

め、樹脂組成物が安定で、触媒パターンの形状が優れて、また、水に対する溶解度が低く、湿式工程において触媒の損失が簡単に生じないと思われる上、フルオロ化銀イオン有機錯化物前駆体を用いることにより塩基性水溶液である無電解メッキ溶液において銀触媒と基材上の吸着力が増大し、均一な蒸着膜を得ることができた。本明細書において用いられた用語「銀イオン有機錯化物前駆体」は触媒として作用するため、還元処理等がされなければならないため触媒として直接的に用いられる前の物質であることを意味する。

【0036】

本発明に好ましい銀イオン有機錯化物前駆体としては、これに制限するものではないが、例えば、銀アセテート系、銀スルホネート系、 β -カルボニルケトン系シルバー(I)錯化物及び β -カルボニルエステル系シルバー(I)錯化物で構成されるグループから選ばれた少なくとも1種以上が単独または2種以上の混合物で用いることができる。

【0037】

銀アセテート系、或いは銀スルホネート系銀イオン有機錯化物としては、これに限定するものではないが、例えば、銀アセテート、銀ラクテート、銀ミリステート、銀シトレート、銀ベンゾエート、銀フェニルアセテート、銀シクロヘキサノアセテート、銀パラトルエンスルホネート、銀オキサレート、銀マロネート、銀サクシネート、または銀アジペート等を用いることができ、フルオロ化物としては銀(I)フルオロサルフェイト、銀(I)トリフルオロアセテート、銀(I)トリフルオロメタンサルフェイト、銀(I)ペンタフルオロプロピオネート、銀(I)ヘプタフルオロブチレート等を用いることができる。

【0038】

β -カルボニルケトン系、或いは β -カルボニルエステル系シルバー(I)錯化物としては、これに限定するものではないが、例えば、シルバー(I)アセチルアセトネート、3-クロロ-2, 4-ペンタンジオネートシルバー(I)錯化物、3, 5-ヘプタンジオネートシルバー(I)錯化物、2-アセチルシクロヘキサノネートシルバー(I)錯化物、3-エチル-2, 4-ペンタンジオネートシルバー(I)錯化物、ベンゾイルアセトンシルバー(I)錯化物、ジベンゾイルメタンシルバー(I)錯化物、2, 2, 6, 6-テトラメチルヘプタンジエンシルバー(I)錯化物、エチルアセトアセテートシルバー(I)錯化物、メチルアセトアセテートシルバー(I)錯化物、イソプロピルアセトアセテートシルバー(I)錯化物、tert-ブチルアセトアセテートシルバー(I)錯化物等を用いることができ、フルオロ化された銀イオン有機錯化物としては1, 5-シクロオクタジエン-ヘキサフルオロアセチルアセトネートシルバー(I)錯化物、1, 1, 1-トリフルオロ-2, 4-ペンタンジオネートシルバー(I)錯化物、5, 5-ジメチル-1, 1, 1-トリフルオロ-2, 4-ヘキサジオネートシルバー(I)錯化物、1-(4-メトキシフェニル)-4, 4, 4-トリフルオロブタンジオネートシルバー(I)錯化物、5, 5, 6, 6, 7, 7, 8, 8, 9, 9, 10, 10, 11, 11, 12, 12, 12-ヘプタデカフルオロデカン-2, 4-ジオネートシルバー(I)錯化物、1, 1, 1, 2, 2, 3, 3-ヘプタフルオロ-7, 7-ジメチル-4, 6-オクタジオネートシルバー(I)錯化物、1, 1, 1, 3, 5, 5, 5-ヘプタフルオロペンタン-2, 4-ジオネートシルバー(I)錯化物、1, 1, 1, 5, 5, 5-ヘキサフルオロペンタン-2, 4-ジオネートシルバー(I)錯化物、5, 5, 6, 6, 7, 7, 8, 8, 8-ノナフルオロオクタン-2, 4-ジオネートシルバー(I)錯化物、5H, 5H-ペルフルオロノナン-4, 6-ジオネートシルバー(I)錯化物、6H, 6H-ペルフルオロウンデカン-5, 7-ジオネートシルバー(I)錯化物、8H, 8H-ペルフルオロペンタデカン-7, 8-ジオネートシルバー(I)錯化物、6H, 6H-ペルフルオロウンデカン-5, 7-ジオネートシルバー(I)錯化物、1-フェニル-2H, 2H-ペルフルオロヘキサン-1, 3-ジオネートシルバー(I)錯化物、1-フェニル-2H, 2H-ペルフルオロウンデカン-1, 3-ジオネートシルバー(I)錯化物、5, 6, 6, 6-テトラフルオロ-5-(ヘプタフルオロプロポキシ)ヘキサン-2, 4-ジオネートシルバー(I)錯化物、1, 1, 5, 5-テトラフルオロペンタン-2, 4-ジオネートシルバー(I)錯化物、5, 5, 6, 6, 7, 7, 8, 8, 9, 9, 9-ウンデカンフルオ

ローノナン-2, 4-ジオネートシルバー(I)錯化物、エチル3-クロロ-4, 4, 4-トリフルオロアセトアセテートシルバー(I)錯化物、エチル-4, 4-ジフルオロアセトアセテートシルバー(I)錯化物、エチル-4, 4, 4-トリフルオロアセトアセテートシルバー(I)錯化物、イソプロピル-4, 4, 4-トリフルオロアセトアセテートシルバー(I)錯化物、メチル-4, 4, 5, 5, 5-ペンタフルオロ-3-オキソペンタノネートシルバー(I)錯化物、エチル-4, 4, 5, 5, 5-ペンタフルオロ-3-オキソペンタノネートシルバー(I)錯化物、及び1, 1, 1, 5, 5, 6, 6, 6-オクタフルオロ-2, 4-ヘキサジオネートシルバー(I)錯化物から選ばれた少なくとも1種以上を用いることができる。上記銀イオン有機錯化物は単独で、或いは2種以上の混合物で用いることができる。

【0039】

本発明の触媒前駆体樹脂組成物中に銀イオン有機錯化物前駆体は、全体有機固形分100重量部に対して、2〜80重量部、好ましくは5〜60重量部で用いることができる。本発明の樹脂組成物において、銀イオン有機錯化物前駆体の含量が2重量部未満であると触媒の量が十分でないために無電解メッキ時に金属膜の製造に長い時間がかかり、均一な膜の形成が困難である。一方、触媒前駆体樹脂組成物中の銀イオン有機錯化物前駆体の含量が80重量部を超えると現像性が落ち20 μ m以下の均一な微細触媒パターンを形成することが困難で、接着特性が低下し微細パターンの金属層の形成が困難である。

【0040】

本発明の触媒前駆体樹脂組成物を構成する溶媒は、特に制限されないが、例えば、メタノール、エタノール、n-プロパノール、イソプロパノール、エチレングリコール、またはプロピレングリコールのようなアルコール類と、アセトン、メチルエチルケトン、シクロヘキサノン、またはn-メチル-2-ピロリドンのようなケトン類と、トルエン、キシレン、またはテトラメチルベンゼンのような芳香族炭化水素類と、セロソルブ、メチルセロソルブ、エチルセロソルブ、3-メトキシプロピルアセテート、プロピレングリコールモノメチルエーテル、プロピレングリコールエチルエーテル、ジプロピレングリコールモノメチルエーテル、またはジプロピレングリコールエチルエーテルのようなグリコールエーテル類と、エチルアセテート、ブチルアセテート、セロソルブアセテート、エチルセロソルブアセテート、ブチルセロソルブアセテート、プロピレングリコールモノメチルエーテルアセテートまたはプロピレングリコールエチルエーテルアセテートのようなアセテート類等からなるグループから選ばれた少なくとも1種以上を単独、或いは混合物で用いることができる。

【0041】

さらに、上記本発明の触媒前駆体樹脂組成物はこれに限定するものではないが、この技術分野に触媒前駆体樹脂組成物の製造時に一般的に用いることができる湿潤剤、接着増進剤等の添加剤を必要に応じてさらに含むことができる。

【0042】

上記触媒前駆体樹脂組成物は固形分含量が10〜50重量%であることができる。固形分含量が50重量%を超えると粘度が高くなり均一にコーティングされず、固形分含量が10重量%未満であると厚さが薄くなり薄膜の機械的強度が落ちるため好ましくない。

【0043】

本発明の他の具現において、本発明による金属パターンの形成方法は上記触媒前駆体樹脂組成物を基材にコーティングし触媒パターン層を形成した後、これを露光及び現像し還元させてから触媒パターン層上に無電解メッキする段階を含んでなることができる。

【0044】

本発明のさらに他の具現において、本発明による金属パターンの製造方法は上記本発明の触媒前駆体樹脂組成物を用いてプリンティング法で基材に触媒パターン層を形成し、還元させてから無電解メッキする段階を含んでなることができる。

【0045】

本発明に用いる基材は、透明性電磁波遮蔽材の製造のために、透明な基材が好ましく用

いられ、具体的にはガラス、ポリカーボネート、アクリル樹脂、PET、TAC (Triacetyl cellulose)、ポリ塩化ビニル樹脂、ポリアミド樹脂、ポリイミド樹脂等のプラスチックシートまたはプラスチックフィルム等を用いることができる。その他基材の厚さ等はこの技術分野において一般的なもので、特に限定しない。

【0046】

上記のような基材に本発明の触媒形成組成物をコーティングする方法は特に限定されず、塗布液の特性や塗布量により異なることができ、例えば、ロールコーティング、グラビアコーティング、ディップコーティング、バーコーティング、スプレーコーティング、またはスピニングコーティング等の通常の方法でコーティングすることができる。

【0047】

本発明の露光及び現像工程は通常知られている方法を用いることができる。例えば、露光工程は露光パターンを有するマスクを用いて接触または非接触露光方式で行うことができる。露光工程で光源としてはハロゲンランプ、高圧水銀灯、メタルハライドランプ等の通常のものを用いることができる。現像工程はスプレー法または浸漬法を用いて現像することができる。露光及び現像により製造された触媒パターン層の形状はラインの幅が30 μm 以下、好ましくは20 μm 以下であることがよい。また、本発明による触媒形成組成物を使用してラインの幅が10 μm 以下の微細パターンを形成することができる。露光現像工程後、パターンのない空間の比率（開口率）が60%以上、より好ましくは70%以上であることがよい。

【0048】

一方、プリンティング法で触媒パターン層を形成する場合にはオフセットプリンティング、インクジェットプリンティング、インプリント及びスクリーンプリンティングで構成されるグループから選ばれた方法で上記基材に本発明による触媒前駆体樹脂組成物を使用して触媒パターン層を形成した後、これを還元させて還元された触媒パターン層に無電解メッキして金属パターンを製造することができる。

【0049】

上記露光及び現像による触媒パターン層形成またはプリンティング法による触媒パターン形成時、触媒パターンを形成した後に無電解メッキ特性を向上させるために銀イオン有機錯化物前駆体が還元されるように還元処理する。

【0050】

銀イオン有機錯化物の還元方法は特に制限されないが、還元剤を用いるか、熱及び／またはUV露光により還元処理することができる。還元剤を用いる場合、公知の還元剤を用いることができる。例えば、水素化ホウ素ナトリウム (NaBH_4) やアスコルビン酸 (Ascorbic acid) 水溶液を用いることができる。

【0051】

一方、銀イオン有機錯化物の種類に従い、無電解メッキ時に無電解メッキ溶液により自発的に還元されることもできるが、無電解メッキ溶液による還元は不十分であるため、この場合にも銀イオン還元工程が必要である。

【0052】

還元剤水溶液の適正濃度は0.01～1.0 Mが適当で、スプレー方式や浸漬方式により還元処理することができる。UV露光や熱を用いて還元させる方法は湿式工程ではないため、触媒の遺失を防ぐ側面で好ましい。還元剤水溶液の濃度が0.01 M未満であると還元力が十分でなく銀イオン有機錯化物前駆体が十分に還元されず、1.0 Mを超える場合には還元程度を制御することが困難でパターン膜が損傷される恐れがある。

【0053】

上記金属パターン層形成時に必要に応じてコーティングした後、前熱硬化及び／または現像してから後熱硬化することができ、このような工程はこの技術分野において一般的なもの、必要に応じて行うことができるもので、これに本発明を限定するものではない。

【0054】

上記のように本発明による触媒前駆体樹脂組成物を用いて触媒パターン層を形成した後

、その上に無電解メッキし金属パターンを形成する。無電解メッキはこの技術分野に一般的に知られている無電解メッキ技術を用いて行うことができる。

【0055】

本発明では銅メッキまたは銀メッキを行うことができ、価額及び電磁波遮蔽性能の側面で銅メッキすることが好ましい。

【0056】

無電解銅メッキは例えば、従来一般的に用いられる公知のメッキ液を用いて行うことができる。これに限定するものではないが、例えば、硫酸銅のような金属イオン塩、ホルマリンのような還元剤、EDTAのような錯化剤と微量の添加剤を含んだ公知のメッキ液を用いることができる。

【0057】

上記本発明による方法により形成される金属パターンを含む最終電磁波遮蔽膜において、触媒パターン層と金属層の総厚さはメッキ浴の金属塩または金属イオン濃度、メッキ温度、蒸着時間等により制御することができる。触媒パターン層及び／または金属層の厚さはパターンの厚さ等により多様に変化することができるもので、この技術分野の技術者は必要に応じて適切な厚さになるように触媒パターン層及び／または金属層の厚さを調節することができ、これに限定するものではないが、触媒パターン層と金属層の総厚さは0.3 μm 以上、好ましくは0.5 μm 以上、より好ましくは1 μm 以上、より好ましくは1-8 μm であることができる。触媒パターン層と金属層の総厚さが0.3 μm 未満であると機械的な強度が不十分で、伝導度が十分でないため遮蔽特性が低下することができる。触媒パターン層と金属層の総厚さが8 μm を超えると、厚さが非常に厚くなり、後工程処理に好ましくない。また、上記触媒パターン層と金属層の総厚さの中の金属層の厚さは伝導度及び電磁波遮蔽性等を考慮し、最小0.1 μm (100 nm)であることが好ましい。

【0058】

このように、本発明による触媒前駆体樹脂組成物を使用して触媒パターン層を形成することにより触媒パターン層の接着性が増大されるため、現像またはメッキ工程のような湿潤工程中の触媒損失が少なく、メッキ速度が向上され無電解メッキ後に均一で微細な金属パターンが形成されることができる。形成された金属パターンを含む電磁波遮蔽材はCRT、PDP、液晶、EL等のディスプレイの前面から発生する電磁波遮蔽膜や軟性回路基板の配線の形成に適合に用いることができる。

【0059】

以下、実施例を通し本発明をより詳細に説明するが、これにより本発明が制限されるものではない。

【0060】

実施例

実施例1

A. 有機高分子樹脂(1)及びこれを用いた触媒前駆体樹脂組成物に用いられる配合物(2)の製造

(1) 250 mLのフラスコにおいて、15.0 g MMA (Methyl methacrylate)と15.0 g MAA (Methacrylic acid)をDPM (dipropylene glycol monomethyl ether) 75.4 gに溶かしてから、0.9 g 3-MPA (3-mercaptopropionic acid)を添加し500 rpmで攪拌した。この混合溶液を窒素雰囲気下で60℃に昇温させた後、1時間の間攪拌した。その後、0.9 g AIBN (2, 2'-azobisisobutyronitrile)をDPM 10.0 gに溶かした溶液を上記60℃の混合溶液に添加し、3時間の間60℃で反応を行った。このようにして得られた有機高分子樹脂の酸価は348.77 mg KOH/g、重量平均分子量は7,933であった。

【0061】

(2) 上記のようにして得られた高分子樹脂溶液5.81 g、DPHA (dipent

aerythritol hexa-acrylate) 溶液 (50wt% in PGMEA) 2.68 g、光開始剤として3-[4-[2,4-ビス(トリクロロメチル)-s-トリアジン-6-イル]フェニルチオ]プロピオン酸 (TPA) を0.185 gを混合し、さらに溶媒としてPGMEA (プロピレングリコールモノメチルエーテルアセテート) 6.23 gを混合して触媒前駆体樹脂組成物に用いられる配合物を製造した。

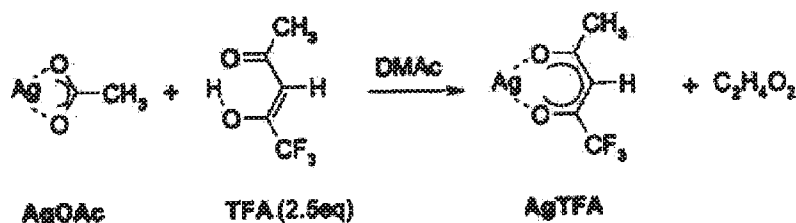
【0062】

B. 銀イオン有機錯化物の製造

常温でシルバーアセテート (AgOAc) 1 gとジメチルアセトアミド (DMAc) 10 gを混ぜ500 rpmで攪拌した。ここに1,1,1-トリフルオロ-2,4-ペンタジオン2.5 gを添加した。シルバーアセテートが1,1,1-トリフルオロ-2,4-ペンタジオンと錯化物をなしながらジメチルアセトアミド (DMAc) 有機溶媒によく溶けている黄色の溶液が形成される。この溶液を0.20 μmシリンジフィルタを介し濾過して得られた固形分を触媒前駆体として使用した。下記の反応式1は上記製造された錯化物の反応式を示すものである。

【0063】

【化1】



【0064】

C. 触媒前駆体樹脂組成物の製造

上記銀イオン有機錯化物と上記触媒前駆体樹脂組成物に用いられる配合物を2:1重量比で混ぜ、攪拌機を用いて500 rpmで攪拌した。樹脂組成物の固形分含量は16.5重量%であった。

【0065】

D. 微細金属パターンの形成

(1) コーティング: 厚さ700 μmのガラス基板に上記Cにおいて製造された触媒前駆体樹脂組成物を1500 rpmで10秒、そして3000 rpmで20秒の間スピンコーティングした。

(2) 前熱硬化: スピンコーティングしてから100℃で90秒の間前熱硬化した。

(3) 露光: 接触方式でフォトマスク (20 μmメッシュのパターン) を通じ330~500 nm波長領域の紫外線を180 mJ/cm² エネルギーで照射し露光させた。

(4) 現像: ENF社のECD-100 (pH13の塩基性水溶液) を72秒の間スプレーし、超純粋 (DI) で洗浄して窒素をブローイングして現像した。

(5) 還元: 現像後、0.1 M アスコルビン酸水溶液に120秒の間浸漬してから、超純粋 (DI) で洗浄して銀触媒を還元させた。

(6) 後熱硬化: 還元させた後、100℃で300秒の間後熱硬化させた。

(7) 銅無電解メッキ: ATOTECH社のCovertron銅メッキ液 (Copper Bath) を用いて60℃で行った。

【0066】

実施例2

本実施例では、330～500nm波長領域の紫外線を 3.9 J/cm^2 で照射し銀有機化合物を還元させたことを除いては実施例1と同じ方法で金属パターン層を形成し、形成された金属パターン層の光学顕微鏡の写真(倍率 $\times 250$)を図3に示した。

【0067】

実施例3

A. 有機高分子樹脂(1)及びこれを用いた触媒前駆体樹脂組成物に用いられる配合物(2)の製造

(1) 250mLのフラスコにおいて、9.0g MMA (Methyl methacrylate)と21.0g MAA (Methacrylic acid)をDPM 75.4gに溶かしてから、0.9g 3-MPA (3-mercaptopropionic acid)を添加して500rpmで攪拌した。この混合溶液を窒素雰囲気下で60℃に昇温させた後、1時間の間500rpmで攪拌した。0.9g AIBN (α, α' -azobisisobutyronitrile)をDPM 10.0gに溶かした溶液を60℃の混合溶液に添加してから、3時間の間60℃で反応を行った。このようにして得られた有機高分子樹脂の酸価は452.32mgKOH/g、重量平均分子量は6,423であった。

【0068】

(2) 上記のようにして得られた高分子溶液5.81g、DPHA (dipentaerythritol hexa-acrylate) 溶液(50wt% in PGMEA) 2.68g、光開始剤として3-(4-[2,4-ビス(トリクロロメチル)-s-トリアジン-6-イル]フェニルチオ)プロピオン酸(TPA) 0.185gを混合し、さらに溶媒としてPGMEA 6.23gを混合して触媒前駆体樹脂組成物に用いられる配合物を製造した。

【0069】

B. 触媒前駆体樹脂組成物の製造

実施例1において製造された銀イオン有機錯化合物と上記実施例3のA(2)において製造された配合物を2:1重量比で混ぜ、攪拌機を用いて500rpmで攪拌して触媒前駆体樹脂組成物を製造した。触媒前駆体樹脂組成物の総固形分含量は16.5重量%であった。

【0070】

C. 微細金属パターン形成

上記実施例3のBの触媒前駆体樹脂組成物を用いたことを除いては実施例2と同じ方法で基材上に金属パターンを形成し、形成された金属パターンの光学顕微鏡の写真(倍率 $\times 250$)を図4に示した。

【0071】

実施例4

A. 有機高分子樹脂(1)及びこれを用いた触媒前駆体樹脂組成物に用いられる配合物(2)の製造

(1) 250mLのフラスコにおいて、3.0g MMA (Methyl methacrylate)と27.0g MAA (Methacrylic acid)をDPM 75.4gに溶かしてから、0.9g 3-MPA (3-mercaptopropionic acid)を添加して500rpmで攪拌した。この混合溶液を窒素雰囲気下で60℃に昇温させた後、1時間の間500rpmで攪拌した。0.9g AIBNをDPM 10.0gに溶かした溶液を上記60℃の混合溶液に添加してから、3時間の間60℃で反応させた。このようにして得られた有機高分子樹脂の酸価は576.69mgKOH/g、重量平均分子量は4,032であった。

【0072】

(2) 上記合成により得られた高分子樹脂溶液5.81g、DPHA (dipentaerythritol hexa-acrylate) 溶液(50wt% in PGM

EA) 2.68 g及び光開始剤として3-〔4-〔2,4-ビス(トリクロロメチル)-s-トリアジン-6-イル〕フェニルチオ〕プロピオン酸(TPA) 0.185 gを混合し、さらに溶媒としてPGMEA 6.23 gを混合し触媒前駆体樹脂組成物に用いられる配合物を製造した。

【0073】

B. 触媒前駆体樹脂組成物の製造

実施例1において製造された銀イオン有機錯化物と上記実施例4のA(2)において製造された配合物を2:1重量比で混ぜ、攪拌機を用いて500 rpmで攪拌し触媒前駆体樹脂組成物を製造した。触媒前駆体樹脂組成物の固形分含量は16.5重量%であった。

【0074】

C. 微細金属パターンの形成

上記実施例4のBの触媒前駆体樹脂組成物を用いたことを除いては実施例2と同じ方法で基材上に金属パターンを形成し、形成された金属パターンの光学顕微鏡の写真(倍率×250)を図5に示した。

【0075】

実施例5

銀イオン有機錯化物として、常温でシルバースセチルアセトネート(silver acetylacetonate) 1 gとジメチルアセトアミド(DMAc) 11.533 gを混ぜ、500 rpmで攪拌して得た溶液を0.20 μmシリンジフィルタを介し濾過して得られた固形分を触媒前駆体に用いたことを除いては実施例1と同じ方法で基材上に金属パターンを形成し、形成された金属パターンの光学顕微鏡の写真(倍率×250)を図6に示した。

【0076】

比較例1

A. 有機高分子樹脂(1)及びこれを用いた触媒前駆体樹脂組成物に用いられる配合物(2)の製造

(1) 250 mLのフラスコにおいて、9.0 g MMA (Methyl methacrylate)と21.0 g MAA (Methacrylic acid)をDPM 75.4 gに溶かしてから、0.9 g 3-MPA (3-mercaptopropionic acid)を添加して500 rpmで攪拌した。この混合溶液を窒素雰囲気下で60℃に昇温させた後、さらに1時間の間500 rpmで攪拌した。0.9 g AIBNをDPM 10.0 gに溶かした溶液を上記60℃の混合溶液に添加してから、3時間の間60℃で反応させた。

【0077】

このようにして得られた有機高分子樹脂の酸価は452.32 mg KOH/g、重量平均分子量は6,423であった。上記合成された有機高分子溶液を80℃に温度を上げてから、酸素雰囲気下で30分の間再び攪拌する。また、溶液の温度を90℃に上昇させてから0.15 g DMAP (dimethyl amino pyridine)を溶媒(DPM) 3 gに溶かした溶液を添加する。この溶液を110℃に上昇させてから、7.44 g GMA (glycidyl methacrylate)を添加し6時間の間攪拌した後、溶液を常温に冷ます。このようにして得られた高分子の酸価は123.74 mg KOH/gで、重量平均分子量は11,635であった。

【0078】

(2) 上記合成により得られた高分子樹脂溶液5.81 gとDPHA (dipentaerythritol hexaacrylate) 溶液(50 wt% in PGM EA) 2.68 g、光開始剤として3-〔4-〔2,4-ビス(トリクロロメチル)-s-トリアジン-6-イル〕フェニルチオ〕プロピオン酸(TPA) 0.185 gを混合し、さらに溶媒としてPGMEA 6.23 gを混合し触媒前駆体樹脂組成物に用いられる配合物を製造した。

【0079】

B. 触媒前駆体の製造

常温で硝酸銀 (AgNO_3) 1 g とジメチルホルムアミド (DMF) 1 g を 500 rpm で攪拌しながら混合し、この溶液を 0.20 μm シリンジフィルタを介し濾過して得られた固形物を触媒前駆体として用いた。

【0080】

C. 触媒前駆体樹脂組成物の製造

上記比較例1のA(2)において用意された配合物と比較例1のBにおいて用意された触媒前駆体を1:1重量比で攪拌機を用いて500 rpm で攪拌しながら混合した。触媒前駆体樹脂組成物の固形分含量は16.5重量%であった。

【0081】

D. 微細金属パターンの形成

上記触媒前駆体樹脂組成物を用いて実施例1と同じ方法で微細金属パターンを形成し、形成された金属パターンの光学顕微鏡の写真(倍率 $\times 250$)を図7に示した。

【0082】

比較例2

触媒前駆体を用いないことを除いては実施例2と同じ方法で微細金属パターンを形成し、形成された微細金属パターンの光学顕微鏡の写真(倍率 $\times 50$)を図8に示した。

【0083】

比較例3

常温でパラジウムアセテート(II) (PdOAc_2) 1 g とジメチルホルムアミド (DMF) 1 g の混合物を攪拌しながら混合した。これを銅無電解メッキの触媒に用いたことを除いては実施例4のような方法で触媒前駆体樹脂組成物を製造した。

【0084】

上記触媒前駆体樹脂組成物は触媒と有機溶媒の相溶性が落ち、また、有機高分子と混練時に相が分離され沈殿が発生し触媒パターンの形成が不可能であった。

【0085】

比較例4

常温でパラジウムアセテート(II) (PdOAc_2) 1 g と、ポリビニルピロリドン (PVP, Mw 10,000) 2.5 g をジメチルアセトアミド (DMAc) 10 g に攪拌しながら混合し触媒相を用意した。上記製造された触媒相と実施例4において用いられた有機高分子を2:1重量比で攪拌しながら混合して触媒前駆体樹脂組成物を製造した。

【0086】

実施例2において用いられた方法により本比較例の触媒前駆体樹脂組成物を用いて触媒パターンを形成しようとしたが、コーティング膜が均一に形成されず、現像されなかったため触媒パターンを形成することができなかった。

【0087】

上記実施例1乃至5のように、銀イオン有機鉛化物を用いた場合は有機高分子、有機溶媒との相溶性は非常に優れて触媒のパターンが非常に均一でパターン内に触媒が均一に分布され、微細な触媒パターンに形成された。また、現像工程及びメッキ工程中に剥離が発生せず、短い時間内に図2乃至6に図示したように優れた微細金属パターンが形成された。

【0088】

還元処理は、化学的に還元処理した場合よりUV露光により還元処理した場合により優れた金属パターンが形成された。

【0089】

無機銀塩を用いた場合(比較例1)には、現像工程及びメッキ工程中に触媒パターン層の一部が剥離され、触媒損失によりメッキ層が遅く形成され金属メッキ層の品質が悪くなった。また、長い時間の無電解メッキ時に触媒パターン層が剥離した。

【0090】

触媒を使用しない比較例2の場合には、金属パターンの透明な基材に対する吸着性が著

しく悪いため、基材にメッキされなかった。

【0091】

比較例3に用いた触媒は、有機溶媒との相溶性が落ち、また、有機高分子と混練時に相が分離され沈殿が発生し均一なパターンの触媒パターン層の形成が不可能であった。

【0092】

混練性を向上させるためにPVPを添加した比較例4の場合は、触媒パターン層が均一でなく、現像もされず触媒パターンを形成することができなかった。

【図面の簡単な説明】

【0093】

【図1】本発明によりフォトリソグラフィ工程を用いて微細な銅薄膜を製造する工程の流れ図である。

【図2】本発明の実施例1による金属パターンの光学顕微鏡の写真（倍率×250）である。

【図3】本発明の実施例2による金属パターンの光学顕微鏡の写真（倍率×250）である。

【図4】本発明の実施例3による金属パターンの光学顕微鏡の写真（倍率×250）である。

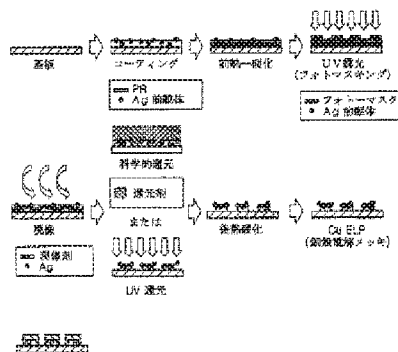
【図5】本発明の実施例4による金属パターンの光学顕微鏡の写真（倍率×250）である。

【図6】本発明の実施例5による金属パターンの光学顕微鏡の写真（倍率×250）である。

【図7】本発明の比較例1による金属パターンの光学顕微鏡の写真（倍率×250）である。

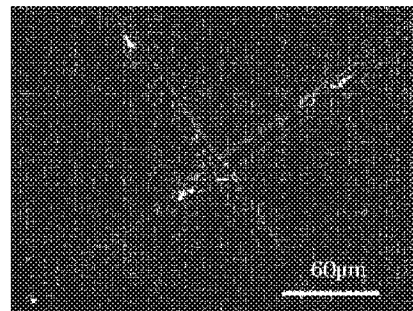
【図8】本発明の比較例2による金属パターンの光学顕微鏡の写真（倍率×50）である。

【図1】



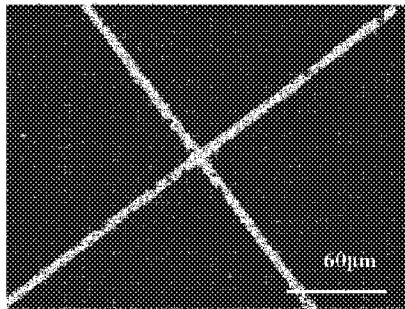
【図2】

[Fig. 2]



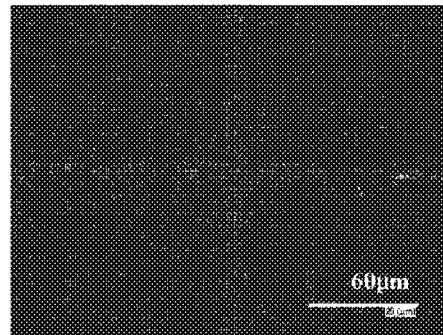
【図3】

[Fig. 3]



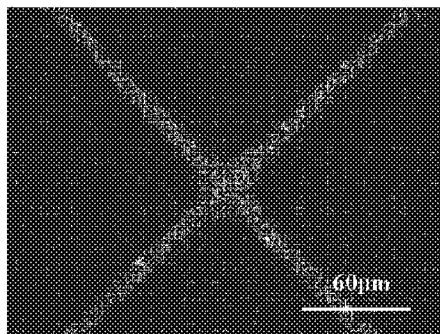
【図4】

[Fig. 4]



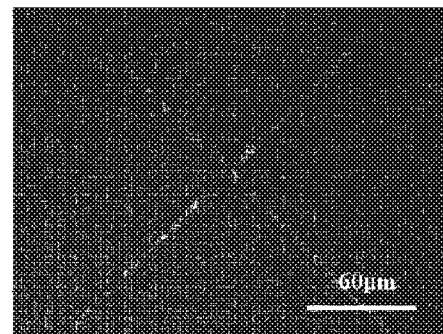
【図5】

[Fig. 5]



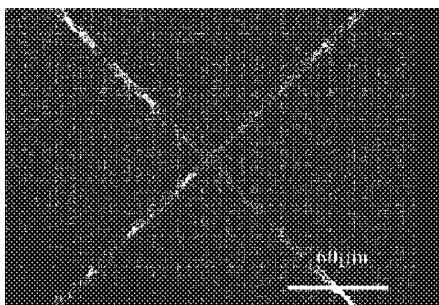
【図7】

[Fig. 7]



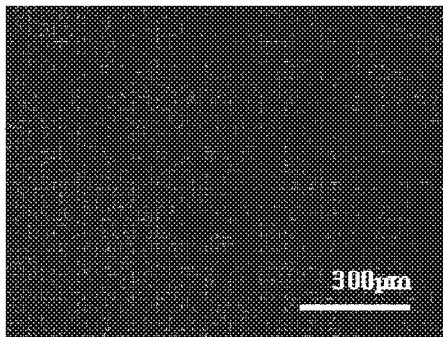
【図6】

[Fig. 6]



【図8】

[Fig. 8]



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A. CLASSIFICATION OF SUBJECT MATTER C08F 4/00(2006.01), G03F 7/027(2006.01) According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC & C08F, G03F Documentation searched other than minimum: documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) eKIPASS, PAJ		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	WO95/36229 A1 (C.F. PLOUCQUET GMBH & CO. et al.) 09 Nov. 1995 Whole document	1-29
☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
<p>* Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&" document member of the same patent family</p>		
Date of the actual completion of the international search 25 JULY 2007 (25.07.2007)		Date of mailing of the international search report 25 JULY 2007 (25.07.2007)
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QA13 QA23 QA24 QA25 RA03 SA01 SA02 SA03 SA04 SA05

SA06 SA21 SA22 SA23 SA31 SA64 SA65 SA78 SA82 SA83

SA84 TA08 UA01 VA01 WA02 WA10

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Espacenet

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METHOD OF FORMING ORGANIC THIN FILM

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Abstract of JP2010094583 (A)

PROBLEM TO BE SOLVED: To provide a method of forming an organic thin film which is easily adaptable to various kinds or sizes of substrates and can uniformly clean even the substrate, whose structure is complicated three-dimension, and by which a cleaning liquid can easily be obtained and preserved for a long period. ;SOLUTION: The method of forming the organic thin film on the surface of the substrate has a process (A) of cleaning the substrate with an alkaline aqueous solution, in which the concentration of an alkaline material is 1-20 mass%, for 1-60 min. The process (A) can be carried out before or after a process (B) of forming the organic thin film. As the alkaline aqueous solution, it is not especially limited as long as it is an aqueous solution exhibiting alkalinity. For example, an aqueous solution containing an inorganic salt such as an alkali metal as the alkaline material is included. Potassium hydroxide or the like is used as the inorganic salt; alkanol amines are used as amines; and an ammonia aqueous solution or the like is used as ammoniums; and these are used singly or in combination thereof. ;COPYRIGHT: (C)2010,JPO&INPIT

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(54) 【発明の名称】 有機薄膜の製造方法

(57) 【要約】

【課題】様々な種類や大きさの基材への対応が容易であって、基材が複雑な三次元構造体であっても基材をムラなく洗浄でき、洗浄液の入手が容易かつ長期保存が可能な、有機薄膜の製造方法を提供する。

【解決手段】基材表面に有機薄膜を形成する有機薄膜の製造方法であって、基材をアルカリ性物質の濃度が1～20質量%であるアルカリ性水溶液で1～60分間洗浄する工程(A)を有する有機薄膜の製造方法である。工程(A)は、有機薄膜を形成する工程(B)の前でも後でもよい。

アルカリ性水溶液としては、アルカリ性を呈する水溶液であれば特に制限されず、例えば、アルカリ性物質としてアルカリ金属等の無機等を含有してなる水溶液が挙げられる。無機塩としては水酸化カリウム等、アミン類としてはアルカノールアミン類、アンモニウム類としてはアンモニア水溶液等を単独、又は組み合わせて使用する。

【選択図】なし

【特許請求の範囲】

【請求項1】

基材表面に有機薄膜を形成する有機薄膜の製造方法であって、基材をアルカリ性物質の濃度が1～20質量％であるアルカリ性水溶液で1～60分間洗浄する工程（A）を有することを特徴とする有機薄膜の製造方法。

【請求項2】

工程（A）が、有機薄膜を形成させる工程（B）の前であることを特徴とする請求項1に記載の有機薄膜の製造方法。

【請求項3】

工程（B）が、真空蒸着法、液相成長法、化学気相成長法、ラングミュア法、スパッタリング法、ディップ法、スプレーコート、スピンコート、ローラーコート、刷毛塗り及びスクリーン印刷からなる群から選ばれる少なくとも1種の方法を用いることを特徴とする請求項2に記載の有機薄膜の製造方法。

【請求項4】

工程（B）が、少なくとも1以上の加水分解性基を有する金属系界面活性剤、及び該金属系界面活性剤と相互作用し得る化合物を含有する有機溶媒溶液に、ディップ法を用いて前記基材を浸漬させることを含む工程（B-1）であることを特徴とする請求項2又は3に記載の有機薄膜の製造方法。

【請求項5】

基材を蒸留水で洗浄する工程（C）、及び／又は基材を有機溶媒で洗浄する工程（D）を、工程（A）より前及び／又は後にさらに有することを特徴とする請求項1～4のいずれかに記載の有機薄膜の製造方法。

【請求項6】

少なくとも1以上の加水分解性基を有する金属系界面活性剤、及び該金属系界面活性剤と相互作用し得る化合物を含有する有機溶媒溶液に接触させた基材を有機溶媒で洗浄する工程（E）、工程（E）で洗浄した基材を乾燥する工程（F）を、工程（B）より後にさらに有することを特徴とする請求項2～5のいずれかに記載の有機薄膜の製造方法。

【請求項7】

少なくとも1以上の加水分解性基を有する金属系界面活性剤が、式（I）

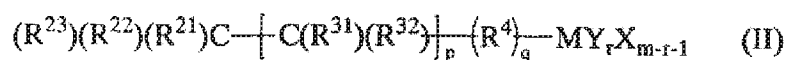


〔式中、 R^1 は、置換基を有していてもよい炭素数1～30の炭化水素基、置換基を有していてもよい炭素数1～30のハロゲン化炭化水素基、連結基を含む炭素数1～30の炭化水素基、又は連結基を含む炭素数1～30のハロゲン化炭化水素基を表し、Mは、ケイ素原子、ゲルマニウム原子、スズ原子、チタン原子、及びジルコニウム原子からなる群から選ばれる少なくとも1種の金属原子を表し、Xは、水酸基又は加水分解性基を表し、mはMの原子価を表す。nは、1から（m-1）のいずれかの正整数を表し、nが2以上の場合、 R^1 は、同一でも相異なってもよい。（m-n）が2以上の場合、Xは同一であっても、相異なってもよいが、Xのうち、少なくとも一個は加水分解性基である。〕で表される化合物であることを特徴とする請求項4～6のいずれかに記載の有機薄膜の製造方法。

【請求項8】

式（I）で表される化合物が、式（II）

【化1】



〔式中、M、X及びmは前記と同じ意味を表す。 R^{21} ～ R^{23} 、 R^{31} 及び R^{32} は、それぞれ独立して水素原子又はフッ素原子を表し、 R^4 は、アルキレン基、ビニレン基、エチニレン基、アリーレン基、又はケイ素原子及び／若しくは酸素原子を含む2価の連結

基を表す。Yは水素原子、アルキル基、アルコキシ基、含フッ素アルキル基又は含フッ素アルコキシ基を表す。pは0又は自然数を表し、qは0又は1を表す。pが2以上のとき、式： $C(R^{31})(R^{32})$ で表される基は同一であっても異なってもよい。rは0又は1から(m-2)のいずれかの正整数を表し、rが2以上のとき、Yは同一でも相異なってもよく、(m-r-1)が2以上のとき、Xは同一でも相異なってもよい。但し、Y及びXのうち、少なくとも一個は水酸基又は加水分解性基である。)で表される化合物であることを特徴とする請求項7に記載の有機薄膜の製造方法。

【請求項9】

金属系界面活性剤と相互作用し得る化合物が、金属酸化物；金属水酸化物；金属アルコキシシド類；キレート化又は配位化された金属化合物；金属アルコキシシド類部分加水分解生成物；金属アルコキシシド類を該金属アルコキシシド類の2倍当量以上の水で処理して得られた加水分解生成物；シラノール縮合触媒から選ばれる少なくとも1種であることを特徴とする請求項7又は8に記載の有機薄膜の製造方法。

【請求項10】

金属酸化物；金属水酸化物；金属アルコキシシド類；キレート化又は配位化された金属化合物；金属アルコキシシド類部分加水分解生成物；金属アルコキシシド類を該金属アルコキシシド類の2倍当量以上の水で処理して得られた加水分解生成物、及びシラノール縮合触媒における金属が、チタン、ジルコニウム、アルミニウム、ケイ素、ゲルマニウム、インジウム、スズ、タンタル、亜鉛、タングステン及び鉛からなる群から選ばれる少なくとも1種以上であることを特徴とする請求項9に記載の有機薄膜の製造方法。

【請求項11】

工程(B-1)において、有機溶媒溶液が、所定の範囲内の水分含量に調整され、かつ保持された有機溶媒溶液であることを特徴とする請求項4～10のいずれかに記載の有機薄膜の製造方法。

【請求項12】

所定の範囲内の水分含量における所定の範囲が、30～1000ppmの範囲であることを特徴とする請求項11に記載の有機薄膜の製造方法。

【請求項13】

有機溶媒溶液の有機溶媒が、炭化水素系溶媒又はフッ化炭素系溶媒であることを特徴とする請求項4～12のいずれかに記載の有機薄膜の製造方法。

【請求項14】

基材が、金属、ガラス、シリコンウェハー、セラミックス、紙、繊維、プラスチック及び鉱物からなる群から選ばれる少なくとも一種から構成されていることを特徴とする請求項1～13のいずれかに記載の有機薄膜の製造方法。

【請求項15】

有機薄膜が、単分子膜であることを特徴とする請求項1～14のいずれかに記載の有機薄膜の製造方法。

【請求項16】

単分子膜が、化学吸着膜及び／又は自己集合膜であることを特徴とする請求項1～15のいずれかに記載の有機薄膜の製造方法。

【請求項17】

工程(B-1)の有機溶媒溶液中において、少なくとも1以上の加水分解性基を有する金属系界面活性剤を含む集合体が形成されていることを特徴とする請求項4～16のいずれかに記載の有機薄膜の製造方法。

【発明の詳細な説明】

【技術分野】

【0001】

本発明は、有機薄膜の製造方法に関するものであり、特に、基材をアルカリ性水溶液で洗浄する工程を含む、有機薄膜の製造方法に関するものである。

【背景技術】

【0002】

基板等の基材表面に有機薄膜を形成する方法として、様々な方法が知られている。例えば、特許文献1には、活性水素を含む基材の表面上への化学吸着膜製造方法において、少なくとも1以上の加水分解性基を有する金属系界面活性剤を、有機溶媒中、金属酸化物、または金属アルコキシド部分加水分解生成物と水で処理した溶液を、前記基材表面に接触させる工程を有することを特徴とする化学吸着膜の製造方法が開示されている。また、特許文献2には、金属原子上に炭化水素基、加水分解性基または水酸基を有する金属化合物、金属系触媒、水を含む有機溶媒溶液を基板に接触させる工程を含む有機薄膜製造方法において、該溶液中の該金属化合物濃度を5～15ミリモル/kgの範囲とし、金属系触媒を酸化物換算で該金属化合物に対して1～20モル%の範囲とし、該溶液中の水の濃度を50～500ppmの範囲とすることを特徴とする有機薄膜製造方法が開示されている。

【0003】

これらの有機薄膜を製造する際、基材表面に有機薄膜を形成させる前に、基材表面の有機物を分解させたり、基材表面に酸化被膜を形成させたりする目的で、一般的に基材にUV/オゾン洗浄が施されることが知られている。また特許文献3には、基材の洗浄にオゾン水又は過酸化水素水を用いた有機薄膜の製造方法が開示されている。さらには基板をアルカリ性の洗浄液で処理することも良く知られている。

【0004】

しかし、基材表面に有機薄膜を形成する有機薄膜の製造において、UV/オゾン洗浄工程を施す場合には、特別に高価な装置が必要であり、また作業員自らが基材を該装置に設置し、その処理後に該装置から該基材を取り出す必要があり、有機薄膜の製造工程において、自動化することができない工程であった。さらに複雑な三次元構造体では洗浄困難であった。オゾン水や過酸化水素水を洗浄剤として用いる場合にはその洗浄剤の有効期間が短く、特にオゾン水は調整直後に使用しなければならない等、その使用に不便な点があった。またアルカリ性の洗浄液では銅などの金属基板では腐食が生じてしまい、一部の金属基板では洗浄に不適であった。

【0005】

【特許文献1】国際公開第03/076064号パンフレット

【特許文献2】特開2005-177533号公報

【特許文献3】特開2007-125548号公報

【発明の開示】

【発明が解決しようとする課題】

【0006】

本発明の課題は、様々な種類や大きさの基材への対応が容易であって、基材が複雑な三次元構造体であっても基材をムラなく洗浄でき、洗浄液の入手が容易かつ長期保存が可能な、有機薄膜の製造方法を提供することにある。

【課題を解決するための手段】

【0007】

本発明者らは、基材表面に有機薄膜を形成する有機薄膜の製造方法において、基材の洗浄に入手が容易かつ長期保存が可能なアルカリ水溶液を用いて、その処理条件を検討することにより様々な種類や大きさの基材への対応が容易であって、かつ基材が複雑な三次元構造体であっても基材をムラなく洗浄することが可能な、有機薄膜の製造方法が得られることを見出し、本発明を完成するに至った。

【0008】

すなわち本発明は、

(1) 基材表面に有機薄膜を形成する有機薄膜の製造方法であって、基材をアルカリ性物質の濃度が1～20質量%であるアルカリ性水溶液で1～60分間洗浄する工程(A)を有することを特徴とする有機薄膜の製造方法、

(2) 工程(A)が、有機薄膜を形成させる工程(B)の前であることを特徴とする上記

(1)に記載の有機薄膜の製造方法、

(3)工程(B)が、真空蒸着法、液相成長法、化学気相成長法、ラングミュア法、スパッタリング法、ディップ法、スプレーコート、スピコート、ローラーコート、刷毛塗り及びスクリーン印刷からなる群から選ばれる少なくとも1種の方法を用いることを特徴とする上記(2)に記載の有機薄膜の製造方法、

(4)工程(B)が、少なくとも1以上の加水分解性基を有する金属系界面活性剤、及び該金属系界面活性剤と相互作用し得る化合物を含有する有機溶媒溶液に、ディップ法を用いて前記基材を浸漬させることを含む工程(B-1)であることを特徴とする上記(2)又は(3)に記載の有機薄膜の製造方法、

(5)基材を蒸留水で洗浄する工程(C)、及び／又は基材を有機溶媒で洗浄する工程(D)を、工程(A)より前及び／又は後にさらに有することを特徴とする上記(1)～(4)のいずれかに記載の有機薄膜の製造方法、

(6)少なくとも1以上の加水分解性基を有する金属系界面活性剤、及び該金属系界面活性剤と相互作用し得る化合物を含有する有機溶媒溶液に接触させた基材を有機溶媒で洗浄する工程(E)、工程(E)で洗浄した基材を乾燥する工程(F)を、工程(B)より後にさらに有することを特徴とする上記(2)～(5)のいずれかに記載の有機薄膜の製造方法、

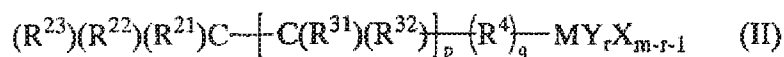
(7)少なくとも1以上の加水分解性基を有する金属系界面活性剤が、式(I)



〔式中、 R^1 は、置換基を有していてもよい炭素数1～30の炭化水素基、置換基を有していてもよい炭素数1～30のハロゲン化炭化水素基、連結基を含む炭素数1～30の炭化水素基、又は連結基を含む炭素数1～30のハロゲン化炭化水素基を表し、Mは、ケイ素原子、ゲルマニウム原子、スズ原子、チタン原子、及びジルコニウム原子からなる群から選ばれる少なくとも1種の金属原子を表し、Xは、水酸基又は加水分解性基を表し、mはMの原子価を表す。nは、1から(m-1)のいずれかの正整数を表し、nが2以上の場合、 R^1 は、同一でも相異なってもよい。(m-n)が2以上の場合、Xは同一であっても、相異なってもよいが、Xのうち、少なくとも一個は加水分解性基である。〕で表される化合物であることを特徴とする上記(4)～(6)のいずれかに記載の有機薄膜の製造方法、

(8)式(I)で表される化合物が、式(II)

【化1】



〔式中、M、X及びmは前記と同じ意味を表す。 R^{21} ～ R^{23} 、 R^{31} 及び R^{32} は、それぞれ独立して水素原子又はフッ素原子を表し、 R^4 は、アルキレン基、ビニレン基、エチニレン基、アリーレン基、又はケイ素原子及び／若しくは酸素原子を含む2価の連結基を表す。Yは水素原子、アルキル基、アルコキシ基、含フッ素アルキル基又は含フッ素アルコキシ基を表す。pは0又は自然数を表し、qは0又は1を表す。pが2以上のとき、式： $C(R^{31})(R^{32})$ で表される基は同一であっても異なってもよい。rは0又は1から(m-2)のいずれかの正整数を表し、rが2以上のとき、Yは同一でも相異なってもよく、(m-r-1)が2以上のとき、Xは同一でも相異なってもよい。但し、Y及びXのうち、少なくとも一個は水酸基又は加水分解性基である。〕で表される化合物であることを特徴とする上記(7)に記載の有機薄膜の製造方法、

(9)金属系界面活性剤と相互作用し得る化合物が、金属酸化物；金属水酸化物；金属アルコキシド類；キレート化又は配位化された金属化合物；金属アルコキシド類部分加水分解生成物；金属アルコキシド類を該金属アルコキシド類の2倍当量以上の水で処理して得られた加水分解生成物；シラノール縮合触媒から選ばれる少なくとも1種であることを特徴とする上記(7)又は(8)に記載の有機薄膜の製造方法、

(10)金属酸化物；金属水酸化物；金属アルコキシド類；キレート化又は配位化された

金属化合物；金属アルコキシド類部分加水分解生成物；金属アルコキシド類を該金属アルコキシド類の2倍当量以上の水で処理して得られた加水分解生成物、及びシラノール縮合触媒における金属が、チタン、ジルコニウム、アルミニウム、ケイ素、ゲルマニウム、インジウム、スズ、タンタル、亜鉛、タングステン及び鉛からなる群から選ばれる少なくとも1種以上であることを特徴とする上記(9)に記載の有機薄膜の製造方法、

(11) 工程(B-1)において、有機溶媒溶液が、所定の範囲内の水分含量に調整され、かつ保持された有機溶媒溶液であることを特徴とする上記(4)～(10)のいずれかに記載の有機薄膜の製造方法、

(12) 所定の範囲内の水分含量における所定の範囲が、30～1000ppmの範囲であることを特徴とする上記(11)に記載の有機薄膜の製造方法、

(13) 有機溶媒溶液の有機溶媒が、炭化水素系溶媒又はフッ化炭素系溶媒であることを特徴とする上記(4)～(12)のいずれかに記載の有機薄膜の製造方法、

(14) 基材が、金属、ガラス、シリコンウェハー、セラミックス、紙、繊維、プラスチック及び鉱物からなる群から選ばれる少なくとも一種から構成されていることを特徴とする上記(1)～(13)のいずれかに記載の有機薄膜の製造方法、

(15) 有機薄膜が、単分子膜であることを特徴とする上記(1)～(14)のいずれかに記載の有機薄膜の製造方法、

(16) 単分子膜が、化学吸着膜及び／又は自己集合膜であることを特徴とする上記(1)～(15)のいずれかに記載の有機薄膜の製造方法、及び、

(17) 工程(B-1)の有機溶媒溶液中において、少なくとも1以上の加水分解性基を有する金属系界面活性剤を含む集合体が形成されていることを特徴とする上記(4)～(16)のいずれかに記載の有機薄膜の製造方法に関する。

【発明の効果】

【0009】

本発明の有機薄膜の製造方法は、様々な種類や大きさの基材への対応が容易であって、基材が複雑な三次元構造体であっても基材をムラなく洗浄でき、洗浄液の入手が容易かつ長期保存が可能である。

【発明を実施するための最良の形態】

【0010】

本発明の有機薄膜の製造方法は、基材表面に有機薄膜を形成する有機薄膜の製造方法であって、基材をアルカリ性物質の濃度が1～20質量%のアルカリ水溶液で1～60分洗浄する工程(A)を有することを特徴とする。基材をアルカリ水溶液で洗浄すると、基材表面に付着した脂質が分解されると共に、基材表面が活性化される。

【0011】

本発明におけるアルカリ性水溶液とは、アルカリ性を呈する水溶液であれば特に制限されない。例えば、アルカリ性物質としてアルカリ金属等の無機塩、アミン類、アンモニウム類等を含む水溶液があげられる。無機塩としては、水酸化カリウム、水酸化ナトリウム、炭酸ナトリウム、リン酸ナトリウム、ケイ酸ナトリウム、ホウ酸ナトリウム等があげられる。アミン類としては、モノエタノールアミン、ジエタノールアミン、トリエタノールアミン等のアルカノールアミン類、アンモニウム類としては、アンモニア水溶液、水酸化テトラメチルアンモニウム水溶液を単独、又は組み合わせて使用する。また、必要であれば界面活性剤やアルコール、ケトンなど水溶性有機溶媒やオゾン水、過酸化水素水を本発明の目的の範囲内で混合して使用してもよい。

【0012】

本発明におけるアルカリ性水溶液のアルカリ性物質濃度は、1～20質量%の範囲内であることが好ましく、1～10質量%の範囲内であることがより好ましい。

【0013】

本発明において基材をアルカリ性水溶液で洗浄する方法は、基材をアルカリ性水溶液に接触させる限り特に制限はされず、例えば、基材にアルカリ性水溶液をスプレーするなどして掛けてもよいし、アルカリ性水溶液中に基材を浸漬してもよい。基材とアルカリ性水

溶液を接触させる時間は、特に制限されないが、基材の洗浄処理の効率と洗浄効果および耐腐食性とのバランスの観点から、1～60分であることが好ましく、5～30分の範囲であることがより好ましい。また、より優れた洗浄効果が得られることから、基材をアルカリ性水溶液に浸漬した状態で、超音波処理することが好ましい。超音波処理の条件は特に制限されないが、周波数25～30KHz、処理時間1～20分、温度20～25℃での処理が好ましく挙げられる。

【0014】

本発明の有機薄膜の製造方法において、工程(A)は、有機薄膜を形成する工程(B)の前でも後でもよい。

本発明における「有機薄膜を形成させる工程」は、有機薄膜を形成させる工程である限り特に制限はないが、真空蒸着法、液相成長法、化学気相成長法、ラングミュア法、スパッタリング法、ディップ法(浸漬法)、スプレーコート、スピンコート、ローラーコート、刷毛塗り及びスクリーン印刷からなる群から選ばれる少なくとも1種の方法を用いることが好ましい。

【0015】

真空蒸着法とは、真空中において、薄膜物質(薄膜の材料となる物質)を加熱して蒸発させ、蒸発温度より低い温度の基材表面で凝結、固化させ薄膜にする方法である。また、液相成長法とは、薄膜物質を過飽和状態になるように高温で溶媒に溶解させ、その溶液に基材を接触させつつ、その溶液を冷却することにより、基材上に薄膜物質の結晶を析出させて薄膜を形成させる方法である。化学気相成長法とは、薄膜物質を含むガスに、熱や光によってエネルギーを与えたり、高周波でプラズマ化したりすることにより、薄膜物質をラジカル化させて反応性を上昇させ、それを基材表面に吸着させて薄膜を形成させる方法である。ラングミュア法とは、水面上に作った単分子膜を一層ずつ固体基材の表面に移しとり、基材上に分子層を累積していく方法である。スパッタリング法とは、固体の薄膜物質(ターゲット物質)に、加速されたイオンを照射するとターゲット物質表面に原子・分子が外部に放出される性質を利用して、基材表面にターゲット物質を付着させて薄膜を形成させる方法である。ディップ法とは、薄膜物質を含む溶液に基材を浸漬させて、基材表面に薄膜を形成させる方法である。スプレーコートとは、薄膜物質を含む溶液を基材にスプレーすることにより基材表面に薄膜を形成させる方法である。スピンコートとは、円盤上に設置した基材に薄膜物質溶液をのせ、円盤を回転させる事によりこれを均一な液膜とし、これを焼成し薄膜を形成させる方法である。ローラーコートとは、ローラーで有機薄膜物質溶液を基材表面上に薄く塗布し薄膜を形成させる方法である。刷毛塗りとは、刷毛で有機薄膜物質溶液を基材表面上に薄く塗布し薄膜を形成させる方法である。スクリーン印刷とは、枠に張ったスクリーン(布)の上から、薄膜物質(ペースト)をのせ、加圧しながら摺動することにより基材上の薄膜を形成させる方法である。

また、ディップ法の場合において、基材を有機溶媒溶液に浸漬する時間は基材の種類等にも左右され、一概にはいえないが、5分～24時間とすることができ、5分～10時間が好ましい。

有機薄膜を形成させるときに用いる有機薄膜材料は、特に制限されないが、例えば、金属系界面活性剤、金属酸化物等が挙げられ、中でも金属系界面活性剤が好ましく挙げられる。

【0016】

また、工程(B)は、少なくとも1以上の加水分解性基を有する金属系界面活性剤、及び該金属系界面活性剤と相互作用し得る化合物を含有する有機溶媒溶液に、ディップ法を用いて前記基材を接触させることを含む工程(B-1)であることが好ましい。これにより、不純物がより少ないより緻密な有機薄膜をより迅速に形成することができる。

【0017】

有機溶媒溶液に基材を接触させる工程は、一度に長い時間行ってもよいし、複数回に分けて短時間で行ってもよい。また、有機薄膜の形成を促進するために超音波を用いることもできる。

【0018】

有機溶媒溶液に基材を接触させる際の有機溶媒溶液の温度は、該溶液が安定性を保てる範囲であれば特に制限されないが、通常、室温から溶液の調製に用いた溶媒の還流温度までの範囲である。有機溶媒溶液を接触に好適な温度とするには、該有機溶媒溶液を加熱してもよいし、基材そのものを加熱してもよいし、その両方を加熱してもよい。

【0019】

本発明における工程(B-1)中の、少なくとも1以上の加水分解性基を有する金属系界面活性剤としては、少なくとも1以上の加水分解可能な官能基と疎水性基とを同一分子内に有するものであれば、特に制限されないが、基材表面上の活性水素と反応して結合を形成することができる加水分解性基を有するものが好ましい。尚、活性水素と反応して結合を形成することができる他の官能基として、水酸基を例示することができる。少なくとも1以上の加水分解性基を有する金属系界面活性剤として、具体的には、前記式(I)で表される化合物を好ましく例示することができる。

【0020】

前記式(I)中、 R^1 は置換基を有していてもよい炭素数1～30の炭化水素基、置換基を有していてもよい炭素数1～30のハロゲン化炭化水素基、連結基を含む炭素数1～30の炭化水素基、又は連結基を含む炭素数1～30のハロゲン化炭化水素基を表し、より好ましくは、置換基を有していてもよい炭素数10～30の炭化水素基、置換基を有していてもよい炭素数10～30のハロゲン化炭化水素基、連結基を含む炭素数10～30の炭化水素基、又は連結基を含む炭素数10～30のハロゲン化炭化水素基を表す。

【0021】

前記置換基を有していてもよい炭素数1～30の炭化水素基の炭化水素基としては、メチル基、エチル基、*n*-プロピル基、イソプロピル基、*n*-ブチル基、イソブチル基、*sec*-ブチル基、*tert*-ブチル基、*n*-ペンチル基、イソペンチル基、ネオペンチル基、*tert*-ペンチル基、*n*-ヘキシル基、イソヘキシル基、*n*-ヘプチル基、*n*-オクチル基、*n*-デシル基等の炭素数1～30のアルキル基；炭素数1～30のアルケニル基；フェニル基、ナフチル基等のアリール基；等が挙げられる。

【0022】

前記置換基を有していてもよい炭素数1～30のハロゲン化炭化水素基のハロゲン化炭化水素基としては、炭素数1～30のハロゲン化アルキル基、炭素数1～30のハロゲン化アルケニル基、ハロゲン化アリール基等が挙げられる。ハロゲン原子としては、フッ素原子、塩素原子、臭素原子等が挙げられ、フッ素原子が好ましい。具体的には、上記例示した炭化水素基中の水素原子の1個以上がフッ素原子、塩素原子又は臭素原子等のハロゲン原子に置換された基が挙げられる。

【0023】

これらの中でも、前記炭素数1～30のハロゲン化炭化水素基としては、炭素数1～30のアルキル基中の水素原子の2個以上がハロゲン原子に置換された基が好ましく、炭素数1～30のアルキル基中の水素原子の2個以上がフッ素原子に置換されたフッ素化アルキル基がより好ましい。また、フッ素化アルキル基が分岐構造を有する場合には、分岐部分は炭素数1～4、好ましくは炭素数1～2の短鎖であるのが好ましい。

【0024】

フッ素化アルキル基としては、末端炭素原子にフッ素原子が1個以上結合した基が好ましく、末端炭素原子にフッ素原子が3個結合した CF_3 基部分を有する基がより好ましく、末端が、フッ素原子が置換しない炭化水素基で内部の炭素鎖にフッ素原子が置換した炭素鎖であっても構わない。末端部分に、アルキル基の全ての水素原子がフッ素原子に置換されたペルフルオロアルキル部分を有し、かつ後述する金属原子Mとの間に、 $-(CH_2)_h-$ (式中、 h は1～6の整数を表し、好ましくは2～4の整数である。)で表されるアルキレン基を有する基が特に好ましい。

【0025】

フッ素化アルキル基中のフッ素原子数は、 $[(\text{フッ素化アルキル基中のフッ素原子数})$

／（フッ素化アルキル基に対応する同一炭素数のアルキル基中に存在する水素原子数）× 100 ％で表現したときに、60 ％以上であることが好ましく、80 ％以上であることがより好ましい。

【0026】

前記置換基を有していてもよい炭素数 1～30 の炭化水素基又は置換基を有していてもよい炭素数 1～30 のハロゲン化炭化水素基の置換基としては、カルボキシル基；アミド基；イミド基；エステル基；メトキシ基、エトキシ基等のアルコキシ基；または水酸基等が挙げられる。これらの置換基の数は 0～3 であることが好ましい。

【0027】

連結基を含む炭素数 1～30 の炭化水素基の炭化水素基としては、具体的には、前記置換基を有していてもよい炭素数 1～30 の炭化水素基の炭化水素基として挙げたものと同様のものが挙げられる。

【0028】

また、連結基を含む炭素数 1～30 のハロゲン化炭化水素基のハロゲン化炭化水素基としては、具体的には、前記置換基を有していてもよい炭素数 1～30 のハロゲン化炭化水素基のハロゲン化炭化水素基として挙げたものと同様のものが挙げられる。

【0029】

前記連結基は、炭化水素基若しくはハロゲン化炭化水素基の炭素－炭素結合間、又は炭化水素基の炭素と後述する金属原子 M との間に存在するのが好ましい。

【0030】

連結基の具体例としては、 $-O-$ 、 $-S-$ 、 $-SO_2-$ 、 $-CO-$ 、 $-C(=O)O-$ 又は $-C(=O)NR^{51}-$ （式中、 R^{51} は、水素原子；メチル基、エチル基、n-プロピル基、イソプロピル基等のアルキル基；を表す。）等が挙げられる。

【0031】

これらの中でも、 R^1 としては、撓水性、耐久性の観点から、炭素数 1～30 のアルキル基、炭素数 1～30 のフッ素化アルキル基、又は連結基を含むフッ素化アルキル基であることが好ましい。

【0032】

R^1 のより好ましい具体例としては、 CH_3- 、 CH_3CH_2- 、 $(CH_3)_2CH-$ 、 $(CH_3)_3C-$ 、 $CH_3(CH_2)_2-$ 、 $CH_3(CH_2)_3-$ 、 $CH_3(CH_2)_4-$ 、 $CH_3(CH_2)_5-$ 、 $CH_3(CH_2)_6-$ 、 $CH_3(CH_2)_7-$ 、 $CH_3(CH_2)_8-$ 、 $CH_3(CH_2)_9-$ 、 $CH_3(CH_2)_{10}-$ 、 $CH_3(CH_2)_{11}-$ 、 $CH_3(CH_2)_{12}-$ 、 $CH_3(CH_2)_{13}-$ 、 $CH_3(CH_2)_{14}-$ 、 $CH_3(CH_2)_{15}-$ 、 $CH_3(CH_2)_{16}-$ 、 $CH_3(CH_2)_{17}-$ 、 $CH_3(CH_2)_{18}-$ 、 $CH_3(CH_2)_{19}-$ 、 $CH_3(CH_2)_{20}-$ 、 $CH_3(CH_2)_{21}-$ 、 $CH_3(CH_2)_{22}-$ 、 $CH_3(CH_2)_{23}-$ 、 $CH_3(CH_2)_{24}-$ 、 $CH_3(CH_2)_{25}-$ 、 CF_3- 、 CF_3CF_2- 、 $(CF_3)_2CF-$ 、 $(CF_3)_3C-$ 、 $CF_3(CH_2)_2-$ 、 $CF_3(CF_2)_3(CH_2)_2-$ 、 $CF_3(CF_2)_5(CH_2)_2-$ 、 $CF_3(CF_2)_7(CH_2)_2-$ 、 $CF_3(CF_2)_9(CH_2)_3-$ 、 $CF_3(CF_2)_7(CH_2)_3-$ 、 $CF_3(CF_2)_5(CH_2)_3-$ 、 $CF_3(CF_2)_7(CH_2)_3-$ 、 $CF_3(CF_2)_4O(CF_2)_2(CH_2)_2-$ 、 $CF_3(CF_2)_4O(CF_2)_2(CH_2)_3-$ 、 $CF_3(CF_2)_7O(CF_2)_2(CH_2)_2-$ 、 $CF_3(CF_2)_7CONH(CH_2)_2-$ 、 $CF_3(CF_2)_7CONH(CH_2)_3-$ 、 $CF_3(CF_2)_3O[CF(CF_3)CF(CF_3)O]_2CF(CF_3)CONH(CH_2)_3-$ 、

$CH_3(CF_2)_7(CH_2)_2-$ 、 $CH_3(CF_2)_8(CH_2)_2-$ 、 $CH_3(CF_2)_9(CH_2)_2-$ 、 $CH_3(CF_2)_{10}(CH_2)_2-$ 、 $CH_3(CF_2)_{11}(CH_2)_2-$ 、 $CH_3(CF_2)_{12}(CH_2)_2-$ 、 $CH_3(CF_2)_7(CH_2)_3-$ 、 $CH_3(CF_2)_9(CH_2)_3-$ 、 $CH_3(CF_2)_{11}(CH_2)_3-$ 、 $CH_3CH_2(CF_2)_6(CH_2)_2-$ 、 $CH_3CH_2(CF_2)_8(CH_2)_2-$ 、 $CH_3CH_2(CF_2)_{10}(CH_2)_2-$ 、 $CH_3(CF_2)_4O(CF_2)_2(CH_2)_2-$

2-、 $\text{CH}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{O}(\text{CH}_2)_3-$ 、 $\text{CH}_3(\text{CF}_2)_8(\text{CH}_2)_2\text{O}(\text{CH}_2)_3-$ 、 $\text{CH}_3(\text{CF}_2)_9(\text{CH}_2)_2\text{O}(\text{CH}_2)_3-$ 、 $\text{CH}_3\text{CH}_2(\text{CF}_2)_6(\text{CH}_2)_2\text{O}(\text{CH}_2)_3-$ 、 $\text{CH}_3(\text{CF}_2)_6\text{CONH}(\text{CH}_2)_3-$ 、 $\text{CH}_3(\text{CF}_2)_8\text{CONH}(\text{CH}_2)_3-$ 、 $\text{CH}_3(\text{CF}_2)_9\text{O}[\text{CF}(\text{CF}_3)\text{CF}(\text{CF}_3)\text{O}]_2\text{CF}(\text{CF}_3)\text{CONH}(\text{CH}_2)_3-$ 、等が挙げられるが、これらに限定されるものではない。

【0033】

Mは、ケイ素原子、ゲルマニウム原子、スズ原子、チタン原子、及びジルコニウム原子からなる群から選ばれる1種の原子を表す。これらの中でも、原料の入手容易性、反応性等の観点からケイ素原子が特に好ましい。

【0034】

Xは、水酸基又は加水分解性基を表し、加水分解性基としては、水と反応して分解する基であれば特に制約されない。具体的には、置換基を有していてもよい炭素数1〜6のアルコキシ基；置換基を有していてもよい炭化水素オキシ基（ただし、アルコキシ基を除く）；置換基を有していてもよいアシルオキシ基；フッ素原子、塩素原子、臭素原子、ヨウ素原子等のハロゲン原子；イソシアネート基；シアノ基；アミノ基；またはアミド基等を例示することができる。

【0035】

炭素数1〜6のアルコキシ基としては、メトキシ基、エトキシ基、*n*-プロポキシ基、イソプロポキシ基、*n*-ブトキシ基、*sec*-ブトキシ基、*tert*-ブトキシ基、*n*-ペンチロキシ基、*n*-ヘキシルオキシ基等が挙げられる。

【0036】

アシルオキシ基としては、アセトキシ基、プロピオニルオキシ基、プロパノイルオキシ基、*n*-プロピルカルボニルオキシ基、イソプロピルカルボニルオキシ基、*n*-ブチルカルボニルオキシ基、プロパノイルオキシ基、脂環式炭化水素オキシ基；シクロプロピルオキシ基、シクロプロピルメチルオキシ、シクロヘキシル基、ノルボニルオキシ基等、アルケニルオキシ基；アリルオキシ基等、アルキニルオキシ基；プロパルギルオキシ基等、アラルキルオキシ基；プロパルギルオキシ基等、アラルキルオキシ基；ビニルオキシ基、ベンジルオキシ基、フェネチルオキシ基等、芳香族炭化水素オキシ基；フェノキシ基、ナフチルオキシ基等、ベンゾイルオキシ基等が挙げられる。

【0037】

炭化水素オキシ基の炭化水素としては、炭素数1〜30のアルケニル基、フェニル基、ナフチル基などのアリール基などが挙げられる。

X中の「置換基を有しても良い」の置換基としては、カルボキシ基、アミド基、イミド基、エステル基、水酸基等が挙げられる。

Xとしては、特に、水酸基、ハロゲン原子、炭素数1〜6のアルコキシ基、アシルオキシ基、又はイソシアネート基が好ましく、炭素数1〜4のアルコキシ基又はアシルオキシ基がより好ましい。

【0038】

mは、金属原子Mの原子価を表す。

【0039】

nは、1から(m-1)のいずれかの正の整数を表す。高密度の有機薄膜を製造する上では、nは1であるのが好ましい。nが2以上のとき、 R^{21} は同一であっても相異なってもよい。また、(m-n)が2以上のとき、Xは同一であっても相異なってもよいが、Xのうち少なくとも一個は加水分解性基であることが好ましい。

【0040】

式(I)で表される化合物中、好ましい態様の一つとして、式(II)で表される化合物を例示することができる。式(II)中、M、X及びmは、式(I)における意味と同じ意味を表す。 $R^{21} \sim R^{23}$ 、 R^{31} 及び R^{32} は、それぞれ独立して水素原子又はフッ素原子を表す。pは0又は自然数を表し、qは0又は1を表す。pが2以上のとき、式C

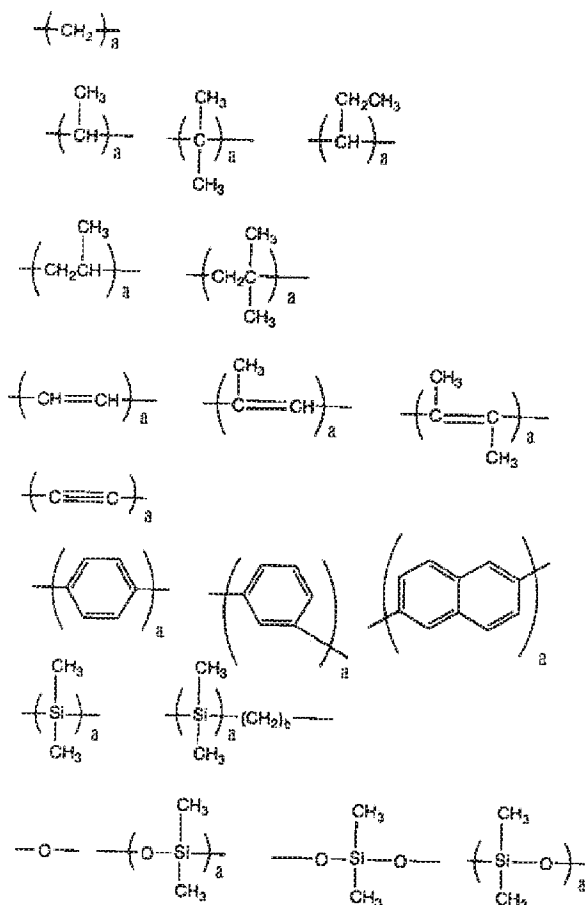
(R³¹) (R³²) で表される基は同一であっても異なってもよい。

【0041】

式(II)中、R⁴は、アルキレン基、ビニレン基、エチニレン基、アリーレン基、または、ケイ素原子及び／または酸素原子を含む2価官能基を表す。具体的には、下記式に示す官能基を例示することができる。

【0042】

【化2】



【0043】

上記式中、a及びbは1以上の任意の自然数を表す。

Yは、水素原子；メチル基、エチル基、n-プロピル基、イソプロピル基、n-ブチル基、イソブチル基、sec-ブチル基、t-ブチル基、n-ペンチル基、イソペンチル基、ネオペンチル基、t-ペンチル基、n-ヘキシル基、イソヘキシル基等のアルキル基；メトキシ基、エトキシ基、n-プロポキシ基、イソプロポキシ基、n-ブトキシ基、sec-ブトキシ基、t-ブトキシ基、n-ペンチルオキシ基、n-ヘキシルオキシ基等のアルコキシ基；アルキル基の一部又はすべての水素原子がフッ素原子に置換された含フッ素アルキル基；又はアルコキシ基の一部若しくはすべての水素原子がフッ素原子に置換された含フッ素アルコキシ基；等を表す。

【0044】

rは、0又は1から(m-2)のいずれかの正整数を表すが、高密度の吸着膜を製造するためには、rは0であることが好ましい。rが2以上の場合に、Yは、それぞれ同一でも相異なってもよい。(m-r-1)が2以上の場合に、Xは、それぞれ同一でも相

異なってもよい。但し、Y及びXのうち、少なくとも一個は水酸基又は加水分解性基である。

【0045】

式(I)で表される化合物の具体例としては、下記に示すものが挙げられる。なお、以下においては、金属原子Mがケイ素原子である化合物を代表例として示しているが、本発明はこれらに限定されるものではない。また、加水分解性基についても、例示した官能基に限定されず他の加水分解性基が結合したものであってもよい。

【0046】

$\text{CH}_3\text{CH}_2\text{O}(\text{CH}_2)_{15}\text{Si}(\text{OCH}_3)_3$
 $\text{CF}_3\text{CH}_2\text{O}(\text{CH}_2)_{15}\text{Si}(\text{OCH}_3)_3$
 $\text{CH}_3(\text{CH}_2)_2\text{Si}(\text{CH}_3)_2(\text{CH}_2)_{15}\text{Si}(\text{OCH}_3)_3$
 $\text{CH}_3(\text{CH}_2)_6\text{Si}(\text{CH}_3)_2(\text{CH}_2)_9\text{Si}(\text{OCH}_3)_3$
 $\text{CH}_3\text{COO}(\text{CH}_2)_{15}\text{Si}(\text{OCH}_3)_3$
 $\text{CF}_3(\text{CF}_2)_5(\text{CH}_2)_2\text{Si}(\text{OCH}_3)_3$
 $\text{CF}_3(\text{CF}_2)_7-(\text{CH}=\text{CH})_3-\text{Si}(\text{OCH}_3)_3$
 $\text{CH}_3\text{CH}_2\text{O}(\text{CH}_2)_{15}\text{Si}(\text{OC}_2\text{H}_5)_3$
 $\text{CH}_3(\text{CH}_2)_2\text{Si}(\text{CH}_3)_2(\text{CH}_2)_{15}\text{Si}(\text{OC}_2\text{H}_5)_3$
 $\text{CH}_3(\text{CH}_2)_6\text{Si}(\text{CH}_3)_2(\text{CH}_2)_9\text{Si}(\text{OC}_2\text{H}_5)_3$
 $\text{CF}_3(\text{CH}_2)_6\text{Si}(\text{CH}_3)_2(\text{CH}_2)_9\text{Si}(\text{OC}_2\text{H}_5)_3$
 $\text{CH}_3\text{COO}(\text{CH}_2)_{15}\text{Si}(\text{OC}_2\text{H}_5)_3$
 $\text{CF}_3\text{COO}(\text{CH}_2)_{15}\text{Si}(\text{OC}_2\text{H}_5)_3$
 $\text{CF}_3\text{COO}(\text{CH}_2)_{15}\text{Si}(\text{OCH}_3)_3$
 $\text{CF}_3(\text{CF}_2)_9(\text{CH}_2)_2\text{Si}(\text{OC}_2\text{H}_5)_3$
 $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{Si}(\text{OC}_2\text{H}_5)_3$
 $\text{CF}_3(\text{CF}_2)_5(\text{CH}_2)_2\text{Si}(\text{OC}_2\text{H}_5)_3$
 $\text{CF}_3(\text{CF}_2)_7(\text{CH}=\text{CH})_3\text{Si}(\text{OC}_2\text{H}_5)_3$
 $\text{CF}_3(\text{CF}_2)_9(\text{CH}_2)_2\text{Si}(\text{OCH}_3)_3$
 $\text{CF}_3(\text{CF}_2)_5(\text{CH}_2)_2\text{Si}(\text{OCH}_3)_3$
 $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{Si}(\text{CH}_3)(\text{OC}_2\text{H}_5)_2$
 $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{Si}(\text{CH}_3)(\text{OCH}_3)_2$
 $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{Si}(\text{CH}_3)_2(\text{OC}_2\text{H}_5)$
 $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{Si}(\text{CH}_3)_2(\text{OCH}_3)$

【0047】

$\text{CF}_3(\text{CH}_2)_2\text{Si}(\text{OCH}_3)_3$
 $\text{CF}_3(\text{CF}_2)_3(\text{CH}_2)_2\text{Si}(\text{OCH}_3)_3$
 $\text{CF}_3(\text{CF}_2)_5(\text{CH}_2)_2\text{Si}(\text{OCH}_3)_3$
 $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{Si}(\text{OCH}_3)_3$
 $\text{CF}_3(\text{CF}_2)_3(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$
 $\text{CF}_3(\text{CF}_2)_5(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$
 $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$
 $\text{CF}_3(\text{CF}_2)_4\text{O}(\text{CF}_2)_2(\text{CH}_2)_2\text{Si}(\text{OCH}_3)_3$
 $\text{CF}_3(\text{CF}_2)_4\text{O}(\text{CF}_2)_2(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$
 $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{O}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$
 $\text{CF}_3(\text{CF}_2)_7\text{CONH}(\text{CH}_2)_2\text{Si}(\text{OCH}_3)_3$
 $\text{CF}_3(\text{CF}_2)_7\text{CONH}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$
 $\text{CF}_3(\text{CF}_2)_3\text{O}[\text{CF}(\text{CF}_3)\text{CF}(\text{CF}_3)\text{O}]_2\text{CF}(\text{CF}_3)-$
 $\text{CONH}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$

【0048】

$\text{CF}_3(\text{CF}_2)_3(\text{CH}_2)_2\text{Si}(\text{CH}_3)(\text{OCH}_3)_2$
 $\text{CF}_3(\text{CF}_2)_5(\text{CH}_2)_2\text{Si}(\text{CH}_3)(\text{OCH}_3)_2$

$\text{CF}_3 (\text{CH}_2)_2 \text{Si} (\text{CH}_3) (\text{OCH}_3)_2$
 $\text{CF}_3 (\text{CF}_2)_3 (\text{CH}_2)_3 \text{Si} (\text{CH}_3) (\text{OCH}_3)_2$
 $\text{CF}_3 (\text{CF}_2)_5 (\text{CH}_2)_3 \text{Si} (\text{CH}_3) (\text{OCH}_3)_2$
 $\text{CF}_3 (\text{CF}_2)_7 (\text{CH}_2)_3 \text{Si} (\text{CH}_3) (\text{OCH}_3)_2$
 $\text{CF}_3 (\text{CF}_2)_4 (\text{CF}_2)_2 (\text{CH}_2)_2 \text{Si} (\text{CH}_3) (\text{OCH}_3)_2$
 $\text{CF}_3 (\text{CF}_2)_4 (\text{CF}_2)_2 (\text{CH}_2)_3 \text{Si} (\text{CH}_3) (\text{OCH}_3)_2$
 $\text{CF}_3 (\text{CF}_2)_4 (\text{CH}_2)_2 \text{O} (\text{CH}_2)_3 \text{Si} (\text{CH}_3) (\text{OCH}_3)_2$
 $\text{CF}_3 (\text{CF}_2)_7 \text{CONH} (\text{CH}_2)_2 \text{Si} (\text{CH}_3) (\text{OCH}_3)_2$
 $\text{CF}_3 (\text{CF}_2)_7 \text{CONH} (\text{CH}_2)_3 \text{Si} (\text{CH}_3) (\text{OCH}_3)_2$
 $\text{CF}_3 (\text{CF}_2)_3 \text{O} [\text{CF} (\text{CF}_3) \text{CF} (\text{CF}_3) \text{O}]_2 \text{CF} (\text{CF}_3) -$
 $\text{CONH} (\text{CH}_2)_3 \text{Si} (\text{CH}_3) (\text{OCH}_3)_2$
 $\text{CH}_3 (\text{CH}_2)_7 \text{Si} (\text{OCH}_3)_3$
 $\text{CH}_3 (\text{CF}_2)_7 (\text{CH}_2)_2 \text{Si} (\text{OCH}_3)_3$
 $\text{CH}_3 (\text{CF}_2)_7 (\text{CH}_2)_2 \text{Si} (\text{CH}_3) (\text{OCH}_3)_2$
 $\text{CH}_3 (\text{CF}_2)_7 (\text{CH}_2)_2 \text{Si} (\text{OCH}_3)_3$
 $\text{CH}_3 (\text{CF}_2)_7 (\text{CH}_2)_2 \text{Si} (\text{NCO})_3$
 $\text{CH}_3 (\text{CF}_2)_8 (\text{CH}_2)_2 \text{Si} (\text{OCH}_3)_3$
 $\text{CH}_3 (\text{CF}_2)_8 (\text{CH}_2)_2 \text{Si} (\text{NCO})_3$
 $\text{CH}_3 (\text{CF}_2)_9 (\text{CH}_2)_2 \text{Si} (\text{OCH}_3)_3$
 $\text{CH}_3 (\text{CF}_2)_9 (\text{CH}_2)_2 \text{Si} (\text{NCO})_3$
 $\text{CH}_3 \text{CH}_2 (\text{CF}_2)_6 (\text{CH}_2)_2 \text{Si} (\text{OCH}_3)_3$
 $\text{CH}_3 \text{CH}_2 (\text{CF}_2)_6 (\text{CH}_2)_2 \text{Si} (\text{NCO})_3$
 $\text{CH}_3 \text{CH}_2 (\text{CF}_2)_8 (\text{CH}_2)_2 \text{Si} (\text{OCH}_3)_3$
 $\text{CH}_3 \text{CH}_2 (\text{CF}_2)_8 (\text{CH}_2)_2 \text{Si} (\text{NCO})_3$
 $\text{CH}_3 \text{CH}_2 (\text{CF}_2)_{10} (\text{CH}_2)_2 \text{Si} (\text{OCH}_3)_3$
 $\text{CH}_3 (\text{CF}_2)_4 \text{O} (\text{CF}_2)_2 (\text{CH}_2)_2 \text{Si} (\text{OCH}_3)_3$
 $\text{CH}_3 (\text{CF}_2)_7 (\text{CH}_2)_2 \text{O} (\text{CH}_2)_3 \text{Si} (\text{OCH}_3)_3$
 $\text{CH}_3 (\text{CF}_2)_8 (\text{CH}_2)_2 \text{O} (\text{CH}_2)_3 \text{Si} (\text{OCH}_3)_3$
 $\text{CH}_3 (\text{CF}_2)_9 (\text{CH}_2)_2 \text{O} (\text{CH}_2)_3 \text{Si} (\text{OCH}_3)_3$
 $\text{CH}_3 \text{CH}_2 (\text{CF}_2)_6 (\text{CH}_2)_2 \text{O} (\text{CH}_2)_3 \text{Si} (\text{OCH}_3)_3$
 $\text{CH}_3 (\text{CF}_2)_6 \text{CONH} (\text{CH}_2)_3 \text{Si} (\text{OCH}_3)_3$
 $\text{CH}_3 (\text{CF}_2)_8 \text{CONH} (\text{CH}_2)_3 \text{Si} (\text{OCH}_3)_3$
 $\text{CH}_3 (\text{CF}_2)_3 \text{O} [\text{CF} (\text{CF}_3) \text{CF} (\text{CF}_3) \text{O}]_2 \text{CF} (\text{CF}_3) -$
 $\text{CONH} (\text{CH}_2)_3 \text{Si} (\text{OCH}_3)_3$

【0049】

$\text{CH}_3 \text{CH}_2 \text{O} (\text{CH}_2)_{15} \text{Si} (\text{OCH}_3) (\text{OH})_2$
 $\text{CF}_3 \text{CH}_2 \text{O} (\text{CH}_2)_{15} \text{Si} (\text{OCH}_3)_1 (\text{OH})_2$
 $\text{CH}_3 (\text{CH}_2)_2 \text{Si} (\text{CH}_3)_2 (\text{CH}_2)_{15} \text{Si} (\text{OCH}_3) (\text{OH})_2$
 $\text{CH}_3 (\text{CH}_2)_6 \text{Si} (\text{CH}_3)_2 (\text{CH}_2)_9 \text{Si} (\text{OCH}_3) (\text{OH})_2$
 $\text{CH}_3 \text{COO} (\text{CH}_2)_{15} \text{Si} (\text{OCH}_3) (\text{OH})_2$
 $\text{CF}_3 (\text{CF}_2)_5 (\text{CH}_2)_2 \text{Si} (\text{OCH}_3) (\text{OH})_2$
 $\text{CF}_3 (\text{CF}_2)_7 (\text{CH}=\text{CH})_3 \text{Si} (\text{OCH}_3) (\text{OH})_2$
 $\text{CH}_3 \text{CH}_2 \text{O} (\text{CH}_2)_{15} \text{Si} (\text{OC}_2\text{H}_5) (\text{OH})_2$
 $\text{CH}_3 (\text{CH}_2)_2 \text{Si} (\text{CH}_3)_2 (\text{CH}_2)_{15} \text{Si} (\text{OC}_2\text{H}_5) (\text{OH})_2$
 $\text{CH}_3 (\text{CH}_2)_6 \text{Si} (\text{CH}_3)_2 (\text{CH}_2)_9 \text{Si} (\text{OC}_2\text{H}_5) (\text{OH})_2$
 $\text{CF}_3 (\text{CH}_2)_6 \text{Si} (\text{CH}_3)_2 (\text{CH}_2)_9 \text{Si} (\text{OC}_2\text{H}_5) (\text{OH})_2$
 $\text{CH}_3 \text{COO} (\text{CH}_2)_{15} \text{Si} (\text{OC}_2\text{H}_5) (\text{OH})_2$
 $\text{CF}_3 \text{COO} (\text{CH}_2)_{15} \text{Si} (\text{OC}_2\text{H}_5) (\text{OH})_2$
 $\text{CF}_3 \text{COO} (\text{CH}_2)_{15} \text{Si} (\text{OCH}_3) (\text{OH})_2$
 $\text{CF}_3 (\text{CF}_2)_9 (\text{CH}_2)_2 \text{Si} (\text{OC}_2\text{H}_5) (\text{OH})_2$

$\text{CF}_3 (\text{CF}_2)_7 (\text{CH}_2)_2 \text{Si} (\text{OC}_2\text{H}_5)_2 (\text{OH})_2$
 $\text{CF}_3 (\text{CF}_2)_5 (\text{CH}_2)_2 \text{Si} (\text{OC}_2\text{H}_5)_2 (\text{OH})_2$
 $\text{CF}_3 (\text{CF}_2)_7 (\text{CH}=\text{CH})_3 \text{Si} (\text{OC}_2\text{H}_5)_2 (\text{OH})_2$
 $\text{CF}_3 (\text{CF}_2)_9 (\text{CH}_2)_2 \text{Si} (\text{OCH}_3)_2 (\text{OH})_2$
 $\text{CF}_3 (\text{CF}_2)_5 (\text{CH}_2)_2 \text{Si} (\text{OCH}_3)_2 (\text{OH})_2$
 $\text{CF}_3 (\text{CF}_2)_7 (\text{CH}_2)_2 \text{Si} (\text{CH}_3)_2 (\text{OH})_2$
 $\text{CF}_3 (\text{CF}_2)_9 (\text{CH}_2)_2 \text{Si} (\text{CH}_3)_2 (\text{OH})_2$

【0050】

$\text{CH}_3 \text{CH}_2 \text{O} (\text{CH}_2)_{15} \text{Si} (\text{OCH}_3)_2 (\text{OH})_2$
 $\text{CF}_3 \text{CH}_2 \text{O} (\text{CH}_2)_{15} \text{Si} (\text{OCH}_3)_2 (\text{OH})_2$
 $\text{CH}_3 (\text{CH}_2)_2 \text{Si} (\text{CH}_3)_2 (\text{CH}_2)_{15} \text{Si} (\text{OCH}_3)_2 (\text{OH})_2$
 $\text{CH}_3 (\text{CH}_2)_6 \text{Si} (\text{CH}_3)_2 (\text{CH}_2)_9 \text{Si} (\text{OCH}_3)_2 (\text{OH})_2$
 $\text{CH}_3 \text{COO} (\text{CH}_2)_{15} \text{Si} (\text{OCH}_3)_2 (\text{OH})_2$
 $\text{CF}_3 (\text{CF}_2)_5 (\text{CH}_2)_2 \text{Si} (\text{OCH}_3)_2 (\text{OH})_2$
 $\text{CH}_3 \text{CH}_2 \text{O} (\text{CH}_2)_{15} \text{Si} (\text{OC}_2\text{H}_5)_2 (\text{OH})_2$
 $\text{CF}_3 (\text{CF}_2)_7 (\text{CH}=\text{CH})_3 \text{Si} (\text{OCH}_3)_2 (\text{OH})_2$
 $\text{CH}_3 (\text{CH}_2)_2 \text{Si} (\text{CH}_3)_2 (\text{CH}_2)_{15} \text{Si} (\text{OC}_2\text{H}_5)_2 (\text{OH})_2$
 $\text{CH}_3 (\text{CH}_2)_6 \text{Si} (\text{CH}_3)_2 (\text{CH}_2)_9 \text{Si} (\text{OC}_2\text{H}_5)_2 (\text{OH})_2$
 $\text{CF}_3 (\text{CH}_2)_6 \text{Si} (\text{CH}_3)_2 (\text{CH}_2)_9 \text{Si} (\text{OC}_2\text{H}_5)_2 (\text{OH})_2$
 $\text{CH}_3 \text{COO} (\text{CH}_2)_{15} \text{Si} (\text{OC}_2\text{H}_5)_2 (\text{OH})_2$
 $\text{CF}_3 \text{COO} (\text{CH}_2)_{15} \text{Si} (\text{OC}_2\text{H}_5)_2 (\text{OH})_2$
 $\text{CF}_3 \text{COO} (\text{CH}_2)_{15} \text{Si} (\text{OCH}_3)_2 (\text{OH})_2$
 $\text{CF}_3 (\text{CF}_2)_9 (\text{CH}_2)_2 \text{Si} (\text{OC}_2\text{H}_5)_2 (\text{OH})_2$
 $\text{CF}_3 (\text{CF}_2)_7 (\text{CH}_2)_2 \text{Si} (\text{OC}_2\text{H}_5)_2 (\text{OH})_2$
 $\text{CF}_3 (\text{CF}_2)_5 (\text{CH}_2)_2 \text{Si} (\text{OC}_2\text{H}_5)_2 (\text{OH})_2$

【0051】

$\text{CF}_3 (\text{CF}_2)_7 (\text{CH}=\text{CH})_3 \text{Si} (\text{OC}_2\text{H}_5)_2 (\text{OH})_2$
 $\text{CF}_3 (\text{CF}_2)_9 (\text{CH}_2)_2 \text{Si} (\text{OCH}_3)_2 (\text{OH})_2$
 $\text{CF}_3 (\text{CF}_2)_5 (\text{CH}_2)_2 \text{Si} (\text{OCH}_3)_2 (\text{OH})_2$
 $\text{CF}_3 (\text{CF}_2)_7 (\text{CH}_2)_2 \text{Si} (\text{CH}_3)_2 (\text{OC}_2\text{H}_5)_2 (\text{OH})_2$
 $\text{CF}_3 (\text{CF}_2)_7 (\text{CH}_2)_2 \text{Si} (\text{CH}_3)_2 (\text{OCH}_3)_2 (\text{OH})_2$

【0052】

$\text{CF}_3 (\text{CH}_2)_2 \text{Si} (\text{OCH}_3)_2 (\text{OH})_2$
 $\text{CF}_3 (\text{CF}_2)_3 (\text{CH}_2)_2 \text{Si} (\text{OCH}_3)_2 (\text{OH})_2$
 $\text{CF}_3 (\text{CF}_2)_5 (\text{CH}_2)_2 \text{Si} (\text{OCH}_3)_2 (\text{OH})_2$
 $\text{CF}_3 (\text{CF}_2)_7 (\text{CH}_2)_2 \text{Si} (\text{OCH}_3)_2 (\text{OH})_2$
 $\text{CF}_3 (\text{CF}_2)_3 (\text{CH}_2)_3 \text{Si} (\text{OCH}_3)_2 (\text{OH})_2$
 $\text{CF}_3 (\text{CF}_2)_5 (\text{CH}_2)_3 \text{Si} (\text{OCH}_3)_2 (\text{OH})_2$
 $\text{CF}_3 (\text{CF}_2)_7 (\text{CH}_2)_3 \text{Si} (\text{OCH}_3)_2 (\text{OH})_2$
 $\text{CF}_3 (\text{CF}_2)_4 \text{O} (\text{CF}_2)_2 (\text{CH}_2)_2 \text{Si} (\text{OCH}_3)_2 (\text{OH})_2$
 $\text{CF}_3 (\text{CF}_2)_4 \text{O} (\text{CF}_2)_2 (\text{CH}_2)_3 \text{Si} (\text{OCH}_3)_2 (\text{OH})_2$
 $\text{CF}_3 (\text{CF}_2)_7 (\text{CH}_2)_2 \text{O} (\text{CH}_2)_3 \text{Si} (\text{OCH}_3)_2 (\text{OH})_2$
 $\text{CF}_3 (\text{CF}_2)_7 \text{CONH} (\text{CH}_2)_2 \text{Si} (\text{OCH}_3)_2 (\text{OH})_2$
 $\text{CF}_3 (\text{CF}_2)_7 \text{CONH} (\text{CH}_2)_3 \text{Si} (\text{OCH}_3)_2 (\text{OH})_2$
 $\text{CF}_3 (\text{CF}_2)_3 \text{O} [\text{CF} (\text{CF}_3) \text{CF} (\text{CF}_3) \text{O}]_2 \text{CF} (\text{CF}_3) \text{CONH} (\text{CH}_2)_3 \text{Si} (\text{OCH}_3)_2 (\text{OH})_2$

【0053】

$\text{CF}_3 (\text{CH}_2)_2 \text{Si} (\text{OCH}_3)_2 (\text{OH})_2$
 $\text{CF}_3 (\text{CF}_2)_3 (\text{CH}_2)_2 \text{Si} (\text{OCH}_3)_2 (\text{OH})_2$
 $\text{CF}_3 (\text{CF}_2)_5 (\text{CH}_2)_2 \text{Si} (\text{OCH}_3)_2 (\text{OH})_2$

$$\begin{array}{l} \text{CF}_3 (\text{CF}_2)_7 (\text{CH}_2)_2 \text{Si} (\text{OCH}_3)_2 (\text{OH}) \\ \text{CF}_3 (\text{CF}_2)_3 (\text{CH}_2)_3 \text{Si} (\text{OCH}_3)_2 (\text{OH}) \\ \text{CF}_3 (\text{CF}_2)_5 (\text{CH}_2)_3 \text{Si} (\text{OCH}_3)_2 (\text{OH}) \\ \text{CF}_3 (\text{CF}_2)_7 (\text{CH}_2)_3 \text{Si} (\text{OCH}_3)_2 (\text{OH}) \\ \text{CF}_3 (\text{CF}_2)_4 \text{O} (\text{CF}_2)_2 (\text{CH}_2)_2 \text{Si} (\text{OCH}_3)_2 (\text{OH}) \\ \text{CF}_3 (\text{CF}_2)_4 \text{O} (\text{CF}_2)_2 (\text{CH}_2)_3 \text{Si} (\text{OCH}_3)_2 (\text{OH}) \\ \text{CF}_3 (\text{CF}_2)_7 (\text{CH}_2)_2 \text{O} (\text{CH}_2)_3 \text{Si} (\text{OCH}_3)_2 (\text{OH}) \\ \text{CF}_3 (\text{CF}_2)_7 \text{CONH} (\text{CH}_2)_2 \text{Si} (\text{OCH}_3)_2 (\text{OH}) \\ \text{CF}_3 (\text{CF}_2)_7 \text{CONH} (\text{CH}_2)_3 \text{Si} (\text{OCH}_3)_2 (\text{OH}) \\ \text{CF}_3 (\text{CF}_2)_3 \text{O} [\text{CF} (\text{CF}_3) \text{CF} (\text{CF}_3) \text{O}]_2 \text{CF} (\text{CF}_3) \text{CONH} (\text{CH}_2)_3 \text{Si} (\text{OCH}_3)_2 (\text{OH}) \end{array}$$

【0054】

$$\begin{aligned}
&\text{CH}_3 (\text{CH}_2)_7 \text{Si} (\text{OCH}_3) (\text{OH})_2 \\
&\text{CH}_3 (\text{CF}_2)_7 (\text{CH}_2)_2 \text{Si} (\text{OCH}_3) (\text{OH})_2 \\
&\text{CH}_3 (\text{CF}_2)_7 (\text{CH}_2)_2 \text{Si} (\text{NCO}) (\text{OH})_2 \\
&\text{CH}_3 (\text{CF}_2)_8 (\text{CH}_2)_2 \text{Si} (\text{OCH}_3) (\text{OH})_2 \\
&\text{CH}_3 (\text{CF}_2)_8 (\text{CH}_2)_2 \text{Si} (\text{NCO}) (\text{OH})_2 \\
&\text{CH}_3 (\text{CF}_2)_9 (\text{CH}_2)_2 \text{Si} (\text{OCH}_3) (\text{OH})_2 \\
&\text{CH}_3 (\text{CF}_2)_9 (\text{CH}_2)_2 \text{Si} (\text{NCO}) (\text{OH})_2 \\
&\text{CH}_3 \text{CH}_2 (\text{CF}_2)_6 (\text{CH}_2)_2 \text{Si} (\text{OCH}_3) (\text{OH})_2 \\
&\text{CH}_3 \text{CH}_2 (\text{CF}_2)_6 (\text{CH}_2)_2 \text{Si} (\text{OCH}_3) (\text{OH})_2 \\
&\text{CH}_3 \text{CH}_2 (\text{CF}_2)_6 (\text{CH}_2)_2 \text{Si} (\text{NCO}) (\text{OH})_2 \\
&\text{CH}_3 \text{CH}_2 (\text{CF}_2)_8 (\text{CH}_2)_2 \text{Si} (\text{OCH}_3) (\text{OH})_2 \\
&\text{CH}_3 \text{CH}_2 (\text{CF}_2)_8 (\text{CH}_2)_2 \text{Si} (\text{NCO}) (\text{OH})_2 \\
&\text{CH}_3 \text{CH}_2 (\text{CF}_2)_{10} (\text{CH}_2)_2 \text{Si} (\text{OCH}_3) (\text{OH})_2 \\
&\text{CH}_3 (\text{CF}_2)_4 \text{O} (\text{CF}_2)_2 (\text{CH}_2)_2 \text{Si} (\text{OCH}_3) (\text{OH})_2 \\
&\text{CH}_3 (\text{CF}_2)_7 (\text{CH}_2)_2 \text{O} (\text{CH}_2)_3 \text{Si} (\text{OCH}_3) (\text{OH})_2 \\
&\text{CH}_3 (\text{CF}_2)_8 (\text{CH}_2)_2 \text{O} (\text{CH}_2)_3 \text{Si} (\text{OCH}_3) (\text{OH})_2 \\
&\text{CH}_3 (\text{CF}_2)_9 (\text{CH}_2)_2 \text{O} (\text{CH}_2)_3 \text{Si} (\text{OCH}_3) (\text{OH})_2 \\
&\text{CH}_3 \text{CH}_2 (\text{CF}_2)_6 (\text{CH}_2)_2 \text{O} (\text{CH}_2)_3 \text{Si} (\text{OCH}_3) (\text{OH})_2 \\
&\text{CH}_3 (\text{CF}_2)_6 \text{CONH} (\text{CH}_2)_3 \text{Si} (\text{OCH}_3) (\text{OH})_2 \\
&\text{CH}_3 (\text{CF}_2)_8 \text{CONH} (\text{CH}_2)_3 \text{Si} (\text{OCH}_3) (\text{OH})_2 \\
&\text{CH}_3 (\text{CF}_2)_3 \text{O} [\text{CF} (\text{CF}_3) \text{CF} (\text{CF}_3) \text{O}]_2 \text{CF} (\text{CF}_3) \text{CONH} (\text{CH}_2)_3 \text{Si} (\text{OCH}_3) (\text{OH})_2
\end{aligned}$$

【0055】

$$\begin{aligned}
&\text{CF}_3 (\text{CF}_2)_3 (\text{CH}_2)_2 \text{Si} (\text{CH}_3) (\text{OCH}_3) (\text{OH}) \\
&\text{CF}_3 (\text{CF}_2)_5 (\text{CH}_2)_2 \text{Si} (\text{CH}_3) (\text{OCH}_3) (\text{OH}) \\
&\text{CF}_3 (\text{CH}_2)_2 \text{Si} (\text{CH}_3) (\text{OCH}_3) (\text{OH}) \\
&\text{CF}_3 (\text{CF}_2)_3 (\text{CH}_2)_3 \text{Si} (\text{CH}_3) (\text{OCH}_3) (\text{OH}) \\
&\text{CF}_3 (\text{CF}_2)_5 (\text{CH}_2)_3 \text{Si} (\text{CH}_3) (\text{OCH}_3) (\text{OH}) \\
&\text{CF}_3 (\text{CF}_2)_7 (\text{CH}_2)_3 \text{Si} (\text{CH}_3) (\text{OCH}_3) (\text{OH}) \\
&\text{CF}_3 (\text{CF}_2)_4 (\text{CF}_2)_2 (\text{CH}_2)_2 \text{Si} (\text{CH}_3) (\text{OCH}_3) (\text{OH}) \\
&\text{CF}_3 (\text{CF}_2)_4 (\text{CF}_2)_2 (\text{CH}_2)_3 \text{Si} (\text{CH}_3) (\text{OCH}_3) (\text{OH}) \\
&\text{CF}_3 (\text{CF}_2)_4 (\text{CH}_2)_2 \text{O} (\text{CH}_2)_3 \text{Si} (\text{CH}_3) (\text{OCH}_3) (\text{OH}) \\
&\text{CF}_3 (\text{CF}_2)_7 \text{CONH} (\text{CH}_2)_2 \text{Si} (\text{CH}_3) (\text{OCH}_3) (\text{OH}) \\
&\text{CF}_3 (\text{CF}_2)_7 \text{CONH} (\text{CH}_2)_3 \text{Si} (\text{CH}_3) (\text{OCH}_3) (\text{OH}) \\
&\text{CF}_3 (\text{CF}_2)_3 \text{O} [\text{CF} (\text{CF}_3) \text{CF} (\text{CF}_3) \text{O}]_2 \text{CF} (\text{CF}_3) \text{CONH} (\text{CH}_2)_3 \text{Si} (\text{CH}_3) (\text{OCH}_3) (\text{OH}) \\
&\text{CH}_3 (\text{CH}_2)_7 \text{Si} (\text{OCH}_3)_2 (\text{OH}) \\
&\text{CH}_3 (\text{CF}_2)_7 (\text{CH}_2)_2 \text{Si} (\text{OCH}_3)_2 (\text{OH})
\end{aligned}$$

$\text{CH}_3 (\text{CF}_2)_7 (\text{CH}_2)_2 \text{Si} (\text{CH}_3) (\text{OCH}_3) (\text{OH})$
 $\text{CH}_3 (\text{CF}_2)_7 (\text{CH}_2)_2 \text{Si} (\text{OCH}_3)_2 (\text{OH})$
 $\text{CH}_3 (\text{CF}_2)_7 (\text{CH}_2)_2 \text{Si} (\text{NCO})_2 (\text{OH})$
 $\text{CH}_3 (\text{CF}_2)_8 (\text{CH}_2)_2 \text{Si} (\text{OCH}_3)_2 (\text{OH})$
 $\text{CH}_3 (\text{CF}_2)_8 (\text{CH}_2)_2 \text{Si} (\text{NCO})_2 (\text{OH})$
 $\text{CH}_3 (\text{CF}_2)_9 (\text{CH}_2)_2 \text{Si} (\text{OCH}_3)_2 (\text{OH})$
 $\text{CH}_3 (\text{CF}_2)_9 (\text{CH}_2)_2 \text{Si} (\text{NCO})_2 (\text{OH})$
 $\text{CH}_3 \text{CH}_2 (\text{CF}_2)_6 (\text{CH}_2)_2 \text{Si} (\text{OCH}_3)_2 (\text{OH})$
 $\text{CH}_3 \text{CH}_2 (\text{CF}_2)_6 (\text{CH}_2)_2 \text{Si} (\text{NCO})_2 (\text{OH})$
 $\text{CH}_3 \text{CH}_2 (\text{CF}_2)_8 (\text{CH}_2)_2 \text{Si} (\text{OCH}_3)_2 (\text{OH})$
 $\text{CH}_3 \text{CH}_2 (\text{CF}_2)_8 (\text{CH}_2)_2 \text{Si} (\text{NCO})_2 (\text{OH})$
 $\text{CH}_3 \text{CH}_2 (\text{CF}_2)_{10} (\text{CH}_2)_2 \text{Si} (\text{OCH}_3)_2 (\text{OH})$
 $\text{CH}_3 (\text{CF}_2)_4 \text{O} (\text{CF}_2)_2 (\text{CH}_2)_2 \text{Si} (\text{OCH}_3)_2 (\text{OH})$
 $\text{CH}_3 (\text{CF}_2)_7 (\text{CH}_2)_2 \text{O} (\text{CH}_2)_3 \text{Si} (\text{OCH}_3)_2 (\text{OH})$
 $\text{CH}_3 (\text{CF}_2)_8 (\text{CH}_2)_2 \text{O} (\text{CH}_2)_3 \text{Si} (\text{OCH}_3)_2 (\text{OH})$
 $\text{CH}_3 (\text{CF}_2)_9 (\text{CH}_2)_2 \text{O} (\text{CH}_2)_3 \text{Si} (\text{OCH}_3)_2 (\text{OH})$
 $\text{CH}_3 \text{CH}_2 (\text{CF}_2)_6 (\text{CH}_2)_2 \text{O} (\text{CH}_2)_3 \text{Si} (\text{OCH}_3)_2 (\text{OH})$
 $\text{CH}_3 (\text{CF}_2)_6 \text{CONH} (\text{CH}_2)_3 \text{Si} (\text{OCH}_3)_2 (\text{OH})$
 $\text{CH}_3 (\text{CF}_2)_8 \text{CONH} (\text{CH}_2)_3 \text{Si} (\text{OCH}_3)_2 (\text{OH})$
 $\text{CH}_3 (\text{CF}_2)_3 \text{O} [\text{CF} (\text{CF}_3) \text{CF} (\text{CF}_3) \text{O}]_2 \text{CF} (\text{CF}_3) \text{CONH} (\text{CH}_2)_3 \text{Si} (\text{OCH}_3)_2 (\text{OH})$

【0056】

$\text{CH}_3 \text{CH}_2 \text{O} (\text{CH}_2)_{15} \text{Si} (\text{OH})_3$
 $\text{CF}_3 \text{CH}_2 \text{O} (\text{CH}_2)_{15} \text{Si} (\text{OH})_3$
 $\text{CH}_3 (\text{CH}_2)_2 \text{Si} (\text{CH}_3)_2 (\text{CH}_2)_{15} \text{Si} (\text{OH})_3$
 $\text{CH}_3 (\text{CH}_2)_6 \text{Si} (\text{CH}_3)_2 (\text{CH}_2)_9 \text{Si} (\text{OH})_3$
 $\text{CH}_3 \text{COO} (\text{CH}_2)_{15} \text{Si} (\text{OH})_3$
 $\text{CF}_3 (\text{CF}_2)_5 (\text{CH}_2)_2 \text{Si} (\text{OH})_3$
 $\text{CF}_3 (\text{CF}_2)_7 (\text{CH}=\text{CH})_3 \text{Si} (\text{OH})_3$
 $\text{CH}_3 \text{CH}_2 \text{O} (\text{CH}_2)_{15} \text{Si} (\text{OH})_3$
 $\text{CH}_3 (\text{CH}_2)_2 \text{Si} (\text{CH}_3)_2 (\text{CH}_2)_{15} \text{Si} (\text{OH})_3$
 $\text{CH}_3 (\text{CH}_2)_6 \text{Si} (\text{CH}_3)_2 (\text{CH}_2)_9 \text{Si} (\text{OH})_3$
 $\text{CF}_3 (\text{CH}_2)_6 \text{Si} (\text{CH}_3)_2 (\text{CH}_2)_9 \text{Si} (\text{OH})_3$
 $\text{CH}_3 \text{COO} (\text{CH}_2)_{15} \text{Si} (\text{OH})_3$
 $\text{CF}_3 \text{COO} (\text{CH}_2)_{15} \text{Si} (\text{OH})_3$
 $\text{CF}_3 (\text{CF}_2)_9 (\text{CH}_2)_2 \text{Si} (\text{OH})_3$
 $\text{CF}_3 (\text{CF}_2)_7 (\text{CH}_2)_2 \text{Si} (\text{OH})_3$
 $\text{CF}_3 (\text{CF}_2)_5 (\text{CH}_2)_2 \text{Si} (\text{OH})_3$
 $\text{CF}_3 (\text{CF}_2)_7 (\text{CH}=\text{CH})_3 \text{Si} (\text{OH})_3$
 $\text{CF}_3 (\text{CF}_2)_9 (\text{CH}_2)_2 \text{Si} (\text{OH})_3$
 $\text{CF}_3 (\text{CF}_2)_5 (\text{CH}_2)_2 \text{Si} (\text{OH})_3$
 $\text{CF}_3 (\text{CF}_2)_7 (\text{CH}_2)_2 \text{Si} (\text{CH}_3)_2 (\text{OH})$
 $\text{CF}_3 (\text{CH}_2)_2 \text{Si} (\text{OH})_3$
 $\text{CF}_3 (\text{CF}_2)_3 (\text{CH}_2)_2 \text{Si} (\text{OH})_3$
 $\text{CF}_3 (\text{CF}_2)_5 (\text{CH}_2)_2 \text{Si} (\text{OH})_3$
 $\text{CF}_3 (\text{CF}_2)_7 (\text{CH}_2)_2 \text{Si} (\text{OH})_3$
 $\text{CF}_3 (\text{CF}_2)_3 (\text{CH}_2)_3 \text{Si} (\text{OH})_3$
 $\text{CF}_3 (\text{CF}_2)_5 (\text{CH}_2)_3 \text{Si} (\text{OH})_3$
 $\text{CF}_3 (\text{CF}_2)_7 (\text{CH}_2)_3 \text{Si} (\text{OH})_3$
 $\text{CF}_3 (\text{CF}_2)_4 \text{O} (\text{CF}_2)_2 (\text{CH}_2)_2 \text{Si} (\text{OH})_3$

$\text{CF}_3 (\text{CF}_2)_4 \text{O} (\text{CF}_2)_2 (\text{CH}_2)_3 \text{Si} (\text{OH})_3$
 $\text{CF}_3 (\text{CF}_2)_7 (\text{CH}_2)_2 \text{O} (\text{CH}_2)_3 \text{Si} (\text{OH})_3$
 $\text{CF}_3 (\text{CF}_2)_7 \text{CONH} (\text{CH}_2)_2 \text{Si} (\text{OH})_3$
 $\text{CF}_3 (\text{CF}_2)_7 \text{CONH} (\text{CH}_2)_3 \text{Si} (\text{OH})_3$
 $\text{CF}_3 (\text{CF}_2)_3 \text{O} [\text{CF} (\text{CF}_3) \text{CF} (\text{CF}_3) \text{O}]_2 \text{CF} (\text{CF}_3) \text{CONH} (\text{CH}_2)_3 \text{Si} (\text{OH})_3$
 $\text{CH}_3 (\text{CH}_2)_7 \text{Si} (\text{OH})_3$
 $\text{CH}_3 (\text{CF}_2)_7 (\text{CH}_2)_2 \text{Si} (\text{OH})_3$
 $\text{CH}_3 (\text{CF}_2)_7 (\text{CH}_2)_2 \text{Si} (\text{OH})_3$
 $\text{CH}_3 (\text{CF}_2)_8 (\text{CH}_2)_2 \text{Si} (\text{OH})_3$
 $\text{CH}_3 (\text{CF}_2)_9 (\text{CH}_2)_2 \text{Si} (\text{OH})_3$
 $\text{CH}_3 \text{CH}_2 (\text{CF}_2)_6 (\text{CH}_2)_2 \text{Si} (\text{OH})_3$
 $\text{CH}_3 \text{CH}_2 (\text{CF}_2)_8 (\text{CH}_2)_2 \text{Si} (\text{OH})_3$
 $\text{CH}_3 \text{CH}_2 (\text{CF}_2)_{10} (\text{CH}_2)_2 \text{Si} (\text{OH})_3$
 $\text{CH}_3 (\text{CF}_2)_4 \text{O} (\text{CF}_2)_2 (\text{CH}_2)_2 \text{Si} (\text{OH})_3$
 $\text{CH}_3 (\text{CF}_2)_7 (\text{CH}_2)_2 \text{O} (\text{CH}_2)_3 \text{Si} (\text{OH})_3$
 $\text{CH}_3 (\text{CF}_2)_8 (\text{CH}_2)_2 \text{O} (\text{CH}_2)_3 \text{Si} (\text{OH})_3$
 $\text{CH}_3 (\text{CF}_2)_9 (\text{CH}_2)_2 \text{O} (\text{CH}_2)_3 \text{Si} (\text{OH})_3$
 $\text{CH}_3 \text{CH}_2 (\text{CF}_2)_6 (\text{CH}_2)_2 \text{O} (\text{CH}_2)_3 \text{Si} (\text{OH})_3$
 $\text{CH}_3 (\text{CF}_2)_6 \text{CONH} (\text{CH}_2)_3 \text{Si} (\text{OH})_3$
 $\text{CH}_3 (\text{CF}_2)_8 \text{CONH} (\text{CH}_2)_3 \text{Si} (\text{OH})_3$
 $\text{CH}_3 (\text{CF}_2)_3 \text{O} [\text{CF} (\text{CF}_3) \text{CF} (\text{CF}_3) \text{O}]_2 \text{CF} (\text{CF}_3) \text{CONH} (\text{CH}_2)_3 \text{Si} (\text{OH})_3$
 $\text{CF}_3 (\text{CF}_2)_3 (\text{CH}_2)_2 \text{Si} (\text{CH}_3) (\text{OH})_2$
 $\text{CF}_3 (\text{CF}_2)_5 (\text{CH}_2)_2 \text{Si} (\text{CH}_3) (\text{OH})_2$
 $\text{CF}_3 (\text{CH}_2)_2 \text{Si} (\text{CH}_3) (\text{OH})_2$
 $\text{CF}_3 (\text{CF}_2)_3 (\text{CH}_2)_3 \text{Si} (\text{CH}_3) (\text{OH})_2$
 $\text{CF}_3 (\text{CF}_2)_5 (\text{CH}_2)_3 \text{Si} (\text{CH}_3) (\text{OH})_2$
 $\text{CF}_3 (\text{CF}_2)_7 (\text{CH}_2)_3 \text{Si} (\text{CH}_3) (\text{OH})_2$
 $\text{CF}_3 (\text{CF}_2)_4 (\text{CF}_2)_2 (\text{CH}_2)_2 \text{Si} (\text{CH}_3) (\text{OH})_2$
 $\text{CF}_3 (\text{CF}_2)_4 (\text{CF}_2)_2 (\text{CH}_2)_3 \text{Si} (\text{CH}_3) (\text{OH})_2$
 $\text{CF}_3 (\text{CF}_2)_4 (\text{CH}_2)_2 \text{O} (\text{CH}_2)_3 \text{Si} (\text{CH}_3) (\text{OH})_2$
 $\text{CF}_3 (\text{CF}_2)_7 \text{CONH} (\text{CH}_2)_2 \text{Si} (\text{CH}_3) (\text{OH})_2$
 $\text{CF}_3 (\text{CF}_2)_7 \text{CONH} (\text{CH}_2)_3 \text{Si} (\text{CH}_3) (\text{OH})_2$
 $\text{CF}_3 (\text{CF}_2)_3 \text{O} [\text{CF} (\text{CF}_3) \text{CF} (\text{CF}_3) \text{O}]_2 \text{CF} (\text{CF}_3) \text{CONH} (\text{CH}_2)_3 \text{Si} (\text{CH}_3) (\text{OH})_2$
 $\text{CH}_3 (\text{CF}_2)_7 (\text{CH}_2)_2 \text{Si} (\text{CH}_3) (\text{OH})_2$

【0057】

これらの化合物は1種単独で、あるいは2種以上を組み合わせて用いることができる。

【0058】

本発明における工程(B-1)中の、少なくとも1以上の加水分解性基を有する金属系界面活性剤と相互作用し得る化合物は、金属系界面活性剤の金属部分又は加水分解性基部分若しくは水酸基部分と、配位結合や水素結合等の化学結合をすることにより、前記金属系界面活性剤の加水分解性基又は水酸基を活性化させ、金属系界面活性剤の縮合を促進させる作用を有する化合物を意味する。工程(B-1)の金属系界面活性剤と相互作用し得る化合物は、前述の作用を有している限り特に制限されないが、なかでも、金属酸化物；金属水酸化物；金属アルコキシド類；キレート化又は配位化された金属化合物；金属アルコキシド類部分加水分解生成物；金属アルコキシド類を2倍当量以上の水で処理して得られた加水分解生成物、及びシラノール縮合触媒から群から選ばれる少なくとも1種の化合物が好ましく、金属アルコキシド類、金属アルコキシド類部分加水分解生成物がより好ま

しい。

【0059】

金属酸化物；金属水酸化物；金属アルコキシド類；キレート化又は配位化された金属化合物；金属アルコキシド類部分加水分解生成物；金属アルコキシド類を2倍当量以上の水で処理して得られた加水分解生成物、及びシラノール縮合触媒における金属としては特に制限されないが、チタン、ジルコニウム、アルミニウム、ケイ素、ゲルマニウム、インジウム、スズ、タンタル、亜鉛、タングステン及び鉛からなる群から選ばれる少なくとも1種であるのが好ましく、チタン、ジルコニウム、アルミニウム又はケイ素であるのがより好ましく、チタン又はケイ素が特に好ましい。

【0060】

金属酸化物は、ゾル、ゲル、固体状等の何れの状態のものも使用することができる。ゲル、ゾルの製造方法は、特に限定されず、例えばシリカゾルを例にとると、珪酸ナトリウム溶液を陽イオン交換する方法、シリコンアルコキシドを加水分解する方法等を例示することができる。特に、有機溶媒中に安定に分散しているゾルが好ましく、さらに、ゾルの粒子径が10～100nmの範囲であることがより好ましく、10～20nmの範囲であることがさらに好ましい。ゾルの形状は特に限定されず、球状、細長い形状等、いずれのものも用いることができる。

【0061】

金属酸化物として、具体的には、メタノールシリカゾル、IPA-ST、IPA-ST-UP、IPA-ST-ZL、NPC-ST-30、DMAC-ST、MEK-ST、MIBK-ST、XBA-ST、PMA-ST（以上、いずれも日産化学工業（株）社製オルガノシリカゾルの商品名を表す。）等を例示することができる。

【0062】

用いる金属酸化物の量は、化学吸着膜の形成を阻害しない量であれば特に制限されないが、金属系界面活性剤に対して触媒量用いることが好ましく、金属系界面活性剤1モルに対して酸化物換算モル数で、0.001～1モルの範囲で用いることがより好ましく、0.001～0.2モルの範囲で用いることがさらに好ましい。これらの金属酸化物は1種単独で、あるいは2種以上を組み合わせ用いることができる。

【0063】

金属水酸化物としては、金属の水酸化物であれば、どのような製造方法で得られたものであってもよい。金属水酸化物の製造方法としては、後述の金属アルコキシド類を加水分解する方法、金属塩を金属水酸化物と反応させる方法等が挙げられる。また、金属水酸化物として市販されているものを、所望により精製して使用することもできる。

【0064】

金属アルコキシド類のアルコキシ基の炭素数は特に限定されないが、含有酸化物濃度、有機物の脱離の容易さ、入手の容易さ等から、炭素数は1～4であることがより好ましい。本発明に用いる金属アルコキシド類の具体例としては、 $\text{Si}(\text{OCH}_3)_4$ 、 $\text{Si}(\text{OC}_2\text{H}_5)_4$ 、 $\text{Si}(\text{OC}_3\text{H}_7-i)_4$ 、 $\text{Si}(\text{OC}_4\text{H}_9-t)_4$ 等のケイ素アルコキシド； $\text{Ti}(\text{OCH}_3)_4$ 、 $\text{Ti}(\text{OC}_2\text{H}_5)_4$ 、 $\text{Ti}(\text{OC}_3\text{H}_7-i)_4$ 、 $\text{Ti}(\text{OC}_4\text{H}_9)_4$ 等のチタンアルコキシド； $\text{Ti}[\text{OSi}(\text{CH}_3)_3]_4$ 、 $\text{Ti}[\text{OSi}(\text{C}_2\text{H}_5)_3]_4$ 等のテトラキストリアルキルシロキシチタン； $\text{Zr}(\text{OCH}_3)_4$ 、 $\text{Zr}(\text{OC}_2\text{H}_5)_4$ 、 $\text{Zr}(\text{OC}_3\text{H}_7)_4$ 、 $\text{Zr}(\text{OC}_4\text{H}_9)_4$ 等のジルコニウムアルコキシド； $\text{Al}(\text{OCH}_3)_3$ 、 $\text{Al}(\text{OC}_2\text{H}_5)_3$ 、 $\text{Al}(\text{OC}_3\text{H}_7-i)_3$ 、 $\text{Al}(\text{OC}_4\text{H}_9)_3$ 等のアルミニウムアルコキシド； $\text{Ge}(\text{OC}_2\text{H}_5)_4$ 等のゲルマニウムアルコキシド； $\text{In}(\text{OCH}_3)_3$ 、 $\text{In}(\text{OC}_2\text{H}_5)_3$ 、 $\text{In}(\text{OC}_3\text{H}_7-i)_3$ 、 $\text{In}(\text{OC}_4\text{H}_9)_3$ 等のインジウムアルコキシド； $\text{Sn}(\text{OCH}_3)_4$ 、 $\text{Sn}(\text{OC}_2\text{H}_5)_4$ 、 $\text{Sn}(\text{OC}_3\text{H}_7-i)_4$ 、 $\text{Sn}(\text{OC}_4\text{H}_9)_4$ 等のスズアルコキシド； $\text{Ta}(\text{OCH}_3)_5$ 、 $\text{Ta}(\text{OC}_2\text{H}_5)_5$ 、 $\text{Ta}(\text{OC}_3\text{H}_7-i)_5$ 、 $\text{Ta}(\text{OC}_4\text{H}_9)_5$ 等のタンタルアルコキシド； $\text{W}(\text{OCH}_3)_6$ 、 $\text{W}(\text{OC}_2\text{H}_5)_6$ 、 $\text{W}(\text{OC}_3\text{H}_7-i)_6$ 、 $\text{W}(\text{OC}_4\text{H}_9)_6$ 等のタングステンアルコキシド； $\text{Zn}(\text{OCH}_3)_2$ 、 $\text{Zn}(\text{OC}_2\text{H}_5)_2$ 、 $\text{Zn}(\text{OC}_3\text{H}_7-i)_2$ 、 $\text{Zn}(\text{OC}_4\text{H}_9)_2$ 等の亜鉛アルコキシド； $\text{Pb}(\text{OCH}_3)_4$ 、 $\text{Pb}(\text{OC}_2\text{H}_5)_4$ 、 $\text{Pb}(\text{OC}_3\text{H}_7-i)_4$ 、 $\text{Pb}(\text{OC}_4\text{H}_9)_4$ 等の鉛アルコキシド； $\text{Bi}(\text{OCH}_3)_3$ 、 $\text{Bi}(\text{OC}_2\text{H}_5)_3$ 、 $\text{Bi}(\text{OC}_3\text{H}_7-i)_3$ 、 $\text{Bi}(\text{OC}_4\text{H}_9)_3$ 等のビスマスアルコキシド； $\text{Sb}(\text{OCH}_3)_3$ 、 $\text{Sb}(\text{OC}_2\text{H}_5)_3$ 、 $\text{Sb}(\text{OC}_3\text{H}_7-i)_3$ 、 $\text{Sb}(\text{OC}_4\text{H}_9)_3$ 等のアンチモンアルコキシド； $\text{As}(\text{OCH}_3)_3$ 、 $\text{As}(\text{OC}_2\text{H}_5)_3$ 、 $\text{As}(\text{OC}_3\text{H}_7-i)_3$ 、 $\text{As}(\text{OC}_4\text{H}_9)_3$ 等のヒ素アルコキシド； $\text{V}(\text{OCH}_3)_5$ 、 $\text{V}(\text{OC}_2\text{H}_5)_5$ 、 $\text{V}(\text{OC}_3\text{H}_7-i)_5$ 、 $\text{V}(\text{OC}_4\text{H}_9)_5$ 等のバナジウムアルコキシド； $\text{Nb}(\text{OCH}_3)_5$ 、 $\text{Nb}(\text{OC}_2\text{H}_5)_5$ 、 $\text{Nb}(\text{OC}_3\text{H}_7-i)_5$ 、 $\text{Nb}(\text{OC}_4\text{H}_9)_5$ 等のニオブアルコキシド； $\text{Mo}(\text{OCH}_3)_6$ 、 $\text{Mo}(\text{OC}_2\text{H}_5)_6$ 、 $\text{Mo}(\text{OC}_3\text{H}_7-i)_6$ 、 $\text{Mo}(\text{OC}_4\text{H}_9)_6$ 等のモリブデンアルコキシド； $\text{Cr}(\text{OCH}_3)_6$ 、 $\text{Cr}(\text{OC}_2\text{H}_5)_6$ 、 $\text{Cr}(\text{OC}_3\text{H}_7-i)_6$ 、 $\text{Cr}(\text{OC}_4\text{H}_9)_6$ 等のクロムアルコキシド； $\text{Mn}(\text{OCH}_3)_5$ 、 $\text{Mn}(\text{OC}_2\text{H}_5)_5$ 、 $\text{Mn}(\text{OC}_3\text{H}_7-i)_5$ 、 $\text{Mn}(\text{OC}_4\text{H}_9)_5$ 等のマンガンアルコキシド； $\text{Co}(\text{OCH}_3)_5$ 、 $\text{Co}(\text{OC}_2\text{H}_5)_5$ 、 $\text{Co}(\text{OC}_3\text{H}_7-i)_5$ 、 $\text{Co}(\text{OC}_4\text{H}_9)_5$ 等のコバルトアルコキシド； $\text{Ni}(\text{OCH}_3)_5$ 、 $\text{Ni}(\text{OC}_2\text{H}_5)_5$ 、 $\text{Ni}(\text{OC}_3\text{H}_7-i)_5$ 、 $\text{Ni}(\text{OC}_4\text{H}_9)_5$ 等のニッケルアルコキシド； $\text{Fe}(\text{OCH}_3)_5$ 、 $\text{Fe}(\text{OC}_2\text{H}_5)_5$ 、 $\text{Fe}(\text{OC}_3\text{H}_7-i)_5$ 、 $\text{Fe}(\text{OC}_4\text{H}_9)_5$ 等の鉄アルコキシド； $\text{Cu}(\text{OCH}_3)_5$ 、 $\text{Cu}(\text{OC}_2\text{H}_5)_5$ 、 $\text{Cu}(\text{OC}_3\text{H}_7-i)_5$ 、 $\text{Cu}(\text{OC}_4\text{H}_9)_5$ 等の銅アルコキシド； $\text{Ag}(\text{OCH}_3)_5$ 、 $\text{Ag}(\text{OC}_2\text{H}_5)_5$ 、 $\text{Ag}(\text{OC}_3\text{H}_7-i)_5$ 、 $\text{Ag}(\text{OC}_4\text{H}_9)_5$ 等の銀アルコキシド； $\text{Hg}(\text{OCH}_3)_6$ 、 $\text{Hg}(\text{OC}_2\text{H}_5)_6$ 、 $\text{Hg}(\text{OC}_3\text{H}_7-i)_6$ 、 $\text{Hg}(\text{OC}_4\text{H}_9)_6$ 等の水銀アルコキシド； $\text{Ca}(\text{OCH}_3)_2$ 、 $\text{Ca}(\text{OC}_2\text{H}_5)_2$ 、 $\text{Ca}(\text{OC}_3\text{H}_7-i)_2$ 、 $\text{Ca}(\text{OC}_4\text{H}_9)_2$ 等のカルシウムアルコキシド； $\text{Sr}(\text{OCH}_3)_2$ 、 $\text{Sr}(\text{OC}_2\text{H}_5)_2$ 、 $\text{Sr}(\text{OC}_3\text{H}_7-i)_2$ 、 $\text{Sr}(\text{OC}_4\text{H}_9)_2$ 等のストロンチウムアルコキシド； $\text{Ba}(\text{OCH}_3)_2$ 、 $\text{Ba}(\text{OC}_2\text{H}_5)_2$ 、 $\text{Ba}(\text{OC}_3\text{H}_7-i)_2$ 、 $\text{Ba}(\text{OC}_4\text{H}_9)_2$ 等のバリウムアルコキシド； $\text{Mg}(\text{OCH}_3)_2$ 、 $\text{Mg}(\text{OC}_2\text{H}_5)_2$ 、 $\text{Mg}(\text{OC}_3\text{H}_7-i)_2$ 、 $\text{Mg}(\text{OC}_4\text{H}_9)_2$ 等のマグネシウムアルコキシド； $\text{Be}(\text{OCH}_3)_2$ 、 $\text{Be}(\text{OC}_2\text{H}_5)_2$ 、 $\text{Be}(\text{OC}_3\text{H}_7-i)_2$ 、 $\text{Be}(\text{OC}_4\text{H}_9)_2$ 等のベリリウムアルコキシド； $\text{Li}(\text{OCH}_3)$ 、 $\text{Li}(\text{OC}_2\text{H}_5)$ 、 $\text{Li}(\text{OC}_3\text{H}_7-i)$ 、 $\text{Li}(\text{OC}_4\text{H}_9)$ 等のリチウムアルコキシド； $\text{K}(\text{OCH}_3)$ 、 $\text{K}(\text{OC}_2\text{H}_5)$ 、 $\text{K}(\text{OC}_3\text{H}_7-i)$ 、 $\text{K}(\text{OC}_4\text{H}_9)$ 等のカリウムアルコキシド； $\text{Rb}(\text{OCH}_3)$ 、 $\text{Rb}(\text{OC}_2\text{H}_5)$ 、 $\text{Rb}(\text{OC}_3\text{H}_7-i)$ 、 $\text{Rb}(\text{OC}_4\text{H}_9)$ 等のルビウムアルコキシド； $\text{Cs}(\text{OCH}_3)$ 、 $\text{Cs}(\text{OC}_2\text{H}_5)$ 、 $\text{Cs}(\text{OC}_3\text{H}_7-i)$ 、 $\text{Cs}(\text{OC}_4\text{H}_9)$ 等のセシウムアルコキシド； $\text{Na}(\text{OCH}_3)$ 、 $\text{Na}(\text{OC}_2\text{H}_5)$ 、 $\text{Na}(\text{OC}_3\text{H}_7-i)$ 、 $\text{Na}(\text{OC}_4\text{H}_9)$ 等のナトリウムアルコキシド； $\text{NH}_4(\text{OCH}_3)$ 、 $\text{NH}_4(\text{OC}_2\text{H}_5)$ 、 $\text{NH}_4(\text{OC}_3\text{H}_7-i)$ 、 $\text{NH}_4(\text{OC}_4\text{H}_9)$ 等のアンモニウムアルコキシド； $\text{Li}(\text{OC}_2\text{H}_5)_2$ 、 $\text{Li}(\text{OC}_3\text{H}_7-i)_2$ 、 $\text{Li}(\text{OC}_4\text{H}_9)_2$ 等のリチウムアルコキシド； $\text{K}(\text{OC}_2\text{H}_5)_2$ 、 $\text{K}(\text{OC}_3\text{H}_7-i)_2$ 、 $\text{K}(\text{OC}_4\text{H}_9)_2$ 等のカリウムアルコキシド； $\text{Rb}(\text{OC}_2\text{H}_5)_2$ 、 $\text{Rb}(\text{OC}_3\text{H}_7-i)_2$ 、 $\text{Rb}(\text{OC}_4\text{H}_9)_2$ 等のルビウムアルコキシド； $\text{Cs}(\text{OC}_2\text{H}_5)_2$ 、 $\text{Cs}(\text{OC}_3\text{H}_7-i)_2$ 、 $\text{Cs}(\text{OC}_4\text{H}_9)_2$ 等のセシウムアルコキシド； $\text{Na}(\text{OC}_2\text{H}_5)_2$ 、 $\text{Na}(\text{OC}_3\text{H}_7-i)_2$ 、 $\text{Na}(\text{OC}_4\text{H}_9)_2$ 等のナトリウムアルコキシド； $\text{NH}_4(\text{OC}_2\text{H}_5)_2$ 、 $\text{NH}_4(\text{OC}_3\text{H}_7-i)_2$ 、 $\text{NH}_4(\text{OC}_4\text{H}_9)_2$ 等のアンモニウムアルコキシド； $\text{Li}(\text{OC}_3\text{H}_7-i)_3$ 、 $\text{Li}(\text{OC}_4\text{H}_9)_3$ 等のリチウムアルコキシド； $\text{K}(\text{OC}_3\text{H}_7-i)_3$ 、 $\text{K}(\text{OC}_4\text{H}_9)_3$ 等のカリウムアルコキシド； $\text{Rb}(\text{OC}_3\text{H}_7-i)_3$ 、 $\text{Rb}(\text{OC}_4\text{H}_9)_3$ 等のルビウムアルコキシド； $\text{Cs}(\text{OC}_3\text{H}_7-i)_3$ 、 $\text{Cs}(\text{OC}_4\text{H}_9)_3$ 等のセシウムアルコキシド； $\text{Na}(\text{OC}_3\text{H}_7-i)_3$ 、 $\text{Na}(\text{OC}_4\text{H}_9)_3$ 等のナトリウムアルコキシド； $\text{NH}_4(\text{OC}_3\text{H}_7-i)_3$ 、 $\text{NH}_4(\text{OC}_4\text{H}_9)_3$ 等のアンモニウムアルコキシド； $\text{Li}(\text{OC}_4\text{H}_9)_4$ 、 $\text{K}(\text{OC}_4\text{H}_9)_4$ 、 $\text{Rb}(\text{OC}_4\text{H}_9)_4$ 、 $\text{Cs}(\text{OC}_4\text{H}_9)_4$ 、 $\text{Na}(\text{OC}_4\text{H}_9)_4$ 、 $\text{NH}_4(\text{OC}_4\text{H}_9)_4$ 等のリチウムアルコキシド； $\text{Li}(\text{OC}_3\text{H}_7-i)_4$ 、 $\text{K}(\text{OC}_3\text{H}_7-i)_4$ 、 $\text{Rb}(\text{OC}_3\text{H}_7-i)_4$ 、 $\text{Cs}(\text{OC}_3\text{H}_7-i)_4$ 、 $\text{Na}(\text{OC}_3\text{H}_7-i)_4$ 、 $\text{NH}_4(\text{OC}_3\text{H}_7-i)_4$ 等のリチウムアルコキシド； $\text{Li}(\text{OC}_2\text{H}_5)_4$ 、 $\text{K}(\text{OC}_2\text{H}_5)_4$ 、 $\text{Rb}(\text{OC}_2\text{H}_5)_4$ 、 $\text{Cs}(\text{OC}_2\text{H}_5)_4$ 、 $\text{Na}(\text{OC}_2\text{H}_5)_4$ 、 $\text{NH}_4(\text{OC}_2\text{H}_5)_4$ 等のリチウムアルコキシド； $\text{Li}(\text{OCH}_3)_4$ 、 $\text{K}(\text{OCH}_3)_4$ 、 $\text{Rb}(\text{OCH}_3)_4$ 、 $\text{Cs}(\text{OCH}_3)_4$ 、 $\text{Na}(\text{OCH}_3)_4$ 、 $\text{NH}_4(\text{OCH}_3)_4$ 等のリチウムアルコキシド； $\text{Li}(\text{OC}_2\text{H}_5)_3$ 、 $\text{K}(\text{OC}_2\text{H}_5)_3$ 、 $\text{Rb}(\text{OC}_2\text{H}_5)_3$ 、 $\text{Cs}(\text{OC}_2\text{H}_5)_3$ 、 $\text{Na}(\text{OC}_2\text{H}_5)_3$ 、 $\text{NH}_4(\text{OC}_2\text{H}_5)_3$ 等のリチウムアルコキシド； $\text{Li}(\text{OC}_3\text{H}_7-i)_3$ 、 $\text{K}(\text{OC}_3\text{H}_7-i)_3$ 、 $\text{Rb}(\text{OC}_3\text{H}_7-i)_3$ 、 $\text{Cs}(\text{OC}_3\text{H}_7-i)_3$ 、 $\text{Na}(\text{OC}_3\text{H}_7-i)_3$ 、 $\text{NH}_4(\text{OC}_3\text{H}_7-i)_3$ 等のリチウムアルコキシド； $\text{Li}(\text{OC}_4\text{H}_9)_3$ 、 $\text{K}(\text{OC}_4\text{H}_9)_3$ 、 $\text{Rb}(\text{OC}_4\text{H}_9)_3$ 、 $\text{Cs}(\text{OC}_4\text{H}_9)_3$ 、 $\text{Na}(\text{OC}_4\text{H}_9)_3$ 、 $\text{NH}_4(\text{OC}_4\text{H}_9)_3$ 等のリチウムアルコキシド； $\text{Li}(\text{OC}_2\text{H}_5)_2$ 、 $\text{K}(\text{OC}_2\text{H}_5)_2$ 、 $\text{Rb}(\text{OC}_2\text{H}_5)_2$ 、 $\text{Cs}(\text{OC}_2\text{H}_5)_2$ 、 $\text{Na}(\text{OC}_2\text{H}_5)_2$ 、 $\text{NH}_4(\text{OC}_2\text{H}_5)_2$ 等のリチウムアルコキシド； $\text{Li}(\text{OC}_3\text{H}_7-i)_2$ 、 $\text{K}(\text{OC}_3\text{H}_7-i)_2$ 、 $\text{Rb}(\text{OC}_3\text{H}_7-i)_2$ 、 $\text{Cs}(\text{OC}_3\text{H}_7-i)_2$ 、 $\text{Na}(\text{OC}_3\text{H}_7-i)_2$ 、 $\text{NH}_4(\text{OC}_3\text{H}_7-i)_2$ 等のリチウムアルコキシド； $\text{Li}(\text{OC}_4\text{H}_9)_2$ 、 $\text{K}(\text{OC}_4\text{H}_9)_2$ 、 $\text{Rb}(\text{OC}_4\text{H}_9)_2$ 、 $\text{Cs}(\text{OC}_4\text{H}_9)_2$ 、 $\text{Na}(\text{OC}_4\text{H}_9)_2$ 、 $\text{NH}_4(\text{OC}_4\text{H}_9)_2$ 等のリチウムアルコキシド； $\text{Li}(\text{OCH}_3)_3$ 、 $\text{K}(\text{OCH}_3)_3$ 、 $\text{Rb}(\text{OCH}_3)_3$ 、 $\text{Cs}(\text{OCH}_3)_3$ 、 $\text{Na}(\text{OCH}_3)_3$ 、 $\text{NH}_4(\text{OCH}_3)_3$ 等のリチウムアルコキシド； $\text{Li}(\text{OC}_2\text{H}_5)_2$ 、 $\text{K}(\text{OC}_2\text{H}_5)_2$ 、 $\text{Rb}(\text{OC}_2\text{H}_5)_2$ 、 $\text{Cs}(\text{OC}_2\text{H}_5)_2$ 、 $\text{Na}(\text{OC}_2\text{H}_5)_2$ 、 $\text{NH}_4(\text{OC}_2\text{H}_5)_2$ 等のリチウムアルコキシド； $\text{Li}(\text{OC}_3\text{H}_7-i)_2$ 、 $\text{K}(\text{OC}_3\text{H}_7-i)_2$ 、 $\text{Rb}(\text{OC}_3\text{H}_7-i)_2$ 、 $\text{Cs}(\text{OC}_3\text{H}_7-i)_2$ 、 $\text{Na}(\text{OC}_3\text{H}_7-i)_2$ 、 $\text{NH}_4(\text{OC}_3\text{H}_7-i)_2$ 等のリチウムアルコキシド； $\text{Li}(\text{OC}_4\text{H}_9)_2$ 、 $\text{K}(\text{OC}_4\text{H}_9)_2$ 、 $\text{Rb}(\text{OC}_4\text{H}_9)_2$ 、 $\text{Cs}(\text{OC}_4\text{H}_9)_2$ 、 $\text{Na}(\text{OC}_4\text{H}_9)_2$ 、 $\text{NH}_4(\text{OC}_4\text{H}_9)_2$ 等のリチウムアルコキシド； $\text{Li}(\text{OCH}_3)_2$ 、 $\text{K}(\text{OCH}_3)_2$ 、 $\text{Rb}(\text{OCH}_3)_2$ 、 $\text{Cs}(\text{OCH}_3)_2$ 、 $\text{Na}(\text{OCH}_3)_2$ 、 $\text{NH}_4(\text{OCH}_3)_2$ 等のリチウムアルコキシド； $\text{Li}(\text{OC}_2\text{H}_5)$ 、 $\text{K}(\text{OC}_2\text{H}_5)$ 、 $\text{Rb}(\text{OC}_2\text{H}_5)$ 、 $\text{Cs}(\text{OC}_2\text{H}_5)$ 、 $\text{Na}(\text{OC}_2\text{H}_5)$ 、 $\text{NH}_4(\text{OC}_2\text{H}_5)$ 等のリチウムアルコキシド； $\text{Li}(\text{OC}_3\text{H}_7-i)$ 、 $\text{K}(\text{OC}_3\text{H}_7-i)$ 、 $\text{Rb}(\text{OC}_3\text{H}_7-i)$ 、 $\text{Cs}(\text{OC}_3\text{H}_7-i)$ 、 $\text{Na}(\text{OC}_3\text{H}_7-i)$ 、 $\text{NH}_4(\text{OC}_3\text{H}_7-i)$ 等のリチウムアルコキシド； $\text{Li}(\text{OC}_4\text{H}_9)$ 、 $\text{K}(\text{OC}_4\text{H}_9)$ 、 $\text{Rb}(\text{OC}_4\text{H}_9)$ 、 $\text{Cs}(\text{OC}_4\text{H}_9)$ 、 $\text{Na}(\text{OC}_4\text{H}_9)$ 、 $\text{NH}_4(\text{OC}_4\text{H}_9)$ 等のリチウムアルコキシド； $\text{Li}(\text{OCH}_3)$ 、 $\text{K}(\text{OCH}_3)$ 、 $\text{Rb}(\text{OCH}_3)$ 、 $\text{Cs}(\text{OCH}_3)$ 、 $\text{Na}(\text{OCH}_3)$ 、 $\text{NH}_4(\text{OCH}_3)$ 等のリチウムアルコキシド； $\text{Li}(\text{OC}_2\text{H}_5)$ 、 $\text{K}(\text{OC}_2\text{H}_5)$ 、 $\text{Rb}(\text{OC}_2\text{H}_5)$ 、 $\text{Cs}(\text{OC}_2\text{H}_5)$ 、 $\text{Na}(\text{OC}_2\text{H}_5)$ 、 $\text{NH}_4(\text{OC}_2\text{H}_5)$ 等のリチウムアルコキシド； $\text{Li}(\text{OC}_3\text{H}_7-i)$ 、 $\text{K}(\text{OC}_3\text{H}_7-i)$ 、 $\text{Rb}(\text{OC}_3\text{H}_7-i)$ 、 $\text{Cs}(\text{OC}_3\text{H}_7-i)$ 、 $\text{Na}(\text{OC}_3\text{H}_7-i)$ 、 $\text{NH}_4(\text{OC}_3\text{H}_7-i)$ 等のリチウムアルコキシド； $\text{Li}(\text{OC}_4\text{H}_9)$ 、 $\text{K}(\text{OC}_4\text{H}_9)$ 、 $\text{Rb}(\text{OC}_4\text{H}_9)$ 、 $\text{Cs}(\text{OC}_4\text{H}_9)$ 、 $\text{Na}(\text{OC}_4\text{H}_9)$ 、 $\text{NH}_4(\text{OC}_4\text{H}_9)$ 等のリチウムアルコキシド； $\text{Li}(\text{OCH}_3)$ 、 $\text{K}(\text{OCH}_3)$ 、 $\text{Rb}(\text{OCH}_3)$ 、 $\text{Cs}(\text{OCH}_3)$ 、 $\text{Na}(\text{OCH}_3)$ 、 $\text{NH}_4(\text{OCH}_3)$ 等のリチウムアルコキシド； $\text{Li}(\text{OC}_2\text{H}_5)$ 、 $\text{K}(\text{OC}_2\text{H}_5)$ 、 $\text{Rb}(\text{OC}_2\text{H}_5)$ 、 $\text{Cs}(\text{OC}_2\text{H}_5)$ 、 $\text{Na}(\text{OC}_2\text{H}_5)$ 、 $\text{NH}_4(\text{OC}_2\text{H}_5)$ 等のリチウムアルコキシド； $\text{Li}(\text{OC}_3\text{H}_7-i)$ 、 $\text{K}(\text{OC}_3\text{H}_7-i)$ 、 $\text{Rb}(\text{OC}_3\text{H}_7-i)$ 、 $\text{Cs}(\text{OC}_3\text{H}_7-i)$ 、 $\text{Na}(\text{OC}_3\text{H}_7-i)$ 、 $\text{NH}_4(\text{OC}_3\text{H}_7-i)$ 等のリチウムアルコキシド； $\text{Li}(\text{OC}_4\text{H}_9)$ 、 $\text{K}(\text{OC}_4\text{H}_9)$ 、 $\text{Rb}(\text{OC}_4\text{H}_9)$ 、 $\text{Cs}(\text{OC}_4\text{H}_9)$ 、 $\text{Na}(\text{OC}_4\text{H}_9)$ 、 $\text{NH}_4(\text{OC}_4\text{H}_9)$ 等のリチウムアルコキシド； $\text{Li}(\text{OCH}_3)$ 、 $\text{K}(\text{OCH}_3)$ 、 $\text{Rb}(\text{OCH}_3)$ 、 $\text{Cs}(\text{OCH}_3)$ 、 $\text{Na}(\text{OCH}_3)$ 、 $\text{NH}_4(\text{OCH}_3)$ 等のリチウムアルコキシド； $\text{Li}(\text{OC}_2\text{H}_5)$ 、 $\text{K}(\text{OC}_2\text{H}_5)$ 、 $\text{Rb}(\text{OC}_2\text{H}_5)$ 、 $\text{Cs}(\text{OC}_2\text{H}_5)$ 、 $\text{Na}(\text{OC}_2\text{H}_5)$ 、 $\text{NH}_4(\text{OC}_2\text{H}_5)$ 等のリチウムアルコキシド； $\text{Li}(\text{OC}_3\text{H}_7-i)$ 、 $\text{K}(\text{OC}_3\text{H}_7-i)$ 、 $\text{Rb}(\text{OC}_3\text{H}_7-i)$ 、 $\text{Cs}(\text{OC}_3\text{H}_7-i)$ 、 $\text{Na}(\text{OC}_3\text{H}_7-i)$ 、 $\text{NH}_4(\text{OC}_3\text{H}_7-i)$ 等のリチウムアルコキシド； $\text{Li}(\text{OC}_4\text{H}_9)$ 、 $\text{K}(\text{OC}_4\text{H}_9)$ 、 $\text{Rb}(\text{OC}_4\text{H}_9)$ 、 $\text{Cs}(\text{OC}_4\text{H}_9)$ 、 $\text{Na}(\text{OC}_4\text{H}_9)$ 、 $\text{NH}_4(\text{OC}_4\text{H}_9)$ 等のリチウムアルコキシド； $\text{Li}(\text{OCH}_3)$ 、 $\text{K}(\text{OCH}_3)$ 、 $\text{Rb}(\text{OCH}_3)$ 、 $\text{Cs}(\text{OCH}_3)$ 、 $\text{Na}(\text{OCH}_3)$ 、 $\text{NH}_4(\text{OCH}_3)$ 等のリチウムアルコキシド； $\text{Li}(\text{OC}_2\text{H}_5)$ 、 $\text{K}(\text{OC}_2\text{H}_5)$ 、 $\text{Rb}(\text{OC}_2\text{H}_5)$ 、 $\text{Cs}(\text{OC}_2\text{H}_5)$ 、 $\text{Na}(\text{OC}_2\text{H}_5)$ 、 $\text{NH}_4(\text{OC}_2\text{H}_5)$ 等のリチウムアルコキシド； $\text{Li}(\text{OC}_3\text{H}_7-i)$ 、 $\text{K}(\text{OC}_3\text{H}_7-i)$ 、 $\text{Rb}(\text{OC}_3\text{H}_7-i)$ 、 $\text{Cs}(\text{OC}_3\text{H}_7-i)$ 、 $\text{Na}(\text{OC}_3\text{H}_7-i)$ 、 $\text{NH}_4(\text{OC}_3\text{H}_7-i)$ 等のリチウムアルコキシド； $\text{Li}(\text{OC}_4\text{H}_9)$ 、 $\text{K}(\text{OC}_4\text{H}_9)$ 、 $\text{Rb}(\text{OC}_4\text{H}_9)$ 、 $\text{Cs}(\text{OC}_4\text{H}_9)$ 、 $\text{Na}(\text{OC}_4\text{H}_9)$ 、 $\text{NH}_4(\text{OC}_4\text{H}_9)$ 等のリチウムアルコキシド； $\text{Li}(\text{OCH}_3)$ 、 $\text{K}(\text{OCH}_3)$ 、 $\text{Rb}(\text{OCH}_3)$ 、 $\text{Cs}(\text{OCH}_3)$ 、 $\text{Na}(\text{OCH}_3)$ 、 $\text{NH}_4(\text{OCH}_3)$ 等のリチウムアルコキシド； $\text{Li}(\text{OC}_2\text{H}_5)$ 、 $\text{K}(\text{OC}_2\text{H}_5)$ 、 $\text{Rb}(\text{OC}_2\text{H}_5)$ 、 $\text{Cs}(\text{OC}_2\text{H}_5)$ 、 $\text{Na}(\text{OC}_2\text{H}_5)$ 、 $\text{NH}_4(\text{OC}_2\text{H}_5)$ 等のリチウムアルコキシド； $\text{Li}(\text{OC}_3\text{H}_7-i)$ 、 $\text{K}(\text{OC}_3\text{H}_7-i)$ 、 $\text{Rb}(\text{OC}_3\text{H}_7-i)$ 、 $\text{Cs}(\text{OC}_3\text{H}_7-i)$ 、 $\text{Na}(\text{OC}_3\text{H}_7-i)$ 、 $\text{NH}_4(\text{OC}_3\text{H}_7-i)$ 等のリチウムアルコキシド； $\text{Li}(\text{OC}_4\text{H}_9)$ 、 $\text{K}(\text{OC}_4\text{H}_9)$ 、 $\text{Rb}(\text{OC}_4\text{H}_9)$ 、 $\text{Cs}(\text{OC}_4\text{H}_9)$ 、 $\text{Na}(\text{OC}_4\text{H}_9)$ 、 $\text{NH}_4(\text{OC}_4\text{H}_9)$ 等のリチウムアルコキシド； $\text{Li}(\text{OCH}_3)$ 、 $\text{K}(\text{OCH}_3)$ 、 $\text{Rb}(\text{OCH}_3)$ 、 $\text{Cs}(\text{OCH}_3)$ 、 $\text{Na}(\text{OCH}_3)$ 、 $\text{NH}_4(\text{OCH}_3)$ 等のリチウムアルコキシド； $\text{Li}(\text{OC}_2\text{H}_5)$ 、 $\text{K}(\text{OC}_2\text{H}_5)$ 、 $\text{Rb}(\text{OC}_2\text{H}_5)$ 、 $\text{Cs}(\text{OC}_2\text{H}_5)$ 、 $\text{Na}(\text{OC}_2\text{H}_5)$ 、 $\text{NH}_4(\text{OC}_2\text{H}_5)$ 等のリチウムアルコキシド； $\text{Li}(\text{OC}_3\text{H}_7-i)$ 、 $\text{K}(\text{OC}_3\text{H}_7-i)$ 、 $\text{Rb}(\text{OC}_3\text{H}_7-i)$ 、 $\text{Cs}(\text{OC}_3\text{H}_7-i)$ 、 $\text{Na}(\text{OC}_3\text{H}_7-i)$ 、 $\text{NH}_4(\text{OC}_3\text{H}_7-i)$ 等のリチウムアルコキシド； $\text{Li}(\text{OC}_4\text{H}_9)$ 、 $\text{K}(\text{OC}_4\text{H}_9)$ 、 $\text{Rb}(\text{OC}_4\text{H}_9)$ 、 $\text{Cs}(\text{OC}_4\text{H}_9)$ 、 $\text{Na}(\text{OC}_4\text{H}_9)$ 、 $\text{NH}_4(\text{OC}_4\text{H}_9)$ 等のリチウムアルコキシド； $\text{Li}(\text{OCH}_3)$ 、 $\text{K}(\text{OCH}_3)$ 、 $\text{Rb}(\text{OCH}_3)$ 、 $\text{Cs}(\text{OCH}_3)$ 、 $\text{Na}(\text{OCH}_3)$ 、 $\text{NH}_4(\text{OCH}_3)$ 等のリチウムアルコキシド； $\text{Li}(\text{OC}_2\text{H}_5)$ 、 $\text{K}(\text{OC}_2\text{H}_5)$ 、 $\text{Rb}(\text{OC}_2\text{H}_5)$ 、 $\text{Cs}(\text{OC}_2\text{H}_5)$ 、 $\text{Na}(\text{OC}_2\text{H}_5)$ 、 $\text{NH}_4(\text{OC}_2\text{H}_5)$ 等のリチウムアルコキシド； $\text{Li}(\text{OC}_3\text{H}_7-i)$ 、 $\text{K}(\text{OC}_3\text{H}_7-i)$ 、 $\text{Rb}(\text$

$\text{OC}_2\text{H}_5)_2$ 等の亜鉛アルコキシド； $\text{Pb}(\text{OC}_4\text{H}_9)_4$ 等の鉛アルコキシド；等が挙げられる。これらの金属アルコキシド類は1種単独で、あるいは2種以上を組み合わせ用いることができる。

【0065】

また本発明においては、金属アルコキシド類として、2種以上の金属アルコキシド類の反応により得られる複合アルコキシド、1種もしくは2種以上の金属アルコキシド類と、1種もしくは2種以上の金属塩との反応により得られる複合アルコキシド、及びこれらの組み合わせを用いることもできる。

【0066】

2種以上の金属アルコキシド類の反応により得られる複合アルコキシドとしては、アルカリ金属又はアルカリ土類金属のアルコキシドと、遷移金属のアルコキシドとの反応により得られる複合アルコキシドや、第3B族元素の組合せにより錯塩の形で得られる複合アルコキシド等を例示することができる。

【0067】

その具体例としては、 $\text{BaTi}(\text{OR})_6$ 、 $\text{SrTi}(\text{OR})_6$ 、 $\text{BaZr}(\text{OR})_6$ 、 $\text{SrZr}(\text{OR})_6$ 、 $\text{LiNb}(\text{OR})_6$ 、 $\text{LiTa}(\text{OR})_6$ 、及び、これらの組合せ、 $\text{LiVO}(\text{OR})_4$ 、 $\text{MgAl}_2(\text{OR})_8$ 、 $(\text{RO})_3\text{SiOAl}(\text{OR}')_2$ 、 $(\text{RO})_3\text{SiOTi}(\text{OR}')_3$ 、 $(\text{RO})_3\text{SiOZr}(\text{OR}')_3$ 、 $(\text{RO})_3\text{SiOB}(\text{OR}')_2$ 、 $(\text{RO})_3\text{SiONb}(\text{OR}')_4$ 、 $(\text{RO})_3\text{SiOTa}(\text{OR}')_4$ 等のケイ素アルコキシドと、前記金属アルコキシド類との反応物及びその縮重合物等が挙げられる。ここで、R及びR'はアルキル基等を表す。

【0068】

1種もしくは2種以上の金属アルコキシド類と1種もしくは2種以上の金属塩との反応により得られる複合アルコキシドとしては、金属塩と金属アルコキシド類との反応により得られる化合物を例示することができる。

【0069】

金属塩としては、金属の塩化物、硝酸塩、硫酸塩、酢酸塩、ギ酸塩、シュウ酸塩等を、金属アルコキシド類としては、上述した金属アルコキシド類をそれぞれ例示することができる。

【0070】

用いる金属アルコキシド類の量は、化学吸着膜の形成を阻害しない量であれば特に制限されないが、金属系界面活性剤に対して触媒量用いることが好ましく、金属系界面活性剤1モルに対して0.001～1モルの範囲で用いることがより好ましく、0.001～0.2モルの範囲で用いることがさらに好ましく、又は酸化物換算モル数で0.001～1モルの範囲で用いることがより好ましく、0.001～0.2モルの範囲で用いることがさらに好ましい。これらの金属アルコキシド類は1種単独で、あるいは2種以上を組み合わせ用いることができる。

【0071】

金属アルコキシド類部分加水分解生成物は、金属アルコキシド類を完全に加水分解する前に得られるものであって、例えば、金属酸化物ゾルの前駆体、またはオリゴマーの状態が存在するもの等を挙げることができる。

【0072】

金属アルコキシド類部分加水分解生成物としては、具体的には、有機溶媒中、酸、塩基及び分散安定化剤からなる群から選ばれる少なくとも1種の非存在下、凝集せずに安定に分散している性質を有する分散質を好ましく例示することができる。この場合、分散質とは、分散系中に分散している微細粒子のことをいい、具体的には、コロイド粒子等を例示することができる。ここで凝集せずに安定に分散している状態とは、有機溶媒中、酸、塩基及び／又は分散安定化剤の非存在下、加水分解生成物の分散質が、凝結して不均質に分離していない状態をいい、好ましくは透明で均質な状態をいう。また透明とは、可視光における透過率が高い状態をいい、具体的には、分散質の濃度を酸化物換算で0.5重量%

とし、石英セルの光路長を1 cmとし、対照試料を有機溶媒とし、光の波長を550 nmとする条件で測定した分光透過率で表して、好ましくは80～100%の透過率を表す状態をいう。加水分解生成物の分散質の粒子径は特に限定されないが、可視光における高い透過率を得るためには、1～100 nmの範囲であることが好ましく、1～50 nmの範囲であることがより好ましく、1～10 nmの範囲であることがさらに好ましい。また、酸、塩基、分散安定化剤については、後述する。

【0073】

金属アルコキシド類の部分加水分解生成物の製造方法としては、有機溶媒中、酸、塩基、及び／又は分散安定化剤の非存在下、上記例示した金属アルコキシド類に対し0.5～2.0倍モル未満の水を用い、-100℃から有機溶媒還流温度範囲で加水分解する方法を好ましく例示することができる。

【0074】

具体的には、(1)有機溶媒中、酸、塩基、及び／又は分散安定化剤の非存在下、金属アルコキシド類に対し0.5～1.0倍モル未満の水を添加する方法、

(2)有機溶媒中、酸、塩基、及び／又は分散安定化剤の非存在下、加水分解を開始する温度以下、又は0℃以下、好ましくは-50～-100℃の範囲で、金属アルコキシド類に対し1.0～2.0倍モル未満の水を添加する方法、

(3)有機溶媒中、酸、塩基、及び／又は分散安定化剤の非存在下、水の添加速度を制御する、添加する水の濃度を水溶性溶媒等を用いて薄める等の方法により加水分解速度を制御しながら、金属アルコキシド類に対し0.5～2.0倍モル未満の水を室温で添加する方法、等を例示することができる。

【0075】

上記(1)の方法においては、任意の温度で所定量の水で処理を行った後、加水分解を開始する温度以下、又は-20℃以下の温度条件下で、水をさらに追加して反応を行うことができる。金属アルコキシド類と水との反応は、有機溶媒を用いずに直接金属アルコキシド類と水を混合することにより行うこともできるが、有機溶媒中で行うのが好ましい。具体的には、金属アルコキシド類の有機溶媒溶液に有機溶媒で希釈した水を添加する方法；水を懸濁若しくは溶解した有機溶媒中に、金属アルコキシド類、又はその有機溶媒溶液を添加する方法；のいずれの方法でも行うことができるが、前者の水を後から添加する方法が好ましい。用いる水は、中性であれば特に制限されないが純水または蒸留水を用いるのが好ましく、その量は、上記規定した範囲であれば特に制限されず、目的とする性質を有する分散質によって任意に選択することができる。

【0076】

有機溶媒中の金属アルコキシド類の濃度は、急激な発熱を抑制し、攪拌が可能な流動性を有する範囲であれば特に限定されないが、5～30重量%の範囲とすることが好ましい。

【0077】

上記(1)の方法における金属アルコキシド類と水との反応温度は特に制限されないが、-100～+100℃の範囲とすることができ、-20℃から用いる有機溶媒又は加水分解によって脱離してくるアルコールの沸点の範囲とすることが好ましい。

【0078】

上記(2)の方法における水の添加温度は、金属アルコキシド類の安定性に依存するものであり、加水分解開始温度以下、又は0℃以下の温度であれば特に限定されないが、金属アルコキシド類の種類によっては、金属アルコキシド類への水の添加を-50℃～-100℃の温度範囲で行うことが好ましい。また、低温で水を添加し、一定時間熟成した後、室温から用いた溶媒の還流温度で加水分解し、さらに脱水縮合反応を行うこともできる。

【0079】

上記(3)の方法における金属アルコキシド類と水との反応は、特殊な冷却装置を用いなくても冷却可能な温度範囲、例えば、0℃から室温の範囲で、水の添加速度を制御する

等の温度以外の方法により加水分解速度を制御することにより行うことができる。一定時間熟成した後、室温から用いる溶媒の還流温度で加水分解し、さらに脱水縮合反応を行うこともできる。

【0080】

用いる有機溶媒としては、その有機溶媒中で、金属アルコキシド類の加水分解生成物が、分散質となって分散できるものであるのが好ましく、金属系界面活性剤を水で処理する反応を低温で行うことができることから、水の溶解度が大きく、低温で凝固しない溶媒がより好ましい。用いる有機溶媒の具体例としては、メタノール、エタノール、イソプロパノール等のアルコール系溶媒；塩化メチレン、クロロホルム、クロロベンゼン等のハロゲン化炭化水素系溶媒；ヘキサン、シクロヘキサン、ベンゼン、トルエン、キシレン等の炭化水素系溶媒；テトラヒドロフラン、ジエチルエーテル、ジオキサン等のエーテル系溶媒；アセトン、メチルエチルケトン、メチルイソブチルケトン等のケトン系溶媒；ジメチルホルムアミド、N-メチルピロリドン等のアミド系溶媒；ジメチルスルホキシド等のスルホキシド系溶媒；メチルポリシロキサン、オクタメチルシクロテトラシロキサン、デカメチルシクロペンタンシロキサン、メチルフェニルポリシロキサン等のシリコーン（特開平9-208438号公報等）等；が挙げられる。これらの溶媒は1種単独で、あるいは2種以上を混合して用いることができる。

【0081】

混合溶媒として用いる場合には、トルエン、キシレン等の炭化水素系溶媒と、メタノール、エタノール、イソプロパノール、n-ブタノール等の低級アルコール系溶媒の組み合わせが好ましい。この場合の低級アルコール系溶媒としては、イソプロパノール、n-ブタノール等の2級以上のアルコール系溶媒を用いるのがより好ましい。混合溶媒の混合比は特に制限されないが、炭化水素系溶媒と低級アルコール系溶媒を、体積比で、99/1～50/50の範囲で用いるのが好ましい。

【0082】

また、金属アルコキシド類の水による加水分解反応においては、酸、塩基又は分散安定化剤を添加してもよい。酸及び塩基は、凝結してできた沈殿を再び分散させる解膠剤として、また、金属アルコキシド類を加水分解、脱水縮合させてコロイド粒子等の分散質を製造するための触媒として、あるいは生成した分散質の分散剤として機能するものであれば特に制限されない。

【0083】

この場合の酸または塩基は、凝結してできた沈殿を再び分散させる解膠剤として、また、前述したように、金属アルコキシド類等を加水分解、脱水縮合させてコロイド粒子等の分散質を製造するための触媒として、及び生成した分散質の分散剤として機能するものであれば特に制限されない。

【0084】

用いる酸としては、例えば、塩酸、硝酸、ホウ酸、ホウフッ化水素酸等の鉱酸、酢酸、ギ酸、シュウ酸、炭酸、トリフルオロ酢酸、p-トルエンスルホン酸、メタンスルホン酸等の有機酸等；ジフェニルヨードニウムヘキサフルオロホスフェート、トリフェニルホスホニウムヘキサフルオロホスフェート等の光照射によって酸を発生する光酸発生剤；が挙げられる。

【0085】

用いる塩基としては、例えば、トリエタノールアミン、トリエチルアミン、1, 8-ジアザビシクロ[5. 4. 0]-7-ウンデセン、アンモニア、ジメチルホルムアミド、ホスフィン等が挙げられる。

【0086】

分散安定化剤は、分散質を分散媒中に安定に分散させる効力を有する剤であり、例えば、解膠剤、保護コロイド、界面活性剤等の凝結防止剤等を分散安定化剤としてあげることができる。具体的には、グリコール酸、グルコン酸、乳酸、酒石酸、クエン酸、リンゴ酸、コハク酸等の多価カルボン酸；ヒドロキシカルボン酸；ピロリン酸、トリポリリン酸等の麟

酸；アセチルアセトン、アセト酢酸メチル、アセト酢酸エチル、アセト酢酸 n-プロピル、アセト酢酸イソプロピル、アセト酢酸 n-ブチル、アセト酢酸 sec-ブチル、アセト酢酸 tert-ブチル、2, 4-ヘキサレンジオン、2, 4-ヘプタレンジオン、3, 5-ヘプタレンジオン、2, 4-オクタレンジオン、2, 4-ノナレンジオン、5-メチル-ヘキサレンジオン等の金属原子に対して強いキレート能力を有する多座配位子化合物；スルパース3000、9000、17000、20000、24000（以上、ゼネカ社製）、Disperbyk-161、-162、-163、-164（以上、ビックケミー社製）等の脂肪族アミン系、ハイドロステアリン酸系、ポリエステルアミン；ジメチルポリシロキサン・メチル（ポリシロキシアルキレン）シロキサン共重合体、トリメチルシロキシケイ酸、カルボキシ変性シリコーンオイル、アミン変性シリコーン等（特開平9-208438号公報、特開平2000-53421号公報等）のシリコーン化合物；等が例示される。

【0087】

用いる金属アルコキシド類部分加水分解生成物の量は、有機薄膜の形成を阻害しない量であれば特に制限されないが、金属系界面活性剤に対して触媒量用いることが好ましく、金属系界面活性剤1モルに対して酸化物換算モル数で、0.001～1モルの範囲で用いることが好ましく、0.001～0.2モルの範囲で用いることがより好ましい。これらの金属アルコキシド類部分加水分解物は1種単独で、あるいは2種以上を組み合わせて用いることができる。

【0088】

本発明に用いられる金属アルコキシド加水分解生成物は、金属アルコキシド類の2倍当量以上の水で加水分解することによって得られる生成物である。該加水分解生成物は、金属アルコキシド類を該金属アルコキシド類の2倍当量以上の水で加水分解することによって得られたものであっても、金属アルコキシド類を該金属アルコキシド類の2倍当量未満の水で部分加水分解することによって、金属アルコキシド類の部分加水分解生成物を得た後、この部分加水分解生成物を、さらに所定量の水（先の部分加水分解に使用した水の量との合計で金属アルコキシド類の2倍当量以上となる量の水）で加水分解することによって得られたものであってもよい。

【0089】

金属アルコキシド類と水との反応は、有機溶媒を用いずに直接金属アルコキシド類と水を混合してもよいし、有機溶媒中で金属アルコキシド類と水とを反応させてもよいが、有機溶媒中で金属アルコキシド類と水とを反応させることが好ましい。ここで用いる水は、中性であれば特に制限されないが、不純物がより少なく、より緻密な有機薄膜を得る観点から、純水、蒸留水又はイオン交換水を用いるのが好ましい。水の使用量は、前記金属アルコキシド類に対し2倍当量以上であることが好ましく、2～8倍当量の範囲であることがより好ましく、3～5倍当量の範囲であることがさらに好ましい。

【0090】

有機溶媒中で金属アルコキシド類と水とを反応させる方法としては、（1）金属アルコキシド類を含む有機溶媒溶液に、水又は有機溶媒で希釈した水を添加する方法、（2）水を懸濁又は溶解した有機溶媒中に、金属アルコキシド類、又は金属アルコキシド類の有機溶媒溶液を添加する方法、等を例示することができる。この場合、金属アルコキシド類の有機溶媒中の濃度は、急激な発熱を抑制し、攪拌が可能な流動性を有する範囲であれば特に限定されないが、反応溶液全量に対して5～30重量%の範囲であることが好ましい。

【0091】

用いる有機溶媒としては、特に制限されないが、その有機溶媒中で、金属アルコキシド類の加水分解生成物が、分散質となって分散できるものであることが好ましく、具体例としては、前記金属アルコキシド類部分加水分解生成物と同様の有機溶媒が好ましい。また、該加水分解生成物においては、有機溶媒以外の水、酸、塩基又は分散安定化剤等についても前記部分加水分解生成物において用いられたものを同様に使用することができる。金属アルコキシド類の加水分解反応温度は、用いる金属アルコキシド類の反応性や安定性

等によるが、 -100°C から有機溶媒の還流温度までの範囲とすることができ、 -100°C ～ -20°C の範囲とすることが好ましい。低温で水を添加し、一定時間熟成した後、反応液の温度を室温から用いた溶媒の還流温度まで昇温して、加水分解、脱水縮合反応をさらに行うこともできる。

【0092】

キレート化又は配位化された金属化合物は、金属化合物の溶液に、該金属化合物の金属と錯体を形成し得るキレート化剤又は配位化合物を添加することで、調製することができる。キレート化剤又は配位化合物としては、金属水酸化物、金属アルコキシド類、又は金属アルコキシド類を水で処理して得られた加水分解生成物の金属にキレート化又は配位して、錯体を形成し得るものであれば特に限定されない。

【0093】

キレート化剤又は配位化合物の具体例としては、酢酸、プロピオン酸、酪酸、吉草酸、ラウリン酸、ミリスチン酸、パルミチン酸、ステアリン酸等の飽和脂肪族カルボン酸類；シュウ酸、マロン酸、コハク酸、グルタル酸、アジピン酸、ピメリン酸、スベリン酸、アゼライン酸、セバシン酸等の飽和脂肪族ジカルボン酸類；アクリル酸、メタクリル酸、クロトン酸、アレイン酸、マレイン酸等の不飽和カルボン酸類；安息香酸、トルイル酸、フタル酸等の芳香族カルボン酸類；クロロ酢酸、トリフルオロ酢酸等のハロゲンカルボン酸類；アセチルアセトン、ベンゾイルアセトン、ヘキサフルオロアセチルアセトン等の β -ジケトン類；アセト酢酸メチル、アセト酢酸エチル等の β -ケトエステル類；テトラヒドロフラン、フラン、フランカルボン酸、チオフェン、チオフェンカルボン酸、ピリジン、ニコチン酸、イソニコチン酸等の複素環化合物類；等が挙げられる。これらは1種単独で、あるいは2種以上を組み合わせる用いることができる。

【0094】

キレート化剤又は配位化合物の添加量は、金属水酸化物、金属アルコキシド類、又は金属アルコキシド類を水で処理して得られた加水分解生成物の金属1モルに対して、0.1～10倍モルであることが好ましく、0.3～2倍モルであることがより好ましく、0.5～1.2倍モルであることがさらに好ましい。

【0095】

キレート化剤又は配位化合物を添加した後は、全容を十分に攪拌することで、金属錯体の溶液を得ることができる。攪拌温度は、特に制限されないが、 0°C から用いる溶媒の沸点までの温度範囲とすることが好ましい。攪拌時間は、特に制限されないが、数分から数時間とすることが好ましい。キレート化又は配位化された金属化合物は、単離したものをすることもできるし、前記金属化合物の溶液にキレート化剤又は配位化合物を添加して得られたキレート化又は配位化された金属化合物の溶液として使用することもできる。また、調製したキレート化又は配位化された金属化合物の溶液は保存しておくことができる。

【0096】

シラノール縮合触媒としては、カルボン酸金属塩、カルボン酸エステル金属塩、カルボン酸金属塩ポリマー、カルボン酸金属塩キレート、チタン酸エステル及びチタン酸エステルキレート等を例示することができる。具体的には、酢酸第一スズ、ジブチルスズジラウレート、ジブチルスズジオクテート、ジブチルスズジアセテート、ジオクチルスズジラウレート、ジオクチルスズジオクテート、ジオクチルスズジアセテート、ジオクタン酸第一スズ、ナフテン酸鉛、ナフテン酸コバルト、2-エチルヘキセン酸鉄、ジオクチルスズビスオクチリチオグリコール酸エステル塩、ジオクチルスズマレイン酸エステル塩、ジブチルスズマレイン酸塩ポリマー、ジメチルスズメルカプトプロピオン酸塩ポリマー、ジブチルスズビスアセチルアセテート、ジオクチルスズビスアセチルラウレート、チタンテトラエトキサイド、チタンテトラブトキサイド、チタンテトライソプロポキシサイド、チタンビス（アセチルアセトニル）ジプロポキシサイド等を例示することができる。

【0097】

本発明の工程（B-1）の有機溶媒溶液に用いる有機溶媒としては、炭化水素系溶媒、

フッ化炭素系溶媒、及びシリコン系溶媒が好ましく、炭化水素系溶媒がより好ましい。
なかでも、沸点が100～250℃のものが特に好ましい。

【0098】

具体的には、n-ヘキサン、シクロヘキサン、ベンゼン、トルエン、キシレン、石油ナフサ、ソルベントナフサ、石油エーテル、石油ベンジン、イソパラフィン、ノルマルパラフィン、デカリン、工業ガソリン、灯油、リグロイン等の炭化水素系溶媒； CBr_2Cl 、 CF_3 、 CClF_2 、 CF_2 、 CCl_3 、 CClF_2 、 CF_2 、 CHFCl 、 CF_3 、 CF_2 、 CHCl_2 、 CF_3 、 CBrFCBrF_2 、 CClF_2 、 CClFCF_2 、 CCl_3 、 $\text{Cl}(\text{CF}_2\text{CFCl})_2$ 、 $\text{Cl}(\text{CF}_2\text{CFCl})_2$ 、 $\text{Cl}(\text{CF}_2\text{CFCl})_3$ 、 $\text{Cl}(\text{CF}_2\text{CFCl})_2$ 、 $\text{Cl}(\text{CF}_2\text{CFCl})_2$ 、 CF_2 、 CCl_3 、 $\text{Cl}(\text{CF}_2\text{CFCl})_3$ 、 $\text{Cl}(\text{CF}_2\text{CFCl})_3$ 等フロン系溶媒、フロリナート（3M社製品）、アフルード（旭ガラス社製品）等のフッ化炭素系溶媒；ジメチルシリコン、フェニルシリコン、アルキル変性シリコン、ポリエーテルシリコン等のシリコン系溶媒；が挙げられる。これらの溶媒は1種単独で、あるいは2種以上を組み合わせ用いることができる。

【0099】

有機溶媒溶液中の金属系界面活性剤の含有量は、特に制限されないが、より緻密な単分子膜を製造する観点から、有機溶媒溶液に対し0.1～30重量%の範囲であることが好ましい。

【0100】

また、工程（B-1）の有機溶媒溶液を用いる場合において、金属系界面活性剤と相互作用し得る化合物の使用量は、形成する単分子の有機薄膜の物性に悪影響を与えない量であれば特に制限されないが、金属系界面活性剤1モルに対して酸化物換算モル数で、0.001～1モルであることが好ましく、0.001～0.2モルであることがより好ましい。

【0101】

本発明の有機薄膜の製造方法は、基材を蒸留水で洗浄する工程（C）、及び／又は基材を有機溶媒で洗浄する工程（D）を、工程（A）より前及び／又は後にさらに有していることが好ましい。これにより、基材表面のゴミ、埃や有機物等の不純物をより高度に取り除き、有機薄膜をより緻密かつ強固に形成することができる。工程（C）と工程（D）を共に有する場合、工程（C）と工程（D）の順序は問わないが、工程（C）の後に工程（D）を有することが好ましい。また、工程（C）及び／又は工程（D）を工程（A）の後に有する場合、工程（C）及び／又は工程（D）を、後述の工程（E）より後に有していてもよいが、工程（E）より前に有していることが好ましい。

【0102】

ここで、工程（C）中の蒸留水は特に制限されないが、より優れた洗浄効果を得る観点から、抵抗値が10メガオーム以上の蒸留水であることが好ましく、抵抗値が15メガオーム以上の蒸留水であることがより好ましい。

【0103】

また、工程（D）中の有機溶媒は、特に制限されないが、エタノール、イソプロパノール等のアルコールが好ましく、エタノール及びイソプロパノールが特に好ましい。

【0104】

また、工程（C）や（D）における洗浄方法は、特に制限されず、例えば、工程（C）の蒸留水や工程（D）の有機溶媒を、基材にスプレーしたり、シャワーするなどして掛けるとよいし、工程（C）の蒸留水や工程（D）の有機溶媒中に基材を浸漬してもよい。より優れた洗浄効果が得られることから、工程（C）の蒸留水や工程（D）の有機溶媒中に基材を浸漬した状態で、超音波処理することが好ましい。超音波処理の具体的な条件としては、上述の、基材をオゾン水又は過酸化水素水に浸漬して超音波処理する場合と同様の条件を例示することができる。また、紫外線やオゾン、プラズマに暴露する物理的な方法をさらに併用すれば、さらに優れた洗浄効果が得られる。

【0105】

本発明の有機薄膜の製造方法は、工程（B）より後に、基材を有機溶媒で洗浄する工程

(E)を含んでいてもよい。このような洗浄工程(E)があると、工程(B)で形成された有機薄膜の表面に付着した余分な試剤や不純物が除去される。また、このような洗浄工程(E)を設けることにより、基材表面に形成された有機薄膜の膜厚を制御することができる。

【0106】

工程(E)における有機溶媒は、特に制限されないが、ヘキサン、ヘプタン、オクタン、ノナン、デカン、ベンゼン、トルエン、キシレン等の炭化水素系溶媒が好ましい。

洗浄方法としては、基材表面の付着物を除去できる方法であれば特に制限されないが、例えば、上記のような有機溶媒中に基材を浸漬させる方法；真空中、又は常圧下で大気中に放置して、基材表面の付着物を蒸発させる方法；乾燥窒素ガス等の不活性ガスをブローして、基材表面の付着物を吹き飛ばす方法；等を例示することができる。また、より優れた洗浄効果が得られることから、基材を前述の有機溶媒に浸漬した状態で、超音波処理することが、より好ましい方法として挙げられる。

【0107】

本発明の有機薄膜の製造方法は、工程(E)より後に、工程(E)で洗浄した基材を乾燥する工程(F)をさらに有することが好ましい。乾燥方法は特に制限はされず、基材表面の溶液をエアナイフなどできってもよいし、自然乾燥させてもよいし、温風をあてるなどの方法が例示できるが、基材表面上に形成された有機薄膜に熱を加えることにより、有機薄膜がより安定化することから、温風をあてる方法が好ましい。

【0108】

なお、基材を乾燥させる際に基材に熱を加えない場合、本発明の有機薄膜の製造方法は、基材に熱を加える工程をさらに含んでいなくてもよいが、有機薄膜がより安定化することから、基材に熱を加える工程(G)をさらに含んでいることが好ましい。工程(G)の順序は、工程(B)、(B-1)、(B-2)又は(B-3)より後であれば特に制限されないが、工程(E)より後であることが好ましい。加熱する温度は、基材及び有機薄膜の安定性によって適宜選択することができるが、例えば、40～70℃の範囲を好ましく挙げることができる。

【0109】

本発明の有機薄膜の製造方法は、工程(A)を含んでいる限り特に制限されず、工程(A)～(F)の他に、それらのいずれか1以上の工程より前及び／又は後に、いかなる工程を含んでいてもよい。

【0110】

本発明の有機薄膜の製造方法に用いる基材は、特に制限されない。本発明の有機薄膜の製造方法に用いる基材としては、有機溶媒溶液中の有機薄膜を形成する分子と相互作用し得る官能基を表面に有する基材でなくてもよいが、有機溶媒溶液中の有機薄膜を形成する分子と相互作用し得る官能基を表面に有する基材であることが好ましく、活性水素を表面に有する基材であることが特に好ましい。活性水素を表面に有する基材を用いると、基材表面の活性水素と、工程(B)中の有機溶媒溶液中の分子とが、化学的な相互作用により基材表面に容易に化学吸着膜を形成することができる。ここで、有機溶媒溶液中の有機薄膜を形成する分子と相互作用し得る官能基を表面に有する基材とは、有機溶媒溶液中の有機薄膜を形成する分子と、化学結合し得る官能基を表面に有する基材を意味する。

【0111】

ここで活性水素とは、プロトンとして解離しやすいものをいい、活性水素を含む官能基としては、水酸基(—OH)、カルボキシル基(—COOH)、ホルミル基(—CHO)、イミノ基(=NH)、アミノ基(—NH₂)、チオール基(—SH)等が挙げられ、なかでも、水酸基が好ましい。

【0112】

基材表面に水酸基を有する基材として、具体的には、アルミニウム、銅、ステンレス、ニッケル等の金属；ガラス；シリコンウェハー；セラミックス；プラスチック；ダイヤモンド等の鉱物；紙；天然繊維、合成繊維等の繊維；皮革；その他親水性の物質；等からな

る基材が挙げられる。なかでも、金属、ガラス、シリコンウェハー、セラミックス、紙、繊維、プラスチック及び鉱物からなる基材が好ましい。

【0113】

プラスチック、ダイヤモンド、合成繊維のように表面に水酸基を持たない材質からなる基材には、予め基材表面を酸素含有のプラズマ雰囲気中で（例えば100Wで20分）処理したり、コロナ処理して親水性基を導入することができる。ポリアミド樹脂又はポリウレタン樹脂等からなる基材は、表面にイミノ基が存在しており、このイミノ基の活性水素と金属系界面活性剤のアルコキシシリル基等とが脱アルコール反応し、シロキサン結合（ $-Si-O-$ ）を形成するので特に表面処理を必要としない。

【0114】

また、表面に活性水素を持たない基材を用いる場合、この基材の表面に、予め $SiCl_4$ 、 $SiHCl_3$ 、 SiH_2Cl_2 、 $Cl-(SiCl_2O)_b-SiCl_3$ （式中、 b は自然数）から選ばれる少なくとも一つの化合物を接触させた後、脱塩化水素反応させることにより、表面に活性水素を有するシリカ下地層を形成しておくこともできる。

【0115】

本発明の工程（B-1）における有機溶媒溶液の調製方法は特に制限されない。本発明の工程（B-1）における有機溶媒溶液は、例えば、少なくとも1以上の加水分解性基を有する金属系界面活性剤、該金属系界面活性剤と相互作用し得る化合物、及び有機溶媒を含む混合物を攪拌するなどして調製することができる。

【0116】

攪拌温度は特に制限されないが、例えば $-100^{\circ}C \sim +100^{\circ}C$ であってもよく、 $-20^{\circ}C \sim +50^{\circ}C$ であることが好ましい。また、攪拌時間も特に制限されないが、数分から数時間行うことができる。

【0117】

調製した有機溶媒溶液中に、金属酸化物等を含む析出物が生じる場合があるが、これらの析出物等の不純物は、不純物のより少ない緻密な単分子の有機薄膜を得るためには、基材に接触させる前に、それらの不純物を除去又は低減しておくことが好ましい。析出物は、濾過、デカント等の操作で簡便に除去又は低減することができる。

【0118】

本発明の工程（B-1）における有機溶媒溶液は、所定の範囲内の水分含量に調整され、又は保持された有機溶媒溶液でなくてもよいが、あらゆる材質の基材に対応して、より緻密でより均質な有機薄膜をより速やかに形成することができることから、所定の範囲内の水分含量になるように調整され、かつ保持された有機溶媒溶液であることが好ましい。

有機溶媒溶液の水分含量が所定の範囲内に調整されていると、より緻密な単分子膜が製造され、膜の形成が促進活性化され、金属系界面活性剤の損失量が減少する。また、有機溶媒溶液の水分含量が所定の範囲内に保持されていると、例えば2つ以上の基材について、同一の有機溶媒溶液を用いて、連続的に該有機溶媒溶液に接触させる工程を行った場合であっても、あらゆる材質の基材に対応して、より緻密でより均質な有機薄膜をより速やかに形成することができる。ここで、同一の有機溶媒溶液とは、1つの基材について工程（B-2）を行った後、その工程に用いた有機溶媒溶液の全部を廃棄して新たな有機溶媒溶液に交換したり、その工程に用いた有機溶媒溶液の一部を廃棄して新たな有機溶媒溶液を追加したりする場合を除く意味である。なお、後述するような何らかの方法で水分量が所定の範囲内に保持された溶液は、ここでいう同一の有機溶媒溶液に含まれる。

【0119】

「所定の範囲内の水分含量」は、用いる基材、金属系界面活性剤、該金属系界面活性剤と相互作用し得る化合物、有機溶媒等の種類により決定することができる。「所定の範囲内の水分含量」として、具体的には、例えば、基材表面への化学吸着がより活発に起こり、より緻密な単分子膜が製造され、かつ、膜の形成が促進活性化される量以上の水分含量や、用いる金属系界面活性剤の損失量がより少なく、該金属系界面活性剤と相互作用し得る化合物がより十分な活性を発揮できるような量以上である水分含量が好ましく挙げられ

る。

【0120】

膜の形成を促進活性化される量とは、例えば、ディップ法により該溶液を基材に接触させる場合、10分以内、好ましくは5分以内の1度の接触（ディップ）で、緻密で均質な有機薄膜を基材全面に形成させることができる程度の量をいう。具体的には、工程（B-2）の有機溶媒溶液中の水分含量が、30ppm以上であることが好ましく、30ppmから有機溶媒への飽和水分量の範囲、より具体的には、30～1000ppmの範囲内であることがさらに好ましく、50～800ppmの範囲内であることがさらに好ましい。水分含量が30ppm以上であると、より迅速に有機薄膜の形成を行うことができ、また、水分含量が1000ppm以下であれば、金属系界面活性剤等がより十分な活性を発揮することができる。

なお、ここで示す水分含量は、有機溶媒溶液の一部を採取してカールフィッシャー法で測定した値を示し、その方法原理を用いた装置で測定した値であれば、測定装置については特に限定されない。なお、有機溶媒溶液が均一である場合には、均一な溶液を一部採取して測定し、有機溶媒層と水分層が2層となっている場合には、有機溶媒層より一部採取して測定し、有機溶媒中に水分層が分散し分離不可能な状態な場合には、その分散液をそのまま採取して測定した値を示す。

【0121】

有機溶媒溶液を所定の範囲内の水分含量に調製する方法は特に制限されないが、

（1）金属系界面活性剤、及び金属系界面活性剤と相互作用し得る化合物を含む有機溶媒溶液に水を添加する方法、

（2）金属系界面活性剤と水を含む有機溶媒溶液に、金属系界面活性剤と相互作用し得る化合物を添加する方法、等を例示することができる。

なお、急激な反応を抑えるためには、（1）の方法において添加する水、（2）の方法において添加する金属系界面活性剤と相互作用し得る化合物は、有機溶媒等で希釈して用いることが好ましい。

【0122】

所定の範囲内に水分含量を調整する、又は保持する方法として、具体的には、（1）有機溶媒溶液に接触して水層を設ける方法、（2）水分を含ませた保水性物質を、有機溶媒溶液に接触させて設ける方法、（3）有機溶媒溶液を、水分を含む気体に接触させる方法、（4）適宜水を添加する方法、等を例示することができる。これらの方法は単独で用いても、2以上を組み合わせ用いてもよい。

【0123】

水分含量の調整又は保持に用いる水は、中性であれば特に制限されないが、純水又は蒸留水であることが好ましい。また、工程（B-1）の有機溶媒溶液に用いる有機溶媒は、無水のものでもよいし、あらかじめ一定量の水分を含むものでもよい。

【0124】

上記（1）の有機溶媒溶液に接触して水層を設ける方法において、炭化水素系溶媒等の、水層と分離する有機溶媒を用いた場合には、有機溶媒層と分離した形で水層を共存させてもよいし、有機溶媒溶液を水層中に循環または通過させた後水槽から分離した有機溶媒層を用いてもよい。低級アルコール等の、水の溶解度が大きく水層と分離しない有機溶媒を用いた場合には、有機溶媒は浸透しないが水は浸透する膜等を介在させて、有機溶媒溶液と水層を接触させる方法を例示することができる。

【0125】

上記（2）の水分を含ませた保水性物質を、有機溶媒溶液に接触させて設ける方法における保水性物質としては、特に制限されないが、有機溶媒溶液中において水を分離せず、かつ有機溶媒溶液中に浮遊しない物質であることが好ましい。具体的には、吸水性高分子等の有機系保水材；ゼオライト、珪酸白土、パーミキュライト、多孔質セラミック等の無機系保水材；界面活性剤等の、溶液中に水を核とするミセル分子を形成することのできる化合物；等が挙げられ、なかでも、ゴミ等の混入が避けられる等の理由から、ガラス繊維

フィルターが特に好ましい。

また、水分を含ませた保水性物質が、有機溶媒溶液に接触させて設けられている場合、保水性物質として、水分を含ませた状態で溶液中に共存しているのが好ましい。

さらに、有機溶媒への水の溶解度をあげるために親水性の溶媒を用いる方法も考えられる。この場合の親水性溶媒についても、本発明における保水性物質に便宜上含まれる。

【0126】

保水性物質に含ませる水分量は特に制限されないが、有機溶媒溶液中で水が保水性物質と分離して遊離していない範囲内の水分量が好ましい。また、保水性物質に水分を適時添加して、保水性物質に水分を補給することもできる。また、保水性物質を、溶液と外気の界面、又は外気から溶液内にかけて連続して設けることによって、外気の湿気等を吸湿させ、有機溶媒溶液に水分を補給することもできる。

【0127】

また、上記(3)の有機溶媒溶液を、水分を含む気体に接触させる方法において、用いる気体は、溶液中の各成分に影響を及ぼさないものであれば特に制限されず、具体的には、空気、窒素ガス、アルゴンガス等を例示することができる。水分を含む気体を得る方法としては、特に制限されないが、気体に水分を含ませる方法；気体を加湿する方法；等が挙げられる。

気体に水分を含ませる方法は、特に制限されないが、ガスを水中に潜らせる、ガスを水または温水表面に接触させる等の水とガスを接触させる方法；水蒸気を含むガスをそのまま用いる方法；等を例示することができる。

気体を加湿する方法は、特に制限されないが、蒸気加湿法、水噴霧加湿法、または気化加熱法等を例示することができる。

【0128】

水分を含む気体と有機溶媒溶液とを接触させる方法は、特に制限されないが、水分を含む気体を有機溶媒溶液中に吹き込む、または有機溶媒溶液表面に吹き付ける方法；有機溶媒溶液を、水分を含む気体雰囲気下に、必要に応じて攪拌しながら放置する方法；有機溶媒溶液を、加湿された雰囲気下に、必要に応じて攪拌しながら放置する方法；等を例示することができる。水分を含む気体を吹き込む方法においては、必要に応じて吹き込み装置、清浄装置、ろ過装置等を付設するのが好ましい。

【0129】

また、上記(4)の適宜水を添加する方法は特に制限されないが、例えば、有機溶媒溶液中の水分量の減少を観測し、減少量に応じて水、又は相溶性を有する有機溶媒もしくは同一の有機溶媒で希釈した水を、有機溶媒溶液へ適宜追加する方法；一定量の水を含有する同一組成の有機溶媒溶液を供給する方法；等を例示することができる。

【0130】

有機溶媒溶液中の水分量を保持しながら、基材を浸漬させる方法としては、具体的には、

(a) 水分調整槽と基材浸漬槽を設け、水分調整槽で水分調整した有機溶媒溶液を基材浸漬槽に循環させる方法、

(b) 基材浸漬槽を複数設け、一つの基材浸漬槽で基材を浸漬している間に他の浸漬槽において有機溶媒溶液の水分調整を行う方法、

(c) 上述したような、所定の範囲内に水分含量を保持する手段を、基材浸漬槽に直接設け、適宜、水分を補給する方法、等が挙げられる。

【0131】

有機溶媒溶液に基材を接触させる工程(B-1)は、湿度が40%RH以上に保持された空間内において実施しなくてもよいが、湿度が40%RH以上に保持された空間内において実施することが好ましく、湿度が60%RH以上に保持された空間内において実施することがより好ましい。このような空間内においては、有機溶媒溶液中の水分量がより好ましく保持され、基材を連続的に有機溶媒溶液に接触させても、より再現性良く、より緻密な単分子膜を形成することができる。

【0132】

本発明の有機薄膜の製造方法は、単分子膜の製造にも、2層以上の多層膜の製造にも用いることができるが、単分子膜の製造には特に好適に用いることができる。また、化学的な吸着により基材表面に有機薄膜を形成させる方法としてだけでなく、物理的な吸着により基材表面に有機薄膜を形成させる方法としても用いることができる。

【0133】

本発明の有機溶媒溶液の保存方法は、少なくとも1以上の加水分解性基を有する金属系界面活性剤と、該金属系界面活性剤と相互作用し得る化合物を含む有機溶媒溶液を水で処理することにより、該有機溶媒溶液中の水分含量を所定の範囲内とし、前記有機溶媒溶液中の水分含量を所定の範囲内に保持した状態で、容器内に密閉する方法等を例示することができる。有機溶媒溶液中の水分含量を所定の範囲内とし、前記有機溶媒溶液中の水分含量を所定の範囲内に保持する方法としては、前述した方法と同様の方法が挙げられる。

【0134】

本発明の有機溶媒溶液を容器内に密閉することにより、有機溶媒とともに水分が大気中に揮散して水分量が減少するのを防ぐことができる。本発明の有機溶媒溶液は、その水分含量が有機薄膜の形成能に影響するため、保存中においても有機溶媒溶液中の水分含量を所定の範囲内に保持することが好ましい。

【0135】

上記の本発明の有機薄膜の製造方法を用いることにより、単分子膜、自己集合膜、化学吸着膜、及びそれらの性質をあわせ持つ有機薄膜を得ることができる。

【0136】

本発明における単分子膜は、化学吸着膜でもなく、自己集合膜でなくともよいが、化学吸着膜及び／又は自己集合膜であることが好ましい。本発明において、自己集合膜とは、外部からの強制力なしに秩序だった構造を形成してなる膜を意味する。工程(B-1)の有機溶媒溶液中において、少なくとも1以上の加水分解性基を有する金属系界面活性剤等の、有機薄膜を形成する分子が集合体を形成している場合には、その有機溶媒溶液を用いて得られる有機薄膜は自己集合膜となる。工程(B-1)中の金属系界面活性剤の分子は、有機溶媒溶液中で、溶媒により溶媒和されて単独に存在するのではなく、幾つかが集まって集合体を形成している。該集合体は、該金属系界面活性剤を、該金属系界面活性剤と相互作用し得る化合物及び水により処理して得ることができる。

【0137】

集合体の形態は、分子が、疎水性部分同士、または親水性部分同士で分子間力、配位結合、または水素結合等により集合した形態；膜を形成する分子が、共有結合により結合して集合した形態；水等の他の媒体が、核もしくは仲介として、ミセル等を形成した形態；またはこれらが組み合わさった形態；等である。

【0138】

集合体の形状は特に限定されず、球状、鎖状、帯状等いずれの形状であってもよい。集合体の平均粒径は、特に限定されないが、10～1000nmの範囲であることが好ましい。

【0139】

本発明における化学吸着膜は、基材上に形成されてなる化学吸着膜であって、該基材が結晶性を有さず、かつ、化学吸着膜が結晶性を有することを特徴とする。すなわち、本発明における化学吸着膜は、基材が結晶性であるかないかにかかわらず結晶性を有する。この場合、結晶性とは、多結晶であっても、単結晶であっても構わない。

【0140】

本発明の基材を有機溶媒溶液に接触させると、該有機溶媒溶液中の金属系界面活性剤が基材表面に吸着され、薄膜が形成される。金属系界面活性剤が基材表面に吸着される機構の詳細は明らかではないが、表面に活性水素を有する基材の場合には次のように考えることができる。すなわち、有機薄膜形成用溶液中においては、金属系界面活性剤の加水分解性基が水により加水分解された状態となっている。そして、この状態の金属系界面活性剤

が基材表面の活性水素と反応して、基材と強固な化学結合を形成してなる薄膜が形成される。この薄膜は、基材の活性水素と反応して形成されるものであって、単分子膜となる。

【0141】

以下、実施例により本発明をより具体的に説明するが、本発明の技術的範囲はこれらの例示に限定されるものではない。

【0142】

[実施例1-1]

(1) 金属系界面活性剤と相互作用し得る化合物溶液の調製

チタンテトライソプロポキシド(A-1:純度99%、酸化チタン換算濃度28.2重量%、日本曹達(株)製)12.4gを4つ口フラスコ中で、トルエン45.0gに溶解し、窒素ガス置換した後、エタノール/液体窒素バス中で-80℃に冷却した。別に、イオン交換水1.3g($H_2O/Ti=1.6$ (モル比))をイソプロパノール11.3gに混合後、-80~-70℃に冷却した状態で、上記4つ口フラスコ中へ攪拌しながら滴下した。滴下中は、フラスコ内の液温を-80~-70℃に維持した。滴下終了後、30分間冷却しながら攪拌後、室温まで攪拌しながら昇温して、無色透明な酸化チタン換算濃度5重量%の部分加水分解溶液(金属系界面活性剤と相互作用し得る化合物溶液:C-1)を得た。

(2) 金属系界面活性剤

有機溶媒溶液の調製用の金属系界面活性剤として、下記のM-1を用いた。

M-1:n-オクタデシルトリメトキシシラン(ODS):Gelest社製

(3) 有機溶媒溶液の調製方法

脱水トルエンにイオン交換水を加え、強く攪拌して、含水トルエンを調製した。この含水トルエンに金属系界面活性剤M-1を最終濃度が0.5重量%になるように加え、室温で30分間攪拌した。次に、この溶液に金属系界面活性剤と相互作用し得る化合物溶液C-1を、所定量滴下し、滴下終了後、室温で3時間攪拌して、有機溶媒溶液(SA-1)を得た。

(4) 蒸留水(純水)中での基材の洗浄

基材として、ステンレス(SUS304)基板(片面鏡面仕上げ)を用意した。15メガオーム以上の抵抗値を有する常温の蒸留水(純水)中に、前記基板を浸し、超音波処理を施しながら10分間超音波洗浄を行った。超音波洗浄は、超音波処理機IUC-7321N(東京超音波技研(株))を用いて、周波数28KHz、温度20℃で行った。超音波洗浄後、約60℃の温風をあてて乾燥処理を行った。

(5) アルカリ性水溶液による洗浄

水酸化ナトリウムを純水に溶解させて、5重量%の水酸化ナトリウム水溶液(5wt% NaOH aq)を調製した。基板をこの水酸化ナトリウム水溶液中に、10分間浸漬し洗浄を行った。基板を引き上げ後、純水で基板をかけ洗いし、エアブローを行って乾燥処理を行った。

(6) 有機薄膜の形成

アルカリ性水溶液で洗浄した基板を、上記の有機溶媒溶液(SA-1)中に1分間浸漬した後、有機溶媒溶液から引き上げた。基板に付着した液を常温の有機溶媒(NSクリーン100:株式会社ジャパンエナジー製)で基板表面をかけ洗いした後、NSクリーン100中で1分間、超音波洗浄を行い、再度NSクリーン100でかけ洗いした。洗浄後、基板表面に約60℃の温風をあてて20分間乾燥処理を行った。その結果、基板表面にきれいに密着して形成された有機薄膜が得られた。

(7) 有機薄膜の評価

以下に示す方法にて有機薄膜を評価した。

各試料の表面にマイクロシリンジから水、又は、テトラデカン(以下、「TD」と略す。)を5 μ l滴下した後、60秒後に、接触角測定器(360S型:エルマ社製)を用いて接触角を測定した。その結果を表1に示す。

【0143】

〔実施例1-2〕

実施例1-1の有機薄膜形成において、アルカリ性水溶液で洗浄した基板を、有機溶媒溶液（SA-1）中に3分間浸漬した他は実施例1-1と同じ方法で行った。有機薄膜評価結果を表1に示す。

【0144】

〔実施例1-3〕

実施例1-1の有機薄膜形成において、アルカリ性水溶液で洗浄した基板を、有機溶媒溶液（SA-1）中に5分間浸漬した他は実施例1-1と同じ方法で行った。有機薄膜評価結果を表1に示す。

【0145】

〔実施例1-4〕

実施例1-1の有機薄膜形成において、アルカリ性水溶液で洗浄した基板を、有機溶媒溶液（SA-1）中に10分間浸漬した他は実施例1-1と同じ方法で行った。有機薄膜評価結果を表1に示す。

【0146】

〔実施例1-5〕

実施例1-1の有機薄膜形成において、アルカリ性水溶液で洗浄した基板を、有機溶媒溶液（SA-1）中に20分間浸漬した他は実施例1-1と同じ方法で行った。有機薄膜評価結果を表1に示す。

【0147】

〔実施例1-6〕

実施例1-1の有機薄膜形成において、アルカリ性水溶液で洗浄した基板を、有機溶媒溶液（SA-1）中に30分間浸漬した他は実施例1-1と同じ方法で行った。有機薄膜評価結果を表1に示す。

【0148】

〔比較例1-1〕

実施例1-6において、アルカリ性水溶液による洗浄を行わなかった以外は実施例1-6と同じ方法で行った。有機薄膜評価結果を表2に示す。

【0149】

〔比較例1-2〕

実施例1-6において、有機薄膜の形成を行わなかった以外は実施例1-6と同じ方法で行った。有機薄膜評価結果を表2に示す。

【0150】

〔比較例1-3〕

実施例1-6において、アルカリ性水溶液による洗浄に代えて、常温でUV/オゾン処理を20分間実施した以外は実施例1-6と同じ方法で行った。有機薄膜評価結果を表2に示す。

【0151】

〔実施例2-1〕

実施例1-1で使用したステンレス基板を銅基板（片面鏡面仕上げ）に代えた他は、実施例1-1と同じ方法で行った。有機薄膜評価結果を表3に示す。

【0152】

〔実施例2-2〕

実施例1-2で使用したステンレス基板を銅基板（片面鏡面仕上げ）に代えた他は、実施例1-2と同じ方法で行った。有機薄膜評価結果を表3に示す。

【0153】

〔実施例2-3〕

実施例1-3で使用したステンレス基板を銅基板（片面鏡面仕上げ）に代えた他は、実施例1-3と同じ方法で行った。有機薄膜評価結果を表3に示す。

【0154】

〔実施例2-4〕

実施例1-4で使用したステンレス基板を銅基板（片面鏡面仕上げ）に代えた他は、実施例1-4と同じ方法で行った。有機薄膜評価結果を表3に示す。

【0155】

〔実施例2-5〕

実施例1-5で使用したステンレス基板を銅基板（片面鏡面仕上げ）に代えた他は、実施例1-5と同じ方法で行った。有機薄膜評価結果を表3に示す。

【0156】

〔実施例2-6〕

実施例1-6で使用したステンレス基板を銅基板（片面鏡面仕上げ）に代えた他は、実施例1-6と同じ方法で行った。有機薄膜評価結果を表3に示す。

【0157】

〔比較例2-1〕

比較例1-1で使用したステンレス基板を銅基板（片面鏡面仕上げ）に代えた他は、比較例1-1と同じ方法で行った。有機薄膜評価結果を表4に示す。

【0158】

〔比較例2-2〕

比較例1-2で使用したステンレス基板を銅基板（片面鏡面仕上げ）に代えた他は、比較例1-2と同じ方法で行った。有機薄膜評価結果を表4に示す。

【0159】

〔比較例2-3〕

比較例1-3で使用したステンレス基板を銅基板（片面鏡面仕上げ）に代えた他は、比較例1-3と同じ方法で行った。有機薄膜評価結果を表4に示す。

【0160】

〔実施例3-1〕

実施例1-1で使用したステンレス基板をニッケル基板（片面鏡面仕上げ）に代えた他は、実施例1-1と同じ方法で行った。有機薄膜評価結果を表5に示す。

【0161】

〔実施例3-2〕

実施例1-2で使用したステンレス基板をニッケル基板（片面鏡面仕上げ）に代えた他は、実施例1-2と同じ方法で行った。有機薄膜評価結果を表5に示す。

【0162】

〔実施例3-3〕

実施例1-3で使用したステンレス基板をニッケル基板（片面鏡面仕上げ）に代えた他は、実施例1-3と同じ方法で行った。有機薄膜評価結果を表5に示す。

【0163】

〔実施例3-4〕

実施例1-4で使用したステンレス基板をニッケル基板（片面鏡面仕上げ）に代えた他は、実施例1-4と同じ方法で行った。有機薄膜評価結果を表5に示す。

【0164】

〔実施例3-5〕

実施例1-5で使用したステンレス基板をニッケル基板（片面鏡面仕上げ）に代えた他は、実施例1-5と同じ方法で行った。有機薄膜評価結果を表5に示す。

【0165】

〔実施例3-6〕

実施例1-6で使用したステンレス基板をニッケル基板（片面鏡面仕上げ）に代えた他は、実施例1-6と同じ方法で行った。有機薄膜評価結果を表5に示す。

【0166】

〔比較例3-1〕

比較例1-1で使用したステンレス基板をニッケル基板（片面鏡面仕上げ）に代えた他

は、比較例1-1と同じ方法で行った。有機薄膜評価結果を表6に示す。

【0167】

[比較例3-2]

比較例1-2で使用したステンレス基板をニッケル基板（片面鏡面仕上げ）に代えた他は、比較例1-2と同じ方法で行った。有機薄膜評価結果を表6に示す。

【0168】

[比較例3-3]

比較例1-3で使用したステンレス基板をニッケル基板（片面鏡面仕上げ）に代えた他は、比較例1-3と同じ方法で行った。有機薄膜評価結果を表6に示す。

【0169】

[実施例4-1]

実施例1-4で使用した5重量%の水酸化ナトリウムを5重量%水酸化カリウム（5wt% KOH aq）に代えた他は、実施例1-4と同じ方法で行った。有機薄膜評価結果を表7に示す。

【0170】

[実施例4-2]

実施例1-4で使用した5重量%の水酸化ナトリウムを5重量%炭酸ナトリウム（5wt% Na₂CO₃ aq）に代えた他は、実施例1-4と同じ方法で行った。有機薄膜評価結果を表7に示す。

【0171】

[実施例4-3]

実施例1-4で使用した5重量%の水酸化ナトリウムを4重量%ケイ酸ナトリウム・9水和物（4wt% Na₂SiO₃・9H₂O aq）に代えた他は、実施例1-4と同じ方法で行った。有機薄膜評価結果を表7に示す。

【0172】

[実施例4-4]

実施例1-4で使用した5重量%の水酸化ナトリウムを5重量%トリエタノールアミン（5wt% N(C₂H₄OH)₃ aq）に代えた他は、実施例1-4と同じ方法で行った。有機薄膜評価結果を表7に示す。

【0173】

[実施例5-1]

実施例2-4で使用した5重量%の水酸化ナトリウムを5重量%水酸化カリウム（5wt% KOH aq）に代えた他は、実施例2-4と同じ方法で行った。有機薄膜評価結果を表8に示す。

【0174】

[実施例5-2]

実施例2-4で使用した5重量%の水酸化ナトリウムを4重量%ケイ酸ナトリウム・9水和物（4wt% Na₂SiO₃・9H₂O aq）に代えた他は、実施例2-4と同じ方法で行った。有機薄膜評価結果を表8に示す。

【0175】

[実施例5-3]

実施例2-4で使用した5重量%の水酸化ナトリウムを5重量%トリエタノールアミン（5wt% N(C₂H₄OH)₃ aq）に代えた他は、実施例2-4と同じ方法で行った。有機薄膜評価結果を表8に示す。

【0176】

[実施例6-1]

実施例3-4で使用した5重量%の水酸化ナトリウムを5重量%水酸化カリウム（5wt% KOH aq）に代えた他は、実施例3-4と同じ方法で行った。有機薄膜評価結果を表9に示す。

【0177】

【実施例6-2】

実施例3-4で使用した5重量%の水酸化ナトリウムを5重量%炭酸ナトリウム（5wt%Na₂CO₃ aq）に代えた他は、実施例3-4と同じ方法で行った。有機薄膜評価結果を表9に示す。

【0178】

【実施例6-3】

実施例3-4で使用した5重量%の水酸化ナトリウムを4重量%ケイ酸ナトリウム・9水和物（4wt%Na₂SiO₃・9H₂O aq）に代えた他は、実施例3-4と同じ方法で行った。有機薄膜評価結果を表9に示す。

【0179】

【実施例6-4】

実施例3-4で使用した5重量%の水酸化ナトリウムを5重量%トリエタノールアミン（5wt%N(C₂H₄OH)₃ aq）に代えた他は、実施例3-4と同じ方法で行った。有機薄膜評価結果を表9に示す。

【0180】

表1〜9中、SUSはステンレス基板、Cuは銅基板、Niはニッケル基板を意味する。

【0181】

【表1】

実施例	基板	基板前洗浄方法	洗浄時間 (分)	SA-1 浸漬 時間 (分)	接触角測定値	
					水 [°]	TD [°]
1-1	SUS	5wt%NaOHaq	10	1	99	34
1-2	SUS	5wt%NaOHaq	10	3	100	37
1-3	SUS	5wt%NaOHaq	10	5	96	35
1-4	SUS	5wt%NaOHaq	10	10	98	37
1-5	SUS	5wt%NaOHaq	10	20	99	34
1-6	SUS	5wt%NaOHaq	10	30	101	34

【0182】

【表2】

比較例	基板	基板前洗浄方法	洗浄時間 (分)	SA-1 浸漬 時間 (分)	接触角測定値	
					水 [°]	TD [°]
1-1	SUS	基板前洗浄なし	—	30	87	13
1-2	SUS	5wt%NaOHaq	10	浸漬なし	45	11
1-3	SUS	UV/オゾン	20	30	105	37

【0183】

【表3】

実施例	基板	基板前洗浄方法	洗浄時間 (分)	SA-1 浸漬 時間 (分)	接触角測定値	
					水 [°]	TD [°]
2-1	Cu	5wt%NaOHaq	10	1	124	28
2-2	Cu	5wt%NaOHaq	10	3	128	29
2-3	Cu	5wt%NaOHaq	10	5	128	25
2-4	Cu	5wt%NaOHaq	10	10	123	28
2-5	Cu	5wt%NaOHaq	10	20	126	29
2-6	Cu	5wt%NaOHaq	10	30	127	27

【0184】

【表4】

比較例	基板	基板前洗浄方法	洗浄時間 (分)	SA-1 浸漬 時間 (分)	接触角測定値	
					水 [°]	TD [°]
2-1	Cu	基板前洗浄なし	—	30	101	23
2-2	Cu	5wt%NaOHaq	10	浸漬なし	46	10
2-3	Cu	UV/オゾン	20	30	110	41

【0185】

【表5】

実施例	基板	基板前洗浄方法	洗浄時間 (分)	SA-1 浸漬 時間 (分)	接触角測定値	
					水 [°]	TD [°]
3-1	Ni	5wt%NaOHaq	10	1	102	32
3-2	Ni	5wt%NaOHaq	10	3	104	33
3-3	Ni	5wt%NaOHaq	10	5	104	29
3-4	Ni	5wt%NaOHaq	10	10	104	33
3-5	Ni	5wt%NaOHaq	10	20	106	34
3-6	Ni	5wt%NaOHaq	10	30	107	31

【0186】

【表6】

比較例	基板	基板前洗浄方法	洗浄時間 (分)	SA-1 浸漬 時間 (分)	接触角測定値	
					水 [°]	TD [°]
3-1	Ni	基板前洗浄なし	—	30	79	10
3-2	Ni	5wt%NaOHaq	10	浸漬なし	67	4
3-3	Ni	UV/オゾン	20	30	107	37

【0187】

【表7】

実施例	基板	基板前洗浄方法	洗浄時間 (分)	SA-1 浸漬時間 (分)	接触角測定値	
					水 [°]	TD [°]
4-1	SUS	5wt% KOH aq	10	10	109.9	35.6
4-2	SUS	5wt% Na ₂ CO ₃ aq	10	10	108.1	31.4
4-3	SUS	4wt% Na ₂ SiO ₃ 9H ₂ O aq	10	10	110.0	37.5
4-4	SUS	5wt% N(C ₂ H ₄ OH) ₃ aq	10	10	105.6	34.3

【0188】

【表8】

実施例	基板	基板前洗浄方法	洗浄時間 (分)	SA-1 浸漬時間 (分)	接触角測定値	
					水 [°]	TD [°]
5-1	Cu	5wt% KOH aq	10	10	111.5	18.3
5-2	Cu	4wt% Na ₂ SiO ₃ 9H ₂ O aq	10	10	110.2	27.7
5-3	Cu	5wt% N(C ₂ H ₄ OH) ₃ aq	10	10	102.1	12.3

【0189】

【表9】

実施例	基板	基板前洗浄方法	洗浄時間 (分)	SA-1 浸漬時間 (分)	接触角測定値	
					水 [°]	TD [°]
6-1	Ni	5wt% KOH aq	10	10	111.5	18.3
6-2	Ni	5wt% Na ₂ CO ₃ aq	10	10	98.2	27.2
6-3	Ni	4wt% Na ₂ SiO ₃ 9H ₂ O aq	10	10	110.2	27.7
6-4	Ni	5wt% N(C ₂ H ₄ OH) ₃ aq	10	10	102.1	12.3

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		B 0 5 D	7/00	F
		B 0 5 D	7/24	3 0 2 A
		B 0 5 D	7/24	3 0 2 B
		B 0 5 D	7/24	3 0 3 A
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ORGANOMETALLIC SOLUTION BASED HIGH RESOLUTION PATTERNING COMPOSITIONS

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Organometallic solutions have been found to provide high resolution radiation based patterning using thin coatings. The patterning can involve irradiation of the coated surface with a selected pattern and developing the pattern with a developing agent to form the developed image. The patternable coatings may be susceptible to positive-tone patterning or negative-tone patterning based on the use of an organic developing agent or an aqueous acid or base developing agent. The radiation sensitive coatings can comprise a metal oxo/hydroxo network with organic ligands. A precursor solution can comprise an organic liquid and metal polynuclear oxo-hydroxo cations with organic ligands having metal carbon bonds and/or metal carboxylate bonds.

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(54) 【発明の名称】 有機金属溶液に基づいた高解像度パターンニング組成物

(57) 【要約】

薄いコーティングを用いて放射線に基づいた高解像度のパターンニングを提供するための有機金属溶液が見出された。パターンニングは、選択されたパターンを有する被覆表面の照射と、現像画像を形成するための現像剤によるパターンの現像とを含むことができる。パターンニング可能なコーティングは、有機現像剤または酸もしくは塩基水溶液現像剤の使用に基づいて、ポジ型パターンニングまたはネガ型パターンニングの影響を受けやすい可能性がある。放射線感受性コーティングは、有機配位子を有する金属オキソ/ヒドロキソネットワークを含むことができる。前駆体溶液は、有機液体と、金属炭素結合および/または金属カルボキシレート結合を有する有機配位子を有する金属多核オキソ-ヒドロキソカチオンとを含むことができる。

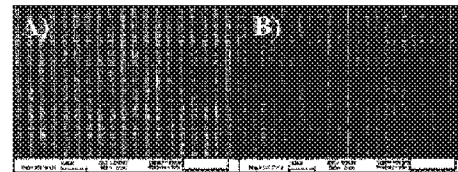


FIG. 12

【特許請求の範囲】

【請求項 1】

放射線により基板をパターン化するための方法であって、

選択されたパターンに沿って被覆基板を照射して、照射コーティングの領域および非照射コーティングの領域を有する照射構造を形成するステップであって、前記被覆基板が、金属炭素結合および／または金属カルボキシラート結合により有機配位子を有する金属オキソヒドロキシネットワークを含むコーティングを含むステップと、

前記照射構造を選択的に現像して、前記照射コーティングまたは前記非照射コーティングの大部分を除去してパターン化基板を形成するステップとを含む方法。

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【請求項 2】

前記照射構造が二者択一的にポジ型画像形成またはネガ型画像形成を受けることができるように、前記照射構造が、塩基水溶液に可溶性である照射コーティングと、有機溶媒に可溶性である非照射コーティングとを有する、請求項 1 に記載の方法。

【請求項 3】

前記非照射コーティングを除去するために、前記現像が有機溶媒を用いて実施される、請求項 1 または 2 に記載の方法。

【請求項 4】

前記選択的な現像が塩基水溶液を用いて実施される、請求項 1 または 2 に記載の方法。

【請求項 5】

前記照射が、電子ビーム、紫外線、極紫外線、ArF レーザーからの照射、KrF レーザーからの照射、またはUV ランプを用いて実施される、請求項 1 ～ 4 のいずれか一項に記載の方法。

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【請求項 6】

エッチングされた前記パターンが、約 60 nm 以下の平均ピッチを有するフィーチャを含む、請求項 1 ～ 5 のいずれか一項に記載の方法。

【請求項 7】

前記非照射コーティングが約 0.1 ～ 約 4 である有機配位子および金属カチオン間のモル比を有し、そして約 1 ミクロン以下の平均コーティング厚さを有する、請求項 1 ～ 6 のいずれか一項に記載の方法。

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【請求項 8】

前記金属がスズイオン、アンチモンイオン、インジウムイオンまたはこれらの組み合わせを含み、前記有機配位子が金属炭素結合を形成し、前記金属炭素結合を形成する配位子がアルキル配位子、アルケニル配位子、アリール配位子、またはこれらの組み合わせ（各配位子は 1 ～ 16 個の炭素原子を含有する）を含み、および／または前記有機配位子が金属-カルボキシル結合を形成し、前記金属-カルボキシル結合が、アルキルカルボキシラート配位子、アルケニルカルボキシラート配位子、アリールカルボキシラート配位子またはこれらの組み合わせ（各配位子は 1 ～ 16 個の炭素原子を有する）によって形成される、請求項 1 ～ 7 のいずれか一項に記載の方法。

【請求項 9】

液体前駆体溶液を付着させ、溶媒を蒸発させてコーティングを凝固させることによって前記コーティングを形成するステップをさらに含む、請求項 1 ～ 8 のいずれか一項に記載の方法。

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【請求項 10】

約 10 ミクロン以下の平均厚さと、コーティングに沿った任意の点において前記平均から約 50 % 以下である厚さ変動とを有する放射線感受性コーティングを含む被覆基板であって、前記コーティングが、金属炭素結合および／または金属カルボキシラート結合により有機配位子を有する金属カチオンを有する金属オキソヒドロキシネットワークを含む、被覆基板。

【請求項 11】

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前記有機配位子および前記金属カチオン間のモル比が約 0.1 ～ 約 4 である、請求項 10 に記載の被覆基板。

【請求項 12】

前記有機配位子および前記金属カチオン間のモル比が約 0.5 ～ 約 3 である、請求項 10 に記載の被覆基板。

【請求項 13】

約 1 ミクロン以下の平均コーティング厚さを有する、請求項 10 ～ 12 のいずれか一項に記載の被覆基板。

【請求項 14】

約 5 nm ～ 約 200 nm の平均厚さを有する、請求項 10 ～ 12 のいずれか一項に記載の被覆基板。

【請求項 15】

前記金属イオンがスズイオン、アンチモンイオン、インジウムイオンまたはこれらの組み合わせを含む、請求項 10 ～ 14 のいずれか一項に記載の被覆基板。

【請求項 16】

前記金属カチオンがさらに、金属および半金属の全含有量の約 50 モル % 以下である別の金属元素および／または半金属元素のカチオンを含む、請求項 15 に記載の被覆基板。

【請求項 17】

前記有機配位子が金属炭素結合を形成し、前記金属炭素結合を形成する配位子が、アルキル配位子、アルケニル配位子、アリール配位子またはこれらの組み合わせ（それぞれ、1 ～ 16 個の炭素原子を含有する）を含む、請求項 10 ～ 16 のいずれか一項に記載の被覆基板。

【請求項 18】

前記有機配位子が金属カルボキシル結合を形成し、前記金属カルボキシル結合が、アルキルカルボキシラート配位子、アルケニルカルボキシラート配位子、アリールカルボキシラート配位子またはこれらの組み合わせ（それぞれ、1 ～ 16 個の炭素原子を有する）によって形成される、請求項 10 ～ 16 のいずれか一項に記載の被覆基板。

【請求項 19】

表面を有する基板と、前記表面に沿って選択された領域に存在し、前記表面に沿って他の領域には存在しない第 1 のコーティングとを含むパターン化基板であって、前記第 1 のコーティングが金属オキソヒドロキソネットワークおよび有機配位子を含み、金属カチオンが金属炭素結合および／または金属カルボキシラート結合によって有機配位子を有しており、二者択一的に、前記第 1 のコーティングが少なくともいくつかの有機液体に可溶性であるか、または前記第 1 のコーティングが塩基水溶液に可溶性である、パターン化基板。

【請求項 20】

前記コーティングが存在しない前記基板の領域において前記基板表面が露出される、請求項 19 に記載のパターン化基板。

【請求項 21】

前記コーティングが少なくともいくつかの有機液体に効果的に可溶性であり、第 1 のコーティングが存在しない領域において前記表面に沿って第 2 のコーティングをさらに含み、前記第 2 のコーティングが塩基水溶液に可溶性である、請求項 19 または 20 に記載のパターン化基板。

【請求項 22】

前記パターン化コーティングが、約 60 nm 以下の平均ピッチを有するフィーチャを含む、請求項 19 ～ 21 のいずれか一項に記載のパターン化基板。

【請求項 23】

有機液体と、金属炭素結合および／または金属カルボキシラート結合を有する有機配位子を有する約 0.01 M ～ 約 1.4 M の金属多核オキソ／ヒドロキソカチオンとを含む前駆体溶液であって、前記前駆体溶液が約 0.5 センチポアズ (cP) ～ 約 150 cP の粘

度を有し、前記有機液体が、少なくとも10℃の引火点と、20℃において約10kPa未満の蒸気圧とを有する、前駆体溶液。

【請求項24】

前記金属がスズを含み、前記有機液体がアルコールである、請求項23に記載の前駆体溶液。

【発明の詳細な説明】

【技術分野】

【0001】

政府の権利に関する陳述

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【0002】

本発明は、有機金属コーティング組成物を用いて材料のパターニングを実施するための放射線に基づく方法に関する。本発明はさらに、放射線により非常に高解像度でパターニング可能な有機金属コーティングを形成するために付着され得る前駆体溶液と、パターニングの前および後の、前駆体溶液により形成された被覆基板およびコーティングとに関する。

【背景技術】

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【0003】

半導体ベースのデバイスおよび他の電子デバイスまたは他の複雑な微細構造を形成する場合、構造を集積するために、材料は一般的にパターン化される。従って、構造は一般的に、種々の材料からパターンが形成される逐次的な付着およびエッチングステップの反復プロセスによって形成される。このようにして、小さい領域に多数のデバイスを形成することができる。技術的ないくつかの進歩は、そのデバイスの設置面積の低減を含むことができ、これは性能の向上のために望ましい可能性がある。

【0004】

放射線パターンを使用してそのパターンに対応して有機組成物の化学構造を変化させるように、放射線パターン化レジストとして有機組成物を使用することができる。例えば、半導体ウェハのパターニングのためのプロセスは、放射線感受性有機材料の薄膜から、所望の画像のリソグラフィ転写を必要とし得る。レジストのパターニングは、一般的に、レジストを(例えば、マスクを介して)選択されたエネルギー源に暴露して潜像を記録し、次に、レジストの選択された領域を現像および除去することを含むいくつかのステップを伴う。ポジ型(positive-tone)レジストの場合、暴露領域が変化されてこのような領域が選択的に除去可能にされるが、ネガ型(negative-tone)レジストの場合には、非暴露領域がより容易に除去可能である。

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【0005】

一般的に、パターンは放射線、反応性ガス、または溶液によって現像され、レジストの選択的に感受性の部分が除去され、レジストの他の部分は保護的なエッチング耐性層としての機能を果たす。液体现像剤は、画像を現像するために特に有効であり得る。基板は、保護レジスト層の残存領域のウィンドウまたはギャップを通して選択的にエッチングされ得る。あるいは、保護レジスト層の残存領域の現像されたウィンドウまたはギャップを通して、下側の基板の露出領域に所望の材料が付着され得る。最後に、保護レジスト層が除去される。プロセスを繰り返して、パターン化材料の付加的な層を形成することができる。機能性無機材料は、化学蒸着、物理蒸着または他の所望の手段を用いて付着され得る。導電性材料の付着またはドーパントの注入などの付加的な処理ステップを使用することができる。マイクロおよびナノファブリケーションの分野において、高集積密度を達成し、そして回路機能を改善するために、集積回路内のフィーチャ(feature)サイズは非常に小さくなっている。

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【発明の概要】

【課題を解決するための手段】

【0006】

第1の態様では、本発明は放射線により基板をパターン化するための方法に関し、本方法は、選択されたパターンに沿って被覆基板を照射して、照射コーティングの領域および非照射コーティングの領域を有する照射構造を形成するステップと、照射構造を選択的に現像して、照射コーティングまたは非照射コーティングの大部分を除去してパターン化基板を形成するステップとを含む。被覆基板は、一般に、金属炭素結合および／または金属カルボキシラート結合により有機配位子を有する金属オキソヒドロキソネットワークを含むコーティングを含む。

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【0007】

さらなる態様では、本発明は、約10ミクロン以下の平均厚さと、コーティングに沿った任意の点において平均から約50%以下である厚さ変動とを有する放射線感受性コーティングを含む被覆基板に関し、コーティングは、金属炭素結合および／または金属カルボキシラート結合により有機配位子を有する金属カチオンを有する金属オキソヒドロキソネットワークを含む。

【0008】

別の態様では、本発明は、表面を有する基板と、表面に沿って選択された領域に存在し、表面に沿って他の領域には存在しない第1のコーティングとを含むパターン化基板に関する。一般に、第1のコーティングは金属オキソヒドロキソネットワークおよび有機配位子を含み、金属カチオンは、金属炭素結合および／または金属カルボキシラート結合によって有機配位子を有している。二者択一的に、第1のコーティングは少なくともいくつかの有機液体に可溶性であるか、または第1のコーティングは塩基水溶液に可溶性である。

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【0009】

付加的な態様では、本発明は、有機液体と、金属炭素結合および／または金属カルボキシラート結合を有する有機配位子を有する約0.01M～約1.4Mの金属多核オキソヒドロキソカチオンとを含む前駆体溶液に関し、前駆体溶液は、約0.5センチポアズ(cP)～約150cPの粘度を有する。有機液体は、少なくとも10℃の引火点と、20℃において約10kPa未満の蒸気圧とを有し得る。

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【図面の簡単な説明】

【0010】

【図1】 潜像を有する放射線パターン化構造の概略斜視図である。

【図2】 図1の構造の側面平面図である。

【図3】 潜像を現像し、非照射コーティング材料を除去してパターン化構造を形成した後の、図1の構造の概略斜視図である。

【図4】 図3のパターン化構造の側面図である。

【図5】 潜像を現像し、照射コーティング材料を除去してパターン化構造を形成した後の、図1の構造の概略斜視図である。

【図6】 図5のパターン化構造の側面図である。

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【図7】 下層をエッチングした後の、図3および図4のパターン化構造の側面平面図である。

【図8】 パターン化された凝縮コーティング材料をエッチングして除去した後の、図7の構造の側面平面図である。

【図9】 「熱凍結(thermal freeze)」ダブルパターンニングのプロセスフローの側面平面図である。図1～図3に示されるプロセスは、第1の層を第2の層に対して不溶性にするベーキングの後に繰り返される。

【図10A】 モノブチルスズオキシド水和物を有する前駆体溶液の時間に対する自己相関散乱強度減衰のプロットである。

【図10B】 4-メチル-2-ペンタノール中にモノブチルスズオキシド水和物を含む前

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駆体溶液の、計算された質量平均粒径分布のヒストグラムである。

【図11A】30kV電子ビームにより $1191\mu\text{C}/\text{cm}^2$ の線量で照射し、4-メチル-2-ペンタノール中で現像した後に、モノブチルスズオキシド水和物を用いて形成されたコーティング材料中に36nmピッチで18nm幅のラインを有するネガ型パターン化コーティングの走査型電子顕微鏡写真である。

【図11B】30kV電子ビームにより $1191\mu\text{C}/\text{cm}^2$ の線量で照射し、乳酸エチル中で現像した後に、モノブチルスズオキシド水和物を用いて形成されたコーティング材料中に36nmピッチで18nm幅のラインを有するネガ型パターン化コーティングの走査型電子顕微鏡写真である。

【図11C】30kV電子ビームにより $1191\mu\text{C}/\text{cm}^2$ の線量で照射し、プロピレングリコールモノメチルエーテル(PGMEA)中で現像した後に、モノブチルスズオキシド水和物を用いて形成されたコーティング材料中に36nmピッチで18nm幅のラインを有するネガ型パターン化コーティングの走査型電子顕微鏡写真である。

【図11D】30kV電子ビームにより $1191\mu\text{C}/\text{cm}^2$ の線量で照射し、酢酸n-ブチル中で現像した後に、モノブチルスズオキシド水和物を用いて形成されたコーティング材料中に36nmピッチで18nm幅のラインを有するネガ型パターン化コーティングの走査型電子顕微鏡写真である。

【図12A】EUV投影リソグラフィを用いて13.5nm放射線により $101\text{mJ}/\text{cm}^2$ の線量で照射し、PGMEAにより現像した後に、モノブチルスズオキシド水和物を用いて形成されたコーティング材料中に44nmピッチで22nm幅のラインを有するネガ型パターン化コーティングの走査型電子顕微鏡写真である。

【図12B】EUV投影リソグラフィを用いて13.5nm放射線により $101\text{mJ}/\text{cm}^2$ の線量で照射し、PGMEAにより現像した後に、モノブチルスズオキシド水和物を用いて形成されたコーティング材料中に36nmピッチで18nm幅のラインを有するネガ型パターン化コーティングの走査型電子顕微鏡写真である。

【図13】モノブチルスズオキシド水和物を用いて形成されたコーティング材料のC-H伸縮モードの吸光度のFTIR透過測定から計算される場合の電子ビーム線量に対する相対的な炭化水素濃度のプロットである。

【図14】30kV電子ビームにより $511\mu\text{C}/\text{cm}^2$ の線量で照射し、2.38%のTMAHにより現像した後に、モノブチルスズオキシド水和物を用いて形成されたコーティング材料中に30nm幅のラインおよび60nmピッチを有するポジ型パターン化コーティングの走査型電子顕微鏡写真である。

【図15A】新たに調製された前駆体溶液から付着され、そして直ちに暴露されてPGMEA中で現像された膜を30kV電子ビームにより $1191\mu\text{C}/\text{cm}^2$ の線量で照射した後に、モノブチルスズオキシド水和物を用いて形成されたコーティング材料中に36nmピッチで18nm幅のラインおよび2.78nmのライン幅ラフネス(LWR)を有するネガ型パターン化コーティングの走査型電子顕微鏡写真である。

【図15B】室温で39日間エージングした前駆体溶液から付着され、そして直ちに暴露されてPGMEA中で現像された膜を30kV電子ビームにより $1191\mu\text{C}/\text{cm}^2$ の線量で照射した後に、モノブチルスズオキシド水和物を用いて形成されたコーティング材料中に36nmピッチで18nm幅のラインおよび2.87nmのLWRを有するネガ型パターン化コーティングの走査型電子顕微鏡写真である。

【図15C】新たに調製された前駆体溶液から付着され、被覆膜として室温で39日間エージングされ、そして暴露されてPGMEA中で現像されたレジスト膜を30kV電子ビームにより $1191\mu\text{C}/\text{cm}^2$ 線量で照射した後に、モノブチルスズオキシド水和物を用いて形成されたコーティング材料中に36nmピッチで18nm幅のラインおよび2.68nmのLWRを有するネガ型パターン化コーティングの走査型電子顕微鏡写真である。

【図16】30kV電子ビームにより $75\mu\text{C}/\text{cm}^2$ の線量で照射し、PGMEA中で現像した後に、ジビニルスズヒドロキシド/オキシドコーティング材料を用いて形成され

たコーティング材料中に100nmピッチのラインを有するネガ型パターン化コーティングの走査型電子顕微鏡写真である。

【図17】30kV電子ビームで暴露された、ジビニルスズヒドロキシド／オキシドコーティング材料を用いて形成されたコーティングのFTIR透過スペクトルから計算される場合の線量に対する相対的なビニル（C—H伸縮）吸光度のプロットである。

【図18】30kV電子ビームにより1500 $\mu\text{C}/\text{cm}^2$ の線量で照射し、PGMEA中で現像した後に、ジブチルスズオキソカルボキシラートコーティング材料を用いて形成されたコーティング材料中に32nmピッチのラインを有するネガ型パターン化コーティングの走査型電子顕微鏡写真である。

【図19】非暴露状態における、そして30kV電子ビームにより800 $\mu\text{C}/\text{cm}^2$ の線量で暴露された後の、ジブチルスズオキソカルボキシラート膜の比較透過モードのFTIR透過スペクトルである。

【発明を実施するための形態】

【0011】

望ましい有機金属前駆体溶液は、一般的に、非水系溶媒を有し、高解像度パターンニングを提供する配位子構造を有しており、この溶液は、良好な放射線感受性を有する放射線パターンニング可能なコーティングの形成のために高度の安定性を有する。金属オキソ／ヒドロキシ錯体を形成するために望ましい配位子はM—C結合またはM—O₂C結合を含むことができ、ここで、Mは選択された金属原子であり、Mがスズ、インジウム、アンチモンまたはこれらの組み合わせである場合に、特に望ましい結果を得ることができる。有機金属前駆体溶液を用いて形成されたコーティングの望ましい特徴は、パターン化金属酸化物コーティングを形成するための優れた直接パターンニングを提供する。特に興味深い実施形態では、放射線への暴露は、照射コーティング材料を現像剤組成物による除去に耐性のある材料に変換するか、あるいはコーティング材料が選択的に除去されるように暴露はその極性を十分に变化させる。従って、いくつかの実施形態では、コーティングは、同じコーティングを用いてネガティブにパターン化されるか、またはポジティブにパターン化されるかのいずれかであり得る。コーティング材料の少なくとも一部の選択的な除去は、下側の基板を露出させるためにコーティングの領域が除去されたパターンを残すことができる。照射に続いてコーティングを現像した後、パターン化酸化物材料は、優れたパターン解像度によりデバイス形成における加工を容易にするために使用することができる。コーティング材料は、極紫外線、紫外線および／または電子ビームなどの選択された放射線に感受性であるように設計され得る。さらに、前駆体溶液は、商品流通のために適切な貯蔵期間を有し、安定であるように配合され得る。

【0012】

本明細書における議論を簡単にするために、M—C配位子結合および／またはM—O₂C配位子結合を有する金属イオンは、有機安定化金属イオンと称することができる。また金属イオンは一般的に、有機配位子に加えて、1つまたは複数のオキソ配位子（すなわち、M—O）および／またはヒドロキシ配位子（すなわち、M—O—H）にもさらに結合される。有機安定化配位子およびオキソ／ヒドロキシ配位子は、金属酸化物への凝縮プロセスに対する著しい制御を提供することによって、前駆体溶液および対応するコーティングに望ましい特徴を提供し、著しい加工の利点を得られる。有機溶媒の使用は溶液の安定性を支持するが、驚くことに、非水系溶液に基づいた加工は、ポジ型パターンニングおよびネガ型パターンニングの両方に対して、優れた現像率コントラストを有する潜像の形成の後に得られたコーティングを選択的に現像する能力を保持する。有機安定化金属イオンが溶解された望ましい前駆体溶液は、微細構造の形成を可能にするために、エッチング耐性に関して高い放射線感受性および優れたコントラストを有し得るコーティングを形成するために便利な溶液ベースの付着を提供する。前駆体組成物の設計は、特定の放射線の種類および／またはエネルギー／波長に対して高い感受性を有するコーティング組成物の形成を提供し得る。

【0013】

放射線感受性コーティング材料は、ポジティブ放射線パターンニング用コーティングまたはネガティブ放射線パターンニング用コーティングのいずれかとして使用することができる。ネガティブパターンニングでは、放射線への暴露により、照射コーティング材料は、非照射コーティング材料と比べて現像剤組成物による除去に対してより耐性のある材料に変換される。ポジティブパターンニングでは、暴露されたコーティング材料が水性溶媒または他の高極性溶媒によって選択的に除去され得るように、暴露は、暴露されたコーティング材料の極性を十分に变化させる（例えば、極性を増大させる）。コーティング材料の少なくとも一部の選択的な除去によって、下側の基板を露出させるために領域が除去されたパターンが残される。

【0014】

集積電子デバイスなどの形成は、一般的に、構造内に個々の素子またはコンポーネントを形成するために材料のパターンニングを含む。このパターンニングは積み重ねられた層の選択された部分を覆う異なる組成物を含むことができ、これは、鉛直および／または水平方向に互いに相互作用をして所望の機能性を誘発する。種々の材料は、選択されたドーパントを有し得る半導体、誘電体、導電体および／または他のタイプの材料を含むことができる。高解像度パターンを形成するために、放射線感受性有機組成物を用いてパターンを導入することが可能であり、選択されたパターンを導入するために選択的な材料の除去を使用することができるように、本組成物の一部は現像／エッチングに対して耐性であるように加工され得るので、本組成物はレジストと呼ぶことができる。選択されたパターンまたはパターンのネガティブと共に放射線を用いてレジストを暴露し、現像剤に耐性の領域および現像剤に溶解する領域を有するパターンまたは潜像を形成することができる。本明細書に記載される放射線感受性有機金属組成物は、デバイス内に所望の無機材料構造を直接形成するために、そして／あるいは有機レジストの代替である放射線パターンニング可能な無機レジストとして使用することができる。いずれの場合も、著しい加工の改善を利用することができるので、そしてパターン化材料の構造も改善され得る。

【0015】

具体的には、前駆体溶液は、約0.1～約3である金属カチオンに対する放射線感受性配位子のモル濃度比を溶液が有するように、十分な放射線感受性有機配位子を含むことができる。前駆体溶液から形成されるコーティングは前駆体溶液中のイオンの配位子構造によって影響され、そして乾燥の際に金属のまわりの配位子構造が同等であってもよいし、あるいは配位子構造はコーティングおよび／または乾燥プロセス中に变化され得る。特に、有機配位子濃度は、前駆体の安定性と、有機溶媒（一般には、極性有機溶媒）で形成された溶液によるネットワーク形成の制御とにおいて驚くほどに大きい改善を提供する。理論によって制限されることは望まないが、放射線感受性配位子濃度の増大は、対応するオキソ配位子および／またはヒドロキソ配位子を有する金属カチオンのアグロメレーションを明らかに低減し、溶液を安定化させる。従って、前駆体溶液は、さらに攪拌することなく、少なくとも1週間、恐らくは著しくより長い（例えば、1ヶ月を超える）期間、固体の沈降に対して安定であり得る。長い安定時間のために、改善された前駆体は、潜在的な商業利用に関する多用途性を増大させた。全体のモル濃度は、所望の安定性レベルと一致して得られる所望のコーティング厚さおよび所望のコーティング特性を達成するように選択することができる。金属-炭素または金属-カルボキシラート結合を有する配位子は望ましい放射線感受性配位子を提供し、特定の配位子には、例えば、アルキル基（例えば、メチル、エチル、プロピル、ブチル、t-ブチル）、アリール基（例えば、フェニル、ベンジル）、アルケニル基（例えば、ビニル、アリル）、カルボキシラート（例えば、アセタート、プロパノアート、ブタノアート、ペンゾアート）基、またはこれらの組み合わせが含まれる。

【0016】

有機配位子を有する多原子金属オキソ／ヒドロキソカチオンは、所望の放射線吸収を達成するように選択され得る。特に、インジウムおよびスズベースのコーティング材料は、193 nm波長の遠紫外線および13.5 nm波長の極紫外線の良好な吸収を示す。表1

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には、モノブチルスズオキシド水和物から形成されて100℃でベーキングされたコーティング材料の選択された波長における光学定数（ n = 屈折率および k = 吸光係数）が記載される。

【0017】

【表1】

表1

波長 (nm)	n	k
193	1.75	0.211
248	1.79	0.0389
365	1.63	0
405	1.62	0
436	1.61	0

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【0018】

いくつかの前駆体溶液は、付加的な金属のブレンドを効果的に取り込んで、コーティング材料の望ましい全体的特性を提供する。前駆体溶液は、リソグラフィのために重要ないくつかの放射線波長の吸収を増大させるために付加的な金属カチオンを含むことができる。金属イオン濃度は、前駆体溶液に所望される特性を提供するように選択することができ、より薄い溶液は、一般的に、より薄いコーティング材料の形成と一致するが、コーティング特性は付着技術にも依存する。

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【0019】

前駆体組成物の配位子構造は、前駆体溶液の望ましい安定性と、放射線パターンニング機能とを提供すると考えられる。特に、放射線の吸収は、金属と有機配位子との間の結合の破壊を提供して、被覆材料の照射および非照射部分において組成物の差別化を生じることができると考えられる。従って、改善された前駆体溶液を形成するための組成の変更は、画像の現像の改善も提供する。特に、照射コーティング材料は、例えば、ポジ型またはネガ型画像のいずれかを現像し得る適切な現像剤の選択によって、現像剤に対する調節可能な応答を有する安定した無機金属酸化物材料をもたらし得る。いくつかの実施形態では、適切な現像剤には、例えば、2.38% TMAH（すなわち、半導体業界標準）が含まれる。コーティング層は、現像後にコーティング材料が残ることが意図される領域からコーティング材料を除去することによる現像中のパターン損失を伴わずに薄くされることが可能である。従来の有機レジストと比較して、本明細書に記載される材料は、商業的に関連する機能層に対する多数のエッチング化学に対して極めて高い耐性を有する。これは、本来ならばマスク機能に関してパターン化有機レジストを補足するために使用され得る中間の犠牲的無機パターン転写層を回避することによって、プロセスの簡素化を可能にする。また、コーティング材料は、便利なダブルパターンニングを提供することができる。具体的には、熱処理の後、コーティング材料のパターン化部分は、さらなる前駆体溶液を含む多数の組成物との接触に関して安定である。従って、既に付着されたハードマスクまたはレジストコーティング材料を除去することなく、多重パターンニングが実施され得る。

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【0020】

所望の機能性材料をパターン化するためのマスクとしてパターン化材料を使用した後、続いてパターン化コーティング材料を除去することができる。あるいは、得られたパターン化材料は、無機金属酸化物材料への少なくともいくつかの凝縮による適切な安定化の後、最終デバイスのコンポーネントとして構造内に組み込むことができる。例えば安定した誘電層としてパターン化無機コーティング材料が構造内に組み込まれる場合、加工手順の多数のステップは、放射線による材料の直接パターンニングの使用によって除外され得る。

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あるいは、短波長の電磁放射線および／または電子ビームを用いて暴露された薄い無機コーティング材料を用いて非常に高解像度の構造が形成され得ること、そして改善されたパターン化構造の形成のためにライン幅ラフネスが非常に低レベルまで低減され得ることが見出された。

【0021】

前駆体溶液は、多核金属オキソ／ヒドロキソカチオンおよび有機配位子を含む。金属亜酸化物カチオンともいわれる多核金属オキソ／ヒドロキソカチオンは、金属元素および共有結合した酸素原子を有する多原子カチオンである。過酸化物ベースの配位子を有する金属亜酸化物カチオンは、参照によって本明細書中に援用される“Patterned Inorganic Layers, Radiation Based Patterning Compositions and Corresponding Methods”という表題の米国特許第8,415,000号明細書(Stowersら)('000号特許)に記載されている。金属亜酸化物または金属水酸化物の水溶液は、ゲル化および／または沈殿に関して不安定な傾向があり得る。特に、溶液は溶媒が除去されると不安定であり、金属カチオンによりオキソ／水酸化物ネットワークを形成し得る。過酸化物などの放射線感受性配位子をこのような溶液中に取り込むと安定性を改善することができるが、ネットワーク形成に関連するバックグラウンドの不安定性は持続し得る。この制御されないネットワーク形成は、照射とは無関係に現像率決定経路を提供することによって、被覆材料の放射線感受性および／または現像率コントラストを効果的に低減する。

【0022】

新しい前駆体溶液は、過酸化物ベースの配位子を有する無機レジスト材料と比べて、改善された安定性およびネットワーク形成および沈殿の制御を備えて配合されている。この場合、配位子が放射線感受性であるという特徴付けは、放射線の吸収の後の金属-配位子結合の不安定性を指し、従って、材料の化学変化を引き起こすために放射線が使用され得る。特に、有機配位子は前駆体溶液を安定化するが、材料の加工に対する制御も提供し、そして金属イオンに対する有機配位子の比率の選択は、溶液および得られたコーティングの特性を制御するように調整され得る。特に、金属カチオンに対する有機配位子のモル比が約0.1〜約3の間であれば、一般的に、より安定した溶液を形成することができる。有機配位子の金属との結合の断裂を放射線により達成し、潜像を有するコーティング材料における現像率コントラストを改善することができるので、より安定した前駆体溶液は、最終照射コーティング材料と非照射コーティング材料との間のより大きいコントラストという追加利点を提供する。

【0023】

より大きい安定性を有する精製前駆体溶液は、基板の放射線暴露部分と非暴露部分との間のより大きい現像率コントラストの可能性を有するコーティング材料も提供し、これは、驚くことに、ポジ型パターンニングまたはネガ型パターンニングのどちらを用いても同時に達成することができる。具体的には、照射コーティング材料または非照射コーティング材料は、適切な現像剤組成物によって比較的より容易に溶解され得る。従って、改善された組成物および対応する材料を用いて、適切な現像剤の選択により、ポジ型またはネガ型画像形成を達成することができる。同時に、隣接する素子間の適切な絶縁、一般には電氣的絶縁と共に、隣接する素子間でピッチは非常に小さくされ得る。照射コーティング組成物はその後の現像／エッチングプロセスに対して非常に感受性であることが可能であり、その結果、コーティング組成物は、基板の表面に照射パターンニング組成物の適切な部分を残しながらコーティング組成物を選択的にきれいに除去することに関して現像プロセスの効力を損なうことなく非常に薄くされ得る。現像剤に対する暴露時間を短くできることは、さらに、コーティングのパターン化部分に損傷を与えることなく薄いコーティングを使用することと一致する。

【0024】

前駆体溶液は、一般的に、以下にさらに記載される任意の合理的なコーティングまたは印刷技術によって付着され得る。コーティングは一般に乾燥され、そして熱が加えられて

、照射の前にコーティングを安定化させることができる。一般に、コーティングは薄く、例えば、10ミクロン未満の平均厚さを有し、非常に小さいフィーチャをパターン化するために非常に薄いサブミクロンのコーティングが望ましいこともある。乾燥されたコーティングは適切な放射線、例えば、極紫外線、電子ビームまたは紫外線にさらされ、コーティング内に潜像を形成することができる。潜像は現像剤と接触されて、物理的な画像、すなわちパターン化コーティングを形成する。パターン化コーティングは、表面にパターン化された残りのコーティングを安定化するためにさらに加熱され得る。パターン化コーティングは、パターンに従ってさらなる加工、例えば、基板のエッチングおよび／または付加的な材料の付着を実施するために物理的なマスクとして使用することができる。加工の適切な時点で、残りのパターン化コーティングは除去することができるが、パターン化コーティングは最終構造に取り込まれることもできる。非常に微細なフィーチャは、本明細書に記載されるパターンニング組成物により効果的に達成され得る。

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【0025】

前駆体溶液

レジストコーティングを形成するための前駆体溶液は、一般的に、有機溶媒（一般的には、有機溶媒）中に適切な有機安定化配位子を有する金属カチオンを含む。前駆体溶液および最終的なレジストコーティングは金属酸化物化学に基づいており、有機配位子を有する金属ポリカチオンの有機溶液は、良好なレジスト特性を有する安定した溶液を提供する。配位子は放射線感受性を提供し、配位子の特定の選択は放射線感受性に影響し得る。特に、前駆体溶液は、金属カチオンおよび関連の配位子の選択に基づいて選択された放射線に対して所望のレベルの放射線吸収を達成するように設計され得る。溶液中の配位子安定化金属カチオンの濃度は、特定の付着手段（例えば、スピニングなど）のために適切な溶液特性を提供するように選択され得る。安定性および加工の有効性に関して特に有効性を有する金属は、第13族、第14族および第15族の金属である。対応して、パターンニングのために一般的に使用される放射線の高い吸収を提供するために、前駆体溶液中にSn、InおよびSb金属を含むことが望ましいが、これらの金属は、特性、特に放射線吸収を調整するために他の金属と組み合わせることも可能である。前駆体溶液は非常に高レベルの安定性を達成するように配合されており、従って、前駆体溶液は商品のために適切な貯蔵寿命を有する。以下のセクションに記載されるように、前駆体溶液は基板表面に塗布され、乾燥され、さらに処理されて、効果的な放射線レジストを形成することができる。前駆体溶液は、少なくとも部分的に溶媒が除去されたときにコーティング組成物を形成するように設計され、最終的には、無機固体は、照射および／または熱処理、プラズマへの暴露、または同様の処理の際に金属酸化物が大半を占める。

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【0026】

前駆体溶液は、一般的に、1つまたは複数の金属カチオンを含む。水溶液中で、金属カチオンは水分子との相互作用のために水和されており、加水分解が生じて酸素原子を金属イオンに結合させ、水酸化物配位子またはオキソ結合を形成し、対応して水素イオンが放出される。相互作用の性質は一般的にpH依存性である。水溶液中で付加的な加水分解が生じるにつれて、溶液は、金属酸化物の沈殿に関して、またはゲル化に関して不安定になり得る。最終的に酸化物材料を形成することが望ましいが、この進行は、有機配位子安定化金属カチオンを有する有機溶媒に基づく前駆体溶液を用いてより良く制御され得る。有機安定化配位子および有機溶媒に基づく前駆体溶液では、酸化物への進行は、まず溶液を処理してコーティング材料にし、そして最終の有機配位子を有する金属酸化物組成物にするための手順の一部として制御され得る。本明細書に記載されるように、有機配位子は、効果的な放射線レジスト組成物へ溶液の処理に対する著しい制御を提供するために使用することができる。

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【0027】

このようにして、金属カチオンの溶液はさらなる処理に備えた状態である。特に、前駆体溶液の添加成分として、多核金属オキソ／ヒドロキソカチオンを使用することが望ましいことがあり、これは、溶液をさらに金属酸化物組成物に対して備えた状態にし得る。一

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般に、前駆体溶液は、約 0.01 M～約 1.4 M、さらなる実施形態では約 0.05 M～約 1.2 M、そして付加的な実施形態では約 0.1 M～約 1.0 M の金属多核オキソ／ヒドロキソカチオンを含む。当業者は、上記の明確な範囲内の金属多核オキソ／ヒドロキソカチオンの付加的な範囲が考慮され、本開示の範囲内に含まれることを認識するであろう。

【0028】

スズ、アンチモンおよび／またはインジウムは、本明細書に記載される前駆体溶液の多核金属オキソ／ヒドロキソカチオンの形成のために特に適した金属である。特に、スズは、有機配位子に基づく望ましい化学的性質を有する。例えば、Ti、Zr、Hf、V、Co、Mo、W、Al、Ga、Si、Ge、P、As、Y、La、Ce、Lu またはこれらの組み合わせを含む付加的な金属は、より複雑な多核金属オキソ／ヒドロキソカチオン配合物を生成するために提供され得る。付加的な金属は、スズイオン、アンチモンイオンおよび／またはインジウムイオン（スズ／アンチモン／インジウムイオン）の代替として、またはこれらに加えて提供され得る。金属イオンのブレンドが使用される場合、いくつかの実施形態では、スズ／アンチモン／インジウムと付加的な金属イオンとのモル比は、各スズ／アンチモン／インジウムイオン当たり約 1 までの非スズ／アンチモン／インジウム金属イオンであり、そしてさらなる実施形態では、スズ／アンチモン／インジウム金属イオン当たり約 0.1～約 0.75 の非スズ／インジウム金属イオンである。金属イオンのブレンドが使用される場合、金属イオンは、溶液中の複雑な複数の金属オキソ／ヒドロキソクラスタ内または別個の金属オキソ／ヒドロキソクラスタ内にあり得る。溶液中の正確なクラスタ形態は分かっているいなくてもよく、得られたコーティングは、一般的に、溶液中のクラスタ構造が既知であるかどうかに関係なく所望の機能を提供することができる。上記のように、溶液中のカチオンの状態は pH 依存性であるので、酸素の配位の初期状態は溶液中で変化し得るが、傾向は加水分解および凝縮に向かっており、酸化物の形成に通じる。有機配位子は、ゲル化および最終的には沈殿をもたらす金属－酸素ネットワークの形成を妨害し得ることが分かった。従って、有機配位子は、選択的な放射線暴露によって酸化物に変換される準備ができた安定な状態を形成するために使用することができる。また有機配位子の使用は、前駆体溶媒および現像剤の選択を拡大し、水系溶媒および有機溶媒の両方を含む。

【0029】

金属は、一般的に、放射線の吸収に著しく影響する。そのため、金属カチオンは、所望の放射線および吸収断面積に基づいて選択され得る。インジウムおよびスズは、13.5 nm における極紫外線の強力な吸収を提供する。有機配位子と組み合わせて、これらは 193 nm 波長における紫外線の良好な吸収も提供する。また Hf も、電子ビーム材料および極紫外線放射の良好な吸収を提供する。放射線吸収のための組成物のさらなるチューニングは、他の金属イオンの添加に基づいて調整することができる。例えば、Ti、V、Mo、もしくは W、またはこれらの組み合わせを含む 1 つまたは複数の金属組成物を前駆体溶液に添加して、吸収端がより長い波長に移動したコーティング材料を形成し、例えば、248 nm 波長の紫外線に対する感受性を提供することができる。吸収されるエネルギーは金属－有機相互作用によって調節され、これは、金属－配位子の断裂および材料特性に対する所望の制御をもたらし得る。

【0030】

有機ベースの配位子は、凝縮に関して組成物を安定化する。特に、有機ベースの配位子の相対濃度が高いと、凝縮金属酸化物または金属水酸化物の形成は、仮に凝縮が室温で自然に生じるとしても、非常にゆっくりである。この安定化特性の発見に基づいて、コーティングを形成するために便利な処理を保持しながら、良好な貯蔵安定性を有する高濃度の放射線感受性配位子を用いて、溶液は形成され得る。放射線感受性配位子は、金属－炭素結合、例えばスズ－炭素結合を形成するカルボキシラートおよび有機部分を含む。吸収された放射線からのエネルギーは、金属－有機配位子結合を破壊し得る。これらの結合が破壊されると、対応する凝縮に関する安定化が低減または喪失される。組成物は、M－O

Hの形成によって、または凝縮してM—O—M結合を形成することによって変化し得る。ここで、Mは金属原子を表す。従って、放射線によって化学変化を制御することができ、高放射線感受性配位子濃度を有する組成物は、水酸化物および凝縮の自然形成の回避に関して非常に安定であり得る。所望の配位子構造を有する一部の適切な金属組成物は、Alpha Aesar (MA, USA) および TCI America (OR, USA) (以下の実施例を参照) などの商業的供給源から購入することができ、他の金属—配位子組成物は以下に記載されるように合成され得る。

【0031】

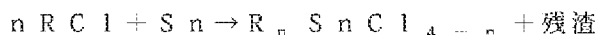
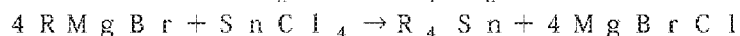
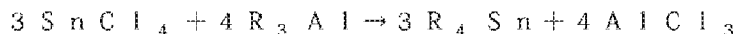
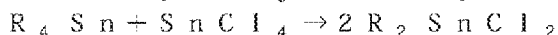
有機配位子は、例えば、アルキル（例えば、メチル、エチル、プロピル、ブチル、t-ブチル、アリール（フェニル、ベンジル））、アルケニル（例えば、ビニル、アリル）、およびカルボキシラート（アセタート、プロパノアート、ブタノアート、ペンゾアート）であり得る。前駆体組成物は、一般に、金属カチオン濃度の約0.25倍～約4倍、さらなる実施形態では約0.5倍～約3.5倍、付加的な実施形態では約0.75倍～約3倍、そして他の実施形態では金属カチオン濃度の約1倍～約2.75倍の配位子濃度を含む。当業者は、上記の明確な範囲内の配位子濃度の付加的な範囲が考慮され、本開示の範囲内に含まれることを認識するであろう。

【0032】

金属イオンに対するオキシ/ヒドロキシ配位子に関して、これらの配位子は、加水分解による加工の間に形成され得る。いくつかの実施形態では、加水分解は、塩基性水溶液中のハロゲン化物配位子の置換と、それに続いて有機溶媒へ移すことを含み得る。特定の例は以下に示される。基本的に、有機安定化配位子およびハロゲン化物配位子を有する金属イオンを含む組成物は有機溶媒に溶解され、これは次に塩基性水溶液と接触され、そこでヒドロキシ配位子によるハロゲン化物配位子の置換が生じ得る。ヒドロキシ配位子を形成するために十分な時間を与えた後、有機液体は水性液体に溶けないとすれば、水溶液は有機相から分離され得る。いくつかの実施形態では、オキシ/ヒドロキシ配位子は、大気水からの加水分解によって形成され得る。加水分解可能な金属イオン組成物は、オキシ/ヒドロキシ配位子がコーティング材料内で直接形成するように、大気水分の存在下で加熱されることが可能であり、これは、高表面積のために比較的容易であり得る。大気水からの加水分解の一例も以下で記載される。

【0033】

有機安定化配位子の形成に関して、これらは溶液中で形成されて、所望の組成物を形成することもできる。カルボキシラート配位子に関して、対応するカルボン酸またはその塩は金属カチオンを有する溶液中に溶解され得る。所望される場合、金属に対するカルボキシラート基の結合を容易にするように溶液のpHを調整することができ、プロセスをさらに駆動するために加熱が適用されてもよい。一般に、反応は水性溶媒中で実施され、続いて有機溶媒へ移されるか、または有機溶媒中で直接実施され得る。またM—C結合も溶液相置換反応において形成され得る。以下の反応は、Sn—C結合を形成するための置換反応の代表的な適切な反応であり、他の金属イオンについても同様の反応が起こる。



式中、Rは有機配位子を表す。一般的に、異なる適切なハロゲン化物は、上記反応において置換され得る。反応は、反応物が合理的な溶解度を有する適切な有機溶媒中で実行され得る。

【0034】

一般に、所望の化合物は、有機溶媒、例えば、アルコール、エステルまたはこれらの組み合わせに溶解され得る。特に、適切な溶媒には、例えば、芳香族化合物（例えば、キシレン、トルエン）、エステル（プロピレングリコールモノメチルエーテルアセタート、酢酸エチル、乳酸エチル）、アルコール（例えば、4-メチル-2-プロパノール、1-ブ

タノール、アニソール）、ケトン（例えば、メチルエチルケトン）などが含まれる。一般に、有機溶媒の選択は、溶解度パラメータ、揮発度、引火性、毒性、粘度、および他の加工材料との潜在的な化学的相互作用によって影響され得る。溶液の成分を溶解させて混ぜ合わせた後、特にコーティングプロセスの間に、部分的な水および凝縮の結果として種々の特性は変化し得る。溶液の組成が本明細書において言及される場合、錯体配合物は、十分に特徴付けし得ない溶液において金属多核種を生じ得るので、その言及は溶液に添加される成分に対するものである。特定の用途のために、有機溶媒は、約10℃以上、さらなる実施形態では約20℃以上、そしてさらなる実施形態では約25℃以上の引火点と、20℃において約10kPa以下、いくつかの実施形態では約8kPa以下、そしてさらなる実施形態では約6kPa以下の蒸気圧とを有することが望ましい。当業者は、上記の明確な範囲内の引火点および蒸気圧の付加的な範囲が考慮され、本開示の範囲内に含まれることを認識するであろう。

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【0035】

一般に、前駆体溶液は、形成される材料の容積に適した適正な混合装置を用いて十分に混合される。適切なる過を用いて、任意の汚染物質または適切に溶解しない他の成分を除去することができる。いくつかの実施形態では、混ぜ合わせて前駆体溶液を組み合わせてから形成することができる別々の溶液を形成することが望ましいこともある。具体的には、以下の：金属多核オキソ／ヒドロキソカチオン、任意の付加的な金属カチオン、および有機配位子のうちの1つまたは複数を含む別々の溶液が形成され得る。多数の金属カチオンが導入される場合、多数の金属カチオンは、同一の溶液および／または別々の溶液中に導入され得る。一般的に、別々の溶液または合わせた溶液は、十分に混合され得る。いくつかの実施形態では、次に、金属カチオン溶液は、有機ベースの配位子が金属カチオンと結合できるように有機ベースの配位子溶液と混合される。得られた溶液は、安定化金属カチオン溶液と呼ぶことができる。いくつかの実施形態では、安定化金属カチオン溶液は安定した配位子形成を提供するために適切な時間反応させられ、配位子形成は、混合金属イオンが導入されるかどうかに関係なく、溶液内のクラスタ形成を含んでいてもそうでなくてもよい。いくつかの実施形態では、溶液の反応または安定化時間は、さらなる加工に先立って、少なくとも約5分間、他の実施形態では少なくとも約1時間、そしてさらなる実施形態では約2時間～約48時間であり得る。当業者は、安定化期間の付加的な範囲が考慮され、本開示の範囲内に含まれることを認識するであろう。

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【0036】

前駆体溶液中の種の濃度は、溶液の所望の物理特性を達成するように選択され得る。特に、より低い濃度は、全体的に、合理的なコーティングパラメータを用いてより薄いコーティングを達成することができるスピンコーティングなどの特定のコーティング手段のために、溶液の望ましい特性をもたらす得る。超微細なパターンニングを達成するため、および材料コストを低減するためにより薄いコーティングを使用することが望ましいことがある。一般に、濃度は、選択されたコーティング手段のために適切であるように選択され得る。コーティング特性はさらに以下に記載される。

【0037】

上記のように、金属カチオンに対する有機ベースの配位子の比較的大きい比率は、前駆体溶液を非常に安定にするために使用することができる。前駆体溶液の安定性は、初期溶液に対する変化に関して評価され得る。具体的には、大きいゾル粒子の生成と共に相分離が生じるか、あるいは溶液が所望のパターン形成を実施するその能力を失えば、溶液は安定性を失っている。本明細書に記載される改善された安定化手段に基づいて、溶液は、少なくとも約1週間、さらなる実施形態では少なくとも約2週間、他の実施形態では少なくとも約4週間、さらに混合することなく安定であり得る。当業者は、安定化時間の付加的な範囲が考慮され、本開示の範囲内に含まれることを認識するであろう。十分な安定化時間を有する溶液を配合することができ、適切な貯蔵期間を有する溶液を商業的に流通させることができる。

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【0038】

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コーティング材料

コーティング材料は、選択された基板への前駆体溶液の付着、およびそれに続く加工によって形成される。基板は一般的にコーティング材料が付着され得る表面を示し、そして基板は、表面が最上層に関連している複数の層を含み得る。いくつかの実施形態では、基板表面は、コーティング材料の接着のための表面を作製するために処理することができる。また、必要に応じて表面は清浄化および／または平滑化され得る。適切な基板表面は、任意の合理的な材料を含むことができる。特に興味深いいくつかの基板は、基板の表面にわたっておよび／または層内に、例えば、シリコンウェハ、シリカ基板、他の無機材料、ポリマー基板、例えば有機ポリマーなど、これらの複合体、およびこれらの組み合わせを含む。比較的薄い円筒形構造などのウェハが便利であり得るが、任意の合理的な形状の構造を使用することができる。ポリマー基板または非ポリマー構造上にポリマー層を有する基板は、その低コストおよび柔軟性に基いて、特定の用途のために望ましいことがあり、適切なポリマーは、本明細書に記載されるパターンニング可能な材料の加工のために使用され得る比較的低い加工温度に基いて選択され得る。適切なポリマーは、例えば、ポリカーボネート、ポリイミド、ポリエステル、ポリアルケン、そのコポリマーおよびその混合物を含むことができる。一般に、基板は、特に高解像度用途のために、平坦な表面を有することが望ましい。

【0039】

一般に、前駆体溶液を基板に供給するために任意の適切なコーティングプロセスが使用され得る。適切なコーティング手段は、例えば、スピンコーティング、スプレーコーティング、ディップコーティング、ナイフエッジコーティング、印刷手段（例えば、インクジェット印刷およびスクリーン印刷）などを含むことができる。これらのコーティング手段のいくつかはコーティングプロセス中にコーティング材料のパターンを形成するが、印刷などから現在得られる解像度は、本明細書に記載される放射線ベースのパターンニングから得られるよりも著しく低いレベルの解像度を有する。コーティングプロセスに対するより大きい制御を提供するために、コーティング材料は多数のコーティングステップで適用され得る。例えば、多数のスピンコーティングを実施して、所望される最終のコーティング厚さをもたらすことができる。以下に記載される熱処理は、各コーティングステップの後、または複数のコーティングステップの後に適用され得る。

【0040】

放射線を用いてパターンニングが実施される場合、スピンコーティングは、基板を比較的均一に被覆するために望ましい手段であり得るが、エッジ効果が存在し得る。いくつかの実施形態では、ウェハは、約500rpm～約10,000rpm、さらなる実施形態では約1000rpm～約7500rpm、そして付加的な実施形態では約2000rpm～約6000rpmの速度で回転され得る。回転速度は、所望のコーティング厚さを得るように調整され得る。スピンコーティングは、約5秒間～約5分間、そしてさらなる実施形態では約15秒間～約2分間の時間で実施され得る。初期低速回転（例えば、50rpm～250rpm）を用いて、基板全体に組成物の初期バルク塗布を実施することができる。任意のエッジビードを除去するために、水または他の適切な溶媒を用いて裏面リンスやエッジビード除去ステップなどを実施することができる。当業者は、上記の明確な範囲内のスピンコーティングパラメータの付加的な範囲が考慮され、本開示の範囲内に含まれることを認識するであろう。

【0041】

コーティングの厚さは、一般的に、前駆体溶液の濃度、粘度およびスピンコーティングの回転速度の関数であり得る。他のコーティングプロセスの場合、厚さは、一般的に、コーティングパラメータの選択によっても調整され得る。いくつかの実施形態では、その後のパターンニングプロセスにおいて小さくかつ高度に改造されたフィーチャの形成を容易にするために薄いコーティングを使用することが望ましいこともある。例えば、乾燥後のコーティング材料は、約10ミクロン以下、他の実施形態では約1ミクロン以下、さらなる実施形態では約250ナノメートル（nm）以下、付加的な実施形態では約1ナノメートル

ル (nm) ~ 約 50 nm、他の実施形態では約 2 nm ~ 約 40 nm、そしていくつかの実施形態では約 3 nm ~ 約 25 nm の平均厚さを有することができる。当業者は、上記の明確な範囲内の厚さの付加的な範囲が考慮され、本開示の範囲内に含まれることを認識するであろう。厚さは、x 線反射率の非接触法および／または膜の光学特性に基づいた偏光解析法を用いて評価され得る。一般に、コーティングは、加工を容易にするために比較的均一である。いくつかの実施形態では、コーティングの厚さの変動は、平均コーティング厚さから ±50% 以下、さらなる実施形態では ±40% 以下、そして付加的な実施形態では平均コーティング厚さに対して約 25% 以下だけ異なる。より大きい基板上の均一性の高いコーティングなどのいくつかの実施形態では、コーティングの均一性の評価は、1 センチメートルのエッジを除外して評価され得る。すなわち、コーティングの均一性は、コーティングのエッジから 1 センチメートル以内の部分については評価されない。当業者は、上記の明確な範囲内の付加的な範囲が考慮され、本開示の範囲内に含まれることを認識するであろう。

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【0042】

多くのコーティングプロセスは、より大きい表面積および／または蒸発を刺激する溶液の移動を有する液滴または他の形態のコーティング材料を形成するので、コーティングプロセス自体が溶媒の一部の蒸発をもたらす得る。溶媒の喪失は、材料中の種の濃度の増大につれてコーティング材料の粘度を増大する傾向がある。コーティングプロセスの間の目標は、十分な溶媒を除去して、さらなる加工のためにコーティング材料を安定化させることであり得る。一般に、コーティング材料は、さらに溶媒を追いついて、コーティング材料の緻密化を促進するために放射線暴露の前に加熱され得る。乾燥したコーティング材料は、一般的に、金属へのオキソ／ヒドロキソ配位子に基づいて高分子金属オキソ／ヒドロキソネットワークを形成することができ、ここで、金属は、いくつかの有機配位子、または有機配位子を有する多核金属オキソ／ヒドロキソ種で構成される分子固体も有する。

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【0043】

溶媒除去プロセスは、コーティング材料中に残存する特定の量の溶媒に関して定量的に制御されてもそうでなくてもよく、得られたコーティング材料の特性の経験的な評価は、一般的に、パターンニングプロセスに有効である加工条件を選択するために実施され得る。プロセス用途の成功のために加熱は必要とされないが、加工を加速し、そして／あるいはプロセスの再現性を増大させるために、被覆基板を加熱することが望ましいこともある。溶媒を除去するために加熱が適用される実施形態では、コーティング材料は、約 45℃ ~ 約 250℃、そしてさらなる実施形態では約 55℃ ~ 約 225℃ 温度まで加熱され得る。溶媒除去のための加熱は、一般的に、少なくとも約 0.1 分間、さらなる実施形態では約 0.5 分間 ~ 約 30 分間、そして付加的な実施形態では約 0.75 分間 ~ 約 10 分間実施され得る。当業者は、上記の明確な範囲内の加熱温度および時間の付加的な範囲が考慮され、本開示の範囲内に含まれることを認識するであろう。コーティング材料の加熱処理および緻密化の結果、コーティング材料は、コントラストを著しく損失することなく屈折率および放射線吸収の増大を示すことができる。

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【0044】

パターン化された暴露およびパターン化されたコーティング材料

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コーティング材料は、放射線を用いて微細にパターン化され得る。上記のように、前駆体溶液の組成、従って対応するコーティング材料の組成は、所望の形態の放射線を十分に吸収するように設計され得る。放射線の吸収は、金属と有機配位子間の結合を破壊できるエネルギーを生じ、その結果、有機ベースの配位子の少なくとも一部はもはや材料を安定化するために利用できない。十分な量の放射線の吸収により、暴露されたコーティング材料は凝縮し、すなわち増強された金属オキソ／ヒドロキソネットワークを形成し、これは、周囲大気から吸収された水を含み得る。放射線は、一般に、選択されたパターンに従って送達され得る。放射線パターンは、照射領域および非照射領域を有するコーティング材料において対応するパターンまたは潜像に転写される。照射領域は、化学的に変化されたコーティング材料を含み、非照射領域は一般的に形成されたままのコーティング材料を含

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む。下記のように、非照射コーティング材料の除去あるいは照射コーティング材料の選択的除去によるコーティング材料の現像の際、非常に鋭いエッジが形成され得る。

【0045】

放射線は、一般的に、マスクを介して被覆基板へ向けられてもよいし、または放射線ビームは基板全体に制御可能に走査されてもよい。一般に、放射線は、電磁放射線、電子ビーム（ベータ放射線）、または他の適切な放射線を含むことができる。一般に、電磁放射線は、可視光、紫外線またはx線などの所望の波長または波長範囲を有することができる。放射線パターンに対して達成可能な解像度は、一般的に、放射線の波長に依存し、より高い解像度パターンは、一般的により短い波長の放射線によって達成され得る。従って、特に高解像度のパターンを達成するために、紫外線、x線または電子ビームを使用することが望ましいこともある。

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【0046】

参照によって本明細書中に援用される国際規格ISO 21348 (2007)に従って、紫外線は、100 nm以上であり400 nm未満である波長間に広がる。フッ化クリプトンレーザーを248 nm紫外線源として使用することができる。紫外線領域は、容認された規格の下、いくつかの方法で、10 nm以上から121 nm未満までである極紫外線（EUV）、および122 nm以上から200 nm未満までである遠紫外線（FUV）などに細分され得る。フッ化アルゴンレーザーからの193 nmラインをFUVにおける放射線源として使用することができる。EUV光は、13.5 nmでリソグラフィのために使用されており、この光は、高エネルギーレーザーまたは放電パルスを用いて励起されたXeまたはSnプラズマ源から発生される。軟x線は、0.1 nm以上から10 nm未満までであると定義され得る。

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【0047】

電磁放射線の量は、暴露時間に対する積分放射フラックスによって得られるフルエンスまたは線量によって特徴付けることができる。適切な放射線フルエンスは、約1 mJ/cm²～約150 mJ/cm²、さらなる実施形態では約2 mJ/cm²～約100 mJ/cm²、そしてさらなる実施形態では約3 mJ/cm²～約50 mJ/cm²であり得る。当業者は、上記の明確な範囲内の放射線フルエンスの付加的な範囲が考慮され、本開示の範囲内に含まれることを認識するであろう。

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【0048】

電子ビームリソグラフィでは、電子ビームは一般的に二次電子を誘発し、これは一般的に照射された材料を変化させる。解像度は、少なくとも部分的に、材料内の二次電子の範囲の関数であり得る。ここで、より高い解像度は一般的により短い範囲の二次電子から得られると考えられる。本明細書に記載される無機コーティング材料を用いて電子リソグラフィにより達成可能な高解像度に基づいて、無機材料中の二次電子の範囲は制限される。電子ビームは、ビームのエネルギーによって特徴付けることができ、適切なエネルギーは、約5 V～約200 kV（キロボルト）、そしてさらなる実施形態では約7.5 V～約100 kVの範囲であり得る。30 kVにおける近接補正ビーム線量は、1平方センチメートル当たり約0.1マイクロクーロン～1平方センチメートル当たり約5ミリクーロン（mC/cm²）、さらなる実施形態では約0.5 μC/cm²～約1 mC/cm²、そして他の実施形態では約1 μC/cm²～約100 μC/cm²の範囲であり得る。当業者は、本明細書中の教示に基づいて、他のビームエネルギーにおいて対応する線量を計算することができ、上記の明確な範囲内の電子ビーム特性の付加的な範囲が考慮され、本開示の範囲内に含まれることを認識するであろう。

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【0049】

コーティング材料の設計に基づいて、凝縮コーティング材料を有する照射領域と、実質的に未変化の有機配位子を有する非照射コーティング材料との間には、材料特性の大きいコントラストが存在する。コントラストは照射後の熱処理によって改善され得るが、いくつかの実施形態では照射後の熱処理がなくても満足な結果を得ることが可能であることが分かった。暴露後の熱処理は、照射コーティング材料をアニーリングして、有機配位子ー

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金属結合の熱破壊に基づいてコーティング材料の非照射領域を有意に凝縮させることなく、その凝縮を増大させると思われる。照射後の熱処理が使用される実施形態の場合、照射後の熱処理は、約45℃～約250℃、付加的な実施形態では約50℃～約190℃、そしてさらなる実施形態では約60℃～約175℃の温度で実施され得る。暴露後加熱は、一般的に、少なくとも約0.1分間、さらなる実施形態では約0.5分間～約30分間、そして付加的な実施形態では約0.75分間～約10分間実施され得る。当業者は、上記の明確な範囲内の照射後加熱温度および時間の付加的な範囲が考慮され、本開示の範囲内に含まれることを認識するであろう。材料特性のこの高いコントラストは、以下のセクションに記載される現像後のパターンにおける鋭いラインの形成をさらに容易にする。

【0050】

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放射線による暴露の後、コーティング材料は、照射領域および非照射領域によりパターン化される。図1および図2を参照すると、基板102、薄膜103およびパターン化コーティング材料104を含むパターン化構造100が示されている。パターン化コーティング材料104は、照射コーティング材料の領域110、112、114、116および非照射コーティング材料の非凝縮領域118、120、122を含む。凝縮領域110、112、114、116および非凝縮領域118、120、122によって形成されたパターン化構造は、コーティング材料内の潜像を表し、潜像の現像は以下のセクションに記載される。

【0051】

現像およびパターン化構造

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画像の現像は、潜像を含むパターン化コーティング材料を現像剤組成物に接触させて、非照射コーティング材料を除去してネガ画像を形成するか、または照射コーティングを除去してポジ画像を形成するかのいずれかを含む。本明細書に記載されるレジスト材料を用いると、一般的には同じコーティングに基づいて適切な現像溶液を用いて、望ましい解像度を有する効果的なネガティブパターンニングまたはポジティブパターンニングを実施することができる。特に、照射領域は少なくとも部分的に凝縮されて金属酸化物の特性が増大され、その結果、照射材料は有機溶媒による溶解に対して耐性であり、非照射組成物は有機溶媒に可溶性のままである。凝縮したコーティング材料への言及は、材料の酸化物特性が初期材料に対して増大するという意味において少なくとも部分的な凝縮を指す。一方、非照射材料は、材料が疎水性であるために弱い塩基または酸水溶液に溶解せず、従って、ポジティブパターンニングのために塩基水溶液を使用して、非照射材料を保持しながら照射材料を除去することができる。

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【0052】

有機安定化配位子を有するコーティング組成物は、本質的に比較的疎水性である材料を生成する。有機金属結合の少なくとも一部を破壊するための照射により、材料はより低疎水性、すなわちより親水性の材料に変化される。この特性の変化は照射コーティングと非照射コーティングとの間に顕著なコントラストを提供し、これにより、同じレジスト組成物を用いてポジ型パターンニングおよびネガ型パターンニングの両方を行うことができるようになる。具体的には、照射コーティング材料はある程度まで凝縮して、金属酸化物のより多い組成物になるが、著しい加熱を伴わなくても凝縮の度合いは一般的に中程度であり、従って、照射材料は比較的、従来の現像剤による現像に対して直接的である。対照的に、過氧化物安定化配位子による金属オキソヒドロキソ化学に基づいた無機レジスト材料は、上記の'000号特許に記載されるように、照射の前は本質的により親水性であり、照射された過氧化物ベースのコーティングは、照射によりより著しい程度まで凝縮されることが可能であり、その結果、非照射レジストは弱い酸または塩基で除去され得るが、照射された過氧化物ベースのコーティングは金属酸化物材料と同様に現像され得る。

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【0053】

ネガ型画像形成に関して、図3および図4を参照すると、図1および図2に示される構造の潜像は現像剤との接触より現像されて、パターン化構造130が形成されている。画像の現像の後、基板102は、開口部132、134を通して上部表面に沿って露出され

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る。開口部132、134、135は、それぞれ非凝縮領域118、120、122の場所に位置する。ポジ型画像形成に関して、図5および図6を参照すると、図1および図2に示される構造の潜像は現像されて、パターン化構造140が形成されている。パターン化構造140は、図3のパターン化構造130の共役像 (conjugate image) を有する。パターン化構造140は、図1～図4の照射領域110、112、114、116 (現像されて開口部142、144、146、148を形成する) の場所で露出された基板102を有する。非凝縮領域118、120、および122は保持される。

【0054】

ネガ型画像形成の場合、現像剤は、前駆体溶液を形成するために使用される溶媒などの有機溶媒であり得る。一般に、現像剤の選択は、コーティング材料 (照射および非照射の両方) に関する溶解度パラメータ、ならびに現像剤の揮発度、引火性、毒性、粘度、および他のプロセス材料との潜在的な化学的相互作用によって影響され得る。特に、適切な現像剤には、例えば、芳香族化合物 (例えば、ベンゼン、キシレン、トルエン)、エステル (例えば、プロピレングリコールモノメチルエステルアセタート、酢酸エチル、乳酸エチル、酢酸n-ブチル、ブチロラクトン)、アルコール (例えば、4-メチル-2-プロパノール、1-ブタノール、イソプロパノール、アニソール)、ケトン (例えば、メチルエチルケトン、アセトン、シクロヘキサノン)、エーテル (例えば、テトラヒドロフラン、ジオキサン) などが含まれる。現像は、約5秒間～約30分間、さらなる実施形態では約8秒間～約15分間、そして付加的な実施形態では約10秒間～約10分間実施され得る。当業者は、上記の明確な範囲内の付加的な範囲が考慮され、本開示の範囲内に含まれることを認識するであろう。

【0055】

ポジ型画像形成の場合、現像剤は、一般に、酸または塩基水溶液であり得る。いくつかの実施形態では、塩基水溶液は、より鋭い画像を得るために使用され得る。現像剤からの汚染を低減するために、金属原子を含まない現像剤を使用することが望ましいこともある。従って、水酸化第4級アンモニウム組成物、例えば、水酸化テトラエチルアンモニウム、水酸化テトラプロピルアンモニウム、水酸化テトラブチルアンモニウムまたはこれらの組み合わせは現像剤として望ましい。一般に、特に興味深い水酸化第4級アンモニウムは、式 R_4NOH (式中、 R = メチル基、エチル基、プロピル基、ブチル基、またはこれらの組み合わせ) で表すことができる。本明細書に記載されるコーティング材料は、一般に、ポリマーレジストのために現在一般に使用されるものと同じ現像剤、具体的には水酸化テトラメチルアンモニウム (TMAH) で現像され得る。市販のTMAHは2.38重量パーセントで利用可能であり、この濃度は、本明細書に記載される処理のために使用され得る。さらに、混合水酸化第4級テトラアルキルアンモニウムが使用され得る。一般に、現像剤は、約0.5～約30重量パーセント、さらなる実施形態では約1～約25重量パーセント、そして他の実施形態では約1.25～約20重量パーセントの水酸化テトラアルキルアンモニウムまたは同様の水酸化第4級アンモニウムを含むことができる。当業者は、上記の明確な範囲内の現像剤濃度の付加的な範囲が考慮され、本開示の範囲内に含まれることを認識するであろう。

【0056】

主要な現像剤組成物に加えて、現像剤は、現像プロセスを容易にするために付加的な組成物を含むことができる。適切な添加剤には、例えば、アンモニウム、d-ブロック金属カチオン (ハフニウム、ジルコニウム、ランタンなど)、f-ブロック金属カチオン (セリウム、ルテチウムなど)、p-ブロック金属カチオン (アルミニウム、スズなど)、アルカリ金属 (リチウム、ナトリウム、カリウムなど)、およびこれらの組み合わせからなる群から選択されるカチオンと、フッ素、塩素、臭素、ヨウ素、硝酸、硫酸、リン酸、ケイ酸、ホウ酸、過氧化物、ブトキシド、ギ酸、エチレンジアミン-四酢酸 (EDTA)、タングステン酸、モリブデン酸など、およびこれらの組み合わせからなる群から選択されるアニオンとを有する溶解塩が含まれる。他の潜在的に有用な添加剤には、例えば、分子キレート剤、例えば、ポリアミン、アルコールアミン、アミノ酸またはこれらの組み合わ

せが含まれる。任意選択の添加剤が存在する場合、現像剤は、約10重量パーセント以下の添加剤、そしてさらなる実施形態では約5重量パーセント以下の添加剤を含むことができる。当業者は、上記の明確な範囲内の添加剤濃度の付加的な範囲が考慮され、本開示の範囲内であることを認識するであろう。添加剤は、コントラスト、感受性およびライン幅ラフネスを改善するように選択され得る。現像剤中の添加剤は、金属酸化物粒子の形成および沈殿も抑制し得る。

【0057】

より弱い現像剤、例えばより低濃度の水性現像剤、希釈した有機現像剤または組成物（コーティングがより低い現像速度を有する）の場合、より高温の現像プロセスを使用して、プロセスの速度を増大させることができる。より強い現像液の場合、現像プロセスの温度は、現像の速度を低下させ、そして／あるいは現像の動態学を制御するために低くすることができる。一般に、現像の温度は、溶媒の揮発度に一致する適切な値の間で調整され得る。さらに、現像剤－コーティング界面付近の溶解したコーティング材料を含む現像剤は、現像の間に超音波処理により分散され得る。

【0058】

現像剤は、任意の合理的な手段を用いてパターン化コーティング材料に適用され得る。例えば、現像剤は、パターン化コーティング材料上にスプレーされ得る。また、スピニングコーティングが使用され得る。自動処理の場合、現像剤をコーティング材料上に静止型式で注ぐことを含むパドル法が使用され得る。所望される場合、スピンリンス（*spin rinsing*）および／または乾燥が使用されて、現像プロセスを完了することができる。適切なすすぎ溶液は、例えば、ネガティブパターンングの場合には、超純水、メチルアルコール、エチルアルコール、プロピルアルコール、およびこれらの組み合わせを含み、ポジティブパターンングの場合には、超純水を含む。画像が現像された後、コーティング材料は、パターンとして基板上に配設される。

【0059】

現像ステップが完了したら、コーティング材料は、材料をさらに凝縮させ、材料をさらに脱水するために熱処理され得る。この熱処理は、最終デバイスに酸化物コーティング材料が取り込まれる実施形態のために特に望ましいことがあるが、さらなるパターンングを容易にするためにコーティング材料の安定化が望ましい場合、コーティング材料がレジストとして使用されて最終的に除去されるいくつかの実施形態に対して熱処理を実施することが望ましいこともある。特に、パターン化コーティング材料のベーキングは、パターン化コーティング材料が所望のレベルのエッチング選択性を示す条件下で実施され得る。いくつかの実施形態では、パターン化コーティング材料は、約100℃～約600℃、さらなる実施形態では約175℃～約500℃、そして付加的な実施形態では約200℃～約400℃の温度まで加熱され得る。加熱は、少なくとも約1分間、他の実施形態では約2分間～約1時間、さらなる実施形態では約2.5分間～約25分間実施され得る。加熱は、空气中、真空中、またはArもしくはN₂などの不活性ガス雰囲気中で実施され得る。当業者は、上記の明確な範囲内の熱処理のための温度および時間の付加的な範囲が考慮され、本開示の範囲内に含まれることを認識するであろう。

【0060】

従来の有機レジストでは、構造のアスペクト比（高さを幅で割った値）が非常に大きくなると、構造はパターン崩壊の影響を受けやすい。パターン崩壊は、加工ステップに関連する力、例えば表面張力が構造要素を変形させるような高アスペクト比構造の機械的不安定性に関連し得る。低アスペクト比構造は、潜在的な変形力に関してより安定である。本明細書に記載されるパターンング可能なコーティング材料を用いると、より薄いコーティング材料層を有する構造を効果的に加工することができるため、高アスペクト比のパターン化コーティング材料を必要とせずに改善されたパターンングを達成することができる。従って、パターン化コーティング材料において高アスペクト比のフィーチャに頼ることなく非常に高解像度のフィーチャが形成されている。

【0061】

得られた構造は、非常に低いライン幅ラフネスを有する、鋭いエッジを有することができる。特に、ライン幅ラフネスを低減できることに加えて、高いコントラストは、小さいフィーチャおよびフィーチャ間の空間の形成、ならびに極めて十分に解像された二次元パターン（例えば、鋭いコーナー）を形成する能力も可能にする。従って、いくつかの実施形態では、隣接する構造の隣り合った直線部分は、約 60 nm 以下、いくつかの実施形態では約 50 nm 以下、そしてさらなる実施形態では約 40 nm 以下の平均ピッチを有することができる。ピッチは設計により評価され、走査型電子顕微鏡法（SEM）、例えばトップダウン画像により確認され得る。本明細書で使用される場合、ピッチは、反復構造要素の空間的周期、すなわち中心間距離を指す。パターンのフィーチャ寸法は、一般にコーナーなどから離れたところで評価されるフィーチャの平均幅に関して表すこともできる。また、フィーチャは、材料要素間のギャップおよび／または材料要素を指すこともできる。いくつかの実施形態では、平均幅は、約 30 nm 以下、さらなる実施形態では約 25 nm 以下、そして付加的な実施形態では約 20 nm 以下であり得る。平均ライン幅ラフネスは、約 3.0 nm 以下、そしてさらなる実施形態では約 1.5 nm ～ 約 2.5 nm であり得る。ライン幅ラフネスの評価は、トップダウン SEM 画像の分析により平均ライン幅からの 3σ 偏差を導くことによって実施される。平均は、高頻度および低頻度の両方のラフネス、すなわちそれぞれ短い相関長および長い相関長を含有する。有機レジストのライン幅ラフネスは主に長い相関長によって特徴付けられるが、本発明の無機コーティング材料は、著しく短い相関長を示す。パターン転写プロセスにおいて、短い相関ラフネスはエッチングプロセスの間に平滑化され、はるかに高い忠実性パターンを生成し得る。当業者は、上記の明確な範囲内のピッチ、平均幅およびライン幅ラフネスの付加的な範囲が考慮され、本開示の範囲内に含まれることを認識するであろう。

【0062】

パターン化コーティング材料のさらなる加工

パターン化コーティング材料を形成した後、コーティング材料は、選択されたデバイスの形成を容易にするためにさらに加工され得る。さらに、構造を完成させるために、一般的にさらなる材料の付着、エッチングおよび／またはパターニングが実施され得る。コーティング材料は、最終的に除去されてもされなくてもよい。パターン化コーティング材料の品質は、いずれの場合も、改善されたデバイス（例えば、より小さい設置面積を有するデバイスなど）の形成のために前進され得る。

【0063】

パターン化コーティング材料は、例えば、図 3 および図 4 に示されるように、下側の基板への開口部を形成する。従来のレジストと同様に、パターン化コーティング材料は、パターンを転写して下側の薄膜を選択的に除去するために使用され得るエッチマスクを形成する。図 7 を参照すると、図 1 における下側の薄膜 103 は、基板 102 の上に、そして凝縮領域 110、112、114 の下方にそれぞれフィーチャ 152、154、156 を残してパターン化される。従来のポリマーレジストと比較して、本明細書に記載される材料は、著しく大きいエッチング耐性を提供することができる。図 5 および図 6 に示されるマスクパターンを用いて同様の加工を行うことができ、代替のマスクパターンから直接得られるパターン化構造はそれに応じて変化する。

【0064】

代替的にまたは付加的に、マスクパターンに従うさらなる材料の付着は、下側の構造の特性を変更させ、そして／あるいは下側の構造との接触を提供することができる。さらなるコーティング材料は、所望の材料特性に基づいて選択することができる。加えて、パターン化無機コーティング材料の密度が、高い注入耐性を提供することができるので、マスクの開口部を介してイオンが下側の構造選択的に注入され得る。いくつかの実施形態では、さらに付着される材料は、誘電体、半導体、導体または他の適切な材料であり得る。さらに付着される材料は、適切な手段、例えば、溶液ベースの手順、化学蒸着（CVD）、スパッタリング、物理蒸着（PVD）、または他の適切な手段を用いて付着され得る。

【0065】

一般に、複数の付加的な層が付着され得る。複数の層の付着に関連して、付加的なパターンニングが実施され得る。所望される場合には、付加的な量の本明細書に記載されるコーティング材料、ポリマーベースのレジスト、他のパターンニング手段またはこれらの組み合わせを用いて任意の付加的なパターンニングが実施され得る。

【0066】

上記のように、パターンニングの後のコーティング（レジスト）材料の層は、除去されてもされなくてもよい。層が除去されない場合、パターン化コーティング（レジスト）材料は構造内に組み込まれる。パターン化コーティング（レジスト）材料が構造内に取り込まれる実施形態の場合、コーティング（レジスト）材料の特性は、所望のパターンニング特性だけでなく、構造内の材料の特性も提供するように選択され得る。

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【0067】

パターン化コーティング材料の除去が所望される場合、コーティング材料は、従来のレジストとしての機能を果たす。パターン化コーティング材料は、レジスト／コーティング材料を除去する前に、後で付着される材料をパターンニングするため、および／または凝縮コーティング材料内の空間を介して基板を選択的にエッチングするために使用される。凝縮コーティング材料は、適切なエッチングプロセスを用いて除去することができる。具体的には、凝縮コーティング材料を除去するために、例えば、 BCl_3 プラズマ、 Cl_2 プラズマ、 HBr プラズマ、 Ar プラズマまたは他の適切なプロセスガスによるプラズマを用いてドライエッチングが実施され得る。代替的または付加的に、パターン化コーティング材料を除去するために、例えば、酸または塩基水溶液、 HF （水）、または緩衝 HF （水）／ NH_4F またはシュウ酸などを用いるウェットエッチングが使用され得る。図8を参照すると、図8の構造は、コーティング材料を除去した後に示される。エッチングされた構造150は、基板102およびフィーチャ152、154、156を含む。

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【0068】

金属オキソ／ヒドロキソベースのコーティング材料は、P. Zimmerman, J. Photopolym. Sci. Technol., Vol. 22, No. 5, 2009, p. 625において従来のレジストについて一般的に記載されるように、熱凍結プロセスを用いて多重パターンニングを実施するために特に便利である。「熱凍結」によるダブルパターンニングプロセスは、図9において概説される。第1のステップでは、図3および図4に関して記載されるように、リソグラフィプロセスおよび現像を用いてコーティング材料が基板162上のパターン160に形成される。加熱ステップ164を実施して、溶媒を除去し、コーティング材料を凝縮させるが、これは、完全な酸化物の形成を伴っていないでもよい。この加熱ステップは、上記の現像セクションに記載される現像後の加熱ステップと同等である。この「熱凍結」プロセスは、その後のコーティング材料の第2の層の付着に対してコーティング材料を不溶性にする。第2のリソグラフィおよび現像ステップ166は、基板162上にダブルパターン化構造168を形成するために実施される。エッチングステップ170の後、産物のダブルパターン化構造172が形成される。このプロセスを多重コーティングおよびパターンニングステップに拡張することは容易であり、このような拡張が考慮され、本開示の範囲内に含まれることに注目されたい。多重パターンニングに関して、本明細書に記載される無機コーティング材料と従来の有機レジストとの間の顕著な違いは、加熱ベーキングの後でも有機レジストが従来のレジストキャストリング溶媒中に可溶性のままなことであり、その結果、有機溶媒に可溶性ではなく、その後のコーティング層を適用することができる。

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【実施例】

【0069】

実施例1 ー 前駆体溶液の調製

この実施例は、スズベースの有機金属組成物を付着して放射線レジストコーティングを形成するための前駆体溶液の調製について記載された。

【0070】

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0.209 g のモノブチルスズオキシド水和物 (BuSnOOH) 粉末 (TCI America) を 10 mL の 4-メチル-2-ペンタノールに添加することによってレジスト前駆体溶液を調製した。溶液を閉鎖バイアルに入れ、24 時間攪拌させた。得られた混合物を 4000 rpm で 15 分間遠心分離し、0.45 μm の PTFE シリンジフィルタによりろ過し、不溶性材料を除去した。溶媒の蒸発および 600 °C におけるこのサンプルのか焼により、 SnO_2 残留質量に基づいて 0.093 M であるスズ濃度が明らかになった。Moebius 装置 (Wyatt Technology) による前駆体溶液の動的光散乱 (DLS) 分析 (図 10A および図 10B) は約 2 nm の平均直径を有する粒子の単峰性分布と一致し、12 量体ブチルスズヒドロキシドオキシド多原子カチオンについて報告された直径 (Eychenne-Baron et al., *Organometallics*, 19, 1940-1949 (2000)) と一致する。従って、結果は、非水系溶液内でのクラスタ形成と一致する。

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【0071】

実施例 2 — レジストコーティング、膜処理、ネガ型画像形成

この実施例は、電子ビーム暴露または極紫外線暴露に基づいて、ネガ型画像形成に基づくレジストパターンの形成を実証する。

【0072】

天然の酸化物表面を有するシリコンウェハ (25 × 25 平方 mm) を薄膜付着のための基板として使用した。付着の前に紫外線オゾン洗浄システムにおいて 10 分間サイクルで Si 基板を処理した。次に、実施例 1 からのレジスト前駆体溶液を、4500 rpm で 30 秒間基板上にスピンコーティングし、ホットプレート上で 100 °C において 2 分間ベーキングして、残留溶媒を除去した。コーティングおよびベーキング後の膜厚は、偏光解析法により、約 22 nm であると測定した。

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【0073】

レジスト膜で被覆された第 1 の基板を、1100 $\mu\text{C}/\text{cm}^2$ の線量でパターンを形成するためにラスタ走査された (rastered) 30 kV の電子ビームに暴露した。次に、パターン化レジストおよび基板に、150 °C で 2 分間暴露後ベーキング (PEB) を行った。次に、暴露した膜を極性有機溶媒に 30 秒間浸漬し、DI H_2O ですすぎ、コーティングの非暴露部分が除去されたネガ型画像を形成した。最後に、200 °C で 5 分間のホットプレートベーキングを現像後に実施した。図 11A ~ 図 11D は、4-メチル-2-ペンタノール (A)、乳酸エチル (B)、プロピレングリコールモノメチルエーテル (PGMEA) (C)、および酢酸 *n*-ブチル (D) 中で現像したレジスト膜中の 36 nm ピッチにおける 18 nm ラインの SEM 画像を示す。

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【0074】

同一の前駆体溶液を用いて別の基板を作製し、コーティング/ベーキングプロセスを使用した後、高解像度パターンニングのために同様に適している極紫外線へ暴露した。それぞれ 44 および 36 nm ピッチにおける 22 および 18 nm ラインのパターンを、13.5 nm 波長および 101 mJ/ cm^2 のイメージング線量で動作する、0.3 のアパーチャを有する投影を用いてレジスト上で暴露した。2 分間の 165 °C のホットプレート PEB の後、膜を PGMEA 中での浸漬により現像し、DI H_2O ですすぎ、そして最後に 200 °C で 5 分間ベーキングした。十分に解像されたライン-空間パターンのネガティブ画像は図 12A および図 12B に示される。

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【0075】

極性変化を誘発する放射線暴露の際に生成される化学的なコントラストは現像率コントラストにおいて明らかになり、レジストの画像形成性能は、フーリエ変換赤外 (FTIR) 分光法を用いて明白に示される。テトラヒドロフラン (THF) 溶媒から非ドーブシリコンウェハ上にスピンコーティングされたブチルスズヒドロキシドオキシドレジスト膜の透過モードの FTIR スペクトルを、30 kV 電子ビームにより暴露線量の関数として集めた。2800 ~ 2900 cm^{-1} からのアルキル C-H 伸縮モードに相当するいくつかの吸収ピークの分析は、アルキル配位子濃度の一貫した低下を線量の関数として示す (図

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【0076】

実施例3 — ポジ型画像形成

この実施例は、実施例1からのレジスト溶液を用いて、ポジ型画像の形成を実証した。

【0077】

実施例1からの同一の前駆体溶液から付着させたレジスト膜で別の基板を被覆し、ホットプレート上で150℃において2分間ベーキングした。レジストコーティングを有するベースのウェハを、 $511\mu\text{C}/\text{cm}^2$ の線量を有する30kVの電子ビームにより暴露し、その後、150℃で2分間の暴露後ベーキングを行った。ポジ型画像形成は、暴露したレジスト膜を塩基水溶液中、例えば2.38%の水酸化テトラメチルアンモニウム (TMAH) 中で現像することによって達成した。2.38%のTMAH中の浸漬により、暴露レジストがエッチングされ、図14のSEM画像に示される30nm (60nmピッチ) ラインが現像された。

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【0078】

実施例4 — レジスト安定性

この実施例は、レジスト前駆体溶液およびエージング後の被覆膜の一貫した画像形成性能によってレジスト前駆体の安定性を実証する。

【0079】

実施例1において既に記載したように調製したレジスト前駆体溶液をスピンコーティングにより一对のウェハ基板に塗布し、これをホットプレート上で100℃において2分間ベーキングした。前駆体溶液の一部を密封バイアル内に保持し、大気環境下、制御されない室温 (20~30℃) で被覆基板の一方 (第1の基板) と共に暗所において貯蔵した。コーティングの後すぐに、30kV電子ビームにより、レジスト膜を有する第2の基板を続いてパターン化し、150℃で2分間ベーキングし、PGMEA中で30秒間現像し、すすぎ、200℃で2分間ハードベーキングした。得られたパターン化第2の基板のSEM画像は図15Aに示される。この暴露および現像プロセスを、39日後に、貯蔵したレジスト膜を有する第1の基板において繰り返した。パターン化第1の基板のSEM画像は図15Bに示される。同様に、元の前駆体溶液の保持された部分を、39日間の貯蔵後の同じ日に使用して、第3のウェハ基板をレジスト膜で被覆し、これを直ちに、最初の2つの基板と同じに処理、暴露、および現像した。パターン化第3の基板のSEM画像は図15Cに示される。同じ36nmピッチおよび18nmライン幅における3つのレジスト膜の画像形成性能は、機能的に同一であり、39日の期間にわたって、被覆レジスト膜または前駆体溶液のエージング後に、画像忠実度、LWR、または感受性において観察可能な低下はないことが分かる。

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【0080】

実施例5 — 有機配位子の選択に基づいた放射線感受性の調節

この実施例は、適切な有機配位子を選択することによってレジストの放射線感受性の調節が観察されることを実証する。

【0081】

ジビニルスズ二塩化物 (Alpha Aesar) を0.1Mの濃度までPGMEAに溶解させた。15mL量のこの溶液を分液漏斗に入れ、これに7.31mLの0.4MのNaOH (水) を添加した。NaOH添加の直後に、容器を約1分間十分に振とうさせ、得られたエマルションを約24時間分離させた。この期間中に、2つの媒体間の相界面で形成された軽い凝集物は消失することが観察され、2つの透明な相が得られた。下側の水相を分液漏斗から除去し、上側のPGMEA相を4Aモレキュラーシーブ (Mallinkrodt、グレード514) 上で約5分間振とうさせて、残留水を除去した。ふるい分けした組成物のアリコート溶媒の蒸発および乾燥により、残留質量SnO₂に基づいてスズ濃度が0.1Mであることが明らかになった。

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【0082】

分離およびふるい分けの後の上記のPGMEA中のジビニルスズ水酸化物溶液を、シリ

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コンウェハ上に1250rpmで直接スピンキャストし、100℃のホットプレートベーキングを2分間行った。ベーキング後の偏光解析測定は、約16nmのレジスト膜厚を示した。30kV電子ビームにより $75\mu\text{C}/\text{cm}^2$ の線量でレジスト膜を暴露した後、100℃で第2のホットプレートベーキングを行い、PGMEA中で現像した。100nmピッチにおけるネガ型ライン/空間パターンのSEM画像は図16に示される。図16を生成するために使用される電子ビームの線量は、実施例2および3で使用したよりも著しく小さかったことに注意されたい。

【0083】

線量の関数として非ドーブシリコンウェハ上に酢酸エチル溶媒から付着された同様のレジスト膜において透過モードのFTIRスペクトルを集めた。電子ビーム線量の関数としての相対的なIR吸収は図17にプロットされる。約3055 cm^{-1} を中心とするビニルC-H伸縮に一致する吸収ピークの面積の分析に基づいて、面積の減少は、暴露の際にスズ配位子としてビニル基が損失されることを示し、これは、図13に示されるブチルスズヒドロキシドオキシドの場合のアルキル配位子の損失よりも、線量に関してはるかに急速かつ包括的である。

【0084】

実施例6 ー 有機スズオキソカルボキシラートレジスト

この実施例は、スズイオンに対してアルキルおよびカルボキシラート配位子を用いて形成された放射線レジストの有効性を実証する。

【0085】

ジブチルスズジアセタート (Alfa-Aesar) をn-プロパノール中に0.025Mの最終濃度に溶解させることによって、レジスト前駆体溶液を調製した。次に、溶液を0.45 μm のPTFEシリンジフィルタによりろ過し、3000rpmで30秒間回転されるシリコンウェハ基板上にスピンキャストした。次に被覆膜を60℃で2分間ベーキングし、残留溶媒を除去した。キャストおよびベーキングの間、ジブチルスズジアセタートは大気水によって部分的に加水分解され、揮発性分子の液体カルボキシラートから固体有機スズオキソカルボキシラートに変換される。偏光解析測定は約22nmのレジスト膜厚を示した。

【0086】

続いて1500 $\mu\text{C}/\text{cm}^2$ の線量でパターンを形成するためにラスタ走査された30kV電子ビームに対するその後の膜の暴露の後、60℃のホットプレートPEBを行い、PGMEA中に30秒間浸漬して、非暴露材料のエッチングによりパターンを現像した。SEM画像形成の前に、最後に100℃で5分間のハードベーキングを実施した。図18は、得られたネガ型ライン/スペースパターンの32nmピッチにける電子顕微鏡写真を含有する。

【0087】

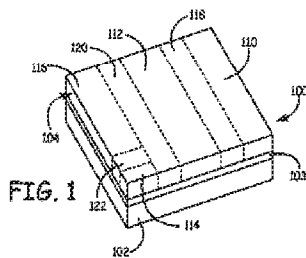
電子ビームによる放射線暴露の際の上記材料における化学的なコントラストの生成は、図19に示されるように、透過FTIR分光法によって観察され得る。30kV電子ビーム(800 $\mu\text{C}/\text{cm}^2$)への暴露の前および後に、非ドーブシリコンウェハ上に付着させて50℃で2分間ベーキングした有機スズオキソカルボキシラート薄膜の透過スペクトルを集めた。簡単な有機スズオキソヒドロキシドと同様に、炭化水素C-H伸縮および変角モードに帰属される吸収ピーク(2957、2924、2858、1391、および1331 cm^{-1})の激しい低下が観察され、暴露時のアルキル配位子の損失が確認された。また、暴露時のカルボキシラート配位子の分解に帰属される1605 cm^{-1} を中心とする吸光度の著しい低下と、それに伴うカルボニルC=O吸収の低減は容易に明らかであり、カルボキシラートに特有である。

【0088】

上記の実施形態は例示的なものであり、限定されることは意図されない。付加的な実施形態は特許請求の範囲の範囲内である。さらに、本発明は特定の実施形態に関して記載されたが、当業者は、本発明の趣旨および範囲から逸脱することなく形態および詳細の変化

がなされ得ることを認識するであろう。上記文献の参照による任意の援用は、本明細書中の明確な開示に反する主題が決して援用されないように限定される。

【図 1】



【図 2】

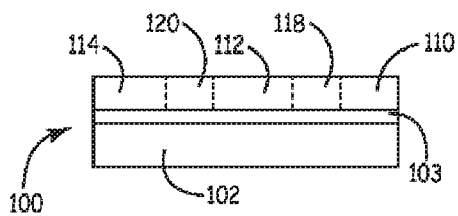
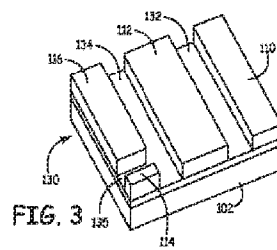


FIG. 2

【図 3】



【図 4】

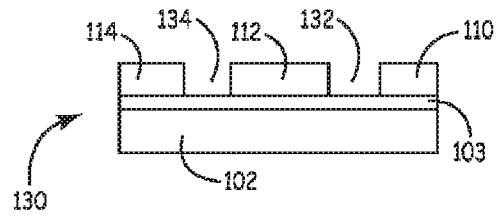


FIG. 4

【図 5】

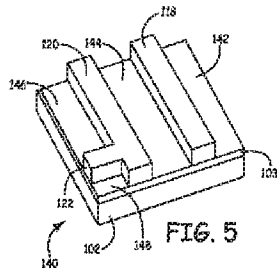


FIG. 5

【図 6】

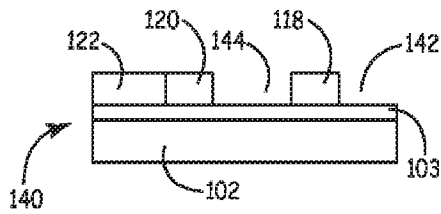


FIG. 6

【図 7】

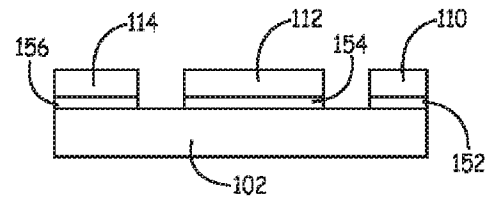


FIG. 7

【図 8】

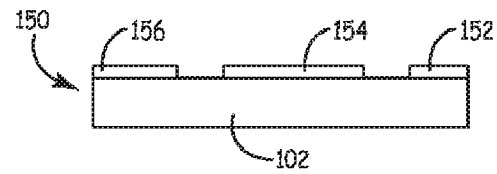


FIG. 8

【図 9】

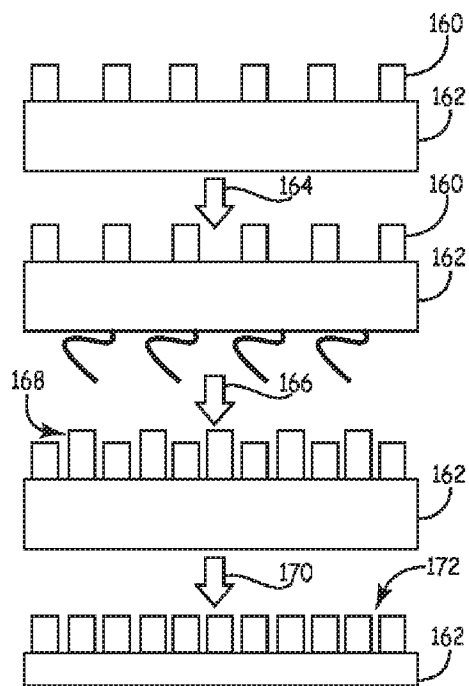


FIG. 9

【図 10】

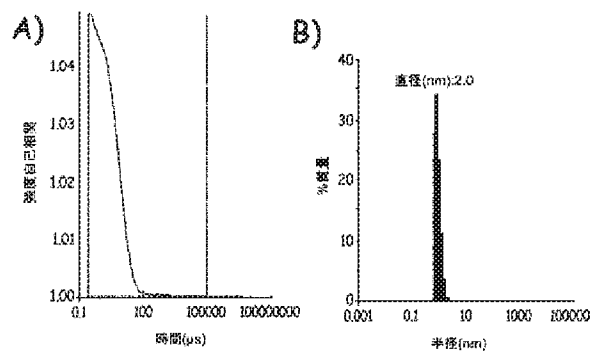


図 10

【図 1 1】

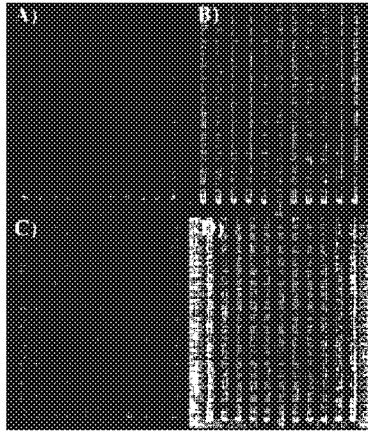


FIG. 11

【図 1 2】

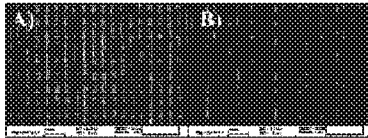


FIG. 12

【図 1 4】

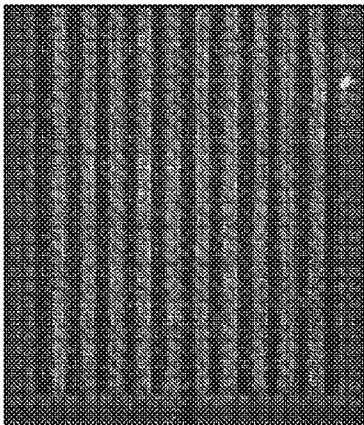


FIG. 14

【図 1 3】

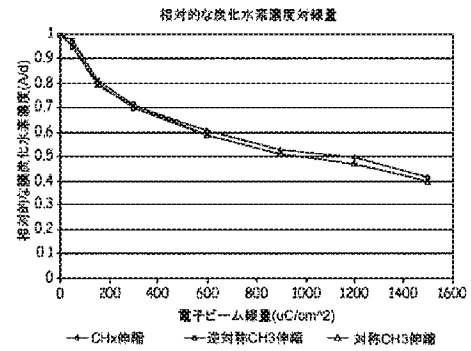


図 13

【図 1 5】

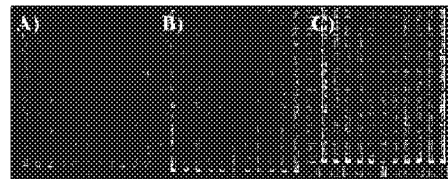


FIG. 15

【図 1 6】

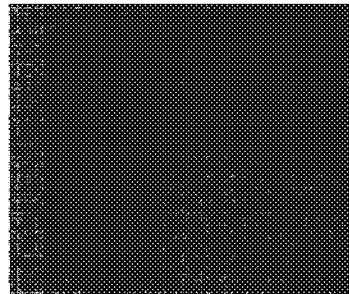


FIG. 16

【図 17】

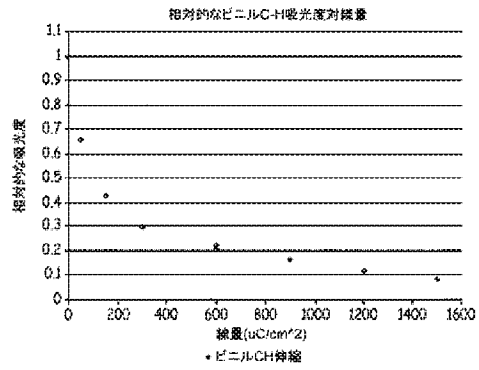


図 17

【図 18】

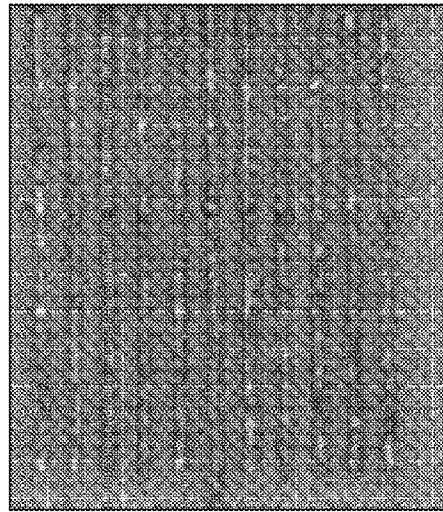


FIG. 18

【図 19】

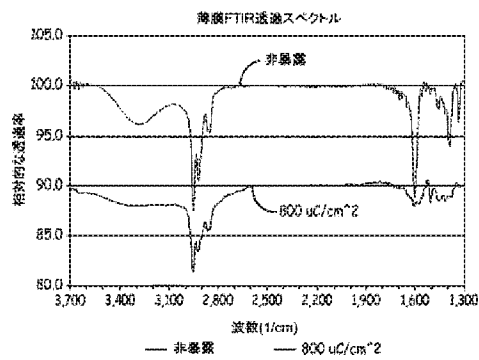


図 19

【国際調査報告】

INTERNATIONAL SEARCH REPORT		International application No. PCT/US 14/48212															
A. CLASSIFICATION OF SUBJECT MATTER IPC(8) - G03C 1/00 (2015.01) CPC - G03F 7/0045; G03F 7/0397; G03F 7/0392 According to International Patent Classification (IPC) or to both national classification and IPC																	
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC(8) - G03C 1/00 (2015.01) CPC - G03F 7/0045; G03F 7/0397; G03F 7/0392 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched USPC-430/270.1, 430/502, 430/56, 428/345, 427/561, 427/566, 427/419.8 Patents and NPL (classification, keyword, search terms below) Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) Databases: Google Scholar, Google Patent, PatBase Search terms used: radiation, irradiating coated substrate, irradiated structure, irradiated coating, un-irradiated coating, metal oxo-hydroxo network, organic ligands, metal carbon bonds, metal carboxylate bonds																	
C. DOCUMENTS CONSIDERED TO BE RELEVANT <table border="1"> <thead> <tr> <th>Category*</th> <th>Citation of document, with indication, where appropriate, of the relevant passages</th> <th>Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td>Y</td> <td>US 2012/0223418 A1 (Stowers et al.) 06 September 2012 (06.09.2012) para [0006]-[0007], [0010], [0012], [0072]-[0074], [0082]-[0084], [0105], [0107], [0109], [0113], [0119], Fig. 2A, Fig. 2C.</td> <td>1-4, 10-14, 19-21 and 23-24</td> </tr> <tr> <td>Y</td> <td>US 2011/0136823 A1 (Lee et al.) 09 June 2011 (09.06.2011) para [0008], [0011]-[0014], [0022], [0089], Table 1.</td> <td>1-4, 10-14, 19-21 and 23-24</td> </tr> <tr> <td>Y</td> <td>US 2011/0244403 A1 (Carosi et al.) 06 October 2011 (06.10.2011) para [0006], [0010], [0056], [0077].</td> <td>2-4</td> </tr> <tr> <td>A</td> <td>US 2003/0124457 A1 (Jung et al.) 03 July 2003 (03.07.2003) para [0008]-[0010].</td> <td>1-4, 10-14, 19-21 and 23-24</td> </tr> </tbody> </table>			Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	Y	US 2012/0223418 A1 (Stowers et al.) 06 September 2012 (06.09.2012) para [0006]-[0007], [0010], [0012], [0072]-[0074], [0082]-[0084], [0105], [0107], [0109], [0113], [0119], Fig. 2A, Fig. 2C.	1-4, 10-14, 19-21 and 23-24	Y	US 2011/0136823 A1 (Lee et al.) 09 June 2011 (09.06.2011) para [0008], [0011]-[0014], [0022], [0089], Table 1.	1-4, 10-14, 19-21 and 23-24	Y	US 2011/0244403 A1 (Carosi et al.) 06 October 2011 (06.10.2011) para [0006], [0010], [0056], [0077].	2-4	A	US 2003/0124457 A1 (Jung et al.) 03 July 2003 (03.07.2003) para [0008]-[0010].	1-4, 10-14, 19-21 and 23-24
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Y	US 2011/0244403 A1 (Carosi et al.) 06 October 2011 (06.10.2011) para [0006], [0010], [0056], [0077].	2-4															
A	US 2003/0124457 A1 (Jung et al.) 03 July 2003 (03.07.2003) para [0008]-[0010].	1-4, 10-14, 19-21 and 23-24															
☐ Further documents are listed in the continuation of Box C. ☐																	
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another mission or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "I" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family																	
Date of the actual completion of the international search 04 February 2015 (04.02.2015)		Date of mailing of the international search report 03 MAR 2015															
Name and mailing address of the ISA/IJS Mail Stop PCT, Attn: ISA/IJS, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201		Authorized officer: Lee W. Young PCT Helpdesk: 571-273-4300 PCT OSP: 571-272-7774															

Form PCT/ISA/210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JS 14/48212

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 5-9, 15-18 and 22
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

Form PCT/ISA/210 (continuation of first sheet (2)) (July 2009)

フロントページの続き

(81)指定国 AP(BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), EA(AM, AZ, BY, KG, KZ, RU, TJ, TM), EP(AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OA(BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG), AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US

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Fターム(参考) 2H197 AB08 AB12 CA03 CA06 CA08 CA09 CA10 CE01 CE10 HA03

JA15 JA21 JA22

2H225 AB03 AN11P AN59P CA12 CB14 CB18 CC01 CC03 CD05



Espacenet

Bibliographic data: JP2018502173 (A) — 2018-01-25

ORGANOMETALLIC SOLUTION BASED HIGH RESOLUTION PATTERNING COMPOSITIONS AND CORRESPONDING METHODS

Inventor(s): スティーブン・ティ・マイヤーズ, ; ジェレミー・アンダーソン, ; ジョセフ・バートン・エドソン, ; カイ・ジアン, ; ダグラス・エイ・ケシュラー, ; マイケル・ケイ・コクシス, ; アラン・ジェイ・テレッキー, ; ブライアン・カーディノー

Applicant(s): インプリア・コーポレイション Inpria Corporation

Classification: - international: C09D1/00; C09D5/00; G03F7/004; G03F7/20
- cooperative: G03F7/0042 (US); G03F7/0043 (EP); G03F7/2004 (US); G03F7/32 (US); G03F7/322 (EP); G03F7/325 (EP)

Application number: JP20170522030 20151022 [Global Dossier](#)

Priority number(s): [US201462067552P 20141023](#) ; [US201562119972P 20150224](#) ; [WO2015US56865 20151022](#)

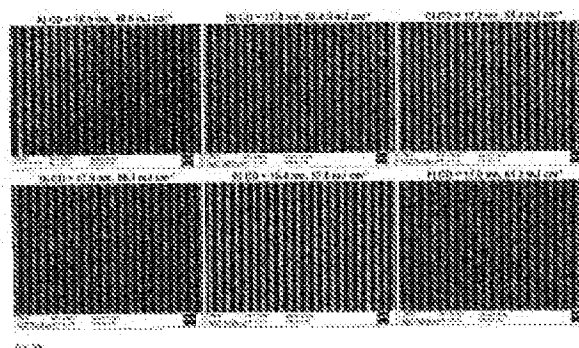
Also published as: [EP3230294 \(A1\)](#) [EP3230294 \(A4\)](#) [KR20170074953 \(A\)](#) [TW201631377 \(A\)](#) [US2016116839 \(A1\)](#) [more](#)

Abstract not available for JP2018502173 (A)

Abstract of corresponding document: WO2016065120 (A1)

Organometallic radiation resist compositions are described based on tin ions with alkyl ligands. Some of the compositions have branched alkyl ligands to provide for improved patterning contrast while maintaining a high degree of solution stability. Blends of compounds with distinct alkyl ligands can provide further improvement in the patterning.

High resolution patterning with a half-pitch of no more than 25 nm can be achieved with a line width roughness of no more than about 4.5 nm. Synthesis techniques have been developed that allow for the formation of alkyl tin oxide hydroxide compositions with very low metal contamination.



(19) 日本国特許庁(JP)

(12) 公表特許公報(A)

(11) 特許出願公表番号

特表2018-502173

(P2018-502173A)

(43) 公表日 平成30年1月25日(2018.1.25)

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C09D 1/00 (2006.01)	C09D 1/00	2H197
G03F 7/004 (2006.01)	G03F 7/004	2H225
G03F 7/20 (2006.01)	G03F 7/004 501	4J038
C09D 5/00 (2006.01)	G03F 7/20 503	
	G03F 7/20 504	

審査請求 未請求 予備審査請求 未請求 (全 54 頁) 最終頁に続く

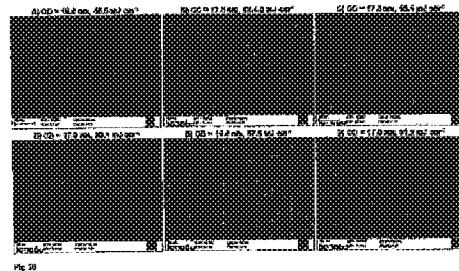
(21) 出願番号	特願2017-522030 (P2017-522030)	(71) 出願人	511130955 インプリア・コーポレーション Inpria Corporation アメリカ合衆国97330オレゴン州コー バリス、スウィート203、ノースウエス ト・モンロー・アベニュー2001番
(86) (22) 出願日	平成27年10月22日 (2015.10.22)	(74) 代理人	100100158 弁理士 飯島 睦
(85) 翻訳文提出日	平成29年6月19日 (2017.6.19)	(74) 代理人	100132263 弁理士 江間 晴彦
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(87) 国際公開番号	W02016/065120		
(87) 国際公開日	平成28年4月28日 (2016.4.28)		
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(32) 優先日	平成26年10月23日 (2014.10.23)		
(33) 優先権主張国	米国 (US)		
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(32) 優先日	平成27年2月24日 (2015.2.24)		
(33) 優先権主張国	米国 (US)		

最終頁に続く

(54) 【発明の名称】 有機金属溶液に基づいた高解像度パターンニング組成物および対応する方法

(57) 【要約】

アルキル配位子を有するスズイオンに基づいて、有機金属放射線レジスト組成物が記載されている。組成物のいくつかは、高度の溶液安定性を保持しながら改善されたパターンニングコントラストを提供するために、分枝状アルキル配位子を有する。別個のアルキル配位子を有する化合物のブレンドは、パターンニングのさらなる改善を提供することができる。25 nm以下のハーフピッチを有する高解像度パターンニングは、約4.5 nm以下のライン幅ラフネスで達成することができる。金属汚染が極めて少ないアルキルスズ酸化物組成物の形成を可能にする合成技術が開発された。



【特許請求の範囲】

【請求項1】

有機溶媒と、式 $R Sn O_{(3/2 - x/2)} (OH)_x$ （式中、 $0 < x < 3$ ）で表される第1の有機金属化合物とを含むコーティング溶液であって、前記溶液中に約0.0025 M～約1.5 Mのスズが含まれ、Rが3～31個の炭素原子を有するアルキル基またはシクロアルキル基であり、前記アルキル基またはシクロアルキル基が第2級または第3級炭素原子においてスズに結合された、コーティング溶液。

【請求項2】

前記第1の有機金属化合物が、tert-ブチルスズ酸化水酸化物（ $R = -C(CH_3)_3$ ）、イソプロピルスズ酸化水酸化物（ $R = -CH(CH_3)_2$ ）、tert-アミルスズ酸化水酸化物（ $R = -C(CH_2CH_3)(CH_3)_2$ ）またはこれらの混合物を含む、請求項1に記載のコーティング溶液。

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【請求項3】

前記第1の有機金属化合物とは異なる、式 $R' Sn O_{(3/2 - x/2)} (OH)_x$ （式中、 $0 < x < 3$ ）で表される第2の有機金属化合物をさらに含み、R'が線状または分枝状アルキル基またはシクロアルキル基である、請求項1または2に記載のコーティング溶液。

【請求項4】

前記有機溶媒がアルコールを含む、請求項1～3のいずれか一項に記載のコーティング溶液。

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【請求項5】

約0.5センチポアズ（cP）～約150 cPの粘度と、約0.01 M～約1.0 Mのスズ濃度とを有する、請求項1～4のいずれか一項に記載のコーティング溶液。

【請求項6】

有機溶媒と、式 $R Sn O_{(3/2 - x/2)} (OH)_x$ （式中、 $0 < x < 3$ であり、Rは3～31個の炭素原子を有するアルキル基またはシクロアルキル基であり、前記アルキル基またはシクロアルキル基は第2級または第3級炭素原子においてスズに結合される）で表される第1の有機金属化合物と、前記第1の有機金属化合物とは異なる、式 $R' Sn O_{(3/2 - x/2)} (OH)_x$ （式中、 $0 < x < 3$ であり、R'は線状または分枝状アルキル基またはシクロアルキル基であり、RおよびR'は同一ではない）で表される第2の有機金属化合物とを含むコーティング溶液。

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【請求項7】

前記第1の有機金属化合物が、tert-ブチルスズ酸化水酸化物（ $R = -C(CH_3)_3$ ）、イソプロピルスズ酸化水酸化物（ $R = -CH(CH_3)_2$ ）、またはtert-アミルスズ酸化水酸化物（ $R = -C(CH_2CH_3)(CH_3)_2$ ）を含む、請求項6に記載のコーティング溶液。

【請求項8】

RおよびR'がそれぞれ独立して分枝状アルキル基またはシクロアルキル基である、請求項6または7に記載のコーティング溶液。

【請求項9】

前記第2の有機金属化合物が、前記コーティング溶液中の有機金属化合物の少なくとも約10重量パーセントに相当する、請求項6～8のいずれか一項に記載のコーティング溶液。

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【請求項10】

式 $R'' Sn O_{(3/2 - x/2)} (OH)_x$ （式中、 $0 < x < 3$ であり、R''は線状または分枝状アルキル基またはシクロアルキル基である）で表される第3の別個の有機金属化合物をさらに含み、前記第3の有機金属化合物が、前記コーティング溶液中の有機金属化合物の少なくとも約10重量パーセントに相当する、請求項6～9のいずれか一項に記載のコーティング溶液。

【請求項11】

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前記溶媒がアルコールを含み、前記有機金属化合物が約0.0025 M～約1.5 Mのスズイオン濃度をもたらす、請求項6～10のいずれか一項に記載のコーティング溶液。

【請求項12】

基板上の膜のパターニング方法であって、

前記膜を約80 mJ / cm² 以下のEUV線量で曝露するステップと、

前記膜を現像して、約25 nm以下のハーフピッチおよび約5 nm以下のライン幅ラフネスでフィーチャを形成するステップと

を含む方法。

【請求項13】

前記EUV線量が約12 mJ / cm² ～約75 mJ / cm² である、請求項12に記載の方法。 10

【請求項14】

前記ハーフピッチが約18 nm以下である、請求項12または13に記載の方法。

【請求項15】

前記有機金属膜が、式 $R Sn O_{(3/2 - x/2)} (OH)_x$ （式中、 $0 < x < 3$ であり、Rは3～31個の炭素原子を有するアルキル基またはシクロアルキル基であり、前記アルキル基またはシクロアルキル基は第2級または第3級炭素においてスズに結合される）で表される第1の有機金属化合物を含む、請求項12～14のいずれか一項に記載の方法。

【請求項16】

曝露の後に前記膜を現像して、前記膜の非曝露部分の除去によりネガティブ画像を形成するステップをさらに含む、請求項12～15のいずれか一項に記載の方法。 20

【請求項17】

曝露の後に前記膜を現像して、前記膜の曝露部分の除去によりポジティブ画像を形成するステップをさらに含む、請求項12～15のいずれか一項に記載の方法。

【請求項18】

基板上の有機金属膜のパターニング方法であって、

前記有機金属膜を約15 mJ / cm² 以下のゲル線量値でEUV放射線に曝露して、少なくとも約6のコントラストを得るステップ

を含む方法。 30

【請求項19】

表面を有する基板と、前記表面に関連したコーティングとを含むパターン化構造であって、前記コーティングの少なくとも一部が式 $(R)_z Sn O_{2 - z/2 - x/2} (OH)_x$ （ $0 < (x + z) < 4$ ）で表され、Rが3～31個の炭素原子を有するアルキル基またはシクロアルキル基であり、前記アルキル基またはシクロアルキル基が第2級または第3級炭素原子においてスズに結合された、パターン化構造。

【請求項20】

zが約1未満である、請求項19に記載のパターン化構造。

【請求項21】

zが約1未満であり、 $(2 - z/2 - x/2) : x$ の比が約1よりも大きい、請求項19に記載のパターン化構造。 40

【請求項22】

前記基板が、ポリマーシート、元素ケイ素および／またはセラミック材料を含む、請求項19～21のいずれか一項に記載のパターン化構造。

【請求項23】

前記コーティングが、約50 nm以下の平均厚さを有する、請求項19～22のいずれか一項に記載のパターン化構造。

【請求項24】

前記コーティングがパターンを形成し、その少なくとも一部が約25 nm以下のハーフピッチを有するフィーチャを形成する、請求項19～23のいずれか一項に記載のパター 50

ン化構造。

【請求項25】

溶媒と、式 $R Sn O_{(3/2 - x/2)} (OH)_x$ (式中、 $0 < x < 3$ であり、R は 1 ～ 31 個の炭素原子を有するアルキル、シクロアルキルまたは置換アルキル部分である) で表される化合物とを含む溶液であって、金属汚染物質の個々の濃度が約 1 重量 ppm 以下である溶液。

【請求項26】

R が 3 ～ 31 個の炭素原子を有するアルキル基またはシクロアルキル基であり、前記アルキル基またはシクロアルキル基が第 2 級または第 3 級炭素原子においてスズに結合された、請求項 25 に記載の溶液。

【請求項27】

個々の金属汚染物質が約 500 重量 ppb 以下であり、金属汚染物質が 100 重量 ppm 未満の濃度を有する、請求項 25 または 26 に記載の溶液。

【請求項28】

個々のアルカリ金属およびアルカリ土類金属の濃度が約 100 重量 ppb 以下である、請求項 25 ～ 27 のいずれか一項に記載の溶液。

【請求項29】

式 $R Sn OOH$ または $R Sn O_{(3/2 - x/2)} (OH)_x$ (式中、 $0 < x < 3$ であり、R は 1 ～ 31 個の炭素原子を有するアルキルまたはシクロアルキル部分である) で表される化合物の合成方法であって、

式 $R Sn X_3$ (式中、X は、ハライド原子 (F、Cl、Br または I)、またはアミド基、またはこれらの組み合わせを表す) を有する前駆体組成物を加水分解するステップを含み、前記加水分解が、加水分解を実現するために十分な水を用いて実施され、前記加水分解生成物が、約 1 重量 ppm 以下であるスズ以外の金属の個々の濃度を有する方法。

【請求項30】

前記加水分解が水酸化第 4 級アンモニウムを用いて実施される、請求項 29 に記載の方法。

【請求項31】

前記加水分解が、加水分解を実現するために十分な水を含む有機溶媒中、制御された反応で実施される、請求項 29 に記載の方法。

【請求項32】

前記水が、測定された量で有機溶媒に添加される、請求項 31 に記載の方法。

【請求項33】

前記水が周囲環境から吸収される、請求項 31 に記載の方法。

【発明の詳細な説明】

【技術分野】

【0001】

関連出願への相互参照

本出願は、2014 年 10 月 23 日に出願された「Organotin Compounds for Forming High Resolution Radiation Patternable Films, Precursor Compounds and Solutions, and Corresponding Methods (高解像度の放射線パターンニング可能な膜、前駆体化合物および溶液を形成するための有機スズ化合物、ならびに対応する方法)」という表題の米国仮特許出願第 62/067,552 号明細書 (Meyer ら) と、2015 年 2 月 24 日に出願された「Organotin Compounds for Forming High Resolution Radiation Patternable Films, Precursor Formulations and Solutions, and Corresponding Methods (高解像度の放射線パターンニング可能な膜、前駆体配合物および溶液を形成するための有機スズ化合物、ならびに対応する方法)」という表題の米国

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仮特許出願第62/119,972号明細書(Meyersら)とに対する優先権を主張し、これらはいずれも参照によって本明細書中に援用される。

【0002】

本発明は、有機金属コーティング組成物を用いて材料のパターニングを実施するための放射線に基づく方法に関する。本発明はさらに、放射線により非常に高解像度でパターニング可能な有機金属コーティングを形成するために付着され得る前駆体溶液と、パターニングの前および後の、前駆体溶液により形成された被覆基板およびコーティングとに関する。

【背景技術】

【0003】

半導体ベースのデバイスおよび他の電子デバイスまたは他の複雑な微細構造を形成する場合、構造を集積するために、材料は一般的にパターン化される。従って、構造は一般的に、種々の材料からパターンが形成される逐次的な付着およびエッチングステップの反復プロセスによって形成される。このようにして、小さい領域に多数のデバイスを形成することができる。技術的ないくつかの進歩は、そのデバイスの設置面積の低減を含むことができ、これは性能の向上のために望ましい可能性がある。

【0004】

放射線パターンを使用してそのパターンに対応して有機組成物の化学構造を変化させるように、放射線パターン化レジストとして有機組成物を使用することができる。例えば、半導体ウェハのパターニングのためのプロセスは、放射線感受性有機材料の薄膜から、所望の画像のリソグラフィ転写を必要とし得る。レジストのパターニングは、一般的に、レジストを(例えば、マスクを介して)選択されたエネルギー源に曝露して潜像を記録し、次に、レジストの選択された領域を現像および除去することを含むいくつかのステップを伴う。ポジ型(positive-tone)レジストの場合、曝露領域が変化されてこのような領域が選択的に除去可能にされるが、ネガ型(negative-tone)レジストの場合には、非曝露領域がより容易に除去可能である。

【0005】

一般的に、パターンは放射線、反応性ガス、または溶液によって現像され、レジストの選択的に感受性の部分が除去され、レジストの他の部分は保護的なエッチング耐性層としての機能を果たす。液体現像剤は、潜像を現像するために特に有効であり得る。基板は、保護レジスト層の残存領域のウィンドウまたはギャップを通して選択的にエッチングされ得る。あるいは、保護レジスト層の残存領域の現像されたウィンドウまたはギャップを通して、下側の基板の露出領域に所望の材料が付着され得る。最後に、保護レジスト層が除去される。プロセスを繰り返して、パターン化材料の付加的な層を形成することができる。機能性無機材料は、化学蒸着、物理蒸着または他の所望の手段を用いて付着され得る。導電性材料の付着またはドーパントの注入などの付加的な処理ステップを使用することができる。マイクロおよびナノファブリケーションの分野において、高集積密度を達成し、そして回路機能を改善するために、集積回路内のフィーチャ(feature)サイズは非常に小さくなっている。

【発明の概要】

【課題を解決するための手段】

【0006】

第1の態様では、本発明は、有機溶媒と、式 $RSnO_{(3/2-x/2)}(OH)_x$ (式中、 $0 < x < 3$)で表される第1の有機金属化合物とを含むコーティング溶液に関し、溶液中に約0.0025M~約1.5Mのスズが含まれ、Rは、3~31個の炭素原子を有するアルキル基またはシクロアルキル基であり、アルキル基またはシクロアルキル基は、第2級または第3級炭素原子においてスズに結合される。

【0007】

さらなる態様では、本発明は、有機溶媒と、式 $RSnO_{(3/2-x/2)}(OH)_x$ (式中、 $0 < x < 3$ であり、Rは3~31個の炭素原子を有するアルキル基またはシクロ

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アルキル基であり、アルキル基またはシクロアルキル基は第2級または第3級炭素原子においてスズに結合される)で表される第1の有機金属化合物と、第1の有機金属化合物とは異なる、式 $R'SnO_{(3/2-x/2)}(OH)_x$ (式中、 $0 < x < 3$ であり、 R' は線状または分枝状アルキル基またはシクロアルキル基であり、 R および R' は同一ではない)で表される第2の有機金属化合物とを含むコーティング溶液に関する。

【0008】

別の態様では、本発明は基板上の膜のパターニング方法に関し、本方法は、膜を約 80 mJ/cm^2 以下のEUV線量で曝露するステップと、膜を現像して、約 25 nm 以下のハーフピッチおよび約 5 nm 以下のライン幅ラフネスでフィーチャを形成するステップとを含む。

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【0009】

付加的な態様では、本発明は基板上の有機金属膜のパターニング方法に関し、本方法は、有機金属膜を約 15 mJ/cm^2 以下のゲル線量(dose-to-gel)値でEUV放射線に曝露して、少なくとも約6のコントラストを得るステップを含む。

【0010】

さらに、本発明は、表面を有する基板と、表面に関連したコーティングとを含むパターン化構造に関し、コーティングの少なくとも一部は式 $(R)_zSnO_{2-z/2-x/2}(OH)_x$ ($0 < (x+z) < 4$)で表され、 R は3~31個の炭素原子を有するアルキル基またはシクロアルキル基であり、アルキル基またはシクロアルキル基は第2級または第3級炭素原子においてスズに結合される。

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【0011】

さらなる態様では、本発明は、溶媒と、式 $RSnO_{(3/2-x/2)}(OH)_x$ (式中、 $0 < x < 3$ であり、 R は1~31個の炭素原子を有するアルキル、シクロアルキルまたは置換アルキル部分である)で表される化合物とを含む溶液に関し、本溶液は、金属汚染物質の個々の濃度が約1重量ppm以下である。

【0012】

さらに、本発明は、式 $RSnOOH$ または $RSnO_{(3/2-x/2)}(OH)_x$ (式中、 $0 < x < 3$ であり、 R は1~31個の炭素原子を有するアルキルまたはシクロアルキル部分である)で表される化合物の合成方法に関し、本方法は、

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式 $RSnX_3$ (式中、 X は、ハライド原子(F 、 Cl 、 Br または I)、またはアミド基、またはこれらの組み合わせを表す)を有する前駆体組成物を加水分解するステップを含み、加水分解は、加水分解を実現するために十分な水を用いて実施され、加水分解生成物は、約1重量ppm以下であるスズ以外の金属の個々の濃度を有する。

【図面の簡単な説明】

【0013】

【図1】潜像を有する放射線パターン化構造の概略斜視図である。

【図2】図1の構造の側面平面図である。

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【図3】潜像を現像し、非照射コーティング材料を除去してパターン化構造を形成した後の、図1の構造の概略斜視図である。

【図4】図3のパターン化構造の側面図である。

【図5】潜像を現像し、照射コーティング材料を除去してパターン化構造を形成した後の、図1の構造の概略斜視図である。

【図6】図5のパターン化構造の側面図である。

【図7】下層をエッチングした後の、図3および図4のパターン化構造の側面平面図である。

【図8】パターン化された凝縮コーティング材料をエッチングして除去した後の、図7の構造の側面平面図である。

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【図9】「熱凍結 (thermal freeze)」ダブルパターニングのプロセスフローの側面平面図である。図1～図3に示されるプロセスは、第1の層を第2の層に対して不溶性にするベーキングの後に繰り返される。

【図10】熱重量分析における温度の関数としての重量損失のプロットである。

【図11】図10の熱重量分析と組み合わせて実施される質量スペクトル分析のサンプル温度の関数としてのプロットである。

【図12】動的光散乱分析から得られた粒径分布を示すヒストグラムである。

【図13】例えば図12のような粒径分布を得るために使用される動的光散乱測定からの代表的な時間相関関数のプロットである。

【図14】実施例3に記載されるような化合物1の溶液の代表的な ^{119}Sn NMRスペクトルである。

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【図15】実施例3に記載されるような化合物1の溶液の代表的な ^1H NMRスペクトルである。

【図16】実施例3に記載されるような化合物1におけるエレクトロスプレー質量分析実験の質量対電荷比の関数としての強度のプロットである。

【図17】別個のアルキル配位子 (*n*-ブチル、イソプロピルおよび*t*-ブチル) を有する3つの異なるコーティング組成物について、ゲル線量の関数としてのコントラストのプロットである。

【図18】34 nmピッチで17 nmラインのパターンを13.5 nm波長のEUV放射線を用いて曝露した後、そして現像の後に、*t*-ブチルスズ酸化水酸化物によりパターン化されたシリコンウェハの走査型電子顕微鏡写真である。

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【図19】+20%バイアスを伴う44 nmピッチの22 nmコンタクトホール of 明視野パターンにおいて13.5 nm波長のEUV放射線を用いて曝露した後、そして現像の後に、イソプロピルスズ酸化水酸化物によりパターン化されたシリコンウェハの走査型電子顕微鏡写真である。

【図20】34 nmピッチで17 nmラインのパターンを13.5 nm波長のEUV放射線を用いて曝露した後、そして現像の後にパターン化されたイソプロピルスズ酸化水酸化物および/または*t*-ブチルスズ酸化水酸化物の種々の組み合わせによる6つの異なる配合物の一連のSEM顕微鏡写真である。

【図21】図20の顕微鏡写真を得るために使用された配合物A～Fについて、コーティング組成物の関数としてプロットされたサイズ線量 (dose-to-size) のプロットである。

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【図22】実施例7に記載されるように調製された*i*-Pr Sn(NMe₂)₃の ^1H NMRスペクトルである。

【図23】実施例7に記載されるように調製された*i*-Pr Sn(NMe₂)₃の ^{119}Sn NMRスペクトルである。

【図24】実施例7の方法1で調製されたイソプロピルスズ酸化水酸化物のサンプルの熱重量分析における温度の関数としての重量のプロットである。

【図25】図24の熱重量分析と関連して実施された質量スペクトル分析である。

【図26】実施例7の方法2で調製されたイソプロピルスズ酸化水酸化物のサンプルの熱重量分析における温度の関数としての重量のプロットである。

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【図27】60 mJ cm⁻²のイメージング線量でEUV放射線に曝露した後、実施例7の方法1を用いて合成されたイソプロピルスズ酸化水酸化物によりパターン化されたシリコンウェハのSEM顕微鏡写真であり、2.9 nmのLWRを有する34 nmピッチでパターン化された14.5 nmレジストラインが得られる。

【図28】実施例10のプロセスを用いて形成されたイソプロピルスズ酸化水酸化物のサンプルの熱重量分析における温度の関数としての重量のプロットである。

【図29】図28の熱重量分析と関連して実施された質量スペクトル分析である。

【図30】実施例11の方法で合成された*t*-Amyl Sn(C≡CPh)₃の ^1H NMRスペクトルである。

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【図31】実施例11の方法で合成された $t\text{-AmylSn}(\text{C}\equiv\text{CPh})_3$ の ^{119}Sn NMRスペクトルである。

【図32】実施例11に記載されるように合成された t -アミルスズ酸化水酸化物の ^{119}Sn NMRスペクトルである。

【図33】実施例11に記載されるように合成された t -アミルスズ酸化水酸化物の ^1H NMRスペクトルである。

【図34】30kEV電子ビームに曝露され、32nmピッチ(上側)および28nmピッチ(下側)で現像された、イソプロピルスズ酸化水酸化物(右側画像)または t -ブチルスズ酸化水酸化物(左側画像)を有するシリコンウェハのSEM顕微鏡写真のセットである。

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【図35】100nm(a)ピッチおよび60nm(b)ピッチによるポジ型画像形成のためのEUV放射線への曝露および現像の後に、イソプロピルスズ酸化水酸化物によりパターン化されたシリコンウェハの2つのSEM顕微鏡写真のセットである。

【発明を実施するための形態】

【0014】

アルキル基、特に分枝状アルキル基(環状配位子を含む)への結合を有する有機スズ化合物は、改善された放射線パターン化前駆体膜形成化合物として使用可能であることが発見された。この化合物により形成された膜は、非常に高解像度のパターンを達成するために望ましい線量の放射線を用いてパターン化することができる。有機スズ化合物のための配位子構造は、コーティングを形成する際に、良好な前駆体溶液安定性および良好な放射線感受性を提供する。分枝状アルキル配位子を有するアルキルスズ化合物は、より低い放射線量で特に改善されたパターンニングを提供することが分かっているが、アルキル配位子の混合物の使用は、得られるコーティングのいくつかの特徴を設計してパターンニングを容易にすることにより、さらなる改善の可能性を提供する。有機金属前駆体溶液を用いて形成されたコーティングの望ましい特徴は、パターン化金属酸化物コーティングを形成するために大きい放射線吸収および優れた直接パターンニングを提供する。有機金属コーティング組成物を構成する金属(例えば、スズ)または金属の組み合わせとは異なる金属汚染が少ない前駆体溶液は、関連の材料およびデバイスにとって金属汚染が不適切であり得る用途のために有用なコーティングの形成を提供する。汚染物質が少ない前駆体溶液の形成のために適切な加工技術が記載されている。前駆体溶液は、適切な技術を用いてコーティングすることができる。放射線パターンニングおよび潜像の現像は、高度の解像度および低ライン幅ラフネスで、非常に小さいパターンフィーチャを有する画像を達成ように実施することができる。

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【0015】

放射線への曝露は照射された有機金属コーティング材料の組成を変化させ、アルキル配位子により画定された構造を破壊し、環境水分などの任意の源からの水分によるさらなる凝縮および反応を可能にする。これらの化学変化に基づいて、適切な現像剤組成物の選択によって膜の照射部分と非照射部分との間で溶解速度が実質的に異なることができ、いくつかの実施形態では、同じコーティングを用いてネガ型パターンニングまたはポジ型パターンニングのいずれかが容易になる。ネガティブパターンニングでは、放射線への曝露およびそれに続く潜在的な凝縮により、照射されたコーティング材料は、有機溶媒ベースの現像剤組成物による除去に対して、非照射コーティング材料よりも耐性である材料に転換される。ポジティブパターンニングでは、曝露は、曝露されたコーティング材料が水性溶媒または他の十分に極性の溶媒によって選択的に除去され得るように、曝露されたコーティング材料の極性を十分に変化させる(例えば、極性を増大させる)。コーティング材料の少なくとも一部の選択的な除去は、コーティングの領域が除去されて下側の基板が露出されたパターンを残すことができる。照射に続いてコーティングを現像した後、パターン化酸化物材料は、優れたパターン解像度を有するデバイス形成における加工を容易にするために使用することができる。コーティング材料は、極紫外線、紫外線および/または電子ビームなどの選択された放射線に感受性であるように設計され得る。さらに、前駆体溶液は、商

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品流通のために適切な貯蔵期間を有し、安定であるように配合され得る。

【0016】

金属イオンは一般的に、有機配位子に加えて、1つまたは複数のオキソ配位子（すなわち、 $M-O$ ）および／またはヒドロキソ配位子（すなわち、 $M-O-H$ ）にもさらに結合される。アルキル配位子およびオキソ／ヒドロキソ配位子は、金属酸化物への凝縮プロセスに対する著しい制御を提供することによって、前駆体溶液および対応するコーティングに望ましい特徴を提供し、著しい加工、パターンニング、およびコーティングの利点が得られる。コーティング溶液中の有機溶媒の使用は溶液の安定性を支持するが、非水溶液に基づいた加工は、非曝露領域に対して曝露領域の溶解度が変化しているために、ポジ型パターンニングおよびネガ型パターンニングの両方について、優れた現像率コントラストを有する潜像の形成の後に得られたコーティングを選択的に現像する能力を保持する。アルキル安定化金属イオンが溶解された望ましい前駆体溶液は、微細構造の形成を可能にするために、エッチング耐性に関して高い放射線感受性および優れたコントラストを有し得るコーティングを形成するために便利な溶液ベースの付着を提供する。前駆体組成物の設計は、特定の放射線の種類および／またはエネルギー／波長に対して高い感受性を有するコーティング組成物の形成を提供し得る。

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【0017】

前駆体有機金属組成物の配位子構造は、前駆体溶液の観察される望ましい安定性と、放射線パターンニング機能とを提供すると考えられる。特に、放射線の吸収は、金属と有機配位子との間の結合の破壊を提供して、被覆材料の照射部分および非照射部分において組成物の差別化を生じることができると考えられる。この差別化は、現像前、現像後、またはその両方において、曝露された膜を適切に加工することによってさらに増幅され得る。従って、改善された前駆体溶液を形成するための組成の変更は、画像の現像の改善も提供する。特に、照射されたコーティング材料は、現像剤に対する調節可能な応答を有する安定した無機金属酸化物材料をもたらし得る。

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【0018】

ポジ型またはネガ型画像のいずれかを現像し得る適切な現像剤の選択によって、現像剤に対する調節可能な応答を有する安定した無機金属酸化物材料をもたらし得る。いくつかの実施形態では、適切な現像剤には、例えば、2.38% TMAH（すなわち、半導体業界標準）が含まれる。コーティング層は、現像後にコーティング材料が残ることが意図される領域からコーティング材料を除去することによる現像中のパターン損失を伴わずに薄くされることが可能である。従来の有機レジストと比較して、本明細書に記載される材料は、商業的に関連する機能層に対する多数のエッチング化学に対して極めて高い耐性を有する。これは、本来ならばマスク機能に関してパターン化有機レジストを補足するために使用され得る中間の犠牲的無機パターン転写層を回避することによって、プロセスの簡素化を可能にする。また、コーティング材料は、便利なダブルパターンニングを提供することができる。具体的には、熱処理の後、コーティング材料のパターン化部分は、さらなる前駆体溶液を含む多数の組成物との接触に関して安定である。従って、既に付着されたハードマスクまたはレジストコーティング材料を除去することなく、多重パターンニングが実施され得る。

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【0019】

前駆体溶液は、多核金属オキソ／ヒドロキソカチオンおよびアルキル配位子を含む。オキソ／ヒドロキソ配位子は、ハライド、アミド、またはアルキニド配位子を有する対応する化合物の加水分解により導入することができる。金属亜酸化物カチオンともいわれる金属オキソ／ヒドロキソカチオンは、1つまたは複数の金属原子および共有結合した酸素原子を有する多原子カチオンである。過酸化物ベースの配位子を有する金属亜酸化物カチオンは、参照によって本明細書中に援用される「Patterned Inorganic Layers, Radiation Based Patterning Compositions and Corresponding Methods（パターン化無機層、放射線ベースのパターンニング組成物および対応する方法）」という表題の米国特許

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第8, 415, 000号明細書(Stowersら)('000号特許)に記載されている。金属亜酸化物または金属水酸化物の水溶液は、ゲル化および／または沈殿に関して不安定な傾向があり得る。特に、溶液は溶媒が除去されると不安定であり、金属カチオンによりオキソー水酸化物ネットワークを形成し得る。過酸化物などの放射線感受性配位子をこのような溶液中に取り込むと安定性を改善することができるが、ネットワーク形成に関連するバックグラウンドの不安定性は持続し得る。任意の制御されないネットワーク形成は、照射とは無関係に現像率決定経路を提供することによって、被覆材料の放射線感受性および／または現像率コントラストを効果的に低減する。アルキル配位子の放射線感受性配位子としての使用は、改善された前駆体溶液安定性を提供し、非常に微細な構造を形成するために大きい放射線吸収および優れたコントラストも提供することが分かった。

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【0020】

本明細書に記載されるように、tert-ブチルまたはイソプロピルなどの分枝状アルキル配位子の使用は、非分枝状アルキル配位子に対して改善されたパターンニング性能を示すことが分かった。分枝状アルキル基の使用は望ましいパターンニング性能を提供することが分かったが、いくつかの実施形態では、分枝状および／または非分枝状アルキル基へのSn-C結合を有する、特に少なくとも1つの分枝状アルキル基を有するアルキルスズ化合物の適切な混合物を配合して、ナノリソグラフィパターンニング性能をさらに改善することができる。アルキル配位子構造の混合物により提供される付加的な柔軟性は、単一の配位子構造内では到達できない多数の組成物特性：例えば、安定性、溶解度、放射線感受性、サイズなどの選択を可能にすると考えられる。従って、別個のアルキル配位子を有する金属イオン混合物の前駆体組成物中の配合物は、後続の実施例で実証される望ましいパターンニング線量およびライン幅ラフネス値を含む様々な性能パラメータの改善の基盤を提供し得る。

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【0021】

放射線レジストコーティングのための有機金属化合物の使用は、参照によって本明細書中に援用される「Organometallic Solution Based High Resolution Patterning Compositions (有機金属溶液に基づいた高解像度パターンニング組成物)」という表題の米国特許出願公開第2015/0056542号明細書(Meyersら)('1542号出願)において一般的に記載されている。'1542号出願では、放射線感受性パターンニング層の形成のためのn-ブチルSn(OH)およびジビニルSn(OH)₂組成物が例示され、スズ、インジウム、アンチモンまたはこれらの組み合わせを有する化合物を含むアルキル配位子の望ましさが記載されている。これらの一般的な組成物は、本明細書に記載される適切な実施形態に関連する。スズに結合され、スズ結合炭素において分枝した(α-炭素分枝)、tert-ブチル、イソプロピル、またはtert-アミル(1,1-ジメチルプロピル)などの分枝状アルキル配位子は、非分枝状配位子を含有するものよりも低い放射線量による放射線パターンニングレジストとして効果的に使用可能であることが発見された。同様に、2-ブチル、シクロヘキシル、シクロペンチル、シクロブチル、シクロプロピル、1-アダマンチル、および2-アダマンチルを含む、α-炭素で分枝した他のアルキルおよびシクロアルキル配位子が考慮され、本明細書に記載されるアルキル配位子を有する化合物の混合物と共に、本開示の範囲内に含まれる。言い換えると、分枝状有機配位子を有するレジストは、第2級または第3級炭素原子によってSn原子に結合したアルキルまたはシクロアルキル配位子、 $R-SnO_{(3/2-x/2)}(OH)_x$ (式中、 $0 < x < 3$ であり、Rは3〜31個の炭素原子を有する第2級または第3級アルキル基またはシクロアルキル基である)を含有する。あるいは、この組成物は $R_1R_2R_3CSnO_{(3/2-x/2)}(OH)_x$ ($0 < x < 3$) で表すことができ、式中、 R_1 および R_2 は独立して1〜10個の炭素原子を有するアルキル基であり、 R_3 は水素、または1〜10個の炭素原子を有するアルキル基であり、ここで、 R_1 、 R_2 は環状炭素鎖を形成することができると共に、 R_3 も任意選択的に環状炭素構造中に含まれ、環状構造の場合、炭素原子の範囲は相加的である。当業者は、 R_1 、 R_2 および R_3 の順序が本質的に任意であり、従って、異

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なる化合物中の基の比較は任意の並べ換えを考慮に入れることができ、化合物または関連する化合物の比較を変化させないことを認識するであろう。同じ概念で、この式は単一のHとR₃との関連を指示するので、HをR₃ではなくR₁またはR₂に任意で割り当てることにより化合物はこの式の範囲を回避しない。理論により制限されることは望まないが、これらの分枝状アルキル配位子の構造は曝露の間にS_n-C結合の開裂を促進し、それにより放射線に対するレジストの感受性が増大されると考えられる。

【0022】

この促進は、関連の第1級アルキル部分に対して増大された第2級および第3級アルキルラジカルまたはカルボカチオン中間体の安定性に起因し得る。S_n-C放射線分解の研究において直接立証されていないが、同様の特性は、一覽にされたC-H結合-解離エネルギーにおいて明白である。従って、本明細書に記載される改善された組成物は、低ライン幅ラフネスを有する高解像度パターンを達成するために、より少ない放射線加工による著しい商業的利点を提供する。低ライン幅ラフネスを有する高解像度パターンは、従って、上記の'000号特許に記載されるような過酸化物ベースの配位子を有する金属酸化物ベースのフォトレジストで達成される同様の優れた解像度および低ライン幅ラフネスと比べて、加工の改善のためにより低い放射線量を用いて達成することができる。

【0023】

新しい前駆体溶液は、過酸化物ベースの配位子を有する無機レジスト材料と比べて、改善された安定性ならびにネットワーク形成および沈殿の制御を備えて配合されている。この場合に放射線感受性であるという配位子の特徴付けは、放射線の吸収の後の金属-配位子結合の不安定性を指し、従って、材料の化学変化を引き起こすために放射線を使用することができる。特に、アルキル配位子は前駆体溶液を安定化するが、材料の加工に対する制御も提供し、金属イオンに対するアルキル配位子の比率の選択は、溶液および得られるコーティングの特性を制御するように調整され得る。

【0024】

異なるアルキル配位子を有する混合物を含む前駆体組成物は、異なる有機配位子を有する2つのアルキルースズ化合物、異なる有機配位子を有する3つのアルキルースズ化合物、または異なるアルキル配位子を有する4つ以上のアルキルースズ化合物の混合物を含むことができる。一般的に、2成分または3成分混合物の場合、混合物は、別個のアルキル配位子を有する少なくとも約8モルパーセントの各成分を含み、いくつかの実施形態では少なくとも約12モルパーセント、さらなる実施形態では少なくとも約25モルパーセントの、別個のアルキル配位子を有する各成分を含む。当業者は、上記の明確な範囲内の混合物成分の付加的な範囲が考慮され、本開示の範囲内に含まれることを認識するであろう。

【0025】

アルキル配位子、特に分枝状アルキル配位子は、曝露のない状態では、凝縮に関して金属カチオンを安定化する。特に、アルキルベースの配位子の濃度が適切な場合、凝縮金属酸化物または金属水酸化物および関連の凝集体の意図されない形成は、仮に室温で自然に生じるとしても、非常にゆっくりである。この安定化特性の発見に基づいて、コーティングを形成するために便利な加工を保持しながら、良好な貯蔵安定性を有する高濃度の放射線感受性配位子を用いて、溶液を形成することができる。吸収された放射線からのエネルギーは、金属-アルキル配位子結合を破壊し得る。これらの結合が破壊されると、対応する凝縮に関する安定化が低減または喪失され、恐らく一過性の中間体として、不飽和価電子状態を有する反応性金属中心が形成され得るが、理論により制限されることは望まない。組成物は、大気中または別に供給されるH₂Oとの反応、M-OHの形成によって、または凝縮してM-O-M結合を形成することによってさらに変化し得る（ここで、Mは金属原子を表す）。従って、放射線によって化学変化を制御することができる。高放射線感受性配位子濃度を有する組成物は、意図されない自然加水分解、凝縮、および凝集の回避に関して非常に安定であり得る。

【0026】

金属イオンに対するオキシ／ヒドロキシ配位子に関して、これらの配位子は、加水分解による処理の間に形成され得る。いくつかの実施形態では、加水分解は、塩基性水溶液中のハロゲン化物配位子の置換または水中のアミド配位子 ($-NR_1R_2$) の置換と、それに続く、沈殿した加水分解物の回収および／または有機溶媒への移動を含み得る。付加的または代替的な実施形態では、加水分解性配位子は、コーティングおよびベーキング中に前駆体と反応する大気中の水分から得られるヒドロキシ配位子によって置換され得る。本明細書に記載されるように、低金属汚染の合成手法は、適切な代替の加水分解手法および高純度のアルキルスズ前駆体を用いて達成することができる。3つのこのような手法は実施例に記載されている：水に反応性のアルキルスズ化合物を利用し、周囲大気から加水分解のための水を手に入れる、または有機溶媒中で加水分解を実現するために制御された量の精製水を添加する、またはアルキルスズハロゲン化物に合わせて金属カチオンを含まない塩基を使用する。水系または非水系の酸または塩基による加水分解に感受性の1つまたは複数の代替配位子は、反応性、合成の容易さ、毒性、及び他の因子などのプロセスおよび合成の考察に依存して、他の実施形態で使用され得る。一般に、適切な加水分解性配位子 ($RSnX_3$ 中のX) は、アルキニド $RC \equiv C$ 、アルコキシド RO^- 、アジド N_3^- 、カルボキシレート $RCOO^-$ 、ハライドおよびジアルキルアミドを含むことができる。

【0027】

特定の合成手順を採用することにより、金属汚染の非常に少ない前駆体アルキルスズ酸化水酸化物化合物を配合することができる。特に、非スズ金属は、通常、1重量百万分率 (ppm) 以下まで低減することができ、アルカリ金属およびアルカリ土類金属は、約100重量十億分率 (ppb) 以下まで低減することができる。化合物の溶液は、それに依拠して形成され得る。得られるコーティングは、下側の基板、隣接層、デバイス、およびプロセス手段に提供する金属汚染リスクを低くすることができる。低金属汚染は、特定の金属汚染、例えばアルカリ金属汚染が望ましくない用途に対してレジスト組成物の有用性を提供することができる。

【0028】

金属汚染物質の少ない前駆体の形成を可能にする処理手法は、金属汚染物質を組成物中に導入する塩基 (例えば、 $NaOH$) などの反応物の使用を回避する。低金属汚染を提供することができる代替塩基には、例えば、水酸化テトラメチルアンモニウムおよび他の水酸化第4級アンモニウムが含まれる。また、大気中から提供される水または制御された量で添加された水を含む有機溶媒中の加水分解の場合は水を直接使用することができる。半導体デバイス製造で規定される非常に少ない微量金属レベル (通常、レジスト組成物に対して <10 ppb) を仮定すると、わずかでも金属汚染物質が導入されれば、配合されたアルキルスズ酸化水酸化物レジストから金属汚染物質を適切に除去するための技術は確認されていない。従って、適切に加水分解可能な配位子、例えば、ハライドまたはアミドは、非スズ金属の実質的な濃度に寄与しない代替の加水分解反応によってオキシ／ヒドロキシ配位子で置換される。加水分解物は、適切な手法、例えば、沈殿、洗浄、ならびに適切な溶媒中での再結晶および／または再溶解などにより、反応副生成物を除去するために精製することができる。

【0029】

一般に、前駆体コーティング溶液は、約0.1～約2である放射線感受性配位子の金属カチオンに対するモル濃度比を溶液が有するように、十分な放射線感受性アルキル配位子を含むことができる。この範囲内の配位子比は、前駆体安定性および溶解度の制約を受けて、適切な化学量論の $RSnX_4$ 、 $RSnX_3$ または R_2SnX_2 前駆体の加水分解によって調製され得る。前駆体溶液から形成されるコーティングは前駆体溶液中のイオンの配位子構造によって影響され、そして乾燥の際に金属のまわりの配位子構造は同等であり得るか、あるいは配位子構造は、コーティングおよび／または乾燥プロセス中に変化され得る。コーティングは、一般に、パターンニング機能を可能にするために放射線への曝露にも影響される。一般に、コーティングは、式 $(R)_zSnO_{2-z/2-x/2}(OH)_x$ ($0 < (x+z) < 4$) によって表すことができ、式中、Rは3～31個の炭素原子を有す

るアルキル基またはシクロアルキル基であり、アルキル基またはシクロアルキル基は、第2級または第3級炭素原子においてスズに結合されている。非照射コーティングでは、 z の値はコーティング溶液の値と同一であるかまたはそれに近い値であり得るが、照射コーティングは通常、より低い z 値を有し、例えばパターニング後などのさらなる加熱および／または照射によってほぼ0に近接し得る。特に、アルキル配位子濃度は、前駆体の安定性と、有機溶媒（一般には、極性有機溶媒）で形成された溶液によるネットワーク形成の制御とにおいて驚くほどに大きい改善を提供する。理論により制限されることは望まないが、適切な範囲の放射線感受性の低極性配位子濃度は、対応するオキソ配位子および／またはヒドロキソ配位子を有する金属カチオンの意図されない凝縮および凝集を明らかに低減し、溶液を安定化させる。従って、前駆体コーティング溶液は、さらに攪拌することなく少なくとも1週間、恐らくは著しくより長い（例えば、一ヶ月を超える）期間、固体の沈降に対して安定であり得る。長い安定時間のために、アルキルスズ酸化水酸化物前駆体は、潜在的な商業利用に関する多用途性を増大させた。全体のモル濃度は、所望の安定性レベルと一致して得られる所望のコーティング厚さおよび所望のコーティング特性を達成するように選択することができる。

[0030]

アルキル配位子を有する多原子金属オキソ／ヒドロキソカチオンは、所望の放射線吸収を達成するように選択することができる。特に、スズベースのコーティング材料は、193 nm波長の遠紫外線および13.5 nm波長の極紫外線の良好な吸収を示す。表1には、モノブチルスズ酸化物水和物から形成されて100℃でベーキングされたコーティング材料の選択された波長における光学定数（ n = 屈折率および k = 吸光係数）が記載される。

[0031]

[表1]

表1

波長 (nm)	n	k
193	1.75	0.211
248	1.79	0.0389
365	1.63	0
405	1.62	0
436	1.61	0

[0032]

パターニングのために一般的に使用される高い放射線吸収を同様に提供するために、前駆体溶液中にSn、InおよびSb金属を含むことが望ましいが、特性、特に放射線吸収を調整するために、これらの金属は他の金属と組み合わせることができる。Hfは電子ビーム材料および極紫外線放射の良好な吸収を提供し、InおよびSbは、13.5 nmにおける極紫外線の強力な吸収を提供する。例えば、Ti、V、Mo、もしくはW、またはこれらの組み合わせを含む1つまたは複数の金属組成物を前駆体溶液に添加して、吸収端がより長い波長に移動したコーティング材料を形成し、例えば、248 nm波長の紫外線に対する感受性を提供することができる。これらの他の金属イオンはアルキル配位子を伴っていてもいなくてもよく、本明細書に記載される前駆体組成物で使用するためのアルキル配位子を伴わない金属イオンの適切な塩には、例えば、コーティング前駆体溶液の溶媒に可溶性である有機または無機塩、アミド、アルコキシドなどが含まれ得る。金属汚染物質の決定に関して、明らかに特別に添加された機能性金属は汚染物質とは考えられず、これらの金属は、通常100重量ppmを超えるレベルで前駆体溶液中に存在することにより確認することができ、このような金属は、特定の用途のために望ましくない汚染を回避

するように選択され得る。

【0033】

一般に、所望の加水分解物は有機溶媒（例えば、アルコール、エステルまたはこれらの組み合わせ）中に溶解されて、前駆体溶液を形成することができる。コーティング溶液中の種の濃度は、溶液の所望の物理特性を達成するように選択され得る。特に、より低い濃度は、全体的に、合理的なコーティングパラメータを用いてより薄いコーティングを達成することができるスピニングなどの特定のコーティング手法のために望ましい溶液の特性をもたらす。超微細なパターンニングを達成するため、および材料コストを低減するためにより薄いコーティングを使用することが望ましいことがある。一般に、濃度は、選択されたコーティング手法のために適切であるように選択することができる。コーティング特性はさらに以下に記載される。

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【0034】

前駆体溶液は、一般的に、以下にさらに記載される任意の合理的なコーティングまたは印刷技術によって付着され得る。コーティングは一般に乾燥され、そして熱が加えられて、照射の前にコーティングを安定化または部分的に凝縮させることができる。一般に、コーティングは薄く、例えば、10ミクロン未満の平均厚さを有し、非常に小さいフィーチャをパターン化するために非常に薄いサブミクロンのコーティング、例えば、約100ナノメートル（nm）以下のコーティングが望ましいこともある。高解像度パターンを形成するために、放射線感受性有機組成物を使用してパターンを導入することができ、組成物の一部分が現像／エッチングに対して耐性であるように処理されて、選択的な材料除去を使用して選択されたパターンを導入することができるので、組成物はレジストと呼ぶことができる。乾燥されたコーティングは選択されたパターンまたはパターンのネガティブ部分を用いて適切な放射線、例えば、極紫外線、電子ビームまたは紫外線にさらされ、現像剤耐性領域および現像剤溶解性領域を有する潜像を形成することができる。適切な放射線への曝露の後、かつ現像の前に、コーティングを加熱、または他の方法で反応させて、潜像を非照射領域とさらに差別化することができる。潜像は現像剤と接触されて、物理的な画像、すなわちパターン化コーティングを形成する。パターン化コーティングをさらに加熱して、表面のパターン化された残存コーティングを安定化させることができる。パターン化コーティングは、パターンに従ってさらなる加工、例えば、基板のエッチングおよび／または付加的な材料の付着を実施するために物理的なマスクとして使用することができる。パターン化レジストを要望通りに使用した後、加工の適切な時点で残りのパターン化コーティングを除去することができるが、パターン化コーティングは、最終構造に組み込むことも可能である。非常に微細なフィーチャは、本明細書に記載されるパターンニング組成物により効果的に達成され得る。

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【0035】

いくつかの実施形態では、得られたパターン化材料は、無機金属酸化物材料への少なくともいくつかの凝縮による適切な安定化の後、最終デバイスのコンポーネントとして構造内に組み込むことができる。例えば安定した誘電層としてパターン化無機コーティング材料が構造内に組み込まれると、放射線による材料の直接パターンニングの使用により加工手順の多数のステップを除外することができる。一般に、短い波長の電磁放射線および／または電子ビームを用いて曝露された薄い無機コーティング材料を用いて非常に高解像度の構造が形成され得ること、そして改善されたパターン化構造の形成のためにライン幅ラフネスが非常に低レベルまで低減され得ることが見出された。

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【0036】

より大きい安定性を有する精製前駆体溶液は、基板の放射線曝露部分と非曝露部分との間のより大きい現像率コントラストの可能性を有するコーティング材料も提供し、これは、驚くことに、ポジ型パターンニングまたはネガ型パターンニングのどちらを用いても同時に達成することができる。具体的には、照射コーティング材料または非照射コーティング材料は、適切な現像剤組成物によって比較的より容易に溶解され得る。従って、改善された組成物および対応する材料を用いて、適切な現像剤の選択により、ポジ型またはネガ型画

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像形成を達成することができる。同時に、隣接する素子間の適切な絶縁、一般には電気的絶縁と共に、隣接する素子間でピッチは非常に小さくされ得る。照射コーティング組成物はその後の現像／エッチングプロセスに対して非常に感受性であることが可能であり、その結果、コーティング組成物は、基板の表面に照射パターンニング組成物の適切な部分を残しながらコーティング組成物を選択的にきれいに除去することに関して現像プロセスの効力を損なうことなく非常に薄くされ得る。現像剤に対する曝露時間を短くできることは、さらに、コーティングのパターン化部分に損傷を与えることなく薄いコーティングを使用することと一致する。

【0037】

集積電子デバイスなどの形成は、一般的に、構造内に個々の素子またはコンポーネントを形成するために材料のパターニングを含む。このパターニングは、鉛直および／または水平方向に互いに相互作用をして所望の機能性を誘発する積み重ねられた層の選択された部分を覆う異なる組成物を含むことができる。種々の材料は、選択されたドーパントを有し得る半導体、誘電体、導電体および／または他のタイプの材料を含むことができる。本明細書に記載される放射線感受性有機金属組成物は、デバイス内に所望の無機材料構造を直接形成するために、そして／あるいは有機レジストの代替である放射線パターンニング可能な無機レジストとして使用することができる。いずれの場合も、著しい加工の改善を利用することができ、そしてパターン化材料の構造も改善され得る。

【0038】

前駆体溶液

レジストコーティングを形成するための前駆体溶液は、一般的に、溶媒（一般的には、有機溶媒）中に適切なアルキル安定化配位子を有するスズカチオンを含む。前駆体溶液および最終的なレジストコーティングは金属酸化物化学に基づいており、アルキル配位子を有する金属ポリカチオンの有機溶液は、良好なレジスト特性を有する安定した溶液を提供する。分枝状アルキル配位子は特に改善されたパターンニング能力を提供する。

【0039】

配位子は放射線感受性を提供し、配位子の特定の選択は放射線感受性に影響し得る。また、前駆体溶液は、金属カチオンおよび関連する配位子の選択に基づいて、選択された放射線に対して所望のレベルの放射線吸収を達成するように設計することができる。溶液中の配位子安定化金属カチオンの濃度は、特定の付着手法（例えば、スピンコーティングなど）のために適切な溶液特性を提供するように選択され得る。前駆体溶液は非常に高レベルの安定性を達成するように配合されており、従って、前駆体溶液は商品のために適切な貯蔵寿命を有する。以下のセクションに記載されるように、前駆体溶液は基板表面に塗布され、乾燥され、さらに処理されて、効果的な放射線レジストを形成することができる。前駆体溶液は、少なくとも部分的に溶媒が除去されたときにコーティング組成物を形成し、最終的に、照射および／または熱処理、プラズマへの曝露、または同様の処理の際に酸化スズが大半を占める無機固体を形成するように設計される。

【0040】

前駆体溶液は、一般的に、1つまたは複数のスズカチオンを含む。水溶液中で、金属カチオンは水分子との相互作用のために水和されており、加水分解が生じて酸素原子を金属イオンに結合させ、水酸化物配位子またはオキソ結合を形成することができ、対応して水素イオンが放出される。相互作用の性質は一般的にpH依存性である。水溶液中で付加的な加水分解が生じるにつれて、溶液は、金属酸化物の沈殿に関して、またはゲル化に関して不安定になり得る。最終的に酸化物材料を形成することが望ましいが、この進行は、アルキル配位子安定化金属カチオンを含む有機溶媒に基づいた前駆体溶液を用いてより良く制御され得る。水蒸気を含む大気に対して配置されると、溶媒は、溶媒と接触する水の分圧と平衡にあるいくつかの溶解した水を含むことができ、実施例により、溶解水を使用して加水分解性配位子の制御された加水分解をもたらすことが実証される。アルキル安定化配位子および有機溶媒に基づいた前駆体溶液では、酸化物への進行は、まず溶液を処理してコーティング材料にし、そして有機配位子を有する最終的な金属酸化物組成物にするた

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めの手順の一部として制御され得る。本明細書に記載されるように、アルキル配位子、特に分枝状アルキル配位子および／またはアルキル配位子の組み合わせは、効果的な放射線レジスト組成物への溶液の処理に対する著しい制御を提供するために使用することができる。

[0041]

一般的に、前駆体化合物は、式 $R_1 S n O_{(3/2 - x/2)} (OH)_x$ ($0 < x < 3$) で表すことができ、式中、R は線状または分枝状（すなわち、金属結合炭素原子において第2級または第3級である）アルキル基である。R は一般的に1～31個の炭素原子を有し、分枝の実施形態では3～31個の炭素原子である。特に、化合物が別の表現で $R_1 R_2 R_3 C S n O_{(3/2 - x/2)} (OH)_x$ ($0 < x < 3$) により表すことができる場合に枝状アルキル配位子が望ましく、ここで、 R_1 および R_2 は独立して、1～10個の炭素原子を有するアルキル基であり、 R_3 は、水素または1～10個の炭素原子を有するアルキル基である。いくつかの実施形態では、 R_1 および R_2 は環状アルキル部分を形成することができ、 R_3 も環状部分の他の基と連結し得る。また前駆体溶液は、異なるアルキル配位子を有する組成物のブレンドを含むこともできる。例示される分枝状アルキル配位子としては、イソプロピル（ R_1 および R_2 がメチル、 R_3 が水素である）、*tert*-ブチル（ R_1 、 R_2 および R_3 がメチルである）、*sec*-ブチル（ R_1 がメチル、 R_2 が $-CHCH_3$ 、 R_3 が水素である）および *tert*-アミル（ R_1 および R_2 がメチル、 R_3 が $-CHCH_3$ である）が挙げられる。環状アルキル配位子を用いる予備実験は、期待できる結果を示した。適切な環状基の例としては、例えば、1-アダマンチル（第3級炭素において金属に結合した $-C(CH_2)_3(CH)_3(CH_2)_3$ またはトリシクロ（3, 3, 1, 1, 3, 7）デカン）、および 2-アダマンチル（第2級炭素において金属に結合した $-CH(CH)_2(CH_2)_4(CH)_2(CH_2)_2$ またはトリシクロ（3, 3, 1, 1, 3, 7）デカン）が挙げられる。従って、金属カチオンの溶液はさらなる処理の準備ができています。特に、前駆体溶液の添加成分として、溶液をさらに酸化スズ組成物に向けて準備可能にする多核スズオキソ／ヒドロキソカチオンを使用することが望ましいことがある。一般に、前駆体溶液は約0.01 M～約1.4 Mの金属多核オキソ／ヒドロキソカチオンを含み、さらなる実施形態では、約0.05 M～約1.2 M、付加的な実施形態では約0.1 M～約1.0 Mの金属多核オキソ／ヒドロキソカチオンを含む。当業者は、上記の明確な範囲内のスズ多核オキソ／ヒドロキソカチオンの付加的な範囲が考慮され、本開示の範囲内に含まれることを認識するであろう。

[0042]

異なる有機配位子を有する混合物を含む前駆体組成物は、異なるアルキル配位子を有する2つのアルキルースズ化合物、異なるアルキル配位子を有する3つのアルキルースズ化合物、または異なるアルキル配位子を有する4つ以上のアルキルースズ化合物の混合物を含むことができる。一般的に、2成分または3成分混合物の場合、混合物は、別個のアリル（*allyl*）配位子を有する少なくとも約8モルパーセントの各成分を含み、いくつかの実施形態では少なくとも約12モルパーセント、さらなる実施形態では少なくとも約25モルパーセントの、別個のアルキル配位子を有する各成分を含む。当業者は、上記の明確な範囲内の混合物成分の付加的な範囲が考慮され、本開示の範囲内に含まれることを認識するであろう。

[0043]

金属は、一般的に、放射線の吸収に著しく影響する。スズは13.5 nmの極紫外線の強力な吸収を提供する。アルキル配位子との組み合わせで、カチオンは193 nm波長の紫外線の良好な吸収も提供する。またスズは電子ビーム放射線の良好な吸収も提供する。吸収されるエネルギーは金属-有機物の相互作用によって調節され、これは、金属-配位子の断裂および材料特性に対する所望の制御をもたらす得る。

[0044]

アルキル配位子は、加水分解物の意図されない自然凝縮および凝集に関して組成物を安定化する。特に、アルキル配位子の相対濃度が高いと、凝縮金属酸化物または金属水酸化

物の形成は、仮に凝縮が室温で自然に生じるとしても、非常にゆっくりである。この安定化特性の発見に基づいて、コーティングを形成するために便利な加工を保持しながら、良好な貯蔵安定性を有する高濃度の放射線感受性配位子を用いて加水分解物溶液を形成することができる。放射線感受性配位子は、スズ-炭素結合を形成するアルキル部分を含む。吸収された放射線からのエネルギーは、スズ-アルキル配位子結合を破壊し得る。これらの結合が破壊されると、対応する凝縮に関する安定化が低減または喪失される。組成物は、M-OHの形成によって、または凝縮してM-O-M結合を形成することによって変化し得る（ここで、Mは金属原子を表す）。従って、放射線によって化学変化を制御することができる。高放射線感受性配位子濃度を有する組成物は、水酸化物および凝縮の自発形成の回避に関して非常に安定であり得る。

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【0045】

所望の配位子構造を有する一部の適切な金属組成物は、Alfa Aesar (MA, USA) およびTCI America (OR, USA) (以下の実施例を参照) などの商業的供給源から購入することができ、他の金属-配位子組成物は以下に記載されるように合成され得る。金属汚染物質が少ない前駆体組成物は、本明細書に記載される方法を用いて合成される。

【0046】

一般に、アルキル配位子は、例えば、メチル、エチル、プロピル、ブチル、および分枝状アルキルであり得る。適切な分枝状アルキル配位子は、例えば、イソプロピル、tert-ブチル、tert-アミル、2-ブチル、シクロヘキシル、シクロペンチル、シクロブチル、シクロプロピル、1-アダマンチルまたは2-アダマンチルであり得る。分枝状アルキル配位子を用いて、改善されたパターンニング結果が得られた。しかし、提供される実施例に示されるように複数のアルキル配位子をブレンドすることにより、本明細書中の教示から、異なる配位子が付与する別個に有利なパターンニング特性（例えば、線量およびライン幅ラフネスなど）を得ることができるので、混合アルキル配位子の使用によって配位子選択のより十分な利点が達成された。

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【0047】

放射線硬化線量は、それぞれの個々の前駆体化合物の放射線量に基づいて、異なるアルキル配位子を有する前駆体化合物の混合物に対してほぼ直線的に比例し得ることが見出された。分枝状アルキル配位子と共に使用可能な放射線量がより低いために、一般的に、混合物は少なくとも1つの分枝状有機配位子を含むことが望ましい。しかしながらそれに応じて、異なる有機配位子を有する前駆体化合物の混合物によりライン幅ラフネスが改善され得ることが発見された。理論により制限されることは望まないが、混合組成物について観察される改善されたライン幅ラフネス値は、パターンのコントラストを著しく低下させることなく混合組成物のエッチングが促進されることに起因し得ることが可能である。これに関連して、観察は、分枝状または非分枝状アルキルを有する有機スズ化合物の組み合わせを含有する混合組成物にまで及ぶことができる。

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【0048】

本明細書に記載されるように、金属汚染の低減を提供する処理手法が開発された。従って、非常に低レベルの非スズ金属を有する前駆体溶液を配合することができる。一般に、非スズ金属濃度は全て、約1重量百万分率(ppm)以下の値まで、さらなる実施形態では約200重量十億分率(ppb)以下、付加的な実施形態では約50ppb以下、他の実施形態では約10ppb以下の値まで個々に低減され得る。いくつかの実施形態では、他の金属元素を添加して処理に影響を与えることが望ましいこともあり、通常、これらは少なくとも約1重量パーセントのレベル、いくつかの実施形態では少なくとも約2重量パーセントのレベルで確認することができ、従って適切な場合には、金属汚染物質とは区別することができる。低減すべき金属汚染物質としては、特に、アルカリ金属およびアルカリ土類金属、Au、Ag、Cu、Fe、Pd、Pt、Co、Mn、およびNiが挙げられる。当業者は、上記の明確なレベルの範囲内の金属レベルの付加的な範囲が考慮され、本開示の範囲内に含まれることを認識するであろう。

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【 0 0 4 9 】

有機スズ酸化水酸化物組成物を形成するための処理は、これまで、かなりの非スズ金属汚染物質（例えば、水酸化ナトリウム塩基からのナトリウムなど）を導入する反応物の使用を含んでいた。本明細書に記載される代替の合成方法は、市販されていることが知られていない化合物および対応する金属汚染物質を有し得る市販の化合物を含む、線状または分枝状アルキル配位子を有する加水分解物を調製するために使用することができる。ナトリウムを十分に低いレベルまで除去する方法は見出されていないので、代替の合成技術が開発された。従って、金属汚染の著しい低減を可能にする代替プロセスが開発された。特に、有機スズ加水分解物を形成するために塩基の添加を必要としない高純度の水反応性前駆体化合物が使用され得る。加水分解物の合成は非水性溶媒中で、あるいは生成化合物が即座に沈殿する水性溶媒を用いて実施することができる。いくつかの実施形態では、水は、加水分解性配位子を加水分解して所望のアルキルスズ酸化水酸化物化合物を形成するためにちょうど十分な量で導入することができる。

【 0 0 5 0 】

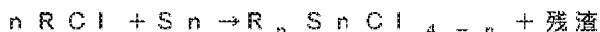
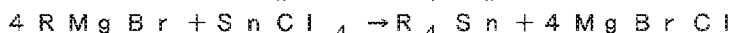
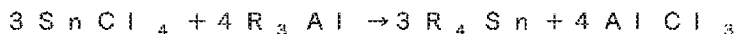
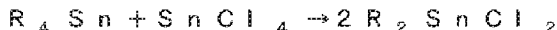
金属イオンに対するオキソ／ヒドロキソ配位子に関して、これらの配位子は、加水分解による処理の間に形成され得る。いくつかの実施形態では、加水分解は、加水分解性配位子を置換して、オキソ（O）および／またはヒドロキソ（-OH）配位子を形成することを含み得る。例えば、ハロゲン化物配位子は、塩基性水溶液中で加水分解し、その後有機溶媒に移すことができる。しかしながら、金属汚染の少ない前駆体組成物を製造するために、代替の反応を用いて加水分解を実施するのが望ましいことが見出された。特定の実施例は、以下に提供される。

【 0 0 5 1 】

いくつかの実施形態では、有機安定化配位子および加水分解性配位子を有するスズイオンを含む組成物は有機溶媒中に溶解され、次に塩基性水溶液と接触され、その結果、ヒドロキソ配位子による加水分解性配位子の置換が生じ得る。ヒドロキソ配位子の形成に十分な時間を与えた後、有機液体は水性液体中に溶解しないと仮定して、水溶液を有機相から分離することができる。いくつかの実施形態では、オキソ／ヒドロキソ配位子は、大気水からの加水分解により形成することができる。加水分解性金属イオン組成物は、コーティング材料中でオキソ／ヒドロキソ配位子が直接形成されるように（これは、表面積が大きいために比較的容易であり得る）、大気水分の存在下で加熱され得る。大気水からの加水分解の一例は、以下においても記載されている。付加的または代替的な実施形態では、加水分解を実現するのに十分な水は、加水分解性配位子を有する前駆体化合物と共に有機溶媒中に溶解される。

【 0 0 5 2 】

アルキル配位子および加水分解性配位子を有する前駆体化合物を形成するために、M-C結合は、溶液相置換反応において形成することもできる。以下の反応は、S_n-C結合を形成するための置換反応の代表的な適切な反応である。



式中、Rはアルキ（alkyl）配位子を表す。一般的に、異なる適切なハライドは、上記反応において置換され得る。反応は、反応物が合理的な溶解度を有する適切な有機溶媒中で実行され得る。

【 0 0 5 3 】

金属汚染物質の少ない前駆体溶液の形成方法に関して、反応物は、加水分解性基を有するアルキルスズ化合物からスズ酸化水酸化物化合物を形成するための加水分解反応の間、金属汚染物質の導入を回避するように選択される。実施例では2つの一般的な手法がうまく使用されている。いくつかの実施形態では、加水分解は有機溶媒中で前駆体化合物を用いて実施され、加水分解を実現するのに十分な水が導入される。加水分解性配位子の加水

分解を完了させるのに十分な水は、環境水蒸気から導入することもできるし、または有機溶媒中に注入して混合することもできる。あるいは、加水分解は、金属汚染物質を導入しない形で触媒塩基が導入された水中で実施することもできる。例えば、実施例では、水酸化テトラメチルアンモニウム (TMAH) 水が使用され、これは、半導体産業で使用するために金属汚染が少ない市販のものである。加水分解性配位子は、実施例に記載される加水分解反応に使用される特定の手法に対して適切に選択することができる。

【0054】

一般に、所望の加水分解化合物は、有機溶媒、例えば、アルコール、エステルまたはこれらの組み合わせに溶解され得る。特に、適切な溶媒には、例えば、芳香族化合物（例えば、キシレン、トルエン）、エーテル（アニソール、テトラヒドロフラン）、エステル（プロピレングリコールモノメチルエーテルアセタート、酢酸エチル、乳酸エチル）、アルコール（例えば、4-メチル-2-プロパノール、1-ブタノール、メタノール、イソプロピルアルコール、1-プロパノール）、ケトン（例えば、メチルエチルケトン）の混合物などが含まれる。一般に、有機溶媒の選択は、溶解度パラメータ、揮発度、引火性、毒性、粘度、および他の加工材料との潜在的な化学的相互作用によって影響され得る。溶液の成分を溶解させて混ぜ合わせた後、特にコーティングプロセスの間に、部分的な水および凝縮の結果として種の特性は変化し得る。溶液の組成が本明細書において言及される場合、錯体配合物は、十分に特徴付けし得ない溶液において金属多核種を生じ得るので、その言及は溶液に添加される成分に対するものである。特定の用途のために、有機溶媒は、約10℃以上、さらなる実施形態では約20℃以上、そしてさらなる実施形態では約25℃以上の引火点と、20℃において約10kPa以下、いくつかの実施形態では約8kPa以下、そしてさらなる実施形態では約6kPa以下の蒸気圧とを有することが望ましい。当業者は、上記の明確な範囲内の引火点および蒸気圧の付加的な範囲が考慮され、本開示の範囲内に含まれることを認識するであろう。

【0055】

一般に、前駆体溶液は、形成される材料の容積に適した適正な混合装置を用いて十分に混合される。適切な過を用いて、任意の汚染物質または適切に溶解しない他の成分を除去することができる。いくつかの実施形態では、混ぜ合わせて前駆体溶液を組み合わせから形成することができる別々の溶液を形成することが望ましいこともある。具体的には、以下の：金属多核オキソ／ヒドロキソカチオン、任意の付加的な金属カチオン、および有機配位子のうちの1つまたは複数を含む別々の溶液が形成され得る。多数の金属カチオンが導入される場合、多数の金属カチオンは、同一の溶液および／または別々の溶液中に導入され得る。一般的に、別々の溶液または合わせた溶液は、十分に混合され得る。いくつかの実施形態では、次に、金属カチオン溶液は、有機ベースの配位子が金属カチオンと結合できるように有機ベースの配位子溶液と混合される。得られた溶液は、安定化金属カチオン溶液と呼ぶことができる。いくつかの実施形態では、安定化金属カチオン溶液は安定した配位子形成を提供するために適切な時間反応させられ、配位子形成は、混合金属イオンが導入されるかどうかに関係なく、溶液内のクラスタ形成を含んでいてもそうでなくてもよい。いくつかの実施形態では、溶液の反応または安定化時間は、さらなる加工に先立って、少なくとも約5分間、他の実施形態では少なくとも約1時間、そしてさらなる実施形態では約2時間～約48時間であり得る。当業者は、安定化期間の付加的な範囲が考慮され、本開示の範囲内に含まれることを認識するであろう。

【0056】

前駆体溶液中の種の濃度は、溶液の所望の物理特性を達成するように選択され得る。特に、より低い濃度は、全体的に、合理的なコーティングパラメータを用いてより薄いコーティングを達成することができるスピンコーティングなどの特定のコーティング手段のために、溶液の望ましい特性をもたらす得る。超微細なパターンングを達成するため、および材料コストを低減するためにより薄いコーティングを使用することが望ましいことがある。一般に、濃度は、選択されたコーティング手段のために適切であるように選択され得る。コーティング特性はさらに以下に記載される。

【0057】

前駆体溶液の安定性は、初期溶液に対する変化に関して評価され得る。具体的には、大きいゾル粒子の生成と共に相分離が生じるか、あるいは溶液が所望のパターン形成を実施するその能力を失えば、溶液は安定性を失っている。本明細書に記載される改善された安定化手段に基づいて、溶液は、少なくとも約1週間、さらなる実施形態では少なくとも約2週間、他の実施形態では少なくとも約4週間、さらに混合することなく安定であり得る。当業者は、安定化時間の付加的な範囲が考慮され、本開示の範囲内に含まれることを認識するであろう。十分な安定化時間を有する溶液を配合することができ、適切な貯蔵期間を有する溶液を商業的に流通させることができる。

【0058】

コーティング材料

コーティング材料は、選択された基板への前駆体溶液の付着、およびそれに続く加工によって形成される。基板は一般的にコーティング材料が付着され得る表面を示し、そして基板は、表面が最上層に関連している複数の層を含み得る。いくつかの実施形態では、基板表面は、コーティング材料の接着のための表面を作製するために処理することができる。また、必要に応じて表面は清浄化および／または平滑化され得る。適切な基板表面は、任意の合理的な材料を含むことができる。特に興味深いいくつかの基板は、基板の表面にわたっておよび／または層内に、例えば、シリコンウェハ、シリカ基板、例えばセラミック材料のような他の無機材料、ポリマー基板、例えば有機ポリマーなど、これらの複合体、およびこれらの組み合わせを含む。比較的薄い円筒形構造などのウェハが便利であり得るが、任意の合理的な形状の構造を使用することができる。ポリマー基板または非ポリマー構造上にポリマー層を有する基板は、その低コストおよび柔軟性に基づいて、特定の用途のために望ましいことがあり、適切なポリマーは、本明細書に記載されるパターンニング可能な材料の加工のために使用され得る比較的低い加工温度に基づいて選択され得る。適切なポリマーは、例えば、ポリカーボネート、ポリイミド、ポリエステル、ポリアルケン、そのコポリマーおよびその混合物を含むことができる。一般に、基板は、特に高解像度用途のために、平坦な表面を有することが望ましい。しかしながら、特定の実施形態では、基板は実質的なトポグラフィを有することがあり、レジストコーティングは、特定のパターンニング用途のために、フィーチャを充填または平坦化することが意図される。レジスト材料のこのような機能は、参照によって本明細書中に援用される「Pre-Patterned Hard Mask for Ultrafast Lithographic Imaging (超高速リソグラフィイメージングのためのプレパターン化ハードマスク)」という表題の米国特許出願公開第2015/0253667 A1号明細書(Bristolら)に記載されている。

【0059】

一般に、前駆体溶液を基板に供給するために任意の適切なコーティングプロセスが使用され得る。適切なコーティング手段は、例えば、スピンコーティング、スプレーコーティング、ディップコーティング、ナイフエッジコーティング、印刷手段(例えば、インクジェット印刷およびスクリーン印刷)などを含むことができる。これらのコーティング手段のいくつかはコーティングプロセス中にコーティング材料のパターンを形成するが、印刷などから現在得られる解像度は、本明細書に記載される放射線ベースのパターンニングから得られるよりも著しく低いレベルの解像度を有する。コーティングプロセスに対するより大きい制御を提供するために、コーティング材料は多数のコーティングステップで適用され得る。例えば、多数のスピンコーティングを実施して、所望される最終のコーティング厚さをもたらすことができる。以下に記載される熱処理は、各コーティングステップの後、または複数のコーティングステップの後に適用され得る。

【0060】

放射線を用いてパターンニングが実施される場合、スピンコーティングは、基板を比較的均一に被覆するために望ましい手段であり得るが、エッジ効果が存在し得る。いくつかの実施形態では、ウェハは、約500rpm～約10,000rpm、さらなる実施形態で

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は約1000rpm～約7500rpm、そして付加的な実施形態では約2000rpm～約6000rpmの速度で回転され得る。回転速度は、所望のコーティング厚さを得るように調整され得る。スピンコーティングは、約5秒間～約5分間、そしてさらなる実施形態では約15秒間～約2分間の時間で実施され得る。初期低速回転（例えば、50rpm～250rpm）を用いて、基板全体に組成物の初期バルク塗布を実施することができる。任意のエッジビードを除去するために、水または他の適切な溶媒を用いて裏面リンスやエッジビード除去ステップなどを実施することができる。当業者は、上記の明確な範囲内のスピンコーティングパラメータの付加的な範囲が考慮され、本開示の範囲内に含まれることを認識するであろう。

[0061]

コーティングの厚さは、一般的に、前駆体溶液の濃度、粘度およびスピンコーティングの回転速度の関数であり得る。他のコーティングプロセスの場合、厚さは、一般的に、コーティングパラメータの選択によっても調整され得る。いくつかの実施形態では、その後のパターンニングプロセスにおいて小さくかつ高度に改造されたフィーチャの形成を容易にするために薄いコーティングを使用することが望ましいこともある。例えば、乾燥後のコーティング材料は、約10ミクロン以下、他の実施形態では約1ミクロン以下、さらなる実施形態では約250ナノメートル（nm）以下、付加的な実施形態では約1ナノメートル（nm）～約50nm、他の実施形態では約2nm～約40nm、そしていくつかの実施形態では約3nm～約25nmの平均厚さを有することができる。当業者は、上記の明確な範囲内の厚さの付加的な範囲が考慮され、本開示の範囲内に含まれることを認識するであろう。厚さは、x線反射率の非接触法および／または膜の光学特性に基づいた偏光解析法を用いて評価され得る。一般に、コーティングは、加工を容易にするために比較的均一である。いくつかの実施形態では、コーティングの厚さの変動は、平均コーティング厚さから±50%以下、さらなる実施形態では±40%以下、そして付加的な実施形態では平均コーティング厚さに対して約±25%以下だけ異なる。より大きい基板上の均一性の高いコーティングなどのいくつかの実施形態では、コーティングの均一性の評価は、1センチメートルのエッジを除外して評価され得る。すなわち、コーティングの均一性は、コーティングのエッジから1センチメートル以内の部分については評価されない。当業者は、上記の明確な範囲内の付加的な範囲が考慮され、本開示の範囲内に含まれることを認識するであろう。

[0062]

多くのコーティングプロセスは、より大きい表面積および／または蒸発を刺激する溶液の移動を有する液滴または他の形態のコーティング材料を形成するので、コーティングプロセス自体が溶媒の一部の蒸発をもたらす得る。溶媒の喪失は、材料中の種の濃度の増大につれてコーティング材料の粘度を増大する傾向がある。コーティングプロセスの間の目標は、十分な溶媒を除去して、さらなる加工のためにコーティング材料を安定化させることであり得る。これらの種は、加水分解物コーティング材料を形成するために、コーティングと、その後の加熱の間に凝縮し得る。一般に、コーティング材料は、さらに溶媒を除去して、コーティング材料の緻密化を促進するために放射線曝露の前に加熱され得る。乾燥したコーティング材料は、一般的に、金属へのオキソ／ヒドロキソ配位子に基づいた高分子金属オキソ／ヒドロキソネットワークを形成することができ、ここで、金属は、いくつかのアルキル配位子、またはアルキル配位子を有する多核金属オキソ／ヒドロキソ種で構成される分子固体も有する。

[0063]

溶媒除去プロセスは、コーティング材料中に残存する特定の量の溶媒に関して定量的に制御されてもそうでなくてもよく、得られたコーティング材料の特性の経験的な評価は、一般的に、パターンニングプロセスに有効である加工条件を選択するために実施され得る。プロセス用途の成功のために加熱は必要とされないが、加工を加速し、そして／あるいはプロセスの再現性を増大させるために、被覆基板を加熱することが望ましいこともある。溶媒を除去するために加熱が適用される実施形態では、コーティング材料は、約45℃～

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約250℃、そしてさらなる実施形態では約55℃～約225℃温度まで加熱され得る。溶媒除去のための加熱は、一般的に、少なくとも約0.1分間、さらなる実施形態では約0.5分間～約30分間、そして付加的な実施形態では約0.75分間～約10分間実施され得る。当業者は、上記の明確な範囲内の加熱温度および時間の付加的な範囲が考慮され、本開示の範囲内に含まれることを認識するであろう。コーティング材料の加熱処理および緻密化の結果、コーティング材料は、コントラストを著しく損失することなく屈折率および放射線吸収の増大を示すことができる。

【0064】

パターン化された曝露およびパターン化されたコーティング材料

コーティング材料は、放射線を用いて微細にパターン化され得る。上記のように、前駆体溶液の組成、従って対応するコーティング材料の組成は、所望の形態の放射線を十分に吸収するように設計され得る。放射線の吸収は、金属とアルキル配位子との間の結合を破壊できるエネルギーを生じ、その結果、アルキル配位子の少なくとも一部はもはや材料を安定化するために利用できない。アルキル配位子または断片を含む放射線分解生成物は、プロセス変数およびこのような生成物の同一性に依拠して膜から拡散してもしなくてもよい。十分な量の放射線の吸収により、曝露されたコーティング材料は凝縮し、すなわち増強された金属オキソ/ヒドロキソネットワークを形成し、これは、周囲大気から吸収された水を含み得る。放射線は、一般に、選択されたパターンに従って送達され得る。放射線パターンは、照射領域および非照射領域を有するコーティング材料において対応するパターンまたは潜像に転写される。照射領域は、化学的に変化されたコーティング材料を含み、非照射領域は一般的に形成されたままのコーティング材料を含む。下記のように、非照射コーティング材料の除去あるいは照射コーティング材料の選択的除去によるコーティング材料の現像の際、非常に鋭いエッジが形成され得る。

【0065】

放射線は、一般的に、マスクを介して被覆基板へ向けられてもよいし、または放射線ビームは基板全体に制御可能に走査されてもよい。一般に、放射線は、電磁放射線、電子ビーム（ベータ放射線）、または他の適切な放射線を含むことができる。一般に、電磁放射線は、可視光、紫外線またはx線などの所望の波長または波長範囲を有することができる。放射線パターンに対して達成可能な解像度は、一般的に、放射線の波長に依存し、より高い解像度パターンは、一般的により短い波長の放射線によって達成され得る。従って、特に高解像度のパターンを達成するために、紫外線、x線または電子ビームを使用することが望ましいこともある。

【0066】

参照によって本明細書中に援用される国際規格ISO 21348（2007）に従って、紫外線は、100nm以上であり400nm未満である波長間に広がる。フッ化クリプトンレーザーを248nm紫外線源として使用することができる。紫外線領域は、容認された規格の下、いくつかの方法で、10nm以上から121nm未満までである極紫外線（EUV）、および122nm以上から200nm未満までである遠紫外線（FUV）などに細分され得る。フッ化アルゴンレーザーからの193nmラインをFUVにおける放射線源として使用することができる。EUV光は、13.5nmでリソグラフィのために使用されており、この光は、高エネルギーレーザーまたは放電パルスを用いて励起されたXeまたはSnプラズマ源から発生される。軟x線は、0.1nm以上から10nm未満までであると定義され得る。

【0067】

電磁放射線の量は、曝露時間に対する積分放射フラックスによって得られるフルエンスまたは線量によって特徴付けることができる。適切な放射線フルエンスは、約1mJ/cm²～約150mJ/cm²、さらなる実施形態では約2mJ/cm²～約100mJ/cm²、そしてさらなる実施形態では約3mJ/cm²～約50mJ/cm²であり得る。当業者は、上記の明確な範囲内の放射線フルエンスの付加的な範囲が考慮され、本開示の範囲内に含まれることを認識するであろう。

【 0 0 6 8 】

電子ビームリソグラフィでは、電子ビームは一般的に二次電子を誘発し、これは一般的に照射された材料を変化させる。解像度は、少なくとも部分的に、材料内の二次電子の範囲の関数であり得る。ここで、より高い解像度は一般的により短い範囲の二次電子から得られると考えられる。本明細書に記載される無機コーティング材料を用いて電子リソグラフィにより達成可能な高解像度に基づいて、無機材料中の二次電子の範囲は制限される。電子ビームは、ビームのエネルギーによって特徴付けることができ、適切なエネルギーは、約5 V～約200 kV（キロボルト）、そしてさらなる実施形態では約7.5 V～約100 kVの範囲であり得る。30 kVにおける近接補正ビーム線量は、1平方センチメートル当たり約0.1マイクロクーロン～1平方センチメートル当たり約5ミリクーロン（ $\mu\text{C}/\text{cm}^2$ ）、さらなる実施形態では約0.5 $\mu\text{C}/\text{cm}^2$ ～約1 mC/cm^2 、そして他の実施形態では約1 $\mu\text{C}/\text{cm}^2$ ～約100 $\mu\text{C}/\text{cm}^2$ の範囲であり得る。当業者は、本明細書中の教示に基づいて、他のビームエネルギーにおいて対応する線量を計算することができ、上記の明確な範囲内の電子ビーム特性の付加的な範囲が考慮され、本開示の範囲内に含まれることを認識するであろう。

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【 0 0 6 9 】

コーティング材料の設計に基づいて、凝縮コーティング材料を有する照射領域と、実質的に未変化の有機配位子を有する非照射コーティング材料との間には、材料特性の大きいコントラストが存在する。投与量におけるコントラストは照射後の熱処理によって改善され得るが、いくつかの実施形態では照射後の熱処理がなくても満足な結果を得ることが可能であることが分かった。曝露後の熱処理は、照射コーティング材料をアニーリングして、有機配位子-金属結合の熱破壊に基づいてコーティング材料の非照射領域を有意に凝縮させることなく、その凝縮を増大させると思われる。照射後の熱処理が使用される実施形態の場合、照射後の熱処理は、約45℃～約250℃、付加的な実施形態では約50℃～約190℃、そしてさらなる実施形態では約60℃～約175℃の温度で実施され得る。曝露後加熱は、一般的に、少なくとも約0.1分間、さらなる実施形態では約0.5分間～約30分間、そして付加的な実施形態では約0.75分間～約10分間実施され得る。当業者は、上記の明確な範囲内の照射後加熱温度および時間の付加的な範囲が考慮され、本開示の範囲内に含まれることを認識するであろう。材料特性のこの高いコントラストは、以下のセクションに記載される現像後のパターンにおける鋭いラインの形成をさらに容易にする。

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【 0 0 7 0 】

放射線による曝露の後、コーティング材料は、照射領域および非照射領域によりパターン化される。図1および図2を参照すると、基板102、薄膜103およびパターン化コーティング材料104を含むパターン化構造100が示されている。パターン化コーティング材料104は、照射コーティング材料の領域110、112、114、116および非照射コーティング材料の非凝縮領域118、120、122を含む。凝縮領域110、112、114、116および非凝縮領域118、120、122によって形成されたパターン化構造は、コーティング材料内の潜像を表し、潜像の現像は以下のセクションに記載される。

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【 0 0 7 1 】

現像およびパターン化構造

画像の現像は、潜像を含むパターン化コーティング材料を現像剤組成物に接触させて、非照射コーティング材料を除去してネガ画像を形成するか、または照射コーティングを除去してポジ画像を形成するかのいずれかを含む。本明細書に記載されるレジスト材料を用いると、一般的には同じコーティングに基づいて適切な現像溶液を用いて、望ましい解像度を有する効果的なネガティブパターンニングまたはポジティブパターンニングを実施することができる。特に、照射領域は少なくとも部分的に凝縮されて金属酸化物の特性が増大され、その結果、照射材料は有機溶媒による溶解に対して耐性であり、非照射組成物は有機溶媒に可溶性のままである。凝縮したコーティング材料への言及は、材料の酸化物特性が

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初期材料に対して増大するという意味において少なくとも部分的な凝縮を指す。一方、非照射材料は、材料が疎水性であるために弱い塩基または酸水溶液に溶解しにくく、従って、ポジティブパターンニングのために塩基水溶液を使用して、非照射材料を保持しながら照射材料を除去することができる。

【0072】

有機安定化配位子を有するコーティング組成物は、本質的に比較的疎水性である材料を生成する。有機金属結合の少なくとも一部を破壊するための照射により、材料はより低疎水性、すなわちより親水性の材料に変化される。この特性の変化は照射コーティングと非照射コーティングとの間に顕著なコントラストを提供し、これにより、同じレジスト組成物を用いてポジ型パターンニングおよびネガ型パターンニングの両方を行うことができるようになる。具体的には、照射コーティング材料はある程度まで凝縮して、金属酸化物のより多い組成物になるが、著しい加熱を伴わなくても凝縮の度合いは一般的に中程度であり、従って、照射材料は比較的、従来の現像剤による現像に対して直接的である。

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【0073】

ネガ型画像形成に関して、図3および図4を参照すると、図1および図2に示される構造の潜像は現像剤との接触より現像されて、パターン化構造130が形成されている。画像の現像の後、基板102は、開口部132、134、135を通して上部表面に沿って露出される。開口部132、134、135は、それぞれ非凝縮領域118、120、122の場所に位置する。ポジ型画像形成に関して、図5および図6を参照すると、図1および図2に示される構造の潜像は現像されて、パターン化構造140が形成されている。パターン化構造140は、パターン化構造130の共役像 (conjugate image) を有する。パターン化構造140は、照射領域110、112、114、116 (現像されて開口部142、144、146、148を形成する) の場所で露出された基板102を有する。

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【0074】

ネガ型画像形成の場合、現像剤は、前駆体溶液を形成するために使用される溶媒などの有機溶媒であり得る。一般に、現像剤の選択は、コーティング材料 (照射および非照射の両方) に関する溶解度パラメータ、ならびに現像剤の揮発度、引火性、毒性、粘度、および他のプロセス材料との潜在的な化学的相互作用によって影響され得る。特に、適切な現像剤には、例えば、芳香族化合物 (例えば、ベンゼン、キシレン、トルエン)、エステル (例えば、プロピレングリコールモノメチルエステルアセタート、酢酸エチル、乳酸エチル、酢酸n-ブチル、ブチロラクトン)、アルコール (例えば、4-メチル-2-ペンタノール、1-ブタノール、イソプロパノール、1-プロパノール、メタノール)、ケトン (例えば、メチルエチルケトン、アセトン、シクロヘキサノン、2-ヘプタノン、2-オクタノン)、エーテル (例えば、テトラヒドロフラン、ジオキサン、アニソール) などが含まれる。現像は、約5秒間〜約30分間、さらなる実施形態では約8秒間〜約15分間、そして付加的な実施形態では約10秒間〜約10分間実施され得る。当業者は、上記の明確な範囲内の付加的な範囲が考慮され、本開示の範囲内に含まれることを認識するであろう。

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【0075】

ポジ型画像形成の場合、現像剤は、一般に、酸または塩基水溶液であり得る。いくつかの実施形態では、塩基水溶液は、より鋭い画像を得るために使用され得る。現像剤からの汚染を低減するために、金属原子を含まない現像剤を使用することが望ましいこともある。従って、水酸化第4級アンモニウム組成物、例えば、水酸化テトラエチルアンモニウム、水酸化テトラプロピルアンモニウム、水酸化テトラブチルアンモニウムまたはこれらの組み合わせは現像剤として望ましい。一般に、特に興味深い水酸化第4級アンモニウムは、式 R_4NOH (式中、 R = メチル基、エチル基、プロピル基、ブチル基、またはこれらの組み合わせ) で表すことができる。本明細書に記載されるコーティング材料は、一般に、ポリマーレジストのために現在一般に使用されるものと同じ現像剤、具体的には水酸化テトラメチルアンモニウム (TMAH) で現像され得る。市販のTMAHは2.38重量

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パーセントで利用可能であり、この濃度は、本明細書に記載される処理のために使用され得る。さらに、混合水酸化第4級テトラアルキルアンモニウムが使用され得る。一般に、現像剤は、約0.5～約30重量パーセント、さらなる実施形態では約1～約25重量パーセント、そして他の実施形態では約1.25～約20重量パーセントの水酸化テトラアルキルアンモニウムまたは同様の水酸化第4級アンモニウムを含むことができる。当業者は、上記の明確な範囲内の現像剤濃度の付加的な範囲が考慮され、本開示の範囲内に含まれることを認識するであろう。

【0076】

主要な現像剤組成物に加えて、現像剤は、現像プロセスを容易にするために付加的な組成物を含むことができる。適切な添加剤には、例えば、アンモニウム、d-ブロック金属カチオン（ハフニウム、ジルコニウム、ランタンなど）、f-ブロック金属カチオン（セリウム、ルテチウムなど）、p-ブロック金属カチオン（アルミニウム、スズなど）、アルカリ金属（リチウム、ナトリウム、カリウムなど）、およびこれらの組み合わせからなる群から選択されるカチオンと、フッ素、塩素、臭素、ヨウ素、硝酸、硫酸、リン酸、ケイ酸、ホウ酸、過酸化物、プトキシド、ギ酸、シュウ酸、エチレンジアミン-四酢酸（EDTA）、タングステン酸、モリブデン酸など、およびこれらの組み合わせからなる群から選択されるアニオンとを有する溶解塩が含まれる。他の潜在的に有用な添加剤には、例えば、分子キレート剤、例えば、ポリアミン、アルコールアミン、アミノ酸、カルボン酸またはこれらの組み合わせが含まれる。任意選択の添加剤が存在する場合、現像剤は、約10重量パーセント以下の添加剤、そしてさらなる実施形態では約5重量パーセント以下の添加剤を含むことができる。当業者は、上記の明確な範囲内の添加剤濃度の付加的な範囲が考慮され、本開示の範囲内であることを認識するであろう。添加剤は、コントラスト、感受性およびライン幅ラフネスを改善するように選択され得る。現像剤中の添加剤は、金属酸化物粒子の形成および沈殿も抑制し得る。

【0077】

より弱い現像剤、例えばより低濃度の水性現像剤、希釈した有機現像剤または組成物（コーティングがより低い現像速度を有する）の場合、より高温の現像プロセスを使用して、プロセスの速度を増大させることができる。より強い現像液の場合、現像プロセスの温度は、現像の速度を低下させ、そして／あるいは現像の動態学を制御するために低くすることができる。一般に、現像の温度は、溶媒の揮発度に一致する適切な値の間で調整され得る。さらに、現像剤-コーティング界面付近の溶解したコーティング材料を含む現像剤は、現像の間に超音波処理により分散され得る。

【0078】

現像剤は、任意の合理的な手段を用いてパターン化コーティング材料に適用され得る。例えば、現像剤は、パターン化コーティング材料上にスプレーされ得る。また、スピンコーティングが使用され得る。自動処理の場合、現像剤をコーティング材料上に静止型式で注ぐことを含むパドル法が使用され得る。所望される場合、スピンリンス（*spin rinsing*）および／または乾燥が使用されて、現像プロセスを完了することができる。適切なすすぎ溶液は、例えば、ネガティブパターンングの場合には、超純水、メチルアルコール、エチルアルコール、プロピルアルコール、およびこれらの組み合わせを含み、ポジティブパターンングの場合には、超純水を含む。画像が現像された後、コーティング材料は、パターンとして基板上に配設される。

【0079】

現像ステップが完了したら、コーティング材料は、材料をさらに凝縮させ、材料をさらに脱水、高密度化、または材料から残存する現像剤を取り除くために熱処理され得る。この熱処理は、最終デバイスに酸化物コーティング材料が取り込まれる実施形態のために特に望ましいことがあるが、さらなるパターンングを容易にするためにコーティング材料の安定化が望ましい場合、コーティング材料がレジストとして使用されて最終的に除去されるいくつかの実施形態に対して熱処理を実施することが望ましいこともある。特に、パターン化コーティング材料のベーキングは、パターン化コーティング材料が所望のレベルの

エッチング選択性を示す条件下で実施され得る。いくつかの実施形態では、パターン化コーティング材料は、約100℃～約600℃、さらなる実施形態では約175℃～約500℃、そして付加的な実施形態では約200℃～約400℃の温度まで加熱され得る。加熱は、少なくとも約1分間、他の実施形態では約2分間～約1時間、さらなる実施形態では約2.5分間～約25分間実施され得る。加熱は、空气中、真空中、またはArもしくはN₂などの不活性ガス雰囲気中で実施され得る。当業者は、上記の明確な範囲内の熱処理のための温度および時間の付加的な範囲が考慮され、本開示の範囲内に含まれることを認識するであろう。同様に、プランケットUV曝露、またはO₂などの酸化性プラズマへの曝露を含む非熱的処理が同様の目的で使用されてもよい。

【0080】

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従来の有機レジストでは、構造のアスペクト比（高さを幅で割った値）が非常に大きくなると、構造はパターン崩壊を起こしやすい。パターン崩壊は、加工ステップに関連する力、例えば表面張力が構造要素を変形させるような高アスペクト比構造の機械的不安定性に関連し得る。低アスペクト比構造は、潜在的な変形力に関してより安定である。本明細書に記載されるパターンニング可能なコーティング材料を用いると、より薄いコーティング材料層を有する構造を効果的に加工することができるため、高アスペクト比のパターン化コーティング材料を必要とせずに改善されたパターンニングを達成することができる。従って、パターン化コーティング材料において高アスペクト比のフィーチャに頼ることなく非常に高解像度のフィーチャが形成された。

【0081】

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得られた構造は、鋭いエッジを有することができ、ライン幅ラフネスは非常に低い。特に、ライン幅ラフネスを低減できることに加えて、高いコントラストも、小さいフィーチャおよびフィーチャ間のスペースの形成、ならびに極めて十分に解像された二次元パターン（例えば、鋭いコーナー）を形成する能力を可能にする。従って、いくつかの実施形態では、隣接する構造の隣り合った直線部分は、約60nm（30nmハーフピッチ）以下、いくつかの実施形態では約50nm（25nmハーフピッチ）以下、そしてさらなる実施形態では約34nm（17nmハーフピッチ）以下の平均ピッチ（ハーフピッチ）を有することができる。

【0082】

ピッチは設計により評価され、走査型電子顕微鏡法（SEM）、例えばトップダウン画像により確認され得る。本明細書で使用される場合、ピッチは反復構造要素の空間的周期、すなわち中心間距離を指し、当該技術分野において一般的に使用されるように、ハーフピッチはピッチの半分である。パターンのフィーチャ寸法は、一般にコーナーなどから離れたところで評価されるフィーチャの平均幅に関して表すこともできる。また、フィーチャは、材料要素間のギャップおよび／または材料要素を指すこともできる。いくつかの実施形態では、平均幅は、約25nm以下、さらなる実施形態では約20nm以下、そして付加的な実施形態では約15nm以下であり得る。平均ライン幅ラフネスは、約5nm以下、いくつかの実施形態では約4.5nm以下、そしてさらなる実施形態では約2.5nm～約4nmであり得る。ライン幅ラフネスの評価は、トップダウンSEM画像の分析により平均ライン幅からの3σ偏差を導くことによって実施される。平均は、高頻度および低頻度の両方のラフネス、すなわちそれぞれ短い相関長および長い相関長を含有する。有機レジストのライン幅ラフネスは主に長い相関長によって特徴付けられるが、本発明の有機金属コーティング材料は、著しく短い相関長を示す。パターン転写プロセスにおいて、短い相関ラフネスはエッチングプロセスの間に平滑化され、はるかに高い忠実性パターンを生成し得る。当業者は、上記の明確な範囲内のピッチ、平均幅およびライン幅ラフネスの付加的な範囲が考慮され、本開示の範囲内に含まれることを認識するであろう。

【0083】

パターン化コーティング材料のさらなる加工

パターン化コーティング材料を形成した後、コーティング材料は、選択されたデバイスの形成を容易にするためにさらに加工され得る。さらに、構造を完成させるために、一般

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的にさらなる材料の付着、エッチングおよび／またはパターニングが実施され得る。コーティング材料は、最終的に除去されてもされなくてもよい。パターン化コーティング材料の品質は、いずれの場合も、改善されたデバイス（例えば、より小さい設置面積を有するデバイスなど）の形成のために前進され得る。

【0084】

パターン化コーティング材料は、例えば、図3および図4に示されるように、下側の基板への開口部を形成する。従来のレジストと同様に、パターン化コーティング材料は、パターンを転写して下側の薄膜を選択的に除去するために使用され得るエッチマスクを形成する。図7を参照すると、下側の薄膜103（図6を参照）は、基板102の上に、凝縮領域110、112、114の下方にそれぞれフィーチャ152、154、156を残してパターン化される。従来のポリマーレジストと比較して、本明細書に記載される材料は、著しく大きいエッチング耐性を提供することができる。図5および図6に示されるマスクパターンを用いて同様の加工を行うことができ、代替のマスクパターンから直接得られるパターン化構造はそれに応じて変化する。

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【0085】

代替的にまたは付加的に、マスクパターンに従うさらなる材料の付着は、下側の構造の特性を変更させ、そして／あるいは下側の構造との接触を提供することができる。さらなるコーティング材料は、所望の材料特性に基づいて選択することができる。加えて、パターン化無機コーティング材料の密度が、高い注入耐性を提供することができるので、マスクの開口部を介してイオンが下側の構造選択的に注入され得る。いくつかの実施形態では、さらに付着される材料は、誘電体、半導体、導体または他の適切な材料であり得る。さらに付着される材料は、適切な手段、例えば、溶液ベースの手順、化学蒸着（CVD）、スパッタリング、物理蒸着（PVD）、または他の適切な手段を用いて付着され得る。

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【0086】

一般に、複数の付加的な層が付着され得る。複数の層の付着に関連して、付加的なパターニングが実施され得る。所望される場合には、付加的な量の明細書に記載されるコーティング材料、ポリマーベースのレジスト、他のパターニング手段またはこれらの組み合わせを用いて任意の付加的なパターニングが実施され得る。

【0087】

上記のように、パターニングの後のコーティング（レジスト）材料の層は、除去されてもされなくてもよい。層が除去されない場合、パターン化コーティング（レジスト）材料は構造内に組み込まれる。パターン化コーティング（レジスト）材料が構造内に取り込まれる実施形態の場合、コーティング（レジスト）材料の特性は、所望のパターニング特性だけでなく、構造内の材料の特性も提供するように選択され得る。

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【0088】

パターン化コーティング材料の除去が所望される場合、コーティング材料は、従来のレジストとしての機能を果たす。パターン化コーティング材料は、レジスト／コーティング材料を除去する前に、後で付着される材料をパターニングするため、および／または凝縮コーティング材料内の空間を介して基板を選択的にエッチングするために使用される。凝縮コーティング材料は、適切なエッチングプロセスを用いて除去することができる。具体的には、凝縮コーティング材料を除去するために、例えば、 BCl_3 プラズマ、 Cl_2 プラズマ、 HBr プラズマ、 Ar プラズマまたは他の適切なプロセスガスによるプラズマを用いてドライエッチングが実施され得る。代替的または付加的に、パターン化コーティング材料を除去するために、例えば、酸または塩基水溶液、 HF （水）、または緩衝 HF （水）／ NH_4F またはシュウ酸などを用いるウェットエッチングが使用され得る。図8を参照すると、図8の構造は、コーティング材料を除去した後に示される。エッチングされた構造150は、基板102およびフィーチャ152、154、156を含む。

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【0089】

金属オキソ／ヒドロキソベースのコーティング材料は、P. Zimmerman, J. Photopolym. Sci. Technol., Vol. 22, No. 5, 2009

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、p. 625において従来のレジストについて一般的に記載されるように、熱凍結プロセスを用いて多重パターンニングを実施するために特に便利である。「熱凍結」によるダブルパターンニングプロセスは、図9において概説される。第1のステップでは、図3および図4に関して記載されるように、リソグラフィプロセスおよび現像を用いてコーティング材料が基板162上のパターン160に形成される。加熱ステップ164を実施して、溶媒を除去し、コーティング材料を凝縮させるが、これは、完全な酸化物の形成を伴っていてもいなくてもよい。この加熱ステップは、上記の現像セクションに記載される現像後の加熱ステップと同等である。この「熱凍結」プロセスは、その後のコーティング材料の第2の層の付着に対してコーティング材料を不溶性にする。第2のリソグラフィおよび現像ステップ166は、基板162上にダブルパターン化構造168を形成するために実施される。エッチングステップ170の後、産物のダブルパターン化構造172が形成される。このプロセスを多重コーティングおよびパターンニングステップに拡張することは容易であり、このような拡張が考慮され、本開示の範囲内に含まれることに注目されたい。多重パターンニングに関して、本明細書に記載される無機コーティング材料と従来の有機レジストとの間の顕著な違いは、加熱ベーキングの後でも有機レジストが従来のレジストキャストリング溶媒中に可溶性のままなことである。本明細書に記載されるレジスト材料は加熱ベーキングにより凝縮されることが可能であり、その結果、有機溶媒に可溶性ではなく、その後のコーティング層を適用することができる。

【実施例】

【0090】

実施例1 — $t\text{-BuSn}(\text{NEt}_2)_3$ の加水分解物

この実施例には、 t -ブチルトリス(ジエチルアミド)スズからの加水分解物前駆体溶液の調製が記載される。

【0091】

公称式 $t\text{-BuSnO}_{(3/2-x/2)}(\text{OH})_x$ (式中、 $0 < x < 3$) を有する加水分解物酸化水酸化物生成物(1)は、参照によって本明細書中に援用される Haensgen, D.; Puff, H.; Beckerman, N. *Journal of Organometallic Chemistry*, 293, 1985, 191-195 で報告された方法に従って合成した t -ブチルトリス(ジエチルアミド)スズ(2)から調製した。気密性シリンジを用いて、4.4gの t -ブチルトリス(ジエチルアミド)スズを150mLのDI H_2O (18M Ω)に絶え間なく(約125 $\mu\text{L}/\text{s}$)添加し、直ぐに沈殿物が形成し、これを5分間放置させた。得られたスラリーを30分間攪拌してから、No. 1のろ紙(Whatman)により吸引ろ過した。得られた固体を1回50mLのDI H_2O により3回すすいだ。ろ過およびすすぎの後に保持された固体を真空(約5トル)下、室温で8時間乾燥させて1.9gの粉末固体の加水分解物1を得た。

【0092】

Microanalysis, Inc. (Wilmington, DE)での粉末サンプルの元素分析によって、22.43% C、4.79% H、および0.11% N(質量)が得られた。これらの結果は、1 t -ブチル:1 Snの組成比(予測値:23.01% C、4.83% H、0.0% N)と一致する。N含量は、 t -ブチルトリス(ジエチルアミド)スズの加水分解の際のジエチルアミンの完全除去を示す。同じ手順で調製された粉末において乾燥空気中で実施される熱重量質量分析は、同様に、図10および11に示されるような加水分解物に対する経験的な近似式(C_4H_9) SnOOH と一致する。段階的な脱水(50~150℃、残留重量約96%)および脱アルキル化/燃焼(200~500℃、約73%)が観察され、最終残留重量は予測される SnO_2 生成物に相当する。

【0093】

実施例2 — $i\text{-PrSnCl}_3$ の加水分解物

この実施例には、 i -プロピルスズ三塩化物からの加水分解物前駆体溶液の調製が記載される。

【0094】

i-プロピルスズ三塩化物(4, i-Pr Sn Cl₃, Gelest)の加水分解物の酸化水酸化物生成物(i-Pr Sn O_(3/2-x/2)(OH)_x、式中、0<x<3)(3)は、150 mLの0.5 MのNaOH(水)に6.5 gの化合物i-プロピルスズ三塩化物を激しく攪拌しながら迅速に添加することによって調製し、すぐに沈殿物が生じた。得られた混合物を室温で1時間攪拌してから、No. 1のろ紙(Whatman)により吸引ろ過した。保持された固体を1回約25 mLのDI H₂Oにより3回洗浄した後、真空(約5トル)下、室温で12時間乾燥させた。

【0095】

i-プロピルスズ三塩化物の加水分解物の乾燥粉末の元素分析(18.04% C、3.76% H、1.38% Cl; Microanalysis, Inc.; Wilmington, DE)により、i-プロピルスズ三塩化物の加水分解の際に塩化物イオンの実質的な除去が起こり、加水分解物の経験的な近似式はi-Pr Sn O_(3/2-x/2)(OH)_x(式中、x≒1)であること(C₃H₈O₂Snの計算値: 18.50% C、4.14% H、0.00% Cl)が示された。結果は、i-プロピルスズ三塩化物の加水分解物に対する経験的な近似式(C₃H₇)SnOOHと一致する。

【0096】

実施例3 - フォトレジスト溶液の調製

この実施例には、加水分解物前駆体からのフォトレジスト溶液の調製が記載される。

【0097】

化合物1(実施例1)の溶液は、0.1 gの乾燥粉末を10 mLのメタノール(ACS, 99.8%)に攪拌しながら添加し、Sn濃度が約0.05 Mの混合物を形成することにより調製した。24時間攪拌した後、混合物を0.45 μmのPTFEシリンジフィルタによりろ過して、不溶性材料を除去した。得られた前駆体溶液の動的光散乱(DLS)分析(Moebius機器(Wyatt Technology))を用いて実施)は、図12に示されるように、約1.9 nmの平均直径を有するクラスターの単峰型質量加重分布と一致する。このような粒径分布を提供する代表的な時間相関関数は図13に示される。

【0098】

核磁気共鳴(NMR)分光法は、d₄-メタノール中で調製した同様の溶液において、Bruker Prodigy™ CryoProbeを備えたBruker Avance-III-HD 600 MHz スペクトロメータを用いて実施した。代表的な¹¹⁹Snスペクトルは図14に示され、代表的な¹Hスペクトルは図15に示される。主要な2セットのプロトン共鳴が観察され、それぞれ、より強い共鳴(1.58、1.40 ppm)およびより弱い共鳴(1.55、1.37 ppm)からなる。これらの位置および積分強度は、クロソ(closo)型十二量体クラスタ[(t-BuSn)₁₂O₁₄(OH)₆]⁺²または密接に関連する化学環境において5配位および6配位のスズ原子に結合した-C(CH₃)₃配位子上のメチルプロトンの予測される化学シフトとほぼ一致する。3.33、および4.90 ppmを中心とする共鳴は、メタノールのCH₃およびOHプロトンに帰属される。2セットの密集した¹¹⁹Sn共鳴は、-333.86および-336.10 ppm、ならびに-520.33および-521.48 ppmにおいて観察される。これらの結果は、参照によって本明細書中に援用されるEychenne-BaronらのOrganometallics 19, 2000, 1940-1949により(n-BuSn)₁₂クラスタについて記載されるように、カチオン性十二量体クラスタにおける2つのスズ環境について予測されるシフトを同様に近似する。

【0099】

エレクトロスプレーイオン化質量分析(ESI-MS)を用いて、同じ加水分解物のメタノール溶液を特徴付けした。代表的な正イオンモードの質量スペクトルは図16に示される。2つの主要なカチオン種がスペクトルにおいて観察される。1つは1219の質量対電荷(m/z)比におけるシグナルであり、2つ目は、m/z=2435におけるより強いシグナルである。これらのm/z比は、加水分解物のメタノール溶液中の二重荷電(

$[(t-BuSn)_2O_4(OH)_6]^{+2}$ 、計算値 $m/z = 1218$ ）、および単一荷電（脱プロトン化、 $[(t-BuSn)_2(O_5(OH)_5)]^{+}$ $m/z = 2435$ ）カチオン性十二量体種の存在に帰属される。 $m/z 2436$ におけるピークの周囲には、いくつかのショルダーおよびサテライトピークがあり、これらは、主要な十二量体種のメトキソおよび溶媒和または水和誘導体の存在を表すことができ、NMRにより観察された密接に関連する ^{119}Sn および ^1H 共鳴に相当すると推定される。

【0100】

化合物3（実施例2）の溶液は、0.16 gの乾燥粉末を10 mLの4-メチル-2-ペンタノール（Alfa-Aesar, 99%）に攪拌しながら添加し、Sn濃度が約0.08 Mの混合物を形成することにより調製した。2時間攪拌した後、混合物を活性化4 Åモレキュラーシーブにより一晩乾燥させて残留水を除去し、次に、0.45 μmのPTFEシリンジフィルタによりろ過して不溶性材料を除去した。

【0101】

実施例4 — レジストコーティング、膜処理、ネガ型画像形成

この実施例は、極紫外放射線曝露によるネガ型画像形成に基づいたレジストパターンの形成を実証する。分枝状アルキルスズ酸化水酸化物フォトレジストをシリコンウェハ上に被覆し、EUV放射線を用いてネガ型の特徴的なコントラスト曲線を作成した。

【0102】

天然の酸化物表面を有するシリコンウェハ（100 mm直径）を、薄膜付着のための基板として使用した。レジスト付着の前にヘキサメチルジシラザン（HMDS）蒸気ブライムによりSi基板を処理した。天然の酸化物表面を有するシリコンウェハ（100 mm直径）を、薄膜付着のための基板として使用した。レジスト付着の前にヘキサメチルジシラザン（HMDS）蒸気ブライムによりSi基板を処理した。i-ブチルおよびt-ブチルスズ酸化水酸化物フォトレジスト溶液を実施例3に記載されるように調製し、それぞれ約0.06および0.05 Mに希釈した。n-ブチルスズ酸化水酸化物（n-BuSnO $_{(3/2-x/2)}(OH)_x$ ）レジスト溶液の前駆体溶液（0.057 MのSn）を上記の1524号出願に記載されるように調製した。前駆体溶液をSi基板上にスピニングし、指示されるrpm/温度で2分間ベーキングしてアルキルスズ酸化水酸化物レジスト薄膜を形成した：1500 rpm/80℃（i-Pr-）；1800 rpm/100℃（n-Bu-）；2000 rpm/100℃（t-Bu-）。

【0103】

EUV光（Lawrence Berkeley National Laboratory Micro Exposure Tool, MET）を用いて、ウェハ上に直線配列の50個の円形パッド（直径約500 μm）を投射した。パッド曝露時間は、各パッドに対して増大するEUV線量（7%の指数関数的ステップ）を提供するように調節した。次に、ホットプレート上で100～200℃において2分間、レジストおよび基板に曝露後ベーキング（PEB）を行った。曝露したフィルムを2-ヘプタノン中に15秒間浸漬し、同じ現像剤でさらに15秒間すすいで、ネガ型画像、すなわちコーティングの非曝露部分が除去された画像を形成した。n-ブチルスズ酸化水酸化物レジスト膜をさらにDI H₂O中で30秒間すすいだ。最後に150℃で2分間のホットプレートベーキングを実施して、プロセスを完了させた。曝露したパッドの残留レジストの厚さを、J. A. Wooliam M-2000分光エリプソメーターを用いて測定した。測定した厚さを測定した最大のレジスト厚さに対して正規化し、曝露線量の対数に対してプロットして、一連のPEB温度における各レジストの特徴的な曲線を形成した。正規化した厚さの最大傾斜対数線量曲線はフォトレジストコントラスト（γ）として定義される。この点で描かれた接線が1に等しい線量値は、フォトレジストのゲル線量（D_g）として定義される。このようにして、フォトレジストの特徴付けに使用される一般的なパラメータは、参照によって本明細書中に援用されるMack, C. Fundamental Principles of Optical Lithography, John Wiley & Sons, Chichester, U.K; pp 271-272, 2007に従って近

似され得る。

【0104】

各レジストの γ 対D₀をプロットすることにより、PEB温度は各レジストに対して増大されるので、線量の低下とコントラストとの間の明白な関係が説明される(図17)。ここで試験される分枝状アルキルスズ酸化水酸化物レジストはいずれも、n-ブチルスズ酸化水酸化物ベースのレジストよりも優れたコントラストを有し、2-ヘプタノン中で現像される場合により低線量(PEBにより調節される)で同等またはより優れたコントラストを維持することが分かる。

【0105】

分枝状アルキルスズ酸化水酸化物フォトレジストから得られる改善された感受性およびコントラストを同様に使用して、EUV放射線への曝露により高解像度パターンを生成した。実施例3からの化合物1の溶液を約0.03MのSnになるようにメタノールで希釈してから、2000rpmで基板上にスピンコーティングし、ホットプレート上、100℃で2分間ベーキングした。コーティングおよびベーキング後の膜厚は、偏光解析法により約23nmであると測定された。

【0106】

被覆基板を極紫外放射線に曝露した(Lawrence Berkeley National Laboratory Micro Exposure Tool)。イメージング線量43mJ/cm²で13.5nm波長の放射線、ダイポール照明、およびアパーチャー0.3を用いて、ウェハ上に34nmピッチの17nmラインのパターンを投射した。次に、ホットプレート上で175℃において2分間、パターン化レジストおよび基板に曝露後ベーキング(PEB)を行った。次に曝露したフィルムを2-ヘプタノン中に15秒間浸漬し、同じ現像剤でさらに15秒間すすぎ、最後にDI H₂Oで30秒間すすいで、ネガ型画像、すなわち、コーティングの非曝露部分が除去された画像を形成した。最後に、150℃で5分間のホットプレートベーキングを現像後に実施した。図18は、34nmピッチでパターン化されて得られた15.4nmのレジストラインのSEM画像を示し、計算されたライン幅ラフネス(LWR)は4.6nmである。

【0107】

i-PrSnO_(3/2-x/2)(OH)_x(実施例2からの化合物3)の溶液を同様の方法で使用して、EUV曝露により高解像度のパターンニングを実現した。実施例3からの3の溶液を約0.06MのSnになるように4-メチル-2-ペンタノール中に希釈してから、1500rpmで第2のSi基板上にスピンコーティングし、ホットプレート上、80℃で2分間ベーキングした。コーティングおよびベーキング後の膜厚は、偏光解析法により約19nmであると測定された。+20%バイアスを伴う44nmピッチの22nmコンタクトホール of the明視野パターンを、イメージング線量36mJ/cm²における四重極照明を用いてウェハ上に投射した。次に、150℃において2分間、パターン化レジストおよび基板にPEBを行った。次に曝露したフィルムを2-オクタノン中に15秒間浸漬し、2-オクタノンでさらに15秒間すすいで、コーティングの非曝露部分が除去されたネガ型画像を形成し、コンタクトホールのパターンが残された。最後に、150℃で5分間のホットプレートベーキングを現像後に実施した。図19は、44nmピッチでパターン化されて得られた22nmホールのSEM画像を示す。

【0108】

実施例5 — 混合アルキル配位子を有するフォトレジスト溶液の調製

この実施例には混合アルキル配位子を含む前駆体溶液の配合が記載されており、パターンニングのためのこれらの配合物の有効性は、以下の実施例に記載される。

【0109】

t-ブチルスズ酸化水酸化物加水分解物(1)は、実施例1において上記した方法に従ってt-ブチルトリス(ジエチルアミド)スズから調製した。気密性シリンジを用いて、4.4g(11mmol)のt-ブチルトリス(ジエチルアミド)スズを150mLのDI H₂O(18MΩ)に添加し、直ぐに沈殿物が形成し、これを5分間放置させた。得

られたスラリーを30分間攪拌してから、No. 1のろ紙(Whatman)により吸引ろ過し、1回60mLのDI-H₂Oにより3回すすいだ。ろ過およびすすぎの後に保持された固体を真空(約5トル)下、室温で17時間乾燥させて、1.85gの粉末固体の加水分解物*t*-ブチルスズ酸化水酸化物(1)を得た。

【0110】

i-プロピルスズ酸化水酸化物加水分解物(3)は、実施例2において上記した方法によって同様に調製した。9.65g(36mmol)量の*i*-プロピルスズ三塩化物(*i*-PrSnCl₃, Gelest)を220mLの0.5MのNaOH(水)に激しく攪拌しながら迅速に添加し、すぐに沈殿物が生じた。得られた混合物を室温で1.25時間攪拌してから、2枚のNo. 5のろ紙(Whatman)により吸引ろ過した。保持された固体を1回約30mLのDI-H₂Oにより3回洗浄した後、真空(約5トル)下、室温で16時間乾燥させた。

【0111】

t-ブチルスズ酸化水酸化物加水分解物(1)および*i*-プロピルスズ酸化水酸化物加水分解物(3)の別個の溶液を、それぞれの粉末から調製した。1.04g量の乾燥粉末*t*-ブチルスズ酸化水酸化物加水分解物を100mLのメタノール(ACS, 99.8%)に添加し、24時間攪拌し、そこで混合物を0.45μmのPTFEフィルタによりシリンジろ過して、不溶性粒子を除去した。溶媒を蒸発させ、続いて空気中700℃において残留固体を熱分解した後の残留質量のサンプルは、化学量論的にSnO₂に転換されたと仮定して、0.035Mの初期Sn濃度と一致した。*i*-プロピルスズ酸化水酸化物加水分解物(3)の溶液は、3.129gの乾燥粉末を80mLの4-メチル-2-ペンタノール(Alfa-Aesar, 99%)に攪拌しながら添加することによって調製した。6時間攪拌した後、混合物を活性化4Åモレキュラーシーブ上で60時間乾燥させた後、0.2μmのPTFE膜フィルタにより真空ろ過して、不溶性材料を除去した。溶液のSn濃度は、酸化物への熱分解により0.16Mであることが分かった。

【0112】

フォトレジスト配合物A~F(表2)は、*t*-ブチルスズ酸化水酸化物加水分解物(1)のメタノール溶液を*i*-プロピルスズ酸化水酸化物加水分解物(3)の4-メチル-2-ペンタノール溶液と混合し、得られた混合物を表2に明記される体積に従って純粋な溶媒で希釈することによって調製した。得られた溶液は、*i*-PrSnO_(3/2-x/2)(OH)_xおよび*t*-BuSnO_(3/2-x/2)(OH)_x加水分解物のブレンドとして特徴付けされ、ここで、*t*-BuSnO_(3/2-x/2)(OH)_xの割合は、全Sn濃度に対して表される。

【0113】

【表2】

表2

配合物	添加体積(mL)				全 Sn に対する t-Bu-Sn (%)
	メタノール	4-メチル 2- ペンタノール	溶液 3	溶液 1	
A	0	0	0	5	100
B	0	0.75	0.5	3.75	62
C	0	0.45	0.8	3.75	50
D	1.033	0.517	1.15	2.3	30
E	0	1.5	1.5	2	22
F	0	2.75	2.25	0	0

【0114】

実施例6 — 混合アルキル配位子前駆体を用いたレジストコーティング、膜処理、ネガ型画像形成

混合配位子有機スズ酸化水酸化物フォトレジストを用いて、極紫外放射線への曝露によりネガ型パターンを生成した。この実施例は、混合アルキル配位子を有する実施例5からの前駆体溶液を用いるパターンニングを研究する。

【0115】

天然の酸化物表面を有するシリコンウェハ(100mm直径)を、薄膜付着のための基板として使用した。レジスト付着の前にヘキサメチルジシラザン(HMDS)蒸気プライムによりSi基板を処理した。実施例5からのレジスト配合物A~Fを2000~2500rpmで基板の上にスピニングし、ホットプレート上、100℃で2分間ベーキングした。コーティングおよびベーキング後の膜厚は、偏光解析法により約30nmであると測定された。被覆基板を極紫外放射線に曝露した(Lawrence Berkeley National Laboratory Micro Exposure Tool)。13.5nm波長の放射線、ダイポール照明、およびアパーチャー0.3を用いて、ウェハ上に34nmピッチで17nmのラインおよびスペースのパターンを投射した。次に、ホットプレート上で170℃において2分間、パターン化レジストおよび基板に曝露後ベーキング(PEB)を行った。次に曝露したフィルムを2-ヘプタノン中に15秒間浸漬し、同じ現像剤でさらに15秒間すすいで、ネガ型画像、すなわち、コーティングの非曝露部分が除去された画像を形成した。最後に、150℃で5分間のホットプレートベーキングを現像後に実施した。

【0116】

図20は、34nmピッチでパターン化されて得られたレジストラインのSEM画像を示す。SUMMIT分析ソフトウェア(EUV Technology Corporation)を使用して、レジスト配合物A~Fを用いてパターン化された17hpラインのSEM画像から、レジストの限界寸法(CD)およびライン幅ラフネス(LWR)を抽出した。各配合物についてのLWRおよびサイズ線量($E_{s, 1\sigma}$)のプロットは、図21に示される。 $t\text{-BuSnO}_{(3/2-x/2)}(\text{OH})_x$ の割合が増大されるにつれて、配合物にわたって線量が低下する明白な傾向(円形ドット)が観察される。さらに、ブレンドされた配合物についての図21のLWR(三角形ドット)は、それぞれ、純粋な $t\text{-BuSnO}_{(3/2-x/2)}(\text{OH})_x$ および $i\text{-PrSnO}_{(3/2-x/2)}(\text{OH})_x$ 配合物AおよびFよりも実質的に低い。

【0117】

実施例7 イソプロピルトリス(ジメチルアミド)スズ前駆体によるイソプロピルスズ酸化水酸化物加水分解物の調製

水反応性前駆体のイソプロピルトリス(ジメチルアミド)スズ($i\text{-PrSn}(\text{NMe}_2)_3$)を不活性雰囲気下で合成し、続いて、 $i\text{-PrSnO}_{(3/2-x/2)}(\text{OH})_x$ 加水分解物を形成するために1)大気中の水分および2)液体 H_2O を用いる2つの方法で加水分解した。

【0118】

アルゴン下、1Lのシュレンク型丸底フラスコに LiNMe_2 (81.75g、1.6mol、Sigma-Aldrich)および無水ヘキサン(700mL、Sigma-Aldrich)を入れて、スラリーを形成した。大型攪拌子を加え、容器を密閉した。アルゴンの正圧下の添加漏斗に、シリンジを介して $i\text{-PrSnCl}_3$ (134.3g、0.5mol、Gelest)を入れ、反応フラスコに取り付けた。フラスコを-78℃に冷却し、 $i\text{-PrSnCl}_3$ を2時間にわたって滴下した。反応を攪拌しながら一晩で室温まで戻し、固体沈殿物を沈降させた。沈降したら、インラインのカニューレフィルタにより反応溶液をアルゴンの正圧下でろ過した。溶媒を真空下で除去し、残渣を減圧下で蒸留(50~52℃、1.4mmHg)して、淡黄色の液体を得た(110g、収率75%)。Bruker DPX-400(400MHz、BBOプローブ)スペクトロメータにおいて収集した C_6D_6 溶媒中の留出物の ^1H および ^{119}Sn NMRスペクトルは、図22および図23にそれぞれ示される。図22に示されるように、観察された ^1H 共鳴(s, 2.82ppm, $-\text{N}(\text{CH}_3)_2$; d, 1.26ppm, $-\text{CH}_3$; m, 1.

60 ppm, -CH) は、 $i\text{-PrSn}(\text{NMe}_2)_3$ の予測スペクトルと一致した。図23に示されるように、-65.4 ppmにおける主要な ^{119}Sn 共鳴は単一のスズ環境を有する主要生成物と一致し、化学シフトは、報告されるモノアルキルスズアミド化合物に相当する。

[0119]

i -プロピルスズ酸化水酸化物加水分解物は、2つの異なる方法を用いる H_2O 加水分解により、 i -プロピルトリス(ジメチルアミド)スズ($i\text{-PrSn}(\text{NMe}_2)_3$)から調製した。

[0120]

方法1:

気密性シリンジを用いて、23.4 g (79.6 mmol) の i -プロピルトリス(ジメチルアミド)スズ($i\text{-PrSn}(\text{NMe}_2)_3$)を150 mL の n -ヘキサン(HPLCグレード、>99.5%ヘキサン、>95% n -ヘキサン)に添加して不透明な懸濁液を形成し、これを空気中で5分間攪拌してから、直径150 mmの6つのペトリ皿に等体積で注いだ。空気中で1.5時間、溶媒を蒸発させながら懸濁液を大気中の水分と反応させると粗固体が残り、これを回収し、結合させ、真空下で15時間乾燥させて、15.8 gの固体加水分解物を得た(化合物3、実施例2)。同じ手順により調製された加水分解物粉末の元素分析(UC Berkeley Microanalytical Facility)は、18.91% C、4.24% H、および0.51% N(質量)の組成物を戻し、ジメチルアミド配位子の実質的な加水分解および得られたアルキルアミンの蒸発と一致した。結果は $\text{C}_3\text{H}_8\text{O}_2\text{Sn}$ の計算値: 18.50% C、4.14% H、0.00% N、および60.94% Sn(質量)と一致する。乾燥空気中の同じサンプルの熱重量分析(図24)は、 SnO_2 への完全分解を仮定して、500°Cにおける残留重量(75.9%)に基づいて、約60%(質量)のSn組成物を示す。同じ分解の質量スペクトル分析(図25)は、 $-\text{C}_3\text{H}_8$ の存在を示す。まとめると、これらの結果は、 $i\text{-PrSnSnO}_{(3/2-x/2)}(\text{OH})_x$ (式中、 $x \approx 1$)の経験的な組成、および少量の残留ジメチルアミドの存在の可能性と一致する。

[0121]

方法2:

気密性シリンジを用いて、1.0 g (3.4 mmol) の i -プロピルトリス(ジメチルアミド)スズ($i\text{-PrSn}(\text{NMe}_2)_3$)を、激しく攪拌しながら直接15 mL のDI H_2O (18.2 M Ω)に迅速に添加してスラリーを形成し、これをさらに60分間攪拌した。次に、このスラリーを0.7 μm のフィルタにより真空ろ過し、保持された固体を10 mL のDI H_2O で洗浄した。次に、固体を回収し、16時間真空乾燥させて、0.7 gの固体加水分解物を得た。同じ手順で調製された加水分解物粉末において乾燥空気中で実施された熱重量分析(図26)は、同様に、3(実施例2)の $i\text{-PrSnSnO}_{(3/2-x/2)}(\text{OH})_x$ (式中、 $x \approx 1$)の経験的な組成と一致する。3の SnO_2 への完全分解に基づいて予測されるように、段階的な脱水(50~175°C、約95.7%残留重量)および脱アルキル化/燃焼(200~500°C、約77%残留重量)に起因する重量損失が観察される。

[0122]

実施例8 — 有機スズ酸化水酸化物フォトレジスト溶液の微量金属分析

レジスト前駆体溶液は、前の実施例の方法1に従って調製した15.8 gの乾燥粉末を810 mLの4-メチル-2-ペンタノール(High Purity Products)に添加し、24時間攪拌することによって調製した。攪拌の後、混合物を0.22 μm のPTFEフィルタにより吸引ろ過して、不溶性材料を除去した。溶媒を蒸発させ、続いて空気中700°Cにおいて固体をか焼した後の残留質量のサンプルは、化学量論的に SnO_2 に転換されたと仮定して、0.072 Mの初期Sn濃度と一致した。

[0123]

上記のレジスト前駆体溶液中の微量金属濃度を、水酸化ナトリウム水および i -プロピ

ルスズ三塩化物を用いて調製された加水分解物に対して評価した。上記で調製した0.072 M溶液を、4-メチル-2-ペンタノールを用いてさらに0.042 M (Sn)まで希釈した。実施例2に記載されるようにNaOH水によるi-PrSnCl₃の加水分解によって、第2のi-プロピルスズ酸化水酸化物前駆体溶液を調製し、同じ高純度の4-メチル-2-ペンタノールを用いて0.42 MのSnになるように希釈した。10十億分率 (ng/g) の検出下限 (LDL) を有する誘導結合プラズマ質量分析 (ICP-MS, Balazs Nanoanalysis, Fremont, CA) を用いて両方の溶液のアリコート进行分析し、22の金属の濃度を決定した。これらの分析の結果は表3・4に示される。いずれの場合も、分析した金属全ての濃度は、ナトリウム (Na) を除いて10 ppb未満であった。NaOH (水) を用いて調製された加水分解物を含有するレジスト溶液 (A) は、18 MΩのDI H₂Oによる3回の洗浄の後でも、34,000 ppbの残留ナトリウムを含有することが分かった。対照的に、i-プロピル(トリス)ジメチルアミドスズの加水分解物から調製されたレジスト溶液 (B) は、無アルカリ加水分解により予測されるように、10 ppb未満のNaを含有することが分かった。

10

【0124】

10 ppbのLDLを有するICP-MSで測定したときのi-PrSnSnO_(3/2-x/2)(OH)_x フォトレジスト前駆体溶液中の微量金属濃度は表3・4に示される。

【0125】

【 表 3 】

表 3

金属	濃度, ppb (ng/g)		
	レジスト		レジスト
	前駆体 A		前駆体 B
	i-PrSnCl ₃		/ i-PrSn(NMe ₂) ₃
	NaOH		/ 空気
アルミニウム	(Al)	< 10	< 10
ヒ素	(As)	< 10	< 10
バリウム	(Ba)	< 10	< 10
カドミウム	(Cd)	< 10	< 10
カルシウム	(Ca)	< 10	< 10
クロム	(Cr)	< 10	< 10
コバルト	(Co)	< 10	< 10
銅	(Cu)	< 10	< 10
金	(Au)	< 10	< 10
鉄	(Fe)	< 10	< 10
リチウム	(Li)	< 10	< 10
マグネシウム	(Mg)	< 10	< 10
マンガン	(Mn)	< 10	< 10

10

20

30

40

【 0 1 2 6 】

【表4】

ニッケル	(Ni)	< 10	< 10	10
パラジウム	(Pd)	< 10	< 10	
カリウム	(K)	< 10	< 10	
銀	(Ag)	< 10	< 10	
ナトリウム	(Na)	34,000	< 10	
チタン	(Ti)	< 10	< 10	
タンガステン	(W)	< 10	< 10	
バナジウム	(V)	< 10	< 10	
亜鉛	(Zn)	< 10	< 10	20

【0127】

実施例9 ー 微量金属汚染の少ないフォトレジストの膜コーティング、処理、およびネガ型画像形成

天然の酸化物表面を有するシリコンウェハ(100mm直径)を、薄膜付着のための基板として使用した。レジスト付着の前にヘキサメチルジシラザン(HMDS)蒸気プライムによりSi基板を処理した。実施例8からの0.072Mのレジスト溶液を、0.45nmシリンジフィルタを通して基板上に分配し、1500rpmでスピンコーティングし、ホットプレート上、100℃で2分間ベーキングした。コーティングおよびベーキング後の膜厚は、偏光解析法により約25nmであると測定された。被覆基板を極紫外放射線に曝露した(Lawrence Berkeley National Laboratory Micro Exposure Tool)。13.5nm波長の放射線、ダイポール照明、およびアパーチャー0.3を用いて、ウェハ上に34nmピッチで17nmのラインおよびスペースのパターンを投射した。次に、ホットプレート上で180℃において2分間、パターン化レジストおよび基板に曝露後ベーキング(PEB)を行った。次に曝露したフィルムを2-ヘプタノン中に15秒間浸漬し、同じ現像剤でさらに15秒間すすいで、ネガ型画像、すなわち、コーティングの非曝露部分が除去された画像を形成した。最後に、150℃で5分間のホットプレートベーキングを現像後に実施した。図27は、60mJcm⁻²のイメージング線量、2.9nmのLWRを有する34nmピッチでパターン化された14.5nmのレジストラインにより画定された、基板上の得られたレジストライン/スペースパターンのSEM画像を示す。

【0128】

実施例10 ー 水性有機塩基を用いたイソプロピルスズ三塩化物の加水分解によるi-プロピルスズ加水分解物の調製

i-PrSnCl₃の加水分解物は、6.5g(24mmol)の化合物4 i-PrSnCl₃を150mLの0.5Mの水酸化テトラメチルアンモニウム(TMAH)水に激しく攪拌しながら迅速に添加することによって調製し、すぐに沈殿物が生じた。TMAHは、導入される金属汚染が少ないように、配合物中に金属カチオンを含まない。得られた混合物を室温で1時間攪拌してから、No.1のろ紙(Whatman)により吸引ろ

過した。保持された固体を1回約25 mLのDI H₂Oにより3回洗浄した後、真空(約5トル)下、室温で12時間乾燥させた。乾燥粉末加水分解物の元素分析(18.67% C、4.22% H、0.03% N、0.90% Cl; Microanalysis, Inc.; Wilmington, DE)は、加水分解およびすすぎの際の塩化物イオンの実質的な除去と一致し、さらに、一般的な化学量論のi-PrSnSnO_(3/2-x/2)(OH)_x(式中、x≒1)と一致した(C₃H₈O₂Snの計算値: 18.50% C、4.14% H、0.00% N、0.00% Cl)。同じ手順で調製された加水分解粉末のTGA-MS分析(乾燥空気)(図28および29)も同じように一致する。SnO₂への完全分解に基づいて予測されるように、段階的な脱水(50~175℃、残留重量約97.0%)および脱アルキル化/燃焼(200~500℃、残留重量約77.5%)に起因する重量損失が観察される。この実験は低金属汚染について特に試験するために実行されたものではないが、本明細書において伴われる実施例で実証されるように、実験は、金属汚染が少ない生成物t-アミルスズ酸化水酸化物が合成される能力を示すように設計される。

【0129】

実施例11 - アルキルスズトリス(アルキニド)の水性加水分解によるアルキルスズ酸化水酸化物加水分解物の調製

t-アミルスズ酸化水酸化物加水分解物、t-AmylSnO_(3/2-x/2)(O<x<3)(化合物6)は、(1,1-ジメチルプロピル)スズトリス(フェニルアセチリド)、t-AmylSn(C≡CPh)₃(化合物7)の水性加水分解により調製した。

【0130】

スズテトラ(フェニルアセチリド)、Sn(C≡CPh)₄、化合物8は、参照によって本明細書中に援用されるLevashov, A. S.; Andreev, A. A.; Konshin, V. V. Tetrahedron Letters, 56, 2015, 56, 1870-1872において報告されるように合成した。次に、Jaumierらの方法(Jaumier P.; Jousseau, B.; Lahcini, M. Angewandte Chemie, International Edition, 38, 1999, 402-404、参照によって本明細書中に援用される)を修正することによって、化合物8の金属交換反応により化合物7を調製した: 150 mLのフラスコ中で、Sn(C≡CPh)₄(9.53 g/19.33 mmol)を無水トルエン(80 mL)に溶解させた。次に、溶液全体に窒素を10分間バブリングし、溶液を氷浴中で冷却した。次に、エーテル中の1,1-ジメチルプロピルマグネシウムブロミド溶液(30 mL/1 N)を液滴で添加した。溶液を室温まで温め、2時間攪拌した。次に、反応混合物をシリカによりろ過し、真空下で凝縮させた。得られた固体を無水ヘキサン中で超音波処理し、ろ過し、上澄みを真空下で凝縮させた。次に、得られたワックス状の固体を-10℃で約2時間にわたって20%のメタノール水(v/v)から再結晶させた。この方法で合成された化合物t-AmylSn(C≡CPh)₃の代表的な¹¹⁹Snおよび¹H NMRスペクトルは、図30および図31に見出される。図30は¹H NMRスペクトルを示す。図31は¹¹⁹Sn NMRスペクトルを示す。

【0131】

tert-アミルスズ酸化水酸化物、t-AmylSnO_(3/2-x/2)(OH)_x(式中、0<x<3)(化合物6)は、非分枝状アルキルスズアルキニドについて記載されるJaumierらの方法を適応させることによって、H₂Oを用いるt-AmylSn(C≡CPh)₃の加水分解により調製した。参照によって本明細書中に援用されるChemical Communications, 1998, 369-370。50 mLのフラスコ中で、t-AmylSn(C≡CPh)₃をテトラヒドロフラン(20 mL/2%の水)および0.5 mLの水に溶解させた。溶液を室温で2日間攪拌し、沈殿物を回収し、クロロホルムに溶解させた。得られた溶液を0.2 μmのPTFEフィルタによりろ過し、溶媒を真空下で除去した。代表的な¹¹⁹Sn(図32)および¹H NMRスペ

クトル(図33)を CDCl_3 中で収集した。 -340.65 および -489.29 ppm で観察された ^{119}Sn 共鳴はそれぞれ、 $[(\text{RSn})_{12}\text{O}_{14}(\text{OH})_6](\text{OH})_2$ の形態のクロソ型十二量体クラスタにおける5配位および6配位のスズ原子に特徴的である。 ^1H 共鳴は同様に2つの化学環境における1,1-ジメチルプロピル配位子の存在を示し、重要なことには、図32および図33に対してごく弱いフェニル共鳴($7.29 \sim 7.60 \text{ ppm}$)しか観察されず、これは、ほぼ完全な加水分解およびフェニルアセチリド配位子の除去を示す。この実験は低金属汚染について特に試験するために実行されたものではないが、本明細書において伴われる実施例で実証されるように、実験は、金属汚染が少ない生成物t-アミルスズ酸化水酸化物が合成されることを可能にする合成手法を提供する。

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【0132】

実施例12 — 電子ビーム曝露を用いたレジストコーティング、膜処理、ネガ型画像形成

t-BuSnO $_{(3/2-x/2)}$ (OH) $_x$ およびi-PrSnSnO $_{(3/2-x/2)}$ (OH) $_x$ レジスト前駆体溶液は、実施例3に記載されるように調製した。溶液をスピンコーティングし、表4に要約されるプロセスパラメータで電子ビームリソグラフィを用いてパターン化した。天然の酸化物表面を有するシリコンウェハ($25 \times 25 \text{ mm}^2$)を、薄膜付着のための基板として使用した。レジストコーティングの前に、15ミリトルにおいて25 Wの O_2 プラズマ中で1分間、基板を洗浄した。0.45 nmシリンジフィルタを通して前駆体溶液を基板上に分配し、指示されるrpmで30秒間スピンコーティングし、ホットプレート上、指示される温度で2分間ベーキングした(適用後ベーキング、PAB)。コーティングおよびベーキング後の膜厚は偏光解析法により測定した。指定される線量でライン/スペースパターンを形成するようにラスターされた30 keVの電子ビームに被覆基板を曝露した。次に、表4に示される温度においてホットプレート上で2分間、パターン化レジストおよび基板に曝露後ベーキング(PEB)を行った。次に曝露したフィルムを現像剤中に15秒間浸漬し、同じ現像剤でさらに15秒間すすいで、ネガ型画像、すなわち、コーティングの非曝露部分が除去された画像を形成した。最後に、150℃で5分間のホットプレートベーキングを現像後に実施した。図34は、32 nm(上側)および28 nm(下側)のピッチで基板上に得られたレジストライン/スペースパターンのSEM画像を示す。

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【0133】

【表5】

表4

レジスト前駆体配合物	$t\text{-BuSnO}_{(3/2-x/2)}(\text{OH})_x$	$i\text{-PrSnSnO}_{(3/2-x/2)}(\text{OH})_x$
溶媒	メタノール	4-メチル-2-ペンタノール
コーティング速度(rpm)	1500	2500
PAB 温度(℃)	100	80
レジスト膜厚(nm)	40	31
PEB 温度(℃)	170	120
現像剤	2-ヘプタノン	2-オクタノン
イメージング線量($\mu\text{C cm}^{-2}$)	1022	696
32 / 28 nm ピッチレジストラインの 限界寸法 (nm)	15.2 / 13.5	16.2 / 15.1

【0134】

実施例13 — EUV 曝露によるポジ型画像形成

分枝状アルキルスズ酸化水酸化物レジストを使用して、EUV 放射線を用いてポジ型画像を生成した。実施例7に記載される方法1を用いて $i\text{-PrSnO}_{(3/2-x/2)}(\text{OH})_x$ 加水分解物(化合物3)を調製し、4-メチル-2-ペンタノール中に溶解させて、約0.07 MのSn前駆体溶液を生じさせた。天然の酸化物表面を有するシリコンウェハ(100 mm直径)を、薄膜付着のための基板として使用した。コーティングの前にウェハ上でヘキサメチルジシラザン(HMDS)蒸気ブライムを実施した。前駆体溶液をピペットにより基板上に分配し、1500 rpmで30秒間スピンコーティングし、ホットプレート上、100℃で2分間ベーキングした。コーティングおよびベーキング後の膜厚は、偏光解析法により約23 nmであると測定された。EUV 曝露は、Berkeley MEITにおいて実行した。13.5 nm波長の放射線およびアパーチャー0.3における環状照明およびイメージング線量 25 mJ cm^{-2} を用いて、様々なピッチの一連のラインおよびスペースパターンをウェハ上に投射した。曝露後すぐに、空気中において、レジストおよび基板をホットプレート上、150℃で2分間ベーキングした。

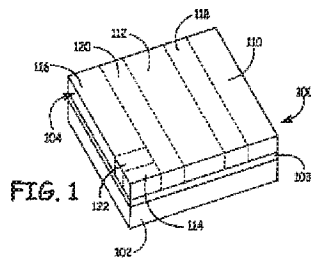
【0135】

曝露したフィルムを0.52 MのNaOH水溶液中に15秒間浸漬し、 H_2O でさらに15秒間すすぎ、ポジ型画像、すなわちコーティングの曝露部分が除去された画像を現像した。最後に、150℃で5分間のホットプレートベーキングを現像後に実施した。100 nm(a)および60 nm(b)ピッチでパターン化されたポジ型レジストラインのSEM画像は図35において見出される。

【 0 1 3 6 】

上記の実施形態は例示的なものであり、限定されることは意図されない。付加的な実施形態は特許請求の範囲の範囲内である。さらに、本発明は特定の実施形態に関して記載されたが、当業者は、本発明の趣旨および範囲から逸脱することなく形態および詳細の変化がなされ得ることを認識するであろう。上記文献の参照による任意の援用は、本明細書中の明確な開示に反する主題が決して援用されないように限定される。

【 図 1 】



【 図 2 】

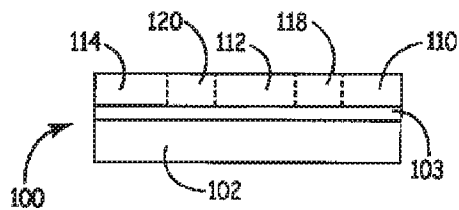


FIG. 2

【 図 3 】

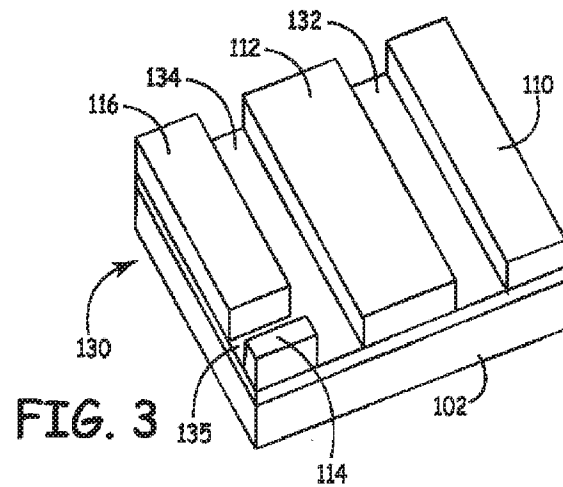


FIG. 3

【 図 4 】

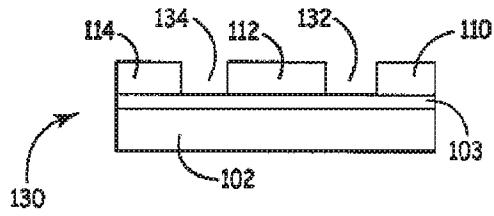


FIG. 4

【 図 5 】

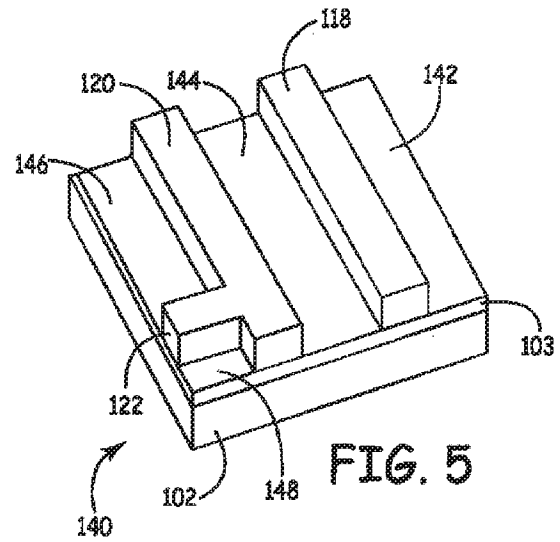


FIG. 5

【 図 6 】

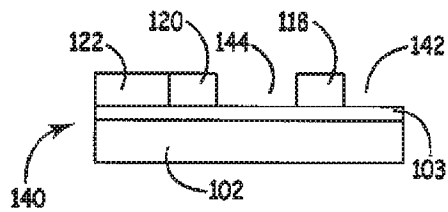


FIG. 6

【 図 8 】

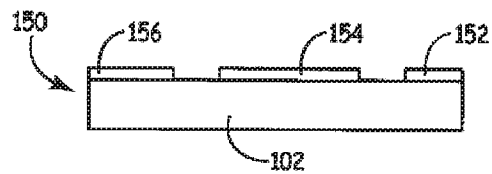


FIG. 8

【 図 7 】

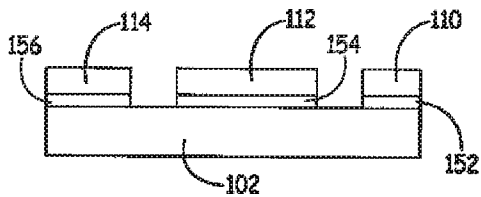


FIG. 7

【 图 9 】

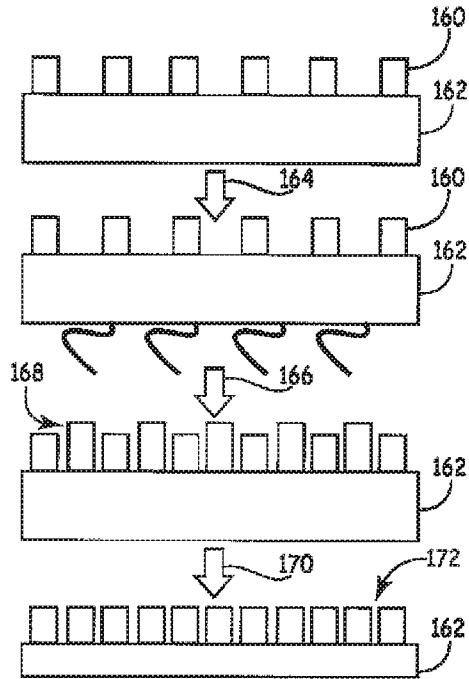


FIG. 9

【 图 10 】

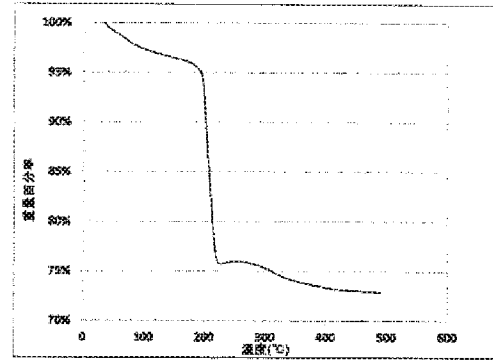


图10

【 图 11 】

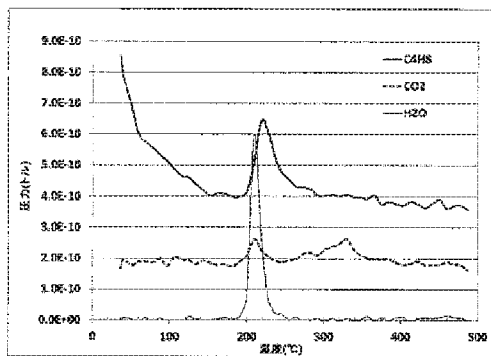


图11

【 图 12 】

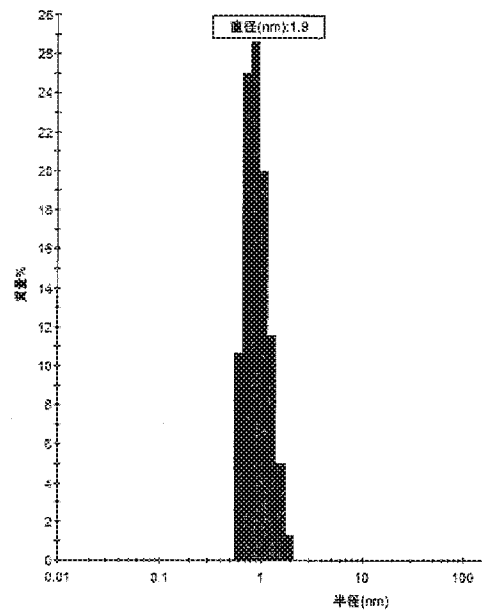


图12

【 図 1 3 】

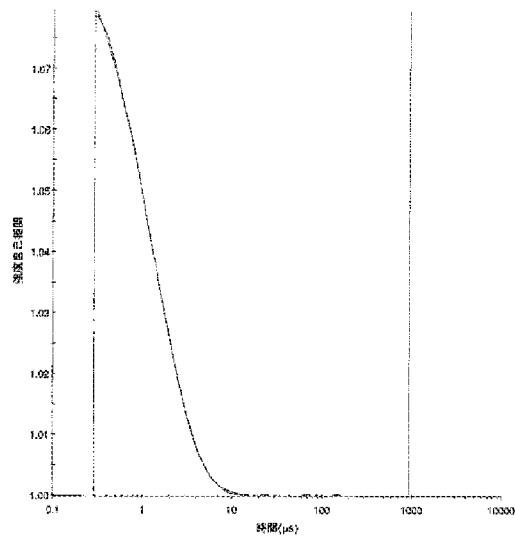


図13

【 図 1 4 】

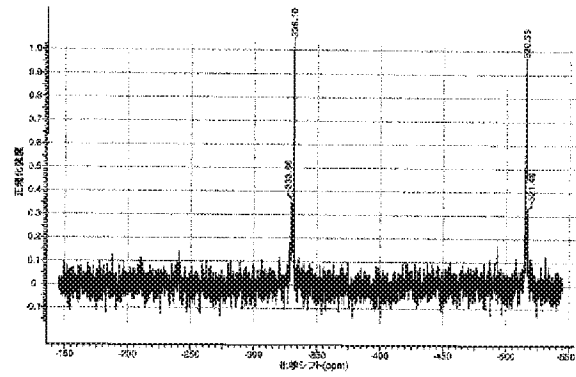


図14

【 図 1 5 】

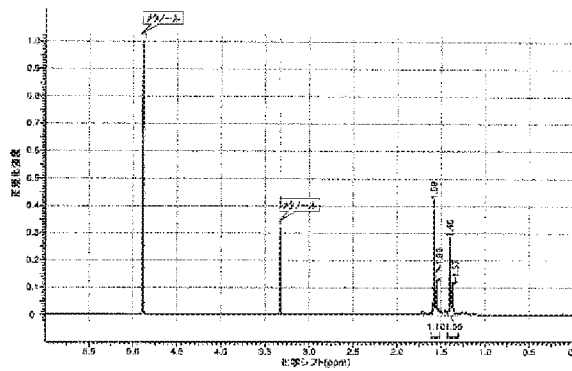


図15

【 図 1 6 】

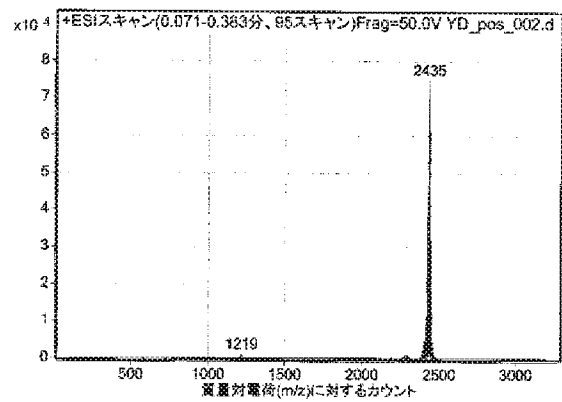


図16

【 図 1 7 】

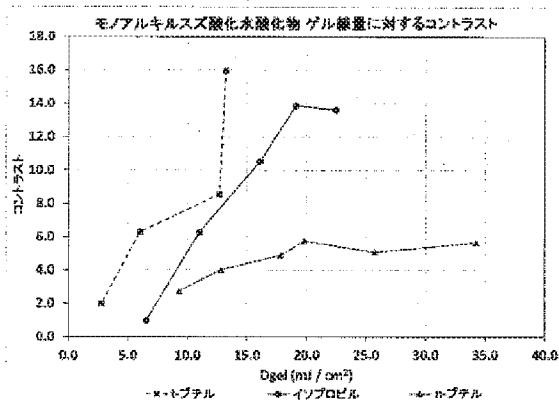


図17

【 図 1 8 】

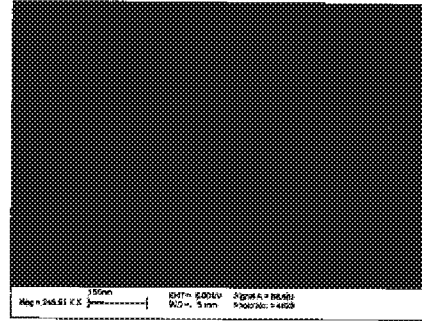


Fig. 18

【 図 1 9 】

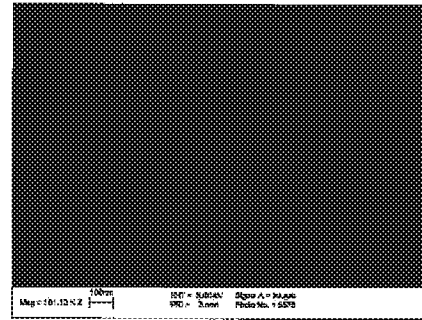
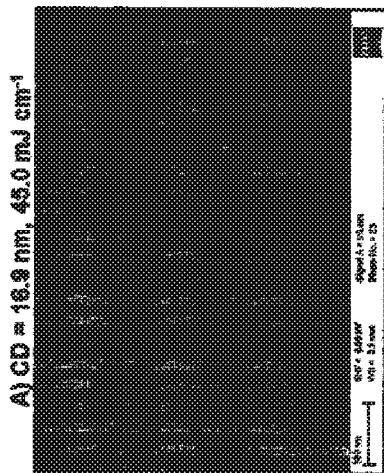
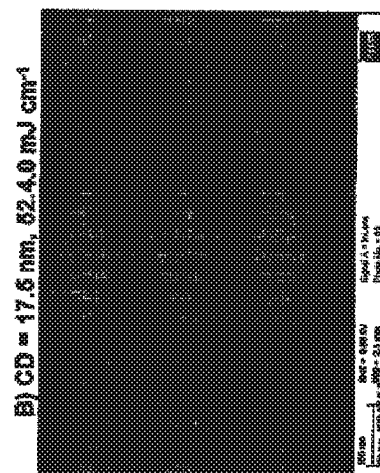


Fig. 19

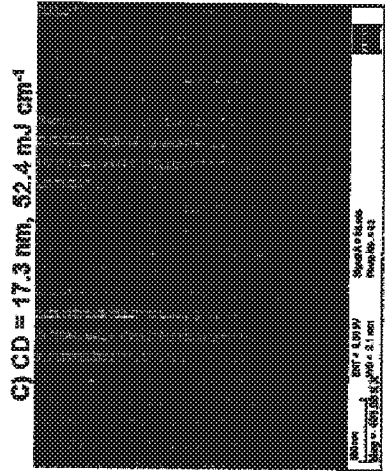
【 図 2 0 A) 】



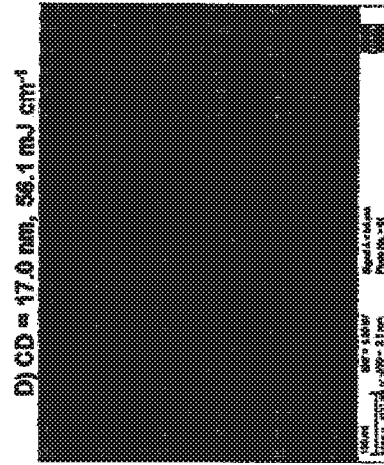
【 図 2 0 B) 】



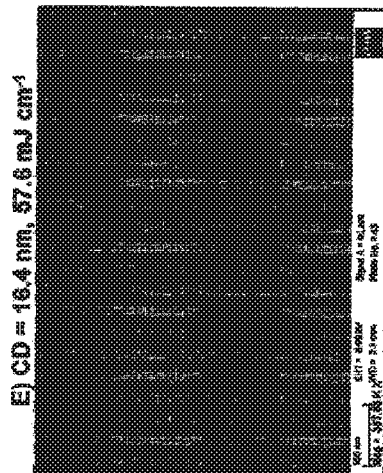
【 図 2 0 C ） 】



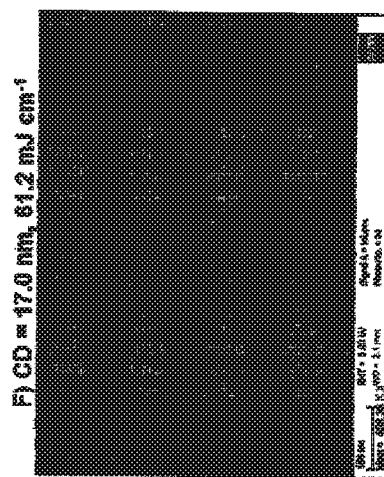
【 図 2 0 D ） 】



【 図 2 0 E ） 】



【 図 2 0 F ） 】



【 図 2 1 】

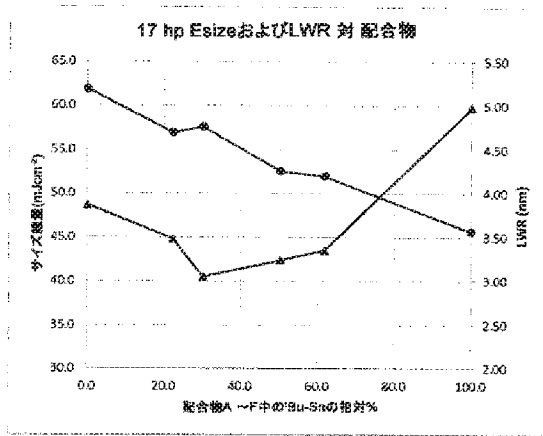


図21

【 図 2 2 】

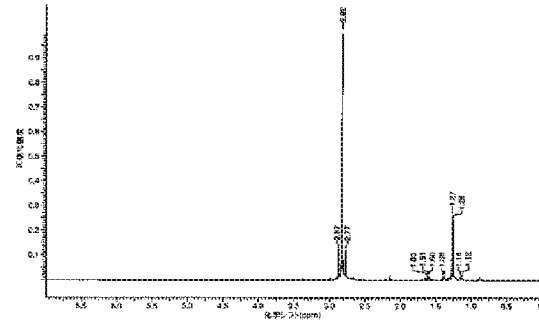


図22

【 図 2 3 】

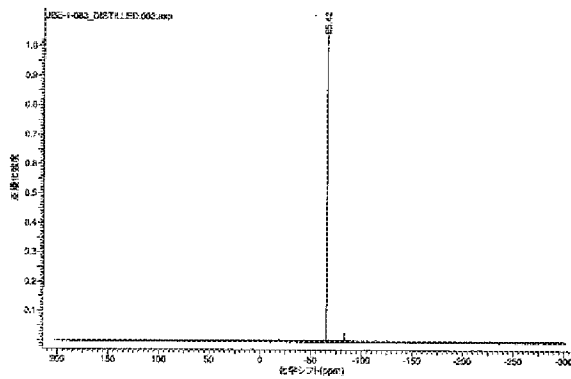


図23

【 図 2 4 】

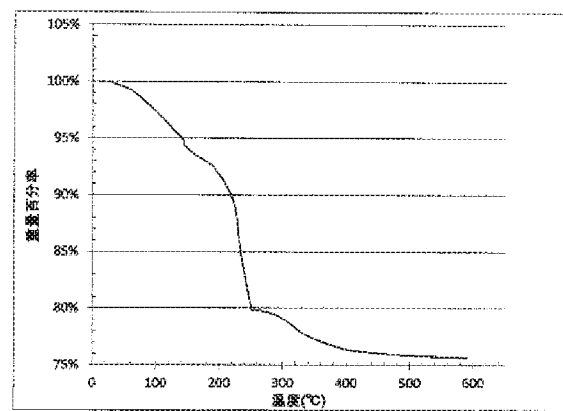


図24

【 図 2 5 】

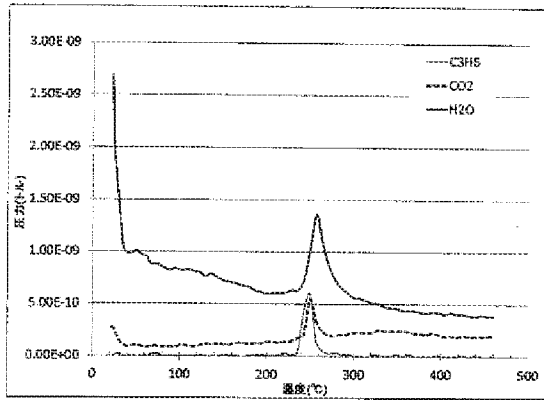


図 25

【 図 2 6 】

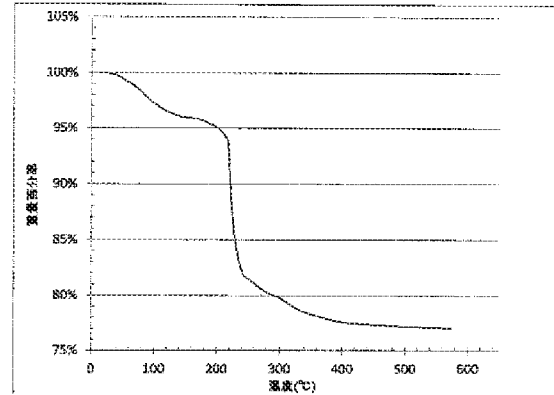


図 26

【 図 2 7 】

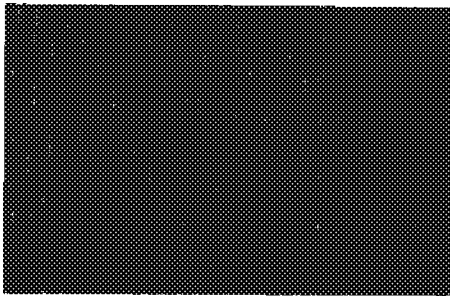


Fig. 27

【 図 2 8 】

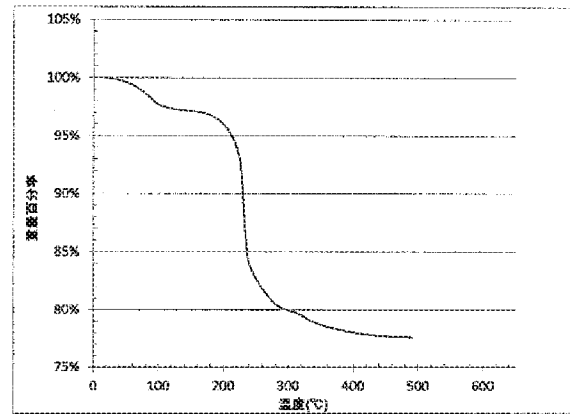


図 28

【 図 2 9 】

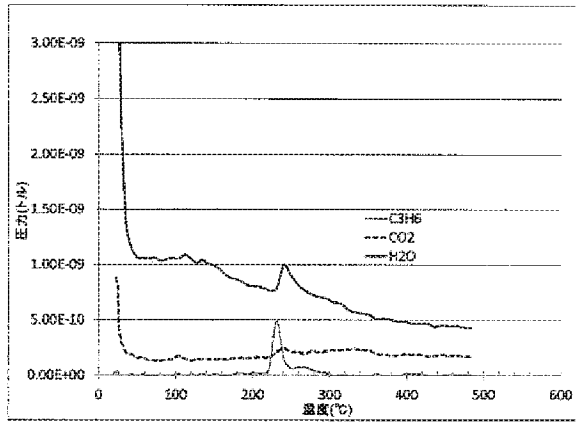
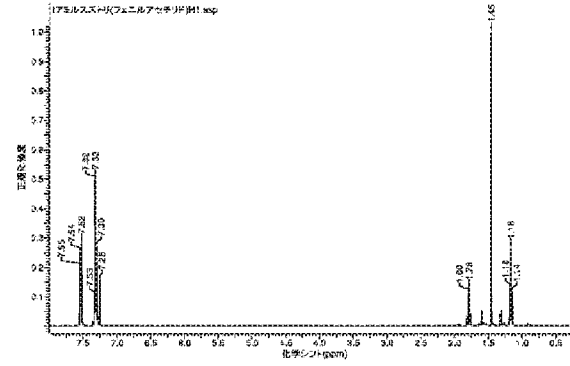


図 29

【 図 3 0 】



【圖 34】

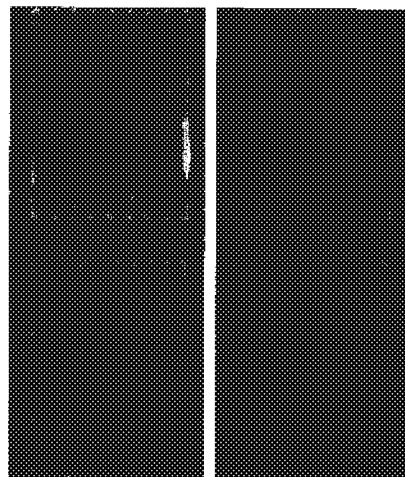


Fig. 36

【 3 5 】

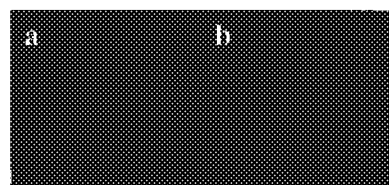


Fig. 35

【 国際調査報告 】

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 15/55866

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - C07F 7/22; G03F 7/004; H05K 3/02 (2016.01)

CPC - C07F7/2232; H01L21/314

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC(8): C07F 7/22; G03F 7/004; H05K 3/02 (2016.01)

CPC: C07F 7/2232; H01L 21/314

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC: 556/89; 430/270.1; 430/313 (key word limited; see search terms below)

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

PatBase, Google Patents, Google Scholar

Search terms used: organotin oxide, hydroxide, tert-butyl, isopropyl, coating, reaction, resist, photoresist

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2014/150411 A1 (THE SHERWIN-WILLIAMS COMPANY) 25 September 2014 (25.09.2014); para [0007], [0044], [0058]	1-2
Y	US 3,835,853 A (STAMM) 18 January 1972 (18.01.1972); col 2 ln 63-72	3, 6-8, 25-27
Y	US 2011/0186268 A1 (DEELMAN et al.) 07 July 2011 (07.07.2011); para [0001], [0012]	3, 6-8
Y	US 2011/0186268 A1 (DEELMAN et al.) 07 July 2011 (07.07.2011); para [0001], [0012]	25-27
A	WO 1998/010508 A1 (E. I. DUPONT DE NEMOURS AND COMPANY) 18 April 1998 (18.04.1998); entire document	1-2

☐ Further documents are listed in the continuation of Box C. ☐

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"Z" document member of the same patent family

Date of the actual completion of the international search

28 January 2016

Date of mailing of the international search report

05 FEB 2016

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents

P.O. Box 1450, Alexandria, Virginia 22313-1450

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Form PCT/ISA/210 (second sheet) (January 2015)

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 15/36865

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 4-5, 9-11, 15-17, 23-24 and 28
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:
--Please see attached sheet--

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1-3, 5-8 and 25-27

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

Form PCT/ISA/210 (continuation of first sheet (2)) (January 2013)

INTERNATIONAL SEARCH REPORT

International application No.

PCT/LUS 15/06885

Attachment to Box No. III:

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1.

Group I: Claims 1-3, 8-6 and 25-27, directed to a coating solution comprising an organic solvent and an organometallic compound represented by the formula $\text{RSnO}(3/2-x/2)(\text{OH})_x$ where $(0 < x < 3)$, where R is an alkyl group or cycloalkyl group with 3-31 carbon atoms, where the alkyl or cycloalkyl group is bonded to the tin at a secondary or tertiary carbon atom.

Group II: Claims 12-14 and 18-22, directed to a method for patterning a film on a substrate, comprising exposing the film to EUV radiation at the specified doses and a patterned structure comprising a surface and a coating associated with the surface wherein at least portions of the coating are represented by the formulation $(\text{R})_x\text{SnO}2-x/2(\text{OH})_x$ $(0 < (x+2) < 4)$, where R is an alkyl group or cycloalkyl group with 3-31 carbon atoms, where the alkyl or cycloalkyl group is bonded to the tin at a secondary or tertiary carbon atom.

Group III: Claims 29-33, directed to a method for synthesizing a compound represented by the formula RSnOOH or $\text{RSnO}(3/2-x/2)(\text{OH})_x$ $(0 < x < 3)$, where R is an alkyl or cycloalkyl moiety having from 1 to 31 carbon atoms.

The groups of inventions listed above do not relate to a single general inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons:

Special Technical Features:

Group I includes the technical feature of a coating solution comprising a solvent and an organometallic compound, not required by Groups II and III.

Group II includes the technical feature of a method of patterning an organometallic film on a substrate and a patterned structure containing an organometallic formulation, not required by Groups I and III.

Group III includes the technical feature of a method of synthesizing an organometallic compound, not required by Groups I and II.

Common technical features:

Groups I-III share the technical feature of an organotin compound.

Groups I and II further share the technical feature of a coating formulation containing an organotin compound.

Groups I and III further share the technical feature of a compound of the formula, $\text{RSnO}(3/2-x/2)(\text{OH})_x$ $(0 < x < 3)$, where R is an alkyl or cycloalkyl moiety having from 1 to 31 carbon atoms.

These shared technical features, however, do not provide a contribution over the prior art, as being anticipated by WO 2014/150411 A1 to Ding et al. published on 25 September 2014 (hereinafter Ding).

Regarding claim 1, Ding discloses a coating solution (para [0007]: "the curable compositions described herein are particularly suited for use in the preparation of paints and coatings for a variety of substrates") comprising an organic solvent (para [0044]: "the curable coating compositions according to the invention may optionally contain a diluent, such as conventional inert organic solvents") and an organometallic compound represented by the formula $\text{RSnO}(3/2-x/2)(\text{OH})_x$ where $(0 < x < 3)$ where R is an alkyl group bonded to the tin at a tertiary carbon atom (para [0058]: tertiary-butyl stannous acid).

As said composition was known in the art at the time of the invention, these cannot be considered special technical features, that would otherwise unify the inventions of Groups I-III.

The inventions of Groups I-III, therefore, lack unity under PCT Rule 13.

Note reg item 4: Claims 4-5, 9-11, 15-17, 23-24 and 28 are unsearchable because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a). These claims are, therefore, not included in the above analysis.

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METHOD OF MAKING ELECTRONIC MATERIALS

Inventor(s):

Applicant(s):

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Abstract not available for KR20030007904 (A)

Abstract of corresponding document: WO0195690 (A1)

The present invention involves fabrication of a hard mask. An embodiment involves the conversion of a precursor into a top-surface imaging layer during a direct patterning step. Another embodiment of the present invention is a method of forming an etched pattern in a substrate. A further embodiment of the present invention is a method of forming an implanted region in a substrate. Preferred precursors are formed from a

metal complex comprising at least one ligand selected from the group consisting of acac, carboxylato, alkoxy, azide, carbonyl, nitrato, amine, halide, nitro, and mixtures thereof and at least one metal selected from the group consisting of Li, Al, Si, Ti, V, Cr, Mn, Fe, Ni, Co, Cu, Zn, Sr, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, In, Sn, Ba, La, Pr, Sm, Eu, Hf, Ta, W, Re, Os, Ir, Pt, Au, Pb, Th, U, Sb, As, Ce, Mg, and mixtures thereof.

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(19) 대한민국특허청(KR)

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(86) 국제출원번호	PCT/US2001/18413		
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(81) 지정국	<p>국내특허 : 알바니아, 아르메니아, 오스트리아, 오스트레일리아, 아제르바이잔, 보스니아-헤르체고비나, 비베아도스, 불가리아, 브라질, 벨라루스, 캐나다, 스위스, 중국, 쿠바, 체코, 독일, 덴마크, 에스토니아, 스페인, 핀란드, 영국, 그루지아, 헝가리, 이스라엘, 아이슬란드, 일본, 케냐, 키르기즈, 북한, 대한민국, 카자흐스탄, 세인트루시아, 스리랑카, 라이베리아, 레소토, 리투아니아, 룩셈부르크, 리트비아, 몰도바, 파타가스카르, 마케도니아, 몽고, 말라위, 멕시코, 노르웨이, 뉴질랜드, 슬로베니아, 슬로바키아, 타지키스탄, 투르크메니스탄, 터키, 트리니다드토바고, 우크라이나, 우간다, 우즈베키스탄, 베트남, 폴란드, 포르투갈, 루마니아, 러시아, 수단, 스웨덴, 싱가포르, 아랍에미리트, 안티구아바부다, 코스타리카, 도미니카연방, 알제리, 모로코, 탄자니아, 남아프리카, 벨리즈, 모잠비크, 콜롬비아, 인도네시아, 그레나다, 가나, 감비아, 인도, 크로아티아, 시에라리온, 유고슬라비아, 짐바브웨, AP, ARIPO.</p> <p>특허 : 케냐, 레소토, 말라위, 수단, 스와질랜드, 우간다, 시에라리온, 가나, 감비아, 짐바브웨, 모잠비크, 탄자니아.</p> <p>EA 유라시아특허 : 아르메니아, 아제르바이잔, 벨라루스, 키르기즈, 카자흐스탄, 몰도바, 러시아, 타지키스탄, 투르크메니스탄.</p> <p>EP 유럽특허 : 오스트리아, 벨기에, 스위스, 독일, 덴마크, 스페인, 프랑스, 영국, 그리스, 아일랜드, 이탈리아, 룩셈부르크, 모나코, 네덜란드, 포르투갈, 스웨덴, 핀란드, 사이프러스, 터키.</p> <p>OA OAPI 특허 : 부르키나파소, 베냉, 중앙아프리카, 콩고, 코트디부아르, 가봉, 가봉, 가나, 말리, 모라타니, 니제르, 세네갈, 차드, 토고, 기네비소.</p>		

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(74) 대리인	허상훈

심사청구 : 없음

(54) 전자 재료 제조 방법

요약

본 발명은 하드 마스크의 제조에 관한 것이다. 한 실시예는 직접 패터닝 단계 동안 전구체를 상면 이미징

층으로 변환하는 것을 포함한다. 본 발명의 다른 실시예는 가판에 예칭된 패턴을 형성하는 방법에 관한다. 본 발명의 다른 실시예는 가판에 주입된 영역을 형성하는 방법에 관한다. 바람직한 전구체는 acac, 카르복실아토, 알콕시, 아지드, 카르보닐, 니트라토, 아민, 할라토, 니트로, 및 그 혼합물로 구성된 그룹 중에서 선택된 적어도 하나의 리간드; 및 Li, Al, Si, Ti, V, Cr, Mn, Fe, Ni, Co, Cu, Zn, Sr, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, In, Sn, Ba, La, Pr, Sm, Eu, Hf, Ta, W, Re, Os, Ir, Pt, Au, Pb, Th, U, Sb, As, Ce, Mg, 및 그 혼합물로 구성된 그룹 중에서 선택된 적어도 하나의 금속을 구비하는 금속 복합체로 형성된다.

대표도

도1

색인어

리간드, 하드 마스크, 직접 패터닝, 전구체, 이미징 층, 가판, 패턴, 주입 영역, acac, 카르복실아토, 알콕시, 아지드, 카르보닐, 니트라토, 아민, 할라토, 니트로, 금속, 금속 복합체

명세서

기술분야

본 발명은 총체적으로 하드 마스크의 형성에 관련된 공정에서 전자 재료의 재조에 관한 것이다. 일 실시예는 직접 패터닝 단계(direct patterning step) 동안 전구체(precursor)를 상면 이미징 층(top surface imaging layer)으로 변환하는 것을 포함한다.

배경기술

다른 것들 중에서, 반도체 및 패키징은, 종래의 공정을 이용하여 그 제품에 얇은 금속 및 금속 산화막을 형성한다. 이와 같은 공정의 예는 증발, 스퍼터 증착 또는 스퍼터링, 화학 증기 증착('CVD') 및 열 산화를 포함한다. 증발은, 증착이 요구되는 가판 근처에서 증착될 재료를 가열시키는 공정이다. 진공 상태에서 정상적으로 도전되는, 증착될 재료는 가판 상에 휘발되고 순차적으로 압축되어 결국 블랭킷(blanket)을 형성하거나, 패턴화되지 않은 소정 재료의 막이 가판 상에 형성되게 된다. 이 방법은, 소정의 막 재료를 높은 온도까지 가열시켜야 하는 조건, 및 높은 진공 상태의 필요성을 포함하는 몇가지 단점을 갖는다. 스크린 또는 채도우가 증발 동안 이용되지 않는 한, 패턴화되지 않은 블랭킷 막이 이 공정으로 인해 형성되게 된다.

스퍼터링은 증발과 유사한 기술로, 증발에서는 증착을 위한 재료를 증기 상(vapor phase)으로 전자사키는 공정은, 재료의 입자들이 증기 상으로 디스로지되(dislodged)되어 순차적으로 가판 상에 압축되도록 충분한 운동 에너지의 입자 원자들로 이 재료에 충격을 가함으로써 이루어진다. 스퍼터링은 증발과 동일한 단점여 있고, 또한 충분한 운동 에너지의 입자 입자를 발생시켜 증착 재료의 입자들을 디스로지시키기 위한 장비 및 소모재를 필요로 한다.

CVD는 증발과 스퍼터링과 유사하지만, 또한 가판 상에 증착되는 입자들이 가판 상에 막을 형성하기 위해 정적 공정 동안 화학 반응이 일어날 것을 필요로 하고 있다. 비록 화학 반응을 위한 조건이 CVD를 증발 및 스퍼터링과는 구별시키지만, CVD 방법은 여전히 정된 장비의 사용, 및 막 증착 동안 온도 및 압력의 극한 조건을 필요로 한다.

열 산화는 또한 온도의 극한 조건 및 산소 분위기를 이용한다. 이 기술에서, 가판 상의 산화막의 블랭킷 층은, 가판 상에 이전에 증착된 비산화 층을 산화시킴으로써 제조된다.

거존의 몇 가지 막 증착 방법은 졸-겔(sol-gel) 및 다른 스핀 방법을 포함하는 분위기 온도 및 압력 조건 하에 수행될 수 있다. 이들 방법에서, 소정의 막 조성으로 순차적으로 변환될 수 있는 전구체 입자를 포함하는 용액이 가판에 도포된다. 이 용액의 도포는 스핀 코팅 또는 스핀 캐스팅(spin-casting)을 통해 달성될 수 있는데, 이 방법에서 용액이 가판의 중간에 떨어뜨려지는 동안에 가판이 축을 중심으로 회전된다. 이와 같은 증착 후에, 코팅된 가판이 고온 처리되어, 전구체 막을 소정 재료의 막으로 변환한다. 따라서, 이들 방법들은 비정질 막의 패턴을 형성하기 위한 직접 이미징(direct imaging)을 허용하지 못하고 있다. 대신에, 이들 방법들은 소정 재료의 블랭킷의 패턴화되지 않은 막을 형성하는 결과가 된다. 이들 방법은 증기 상 방법보다 덜 엄격한 장비 조건을 가지지만, 소정 막을 소정 재료로 변환하기 위해 여전히 극한 온도를 사용할 것을 필요로 한다.

블랭킷 막을 패턴화하는 한 방법에서, 블랭킷 막은 감광막 코팅으로 코팅된다(종래에 스핀 코팅 또는 다른 용액에 기초한 코팅 방법에 의해, 또는 감광 건식 막의 도포에 의해). 이 감광층은 마스크를 통해 특정 파장의 광에 선택적으로 노출된다. 노광은, 노출된 면적 또는 노출되지 않은 면적이 현상액을 사용하여 선택적으로 제거될 수 있도록, 감광층의 노출된 면적의 용해성을 변화시킨다. 다음에 나머지 재료가 소정의 재료의 막을 패턴화시키는 에칭 매체에 대해 패턴 전사 매체 또는 마스크로서 사용된다. 이 에칭 단계 후에, 나머지(이전의 감광)재료가 제거되고, 필요에 따라 에칭 공정 동안 발생된 임의의 부산물이 제거된다.

가판 상에 패턴화된 막을 형성하는 다른 방법에서, 감광 재료는 성숙한 바와 같이 패턴화될 수 있다. 패턴화 후, 소정 재료의 동적 불렛이 패턴화된(이전의 감광) 재료의 상부에 증착될 수 있고, 다음에 패턴화된 재료를 갖는 가판 및 소정 재료의 불렛 막이 이전의 감광 재료를 손상시키는 처리에 노출될 수 있다. 이 처리는 이전의 나머지 감광 재료 및 상부 상의 소정 재료의 불렛 막의 일부를 제거한다. 이와 같이, 소정 재료의 패턴화된 막의 결과가 되고, 이 '리프트오프(liftoff)' 공정에서 어떠한 에칭 단계도 필요하지 않다. 그러나, 중간 패턴 전사 매체(감광 재료)의 사용이 여전히 요구되고, 이는 이 방법의 단점이다. 또한, '리프트오프' 방법은 소정 재료의 패턴에 의해 결정될 수 있는 해상도(최소 크기)와 관련된 엄중한 한계를 가지고 있다. 이 단점은 이 방법의 유용성을 극히 제한한다.

따라서, 순차적으로 패턴화될 필요가 있는 불렛의 증착은 몇 가지 값비싸고 어려운 공정 단계의 필요성을 포함한다.

패턴화된 막을 형성하는 또 다른 방법에서, 소정 재료의 불렛 막은, 상술된 방법들 중의 하나에 의해, 이전에 설명된 것과 같은 에칭 공정에 의해 이전에 패턴화된 가판 상에 증착될 수 있다. 불렛 막은, 그 두께가 채워져 가판 내의 기존의 패턴을 완전히 덮도록 증착된다. 다음에 불렛 막의 일부는, 나머지 소정 재료 및 이전에 패턴화된 가판이 동일한 높이에 놓일 때까지 이방성으로 제거된다. 따라서, 이전에 패턴화된 가판에 내장된 패턴에 소정의 재료가 존재하게 된다. 소정 재료의 이방성 제거는 에칭 공정을 거쳐 달성될 수 있는데, 흔히 반도체 소자를 형성하는 경우에, 이 제거는 화학 기계적 평탄화('CMP')라고 하는 공정을 통해 실시된다. 이는 화학 용제와 관련된 입자의 슬러리(slurry)를 사용하여 화학 및 기계적 작용의 조합을 통해 대부분의 소정 재료를 제거하여, 패턴화된 가판에 내장된 소정 위치에 소정 재료를 남기는 것을 포함한다. 패턴화된 막을 형성하는 이 방법은 값이 비싸고 복잡한 평탄화 장비, 및 평탄화 패드를 포함하는 소모재, 슬러리 및 화학제의 사용을 필요로 한다. 부수적으로, 작은 슬러리 입자의 사용은, 이들 입자들이 다음에 평탄화된 표면으로부터 제거될 것을 필요로 하여, 잉여의 공정 단계를 필요로 한다.

비록 이들 방법들 중의 일부가 다른 것들보다 보다 정비에 집중적이고 용액 또는 증기 상 방법의 사용에서 다르지만, 금속 및 금속 산화막을 형성하는 이와 같은 종래의 공정은, 예를 들어 이들 각각이 비싼 장비를 필요로 하고, 시간을 허비하고, 소정 결과를 달성하기 위해 고온의 사용을 필요로 하여 불렛 패턴화되지 않은 막의 결과가 되기 때문에 최적이지 아니며, 만일 패턴화가 요구되면, 또 다른 패턴화 단계가 필요하다. 이들 방법들 중의 대부분은, 많은 경우에, 다양한 어플리케이션에 적합하지 않을 수 있는 다결정막을 형성하는 부수적인 단점이다. 이들 방법에 대한 바람직한 대안은 가판에 도포되어, 선택적으로 어마지되고 패턴화되어 중간 단계의 필요성이 없어 비정질 막을 형성할 수 있는 전구체의 사용일 것이다.

반도체 처리에서 박막의 한가지 사용은, 얇은 상면 이미징(thin top-surface imaging)(이하 'TSI'라고 함) 중, 전형적으로 이미 가판에 도포된 원자 유기층을 형성하기 위한 것이다. 이 경우, 유기층은, 증착된 박막이 종래의 방법을 사용하여 다음에 패턴화될 것이기 때문에 광활성일 필요는 없다. TSI를 위한 이들 박막의 사용은 포토레지스트 마스크의 사용에 의해 제공되지 않는 플라즈마 에칭에 대한 저항, 및 극히 얇은 막에 의해 제공되지 않은 리소그래픽 공정의 증가된 해상도를 포함하는 몇 가지 공정 상의 단점이다. TSI를 위한 전형적인 박막은 금속, 실리콘 질화물 및 산화막을 포함하고, 실리레이션(silylation)이라고 하는 공정에 대해 많은 연구가 실시되고 있다. 이 공정은 이전에 증착된 유기층의 상부에 실리콘 함유 종의 박막을 증가 증착하는 것을 포함한다. 다음에 이와 같은 실리콘 종의 박막이 어마되어 실리콘 산화물의 박막을 형성하고, 이는 밀의 유기층의 산소 플라즈마 패턴화 동안 TSI 중에 작용한다. 반도체 및 패키징 업계에 의한 실리레이션 공정의 수용은 많은 공정 및 비용 한계로 인해 중요하지 않게 되고 있다.

반도체 공정에서 박막의 다른 사용은, 즉 주입 공정용의 하드 마스크를 형성하기 위한 것이다. 이온 주입은, 예를 들어 가판 제조 동안 가판에 도핑된 영역을 형성하는데 있어서 사용되는 잘 공지된 기술이다. 이온 주입은 흔히 이온들이 선정된 영역 내로만 주입되게 하는 또한 하드 마스크라고 하는 패턴화된 차단층을 필요로 한다. 예를 들어, Shimozu 등에 허여된 미국특허 제5,436,176호는 '실시예 1'에서, 붕소 원자로 세 번 주입되는 것으로 개시된, 실리콘 산화막에 의해 덮여진 실리콘 가판의 무마스크 주입(maskless implantation)을 개시하고 있다. 선택적으로, 이 기술은 '실시예 3'에서, 실리콘 산화막에 의해 덮여진 실리콘 가판 상에 마스크를 형성하고, 인(P)을 주입하고, 제2 마스크를 형성하고, 붕소를 주입하고, 마지막으로 열처리하는 순차적인 단계를 포함하는 세 번의 반복되는 방법에서 다수의 하드 마스크를 사용하여 주입하는 것을 개시하고 있다.

이전에 설명한 바와 같이, 이들 공정중의 어느 것에 의해 하드 마스크를 형성하는 것은, 비교적 많은 수의 공정 단계를 필요로 한다. 예를 들어 사용될 공정을 단순화시키고, 그 효율을 증가시키며, 그 비용을 감소시키기 때문에, 에칭 또는 이온 주입 이전에 이들 단계의 일부를 제거하는 것이 유익할 것이다.

이 문제를 해결하는 한가지 접근 방법은, 포토레지스트를 마스크로서 사용하는 것을 포함한다. 그러나, 포토레지스트가, 특히 중간 보호층으로서 이용될 수 있거나 저유전상수('low-k') 유전체 및 이온에 대한 저 정지력(low stopping power)으로서 점차적으로 사용이 증가하는 유기층의 패턴화를 위해, 임의의 플라즈마 에칭 화학처리제에 대한 저 에칭 저항(low etch resistance)을 갖는다는 것을 공지되어 있다. 따라서, 바람직하지 않게 두꺼운 포토레지스트 막들은, 종의 완전한 에칭이 마스크 종의 완전한 부식 이전에 패턴화되게 하거나 또는 도포되는 가판의 면적의 주입을 방지할 필요가 있다. 다른 단점은, 이온 주입된 포토레지스트가 웨어퍼로부터 제거하기가 지나치게 힘들 수 있다는 것이다. 이 문제에 대한 다른 해결 방법은 예를 들어, 먼저 하드 마스크를 도포한 후 하드 마스크 상에, 포토레지스트 층을 도포하고 다음에 에칭 또는 이온 주입이 발생하기 전에 패턴화함으로써 시도되고 있다. 플라즈마 에칭 또는 이온 주입 이전에 종래 기술의 방법에서 개시된 많은 단계를 종의 결합 일부 또는 이들중 하나 이상의 심지어 제거는 이들 공정을 단순화시키는데 도움이 될 것이다. 따라서, 플라즈마 패턴화 또는 이온 주입 공정에서 단계들을 제거하는 방법이 극히 바람직할 것이다.

금속 합성물 전구체 증착을 위한 현재의 공정은 금속 및 금속 산화 하드 마스크 막을 형성하기 위한 적은 비용의 방법으로 발전되고 있다. 이 공정, 광화학 금속 유기 증착 중의 한 실시예는 금속 합성물 전구체를 위한 금속 유기물, 및 입사 복사 또는 열 에너지와 같이 금속 유기물을 금속 또는 금속 산화막으로

변환하기 위한 수단의 사용을 필요로 한다. 특히, 이 공정에서, 전구체 금속 유기물은 예를 들어, 양의의 공치된 수단에 의해 표면에 증착되는 전구체 용액을 형성하기 위해 적합한 유기 용제에서 용해시키므로써 표면에 도포된다. 다음에 전구체는, 에너지원에의 노출, 즉 광, 아온 빔 충격, 전자 빔 충격 또는 열 또는 가열 처리 또는 열처리에 의한 것과 같은, 부분 변환 수단 및/또는 변환 수단에 의해 금속 또는 금속 산화층으로 적어도 부분적으로 변환된다. 따라서, 본 공정은 즉 반도체 및 패키징 업계에서 이용가능성이 있다.

Hill 등에 하여온 미국특허 제5,534,312호는, 기판의 표면에 금속 합성물의 비정밀 막을 증착하고, 선택된 분위기에 막을 위치시키고, 막의 선택된 영역을 전자가 복사, 바람직하게 자외선 선택적으로 마스크를 통해 노출시켜, 선택된 영역 내의 금속 합성물이 광화학 반응하게 하는 단계를 포함하는, 기판 상에 패턴화된 금속 함유 재료를 제조하는 포토레지스트(free photoresist) 방법을 개시한다.

Thomson 등에 하여온 미국특허 제6,071,676호는, 그 집적 회로 제조 공정이 화합물이 복사 또는 입자 빔에 의해 접촉되는 도포된 화합물의 열화를 초래한다는 것을 개시한다. 다른 말로 해서, 화합물의 열화에 의해 유발된 증착물의 치수는 복사하는 빔의 초점 쪽에 비례한다. 나노스케일 치수(nanoscale dimensions)가 이 공정에 의해 달성가능한 것으로 개시된다. 화합물이 열화하여 금속 또는 다른 도전성 기판의 증착물을 형성하는 경우, 이 방법은 기판 상에 직접 집적 회로를 제조하는데 사용될 수 있다. 이 증착물은, 바람직하게 금속 또는 금속 합금인 것으로 교차되며, 금속들은 금, 주석 또는 크롬일 수 있거나, 증착물은 갈륨과 같은 도전성 비금속 또는 반금속일 수 있다. 다른 특징에서, 복사 또는 입자 빔의 효과 하에 열화하여 도전성, 바람직하게 금속성 증착물을 만드는 화합물을 기판에 도포하고, 복사 또는 입자 빔을 화합물의 선택된 표면 영역에 도포하고, 열화된 화합물 및 영향을 받지 않은 화합물을 기판으로부터 제거하는 것을 포함하는 집적 회로의 제조 방법이 제공된다.

발명의 상세한 설명

본 발명의 공정은 패턴화된 하드 마스크를 제공하여, 종래의 TSI 및 아온 주입 공정에 사용되는 산화물 및 포토레지스트 층 모두를 교체하고, 예를 들어, 수행되어야 하는 공정 단계의 수를 감소시켜 방법을 단순화시킨다. 본 발명의 다른 장점은 만들어지는 재료가 플라즈마 에칭 화학처리에 대해 보다 나은 에칭 저항을 갖는다는 점이다. 이는 하드 마스크로서 극히 얇은 막의 사용을 가능하게 하여, 포토레소그래픽 공정의 궁극적인 해상도를 증가시키고 보다 작고 정교한 피처(features)의 형성을 가능하게 한다. 본 발명의 또 다른 장점은, 만들어지는 재료가 보다 나은 아온 주입 차단 및 정지력을 갖는다는 점이다. 부수적으로, 본 발명의 공정은, 기술 분야에서 종래의 공정에 의해서는 예칭하기가 힘들거나 불가능한 것으로 알려진, 플레타늄, 아리듐, 아리듐 산화물, 루테튬 및 루테튬 산화물과 같은 패턴화 층을 위한 새로운 재료의 사용을 용이하게 한다는 점이다.

본 발명의 한 실시예는:

- 적어도 하나의 전구체 재료를 선택하는 단계,
- 기판 위에 전구체를 구비하는 층을 형성하는 단계,
- 전구체 층을 현상하여, 전구체 층에 패턴을 형성하는 단계, 및
- 패턴을 기판으로 전사하여 패턴을 형성하는데 포토레지스트가 사용되지 않게 되는 방법을 포함하는, 기판 상에 하드 마스크를 형성하는 방법이다.

전구체 층의 변환되지 않은 부분은 현상제로 현상될 수 있다. 선택적으로, 전구체 층의 변환된 부분은 현상제로 현상될 수 있다. 현상제는, 적어도 하나의 알콜과 적어도 하나의 케톤(ketone)을 구비하는 액체 현상제일 수 있는데, 여기서, 알콜 모두의 전체 체적은 알콜의 전체 체적과 액체 현상제에 있는 케톤의 전체 체적의 합이 50% 이상이다. 바람직하게, 현상제의 적어도 하나의 알콜은 이소프로필 알콜(isopropyl alcohol)이고, 적어도 하나의 케톤은 메틸 이소부틸 케톤이고, 이소프로필 알콜:메틸 이소부틸 케톤의 비율은 체적으로 약 1:1 이상 체적으로 약 40:1 미만 범위이다.

본 발명의 다른 실시예는:

- 적어도 하나의 전구체 재료를 선택하는 단계,
- 선택적으로, 기판 위에 보호층을 형성하는 단계,
- 보호층 위에 변환되지 않은 전구체를 구비하는 층을 형성하는 단계,
- 변환되지 않은 전구체 층의 적어도 일부를 부분적으로 변환하는 단계,
- 변환되지 않은 전구체 층의 적어도 일부를 실질적으로 제거하여 패턴을 형성하는 단계, 및
- 부분적으로 변환된 전구체 층의 적어도 일부를 변환하여 하드 마스크를 형성하는 단계를 포함하는, 기판 상에 하드 마스크를 형성하는 방법이다.

부분 변환은 에너지를 실질적으로 투과하는 적어도 한 부분을 구비하는 패턴화된 마스크를 통해, 광, 전자 빔 복사, 아온 빔 복사 및 그 혼합 중에서 선택된 에너지원으로 달성될 수 있다. 변환되지 않은 전구체 층의 적어도 일부는 현상제를 사용하여 실질적으로 제거될 수 있다. 변환은 광, 전자 빔 복사, 아온 빔 복사, 열처리 및 그 혼합 중에서 선택된 에너지원으로 달성될 수 있다.

본 발명의 대체 실시예는:

- 적어도 하나의 전구체 재료를 선택하는 단계,

- 기판 위에 변환되지 않은 전구체를 구비하는 층을 형성하는 단계,
- 변환되지 않은 전구체 층의 적어도 일부를 부분적으로 변환하는 단계,
- 변환되지 않은 전구체 층의 적어도 일부를 실질적으로 제거하는 단계,
- 부분적으로 변환된 전구체 층의 적어도 일부를 변환하여 하드 마스크를 형성하는 단계, 및
- 하드 마스크에 의해 실질적으로 덮이지 않은 기판의 적어도 일부를 에칭하여 기판에 적어도 하나의 패턴화된 영역을 형성하는 단계를 포함하는, 기판에 에칭된 패턴을 형성하는 방법이다.

본 발명의 또 다른 실시예는:

- 금속 복합체(metal complex)를 구비하는 적어도 하나의 전구체 재료를 선택하는 단계,
- 기판 상에 패턴 전사 층을 형성하는 단계,
- 패턴 전사 층 위에 변환되지 않은 전구체를 구비하는 층을 형성하는 단계;
- 광을 실질적으로 투과하는 적어도 한 부분을 구비하는 패턴화된 마스크를 통해 변환되지 않은 전구체 층의 일부를 광에 노출시켜, 노출된 부분을 부분적으로 변환시키는 단계,
- 변환되지 않은 전구체 층의 적어도 일부를 실질적으로 제거하는 단계,
- 부분적으로 변환된 전구체 층의 적어도 일부를 변환하여 하드 마스크를 형성하는 단계,
- 적어도 부분적으로 변환된 전구체 및 패턴 전사층의 덮이지 않은 부분을 에칭하여, 덮이지 않은 패턴 전사층으로부터 적어도 하나의 에칭된 부분을 형성하는 단계, 및
- 나머지 적어도 하나의 부분적으로 변환된 전구체 층 및 패턴 전사층을 실질적으로 제거하여, 기판의 적어도 한 일부를 벗기는 단계를 포함하는, 패턴화된 얇은 상면을 형성하는 방법이다.

패턴 전사층은 포토레지스트, 폴리머마드, 폴리(메탈 메타아크릴레이트), Novolac 및 에폭시로부터 선택될 수 있다.

본 발명의 다른 실시예는:

- 금속 복합체(metal complex)를 구비하는 적어도 하나의 전구체 재료를 선택하는 단계,
- 기판 상에 릴리스 층(release layer)을 형성하는 단계,
- 릴리스 층 위에 리프트오프 층을 형성하는 단계,
- 리프트오프 층 위에 변환되지 않은 전구체를 구비하는 층을 형성하는 단계,
- 광을 실질적으로 투과하는 적어도 한 부분을 구비하는 패턴화된 마스크를 통해 변환되지 않은 전구체 층의 일부를 광에 노출시켜, 노출된 부분을 부분적으로 변환시키는 단계,
- 변환되지 않은 전구체 층의 적어도 일부를 실질적으로 제거하여, 리프트오프 층의 나머지 부분이 부분적으로 변환된 전구체 층에 의해 덮인 리프트오프 층의 적어도 일부를 노출시키는 단계,
- 부분적으로 변환된 전구체 층의 적어도 일부를 변환하여 하드 마스크를 형성하는 단계,
- 적어도 부분적으로 변환된 전구체 및 리프트오프 층의 덮이지 않은 부분을 여방성 제거 수단에 노출시켜, 리프트오프 층의 덮이지 않은 부분 및 리프트오프 층의 덮이지 않은 부분 하부의 릴리스 층의 적어도 일부를 실질적으로 제거하고, 기판의 적어도 일부를 노출시키는 단계,
- 적어도 부분적으로 변환된 전구체, 리프트오프 층의 덮인 부분, 및 리프트오프 층의 덮인 부분 밑의 릴리스 층의 적어도 일부를 등방성 제거 수단에 노출시키는 단계,
- 노출된 기판의 적어도 일부 위 및 적어도 부분적으로 변환된 전구체 위에 금속의 막을 증착시키는 단계,
- 적어도 부분적으로 변환된 전구체 위의 금속을 실질적으로 제거하는 단계, 및
- 나머지 적어도 부분적으로 변환된 전구체, 리프트오프 층, 릴리스 층을 실질적으로 제거하여, 기판 위에 금속의 패턴을 형성하는 단계를 포함하는, 리프트오프 층(liftoff layer) 위에 패턴화된 얇은 상면을 형성하는 방법이다.

본 발명의 부수적인 실시예는:

- 금속 복합체(metal complex)를 구비하는 적어도 하나의 전구체 재료를 선택하는 단계,
- 기판 상에 변환되지 않은 전구체 재료를 구비하는 층을 형성하는 단계,
- 변환되지 않은 전구체 층의 적어도 일부를 부분적으로 변환하는 단계,
- 변환되지 않은 전구체 층의 적어도 일부를 실질적으로 제거하여, 부분적으로 변환된 전구체 부분에 안쪽으로 테이퍼진 측면 프로필을 형성하고, 기판의 적어도 일부를 노출시키는 단계,
- 부분적으로 변환된 전구체 층의 적어도 일부를 변환시켜 하드 마스크를 형성하는 단계,
- 노출된 기판의 적어도 일부 위 및 적어도 부분적으로 변환된 전구체 위에 금속의 막을 증착시키는 단계,
- 적어도 부분적으로 변환된 전구체 위의 금속을 실질적으로 제거하는 단계, 및
- 나머지 적어도 부분적으로 변환된 전구체를 실질적으로 제거하여 기판 위에 금속의 패턴을 형성하는 단

계를 포함하는, 리프트오프 층(lift-off layer) 위에 패턴화된 얇은 상면을 형성하는 방법이다.

부분 변환은 에너지를 실질적으로 투과하는 적어도 한 부분을 구비하는 패턴화된 마스크를 통해, 광, 전자 빔 복사, 이온 빔 복사 및 그 혼합 중에서 선택된 에너지원으로 달성될 수 있다. 변환은 광, 전자 빔 복사, 이온 빔 복사, 열처리 및 그 혼합 중에서 선택된 에너지원으로 달성될 수 있다. 이온들은 덮이지 않은 기판을 이온 빔에 노출시켜 주입될 수 있다.

본 발명의 다른 실시예는:

- 적어도 하나의 전구체 재료를 선택하는 단계,
- 기판 위에 특성 두께를 갖는 유전체 층을 형성하는 단계,
- 유전체 층 위에 제1 변환되지 않은 전구체를 포함하는 층을 형성하는 단계,
- 제1 부분 변환 수단을 사용하여, 제1 변환되지 않은 전구체 층의 적어도 일부 위에 제1 전구체 층의 부분적으로 변환된 부분을 형성하는 단계,
- 제1 제거 수단을 사용하여 적어도 부분적으로 변환된 제1 전구체 층에 의해 덮이지 않은 제1 패턴을 형성하기 위해, 제1 변환되지 않은 전구체 층의 적어도 일부를 실질적으로 제거하여 유전체 층의 적어도 일부를 노출시키는 단계,
- 제1 변환 수단을 사용하여, 부분적으로 변환된 제1 전구체 층의 적어도 일부 위에 하드 마스크를 형성하는 단계,
- 유전체 층의 노출된 부분 위 및 적어도 부분적으로 변환된 제1 전구체 층 위에 스핀 평탄화 층을 형성하는 단계,
- 스핀 평탄화 층 위에 제2 변환되지 않은 전구체를 포함하는 층을 형성하는 단계,
- 제2 부분 변환 수단을 사용하여, 변환되지 않은 제2 전구체 층의 적어도 일부 위에 제2 전구체의 적어도 부분적으로 변환된 부분을 형성하는 단계,
- 제2 제거 수단을 사용하여 적어도 부분적으로 변환된 제2 전구체 층에 의해 덮이지 않은 제2 패턴을 형성하기 위해, 제2 변환되지 않은 전구체 층의 적어도 일부를 실질적으로 제거하여 스핀 평탄화 층의 적어도 일부를 노출시키는 단계,
- 제2 변환 수단을 사용하여, 부분적으로 변환된 제2 전구체 층의 적어도 일부 위에 하드 마스크를 형성하는 단계,
- 유전체 층의 두께 마만이 제1 예정 수단에 의해 제거되도록, 제1 예정 수단을 사용하여, 유전체 층의 적어도 일부 및 제2 하드 마스크에 의해 실질적으로 덮이지 않은 위의 스핀 평탄화 층 위에 유전체 층 내의 적어도 제2 패턴화된 영역을 형성하는 단계,
- 제3 제거 수단을 사용하여, 나머지 적어도 부분적으로 변환된 제2 전구체 층 및 스핀 평탄화 층을 실질적으로 제거하여, 적어도 부분적으로 변환된 전구체 층을 노출시키는 단계,
- 유전체 층 두께 마만이 제1 패턴화된 영역 내의 제2 예정 수단에 의해 제거되고 유전체의 실질적으로 전체 두께가 제2 패턴화된 영역 내의 제2 예정 수단에 의해 제거되도록, 제2 예정 수단을 사용하여, 제1 하드 마스크에 의해 실질적으로 덮이지 않은 유전체 층의 적어도 일부 위에 유전체 층 내의 적어도 하나의 제1 패턴화된 영역을 형성하여, 기판의 적어도 일부를 노출시키는 단계, 및
- 선택적으로, 제4 제거 수단을 사용하여 나머지 적어도 부분적으로 변환된 제1 전구체 층을 실질적으로 제거하는 단계를 포함하는, 유전체 층에 이중 다마신 아키텍처를 형성하는 방법이다.

바람직하게, 유전체 층은 저 유전상수 유전체 재료이다.

여들 실시예의 각각에서, 바람직한 전구체 재료는 acac, 카르복실아토(carboxylato), 알콕시(alkoxy), 아지드(azide), 카르보닐(carbonyl), 니트라토(nitrato), 아민, 할리드(halide), 나트로, 및 그 혼합물로 구성된 그룹 중에서 선택된 적어도 하나의 리간드(ligand): 및 Li, Al, Si, Ti, V, Cr, Mn, Fe, Ni, Co, Cu, Zn, Sr, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, In, Sn, Ba, La, Pr, Sm, Eu, Hf, Ta, W, Re, Os, Ir, Pt, Au, Pb, Th, U, Sb, As, Ce, Mg, 및 그 혼합물로 구성된 그룹 중에서 선택된 적어도 하나의 금속을 구비하는 금속 복합체(metal complex)이다.

도면의 간단한 설명

본 발명의 부수적인 목적 및 특징은 도면을 참조하여 설명된 발명의 상세한 설명 및 특허청구의 범위로부터 명확할 것이다.

도 1은 공정 단계에 의한 공정 변수를 식별하는 공정 순서도.

도 2는 본 발명에 따른 공정의 한 실시예에서 단계의 기본적인 순서를 도시하는 도면.

도 3은 반도체 상호접속부에 사용되는 하드 마스크의 종래 기술에 따른 제조 및 사용 방법을 도시하는 도면.

도 4는 본 발명에 따른 하드 마스크의 제조 및 사용 방법을 도시하는 도면.

도 5는 TSI에 의한 종래 기술의 패터닝 방법을 도시하는 도면.

- 도 6은 본 발명에 따른 TSI 층의 제조 및 사용 방법을 도시하는 도면,
 도 7은 리프트오프 공정을 실시하는 종래 기술의 방법을 도시하는 도면,
 도 8은 본 발명에 따른 리프트오프 공정을 실시하는 방법을 도시하는 도면,
 도 9는 본 발명에 따른 리프트오프 공정을 실시하는 다른 방법을 도시하는 도면,
 도 10은 이중 다마신 공정 집적을 위한 종래 기술의 방법을 도시하는 도면,
 도 11은 도 10보다 적은 단계를 포함하는 본 발명에 따른 이중 다마신 공정 집적의 방법을 도시하는 도면,
 도 12는 어온 주입 하드 마스크를 제조하고 그와 함께 어온을 주입하는 종래 기술의 방법을 도시하는 도면,
 도 13은 본 발명의 일 실시예에 따른 어온 주입 하드 마스크의 제조 및 그와 함께 어온을 주입하는 방법을 도시하는 도면,
 도 14는 두 개의 서로 다른 전구체로 형성된 ZrO_2 막에 의해 나타내어진 서로 다른 굴절률 성질을 도시하는 도면,
 도 15는 열 및 광화학 변환에 의해 형성된 다양한 ZrO_2 막의 굴절률을 도시하는 도면,
 도 16은 전구체 용액을 기판에 도포 한 후에 특정 용제의 사용에 의해 유발되는 중무늬를 도시하는 도면,
 도 17은 BST를 위한 열 접촉 곡선을 도시하는 도면,
 도 18은 BST를 위한 광화학 접촉 곡선을 도시하는 도면,
 도 19는 BST를 위한 결합된 열/광화학 접촉 곡선을 도시하는 도면,
 도 20은 하드 베이킹된 노볼락(hard baked Novolac)을 위한 두께 대 예칭 시간의 그래프, 및
 도 21은 완전히 변환된 PZT 대 TiO_2 를 위한 두께 대 예칭 시간의 그래프.

실시예

본 발명은 다른 막 증착 및 형성 방법으로는 이용가능하지 않은 장점을 가능하게 한다. 결국, 사용자로 하여금 결과로 나타나는 막의 특성을 제어하고 조작하여 소정의 어플리케이션에 적합하게 할 수 있는 보다 큰 능력을 제공한다. 따라서, 본 발명에 따른 공정은 광범위한 어플리케이션에 이용 가능하다.

본 발명은, 소정의 재료의 패턴 막을 제조하는 공정을 제공한다. 비정질 막은 다결정 및 결정막과 구별되는 한편, 비정질 막은 보다 정렬된 막에 의해 형성된 서로 다른 비정질 막과는 구별되며, 또한 서로 다른 막 형성 방법에 의해 형성된 서로 다른 비정질 막들이 상호 다르다는 것을 인식하는 것은 중요하다. 더욱이, 서로 다른 방법에 의해 형성된 서로 다른 비정질 막의 서로 다른 성질은 제어될 수 있고, 예를 들어 반도체 장치 및/또는 그 제조에서 층(들)으로서 특정 어플리케이션에 유용한 특정 화학적, 물리적 기계적 성질에 영향을 받는다. 이와 같은 비정질 막을 적어도 부분적으로 변환하는 단계를 포함하는 본 발명에 의해 형성된 하드 마스크는 바람직하게 패턴화되고, 따라서 기판으로 패턴을 전사하는데 유용하다. 하드 마스크는 주입 마스크, 예칭 마스크 및 패턴 전사층(pattern transfer layer) 또는 마스크, 즉 리프트오프 마스크(liftoff mask)를 포함하지만 이에 한정되지 않는다.

본 공정의 한 실시예의 한 가지 장점은, 패턴을 형성하는데 있어서, 종래의 패턴링 재료, 즉 포토레지스트를 사용하지 않고 패턴화된 전자 재료를 만든다는 점이다. 본 공정의 다른 장점은, 형성될 수 있는 전구체 재료의 비정질 막이 중간 패턴링 재료를 사용하지 않고 기판 상에 광학적으로 직접 패턴화될 수 있다는 점이다. 공정 변수의 이해의 결과, 다른 막 형성 및 증착 방법을 사용하지 않는 본 증착 공정을 통해 중요하고 유일한 성질이 얻어질 수 있다. 도 1은 특정 어플리케이션을 위한 최적화된 성질을 갖는 소정의 재료의 막을 얻기 위해 실시될 수 있는 예시적인 단계를 도시하는 공정 순서도에 의해 본 공정의 개요를 제공한다. 많은 이들 단계들은 막의 궁극적인 어플리케이션에 기초하여 완전히 광학적이다. 본 발명은 또한 이들 단계에 한정되어 있지 않고, 막의 궁극적인 어플리케이션에 기초하여 다른 단계를 포함할 수 있다. 기술분야의 숙련자는 특정 어플리케이션을 위한 소정 결과를 얻기 위해 어떤 단계들이 포함되거나 제외되어야 하는 지를 알 것이다.

각각의 단계에서, 결과로 나타나는 막에 영향을 미치도록 조작될 수 있는 변수가 존재한다. 예를 들어, 도 1의 단계 1에서, 변수들은 전구체 재료, 용제가 전구체 재료에 사용되는 자에 따라 전구체 재료에 사용된 용제, 전구체 재료와 함께 사용될 수 있는 첨가물 및/또는 전구체 재료와 함께 포함될 수 있는 속도 증강제의 조합을 포함할 수 있다.

도 1의 단계 2에서, 변수는 기판의 클리닝, 장벽층의 증착, 접착 개선제의 증착, 및/또는 반응층의 사용을 포함할 수 있다.

도 1의 단계 3에서, 변수는 전구체 막을 도포하는 방법, 전구체가 도포되는 분위기, 및/또는 증착 온도를 포함할 수 있다.

도 1의 단계 4에서, 변수는 열 처리, 전자 빔에 의한 열 처리, 어온 빔에 의한 열 처리, 마이크로웨이브를 사용한 처리, 및/또는 특정 분위기의 사용을 포함할 수 있다.

도 1의 단계 5에서, 변수는 막이 노출되거나 패턴화된 물렁킷인지 또는 각각의 혼합물 및/또는 특정 분위기의 사용을 포함할 수 있다.

도 1의 단계 6에서, 변수는 열 처리, 마이크로웨이브를 이용한 처리, 전자 빔에 의한 처리, 이온 빔에 의한 처리, 도금, 및/또는 특정 분위기의 사용을 포함할 수 있다.

도 1의 단계 7에서, 변수는 습식 또는 건식 기술에 의한 패터닝을 포함할 수 있다.

도 1의 단계 8에서, 변수는 열처리 및/또는 특정 분위기의 사용을 포함할 수 있다. 또한, 이 단계에서, 형성되는 임의의 비정질 막은, 즉 상승된 온도를 인가 또는 광 유도 핵화와 같은 다양한 다른 핵화 공정에 의해 다결정 또는 결정막으로 변형될 수 있고, 일부 어플리케이션을 위해 이는 바람직한 공정 단계일 수 있다.

여들 변수는 예로서 의도되었고, 결과로 나타나는 막의 성질에 영향을 미쳐도록 조작될 수 있는 모든 변수인 것으로 간주되어서는 않는다. 본 발명의 보다 특정한 예 및 실시예가 이하에 상세히 설명된다.

패터닝된 막이 필요하면, 이하에 설명되는 공정은 중간 패터닝 재료, 즉 포토레지스트를 사용하지 않고 광 화학적으로 진행할 수 있고, 분위기 조건 하에서 진행되거나 또는 공기 또는 다른 조성 분위기와 같은 다른 조건 및/또는 다양한 압력, 분위기, 보다 높거나 낮은 분위기 하에서 수행될 수 있고, 유일한 재료, 층 및 구조를 만들기 위해 다양한 다른 공정 단계와 결합하여 사용될 수 있다.

공정이 광분해적으로 수행되는 경우, 공정은 실질적으로 분위기 온도에서 진행되는 한편, 다른 종래 기술의 방법은 패턴 전사를 실시하기 위해 상승된 온도 흔히 100°C 이상의 온도의 사용을 필요로 한다. 이와 같은 한계는 제조 관점에서 볼 때 엄격한 공정 한계를 제시하며, 방법의 어플리케이션에 연관된 장치의 조립에 사용되는 재료의 선택을 제한한다.

본 발명의 공정은, 흔히 실질적으로 분위기 온도 하에서 만족할 만하게 진행된다. 이와 대조적으로, 대부분의 종래 기술의 증착 방법은, 상술한 한계를 갖는 것 이외에, 높은 진공 조건 하에서 수행되어야 하기 때문에, 실행하고 유지하기 힘든 값비싸고 복잡한 장치를 필요하게 된다.

본 발명의 공정들은 전구체 재료로부터 기판 상에 얇은 층의 형성을 용이하게 한다. 전구체는, 특히 균일한 방식으로 기판을 코팅하여, 고 광학 품질의 막, 본 공정의 경우에 광광성을 갖는 능력을 갖도록 설계된 분자를 구비한다. 전구체 분자는 큰 변수 - 적어도 하나의 금속('M') 및 적어도 하나의 적합한 리간드(ligand) ('L') 또는 리간드들을 구비하는 공식 $MaLb$ (여기서, a는 적어도 1인 정수이고 b는 적어도 1인 정수임)의 광범위한 금속 합성물이다.

만일 복수의 금속들이 사용되면, 모든 금속 원자들은 동일하고, 모두 서로 다른 원자를 가질 수 있거나/있거나 서로 다른 원자가, 즉 $BaNa$ 또는 $Fe(II)Fe(III)$ 를 가질 수 있거나, 일부는 동일하지만 다른 것은 서로 다른 원자를 가질 수 있고/있거나 서로 다른 원자가, 즉 $Ba2Fe(II)Fe(III)$ 를 가질 수 있다. 어떠한 경우에도, 금속 M은 알칼리 또는 알칼리 토류, 예를 들어 Ba 또는 Li , 전이 금속, 예를 들어 Cr 또는 Ni , 주 그룹 금속(main group metal), 예를 들어 Al 또는 Sn , 또는 악티나이드(actinide) 금속, 예를 들어 U 또는 Th 일 수 있다. 바람직하게, 각각의 금속은 Li , Al , Si , Ti , V , Cr , Mn , Fe , Ni , Co , Cu , Zn , Sr , Y , Zr , Nb , Mo , Ru , Rh , Pd , Ag , In , Sn , Ba , La , Pr , Sm , Eu , Hf , Ta , W , Re , Os , Ir , Pt , Au , Pb , Th , U , Sb , As , Ce 및 Mg 중에서 독립적으로 선택된다.

만일 복수의 리간드가 사용되면, 모든 리간드들은 동일한 수 있는, 이들은 서로 다른 수 있거나, 또는 일부는 동일하고 다른 것들은 다를 수 있다. 어떠한 경우에도, 리간드 L은, 실질적으로 변형되지 않은 전구체 합성물이 형성될 수 있고 성질이 다음과 같도록 선택된다:

- 1) 기판 상에 비정질막에 증착될 수 있다.
- 2) 비정질 막은 안정하거나 또는 적어도 준안정이다.
- 3) 에너지의 흡수시, 즉 요구되는 에너지의 광자의 흡수시, 막은 화학 반응을 통해 서로 다른 금속 함유 재료에 변형될 수 있다.
- 4) 에너지 유도 화학 반응의 어떠한 부산물도 제거할 수 있어야, 즉 막으로부터 제거할 수 있도록 하기 위해 충분히 휘발성이어야 한다.

여들 결과중 첫 번째 두 개를 달성하기 위해, 합성물은 저 극성 및 낮은 분자간력(low intermolecular force)을 가져야 한다. 유기 그룹은 흔히 낮은 분자간력을 가지기 때문에, 그 외각 주변에 유기 그룹을 갖는 리간드는 첫 번째 두 가지 조건을 만족시키는 경향이 있다. 만일 흡수된 에너지가 광이면, 단계(3)의 화학 반응은 광 유도 반응으로서 알려졌다.

실질적으로 변형되지 않은 전구체의 증착막은 비정질 또는 적어도 실질적으로 비정질이다. 따라서, 금속 합성물이 결정화에 저항하도록 하기 위해서는, 리간드(L)는 바람직하게, 합성물이 비대칭이 되도록 되어야 한다. 합성물은 그 자신이 두 개 이상의 입체 이성체 형태를 갖는 리간드를 사용하여 비대칭으로 될 수 있다. 예를 들어, 만일 L이 2-에틸헥사노에이트(2-ethylhexanoate)이면, 합성물이 몇 개의 서로 다른 입체 이성체 형태를 갖기 때문에 결과로 나타나는 금속 합성물은 비대칭이다. 리간드의 유기 부분의 형태 및 크기는 막 안정성을 최적화시키고, 선택된 막 증착 공정에 의해 증착될 막의 두께를 조정하도록 선택될 수 있다.

결정화에 대한 비정질 막의 안정성은 또한 각각의 금속 원자에 부착된 몇 개의 서로 다른 리간드를 갖는 합성물의 막을 제조함으로써 증가될 수 있다. 이와 같은 금속 합성물들은 이성체 형태를 갖는다. 예를 들어, 니켈(II) 염 및 $KNCS$ 의 합성에 대한 $CH_3HNCCH_2CH_2NHCH_3$ 의 반응으로 이성체의 합성물이 제조되게 된다. 서로 다른 이성체의 화학적 성질은 크게 다르지 않은 것으로 공지되어 있지만, 막 내의 몇몇 이성체의 존재는 막 내의 합성물의 결정화를 손상시킨다.

합성물은 또한, 공정 조건 하에서 급속하게 그리고 순간적으로 분해하지 않는 안정하거나 적어도 준안정하여야 한다. 소정 금속의 합성물의 안정성은, 예를 들어 합성물 내의 금속의 산화 상태에 따라 다를 수 있다. 예를 들어, $Ni(0)$ 합성물은 대기에서 불안정한 한편 $Ni(II)$ 합성물은 대기 안정하다. 결국, 대기 분

여기에서 공정 단계를 포함하는 Ni 기본 막을 증착하는 공정은 Ni(0) 합성물 보다 우선하여 Ni(II) 합성물을 포함하여야 한다.

부분적인 변환 및 변환은, 부분적으로 변환되거나 변환된 영역을 소정의 변환된 재료로 변경시키는 막 내의 화학 반응의 결과이다. 이상적으로, 합성물이 부분적인 변환 수단 및/또는 변환 수단의 영향에 의해 여기 상태로 상승될 때, 적어도 하나의 리간드가 쪼개어진 본드에 의해 합성물에 반응하고 부착되어야 한다. 바람직하게, 반응 그룹은 부분 변환 수단 및/또는 변환 수단으로서 빛, 보다 바람직하게 자외선에 의해 추가화되는 광화학 반응에서 합성물로부터 분리된다. 공정에서의 이와 같은 광화학 단계(들)들이 보다 효율적으로 되기 위해서는, 반응 그룹이 불안정하고 순간적으로 쪼개어질 때 만들어지는 중간 재료가 소정의 새로운 재료 및 휘발성 부산물(들)로 변환되는 것이 극히 바람직하다.

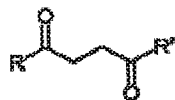
적절한 광화학 반응을 발생시킬 수 있는 몇가지 메커니즘이 존재한다. 본 발명에 따라 개별적으로 또는 조합하여 운영할 수 있는 적합한 반응 메커니즘의 일부 예는 다음과 같다:

(a) 광자의 흡수는 리간드(ligand) 내의 복합체(complex)를 금속 복합체에서 금속 대 리간드 결합(metal-to-ligand bond)이 불안정한 금속 전하 전달 여기 상태(ligand to metal charge transfer excited state)로 높게 할 수 있고, 결합은 파괴되고 복합체의 나머지 부분은 순간적으로 분해한다. (b) 광자의 흡수는 복합체를 복합체 내의 금속 대 리간드 결합이 불안정한 금속 대 리간드 전하 전달 여기 상태(metal-to-ligand charge transfer excited state)로 높게 할 수 있고, 결합은 파괴되고 복합체의 나머지 부분은 순간적으로 분해한다. (c) 광자의 흡수는 복합체는 복합체 내의 금속 대 리간드 결합이 불안정한 분자간 전하 전달 여기 상태로 높게 할 수 있고, 결합은 파괴되고 복합체의 나머지 부분은 순간적으로 분해한다. (d) 광자의 흡수는 복합체를 복합체 내의 금속 대 리간드 결합이 불안정한 국부화된 리간드 여기 상태(localized ligand excited state)로 높게 할 수 있고, 결합은 파괴되고 복합체의 나머지 부분은 순간적으로 분해한다. (e) 광자의 흡수는 복합체를 복합체 중의 적어도 하나의 리간드가 불안정하고 분해하도록 분자간 전하 전달 여기 상태로 만들고, 복합체의 나머지 부분은 불안정하고 순간적으로 분해한다. (f) 광자의 흡수는 복합체 중의 적어도 하나의 리간드를 여기된 리간드가 불안정하고 분해하는 국부화된 리간드 여기 상태로 만들고, 복합체의 나머지 부분은 불안정하고 순간적으로 분해한다. (g) 광자의 흡수는 복합체 중의 적어도 하나의 리간드가 불안정하고 분해하는 금속 대 리간드 전하 전달 여기 상태로 만들고, 복합체의 나머지 부분은 불안정하고 순간적으로 분해한다. 그 광범위한 특정에서, 본 발명은 이들 반응 메커니즘에 한정되지 않는다.

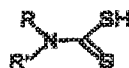
예시적인 금속 복합체, 및 그 금속 및 리간드 성분은 그 전문에 본 발명의 참조로서 일체화되는 미국특허 제5,534,312호에 개시된다. 바람직한 금속 복합체 전구체는 위의 기준을 만족하는 리간드를 포함한다. 보다 바람직하게, 리간드는 아세틸아세토네이트(acetylacetonate) (또한 'acac' 또는 2,4-pentanedione라고도 함) 및 그 음이온, 대체 아세틸아세토네이트, 즉



및 그 음이온, 아세토닐아세톤(acetonylacetone)(2,5-hexanedione라고도 함) 및 그 음이온, 대체 아세토닐아세톤, 즉



및 그 음이온, 디아킬디티오카바메이트(diacyldithiocarbamates), 즉



및 그 음이온, 카복실산(carboxylic acids), 즉



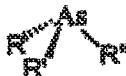
예를 들어, 헥사노익(hexanoic) (여기서 R=CH₃(CH₂)₄, 카복실레이트



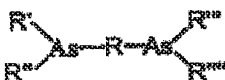
예를 들어, 헥사노에이트(hexanoate) (여기서 $R=CH_3(CH_2)_4$, 피리딘(pyridine) 및/또는 대체 피리딘, 즉



아지드(azide), 즉 N_3^- , 이만, 즉 RNH_2 , 다이민, 즉 H_2NRNH_2 , 아르신(arsine), 즉



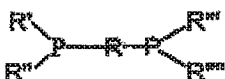
디아리신(diarsines), 즉



포스파인(phosphines), 즉



디포스파인(diphosphines), 즉



아레스(arenes), 즉



을 구성된 그룹 중에서 선택된다.

하이드록시, 즉 OH^- , 알콕시 리간드, 즉 RO^- , $(C_2(H_5)_2NCH_2CH_2O^-)$ 와 같은 리간드, 알킬 리간드, 즉 R^- , 아릴(aryl) 리간드, 및 그 혼합물 (여기서, R , R' , R'' , R''' 및 R'''' 은 유기 그룹중에서 독립적으로 선택되고 바람직하게 알킬(alkyl), 알케닐(alkenyl), 아릴킬(arylalkyl) 및 아릴케닐(arylkenyl) 그룹중에서 독립적으로 선택된다.

본 발명에 사용되는 바와 같이, '알킬'이라는 용어는 직선 또는 분기 탄화수소 체인을 지칭한다. 본 발명에 사용되는 바와 같이, 위상 직선 체인 또는 분기된 체인 탄화수소 체인은 알칸(alkanes), 알케인(alkenes) 및 알카인(alkynes)을 포함하는 영역의 대체 또는 대체되지 않은 아사이클릭(acyclic) 탄소 함유 화합물을 의미한다. 알킬 그룹의 예는 저 알킬, 예를 들어, 메틸, 에틸, n-프로필, 이소프로필, n-부틸, 이소부틸, tert-부틸(tert-butyl) 또는 이소헥실(iso-hexyl); 상부 알킬, 예를 들어 n-헵틸, -옥틸(octyl), 이소옥틸, 노닐(nonyl), 데실(decyl) 등; 하부 알킬렌, 예를 들어 에틸렌, 프로필렌(propylene), 프로필라니(propylene), 부틸렌, 부타딘, 펜틴, n-헥센(hexene) 또는 이소부틴; 및 상부 알킬렌, 예를 들어 n-헵텐, n-옥텐, 이소옥텐, 노넨, 디센 등을 포함한다. 기술분야의 숙련자는 본 발명의 범위에 포함되는, 무수히 많은 직선, 즉 선형 및 분기 알킬 그룹을 알 것이다. 또한, 이와 같은 알킬 그룹은 또한, 하나 이상의 수소 원자가 기능성 그룹 또는 인-체인(in-chain) 기능성 그룹에 의해 교체되는 다양한 대체물을 포함한다.

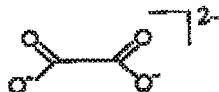
본 발명에 사용되는 바와 같이, '알케닐(alkenyl)'이라는 용어는 탄소-탄소 연결중의 적어도 하나가 탄소-탄소 이중 결합인 직선 또는 분기된 탄화수소 체인을 지칭한다. 본 발명에 사용되는 바와 같이, '아릴킬(arylalkyl)'이라는 용어는 적어도 하나의 아릴 그룹, 즉 용어상으로 벤조닐로 대체되는 알킬 그룹을 지칭한다. 본 발명에 사용되는 바와 같이, '아릴케닐(arylkenyl)'이라는 용어는 적어도 하나의 아릴 그룹으로 용어상으로 교체되는 알케닐 그룹을 지칭한다. 본 발명에 사용되는 바와 같이, '아릴(aryl)'이라는 용어는 흔히 적어도 5π (pi) 전자를 포함하는 공액 이중 결합 시스템을 띠는 탄화수소 링을 지칭한다. 아릴 그룹의 예는 페닐, 나프틸(naphthyl), 아니실(anisyl), 톨루일(toluy), 자레닐(xylenyl)등을 포함하지만 이에 한정되지 않는다.

본 발명의 문장에서 '기능성 그룹(functional group)'이라는 용어는 기술분야의 숙련자가 알 수 있는 바와 같이, 부분 소유 인-체인(moiety possessing in-chain) 및/또는 종단 기능(terminal functionality)을 광범위하게 지칭한다. 인-체인 기능 그룹의 예는, 에테르, 에스터, 아마이드, 우레탄, 및 그 황(thio)-파생물일 수 있는데, 여기서 적어도 하나의 산소 원자는 황 원자에 의해 교체된다. 페던트(pendant) 및/또는 종단 기능 그룹의 예는 플루오르 및 클로로와 같은 할로겐, 및 하이드록실, 아미노, 카복실, 황 및 아마이드(amido), 이소시아네이트, 사이노(cyano), 에폭시, 및 아릴리(allyl), 아크릴로일(acryloyl) 및 메타아크릴로일(methacryloyl)과 같은 에틸렌티칼리 포화되지 않은 그룹, 말레이트(maleate) 및 말레이미도

(maleimido)일 수 있다.

순간적으로 열적으로 분해하는 광화학 반응의 제품의 경향을 포함하는 소정의 광화학 특성을 증가시키기 위해, 다른 그룹을 포함하고/하거나 이들 중의 하나 이상 중에서 선택된 리간드가 단독으로 사용되거나 또는 열거된 리간드와 결합하여 사용될 수 있다. 즉 옥소(oxo),

옥사라토(oxalato), 즉



할라이드(halide), 수소, 수소화물, 즉 H-, 이수소화물, 즉 H₂, 하이드록시, 사이네오(cyano), 즉 CN-, 카보닐, 니트로(nitro), 즉 NO₂, 니트리로(nitrito), 즉 NO₂-, 니트라테(nitrate), 즉 NO₃, 니트리로(nitrito), 즉 NO₃-, 니트로실(nitrosyl), NO, 에틸렌, 아세틸렌 등.

티아시아네이트(thiocyanato), 즉 SCN-, 이소티아시아네이트, 즉 NCSN-, 아퀴오(aquo), 즉 H₂O, 아지드(azide), 카보네이트, 즉 CO₃-2, 아민, 및 티오카르보닐 (여기서, 각각의 R 및 R'는 유기 그룹 중에서 독립적으로 선택되고, 바람직하게는 알킬, 알케닐, 아릴킬 및 아릴케닐 그룹 중에서 독립적으로 선택된다. 보다 바람직하게, 각각의 리간드는 acac, 카르복실레이트, 알콕시, 옥소라토(oxalato), 아지드(azide), 카르복실, 니트로, 니트라토, 아민, 할로겐 및 그 음이온 중에서 독립적으로 선택된다.

바람직하게, 금속 복합체 전구체는 acac, 카르복실라토(carboxylato), 알콕시, 아지드(azide), 카르복실, 니트라토, 아민, 할로겐, 니트로 및 그 혼합물, 및 Li, Al, Si, Ti, V, Cr, Mn, Fe, Ni, Co, Cu, Zn, Sr, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, In, Sn, Ba, La, Pr, Sm, Eu, Hf, Ta, W, Re, Os, Ir, Pt, Au, Pb, Th, U, Sb, As, Ce, Mg 및 그 혼합물로 구성된 그룹 중에서 선택된 적어도 하나의 금속 중에서 선택된다.

전구체는 기판에 직접 도포될 수 있다. 선택적으로 그리고 바람직하게, 전구체는 용제 또는 용제들에서 용해되어 전구체 용액을 형성한다. 이는 용액을 기판에 스핀 또는 스프레이 도포와 같은 것에 의해, 기술 분야의 숙련자에 공지된 다양한 수단에 의해 기판에 도포를 용이하게 한다. 용제는 전구체를 용해시키는 용제의 능력, 전구체에 대한 용제의 불활성, 용제의 점도, 용제 내의 산소 또는 다른 분위기 또는 다른 기체의 용해성, U 용제의 V, 가시광선, 및/또는 적외선 흡수 스펙트럼, 전자 및/또는 이온 빔에 대한 용제의 흡수 단면, 용제의 휘발성, 다음에 형성되는 막을 통해 확산하는 용제의 능력, 서로 다른 용제 이성체의 존재에 대한 용제의 순도, 용제의 열 안정성, 다음에 형성되는 막 내의 결함 또는 핵 사이트에 영향을 미치는 용제의 능력, 및 용제에 관련된 환경 고려를 포함하는, 몇가지 기준에 기초하여 개별적으로 또는 결합하여 선택될 수 있다. 예시적인 용제는 핵산과 같은 일가단, 메틸 아소부틸 케톤('MEBK') 및 메틸 에틸 케톤('MEK')과 같은 케톤(ketones), 및 프로판올, 글리콜, 모노메틸 에테르 아세테이트('PMEA')를 포함한다.

용액 내의 전구체의 농도는 광범위한 범위에 걸쳐 다를 수 있고, 기술분야의 숙련자에 의해, 그 두께 및/또는 광 또는 입자 빔에 의한 자극에 대한 감도를 포함하는 전구체 막의 성질이 소정의 어플리케이션에 적합하도록 최소 루틴 실험에 따라 선정될 수 있다.

그러나, 전구체의 선정은 기술 분야의 숙련자에 의해 용이하게 예측할 수 없는 소정의 막의 성질에 큰 영향을 미칠 수 있다. 예를 들어, 각각 금속 M과 서로 다른 리간드 세트 L 또는 L' 중의 하나로 구성된 두 개의 전구체 ML 및 ML'은, 상호 다른 리간드의 부분들이 하드 마스크로 전구체를 변환시키는 동안 제거될 것이기 때문에, 동일한 소정의 재료의 막을 형성하는 것으로 예상될 수 있다. 실제로, 이들 두 개의 유사한 반응물의 가정되는 동일한 막 재물은 그 성질이 다를 수 있다. 본 공정에서 영향을 받을 수 있는 성질의 예는 유전상수, 및 막에서 임의의 보조 또는 제3기 구조의 존재/부재를 포함한다. 이와 같은 차이를 위한 가능한 이유는 비정질 재료의 형성 속도 및 소정의 재료의 광 유도 막으로부터 에너지를 제거하는 광 분해 리간드의 능력에 관련될 수 있다. 노광 공정 동안 리간드 입자의 존재는 또한 막 형성 공정에 영향을 미칠 수 있고, 막의 확산 성질, 핵화 및 결정 성장과 같은 현 상에 영향을 미친다.

더우기, 막 형성 및 광화학 노광시 전구체의 선택은, 예를 들어 소정의 막이 형성되는 분위기의 기체 구성 요소로서 소정의 재료의 막의 부수적인 반응성에 큰 영향을 미친다. 이는 예를 들어, 고 또는 저 속도가 소정의 제품에 따른 정정할 수 있을 때 증착된 막의 신뢰 속도에 영향을 미칠 수 있다. 부수적으로, 막의 자유 능력에 대한 전구체의 효과 즉 균열을 최소화시키는 능력, 및 막의 수축 또는 거칠어짐은 기술분야의 숙련자에 의해 동일한 결과를 만들어내는 것으로 보일 전구체의 선택에 의해 큰 영향을 받을 수 있는 것으로 알려져 있다.

화학 첨가물은 선택적으로 전구체 또는 전구체 용액으로 제시된다. 이들은 다음 이유중 임의 또는 몇 가지 이유: 실질적으로 증착된 전구체 또는 막의 감광성을 재어하고, 균일하고 결함 없는 막을 기판에 증착하는 것을 보조하고, 용액의 점도를 수정하고, 막 형성의 속도를 증가시키고, 증착된 막의 후속하는 노출 동안 막의 균열을 방지하는 것을 돕고, 용액의 다른 물리 성질을 수정하고, 그리고 소정의 재료의 막의 성질을 중요한 방식으로 수정하기 위해 제시된다. 첨가물은 적합한 용제를 선택할 때 이용되는 기준 이외에 이들 기준에 따라 선정된다. 전구체 또는 전구체 용액은 그 막 형성 성질을 개선하기 위해 특별한 오염이 없는 것이 바람직하다.

만일 사용되지 않는다면, 비록 전구체 막의 증착 방법 및 증착을 위한 용제에 영향을 미칠지라도, 전구체가 도포되는 기판의 성질은 공정에 중요하지 않다. 기판은 CaF₂과 같은 염분, 실리콘을 포함하는 반도체

표면, 실리콘 게르마늄 및 III-V 및 II-VI 반도체를 포함하는 화합물 반도체, 인쇄되고/되거나 박막화된 기판, 금속, 세라믹, 및 글래스를 포함하지만 이에 한정되지 않는다. 실리콘 웨이퍼, 세라믹 기판 및 인쇄회로 기판은 광범위하게 사용되고 있다. 본 공정에서 그 사용 이전에, 기판은 유전체 층, 포토레지스트, 폴리머, 금속 산화물, 열 산화물, 도전 재료, 절연 재료, 감작성 재료 또는 전자 소자의 구성에 사용되는 다른 재료와 같은 단일 또는 복수의 층으로 코팅될 수 있다. 산소 플라즈마에 의해 패터닝이 영향을 받고 전구체 재료가 TSI 재료로 이용되려는 경우, 하부의 층은 Novolac 수지, 폴리(메틸 메타크릴레이트(methyl methacrylate)) ('PMMA'), 폴리(메틸 글루타리미드(methyl glutarimide)) ('PMGI'), 폴리머이드, 및 폴리(p-하이드록시스티렌(hydroxystyrene)) ('PHOST')를 포함하지만 이에 한정되지 않는다.

일단 형성된 하드 마스크에서 금속 원자가 후속하는 단계 동안 하부의 기판에 '충돌(bumped)' 되는 정도로, 이는 전구체 형성 조건 및/또는 두께를 주의 깊게 선택하여 극복될 수 있다. 선택적으로, 기판, 및 하드 마스크 형성 공정이 완료된 후에 기판을 보호하도록 남는 전구체 층 간에 선택적인 보호층이 사용될 수 있다. 선택적으로, 기판은, 전구체 또는 전구체 용액이 도포되기 전에 적어도 하나의 보호층으로 코팅될 수 있다. 보호층은 기술분야의 숙련자에 의해 다양한 수단으로 기판에 도포될 수 있다. 보호층들은 공정이 어떤 주입 단계를 포함할 때 특히 바람직하다.

전구체 막의 증착 이전에 기판의 준비는 소정의 하드 마스크의 공극적인 성질에 큰 영향을 미칠 수 있다. 따라서, 양의 표면 준비는 바람직하거나 또는 역으로 사용된 특정 하드 마스크에 따라 피할 필요가 있다. 기판 준비는 기판 표면으로부터 원치 않는 증류를 제거하기 위한 간단 클리닝 공정, 사전 패터닝 단계, 장벽 재료의 증착, 접착 개선 재료의 증착, 또는 증착된 재료, 즉 결합체의 막에서 화학 변화를 감소시켜도 될 수 있는 반응 재료의 증착을 포함할 수 있다.

전구체 또는 전구체 용액의 도포 방법은, 기판 및 의도하는 어플리케이션에 따라 선정될 수 있다. 기술분야의 숙련자에 공지된 다양한 코팅 방법들의 몇 가지 예는 스프레이, 스프레이, 딥(dip) 및 롤러 코팅(roller coating), 스탬핑(stamping), 메니커스(meniscus), 및 다양한 연결 방법, 즉 잉크젯팅 방법을 포함한다. 코팅 공정에서의 변수는 증착된 막의 두께 및 균일성을 제어하고, 예지 효과 및 막 내의 보이드 또는 핀홀의 형성을 최소화시키고, 코팅 공정 동안 소비되는 전구체 또는 전구체 용액의 요구되는 양보다 덜 소비되게 하기 위해 선정될 수 있다. 전구체 막의 최적의 어플리케이션은 바람직하게 극히 부드러운 막을 만들 수 있다.

증착된 막은 선택적으로, 증착된 막에 존재하는 양의 잔류 용제를 제거하는 베이킹 또는 진공 단계 처리될 수 있다. 만일 베이킹 단계가 이용되면, 물론 이 단계의 온도를 전구체 분자가 열분해적으로 분해하는 온도 이하로 유지하는 것이 중요하다. 본 발명의 공정으로, 소정 재료의 균일한 불렛팅 코팅으로 열분해적으로 변환하거나 또는 열 처리없이 가능한 패터닝을 위한 변환 수단 및/또는 보다 낮은 부분 변환 수단을 필요로 하는 막을 만들기 위해 전구체 캐스트(cast) 막의 불렛팅 열 및 가열 처리 또는 열처리(annealing)가 가능하게 된다. 증착된 막은, 공정의 이 단계에서, 불렛팅 광화학 또는 전자 빔 노출 및 마이크로웨이브 처리를 포함하지만 이에 한정되지 않는 다른 처리가 수행될 수 있다.

공정의 이 단계에서의 베이킹 단계는 전구체 막으로부터 용제를 계속 분출시키고 또한 열 분해 공정을 개시하는 것을 알아야 한다. 이를 제거하는 모든, 예를 들어 후속하는 부분 변환 및/또는 변환 단계 동안 보다 낮은 도우즈 조건에 결과가 되는, 공정의 전반적인 효율을 보존할 수 있다. 또한, 이와 같은 베이킹 단계 동안, 증착된 막 또는 소정 재료의 막과는 다른 새로운 재료가 형성될 수 있다는 것을 알아야 한다. 이의 효과는, 기술분야의 숙련자가 용이하게 알 수 없는 방식으로 유전상수, 화학, 특화, 및 결정화 행위를 포함하는 소정 재료의 후속하는 성질을 크게 변화시킨다. 예를 들어, 하나의 재료가 프리-베이킹 단계에서 활성화되는 한편 다른 성분(들)이 광화학 또는 보다 높은 에너지 열 공정 단계에서 활성화되도록 선택되는 두 가지 성분 시스템이 양의 어플리케이션에 채택될 수 있다. 전구체의 혼합물로부터 이와 같은 증착은 시스템의 효율적인 설계를 가능하게 하여, 베이킹 및 후속하는 부분 변환 및/또는 변환 단계(들)로부터 형성되는 재료의 서로 다른 화학적 성질의 장점을 취할 수 있게 한다.

다음에, 증착된 막은 전구체가 적어도 부분적으로 변환되도록 에너지원에 의해, 부분 변환 수단 및/또는 변환 수단에 의해 처리된다. 전체 막 또는 증착된 전구체 막의 선택된 영역이 에너지원에 노출된다. 에너지원은, 즉 특정 파장의 광원, 특정 파장 또는 파장의 코히어런트 광원, 광대역 광원, 전자빔('e-빔')원, 또는 아온 빔 원일 수 있다. 약 150nm 내지 약 600nm의 파장 범위의 광이 적합하게 사용된다. 바람직하게, 광의 파장은 약 157 내지 약 436nm이다.

본 발명의 양의 실시예에서, 에너지원은 표면상의 이미지를 정의하는데 사용되는 광학 마스크를 통해 검출되는 광원이다. 마스크는 실질적으로 투명하고 실질적으로 불투명하거나 또는 광 흡수 영역으로 구성된다. 이 마스크는 또한 위상 쉬프트 기술과 같은 광학 증가 피쳐(optical enhancing feature)를 포함한다. 그러나, 에너지원은 마스크를 통해 배향될 필요가 없다. 예를 들어, 만일 재료를 패터닝할 필요가 없다면, 열 에너지 또는 넓은 광범에 의해 제공되는 바와 같은, 플러드(flood) 또는 블랭킷 에너지 노출(blanket energy exposure)이 사용될 수 있다.

증착된 막이 적어도 부분적으로 변환되게 하는 대기 및 양력은 전체적으로 그리고 부분적으로 중요한 공정 변수일 수 있다. 흔히, 대기는 공기인 것이 편리하고 경제적이지만, 적어도 부분적인 변환 동안 제시되는 대기의 조성을 바꾸는 것이 바람직할 수 있다. 이에 대한 한 가지 이유는, 만일 짧은 파장 광이 사용되면, 이와 같은 광이 공기에 의해 감쇄될 수 있기 때문에 노출되는 광의 전송을 증가시키기 위한 것이다. 따라서, 광의 제거, 즉 이를 증가시키므로써, 막내의 열 반응을 개시시켜 재물 막을 생성하는 것이 가능하다. 또한 대기의 조성을 바꾸어 재물 막의 조성 또는 성질을 바꾸는 것이 바람직할 수 있다. 예를 들어, 동 복합체의 노출로 공기 또는 산소 분위기에서 동 산화물이 형성되게 된다. 대기로부터 산소를 가성적으로 제거하므로써, 주로 감소된 동 종류를 구비하는 막이 형성될 수 있다. 예를 들어, 만일 변환된 전구체가 유전체 막이거나, 또는 수소와 같은 환원하는 기체의 존재시 만일 변환된 전구체가 금속 막일 때, 부분적인 변환 또는 변환 단계는 바람직하게 산소의 존재 시에 수행된다. 부수적으로, 막 내의 수분의 양은 대기의 습도를 바꿈으로써 변경될 수 있다.

또한 '기판 전처리'라고 하는, 부분적인 변환 단계, 또는 연속적으로 서로 다른 변환 단계들의 사용은, 예

를 들어 기관 상의 전구체가 스텝퍼와 같은 값어치 비싼 장치에 노출될 필요가 있는 시간을 최소화시키기 위해 공정 흐름 관점에서 바람직할 수 있다.

증착된 전구체의 적어도 부분적인 변환 후에, 전구체는 선택적으로 변환되지 않은 전구체 층의 적어도 일부를 제거하기 전에 기술분야에 공지된 다양한 방법에 의해 처리될 수 있다. 이들 방법은 열, 레이저 또는 플라즈마 어닐링 단계, 특정 분위기에의 노출, 즉 산화 또는 환원, 이온 주입, 마이크로웨이브 처리 및 전자 빔 처리와 같은 열처리를 포함하지만 이에 한정되지 않는다. 만일 적어도 부분적인 변환 영역(들)이 전구체의 변환되지 않은 영역(들)에 대해 무전해 도금 핵 사이트로서의 역할을 할 수 있다면, 이때 선택적인 도금 단계가 이 단계에서 사용될 수 있다.

다음에, 증착된 막의 노출되지 않은 영역, 또는 그 일부는 제거 (또는 현상) 수단에 제거될 수 있다. 예를 들어, 현상 수단은 퍼들(puddle) 현상 또는 침전 습식 현상 공정에서 액체 또는 용액으로서 도포될 수 있는 현상제 화합물을 구비할 수 있다. 선택적으로, 반도체 업계에 의해 종래에 사용되는 건식 패터닝 단계와 유사한 건식 현상 공정이 현상 수단으로서 이용될 수 있다. 바람직한 제거 수단은 스프레이 현상, 퍼들 현상, 및 침전 습식 현상을 포함한다.

현상제는 용해도 차이가 노출되고 노출되지 않은 막의 영역 사이에 존재하도록 하는 조건하에 정형화되거나/되거나 사용되어야 한다. 이 용해도 차이는 기관 상에 남는 것이 필요한 영역들이 실질적으로 그대로 유지되는 동안 막의 임의의 선택된 영역들이 현상제에 의해 실질적으로 제거되도록, 막의 선택된 영역들을 제거하는데 사용된다. 현상제의 정형화를 최적화시키기 위해 상당한 실험이 필요할 수 있다. 예를 들어, 입사 에너지에 노출된 영역들이 기관 상에 남는 것이 필요한 공정에서, 입사 특성에의 노출 후에 막을 현상하기 위해 캐스팅 용제(casting solvent)를 사용하는 것은 너무 자극적이다. (a) 캐스팅 용제가 혼합될 수 있고 (b) 막의 노출되지 않은 영역이 결핍되게(반드시 완전하지 않음) 용해될 수 있고, (c) 막의 노출된 영역들이 실질적으로 용해될 없는 다른 액체에서 캐스트 용제의 희석 용액은 개선된 현상 공정을 제공한다.

예를 들어, 본 발명의 바람직한 한 실시예에서, 비정질 막은 케톤 용액(ketone solution)으로부터 캐스트될 수 있다. 현상제로서 케톤 만의 사용 또는 알콜과 케톤의 케톤이 풍부한 혼합물, 즉 케톤이 50vol.% 이상인 혼합물은, 알콜이 주 성분일 때 덜 효과적인 현상 공정의 결과가 된다. 예를 들어, 10:1(vol/vol) IPA:MeBK 용액은 MeBK 또는 1:1(vol/vol) IPA:MeBK 보다 BaxSryTizO3에 대해 보다 효과적인 현상제이다. 또한 10:1 혼합물은 20:1 IPA:MeBK보다 덜 효과적이다. 그러나, 10:1 및 20:1 용액 모두는 40:1(vol/vol) IPA:MeBK의 용액보다 효과적이다. 더욱이, 이들 용액의 상대적 효과는, 예를 들어 입사 복사의 종류 및 에너지, 코팅 및 패터닝 동안 기관의 온도를 포함하는 패터닝된 막의 형성에 이용되는 다른 공정에 크게 의존한다. 따라서, 본 발명을 위한 적합한 현상제 정형화의 결정은 실험을 필요로 하고, 기술분야의 숙련자에 명확하지 않다. 액체 및/또는 용액에 기초한 현상제는, 예를 들어 위에서 설명된 것과 같은 포토레지스트에 기초한 공정에 이용되는 현상 방법과 유사한 방식으로 물리적으로 도포될 수 있다.

현상 후에, 적어도 부분적으로 변환된 전구체는 선택적으로 변환 수단에 의해 처리되기 전에 기술분야에 공지된 다양한 방법에 의해 처리될 수 있다. 이들 방법은 열처리, 레이저 또는 플라즈마 열처리와 같은 열처리를 포함하지만 이에 한정되지 않는다. 이와 같은 열처리의 온도 및 시간은 중요한 변수이다. 열처리 단계는 또한, 시전 표면 처리, 예를 들어 산소 플라즈마, 레이저 또는 금속 열처리(RTA) 공정에 의해 영향을 받을 수 있다. 그 물리적 또는 전기적 성질이 바람직하게 변경되는 동안 열처리된 적어도 부분적으로 변환된 전구체가 그 비정질 성질을 유지하도록 적당한 조건을 선택하는 것이 가능하다. 선택적으로, 막이 그 결정 상태, 즉 고온으로 변환시키게 하는 열처리 조건은 막이 사용될 어플리케이션에 따라 바람직할 수 있다. 예를 들어, 이 단계에서의 적당한 열처리를 사용하여 전구체 또는 적어도 실질적으로 비정질인 적어도 부분적으로 변환된 전구체로부터 극단적으로 배향된 결정 막을 형성하는 것을 유도할 수 있다. 이와 같이, 비정질 막의 성질은 정밀하게 조정될 수 있거나 또는 그 물리적 성질은, 한 극단에서 완전히 비정질인 단계에서 반 결정 중간 위상을 거쳐 다른 극단에서 단일 배향 결정 위상까지의 광범위한 범위에 걸쳐 변환될 수 있다. 이와 같은 열처리는 흔히 전구체를 더욱 변환시키도록 작용할 것이다.

만일 전구체가 실질적으로 완전히 변환될 필요가 없다면, 다음에 전구체 막은, 전구체가 실질적으로 완전히 변환되도록 선택적으로 그러나 전형적으로 변환 수단에 의해 처리된다. 전구체 막의 전체 막 또는 선택된 영역들은 에너지원에 노출될 수 있다. 변환 수단은, 이전에 사용된 임의의 부분적인 변환 수단과 동일하거나 또는 동일할 수 있는 에너지원일 수 있다. 더욱이, 변환 수단은, 특정 파장의 광원, 특정 파장의 코히어런트 광원, 광대역 광원, 전자 빔 원 및/또는 이온 빔 원일 수 있다. 본 발명의 임의의 실시예에서, 에너지원 또는 에너지원의 적어도 일부는 이전에 설명한 바와 같이 표면 상의 이미지를 정의하는데 사용되는 광학 마스크를 통해 배향된다. 그러나, 에너지원은 마스크를 통과해서 배향될 필요는 없다. 예를 들어, 전구체가 이미 패터닝될 수 있고, 따라서, 플러드 또는 블랭킷 노광이 변환 수단으로서 사용될 수 있기 때문에, 변환 단계 동안 재료를 패터닝할 필요가 없을 수 있다. 바람직한 변환 수단은 광, 전자 빔, 이온 빔 및 열 처리를 포함한다. 부분적인 변환에 대해 설명한 바와 같이 그리고 또한 본 발명에 적용가능한 바와 같이, 증착된 막을 변환시키는, 분위기 조성, 전체 또는 부분적으로 압력, 및 습도와 같은 분위기가 조건은 중요한 공정 변수일 수 있다. 변환 동안 이들 변수는 임의의 이전의 부분적인 변환 단계에 사용된 그 설정과 동일하거나 다를 수 있다.

물론, 바람직한 박막으로서, 하드 마스크는 부분적으로 변환된 전구체 층의 적어도 한 일부를 실질적으로 완전히 변환시킴으로서 형성될 수 있다는 것을 알아야 한다. 여기서, '실질적으로 완전히 변환된 전구체', '완전히 변환된 전구체', '변환된 전구체', '실질적으로 완전히 변환된 부분적으로 변환된 전구체', '완전히 변환된 부분적으로 변환된 전구체' 및 '변환된 부분적으로 변환된 전구체'라는 용어는 모두 이와 같은 박막을 지칭한다.

전구체를 소정 재료의 막의 두께로 부분적으로 변환 및/또는 실질적으로 완전히 변환하는 공정 동안, 막의 일부 수축, 즉 소정 재료의 막의 두께가 변환되지 않은 전구체 막의 두께 미만일 수 있다는 것을 알아야 한다. 이와 같은 두께의 변화는 본 발명의 중요한 특징으로, 소정 재료의 막에 유용한 성질을 제공한다. 예를 들어, 극히 얇은 막의 형성은, 캐패시터를 최대화시키는 것과 관련하여 장점을 가질 수 있는 한편, 동시에 이와 같은 박막의 형성은 제조 관점으로 볼 때 힘들 것이다. 본 발명의 공정은, 비교적 두꺼운 캐스트

막(cast film)을 적용하는 능력을 제공하여, 보다 큰 재조를 제공할 뿐 아니라, 소정의 적어도 부분적으로 변환된 전구체 재료의 비교적 낮은 막을 제공하여 소정 재료의 막에 개선된 성질을 제공한다. 소정 막의 수축 성질은, 전구체의 선택, 용제의 선택 및 양, 전구체 첨가물의 종류, 증착 공정에 의해 결정되는 것으로서 전구체 막의 두께, 막의 패터닝 이전, 중간 및 이후에 열 처리의 사용, 및 노출된 막의 현상을 포함하는 공정 변수의 신중한 조절에 의해 목표로 하는 변수에 맞게 제어되고 맞추어질 수 있다. 본 발명의 공정은 용스트롬 범위에서 파라미터 범위에서 걸치는 전체 두께에 걸치는 소정 막의 정밀한 두께 제어를 가능하게 한다.

변환 후에, 후속하는 선택적 공정 단계는 위에 설명된 신규한 현상 방법, 및 후 현상 처리 단계를 포함하지만 이에 한정되지 않은, 후 변환 처리, 현상을 포함할 수 있다. 선택된 특정 단계는 제품의 궁극적인 사용에 따라 다를 수 있다. 예를 들어, 사용 방법은, 각각 본 발명의 참조로서 그 전문에 일체화된 미국 특허 제5,534,312, 5,821,017 및 6,071,676호에 개시되어 있다.

본 공정의 임의의 실시예에서, 변환 다음에는 주입 단계가 오는데, 여기서 적어도 하나의 주입된 영역이, 하드 마스크에 의해 실질적으로 덮이지 않은 기판의 적어도 일부 상에 주입 수단을 사용하여 기판에 형성된다. 주입 수단으로서 어온 빔의 사용은 기술분야에 공지되어 있다. 그러나, 본 공정은 어온 빔의 사용에 한정되지 않고, 임의의 효과적인 주입 방법이 사용될 수 있다. 주입에 적합한 이온들은 비소, 붕소 및 안을 포함하지만 이에 한정되지 않는다. 어온 주입은 고 에너지, 즉 저 도우즈(low dose), 즉 약 1020 atm/cm² 미만과 결합된 즉 약 300KeV 이상의 조건, 또는 저 에너지, 즉 고 도우즈, 즉 약 1020 atm/cm² 이상과 결합된 약 300KeV 미만의 조건 하에 실시될 수 있다. 선택적으로, 하드 마스크 층은 주입 후에 제거될 수 있다. 선택적으로, 주입된 기판은, 열처리와 같은 것에 의해 더 처리되어, 주입된 기판 영역을 도핑된 영역으로 변환할 수 있다. 만일 이들 선택적 단계의 모두가 수행되면, 이들이 수행되는 순서는 본 발명이 지향하는 특정 어플리케이션에 적합하도록 조정될 수 있다.

본 변환의 다른 실시예에서, 본 발명에 의해 형성된 적어도 부분적으로 변환된 전구체는 예정 레지스트 층으로서 작용한다. 예정 단계 또는 단계들에서, 플라즈마, 반응성 어온 또는 습식 예정 용액과 같은 예정 수단은 하드 마스크에 의해 제공된 패턴을 통해 기판의 선택된 영역에 접촉한다. 선택적으로, 실리콘 이산화물 및 실리콘 질화물과 같이 종래에 도포된 재료의 하드 마스크가 예정을 이용하는 전자 제조 공정에서 보호 마스크로서 사용된다.

본 변환의 바람직한 실시예에서, 본 공정에 의해 형성된 적어도 부분적으로 변환된 전구체 또는 하드 마스크는 예정 레지스트 층으로서 작용한다. 예정 단계 또는 단계들에서, 플라즈마, 반응성 어온 또는 습식 예정 용액과 같은 예정 수단은 즉 하드 마스크에 의해 제공되는 패턴을 통해 기판의 선택된 영역에 접촉하여, 소정의 영역만의 기판을 제거하게 된다. 현재, 실리콘 이산화물 및 실리콘 질화물과 같은 종래에 도포된 재료의 하드 마스크는 예정을 이용하는 전자 제조 공정에서 보호 마스크로서 사용된다.

도 2는 본 발명에 따른, 처리 이전에 단계(2A)에 도시된 바와 같이 기판(10) 상에 도전되는, 공정의 한 실시예에서 단계들, 즉 단계(2A, 2B, 2C 및 2D)의 기본적인 순서를 도시한다. 기판(10)은 예를 들어, 유기 층으로 코팅된 실리콘 웨이퍼일 수 있다. 단계(2B)에서, 변환되지 않은 전구체(11)가 기판(10)에 도포된다. 단계(2C)에서, 광화학 금속 유기 증착 공정 또는 열 또는 가열 처리에서 광과 같은 변환 수단이 변환되지 않은 전구체(11)의 적어도 한 선택된 부분에 도포되어, 변환된 전구체 층(12)을 형성한다. 단계(2D)에서, 현상제 화합물과 같은 제거 수단을 사용하여, 변환되지 않은 전구체 층(11)의 적어도 일부 및 바람직하게 실질적으로 모든 부분을 제거하여, 변환된 전구체(12)를 그대로 남김으로서 기판(10)을 위한 하드 마스크를 형성한다. 이와 같은 마스크는 임의의 패터닝 수단으로부터 임의의 다른 기판 영역을 마스크하거나 차단하면서 기판의 소정 영역을 통과할 수 있게 한다.

선택적으로, 도 2의 단계(2C)에서, 광 또는 열 또는 가열 처리와 같은 부분적인 변환 수단이 변환되지 않은 전구체(11)의 적어도 하나의 선택된 부분에 도포되어, 부분적으로 변환된 전구체 층(12)을 형성할 수 있다. 단계(2D)에서, 현상제 화합물과 같은 제거 수단을 사용하여 변환되지 않은 전구체 층(11)의 적어도 일부 바람직하게 모두를 제거하여, 부분적으로 변환된 전구체(12)를 그대로 남긴다. 부분적으로 변환된 전구체의 적어도 일부 상에 대해 도시되지 않은 광 또는 열 또는 가열 처리와 같은 변환 수단을 사용하여 그 부분을 실질적으로 제거하므로써, 하드 마스크를 형성한다. 부분적인 변환 수단은 변환 수단과 동일하거나 또는 다를 수 있다. 도 2는 본 발명의 공정에 의해 패턴화된 하드 마스크를 형성하는데 있어서 단계들의 경계성을 증명한다.

대조적으로 도 3은 패턴화된 하드 마스크를 형성하기 위한 종래 기술에 따른 제조 방법을 도시한다. 단계(3A)에서, 기판(200)이 도 2에 도시된 바와 같이 제공된다. 단계(3B)에서, 하드 마스크층(210)이 기판 상에 형성된다. 예를 들어, 하드 마스크 층(210)은 실리콘 산화물일 수 있다. 단계(3C)에서, 포토레지스트 층(220)은 하드 마스크 층(210)의 상부에 도포된다. 단계(3D)에서, 포토레지스트 층(220)은 마스크(235)를 통해 광선(230)에 노출된다. 마스크(235)는 광선에 대해 실질적으로 불투명한 영역(250)을 갖는 투명 유리 기판(240)을 구비하여, 광선의 일부를 차단하고 포토레지스트 층의 노출된 부분(22) 상에 패턴을 형성한다. 단계(3E)에서, 노출된 포토레지스트 영역(222)이 현상되어 하드 마스크 층(210)을 노출시킨다. 단계(3F)에서, 하드 마스크 층(210) 내에 적합한 예정 조성을 갖는 하드 마스크 층(210)의 보호되지 않은 부분을 예정하므로써 계구부(255)가 형성된다. 단계(3G)에서, 포토레지스트 층(220)의 나머지 부분이 제거된다. 단계(3H)에서, 하드 마스크 층(210)을 제외한 기판(200)을 예정하도록 선택된 플라즈마 예정 화학 처리(260)가 기판(200)을 패턴화한다. 따라서, 도 3으로부터 종래의 공정은 패턴화된 하드 마스크를 형성하기 위한, 즉 본 발명의 공정 보다 패턴화된 마스크를 통해 어온을 주입하기 위한 보다 많은 단계를 필요로 한다는 것을 알 수 있다.

도 4는 하드 마스크 예정과 연관된 단계들, 즉 상술된 단계(3C 내지 3G) 모두를 제거하는 패턴화된 하드 마스크를 형성하기 위해 금속 복합체를 사용하여 하드 마스크를 제조하는 것이 적용되는 본 발명의 바람직한 실시예를 도시한다. 단계(4A)에서, 기판(300)이 도 2에 도시된 바와 같이 제공된다. 단계(4B)에서, 금속 복합체를 포함하는 층과 같은 전구체 층(310)이 기판(300)의 상부에 형성된다. 단계(4C)에서, 전구체(310)는 부분적인 변환 수단, 마스크(320)를 통과하도록 배향된 본 발명에 설명되는 광선(315)에 노출된다. 마스크(320)는 부분적인 변환 수단에 실질적으로 불투명한 영역(340)을 갖는 투명 유리 기판(330)을

포함한다. 부분 변환 수단(315)에 노출된 전구체(310)의 일부가 적어도 부분적으로 변환되거나 반응되어 부분적으로 변환된 전구체(350)의 영역을 형성한다. 단계(40)에서, 조합체가 액체 현상제와 같은 제거 수단(도시되지 않음)에 노출된다. 실질적으로 변환되지 않은 전구체(310)는 현상제 또는 제거 수단에 의해 제거되어, 기판(300)을 노출시키는 한편, 부분 변환 전구체(350)는 제거 수단에 저항하여 그대로 남는다. 단계(4E)에서, 변환 수단(도시되지 않음)이 부분 변환 전구체(350)에 도포되어, 실질적으로 완전히 변환된 전구체(360), 즉 패턴화된 하드 마스크를 형성한다. 이 변환은 블랭킷 광 노출 단계 또는 열 또는 가열 열처리 단계에 의해 수행될 수 있다. 단계(4C 및 4E)의 각각에서, 변환은 바람직하게, 산소의 존재시에 변환된 전구체(360)가 유전체막일 때 또는 수소와 같은 환원 기체의 존재 시에, 변환된 전구체(360)가 금속막일 때 수행된다. 단계(4F)에서, 애칭 수단, 본 발명에서 하드 마스크 층(360)을 제외한 기판(300)을 애칭하도록 선택된 플라즈마 애칭 화학처리(370)는 기판(300)을 패턴화한다. 그 결과 패턴화된 피쳐(features)(390)가 단계(4C)에 도시된 바와 같이 정의되게 된다.

도 5는 예를 들어, 흔히 탑 실리레이션 이미징(top silylation imaging)이라고 하는 공정에 의해 포토레지스트에 TSI를 형성하는 종래 기술의 방법을 도시한다. 단계(5A)에서, 기판(400)이 제공된다. 단계(5B)에서, 기판(400)은 탑 실리레이션에 적합한 포토레지스트 층(410)으로 코팅된다. 단계(5C)에서, 포토레지스트 층(410)이 마스크(435)를 통해 광선(430)에 노출된다. 마스크(435)는 노출 수단에 실질적으로 불투명한 영역(450)을 갖는 투명 유리 기판(400)을 포함하여, 광선의 일부를 차단하고, 포토레지스트 층의 노출된 부분(432)에 패턴을 형성한다. 노출된 포토레지스트 영역(432)은 그 노광 결과로서 서로 소정의 소정의 화학 및/물리적 성질을 갖는다. 단계(5D)에서, 기판(400), 포토레지스트 층(410) 및 노출된 포토레지스트 영역(432)은, 노출된 포토레지스트 영역(432)에 선택적으로 흡수하는 거채상 TSI 레전트(reagent)(460)에 노출되어, 수정된 포토레지스트 표면(470)을 형성한다. 기술분야에 공지된 TSI 레전트(460)의 예는 실리콘 함유 기체를 포함한다.

단계(5E)에서, 표면이 플라즈마 처리(480)에 노출되어, 수정된 포토레지스트 표면(470)을 화학적으로 불활성으로 만들어, 레지스트 하드 마스크 표면(490) 바로 밑의 나머지 포토레지스트(410)을 제거한다. 단계(5F)에서, 플라즈마 처리(497)를 이용하여, 포토레지스트 층(410), 수정된 포토레지스트 표면(470) 및 레지스트 하드 마스크 표면(490)으로 형성된 복합체 스택(complex stack)을 이용하여 기판(400)을 패턴화하여, 기판(400)으로 전사된 패턴을 정의한다. 결과로 나타나는 패턴이 단계(5H)에서 애칭된 영역(499)로 도시된다. 단계(5I)에서, 제거 수단(도시되지 않음)을 이용하여 포토레지스트 층(410), 수정된 포토레지스트 표면(470) 및 레지스트 하드 마스크 표면(490)으로 형성된 복합체 스택을 제거한다. 비록 도 5에 도시된 방법이 없어질 수 있는 해상도를 개선하고 초점 깊이 조건의 변화를 돕는 패턴링을 위한 얇은 표면 층을 형성하는 장점을 제공하지만, 이는 TSI 레전트(460)를 필요로 하고, 다수의 플라즈마 열처리 단계를 필요로 하고, 다른 종래의 기법에 제시되지 않는 패턴 전사에서 부수적인 비용 및 복잡성을 제공하는 단점이 있다.

여와 대조적으로, 도 6은 금속 복합체 전구체를 사용하여 패턴화된 얇은 상면을 형성하는 TSI에 적용되는 본 발명에 따른 공정의 바람직한 실시예를 도시한다. 단계(6A)에서, 패턴 전사층(505)로 코팅된 기판(500)이 제공된다. 패턴 전사층(505)은 포토레지스트, 폴리이미드, PMMA, Novolac, 애폭시, 및 기술분야에 공지된 다른 유기 또는 관련된 코팅을 포함하는 유기 막 형성 수지를 선택적으로 구비할 수 있다. 단계(6B)에서, 전구체 층(510)이 기판(500)의 상부 및 패턴 전사층(505)의 바로 위에 형성된다. 이 경우, 전구체(510)는 금속 복합체를 구비한다. 단계(6C)에서, 전구체(510)는 부분 변환 수단, 마스크(520)를 통과하도록 배향된 본 발명에 도시된 광선(510)에 노출된다. 마스크(520)는 본 발명에서 유리로서 예시된, 부분적으로 변환되지 않은 전구체(510)는 제거 수단, 즉 현상제에 의해 제거되어, 패턴 전사 층(505)을 노출시키는 한편, 부분적으로 변환된 부분 변환 전구체(550)는 제거 수단에 저항하여 그대로 남는다. 선택적인 단계(6E)에서, 변환 수단(도시되지 않음)이 부분 변환 전구체(550)에 도포되어, 실질적으로 완전히 변환된 전구체(560)를 형성한다. 이와 같은 변환은, 즉 블랭킷 광 노출 단계 또는 열 또는 가열 열처리 단계에 의해 수행될 수 있다.

단계(6F)에서, 표면이, 예시된 플라즈마 애칭 화학 처리와 같은 애칭 수단(570)에 노출된다. 예를 들어, 플라즈마 애칭 수단은 반드시 산소를 구비한다. 애칭 수단은 패턴 전사 층(505)의 노출된 영역을 제거하는 한편, 부분적으로 변환되거나 실질적으로 완전히 변환된 전구체 층(560)이 선택되어 애칭 수단(570)을 향해 실질적으로 불활성하는 방식으로 처리되어, 애칭된 영역(580)이 형성되게 된다. 단계(6G)에서, 기판(500)의 후속하는 패턴링(도시되지 않음)이, 적어도 부분 변환 전구체(560) 밑의 패턴 전사 층(505)에 형성된 패턴을 이용하여 애칭 수단에 의해 실시되어, 애칭된 영역(580)을 형성한다. 단계(6H)에서, 제거 수단(도시되지 않음)은 나머지 패턴 전사 층(505) 및 적어도 부분 변환 전구체(560) 모두를 제거하여, 애칭된 영역(590)을 갖는 소정의 패턴화된 기판(500)을 노출시킨다. 도 6의 방법은, 적은 단계, 적은 플라즈마 단계를 필요로 하고, 어떠한 TSI 레전트를 필요로 하지 않기 때문에 도 5에 도시된 방법보다 우수하다. 동시에, 도 6의 방법은 도 5의 방법을 이용함으로써 제공되는 모든 장점을 얻는다.

도 7은 기판 상부에 패턴화된 금속층을 증착하는 종래 기술의 방법을 도시한다. 이 방법은, 소정의 금속이 애칭되기 힘든, 즉 금 또는 플래티넘일 때 종래에 이용되나, 단계(7A)에서, 기판(600)이 제공된다. 단계(7B)에서, 릴리스 층(release layer)(605)이 기판(600) 상부에 코팅되고, 릴리스 층(605)의 상부에 리프트오프 층(liftoff layer)(610)이 도포된다. 단계(7C)에서, 선택적인 하드 마스크 층(620)이 리프트오프 층(610)의 상부에 증착된다. 단계(7D)에서, 포토레지스트 층(630)이 선택적 하드 마스크 층(620), 리프트오프 층(610) 및 릴리스 층(605)으로 구성된 복합체 스택의 상부에 도포된다. 단계(7E)에서, 포토레지스트 층(630)이 마스크(635)를 통해 광선(645)에 노출된다. 마스크(635)는 노광 수단에 실질적으로 불투명한 영역(650)을 갖는 투명 유리 기판(640)을 구비하여, 광선의 일부를 차단하고 포토레지스트 층의 노출된 부분(632) 상에 패턴을 형성한다. 단계(7F)에서, 습식 현상제와 같은 제거 수단이 도포되어 포토레지스트 층(630) 내의 노출된 부분(632)을 제거한다.

단계(7G)에서, 플라즈마 애칭 화학 처리(660)를 사용하여, 존재하는 선택적 하드 마스크 층(620)을 애칭한

다. 플라즈마 예칭 화학 처리(660)는 또한 포토레지스트 층(630)의 두께의 실질적인 부분을 침식하는 효과를 가질 수 있다. 단계(74)에서, 플라즈마 예칭 화학 처리(670)를 사용하여 리프트오프 층(610) 및 릴리스 층(605)을 에칭한다. 이 단계 동안 바람직하게 플라즈마 내의 충전된 종류가 주로 수직 방향으로 이동하도록 플라즈마 예칭 화학 처리(670)를 이방성 모드로 이용한 다음, 에칭을 담당하는 플라즈마 내의 대전된 종류가 균일하게 모든 방향으로 이동하게 하는 등방성 모드로 전환함으로써 도 7H에 도시된 바와 같이 굴곡된 측벽을 생성하는 것이 가능하다. 이와 같은 조작의 결과가 단계(7H)에 도시되어 있다. 단계(71)에서, 증착 수단을 이용하여 소정의 금속(680)(즉, 금, 플래티넘 또는 다른 소정의 금속)으로 표면의 파지를 덮는다. 단계(7J)에서, 제거 수단(도시되지 않음)을 이용하여 용제 처리에 의해 나머지 릴리스 층(605), 리프트오프 층(610), 하드 마스크 층(620)(만일 존재하면) 및 포토레지스트 층(630) 모두를 리프트 오프한다. 따라서 기판(600) 상에 소정 금속(680)의 소정 패턴만이 남게 된다. 패턴화된 금속 증착의 이와 같은 방법은, 많은 단계를 포함하고 포토레지스트의 두꺼운 층의 사용을 필요로 하기 때문에 힘들다. 이와 같이 두꺼운 층들은, 값비싼 포토레지스트의 바람직한 양 이상의 양이 소비될 것을 필요로 한다. 또한, 포토레지스트의 제거는 다른 경우보다 그 극한 두께에 의해 보다 힘들게 된다.

도 8은 금속 복합체 전구체를 사용하여 패턴화된 얇은 상부면을 리프트오프 층 위에 형성하기 위한 리프트오프 공정에 적용되는 본 발명에 따른 바람직한 실시예를 도시한다. 단계(8A)에서, 기판(700)이 제공된다. 단계(8B)에서, 기판(700)이 릴리스 층(705)로 코팅되고, 릴리스 층(705)이 리프트오프 층(710)으로 코팅된다. 단계(8C)에서, 전구체 층(720)이 리프트오프 층(710) 위에 코팅된다. 이 경우에, 전구체 층(720)은 금속 복합체를 구비한다. 단계(8D)에서, 전구체(720)가 본 발명에서 광선(745)으로 예시되고 마스크(735)를 통과하는 것으로 배향된 부분 변환 수단(740)에 노출된다. 마스크(735)는 부분 변환 수단(740)에 실질적으로 불투명한 영역(735)을 갖는 투명 유리 기판(740)을 포함한다. 부분 변환 수단(745)에 노출된 전구체(720)의 부분이 적어도 부분적으로 변환되거나 반응되어, 부분 변환 전구체(732)의 영역을 형성한다. 단계(8E)에서, 조립체가 액체 현상제와 같은 제거 수단(도시되지 않음)에 노출된다. 실질적으로 변환되지 않은 전구체(720)는 현상제 또는 제거 수단에 의해 제거되어, 리프트오프 층(710)을 노출시키는 한편, 부분적으로 변환된 부분 변환 전구체(732)는 제거 수단에 저항하여 그대로 남는다. 선택적인 단계(도시되지 않음)에서, 변환 수단(도시되지 않음)이 부분 변환 전구체(732)에 도포되어, 실질적으로 완전히 변환된 전구체를 형성한다.

단계(8F)에서, 제거 수단(760)은 예를 들어, 플라즈마 예칭 화학처리가 이방성 모드로 이용되어, 리프트오프 층(710) 및 하부의 전구체(732)가 아닌 하부의 릴리스 층(705)의 그와 같은 영역을 제거한다. 단계(8G)에서, 도시된 바와 같이 리프트오프 곡선 프로파일은, 제거 수단(760)으로 하여금 리프트오프 층(710) 및 릴리스 층(705)을 이방성으로 에칭하게 하므로써 형성된다. 단계(8H)에서, 소정 금속(770)의 얇은 부분은, 현상 수단, 예를 들어, 용제 또는 건식 현상 공정에 의해 전구체(732), 리프트오프 층(710) 및 릴리스 층(705)과 함께 제거되어, 기판(710)의 상부에 소정의 금속(770)의 소정 패턴을 뒤에 남는다. 이 방법은 적은 공정 단계를 필요로 하고 포토레지스트의 사용을 필요로 하지 않기 때문에 도 7에서 얻어지는 종래 기술의 방법에 비해 바람직하다.

도 9는 금속 복합체 전구체를 이용하여 리프트오프 층 위에 패턴화된 얇은 상면막을 형성하는 리프트오프 공정에 적용되는 본 발명의 바람직한 다른 실시예를 도시한다. 단계(9A)에서, 기판(800)이 제공된다. 단계(9B)에서, 전구체 층(810)이 기판(800) 위에 코팅된다. 이 경우, 전구체(810)는 금속 복합체를 구비한다. 단계(9C)에서, 전구체 층(810)은 부분 변환 수단, 여기서 예시되고 마스크(835)를 통과하도록 배향된 광선(845)에 노출된다. 마스크(835)는 부분 변환 수단(845)에 실질적으로 불투명한 영역(850)을 갖는 투명 유리 기판(840)을 구비한다. 부분 변환 수단(845)에 노출된 전구체(810)의 부분은 적어도 부분적으로 변환되거나 반응되어 노출된 영역(845)의 영역을 형성한다. 단계(9D)에서, 조립체가 액체 현상제와 같은 제거 수단(도시되지 않음)에 노출된다. 실질적으로 변환되지 않은 전구체(810)는 제거 수단에 의해 제거되어, 기판(800)을 노출시키는 한편, 부분적으로 변환된 노출된 영역(832)은 제거 수단에 저항하여 그대로 남는다. 선택적으로, 본 발명의 다른 바람직한 실시예에서 설명된 바와 같이, 노출된 영역(832)은 제거 수단 단계(9D) 이후에 추가적으로 변환될 수 있다. 노출된 영역(832)에 제시된 안쪽으로 테이퍼진 측벽 프로파일은 단계(9D)에 도시된 바와 같이, 각각 즉 단계(8D, 8F 및 8G)에서 설명된 바와 같이 노광 및 단계(9C 및 9D)에서 표현된 제거 수단을 적절히 제어함으로써 얻어진다. 단계(9E)에서, 소정의 금속(870) 막이 조립체 위에 증착 수단에 의해 증착된다. 단계(9F)에서, 소정 금속(870)의 얇은 부분은 현상 수단, 예를 들어 용제 또는 건식 현상 공정에 의해 전구체(832)와 함께 제거되어, 기판(800)의 상부에 금속(870)의 소정의 패턴을 남긴다.

본 공정의 다른 바람직한 실시예에서, TSI 층 집적의 사용은 반도체 상호접속부 구조내에 동 집적을 위한 여중 다마신 아커막적을 구성하는데 사용될 수 있다. 도 10의 단계(A 내지 H)는 '바아-퍼스트(via-first)' 방법이라고 하는 다마신 아커막적을 구성하는 종래 기술의 방법을 도시한다. 단계(10A)에서, 표시된 바와 같이, 제1 유전체 층(905), 장벽층(910), 제2 유전체 층(910) 및 하드 마스크(920)으로 연속적으로 코팅된 기판(900)이 제공된다. 유전체 층(905, 910)은 흔히 그러나 반드시 동일한 재료가 아닌 한편, 장벽 및 하드 마스크 층(915, 920)은 동일한 재료이거나 동일한 재료일 수 없지만, 흔히 실리콘 질화물 및/또는 실리콘 산화물이다. 단계(10B)에서, 조립체가 바닥 반반사 코팅(bottom anti-reflective-coating)(BARC)(925) 및 포토레지스트 층(930)과 함께 하드 마스크(920) 위에 코팅된다. 도시된 바와 같이, 포토레지스트 층은 종래 방법에 의해 현상되고 패턴화된다. 단계(10C)에서, 플라즈마 예칭 화학 처리를 사용하여 BARC 층(925), 하드 마스크(920), 유전체 층(910), 장벽층(915), 및 유전체 층(925)의 표시된 부분을 제거한다. 단계(10D)에서, 나머지 포토레지스트(920) 및 BARC(925)이 단계(10C)의 플라즈마 공정 다음에 조립체로부터 제거된다. 단계(10E)에서, 제2 BARC 층(935) 및 제2 포토레지스트 층(940)이 도포되어 하드 마스크(920) 상부에 조립하고, 도시된 바와 같이, 포토레지스트 층(940)은 종래 방법에 의해 현상되고 패턴화된다. 단계(10F)에서, 제2 플라즈마 예칭 화학 처리 단계를 사용하여 BARC 층(935) 및 유전체 층(910)의 표시된 부분을 제거한다. 단계(10G)에서, 단계(10F)의 플라즈마 공정 다음에, 나머지 포토레지스트(940) 및 BARC(935)가 제거된다.

이와 대조적으로, 도 11은 본 발명의 공정이 많이 적은 공정 단계로서 어떻게 여중 다마신 아커막적의 조립을 달성하는지를 도시한다. 단계(11A)에서, 유전체 층(1005)로 코팅된 기판(1000)이 제공된다. 단계

(11B)에서, 금속 복합체를 구비하는 전구체 층 유전체 층의 상부에 도포되고, 적어도 부분적인 변환에 의해 패터닝된 다음, 본 발명의 다른 실시예에서 이전에 설명한 것과 같은 기술에 의해 형성되어, 도시된 바와 같이 패턴화 층(1010)을 만든다. 예를 들어, 패턴 형성 단계는 이전에 설명한 바와 같이, 용해 또는 건식 현상 공정에 의해 수행될 수 있다. 다음에 스핀 평탄화 층(1015)이 패턴화 층(1010) 상에 도포된다. 스핀 평탄화 층(spin planarization layer)(1015)은 조립체에 대해 스핀될 수 있는 임의의 유기물에 기초한 코팅일 수 있다. 단계(11C)에서, 제2 패턴화 층(1020)이 패턴화 층(1010)의 형성에 이용된 것과 동일한 기술을 사용하여, 증착되고, 패턴화되고 현상된다. 단계(11D)에서, 플라즈마 에칭 화학처리와 같은 에칭 수단(도시되지 않음)을 이용하여 스핀 평탄화 층(1015)의 도시된 영역 및 유전체 층(1005)의 두께의 부분을 제거한다. 도시된 바와 같이, 유전체 층(1005)의 두께의 부분만이 제거되도록 에칭 수단을 제어하는 것이 중요하다. 예를 들어, 전체 유전체 층 두께를 통해 에칭하는데 필요할 만한 시간에 한정된 플라즈마 에칭 노광이 사용될 수 있다.

단계(11E)에서, 패턴화 층(1020) 및 스핀 평탄화 층(1015)은, 스핀 평탄화 층(1015)가 용해가능하고 조립체의 다른 부분에 큰 영향력을 주지 않는 조립체의 처리와 같은 제거 수단에 의해 제거된다. 단계(11F)에서, 이전에 설명한 플라즈마 에칭 화학처리와 같은 제어되는 에칭 수단(도시되지 않음)을 이용하여 유전체 층(1005)의 도시된 영역을 제거한다. 이 제어되는 에칭은 패턴화 층(1020)에 의해 형성된 패턴에서 유전체 층(1005)의 나머지 두께를 동시에 제거하지만, 패턴화 층(1010)에 의해 형성된 패턴에서 유전체 층(1005)의 두께의 일부만을 제거한다. 이중 다마신 물드가 이와 같이 조립될 수 있다.

패턴화 층(1010)은 선택적으로 다음 단계(11F)(도시되지 않음) 다음에 제거될 수 있는데, 선택적으로 본 발명의 다른 실시예에서, 패턴화 층(1010)은 동 증착 및 평탄화 다음에 CMP 절차로서 이용되도록 남는다.

도 11에 도시된 공정은, 많은 적은 공정 단계를 포함하고, 다수의 포토레지스트 및 BARC 단계를 필요로 하지 않으며, 종래의 공정에서 이용된 장비 및 하드 마스크의 필요성을 없앴다는 점에서 도 10에 도시된 종래 기술의 방법에 비해 뛰어나다.

도 12는 패턴화된 아연 주입 하드를 형성하기 위한 종래 기술의 방법에 의해 이용되는 아연을 주입하기 위한 복잡한 방법을 도시한다. 단계(12A)에서, 도 2에 도시된 바와 같이 기판(1200)이 제공된다. 단계(12B)에서, 선택적인 보호층(1205)은 주입 마스크 층(1210) 다음에 기판(1200) 상에 형성된다. 한 예에서, 주입 마스크 층(1210)은 실리콘 산화물이다. 단계(12C)에서, 포토레지스트 층(1220)이 주입 마스크 층(1210)의 상부의 기판(1200)에 도포된다. 단계(12D)에서, 포토레지스트 층(1220)이 마스크(1235)를 통해 광선(1230)에 노출된다. 마스크(1235)는 노광 수단(1250)에 실질적으로 불투명한 영역을 갖는 투명 유리 기판(1240)을 구비하여, 광선의 일부를 차단하고, 포토레지스트 층의 노출된 부분(1222) 상의 패턴을 형성한다. 단계(12E)에서, 노출된 포토레지스트 영역(1222)이 현상되어 주입 마스크 층(1210)을 노출시킨다. 단계(12F)에서, 적합한 에칭 조성에 의해 주입마스크 층(1210)의 보호되지 않은 부분을 에칭하여 주입 마스크 층(1210)에 개구부(1255)를 형성한다. 단계(12G)에서, 포토레지스트 층(1220)의 나머지 부분이 제거된다. 단계(12H)에서, 주입 마스크 내의 개구부(1255) 바로 밑에 주입된 영역(1270)을 형성하기 위해 기판(1200)이 아연 밤(1260)에 노출된다. 선택적인 단계(12I)에서, 주입 마스크 층(1210)이 제거되고, 기판이 열처리되어, 주입된 영역(1270)을 도핑된 영역(1280)으로 변환시킨다. 따라서, 도 12로부터 종래의 공정은 본 발명의 공정보다도, 패턴화된 주입 마스크를 형성, 즉 패턴화된 마스크를 통해 아연을 주입하기 위한 많은 단계를 필요로 한다는 것을 알 수 있다.

이와 대조적으로, 도 13은 주입 마스크 에칭과 연관된 모든 단계들, 즉 위에 설명된 단계(12C 내지 12G) 모두를 제거하는 패턴화된 주입 마스크를 형성하기 위해 금속 복합체 전구체를 이용하는 아연 주입 하드 마스크를 제조하는데 적용되는, 본 발명의 다른 일 실시예를 도시한다. 단계(13A)에서, 기판(1300)이 제공된다. 단계(13B)에서, 선택적 보호층(1312)이 기판(1300) 상에 형성되고, 전구체(1310)의 층이 보호층(1312)의 상부에 형성된다. 이 경우, 전구체(1310)는 금속 복합체이다. 단계(13C)에서, 전구체(1310)는 부분 변환 수단, 즉 마스크(1310)를 통과하도록 배향된 광선(1315)에 노출된다. 마스크(1320)는 부분 변환 수단에 실질적으로 불투명한 영역(1340)을 갖는 투명 유리 기판(1330)을 포함한다. 부분 변환 수단(1315)에 노출된 전구체(1310)의 부분은 적어도 부분적으로 변환되거나 반응되어 부분 변환 전구체(1350)의 영역을 형성한다. 단계(13D)에서, 조립체가 액체 현상제와 같은 제거 수단(도시되지 않음)에 노출된다. 변환되지 않은 전구체(1310)는 현상제 또는 제거 수단에 의해 제거되어, 보호층(1312)을 노출시키는 한편, 부분적으로 변환된 부분 변환 전구체(1332)는 제거 수단에 저항하여 그대로 남는다. 단계(13E)에서, 변환 수단(도시되지 않음)이 부분 변환 전구체(1350)에 도포되어 실질적으로 완전히 변환된 전구체(1360)를 형성한다. 이와 같은 변환은 불렛 노광 단계 또는 열 처리 단계에 의해 수행될 수 있다. 단계(13C 내지 13E)의 각각에서, 바람직하게 산소의 존재시 변환된 전구체(1360)이 유전체막일 때 변환이 수행되거나, 또는 수소와 같은 환원 가스의 존재 시에는 변환된 전구체(1360)이 금속막일 때 변환이 수행된다. 단계(13E)에서, 기판에 주입된 영역(1380)을 형성하기 위해 기판(1300)이 아연 밤(1370)과 같은 주입 수단에 의해 처리된다. 선택적인 단계(13G)에서, 주입 마스크가 제거되고, 주입된 영역(1370)을 기판내의 도핑된 영역(1390)으로 변환하기 위해 열처리 공정이 수행된다.

본 발명의 공정의 광범위한 범위는 광범위한 가능한 어플리케이션을 가능하게 한다. 본 발명의 바람직한 실시예는 인쇄 와이어 기판(printed wire board)('PWB') 내의 통합 캐패시터 구조를 형성하는데 사용되는 비정질 금속 산화막을 구비하는데, 여기서, PWB 기판은 적합한 전구체 용액을 사용하여 본 발명의 다른 공정에 의해 코팅되고 직접 어마지화된다. 본 발명의 장점은, 다른 공정 단계의 직접적인 어마지 및 연관된 제거 능력, PWB 공정에 필요한 분위기 온도 및 압력의 사용, 및 수작가능한 높은 캐패시턴스를 갖는 막의 형성을 포함한다.

다른 바람직한 실시예에서, 패턴화된 금속 산화물 또는 합성 금속 산화막은, 본 공정에 의해 투명 기판 상에 불투명한 패턴으로 형성된다. 이와 같은 실시는 반도체 제조 공정 동안 패턴의 리소그래픽 전사를 위한 패턴된 마스크로서 사용될 수 있다.

본 발명의 또 다른 바람직한 실시예에서, 비정질 금속 산화물 또는 합성 금속 산화막을 사용하여, 수정된 실리콘 기판이 적당한 전구체 용액을 이용한 본 발명에 따른 공정에 의해 코팅되고 직접 어마지화되는, 개선된 상호접속 반도체 장치의 상호접속 레벨 내에서 디커플링(decoupling) 캐패시터 구조를 형성한다. 본

로를 형성하기 위해 전구체의 액상 침투 및 후속하는 열 변환; 폴리머 용액에의 첨가물을 사용하여 나노 합성물을 형성함으로써 결과로 나타나는 재료의 물리적, 화학적, 광학적 및 전기적 성질을 변화시킴; 위에 언급된 공정으로부터 VOC 방출을 감소시키기 위해 수분 용해 전구체의 합성 및 형성; 게이트 전극 재료: 평판 패널 디스플레이; FeRAM; 직접-기록 재료; 마이크로유체; 마스크 및 도파관을 포함한다.

전자 재료의 제조를 위한 공정의 부수적인 설명은 본 개시가 본 발명의 참조로서 일체화된 'Method of And Apparatus for Substrate Pretreatment'라는 제목의 현재 출원중인 미국특허출원 제.09/.....에 설명된 것을 포함한다.

예

다음 예는 본 발명의 임의의 실시예들을 더 예시한다. 이들 예는 예시적인 목적으로 제시되며, 어떤 경우 예는 본 발명의 범위를 제한하지 않는다.

예 1

서로 다른 지르코늄-함유 전구체, $Zr(\text{아세틸아세톤})_4$, (또한 $Zr(\text{acac})_4$, 테트라키스(tetrakis(2,4-펜타네디오네이트(pentanedionate)지르코늄(IV) 및 $Zr(\text{카르복시레이트})_4$ 라고도 함)의 두 막이, 적당한 용매에 용해시켜 실리콘 웨이퍼의 표면 상에 용액을 스핀 코팅함으로써 캐스트된다. 각각은 전구체 막 두께에 어떠한 추가적인 변화도 없을 때까지 연장된 불렛 열 처리된다. 이 처리 다음에, 각 샘플의 굴절률이 가변 각도 스펙트로스코프 일립소메트리(variable angle spectroscopic ellipsometry)('VASE')를 사용하여 파장의 함수로서 측정된다. 그 결과가 도 14에 도시된다. 도 14에서, 라인(101)은 $Zr(\text{acac})_4$ 전구체로 형성된 샘플로부터 인한 것이고, 라인(102)는 $Zr(\text{acac})_4$ 전구체로 형성된 샘플로부터 인한 것이다. 이들 결과는 전구체의 화학적 조성에 직접 관련된 샘플들의 각각에 대한 굴절을 성질에 큰 차이가 있다는 것을 증명한다. $Zr(\text{acac})_4$ 전구체는 $Zr(\text{카르복시레이트})$ 로 형성된 막보다 약 3% 이상의 굴절률을 갖는 막을 형성한다.

예 2

먼저 두 개의 서로 다른 동 전구체가 준비된다: $\text{Cu}_2(\text{OH}_2)_2(\text{O}_2\text{C}(\text{CH}_2)_4\text{CH}_3)_4$ 및 $(\mu-(\text{C}_2\text{H}_5)_2\text{NCH}_2\text{CH}_2\text{O})_2\text{Cu}_2(\text{N}_3)_2$. 각각의 전구체는 광화학 처리되어, 리간드의 손실 및 동 원자를 만들게 된다. 동 원자들은 상호 각각 결합되어 동 금속을 만들거나 또는 산소화 결합하여 동 산화물을 형성하지만, 산화물의 형성은 또한 먼저 형성된 동 금속의 산화결과로서 발생할 수 있다. 종래 기술의 화학에 기초하여, 막 형성 성질 및 반응의 효율이 전구체의 선택의 결과로서 광범위하게 변할 수 있지만, 이들 서로 다른 전구체가 유사한 반응 조건 하에 서로 다른 재료를 제공할 것이라고 가정하는 이유가 없다.

따라서, 이들 두 개의 전구체의 각각이 용해되고, 각각의 용액이 스핀 코팅에 의해 실리콘 칩에 증착되며, 코팅된 칩의 각각 위의 전구체 층이 진공하에서 광과 광분해함으로써 실질적으로 완전히 변환되었다. 광분해는 리간드와 연관된 어떠한 흡수도 막의 FTIR 스펙트럼에 관찰되지 않을 때까지 계속되었다. 다음에 샘플들은 노로 보내져 약 400°C의 온도하에 가열되었다.

다음에, 각각의 샘플은 공지된 광학 x선 회절 방법에 의해 조사되었다. $\text{Cu}_2(\text{OH}_2)_2(\text{O}_2\text{C}(\text{CH}_2)_4\text{CH}_3)_4$ 전구체는 변환 후에 하나 이상의 동 산화물을 만들든 반면, $(\mu-(\text{C}_2\text{H}_5)_2\text{NCH}_2\text{CH}_2\text{O})_2\text{Cu}_2(\text{N}_3)_2$ 전구체는 보다 많은 결정 금속 동을 만든 것을 알았다. 이들 결과는 공정의 의존성, 즉 변환후에 거울에 의해 이전에 가정되지 않은 방식으로 전구체 조성에 의존한다는 것을 증명한다.

소정의 전구체 재료의 막을 열 또는 광분해 공정에 의해 비정질 막으로 변환시키는 방법은, 막의 성질에 큰 충격을 줄 수 있다. 이는 광학 굴절률을 요약하는 데이터에 도시되어 있고, 또한 예 3 및 4에 도시된 바와 같이, 유전상수의 비교에 의해 명확히 증명된다.

예 3

Chaemat Technology, Inc.에 의한 $Zr(\text{acac})_4$ (지르코늄(IV) 아세틸아세톤은 톨로엔에 용해되고, 이 용액은 30 초 동안 1250rpm으로 실리콘 웨이퍼 상에서 스핀되었다. 결과로 나타나는 변환되지 않은 전구체 막은 436Å의 두께를 가졌다. ZrO_2 로의 열 변환이 1 시간 동안 180°C에서 핫 플레이트(hot plate) 상에서 수행되었다. 연장된 열 변환이 180°C로 핫 플레이트 상에서 수행되었다. ZrO_2 로의 광화학 변환이 220nm 쿨드 미러(cold mirror)를 갖는 Karl Suss MJB-3 마스크 정렬기를 사용하여 수행되었다. 깊은 UV($\text{dir } 0.38\text{mW/cm}^2$)에서 마스크 정렬기의 저 강도 출력으로 인해, 부수적인 노광이 추가적인 두께 강소를 초래하는 도우즈인 것으로 밝혀졌기 때문에 5 시간의 노광 시간이 사용되었다. 두께 및 굴절률의 결과로 나타나는 막에 대한 파장의 함수로 VASE를 사용하여 측정되었다. 이들 막의 측정된 두께는 다음과 같다:

변환되지 않은 $Zr(\text{acac})_4$ 전구체 436Å

열적으로 변환된360Å

연장된 열 변환316Å

광변환된330Å

Chemat Technology, Inc. (Northridge CA USA)로부터 입수할 수 있는 $Zr(\text{O}(\text{O})\text{CC}_7\text{H}_{15})_4$ (지르코늄(IV)-에틸 헥사노에이트(hexanoate)는 헥산에서 용해되고, 용액이 30초 동안 1500rpm으로 실리콘 웨이퍼 상에서 회전되었다. 결과로 나타나는 변환되지 않은 전구체는 2335Å의 두께를 가졌다. ZrO_2 로의 열 변환이 3시간 동안 180°C에서 핫 플레이트 상에서 수행되었다. 3 시간의 열 변환 시간을 포함하는 전체 6시간 동안 180°C에서 핫 플레이트 상에서 연장된 열 변환이 수행되었다. ZrO_2 로의 광화학 변환은, 상술된 바와 같이, $Zr(\text{O}(\text{O})\text{CC}_7\text{H}_{15})_4$ 전구체의 저강도 및 저노출 세기 때문에 약 30 시간의 노광 시간이 사용되었다는 것을 제외하고 $ZrO(\text{acac})_2$ 전구체에 대해 수행되었다. 다시 각각의 결과로 나타나는 막에 대한 파장의 함수로서 두께 및 굴절률이 VASE를 사용하여 측정되었다. 이들 막의 측정된 두께는 다음과 같다:

변환되지 않은 $r(\text{O}(\text{O})\text{CC}_7\text{H}_{15})_4$ 2335Å

열적으로 변환된 1141 Å

연장된 열 변환 977 Å

광변환된 1487 Å

굴절률 결과가 도 15에 도시되는데, 여기서 $Zr(acac)_4$ 광화학적으로 변환된 것은 라인 1, $Zr(acac)_4$ 열적으로 변환된 것은 라인 2, $Zr(O(0)CC7H15)_4$ 열적으로 변환된 것은 라인 3, $Zr(O(0)CC7H15)_4$ 광화학적으로 변환된 것은 라인 4, 연장된 열 변환에 의해 변환된 $Zr(O(0)CC7H15)_4$ 은 라인 5, 및 연장된 열 변환에 의해 변환된 $Zr(acac)_4$ 은 라인 6이다.

결과는, 전구체의 화학 조성 및 준비되는 방법에 직접 관련된 샘플들의 각각에 대한 굴절률 성질에서 큰 차이가 있다는 것을 증명한다.

예 4

알루미늄-코팅 실리콘 웨어퍼가 hexanes 용액에서 적어도 부분적인 변환 후에, BST를 만들도록 설계된 전구체의 약 7000 Å으로 스핀 코팅되었다. BST의 전구체 막은 1:0.8:1의 Ba:Sr:Ti(IV) 몰비(molar ratio)에 대응하여, 3.7g Ti(bis(아세틸아세테이트)di(아소프로폭사이드(isopropoxide))), 2.8g 배리움 2-에틸헥사노에이트, 및 182g hexanes에서 5.6 2-에틸헥사노에이트(2-에틸헥사노에이트 산에서 40% w/w)를 용해시켜 준비되었다. 전구체 막들은 열 처리 또는 광분해 처리에 의해 BST 막들로 변환되었다. 결과로 나타나는 얇은 BST 막들은 박막 캐패시터로 제조되고, 막의 전기적 성질이 측정되었다. 다음의 결과로부터 알 수 있는 바와 같이, 각 막의 유전상수 및 평균 컨덕턴스가 극적으로 달랐다.

열 변환으로부터의 BST

유전상수 4.86

평균 컨덕턴스 0.008992 S

광화학 변환으로부터의 BST

유전상수 27.26

평균 컨덕턴스 0.04311 S

이들 결과는, 변환된 전구체가 준비되는 방법에 직접 관련된 샘플들의 각각에 대한 전기적 성질에서 큰 차이가 있다는 것을 증명한다.

예 5

용제의 선택, 예를 들어, 막 전구체의 스핀 코팅은 막의 광학적 품질에 영향을 미칠 수 있기 때문에 중요하다. 예를 들어, 이 샘플은 BST로 변환되도록 설계된 전구체를 구비하는 막이 MIBK 및 n-헵타인(heptane)의 각각에서 용액으로부터 노 광학 품질의 막을 만드는 한편, '스트리크(streaky)' 막이 PGMEA의 용액으로부터 형성되었다.

전구체 용액들이 용제에 전구체를 용해시키거나 또는 전구체 용액에서 용제의 일부 또는 전부를 소정의 용제로서 교체함으로써 이들 세가지 용제의 각각에서 형성되었다. 각각의 용액은 스핀 코팅에 의해 알루미늄-코팅 Si 웨어퍼 상에 증착되었다. 웨어퍼는 30 초 동안 1500rpm으로 스핀되었다. 스퍼닝 다음에, 입자의 나머지 용제를 제거하기 위해 2 분 동안 110°C에서 핫 플레이트 상에서 배이크되었다. 전구체 막들은 1.2mW/cm²의 세기로 220nm 파장 파를 갖는 Karl Suss MJB-3 마스크를 사용하여 산화물로 변환되었다. 각각의 웨어퍼가 완전한 노광을 위해 1.5 시간 동안 노출되었다. 변환 후에, 현상 또는 제거 단계를 수행하여, 샘플을 스핀 코팅하는데 사용되는 동일한 용제로서 린스함으로써 각각의 전구체 막의 변환되지 않고 노출되지 않은 부분들을 씻어내었다. 변환전, 즉 변환 바로 직후 및 현상 바로 직후의 변환되지 않은 막 두께를 VASE를 사용하여 측정하였다.

MIBK 및 n-헵타인으로부터 만들어진 것과 같은 고 광학 품질의 전구체 막은 반드시 피쳐없는(featureless) 표면을 가지고 있었고, 따라서 어떠한 도면도 이를 도시하지 않는다. 이와 대조적으로, PGMEA 용액으로부터 스핀 코팅된 BST 전구체 막은, 도 16으로부터 볼 수 있는 바와 같이 큰 스트리킹(streaking)을 나타내었다. 위의 용제들 중에서, MIBK는 가장 균일하고 재생가능한 막을 만들었다.

예 6

열 처리가 전구체 막을 소정 재료의 비정질 막으로 변환하기 위해 어떻게 사용될 수 있는지의 예에서, 일련의 배어 실리콘 웨어퍼(bare silicon wafers)가 변환시 BST를 형성하도록 설계된 전구체의 용액으로 스핀 코팅되었다. 웨어퍼들은 10분 간격으로 전체 120분 동안 160°C에서 핫 플레이트 상에서 각각 가열시켜 적어도 부분적인 변환 단계 처리되었다. 각각의 변환 간격 후에, 전구체 패턴은 변환되지 않은 전구체를 제거하기 위해 아소프로판올(isopropanol)로 린스하여 현상되었다. 이는 막을 열적으로 프린트하는데 필요한 시간의 결정이 IPA로의 현상 후에 남은 막의 대부분을 갖게 하게 한다. 도 17에 도시된 바와 같이, 이 시간은 열 변환 동안 약 20분인 것으로 판단되었다.

열 변환 동안, 광화학 변환을 대체함으로써 유사한 실험을 수행하였다. 이들 결과가 도 18에 도시되어 있다. 이 도면은, 막을 광화학적으로 프린트하는데 필요한 시간이 30 내지 60 분 범위 내에 있다는 것을 증명한다. 광화학 변환과 열 부분 변환 또는 전처리를 결합시키도록 설계된 세 번째 실험에서, 웨어퍼들은 10분 동안 160°C의 열 전처리된 다음, 위에 설명된 광화학 변환 처리되었다. 열/광화학 프린트 결과가 도 19에 도시되어 있는데, 도 19는 결합된 열/광화학 변환 공정에 의해 변환에 필요한 시간, 즉 패턴을 형성하는데 필요한 최소 시간이 광화학 변환만을 위해 30 내지 60분에 걸쳐 약 20분으로 감소되었다는 것을 증명한다.

예 7

광 투사 시스템의 해상도는, 이미지 광의 파장을 감소시키고, 렌즈 시스템의 개구수를 증가시키므로써 향상될 수 있다. 그러나, 레지스트 전체를 통해 이미지를 초점 맞추는 능력은 그 두께가 감소함에 따라 감소한다. 초점의 깊이는 레지스트 막의 두께를 감소시켜서 유지될 수 있지만, 최소 레지스트 두께는 패턴 전사 단계에 필요한 에칭 조건에 의해 제한된다. 초점 한계의 깊이를 완화시키기 위해, 박막 이미지를 사용하여 레지스트의 상부 층만을 패터닝하고 있다. 상부 층의 레지스트를 이미징한 후에, 패턴이 현상된 다음, 에칭 공정을 사용하여 기판으로 전사된다.

금속 복합체 전구체를 사용한 이중층 방법의 경우, 하부층과 금속 복합체 전구체를 구비하는 2 스택 막이 각각의 층으로 사용, 즉 스펀 코팅될 수 있다. 금속 복합체 전구체는 에칭 마스크의 필요성을 제공하지만, 하부층은 에칭에 의해 패턴을 기판으로 전사하는데 사용된다. 세 가지 서로 다른 하부층들이 테스트되었다. PMMA, PHOST 및 Novolac. PHOST 및 Novolac은 금속 복합체 전구체의 스펀 코팅 이전에 2시간 동안 160°C에서 핫 플레이트 상에서 하드 베이킹(hard baked)되었다. 실험에 사용된 금속 복합체 전구체는 BST, PZT 또는 티타늄 이산화물(TiO₂)을 형성하도록 설계되었다. BST 전구체는 예 4에 설명된 절차에 따라 준비되었다. PZT 전구체는 57.4g 헥사네(hexanes)에서 리드(II)-에틸헥사노에이트의 18.48g을 용해시키고, 24.2g 지르코늄(IV)-에틸헥사노에이트 및 9.5g Ti(bis(에세틸에세톤)di(이소프로폭사이드)를 첨가하고, 다음에 2.5:1:1.3의 Pb(II):Zr(IV):Ti(IV) 몰비에 대응하여 부수적인 헥사네의 327g을 첨가하여 준비하였다. 다음 표는 사용된 서로 다른 조합 및 하부층 및 금속 복합체 전구체가 어떻게 호환하는 것으로 간주되는 지를 열거한다.

하부층 전구체 헥사네 캐스팅 용제를 이용한
상대 호환성

PMMA BST불량
PMMA PZT불량
PHOST BST불량
PHOST PZT불량
Novolac BST양호
Novolac PZT양호
Novolac TiO₂양호

하드 베이킹된 Novolac은 BST, PZT 및 TiO₂ 전구체와 호환하는 한편, 테스트된 PMMA 및 PHOST 하부 재료는 금속 복합체 층의 스펀 코팅 동안 용해되는 것을 밝혀졌다. PMMA 및 PHOST는 BST 및 PZT 전구체에 사용된 캐스팅 용제 헥사네의 조제에 용해되었다. BST 및 PZT와 하드 베이킹된 Novolac의 호환성은 패턴의 패턴링 및 전사를 허용하였다.

예 8

하드 베이킹된 Novolac 및 두 개의 금속 복합체들 간의 에칭 선택도는 에칭시 두께 변화를 모니터링하므로써 결정되었다. 예 7에 따라 준비된, 하드 베이킹된 Novolac 및 완전히 변환된 PZT 또는 TiO₂의 샘플들이 에칭 챔버에 로드되고, 적어도 120초까지 30초 간격으로 산소 플라즈마로 에칭되었다. 각각의 간격 후에 샘플 두께가 측정되었다. 각 샘플에 대한 에칭 속도는 두께 대 에칭 시간의 도면 슬로프로부터 결정되었다. 하드 베이킹된 Novolac의 두께 대 에칭 시간 도면이 도 20에 도시되어 있고, 완전히 변환된 PZT 또는 TiO₂를 위해 샘플링한 도면이 도 21에 도시되었다. 다음 표는 선택 최소 정방향 러인의 각각의 슬로프와 교정 계수를 열거한다.

산소 에칭중 두께 대 에칭 시간 교정 계수
도면의 슬로프

하드 베이킹된 -76.3 0.999
Novolac
완전히 변환된 -0.1950.985
PZT
완전히 변환된 -0.0866 0.992
PZT 또는 TiO₂

각각의 예칭 속도 도면의 슬로프의 비로부터 예칭 선택도가 결정되었다. 하드 베이크된 Novolac 및 완전히 변환된 PZT 간의 예칭 선택도는 약 390:1이었다. 하드 베이크된 Novolac 및 완전히 변환된 TiO₂ 간의 예칭 선택도는 약 880:1이었다. TiO₂의 예칭 선택도는 동일한 조건하에서 SiO₂의 그것에 상당하다.

예 9

각 재료의 완전히 변환된 일련의 막을 노출시켜 e-빔의 도우즈를 증가시키고, 현상 후에, 막의 일부가 재료에 남는 최고 도우즈 및 남의 막의 일부가 약 1의 값에 도달하는 최저 도우즈를 왕으로서 이들 재료의 광속도를 결정하기 위해 BZT 및 PZT의 E-빔 콘트라스트를 수행하였다. PZT 및 BST에 대한 콘트라스트는 약 60 내지 100 $\mu\text{C}/\text{cm}^2$ 까지 각각에 대해 약 동일한 범위로 발생한다.

산업상 이용가능성

바람직한 발명이 몇몇 특정 실시예를 참조로 설명되었지만, 이 설명은 본 발명의 예시일 뿐이며 본 발명을 제한하는 것으로 간주되어서는 안된다. 기술분야의 숙련자에게는 첨부하는 특허청구의 범위에 정의된 본 발명의 참된 의도 및 범위를 이탈하지 않고 다양한 수정이 발생할 수 있다.

(57) 청구의 범위

청구항 1

가판 상에 하드 마스크를 형성하는 방법에 있어서,

적어도 하나의 전구체 재료를 선택하는 단계;

상기 기판 위에 전구체를 구비하는 층을 형성하는 단계;

상기 전구체 층을 현상하여, 상기 전구체 층에 패턴을 형성하는 단계; 및

상기 패턴을 상기 기판으로 전사하여, 상기 패턴을 형성하는데 포토레지스트가 사용되지 않게 하는 단계를 포함하는 방법

청구항 2

제1항에 있어서, 현상제로 상기 전구체 층의 변환되지 않은 부분(unconverted portion)을 현상하는 단계를 더 포함하는 방법.

청구항 3

제2항에 있어서, 상기 현상제는, 적어도 하나의 알콜과 적어도 하나의 케톤(ketone)을 구비하는 액체 현상제이고, 상기 알콜 모두의 전체 체적은 상기 알콜의 전체 체적과 상기 액체 현상제에 있는 케톤의 전체 체적의 합의 50% 이상인 방법.

청구항 4

제3항에 있어서, 상기 적어도 하나의 알콜은 이소프로필 알콜(isopropyl alcohol)이고, 상기 적어도 하나의 케톤은 메틸 이소부틸 케톤이고, 이소프로필 알콜:메틸 이소부틸 케톤의 비율은 체적으로 약 1:1 이상 체적으로 약 40:1 미만 범위인 방법.

청구항 5

제1항에 있어서, 현상제로 상기 전구체 층의 변환된 부분을 현상하는 단계를 더 포함하는 방법.

청구항 6

제5항에 있어서, 상기 현상제는, 적어도 하나의 알콜과 적어도 하나의 케톤(ketone)을 구비하는 액체 현상제이고, 상기 알콜 모두의 전체 체적은 상기 알콜의 전체 체적과 상기 액체 현상제에 있는 케톤의 전체 체적의 합의 50% 이상인 방법.

청구항 7

제6항에 있어서, 상기 적어도 하나의 알콜은 이소프로필 알콜(isopropyl alcohol)이고, 상기 적어도 하나의 케톤은 메틸 이소부틸 케톤이고, 이소프로필 알콜:메틸 이소부틸 케톤의 비율은 체적으로 약 1:1 이상 체적으로 약 40:1 미만 범위인 방법.

청구항 8

제1항에 있어서, acac, 카르복실아토(carboxylato), 알콕시(alkoxy), 아지드(azide), 카르보닐(carbonyl), 니트라토(nitrato), 아민, 할라이드(halide), 니트로, 및 그 혼합물로 구성된 그룹 중에서 선택된 적어도 하나의 리간드(ligand): 및 Li, Al, Si, Ti, V, Cr, Mn, Fe, Ni, Co, Cu, Zn, Sr, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, In, Sn, Ba, La, Pr, Sm, Eu, Hf, Ta, W, Re, Os, Ir, Pt, Au, Pb, Th, U, Sb, As, Ce, Mg 및 그 혼합물로 구성된 그룹 중에서 선택된 적어도 하나의 금속을 구비하는 금속 복합체(metal complex)로부터 상기 적어도 하나의 전구체 재료를 선택하는 단계를 더 포함하는 방법.

청구항 9

가판 상에 하드 마스크를 형성하는 방법에,

적어도 하나의 전구체 재료를 선택하는 단계;

선택적으로, 상기 기판 위에 보호층을 형성하는 단계;

상기 보호층 위에 변환되지 않은 전구체를 구비하는 층을 형성하는 단계;

상기 변환되지 않은 전구체 층의 적어도 일부를 부분적으로 변환하는 단계;

상기 변환되지 않은 전구체 층의 적어도 일부를 실질적으로 제거하여 패턴을 형성하는 단계; 및

상기 부분 변환 전구체 층의 적어도 일부를 변환하여 하드 마스크를 형성하는 단계를 포함하는 방법.

청구항 10

제9항에 있어서, 에너지원을 실질적으로 투과하는 적어도 한 부분을 구비하는 패턴화된 마스크를 통해, 광, 전자 빔 복사, 이온 빔 복사 및 그 혼합 중에서 선택된 에너지원으로 부분적으로 변환하는 단계를 더 포함하는 방법.

청구항 11

제9항에 있어서, 현상제를 사용하여 상기 변환되지 않은 전구체 층의 적어도 일부를 실질적으로 제거하는 단계를 더 포함하는 방법.

청구항 12

제9항에 있어서, 광, 전자 빔 복사, 이온 빔 복사, 열처리 및 그 혼합 중에서 선택된 에너지원으로 변환함으로써 상기 하드 마스크를 형성하는 더 포함하는 방법.

청구항 13

제9항에 있어서, acac, 카르복실아토(carboxylato), 알콕시(alkoxy), 아지드(azide), 카르보닐(carbonyl), 니트라토(nitrato), 아민, 할라이드(halide), 니트로, 및 그 혼합물로 구성된 그룹 중에서 선택된 적어도 하나의 리간드(ligand); 및 Li, Al, Si, Ti, V, Cr, Mn, Fe, Ni, Co, Cu, Zn, Sr, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, In, Sn, Ba, La, Pr, Sm, Eu, Hf, Ta, W, Re, Os, Ir, Pt, Au, Pb, Th, U, Sb, As, Ce, Mg, 및 그 혼합물로 구성된 그룹 중에서 선택된 적어도 하나의 금속을 구비하는 금속 복합체(metal complex)로부터 상기 적어도 하나의 전구체 재료를 선택하는 단계를 더 포함하는 방법.

청구항 14

거품에 예칭된 패턴을 형성하는 방법에,

적어도 하나의 전구체 재료를 선택하는 단계;

상기 기판 위에 변환되지 않은 전구체를 구비하는 층을 형성하는 단계;

상기 변환되지 않은 전구체 층의 적어도 일부를 부분적으로 변환하는 단계;

상기 변환되지 않은 전구체 층의 적어도 일부를 실질적으로 제거하는 단계;

상기 부분 변환 전구체 층의 적어도 일부를 변환하여 하드 마스크를 형성하는 단계; 및

상기 하드 마스크에 의해 실질적으로 덮여지 않은 기판의 적어도 일부를 예칭하여 상기 기판에 적어도 하나의 패턴화된 영역을 형성하는 단계

를 포함하는 방법.

청구항 15

제14항에 있어서, acac, 카르복실아토(carboxylato), 알콕시(alkoxy), 아지드(azide), 카르보닐(carbonyl), 니트라토(nitrato), 아민, 할라이드(halide), 니트로, 및 그 혼합물로 구성된 그룹 중에서 선택된 적어도 하나의 리간드(ligand); 및 Li, Al, Si, Ti, V, Cr, Mn, Fe, Ni, Co, Cu, Zn, Sr, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, In, Sn, Ba, La, Pr, Sm, Eu, Hf, Ta, W, Re, Os, Ir, Pt, Au, Pb, Th, U, Sb, As, Ce, Mg, 및 그 혼합물로 구성된 그룹 중에서 선택된 적어도 하나의 금속을 구비하는 금속 복합체(metal complex)로부터 상기 적어도 하나의 전구체 재료를 선택하는 단계를 더 포함하는 방법.

청구항 16

패턴화된 얇은 상면을 형성하는 방법에,

금속 복합체(metal complex)를 구비하는 적어도 하나의 전구체 재료를 선택하는 단계;

상기 기판 상에 패턴 전자 층을 형성하는 단계;

상기 패턴 전자 층 위에 변환되지 않은 전구체를 구비하는 층을 형성하는 단계;

광을 실질적으로 투과하는 적어도 한 부분을 구비하는 패턴화된 마스크를 통해 상기 변환되지 않은 전구체 층의 일부를 상기 광에 노출시켜, 상기 노출된 부분을 부분적으로 변환시키는 단계;

상기 변환되지 않은 전구체 층의 적어도 일부를 실질적으로 제거하는 단계;

상기 부분 변환 전구체 층의 적어도 일부를 변환하여 하드 마스크를 형성하는 단계;

상기 적어도 부분 변환 전구체 및 상기 패턴 전사 층의 덮이지 않은 부분을 에칭하여, 상기 덮이지 않은 패턴 전사 층으로부터 적어도 하나의 에칭된 부분을 형성하는 단계; 및

나머지 적어도 하나의 부분 변환 전구체 층 및 패턴 전사 층을 실질적으로 제거하여, 상기 기판의 적어도 한 일부를 벗기는 단계

를 포함하는 방법.

청구항 17

제16항에 있어서, 포토레지스트, 폴리머이드, 폴리(메탈 메타아크릴레이트), Novolac 및 에폭시로부터 상기 패턴 전사 층을 선택하는 단계를 더 포함하는 방법.

청구항 18

제16항에 있어서, acac, 카르복실아토(carboxylato), 알콕사(alkoxy), 아지드(azide), 카르보닐(carbonyl), 니트라토(nitrato), 아민, 할리드(halide), 니트로, 및 그 혼합물로 구성된 그룹 중에서 선택된 적어도 하나의 리간드(ligand); 및 Li, Al, Si, Ti, V, Cr, Mn, Fe, Ni, Co, Cu, Zn, Sr, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, In, Sn, Ba, La, Pr, Sm, Eu, Hf, Ta, W, Re, Os, Ir, Pt, Au, Pb, Th, U, Sb, As, Ce, Mg, 및 그 혼합물로 구성된 그룹 중에서 선택된 적어도 하나의 금속을 구비하는 금속 복합체(metal complex)로부터 상기 적어도 하나의 전구체 재료를 선택하는 단계를 더 포함하는 방법.

청구항 19

리프트오프 층(liftoff layer) 위에 패턴화된 얇은 상면을 형성하는 방법예,

금속 복합체(metal complex)를 구비하는 적어도 하나의 전구체 재료를 선택하는 단계;

상기 기판 상에 릴리스 층(release layer)을 형성하는 단계;

상기 릴리스 층 위에 리프트오프 층을 형성하는 단계;

상기 리프트오프 층 위에 변환되지 않은 전구체를 구비하는 층을 형성하는 단계;

광을 실질적으로 투과하는 적어도 한 부분을 구비하는 패턴화된 마스크를 통해 상기 변환되지 않은 전구체 층의 일부를 상기 광에 노출시켜, 상기 노출된 부분을 부분적으로 변환시키는 단계;

상기 변환되지 않은 전구체 층의 적어도 일부를 실질적으로 제거하여, 상기 리프트오프 층의 나머지 부분이 상기 부분 변환 전구체 층에 의해 덮인채 상기 리프트오프 층의 적어도 일부를 노출시키는 단계;

상기 부분 변환 전구체 층의 적어도 일부를 변환하여 하드 마스크를 형성하는 단계;

상기 적어도 부분 변환 전구체 및 상기 리프트오프 층의 덮이지 않은 부분을 어방성 제거 수단에 노출시켜, 상기 리프트오프 층의 상기 덮이지 않은 부분 및 상기 리프트오프 층의 상기 덮이지 않은 부분 하부의 상기 릴리스 층의 적어도 일부를 실질적으로 제거하고, 상기 기판의 적어도 일부를 노출시키는 단계;

상기 적어도 부분 변환 전구체, 상기 리프트오프 층의 상기 덮인 부분, 및 상기 리프트오프 층의 상기 덮인 부분 밑의 상기 릴리스 층의 적어도 일부를 등방성 제거 수단에 노출시키는 단계;

상기 노출된 기판의 상기 적어도 일부 위 및 상기 적어도 부분 변환 전구체 위에 금속의 막을 증착시키는 단계;

상기 적어도 부분 변환 전구체 위의 상기 금속을 실질적으로 제거하는 단계; 및

상기 나머지 적어도 부분 변환 전구체, 상기 리프트오프 층, 상기 릴리스 층을 실질적으로 제거하여, 상기 기판 위에 상기 금속의 패턴을 형성하는 단계

를 포함하는 방법.

청구항 20

제19항에 있어서, acac, 카르복실아토(carboxylato), 알콕사(alkoxy), 아지드(azide), 카르보닐(carbonyl), 니트라토(nitrato), 아민, 할리드(halide), 니트로, 및 그 혼합물로 구성된 그룹 중에서 선택된 적어도 하나의 리간드(ligand); 및 Li, Al, Si, Ti, V, Cr, Mn, Fe, Ni, Co, Cu, Zn, Sr, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, In, Sn, Ba, La, Pr, Sm, Eu, Hf, Ta, W, Re, Os, Ir, Pt, Au, Pb, Th, U, Sb, As, Ce, Mg, 및 그 혼합물로 구성된 그룹 중에서 선택된 적어도 하나의 금속을 구비하는 금속 복합체(metal complex)로부터 상기 적어도 하나의 전구체 재료를 선택하는 단계를 더 포함하는 방법.

청구항 21

리프트오프 층(liftoff layer) 위에 패턴화된 얇은 상면을 형성하는 방법예,

금속 복합체(metal complex)를 구비하는 적어도 하나의 전구체 재료를 선택하는 단계;

상기 기판 상에 변환되지 않은 전구체 재료를 구비하는 층을 형성하는 단계;

상기 변환되지 않은 전구체 층의 적어도 일부를 부분적으로 변환하는 단계;

상기 변환되지 않은 전구체 층의 적어도 일부를 실질적으로 제거하여, 상기 부분 변환 전구체 부분에 안쪽으로 테이퍼진 측면 프로파일(inwardly-tapering sidewall profile)을 형성하고, 상기 기판의 적어도 일부를 노출시키는 단계;

상기 부분 변환 전구체 층의 적어도 일부를 변환시켜 하드 마스크를 형성하는 단계;

상기 노출된 기판의 상기 적어도 일부 위 및 상기 적어도 부분 변환 전구체 위에 금속의 막을 증착시키는 단계;

상기 적어도 부분 변환 전구체 위의 상기 금속을 실질적으로 제거하는 단계; 및

나머지 상기 적어도 부분 변환 전구체를 실질적으로 제거하여 상기 기판 위에 상기 금속의 패턴을 형성하는 단계

를 포함하는 방법.

청구항 22

제21항에 있어서, acac, 카르복실아토(carboxylato), 알콕사(alkoxy), 아지드(azide), 카르보닐(carbonyl), 니트라토(nitrato), 아민, 할라이드(halide), 니트로, 및 그 혼합물로 구성된 그룹 중에서 선택된 적어도 하나의 리간드(ligand); 및 Li, Al, Si, Ti, V, Cr, Mn, Fe, Ni, Co, Cu, Zn, Sr, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, In, Sn, Ba, La, Pr, Sm, Eu, Hf, Ta, W, Re, Os, Ir, Pt, Au, Pb, Th, U, Sb, As, Ce, Mg, 및 그 혼합물로 구성된 그룹 중에서 선택된 적어도 하나의 금속을 구비하는 금속 복합체(metal complex)로부터 상기 적어도 하나의 전구체 재료를 선택하는 단계를 더 포함하는 방법.

청구항 23

기판에 주입된 영역(implanted region)을 형성하는 방법에,

적어도 하나의 전구체 재료를 선택하는 단계;

선택적으로, 상기 기판 상에 보호층을 형성하는 단계;

상기 보호층 위에 적어도 하나의 변환되지 않은 전구체 재료를 구비하는 층을 형성하는 단계;

상기 변환되지 않은 전구체 층의 적어도 일부를 부분적으로 변환시켜, 상기 전구체 층의 부분적으로 변환된 부분을 형성하는 단계;

현상제를 사용하여, 상기 변환되지 않은 전구체 층의 적어도 일부를 실질적으로 제거하는 단계;

상기 부분 변환 전구체 층의 적어도 일부를 변환시켜 하드 마스크를 형성하는 단계; 및

상기 하드 마스크에 의해 실질적으로 덮이지 않은 상기 기판의 적어도 일부에 이온을 주입하여, 상기 기판에 적어도 하나의 주입된 영역을 형성하는 단계

를 포함하는 방법.

청구항 24

제23항에 있어서, 에너지원을 실질적으로 투과하는 적어도 한 부분을 구비하는 패턴화된 마스크를 통해, 광, 전자 빔 복사, 이온 빔 복사 및 그 혼합 중에서 선택된 에너지원으로 부분적으로 변환하는 단계를 더 포함하는 방법.

청구항 25

제23항에 있어서, 광, 전자 빔 복사, 이온 빔 복사, 열처리 및 그 혼합 중에서 선택된 에너지원으로 변환함으로써 상기 하드 마스크를 형성하는 더 포함하는 방법.

청구항 26

제23항에 있어서, 상기 변환되지 않은 기판을 이온 빔에 노출시켜 이온을 주입하는 단계를 더 포함하는 방법.

청구항 27

제23항에 있어서, acac, 카르복실라토(carboxylato), 알콕사(alkoxy), 아지드(azide), 카르보닐(carbonyl), 니트라토(nitrato), 아민, 할라이드(halide), 니트로, 및 그 혼합물로 구성된 그룹 중에서 선택된 적어도 하나의 리간드(ligand); 및 Li, Al, Si, Ti, V, Cr, Mn, Fe, Ni, Co, Cu, Zn, Sr, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, In, Sn, Ba, La, Pr, Sm, Eu, Hf, Ta, W, Re, Os, Ir, Pt, Au, Pb, Th, U, Sb, As, Ce, Mg, 및 그 혼합물로 구성된 그룹 중에서 선택된 적어도 하나의 금속을 구비하는 금속 복합체(metal complex)로부터 상기 적어도 하나의 전구체 재료를 선택하는 단계를 더 포함하는 방법.

청구항 28

유전체 층에 이중 다마신 아키텍처를 형성하는 방법에 있어서,

적어도 하나의 전구체 재료를 선택하는 단계;

기판 위에 특정 두께를 갖는 상기 유전체 층을 형성하는 단계;

상기 유전체 층 위에 제1 변환되지 않은 전구체를 포함하는 층을 형성하는 단계;

제1 부분 변환 수단을 사용하여, 상기 제1 변환되지 않은 전구체 층의 적어도 일부 위에 상기 제1 전구체 층의 부분적으로 변환된 부분을 형성하는 단계;

제1 제거 수단을 사용하여 상기 적어도 부분적으로 변환된 제1 전구체 층에 의해 덮이지 않은 제1 패턴을 형성하기 위해, 상기 제1 변환되지 않은 전구체 층의 적어도 일부를 실질적으로 제거하여 상기 유전체 층

의 적어도 일부를 노출시키기는 단계;

제1 변환 수단을 사용하여, 상기 부분적으로 변환된 제1 전구체 층의 적어도 일부 위에 하드 마스크를 형성하는 단계;

상기 유전체 층의 노출된 부분 위 및 상기 적어도 부분적으로 변환된 제1 전구체 층 위에 스핀 평탄화 층을 형성하는 단계;

상기 스핀 평탄화 층 위에 제2 변환되지 않은 전구체를 포함하는 층을 형성하는 단계;

제2 부분 변환 수단을 사용하여, 상기 변환되지 않은 제2 전구체 층의 적어도 일부 위에 상기 제2 전구체의 적어도 부분적으로 변환된 부분을 형성하는 단계;

제2 제거 수단을 사용하여, 상기 적어도 부분적으로 변환된 제2 전구체 층에 의해 덮이지 않은 제2 패턴을 형성하기 위해, 상기 제2 변환되지 않은 전구체 층의 적어도 일부를 실질적으로 제거하여 상기 스핀 평탄화 층의 적어도 일부를 노출시키기는 단계;

제2 변환 수단을 사용하여, 상기 부분적으로 변환된 제2 전구체 층의 적어도 일부 위에 하드 마스크를 형성하는 단계;

상기 유전체 층의 두께 미만이 제1 에칭 수단에 의해 제거되도록, 상기 제1 에칭 수단을 사용하여, 상기 유전체 층의 적어도 일부 및 상기 제2 하드 마스크에 의해 실질적으로 덮이지 않은 위의 스핀 평탄화 층 위에 상기 유전체 층 내의 적어도 제2 패턴화된 영역을 형성하는 단계;

제3 제거 수단을 사용하여, 나머지 상기 적어도 부분적으로 변환된 제2 전구체 층 및 상기 스핀 평탄화 층을 실질적으로 제거하여, 상기 적어도 부분 변환 전구체 층을 노출시키기는 단계;

상기 유전체 층 두께 미만이 상기 제1 패턴화된 영역 내의 상기 제2 에칭 수단에 의해 제거되고 상기 유전체의 실질적으로 전체 두께가 상기 제2 패턴화된 영역 내의 상기 제2 에칭 수단에 의해 제거되도록, 제2 에칭 수단을 사용하여, 상기 제1 하드 마스크에 의해 실질적으로 덮이지 않은 유전체 층의 적어도 일부 위에 상기 유전체 층 내의 적어도 하나의 제1 패턴화된 영역을 형성하여, 상기 기판의 적어도 일부를 노출시키기는 단계; 및

선택적으로, 제4 제거 수단을 사용하여 나머지 상기 적어도 부분적으로 변환된 제1 전구체 층을 실질적으로 제거하는 단계

를 포함하는 방법.

청구항 29

제28항에 있어서, 저 유전상수 유전체 재료로 구성된 그룹 중에서 상기 유전체 층을 선택하는 단계를 더 포함하는 방법.

청구항 30

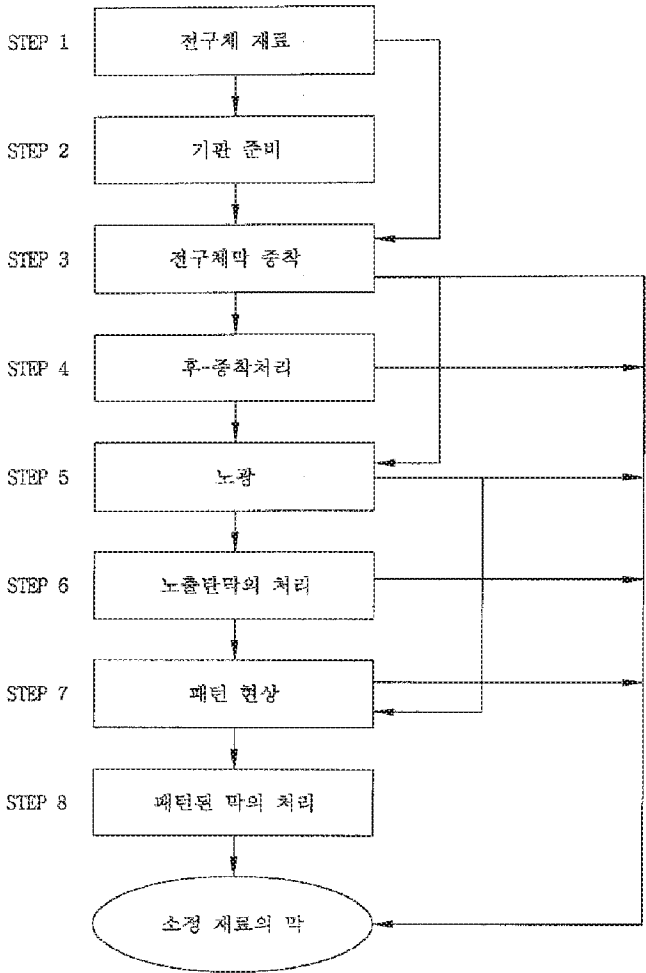
제28항에 있어서, acac, 카르복실아토(carboxylato), 알콕사(alkoxy), 아지드(azide), 카르보닐(carbonyl), 니트라토(nitrato), 아민, 할라이드(halide), 니트로, 및 그 혼합물로 구성된 그룹 중에서 선택된 적어도 하나의 리간드(ligand): 및 Li, Al, Si, Ti, V, Cr, Mn, Fe, Ni, Co, Cu, Zn, Sr, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, In, Sn, Ba, La, Pr, Sm, Eu, Hf, Ta, W, Re, Os, Ir, Pt, Au, Pb, Th, U, Sb, As, Ce, Mg, 및 그 혼합물로 구성된 그룹 중에서 선택된 적어도 하나의 금속을 구비하는 금속 복합체(metal complex)로부터 상기 적어도 하나의 전구체 재료를 선택하는 단계를 더 포함하는 방법.

청구항 31

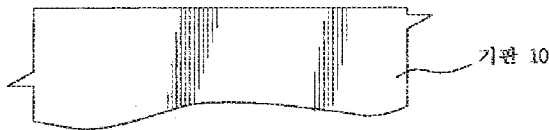
제28항에 있어서, 산소를 포함하는 이방성 플라즈마로서 상기 제1 및 제2 에칭 수단중의 적어도 하나를 선택하는 단계를 더 포함하는 방법.

도면

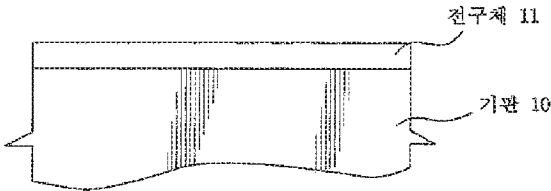
도면1



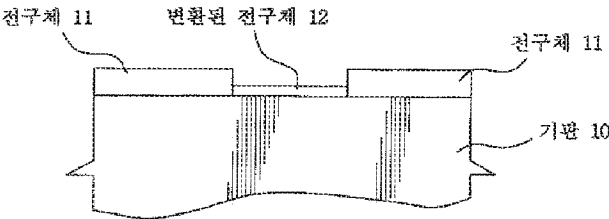
도면2a



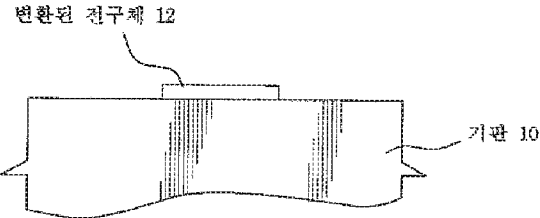
도면2b



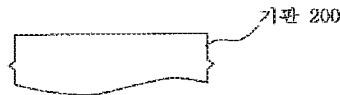
도면2c



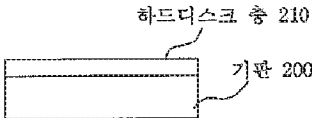
도면2d



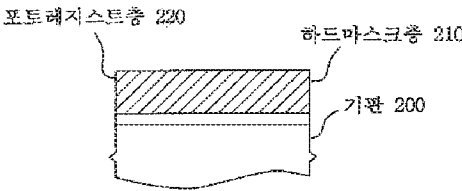
도면3a



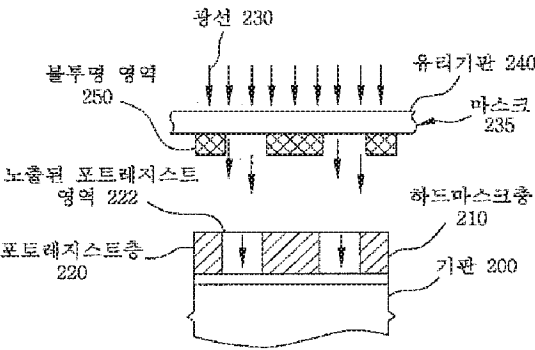
도면3b



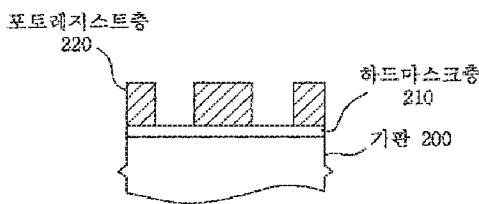
도면3c



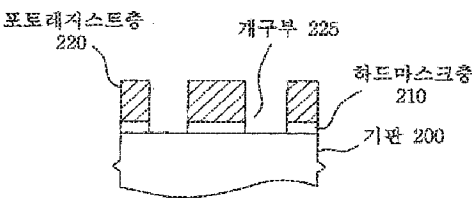
도면3d



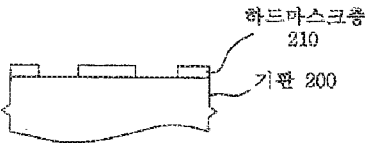
도면3e



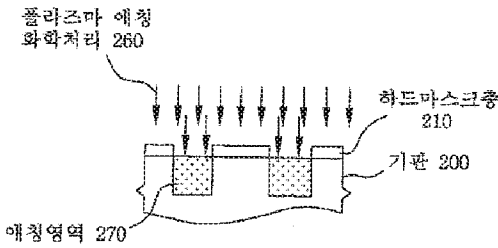
도면3f



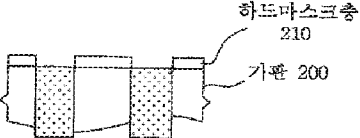
도면3g



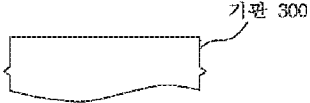
도면3h



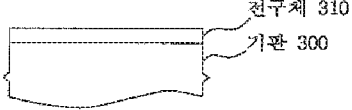
도면3i



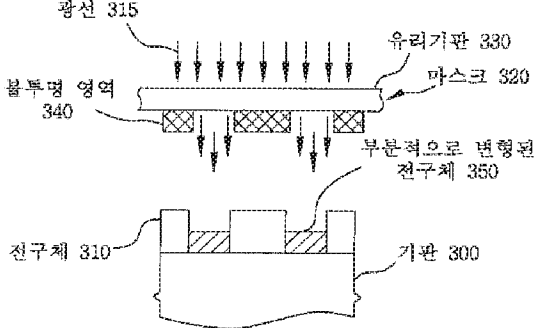
도면4a



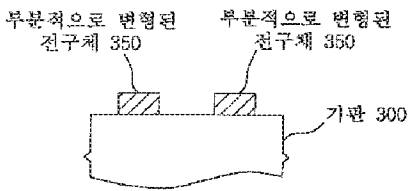
도면4b



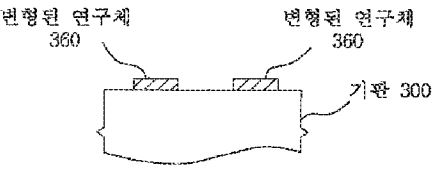
도면4c



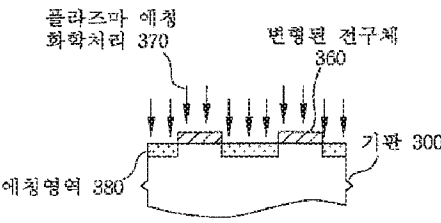
도면4d



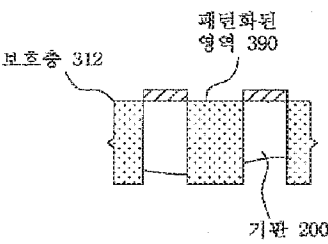
도면4e



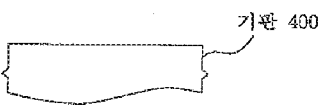
도면4f



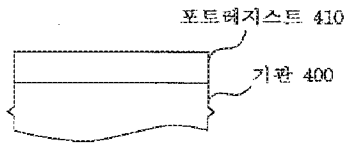
도면4g



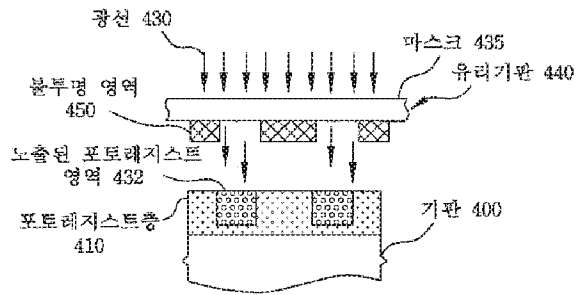
도면5a



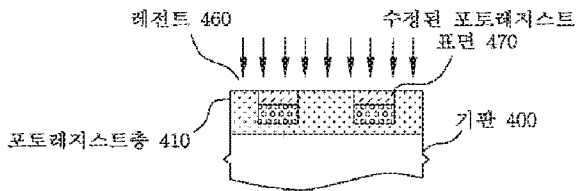
도면5b



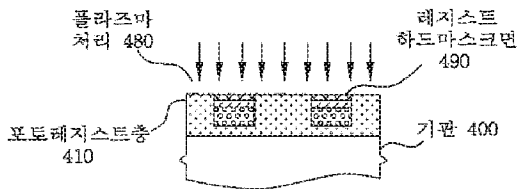
도면5c



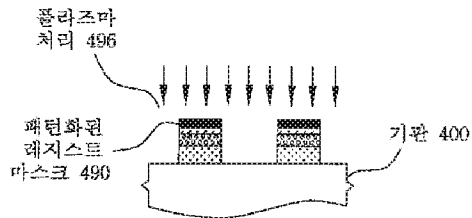
도면5d

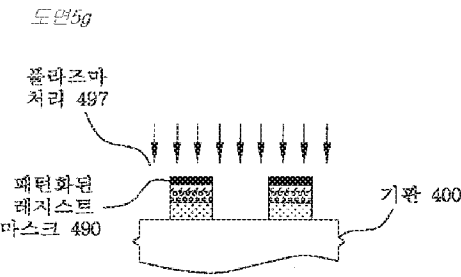
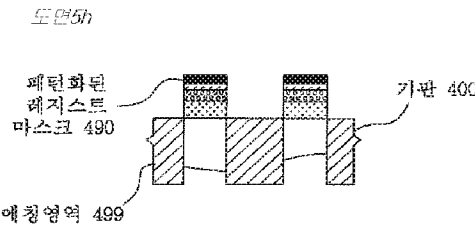
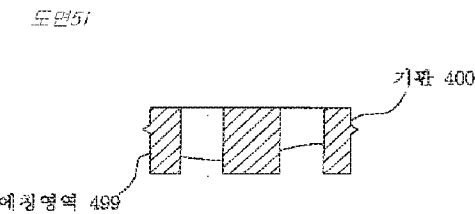
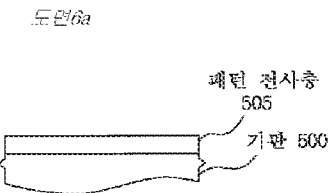
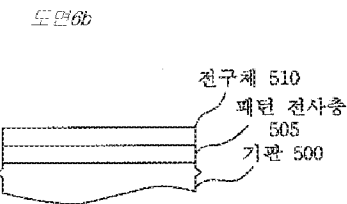


도면5e

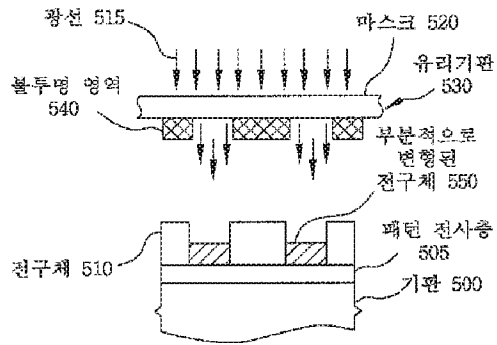


도면5f

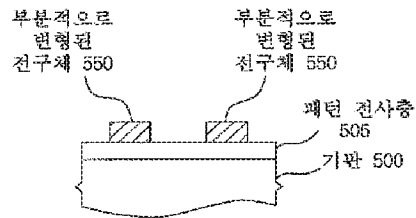




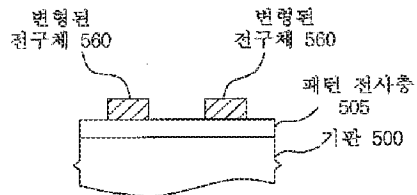
도면6c



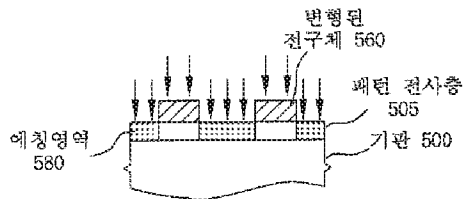
도면6d



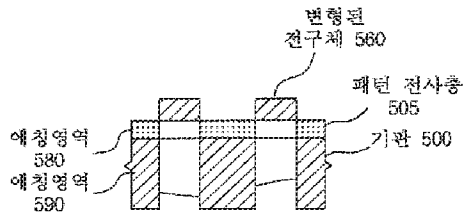
도면6e



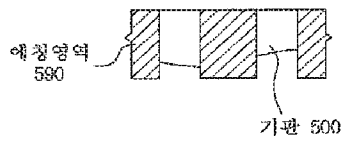
도면6f



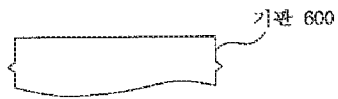
도면6g



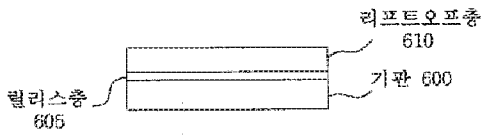
도면6h



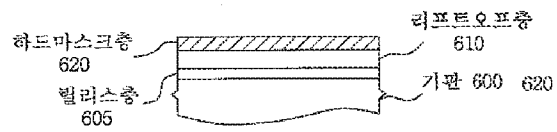
도면7a



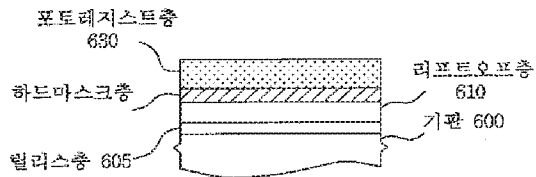
도면7b



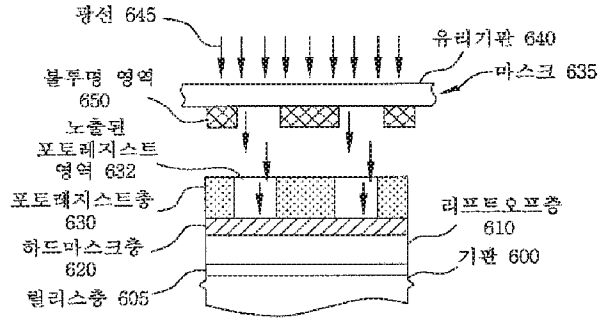
도면7c



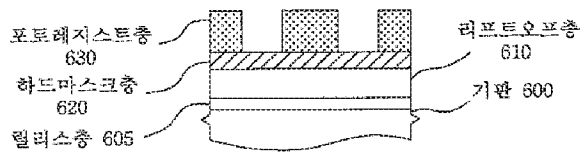
도면7d



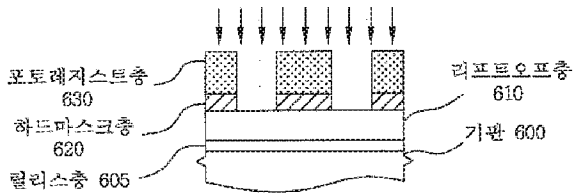
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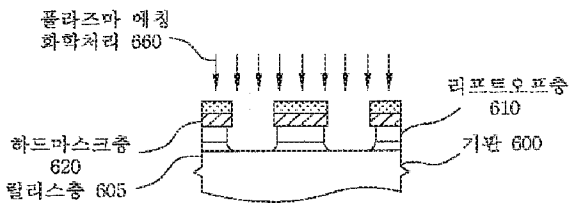
도면7f



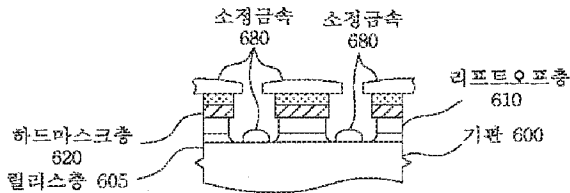
도면7g



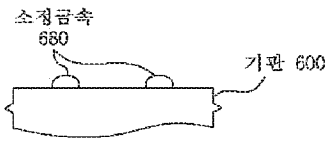
도면7h



도면7i



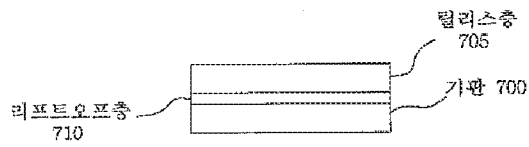
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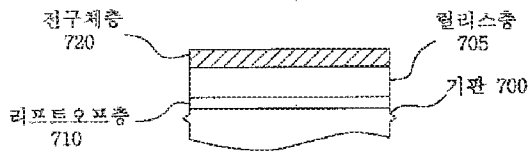
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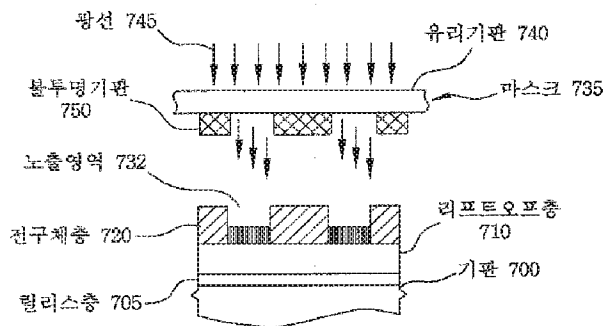
도면8b



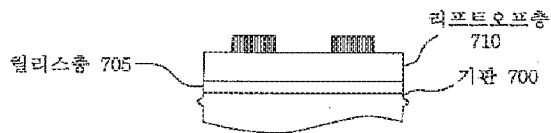
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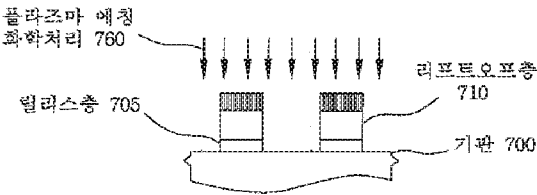
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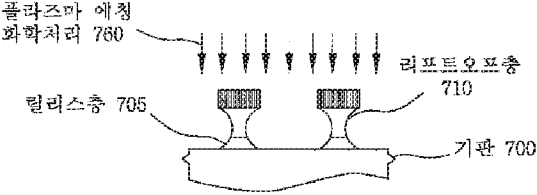
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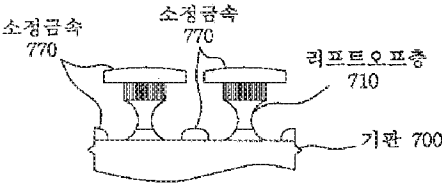
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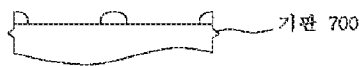
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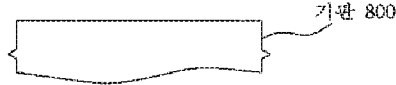
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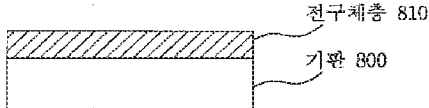
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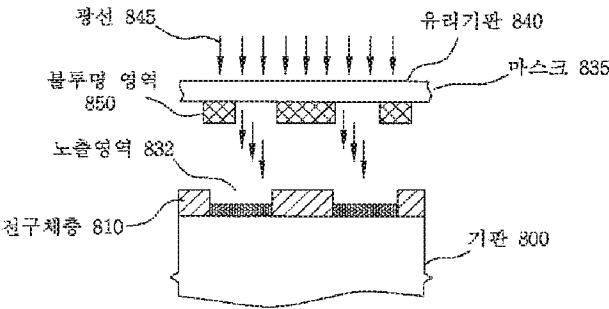
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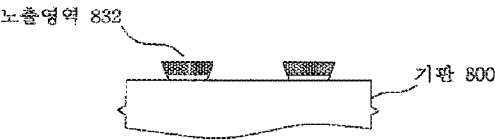
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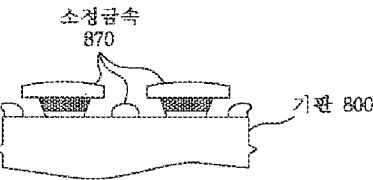
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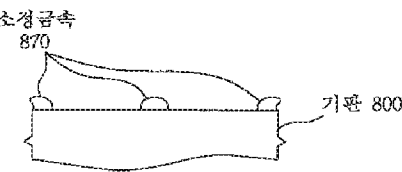
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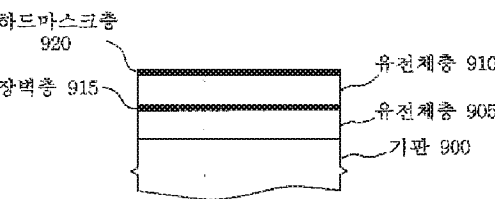
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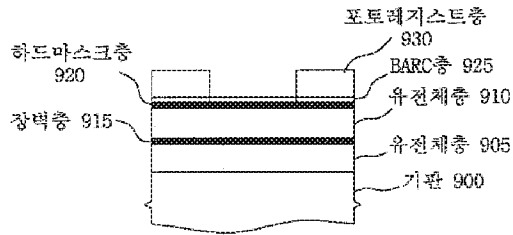
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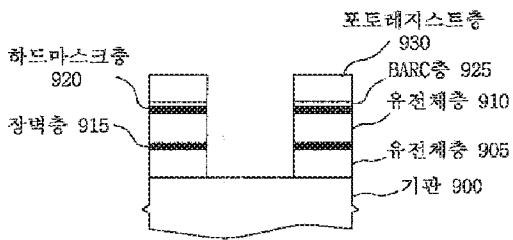
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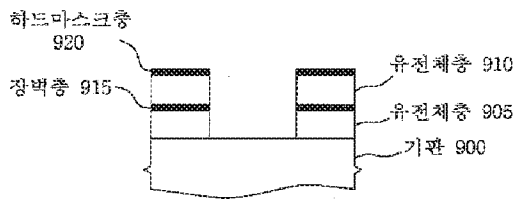
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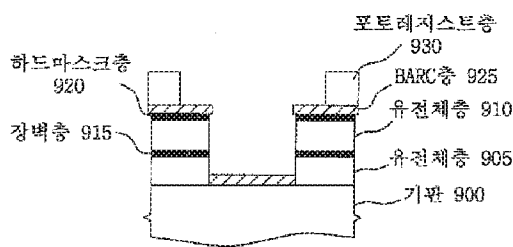
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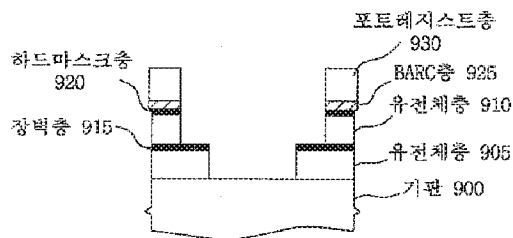
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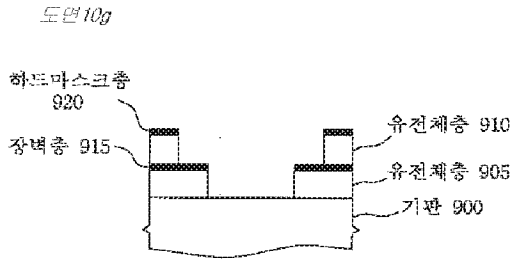
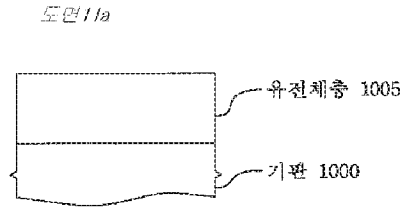
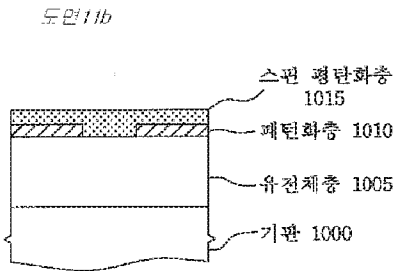
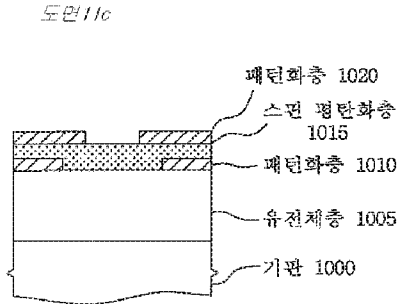
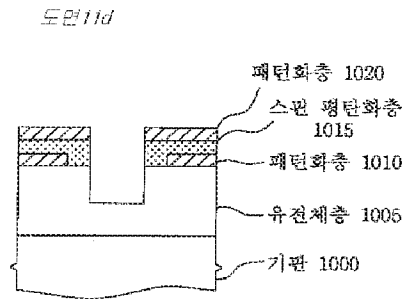


도면 10e

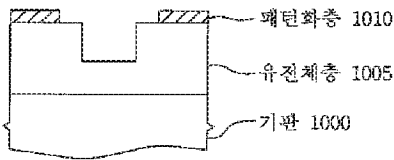


도면 10f

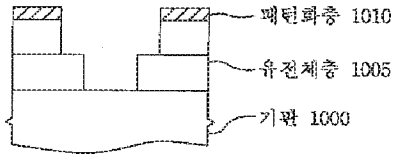




도면11e



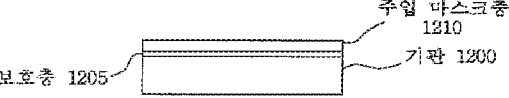
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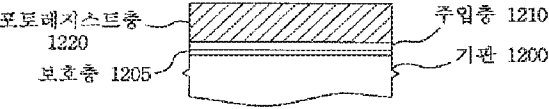
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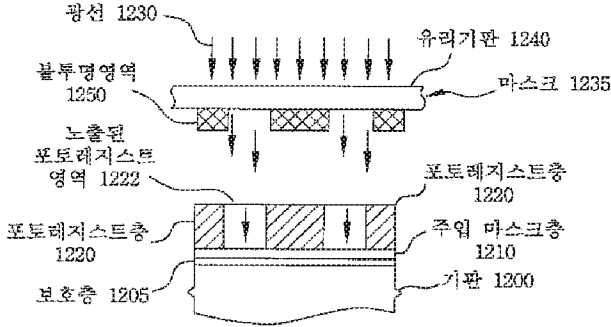
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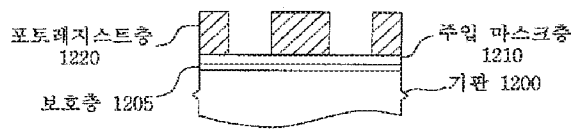
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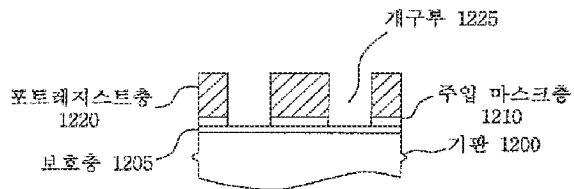
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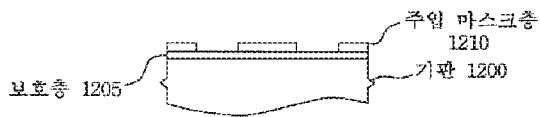
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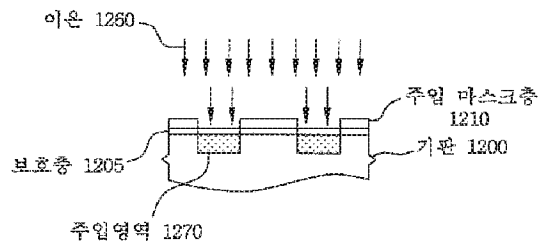
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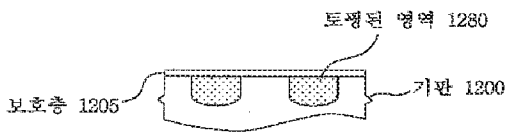
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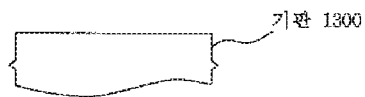
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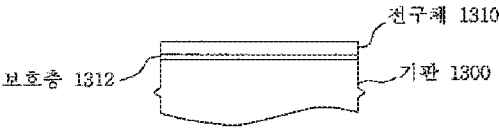
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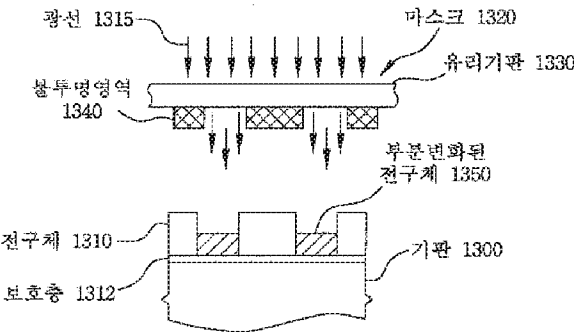
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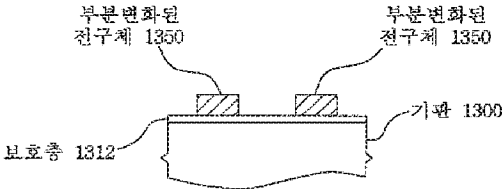
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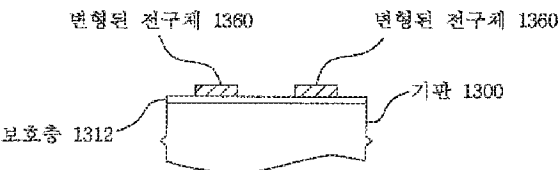
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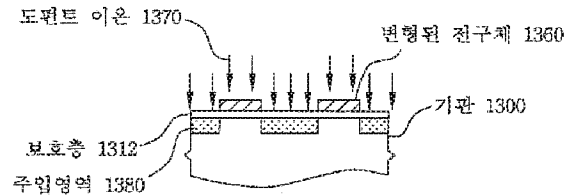
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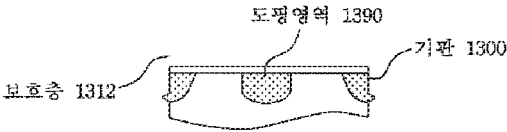
도면 13e



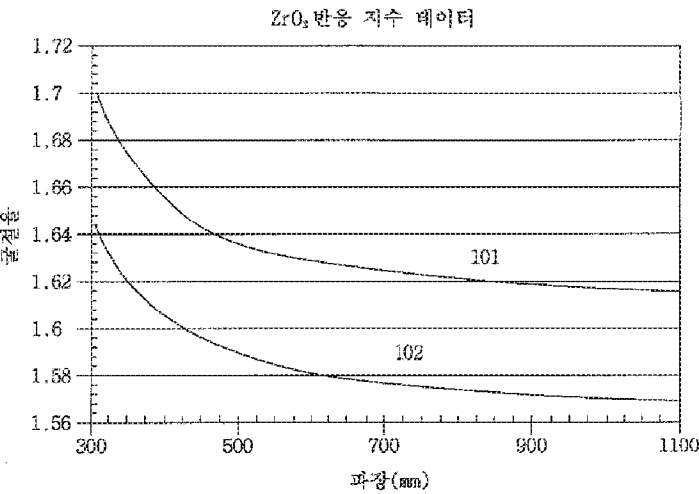
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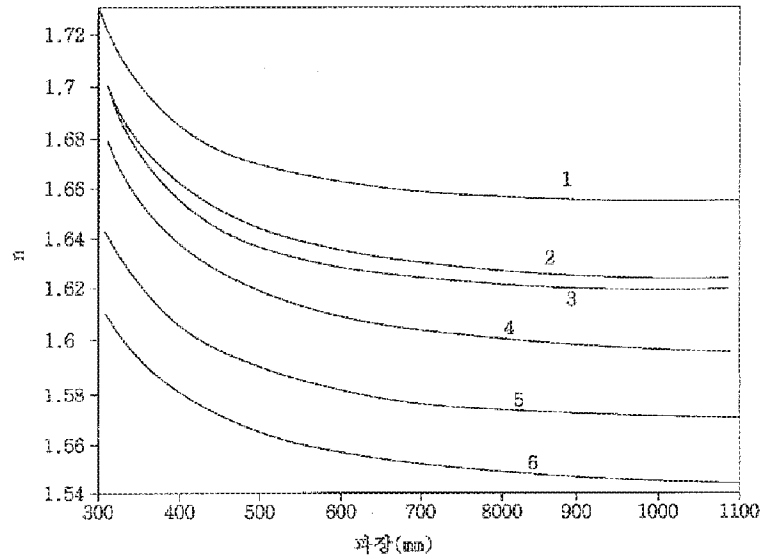
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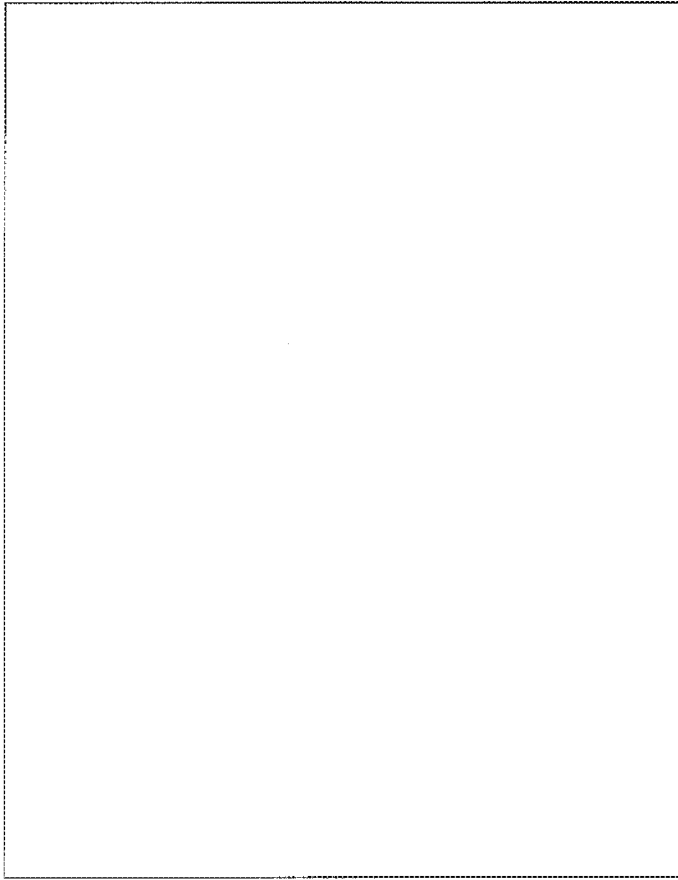
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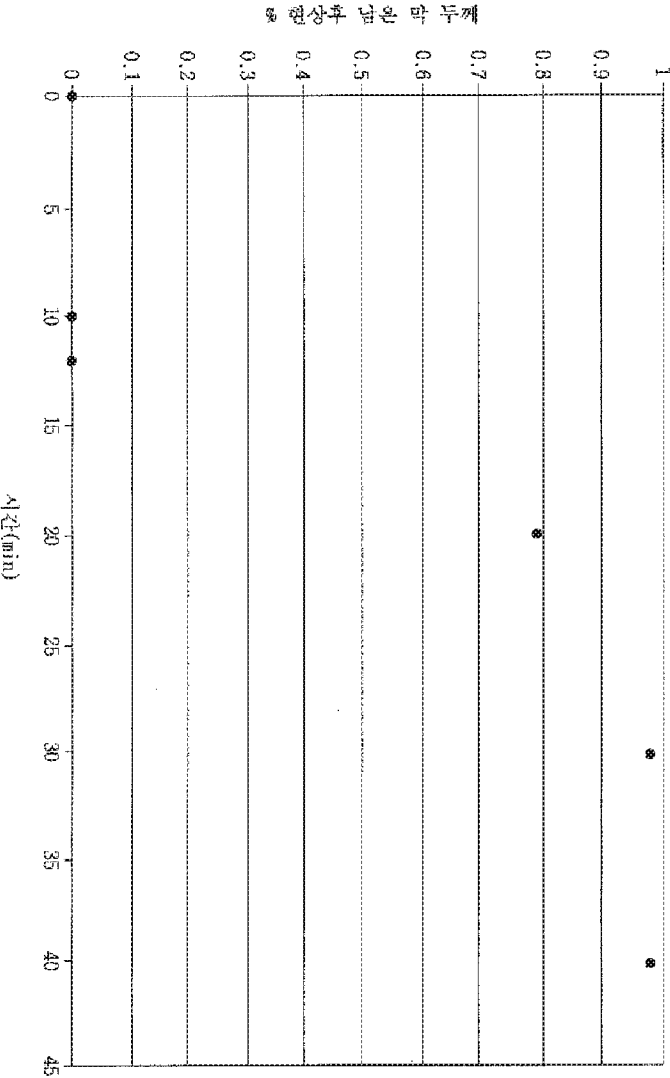
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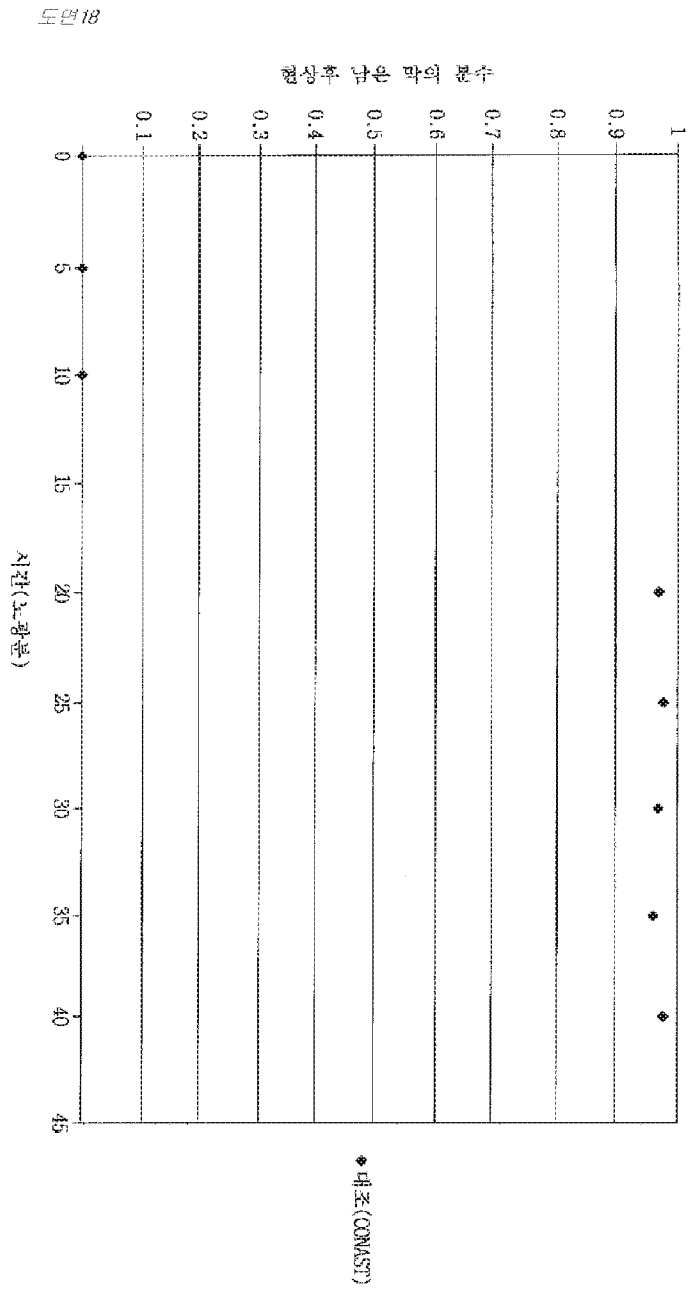


도면16

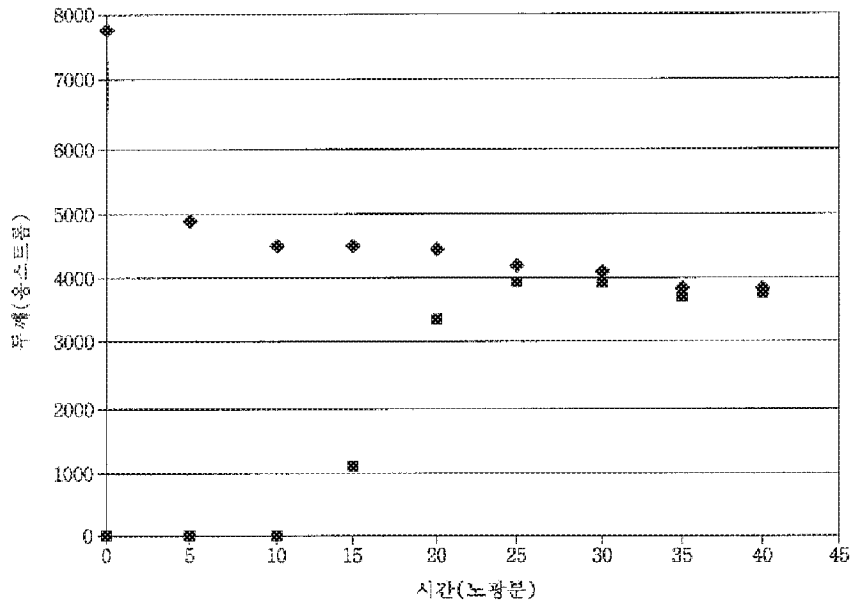


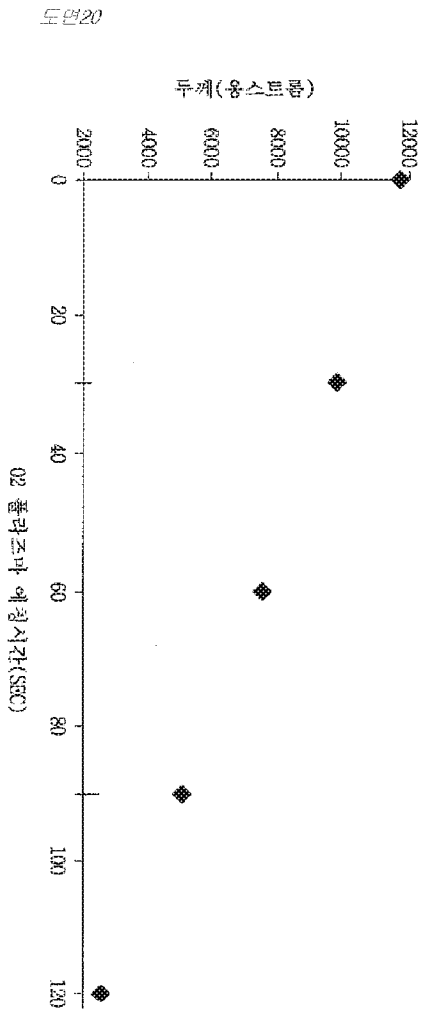
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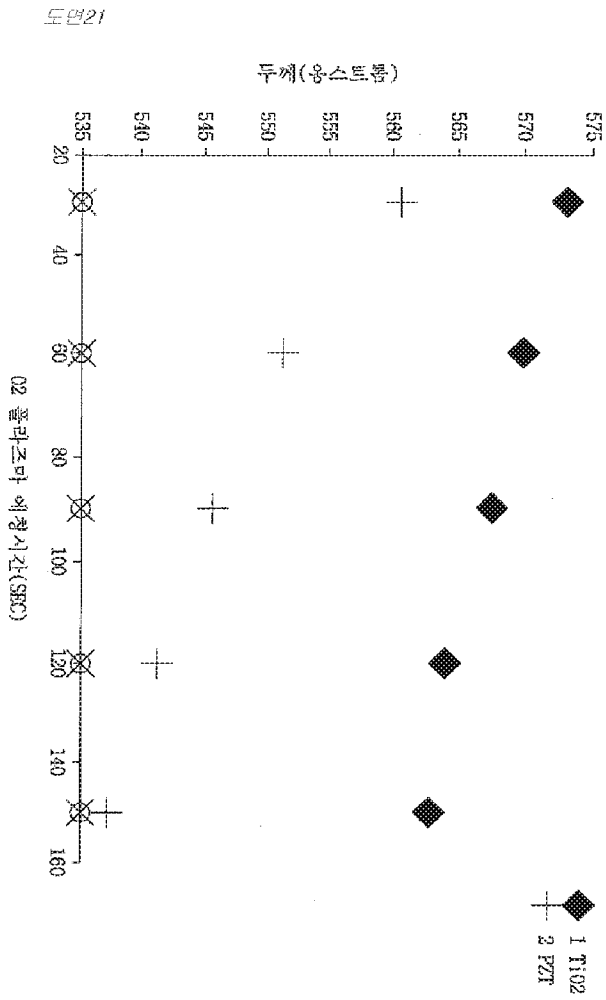




도면 19









Espacenet

Bibliographic data: KR20110132288 (A) — 2011-12-07

PATTERNED INORGANIC LAYERS, RADIATION BASED PATTERNING COMPOSITIONS AND CORRESPONDING METHODS

Inventor(s): STOWERS JASON K [US]; TELECKY ALAN J [US]; KESZLER DOUGLAS A [US]; GRENVILLE ANDREW [US] ± (STOWERS JASON K, ; TELECKY ALAN J, ; KESZLER DOUGLAS A, ; GRENVILLE ANDREW)

Applicant(s): INPRIA CORP [US] ± (INPRIA CORPORATION)

Classification: - international: G03F7/00; G03F7/004
 - cooperative: G03F7/00 (KR); G03F7/0002 (KR); G03F7/004 (KR); G03F7/0042 (EP, KR, US); G03F7/0043 (US); G03F7/0045 (KR); G03F7/0047 (KR); G03F7/20 (US); G03F7/327 (US); Y10T428/24355 (EP, US)

Application number: KR20110052919 20110601 Global Dossier

Priority number(s): US20100850867 20100805 ; US20100350103P 20100601

Also published as: CN102269929 (A) CN102269929 (B) EP2392969 (A2) EP2392969 (A3) EP2392969 (B1) EP2988172 (A1) JP2011253185 (A) JP2016029498 (A) JP2018041099 (A) JP5872189 (B2) JP6280904 (B2) KR101364953 (B1) TW201222144 (A) TWI446108 (B) US2011293888 (A1) US2012070613 (A1) US2016011505 (A1) US2018039172 (A1) US8415000 (B2) US9176377 (B2) US9823564 (B2) less

Abstract of KR20110132288 (A)

PURPOSE: A patterned inorganic layer, a patterning composition based on radiation ray, and a method for the same are provided to form features of high resolution in a patterned coating material and to protect features of high aspect ratio in the patterned coating material. CONSTITUTION: An inorganic patterning precursor aqueous solution includes the mixture of water, metal suboxide cation, inorganic polyatomic anion, and radiation-sensitive ligand containing a peroxide group. The molar ratio of the ligand with respect to the metal suboxide cation is more than or equal to about 2. The precursor aqueous solution is stable to phase separation for about 2 hours without additional mix.

The concentration of the metal suboxide cation is between about 0.01 and 1.4M. The metal suboxide cation includes HfO^{+2} , ZrO^{+2} , and the combination of the same.

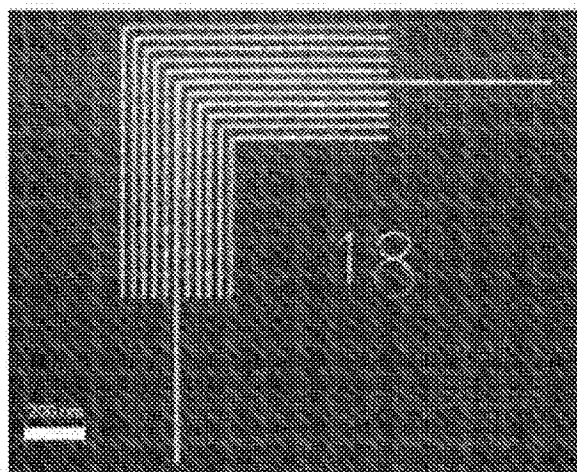


Fig. 11

	(19) 대한민국특허청(KR) (12) 공개특허공보(A)	(11) 공개번호 10-2011-0132288 (43) 공개일자 2011년12월07일
(51) 국제특허분류(Int. Cl.) G03F 7/004 (2006.01) G03F 7/00 (2006.01)		(71) 출원인 인프리아 코퍼레이션 미국 오레건주 97330 코볼리스 스위트 203 노스웨스트 먼로 애비뉴 2001
(21) 출원번호 10-2011-0052919	(22) 출원일자 2011년06월01일 심사청구일자 2011년06월01일	(72) 발명자 스타우어즈 제이슨 케이 미국 오레건주 97330 코볼리스 노스웨스트 위트햄 드라이브 805 텔레키 앨런 제이 미국 오레건주 97333 코볼리스 사우스웨스트 55번가 720 (74) 대리인 김진희, 김성기
(30) 우선권주장 12/850,867 2010년06월05일 미국 (US) 61/350,103 2010년06월01일 미국 (US)		

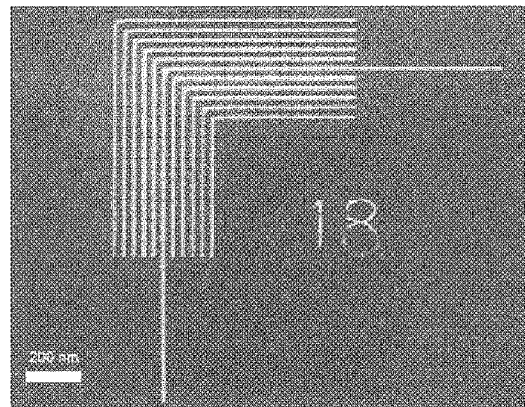
전체 청구항 수 : 총 38 항

(54) 발명의 명칭 패턴닝된 무기층, 방사선에 기초한 패턴닝 조성물 및 해당 방법

(57) 요약

안정화된 전구체 용액을 사용하여 방사선 무기 코팅 물질을 형성할 수 있다. 전구체 용액은 일반적으로 금속 산화물 양이온, 에폭시드계 리간드 및 다원자 음이온을 포함한다. 전구체 용액은 높은 안정도 수준의 전구체 용액을 얻을 수 있도록 설계될 수 있다. 생성되는 코팅 물질은 자외광, x-선 방사선 또는 전자빔 방사선과 같은 선택된 방사선으로 패턴닝하도록 설계될 수 있다. 방사선 패턴닝된 코팅 물질은 물질 특성에 대하여 높은 콘트라스트를 가질 수 있으므로, 잠상의 현상이 성공적이어서 매우 낮은 선폭 거칠기를 갖는 선 및 매우 작은 피치를 갖는 인접 구조체가 형성될 수 있다.

도면 - 도11



(72) 발명자

케스즐러 더글라스 에이

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레이스 8927

그랜빌 앤드류

미국 오레건주 97403 유진 패어마운트 볼러바드
1925

복합청구의 범위

청구항 1

물, 금속 아산화물 양이온, 다원자 무기 음이온 및 퍼옥시드 기를 포함하는 방사선 감수성 리간드의 혼합물을 포함하는 무기 패터닝 전구체 수용액으로서, 상기 조성물은 금속 아산화물 양이온에 대한 리간드의 몰농도 비가 약 2 이상이고 상기 전구체 용액은 추가의 혼합 없이 약 2 시간 이상 동안 상 분리에 대하여 안정한 무기 패터닝 전구체 수용액.

청구항 2

제1항에 있어서, 약 0.01 M 내지 약 1.4 M의 금속 아산화물 양이온 농도를 갖는 수성 무기 패터닝 조성물.

청구항 3

제2항에 있어서, 금속 아산화물 양이온 농도의 약 0.75배 내지 약 1.5배의 다원자 음이온 농도를 갖는 수성 무기 패터닝 조성물.

청구항 4

제1항에 있어서, 금속 아산화물 양이온이 HfO_4^{4-} , ZrO_4^{4-} 또는 이의 조합을 포함하는 것인 수성 무기 패터닝 조성물.

청구항 5

제1항에 있어서, 다원자 음이온이 황산염을 포함하는 것인 수성 무기 패터닝 조성물.

청구항 6

제1항에 있어서, 다원자 음이온이 붕산염, 인산염, 텅스텐산염, 규산염 또는 이의 조합을 포함하는 것인 수성 무기 패터닝 조성물.

청구항 7

제1항에 있어서, 금속 아산화물 양이온에 대한 리간드의 몰농도 비가 약 5 이상인 것인 수성 무기 패터닝 조성물.

청구항 8

제1항에 있어서, 금속 아산화물 양이온에 대한 리간드의 몰농도 비가 약 7 이상인 것인 수성 무기 패터닝 조성물.

청구항 9

제1항에 있어서, 추가의 혼합 없이 24 시간 이상 안정한 것인 수성 무기 패터닝 조성물.

청구항 10

제1항에 있어서, 적절한 산화된 이온 내에 Cu, Al, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, Y, Zr, Nb, Mo, In, Sn, Sb, Hf, Ta, W, Ir, Pt, La, Ce, Pr, Nb, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu 또는 이의 조합을 포함하는 것인 수성 무기 패터닝 조성물.

청구항 11

금속 아산화물 양이온을 포함하는 제1 수용액, 퍼옥시드 기를 갖는 리간드를 포함하는 착화 용액 및 다원자 무기 음이온을 포함하는 조성물을 합하여 코팅 전구체 용액을 형성하는 단계를 포함하고 금속 아산화물 양이온에 대한 리간드의 몰농도 비가 약 2 이상인 방사선 감수성 무기 코팅 전구체 용액의 형성 방법.

청구항 12

제11항에 있어서, 제1 수용액을 착화 용액과 혼합하여 리간드-양이온 혼합물 용액을 형성한 후 무기 음이온을 도입하는 것인 방법.

청구항 13

제12항에 있어서, 리간드-양이온 혼합물 용액을 약 5분 이상 노화시킨 후 다원자 음이온을 포함하는 용액을 첨가하는 것인 방법.

청구항 14

용매, 금속 아산화물 양이온, 피옥시드 기를 포함하는 리간드 및 무기 다원자 음이온을 포함하는 방사선 패터닝 가능한 코팅 물질의 층을 형성하여 코팅된 기판을 형성하는 단계;

상기 코팅된 기판을 가열하여 용매의 적어도 일부를 제거하는 단계;

상기 코팅된 기판을 방사선 패턴에 조사하여 조사된 위치에서 코팅을 축합시키는 단계; 및

조사 후 코팅된 기판을 약 45℃ 이상의 온도까지 가열한 후 코팅을 현상제와 접촉시키는 단계

를 포함하는 기판에서 무기 물질을 패터닝하는 방법.

청구항 15

제14항에 있어서, 방사선은 자외광인 방법.

청구항 16

제14항에 있어서, 방사선은 약 193 nm의 파장을 갖는 광인 방법.

청구항 17

제14항에 있어서, 방사선은 극자외광인 방법.

청구항 18

제14항에 있어서, 방사선은 전자빔을 포함하는 것인 방법.

청구항 19

제14항에 있어서, 금속 아산화물 양이온은 HfO^{2+} , ZrO^{2+} 또는 이의 조합을 포함하고, 다원자 음이온은 황산염 음이온을 포함하는 것인 방법.

청구항 20

제14항에 있어서, 코팅 물질은 금속 아산화물 양이온에 대한 리간드의 몰농도 비가 약 5 이상인 것인 방법.

청구항 21

제14항에 있어서, 스핀 코팅, 분무 코팅, 침지 코팅 또는 나이프 에지 코팅을 이용하여 코팅의 형성을 수행하는 것인 방법.

청구항 22

제14항에 있어서, 코팅 물질층의 평균 두께가 약 1 nm 내지 약 40 nm인 방법.

청구항 23

제14항에 있어서, 방사선을 마스크를 통해 겨냥하여 코팅된 기판의 선택된 부분을 노광시키는 것인 방법.

청구항 24

제14항에 있어서, 레이저빔 또는 전자빔을 코팅된 기판 상에서 스캐닝하여 코팅된 기판의 선택된 부분을 노광시키는 것인 방법.

청구항 25

제14항에 있어서, 코팅된 기판을 현상 조성물로 노광하여 비노광 위치에서 코팅 조성물을 적어도 부분적으로 제거하는 단계를 더 포함하는 것인 방법.

청구항 26

제25항에 있어서, 현상 조성물을 약 75초 이하 동안 코팅된 기판과 접촉시키는 것인 방법.

청구항 27

제25항에 있어서, 현상 조성물은 테트라메틸 암모늄 하이드록시드를 포함하는 것인 방법.

청구항 28

제27항에 있어서, 현상 조성물은 약 2.38 중량%의 테트라메틸 암모늄 하이드록시드 농도를 갖는 것인 방법.

청구항 29

제14항에 있어서, 방사선 패터닝 가능한 코팅 물질의 형성 전에 기판을 친수성 표면 처리로 표면을 따라 처리하는 것인 방법.

청구항 30

제14항에 있어서, 방사선 패터닝 가능한 코팅 물질의 형성은 선택된 두께의 코팅 물질을 형성하는 복수의 코팅 단계를 포함하는 것인 방법.

청구항 31

기판 및 기판 표면 상의 패터닝된 무기 물질을 포함하는 구조체로서, 상기 패터닝된 무기 물질은 약 60 nm 이하의 피치에서 약 2.25 nm 이하의 평균 선폭 거칠거리를 갖는 애지를 갖거나 개개의 피치(feature)에 대하여 약 30 nm 이하의 평균 폭을 갖는 구조체.

청구항 32

제31항에 있어서, 상기 패터닝된 무기 물질은 금속 아산화물 조성물을 포함하는 것인 구조체.

청구항 33

제31항에 있어서, 상기 패터닝된 무기 물질은 패터닝된 반도체 물질 또는 패터닝된 유전체 물질을 포함하는 것인 구조체.

청구항 34

제31항에 있어서, 평균 선폭 거칠거리가 약 1.2 nm 내지 약 2.0 nm인 구조체.

청구항 35

기판 및 기판 표면 상의 패터닝된 무기 물질을 포함하는 패터닝된 구조체의 형성 방법으로서,

약 100 mJ/cm² 이하의 용량에서 극자외광으로 또는 30 kV에서 약 300 pC/cm² 이하에 상당하는 용량에서 전자빔으로 코팅 물질층을 조사하는 단계; 및

상기 조사된 층과 현상 조성물을 접촉시켜 비조사 물질을 용해시켜 패터닝된 무기 물질을 형성하는 단계를 포함하며, 상기 패터닝된 무기 물질은 약 60 nm 이하의 평균 피치를 갖거나 개개의 피치에 대하여 약 30 nm 이하의 평균 폭을 갖는 형성 방법.

청구항 36

제35항에 있어서, 상기 패터닝된 무기 물질은 금속 아산화물 조성물을 포함하는 것인 방법.

청구항 37

제35항에 있어서, 상기 패터닝된 무기 물질은 약 40 nm 이하의 평균 피치를 갖거나 개개의 피치에 대하여 약 20 nm 이하의 평균 폭을 갖는 것인 방법.

청구항 38

제35항에 있어서, 상기 패터닝된 무기 물질은 패터닝된 반도체 물질 또는 패터닝된 유전체 물질을 포함하는 것인 방법.

명세서

기술분야

[0001] 관련 출원 참조

[0002] 본 출원은 본 명세서에 참고문헌으로 포함된 "Photopatternable Inorganic Hardmask"라 표제된 Stowers 등의 공동계류중인 미국 가특허 출원 61/350,103호를 우선권으로 주장한다.

[0003] 정부 권리에 대한 언급

[0004] 본 명세서에 개시된 발명의 개발은 미국 국립 과학 재단 지원금 DGE-0549503 및 IIP-0912921을 통해 적어도 일부 정부 자금 지원을 받았으며, 미국 정부는 본 발명에 일정한 권리를 가진다.

[0005] 기술 분야

[0006] 본 발명은 소자의 요소의 형성 및/또는 다른 물질의 패터닝을 촉진하기 위한 레지스트로서 사용될 수 있는 패터닝된 무기층에 관한 것이다. 본 발명은 또한 침착되어 방사선에 의하여 매우 높은 해상도로 패터닝될 수 있는 코팅을 형성할 수 있는 전구체 용액 및 방사선에 기초한 패터닝 수행 방법에 관한 것이다.

배경 기술

[0007] 반도체 기반 소자 및 다른 전자 소자의 형성을 위하여, 일반적으로 물질을 패터닝하여 구조를 집적시킨다. 따라서, 구조는 일반적으로 각종 물질로 패터닝이 형성되는 순차적 침착 및 에칭 단계의 반복 공정을 통하여 형성된다. 이러한 식으로, 다수의 소자가 작은 면적으로 형성될 수 있다. 업계의 일부 진보는 성능의 증대에 바람직할 수 있는 소자의 차가 공간 감소를 동반할 수 있다.

[0008] 유기 조성물을 방사선 패터닝되는 레지스트로서 이용하여, 패턴으로 해당 유기 조성물의 화학적 구조를 변경시키는 데 방사선 패턴을 이용한다. 예컨대, 반도체 웨이퍼 패터닝 공정은 방사선 감수성 유기 물질의 박막으로부터 소정 화상의 리소그래피 전사를 수반할 수 있다. 레지스트의 패터닝은 일반적으로 레지스트를 에컨대 마스크를 통해 선택된 에너지원에 노광시켜 감광을 기록하는 단계 및 이어서 레지스트의 선택된 영역을 현상 및 제거하는 단계를 포함한 몇몇 단계를 수반한다. 포지티브-톤 레지스트에서, 노광된 영역은 이러한 영역이 선택적으로 제거될 수 있도록 변형되는 반면, 네거티브-톤 레지스트에서는, 비노광 영역이 더 용이하게 제거될 수 있다.

[0009] 일반적으로, 패턴을 방사선, 반응성 기체 또는 액체 용액으로 현상하여 레지스트의 감수성 부분을 선택적으로 제거할 수 있는 한편, 레지스트의 다른 부분은 보호성 내에칭층으로서 작용한다. 그러나, 액체 현상제가 화상 현상에 효과적으로 이용될 수 있다. 기판은 보호성 레지스트 층의 나머지 영역에서 윈도우 또는 갭을 통해 선택적으로 에칭될 수 있다. 대안으로, 보호성 레지스트 층의 나머지 영역에서 현상된 윈도우 또는 갭을 통해 아래 기판의 노광된 영역으로 소정 물질을 침착시킬 수 있다. 최종적으로, 보호성 레지스트 층을 제거한다. 공정을 반복하여 패터닝된 물질의 추가의 층들을 형성할 수 있다. 작용성 무기 물질을 화학적 증기 증착, 물리적 증기 증착 또는 기타 바람직한 방법을 이용하여 침착시킬 수 있다. 전도성 물질의 침착 또는 도펀트의 주입과 같은 추가 가공 단계를 이용할 수 있다. 마이크로 및 나노 제조 분야에서, 집적 회로 내의 피쳐(feature) 크기는 고 집적 밀도를 달성하고 회로 기능을 개선하기 위하여 매우 작아져 왔다.

발명의 내용

[0010] 발명의 개요

[0011] 제1 측면에서, 본 발명은 물, 금속 아산화물 양이온, 다원자 무기 음이온 및 퍼옥시드 기를 포함하는 리간드의

혼합물을 포함하는 무기 패터닝 전구체 수용액에 관한 것으로, 상기 조성물은 금속 아산화물 양이온에 대한 리간드의 몰농도 비가 약 2 이상이고 상기 레지스트 조성물은 추가의 혼합 없이 약 2 시간 이상 동안 상 분리에 대하여 안정하다.

- [0012] 추가의 측면에서, 본 발명은 방사선 감수성 무기 코팅 전구체 용액의 형성 방법에 관한 것으로, 상기 방법은 금속 아산화물 양이온을 포함하는 제1 수용액, 피옥사이드 기를 갖는 리간드를 포함하는 착화 용액 및 다원자 무기 음이온을 포함하는 조성물을 합하여 코팅 전구체 용액을 형성하는 단계를 포함한다. 일부 구체예에서, 금속 아산화물 양이온에 대한 리간드의 몰농도 비는 약 2 이상이다.
- [0013] 다른 측면에서, 본 발명은 기판 상에 무기 물질을 패터닝하기 위한 방법에 관한 것으로, 상기 방법은 방사선으로 패터닝 가능한 코팅 물질의 층을 형성하여 코팅된 기판을 형성하는 단계, 상기 코팅된 기판을 가열하여 용매의 적어도 일부를 제거하는 단계, 상기 코팅된 기판을 방사선 패턴에 노광시키는 단계 및 조사 후 상기 코팅된 기판을 가열하는 단계를 포함한다. 일반적으로, 패터닝된 코팅 물질은 금속 아산화물 양이온, 피옥사이드 기를 포함하는 리간드 및 무기 다원자 음이온을 포함한다. 코팅된 기판의 조사는 조사된 위치에서 코팅을 축합시킬 수 있다. 조사 후 코팅된 기판을 약 45°C 이상의 온도까지 가열한 후 코팅을 현상제와 접촉시킬 수 있다.
- [0014] 다른 측면에서, 본 발명은 기판 및 기판의 표면 상에 패터닝된 무기 물질을 포함하는 패터닝 구조체에 관한 것이다. 패터닝된 무기 물질은 패터닝된 반도체 물질 또는 패터닝된 유전체 물질을 포함할 수 있고, 패터닝된 무기 물질은 약 60 nm 이하의 피처에서 약 2.25 nm 이하의 평균 선폭 거칠기를 갖는 에지를 가질 수 있거나 개개의 피처에 대하여 약 30 nm 이하의 평균 폭을 가진다.
- [0015] 다른 측면에서, 본 발명은 기판 및 기판의 표면 상에 패터닝된 무기 물질을 포함하는 패터닝 구조체의 형성 방법에 관한 것이다. 상기 방법은 약 100 mJ/cm² 이하의 용량에서 극자외광으로 또는 30 kV에서 약 300 pC/cm² 이하에 상당하는 용량에서 전자빔으로 코팅 물질의 층을 조사하고 상기 조사된 층과 현상 조성물을 접촉시켜 미조사 물질을 용해시켜 패터닝된 무기 물질을 형성하는 단계를 포함한다. 일부 구체예에서, 패터닝된 무기 물질은 약 60 nm 이하의 평균 피처를 갖거나 개개의 피처에 대하여 약 30 nm 이하의 평균 폭을 가진다.
- [0016] 발명의 상세한 설명
- [0017] 무기 전구체 용액에서 유의적인 개선은 다원자 이온을 포함하는 무기 산화물 물질에 대한 우수한 직접 패터닝 결과를 제공한다. 전구체 용액은 방사선 감수성인 무기 코팅 물질을 침착시키기 위하여 사용될 수 있다. 특히 주목되는 구체예에서, 방사선에 의한 노광은 조사된 코팅 물질을 현상제 조성물에 의한 제거에 대해 내성인 축합된 물질로 전환시킨다. 미조사 코팅 물질의 적어도 일부를 선택적으로 제거하면 축합된 코팅 물질 영역 및 미조사 코팅 물질이 제거되어 아래 기판이 노출된 영역을 포함하는 패턴이 남는다. 코팅 물질은 자외광 및/또는 전자빔과 같은 선택된 방사선에 감수성하도록 설계될 수 있다. 또한, 전구체 용액은 유통을 위한 적절한 저장 수명을 갖고 안정하도록 조제될 수 있다.
- [0018] 개선된 전구체 용액을 형성하기 위한 조성 변화는 또한 개선된 화상 현상을 제공한다. 특히, 조사된 코팅 물질은 예컨대 미조사 코팅 물질을 용해시키는 적당한 액체와 같은 현상제에 대하여 높은 수준의 내성을 갖는 안정한 무기 물질을 생성할 수 있다. 따라서, 코팅층은 현상 동안 축합된 코팅 물질의 제거 없이 쉽게 제조될 수 있다. 종래의 유기 레지스트에 비하여, 본 명세서에 개시된 무기 물질은 상업적으로 적합한 기능층을 위한 다수의 에칭 화학약품에 대하여 매우 높은 내성을 가진다. 이로써 마스크 기능과 관련하여 패터닝된 유기 레지스트를 보충하기 위하여 사용되는 중간 희생막 무기 패턴 전사층을 생략함으로써 공정을 간략화할 수 있다. 또한, 코팅 물질은 종래의 이중 패터닝을 제공한다. 특히, 열처리 후, 조사된 코팅 물질의 축합 부분은 추가의 전구체 용액을 포함하는 다수의 조성물과의 접촉에 있어서 안정하다. 따라서, 전에 침착된 하드마스크 코팅 물질의 제거 없이 이중 패터닝을 수행할 수 있다.
- [0019] 이후 패터닝된 무기 코팅 물질은 소경의 가능성 물질을 패터닝하는 마스크로서 사용된 후 제거될 수 있다. 대안으로, 생성되는 패터닝된 무기 물질은 소자(들)의 부품으로서 구조체에 통합될 수 있다. 패터닝된 무기 코팅 물질이 구조체에 통합되는 경우, 방사선에 의한 물질의 직접 패터닝을 이용함으로써 가공 절차의 많은 단계를 생략할 수 있다. 대안으로, 단파장 전자기 방사선 및/또는 전자빔을 이용하여 노광된 얇은 무기 코팅 물질을 사용하여 매우 고해상의 구조체를 형성할 수 있고, 선폭 거칠기가 개선된 패터닝된 구조체의 형성을 위한 매우 낮은 수준까지 감소될 수 있음을 발견하였다.
- [0020] 통합된 전자 소자 등의 형성은 물질을 패터닝하여 구조체 내에 개개의 요소 또는 부품을 형성하는 것을 수반한다. 일반적으로, 이러한 패터닝은 서로 접속되어 소경의 기능성을 유도하는 층들의 부분들을 커버하는 상이한

조성을 수반한다. 각종 물질은 반도체를 포함할 수 있으며, 이것은 선택된 도펀트, 유전체, 전기 전도체 및/또는 다른 유형의 물질을 가질 수 있다. 고해상 패턴을 형성하기 위하여, 방사선 감수성 유기 조성물을 사용하여 패턴을 도입할 수 있으며, 상기 조성물은 상기 조성물의 부분들이 현상/에칭에 대하여 내성하도록 가공되어 선택적 물질 제거를 이용한 선택된 패턴의 유도가 가능하므로 레지스트라 언급될 수 있다. 방사선과 선택된 패턴 또는 패턴의 네거티브를 이용하여 레지스트를 노광시키고 현상제 내성 영역 및 현상제 용해성 영역을 갖는 패턴 또는 감상을 형성할 수 있다. 본 명세서에 개시된 방사선 감수성 무기 조성물은 소자 내부의 소정 무기 물질 구조체의 직접 형성을 위해 및/또는 유기 레지스트의 대체물인 방사선 패턴링 가능한 무기 레지스트로서 사용될 수 있다. 어떤 경우든, 유익적인 가공 개선이 활용될 수 있고, 패턴링된 물질의 구조체도 개선될 수 있다.

[0021] 코팅 물질을 형성하기 위하여, 전구체 용액을 웨이퍼 등과 같은 기판의 표면에 도포한다. 일부 구체예에서, 무기 전구체 용액은 코팅 조성물의 레올로지, 예컨대 점도가 기판 상에 얇은 코팅의 형성을 허용하도록 비교적 저농도의 금속 양이온을 가질 수 있다. 더 얇은 코팅의 사용은 방사선에의 노광 및 패턴의 현상 사이에 고해상 구조체의 형성과 양립된다. 코팅 물질의 독립적으로 가공가능한 화학적 부분의 비교적 높은 밀도 및 작은 공간 치수는 감소된 선폰 거칠기, 작은 피치 크기 및/또는 매우 높은 해상도를 갖는 구조의 형성에 이용될 수 있다.

[0022] 본 명세서에 개시된 코팅 물질은 특정 방사선 유형과 사용하도록 설계될 수 있으며, 이에 상응하여 전구체 용액은 소정 코팅 물질 조성을 제공하도록 조절될 수 있다. 특히, 코팅 물질은 선택된 방사선의 소정 흡수를 갖도록 제작될 수 있으며, 방사선 흡수 단면적이 더 큰 코팅 물질을 사용하면 그 만큼 더 낮은 방사선 용량을 사용할 수 있다. 조성을 적절히 선택하면, 패턴링 조성물은 예컨대 자외광, X-선 또는 전자빔 및 각 방사선 유형에서 특정 파장 또는 파장 범위에 대하여 감수성일 수 있다. 이들 특정 방사선 유형은 짧은 방사선 파장에 기초한 작은 패턴의 형성능으로 인하여 바람직하다. 따라서, 본 명세서에 개시된 코팅 물질을 사용하는 것은, 소자 형성능을 증대시킬 수 있는 낮은 선폰 거칠기를 갖도록 효과적으로 형성될 수 있다. 또한, 방사선 패턴링된 코팅 물질은 얇고 적절한 현상제에 대한 감수성과 관련하여 높은 콘트라스트를 가지므로, 미조사 코팅 물질의 제거 후, 구조체들은 연결 구조체 사이에 작은 피치를 가질 수 있다.

[0023] 전구체 용액은 금속 아산화물 양이온, 퍼옥시드 기를 포함하는 방사선 감수성 리간드 및 다원자 음이온을 갖는 수용액을 포함한다. 금속 아산화물 양이온은 금속 원소 및 공유 결합된 산소 원자를 갖는 다원자 양이온이다. 금속 아산화물 또는 금속 수산화물의 수용액은 겔화 및/또는 침전에 대하여 불안정한 경향이 있을 수 있다. 특히, 용액은 용매 제거시 불안정하며 금속 양이온을 갖는 옥소-히드록시드 네트워크를 형성할 수 있다. 그럼에도 불구하고, 침전된 물질은 이하 개시되는 바와 같은 유용한 특성을 가질 수 있다. 전구체 용액은 방사선을 사용하여 물질내 변화를 유도할 수 있도록 개선된 안정성 및 침전 조절성을 갖도록 조절되어 왔다. 특히, 퍼옥시드계 리간드는 물질의 가공성에 대한 제어성을 제공하면서 전구체 용액을 안정화시킨다.

[0024] 특히, 전구체 용액은 금속 아산화물 양이온에 대한 방사선 감수성 리간드의 몰농도 비가 약 2 이상, 일부 구체예에서 약 5 이상이도록 충분한 방사선 감수성 리간드를 포함할 수 있다. 특히, 퍼옥시드계 리간드 농도가 높을수록 전구체 안정성이 높답도록 크게 개선된다. 이론에 의해 한정되는 것을 원치 않으나, 방사선 감수성 리간드 농도 증가는 금속 양이온의 응집을 확실히 감소시켜 용액을 안정화시킨다. 따라서, 전구체 용액은 2 시간 이상 동안, 심지어 한달을 초과하는 것과 같은 현저히 장시간 동안 더 교반하는 일 없이 교형분의 침강에 대하여 안정할 수 있다. 안정 시간이 길기 때문에, 개선된 전구체는 상업적 사용 가능성에 있어서 다양성을 증가시켰다. 다른 무기 퍼옥시드도 격합할 수 있으나 과산화수소가 바람직한 방사선 감수성 리간드를 제공한다. 일부 구체예에서, 유기 퍼옥시드를 사용할 수 있으나, 적어도 일부 전자제품 분야에서 최종 제품의 형성을 위해 일반적으로 유기 성분들은 철저히 제거되어야 한다.

[0025] 또한, 금속 아산화물 양이온 및 다원자 음이온으로 형성된 물질은 이것이 전자 소자 등의 부품에 적합하도록 하는 유용한 품질 특성을 제공할 수 있다. 특성을 조절하기 위하여 추가의 금속 양이온 및 음이온을 물질에 포함시킬 수 있다. 이들 일반적 전구체 용액은 본 명세서에 참고문헌으로 포함된 "Solution Processed Thin Films and Laminates, Devices Comprising Such Thin Films and Laminates, and Methods for the Use and Manufacture"라 표제된 Keszler 등의 공개된 PCT 출원 WO 2009/120169호(이하 "Keszler PCT 특허")에 더 개시된다. 본 명세서에 개시된 바와 같이, 현저히 높은 방사선 감수성 리간드 농도를 사용함으로써 전구체 용액의 현저한 개선이 달성되었다. 더욱 더 놀랍게도, 전구체 용액 중의 방사선 감수성 리간드 농도가 유의적으로 증가하면 방사선 노광 후 콘트라스트가 더 큰 코팅 물질이 얻어져 놀랍게도 전구체 용액의 안정화로 개선된 패턴링과 현상 시간 단축이 추가로 달성된다는 이점이 추가된다.

[0026] 소정 방사선 흡수를 달성하기 위하여 금속 아산화물 양이온을 선택할 수 있다. 특히, ZrO₂계 코팅 물질은 193

nm 파장에서 양호한 원자외광 흡수를 나타낸다. HfO_2 계 코팅 물질은 x-선 방사선 및 전자빔 방사선의 양호한 흡수를 보이며, 또한 밀도 및 평활도와 같은 바람직한 특성을 코팅 물질에 부여할 수 있다. 코팅 물질의 바람직한 전체 특성을 제공하기 위하여 일부 전구체 용액은 ZrO_2 및 HfO_2 양이온의 플렌드를 효과적으로 포함한다. 전구체 용액은 리소그래피에 중요한 일부 방사선 파장의 흡수를 증가시키기 위하여 추가의 금속 양이온을 포함할 수 있다. 금속 양이온은 물과의 상호작용으로 다양한 가수분해도를 가질 수 있으며, 물을 이용한 가수분해 상태는 일반적으로 매우 pH 의존적이다. 금속 이온 농도는 전구체 용액에 대한 소정 특성을 제공하도록 선택될 수 있는데, 더 희석된 용액은 일반적으로 더 얇은 코팅 물질의 형성과 양립한다.

- [0027] 황산염 음이온이 전구체 용액에 포함시키기에 바람직한 다원자 음이온일 수 있으나, 다른 다원자 음이온도 황산염 음이온의 바람직한 대체물 또는 부가물일 수 있다. 다원자 음이온의 농도는 다양한 현상제 조성물에 대한 코팅 물질의 선택성과 상관관계가 있는 것이 발견되었다. 일부 다원자 음이온은 히드록시드 기 및/또는 산소 원자와의 공유 결합을 갖는 금속 원자를 포함하며, 음이온 구조도 pH 의존적일 수 있다.
- [0028] 알정성이 더 큰 정제된 전구체 용액은 또한 기관의 방사선 노광 및 비노광 부분 사이에 더 큰 콘트라스트 가능성을 갖는 코팅 물질을 제공한다. 특히, 미조사 코팅 물질은 적합한 현상제 조성물에 의하여 비교적 더 용이하게 용해될 수 있는 반면, 노광된 코팅 물질은 현상제 조성물에 대하여 적절히 내성하도록 유지될 수 있다. 미조사 코팅 물질은 조사된 코팅 물질에 비하여 현상제로 비교적 더 용이하게 용해될 수 있으므로, 코팅 조성물의 바람직한 제거가 여전히 유지되면서 현상제와의 접촉 시간이 감소될 수 있다. 특히, 개선된 조성을 및 해당 물질로, 선택 거칠기가 놀랍도록 낮은 수준으로 감소되었다. 따라서, 이웃하는 소자들 사이가 적절히 분리, 일반적으로 절연되면서, 이웃하는 소자들간 피치가 매우 작아질 수 있다. 조사된 코팅 조성물은 기관의 표면 상에 조사된 패터닝 조성물의 적절한 일부를 남기면서 미조사 코팅 조성물을 깨끗히 제거하는 것과 관련하여 현상 공정의 효율을 손상시키지 않으면서 매우 얇게 제조될 수 있도록 현상/에칭 공정에 매우 내성일 수 있다. 현상제에 대한 노광 시간 단축능은 또한 코팅의 노광 부분을 손상시키지 않고 얇은 코팅의 사용량 양립한다.
- [0029] 패터닝을 수행하기 위하여, 전구체 용액을 일반적으로 기관의 전체 표면 또는 이의 선택된 부분에 도포한다. 전구체 조성물은 예컨대 종래의 코팅 방법을 이용하여 기관에 침착시킬 수 있다. 코팅 물질의 도포 전에, 친수성 표면 처리를 이용하여 기관 표면을 준비함으로써 표면 친수성을 증가시켜 전구체 수용액에 의한 습윤성을 개선시킬 수 있다. 예컨대, 전구체 용액을 스핀 코팅을 이용하여 웨이퍼 또는 다른 기관에 코팅할 수 있으나, 분무 코팅, 나이프 애저 코팅 또는 기타 적절한 기술과 같은 다른 코팅법도 이용할 수 있다. 전구체 용액의 도포에 스크린 인쇄, 잉크젯 인쇄 등과 같은 인쇄 기술을 이용할 수 있다. 그러나, 미세 패터닝은 인쇄보다는 방사선에 기초한 패터닝으로 수행된다. 용매의 적어도 일부를 제거하면 추가 처리에 대하여 코팅 물질을 안정화시킬 수 있다. 용매는 코팅 공정 자체 동안 일부 제거될 수 있다. 또한, 기관과 코팅 물질을 가열하여 용매의 제거에 기여할 수 있다. 충분한 용매의 제거 후, 코팅 물질은 일반적으로 비교적 안정하여 패터닝될 수 있고 패터닝을 위해 더 처리될 수 있다.
- [0030] 코팅 물질은 방사선에의 노광이 조사된 영역에서 코팅 물질 조성물을 잠상으로서 변화시키도록 일반적으로 방사선 감수성이다. 방사선 패턴은 물리적 마스크를 통한 방사선의 통과 또는 반사를 통하여 유도될 수 있으며 적절한 광학장치를 이용하여 코팅 물질에 패터닝된 방사선을 전달할 수 있다. 추가로 또는 대안으로, 방사선 빔을 코팅 물질에 거쳐 스캐닝하여 코팅 물질 중의 패턴을 방사선에 대한 노광에 기초하여 잠상으로서 형성할 수 있다. 방사선 흡수로 코팅 물질의 조사된 부분이 축합된다. 즉, 방사선 흡수로 인한 에너지로 금속 이온이 응집되어 조사된 물질의 특성이 변화된다.
- [0031] 이론에 의하여 한정되는 것을 원치 않으나, 방사선의 흡수서, 퍼옥사이드 작용기가 절편화되고 이에 따라 가교 금속-산소 결합의 형성을 통해 조성물이 축합된다고 생각된다. 축합 반응을 통해, 방사선 패턴은 코팅 물질 중의 패턴으로 전사된다. 특히, 조사된, 따라서 축합된 코팅 물질 및 코팅 물질의 패터닝 조사 전의 조성으로부터 실질적으로 불변인 미조사 코팅 물질의 패턴이 존재한다.
- [0032] 조사후 물질의 가열을 통해 축합된 코팅 조성물 및 미조사된 코팅 조성물 간에 물질 특성의 대비가 증대될 수 있음을 발견하였다. 특히, 가열 공정은 조사된 코팅 조성물의 축합을 증가시키는 것으로 발견되었다. 가열은 현상 단계에서 미조사된 물질을 제거하는 능력을 유익적으로 변화시키지 않는다.
- [0033] 패터닝된 코팅 조성물은 코팅 물질의 미조사된 부분을 제거하는 2.38 중량% 테트라메틸 암모늄 히드록시드 (반도체 리소그래피에서 표준 현상제)와 같은 현상제액에 노광될 수 있다. 현상제 조성물의 적절한 선택을 기초로 단시간에 현상을 수행할 수 있다. 또한, 축합된, 조사된 코팅 물질의 안정화로 인하여, 축합된 코팅 물질은 현상제에 대하여 매우 안정할 수 있다. 축합된 코팅 물질은 매우 단단한 마스크 물질을 형성한다.

- [0034] 코팅 물질의 패터닝 후, 추가의 물질층을 패터닝 상에 도포할 수 있고/있거나 미조사된 코팅 물질을 제거함으로써 생성되는 윈도우를 통해 추가의 에칭을 수행하여 패터닝된 코팅 물질 중의 감광을 기초로 기판 물질을 선택적으로 제거할 수 있다. 이러한 방식으로, 패터닝된 코팅 물질을 이용하여 다양한 조성의 추가의 상보적 패터닝을 갖는 구조를 어셈블링할 수 있다. 이온도 전기적 특성의 조절을 위해 패터닝된 코팅 물질의 윈도우를 통해 기판에 선택적으로 주입될 수 있다. 패터닝된 무기 코팅의 치밀성은 종래의 유기 패터닝 코팅에 비하여 더 높은 주입 내성을 제공한다. 패터닝된 코팅 물질 자체는 구조에 소정 특성을 포함시킬 수 있는 무기 물질이므로, 패터닝된 코팅 물질은 소자에 직접 포함될 수 있다. 코팅 물질이 구조에 직접 포함되는 구조예의 경우, 패터닝 및 레지스트 제거를 수행하는 구분된 단계들이 생략되어 매우 유의적인 가공 이점이 달성될 수 있다. 이들 용도는 이하의 논의에서 설명된다.
- [0035] 상기 기재된 바와 같이, 본 명세서에 개시된 방사선 감수성 코팅 물질은 네거티브 레지스트로서 사용될 수 있다. 패터닝된 코팅 물질을 현상하여 미조사된 코팅 물질을 제거한 후, 패턴을 추가의 가공 단계에 이용할 수 있다. 특히, 기판은 패터닝된 코팅 중의 갭을 통해 에칭될 수 있다. 또한, 추가의 물질을 패터닝된 코팅 물질 중의 갭을 통해 침투시켜 아래 기판에 도달하는 추가의 물질과 함께 침착시킬 수 있다. 일부 구체예에서, 코팅 물질 중의 패턴을 기초로 에칭 및 침착을 조합할 수 있다. 패터닝된 코팅 물질을 기초로 추가의 가공을 수행한 후, 무기 코팅 물질, 즉 무기 레지스트를 적당한 에칭 조성물 또는 다른 에칭 공정을 이용하여 제거할 수 있다. 예컨대, 조사된 코팅 물질은 건식 BCl_3 플라즈마 에칭 또는 수성 HF 습식 에칭으로 제거될 수 있다. 포지티브 레지스트의 일부 구체예 및 네거티브 레지스트로서 유사한 조성물의 사용은 본 명세서에 참고문헌으로 포함된 Keszler PCT 출원에 개시된다. 유기 레지스트에 비하여, 무기 코팅 물질은 노광 및 비노광 영역 사이의 높은 콘트라스트 및 선택된 방사선의 흡수에 있어서 눈에 띄는 이점을 제공하므로 적당한 방사선 용량으로 고해상도가 달성될 수 있다.
- [0036] 패터닝된 방사선 감수성 무기 코팅 물질의 직접 사용은 유기 레지스트를 별도로 사용하지 않아도 패터닝된 무기층을 형성할 수 있는 능력을 제공한다. 무기 코팅 물질의 조사된 및 미조사된 영역 사이의 큰 특성 대비는 현상 공정 동안 코팅 물질의 축합 부분의 유의적인 손상 없이 미조사된 부분이 깨끗하게 제거될 수 있는 얇은 패터닝된 층들을 형성할 수 있는 능력을 제공한다. 패터닝된 무기 코팅 물질의 밀도 및 일반적인 에칭 내성으로 인하여, 얇은 패터닝된 코팅 물질이 마스크로서 패터닝된 무기 코팅 물질에 의하여 가이드되는 예컨대 에칭 및 이온 주입을 비롯한 구조의 추가 가공에 효과적으로 사용될 수 있다. 일부 구체예에서, 축합된 무기 코팅 물질은 기능성 요소로서 소자 내에 직접 포함되기 위하여 적절한 두께 및 물리적 특성을 갖도록 설계될 수 있다. 예컨대, 생성된 금속 산화물을 조성물을 본 명세서에 참고문헌으로 포함된 "Dielectric Material"이라 표제된 Herman 등의 공개된 미국 특허 출원 2005/0242330A호에 개시된 바와 같이 유전체로서 사용할 수 있다. 또한, 금속 산화물 조성물의 일부 구체예는 본 명세서에 참고문헌으로 포함된 "Semiconductor Film Composition"라 표제된 Herman 등의 공개된 미국 특허 출원 2010/0044698호에 개시된 바와 같은 반도체 특성을 나타낸다. 따라서, 코팅 물질은 적절한 작용성을 갖도록 선택될 수 있다.
- [0037] 리소그래피 절차의 일반적인 사용은 전자 업계에 잘 알려져 있다. 예컨대 본 명세서에 참고문헌으로 포함된 "Method for Manufacturing Printed Circuit Board"라 표제된 Lee 등의 미국 특허 7,208,341호, Harry J. Levinson, "Principles of Lithography," 2판, SPIE Press, Monograph Vol. PM146 (2005), 및 Chris Mack, "Fundamental Principles of Optical Lithography, The Science of Microfabrication," Wiley-Interscience (2007)를 참고하시오. 일반적으로, 기판은 다른 층을 포함할 수 있는 단결정 규소 웨이퍼이나, 중합체와 같은 다른 기판에 사용될 수 있다. 특히, 본 명세서에 개시된 바와 같은 패터닝된 무기 물질의 형성이 예컨대 600°C 초과와 고온에서 손상 없이 가공될 수 없는 기판 상에서 매우 고해상도로 수행될 수 있도록 본 명세서에 개시된 무기 코팅 물질의 가공 온도는 비교적 낮다. 요소들이 본 명세서에 개시된 무기 코팅 물질을 이용하여 패터닝될 수 있는 적합한 소자는 예컨대 집적 전자 회로, 태양 전지, 전자 디스플레이 등을 포함한다.
- [0038] 전구체 용액
- [0039] 전구체 용액은 매우 높은 수준의 안정성을 달성하여 시판 제품을 위한 적절한 저장 수명을 갖도록 조제되어 왔다. 또한, 전구체 용액 제제는 금속 양이온의 선택에 기초하여 선택된 방사선에 대하여 소정 수준의 방사선 흡수를 달성하도록 설계될 수 있다고 발견되었다. 전구체 용액은 금속 양이온과 다원자 음이온의 수용액 및 금속 산화물 화학에 기초한다. 전구체 용액은 적어도 부분적인 용매 제거시 코팅 조성물 및 궁극적으로 금속 산화물과 다원자 음이온을 갖는 무기 고체를 형성하도록 설계된다. 금속 양이온에 대한 방사선 감수성 리간드, 특히 퍼옥시드 리간드의 높은 농도에 기초하여 전구체용액을 조정한다. 특히, 금속 양이온에 대한 퍼옥시드 거의 몰비가 2 이상일 경우, 더 안정한 용액이 형성될 수 있다. 더 안정한 전구체 용액은 조사된 코팅 물질 및 미조

사된 코팅 물질간 콘트라스트가 더 크다는 추가의 이점을 제공한다.

- [0040] 전구체 수용액은 일반적으로 하나 이상의 금속 양이온을 포함한다. 수용액에서, 금속 양이온은 물 분자와의 상호작용으로 수화된다. 상호작용성은 일반적으로 pH 의존적이다. 특히, 가수분해가 일어나 금속 이온에 산소 원자를 결합시켜 하이드록시드 리간드 또는 옥소 결합을 형성하면서 수소 이온을 방출할 수 있다. 추가의 가수분해가 일어날 때, 용액은 금속 산화물의 침전에 대하여 또는 겔화에 대하여 불안정해질 수 있다. 궁극적으로, 산화물 물질을 형성하는 것이 바람직하나, 이러한 산화물로의 전행은 용액을 먼저 코팅 물질로, 이어서 다원자 음이온을 갖는 금속 산화물 조성물로 가공하기 위한 절차의 일부로서 제어된다. 용매 제거는 산화물의 형성에 기여할 수 있으나, 이러한 방법은 본 명세서에 개시된 바와 같은 퍼옥시드계 리간드의 사용 없이는 유의적인 공정 제어를 제공하지 않는다. 이하 개시된 바와 같이, 퍼옥시드계 리간드를 사용하여 용액의 가공을 유의적으로 제어할 수 있다.
- [0041] 따라서, 금속 양이온의 수용액은 추가의 가공에 대하여 준비된다. 특히, 전구체 용액을 조성물에 대하여 더 준비시킬 수 있는 금속 아산화물 양이온을 전구체 용액의 추가 성분으로서 사용하는 것이 유리할 수 있다. 일반적으로, 전구체 용액은 약 0.01M 내지 약 1.4M 금속 아산화물 양이온, 다른 구체예에서 약 0.05M 내지 약 1.2M, 추가의 구체예에서 약 0.1M 내지 약 1.0M의 금속 아산화물 양이온을 포함한다. 당업자라면 상기 명시 범위에 속하는 추가 범위의 금속 아산화물 양이온이 고려되며 본 발명의 개시내용을 인식할 것이다. 금속 아산화물은 할로겐화물 염, 예컨대 염화물, 불화물, 브롬화물, 요오드화물 또는 이의 조합과 같은 적당한 염으로서 첨가될 수 있다. 전구체 용액에 금속 아산화물 이온의 사용을 기초로, 비교적 낮은 수준의 가열을 이용하여 방사선 감수성 리간드의 사용에 기초한 용액의 양호한 제어를 유지하면서 산화물을 형성할 수 있다.
- [0042] 다양한 금속 이온이 VO^{2+} , SbO^{3+} , ReO_3^{4+} , TiO^{2+} , TaO^{3+} , TaO_2^{4+} , YO^{3+} , NbO^{2+} , MoO^{2+} , WO^{4+} , WO_2^{2+} , AlO^{3+} , GaO^{3+} , CrO^{3+} , FeO^{3+} , BiO^{3+} , LaO^{3+} , CeO^{3+} , PrO^{3+} , NdO^{3+} , PmO^{3+} , SmO^{3+} , EuO^{3+} , GdO^{3+} , TbO^{3+} , DyO^{3+} , HoO^{3+} , ErO^{3+} , TmO^{3+} , YbO^{3+} , LuO^{3+} , $\text{TiO}_2(\text{OH})_2^{(4-2y-z)+}$, $\text{TaO}_2(\text{OH})_2^{(5-2y-z)+}$, $\text{YO}_2(\text{OH})_2^{(3-2y-z)+}$, $\text{NbO}_2(\text{OH})_2^{(4-2y-z)+}$, $\text{MoO}_2(\text{OH})_2^{(4+2y-z)+}$, $\text{WO}_2(\text{OH})_2^{(6-2y-z)+}$, $\text{AlO}_2(\text{OH})_2^{(3-2y-z)+}$, $\text{GaO}_2(\text{OH})_2^{(3-2y-z)+}$, $\text{Zn}(\text{OH})_2^{+}$, $\text{CrO}_2(\text{OH})_2^{(3-2y-z)+}$, $\text{FeO}_2(\text{OH})_2^{(3-2y-z)+}$, $\text{BiO}_2(\text{OH})_2^{(3-2y-z)+}$, $\text{LaO}_2(\text{OH})_2^{(3-2y-z)+}$, $\text{CeO}_2(\text{OH})_2^{(3-2y-z)+}$, $\text{PrO}_2(\text{OH})_2^{(3-2y-z)+}$, $\text{NbO}_2(\text{OH})_2^{(3-2y-z)+}$, $\text{PmO}_2(\text{OH})_2^{(3-2y-z)+}$, $\text{SmO}_2(\text{OH})_2^{(3-2y-z)+}$, $\text{EuO}_2(\text{OH})_2^{(3-2y-z)+}$, $\text{GdO}_2(\text{OH})_2^{(3-2y-z)+}$, $\text{TbO}_2(\text{OH})_2^{(3-2y-z)+}$, $\text{DyO}_2(\text{OH})_2^{(3-2y-z)+}$, $\text{HoO}_2(\text{OH})_2^{(3-2y-z)+}$, $\text{ErO}_2(\text{OH})_2^{(3-2y-z)+}$, $\text{TmO}_2(\text{OH})_2^{(3-2y-z)+}$, $\text{YbO}_2(\text{OH})_2^{(3-2y-z)+}$, $\text{LuO}_2(\text{OH})_2^{(3-2y-z)+}$, 또는 이의 조합과 같은 금속 아산화물 양이온으로서 제공될 수 있다. y 및 z 매개변수는 이온이 금속 원자의 특정 산화 상태에 기초하여 양전하를 갖도록 선택될 수 있다. 특히 주목되는 금속 아산화물 양이온은 예컨대 ZrO^{2+} , ZrOOH^{+} , $\text{Zr}(\text{OH})_2^{2+}$, $\text{Zr}(\text{OH})_3^{+}$, HfO^{2+} , HfOOH^{+} , $\text{Hf}(\text{OH})_2^{2+}$, $\text{Hf}(\text{OH})_3^{+}$, 이의 조합 및/또는 다른 금속 아산화물 양이온과의 조합을 포함한다. 또한, 용액은 하프늄(Hf^{4+}), 티타늄(Ti^{4+}), 지르코늄(Zr^{4+}), 세륨(Ce^{4+}), 주석(Sn^{4+}), 탄탈(Ta^{5+}), 니오븀(Nb^{5+}), 이트륨(Y^{3+}), 몰리브덴(Mo^{6+}), 텅스텐(W^{6+}), 알루미늄(Al^{3+}), 갈륨(Ga^{3+}), 아연(Zn^{2+}), 크롬(Cr^{3+}), 철(Fe^{3+}), 비스무트(Bi^{3+}), 스칸듐(Sc^{3+}), 바나듐(V^{4+}), 망간(Mn^{4+} , Mn^{3+} , Mn^{2+}), 코발트(Co^{4+} , Co^{3+}), 니켈(Ni^{4+} , Ni^{3+}), 인듐(In^{3+}), 안티몬(Sb^{5+}), 이리듐(Ir^{4+} , Ir^{3+}), 백금(Pt^{4+} , Pt^{3+}), 란타넘(La^{3+}), 프라세오디뮴(Pr^{3+}), 네오디뮴(Nd^{3+}), 프로메티움(Pm^{3+}), 사마륨(Sm^{3+}), 유로퓸(Eu^{3+}), 가돌리늄(Gd^{3+}), 테르븀(Tb^{3+}), 디스프로슘(Dy^{3+}), 홀름(Ho^{3+}), 에르븀(Er^{3+}), 툴리움(Tm^{3+}), 이터븀(Yb^{3+}), 루테튬(Lu^{3+})의 양이온 또는 이의 조합과 같은 추가의 금속 양이온을 포함할 수 있다. 상기 기재된 바와 같이, 용액중 양이온의 상태는 pH 의존적이며 산소 배위결합의 초기 상태가 용액 중에서 변화될 수 있으나, 가수분해 경향으로 산화물 형성이 유도된다. 퍼옥시드계 리간드는 겔화 및 궁극적으로 침전을 유도하는 금속-산소 네트워크의 형성을 방해할 수 있다는 것이 발견되었다. 따라서, 퍼옥시드를 사용하여 퍼옥시드 결합이 깨질 때 빠르게 축합될 수 있는 안정한 상태를 형성할 수 있다.
- [0043] 금속 양이온은 일반적으로 방사선의 흡수에 유의적으로 영향을 준다. 따라서, 금속 양이온은 소정 방사선 및 흡수 단면을 기초로 선택될 수 있다. ZrO^{2+} 는 193 nm 파장에서의 자외광 및 다른 원자외선의 양호한 흡수를 제공하는 것이 발견되었다. HfO^{2+} 는 극자외선 및 원자빔 물질의 양호한 흡수를 제공한다. 방사선 흡수를 위한 조성의 추가 조성은 다른 금속 이온의 첨가를 기초로 조절될 수 있다. 예컨대, 티탄, 아연, 갈륨, 인듐, 주석, 안티몬, 비스무트 또는 이의 조합을 포함하는 하나 이상의 이온(양이온 또는 음이온)을 전구체 용액에 첨가하여 정파장으로 이동된 흡수 한계를 갖는 코팅 물질을 형성함으로써 248 nm 파장 자외광에 대한 감수성을 제공할 수 있다. 또한, 마그네슘, 붕소, 칼슘, 알루미늄, 규소, 인 또는 이의 조합을 포함하는 하나 이상의 이온(양이온 또는 음이온)을 사용하여 단파장에서 흡수 단면을 증가시킬 수 있다. 흡수된 에너지는 퍼옥시드 결합을 깰 수 있는 퍼옥시드 리간드로 옮겨져, 물질 특성에 대한 바람직한 제어를 제공한다.
- [0044] 전구체 용액은 또한 일반적으로 산소계인 다원자 음이온을 포함할 수 있다. 최종 무기 산화물의 형성을 통해, 산소계 다원자 음이온은 최종 고체 물질 내부의 산화물로 운반될 수 있다. 양이온과 마찬가지로, 음이온성은 pH

의존적일 수 있다. 적당한 산소계 다원자 음이온은 예컨대 SO_4^{2-} , BO_3^{3-} , AsO_4^{3-} , MoO_4^{2-} , PO_4^{3-} , WO_4^{2-} , SeO_4^{2-} , SiO_4^{4-} , 이들의 양성자화된 형태 및 이들의 조합을 포함한다. 일반적으로, 전구체 용액은 금속 아산화물 양이온 농도의 약 0.5 내지 2.0배, 다른 구체예에서 약 0.75 내지 약 1.5배, 추가의 구체예에서 약 0.8 내지 약 1.3배의 다원자 음이온 농도를 포함한다. 당업자라면 상기 명시 범위에 속하는 추가 범위의 음이온 농도가 고려되며 본 발명의 개시내용을 인식할 것이다. pH 조절이 적합할 경우 다원자 음이온은 산으로서 첨가될 수 있고/있거나 다원자 음이온은 소정 금속 양이온과 함께 첨가될 수 있다. 전구체 용액은 일반적으로 금속 아산화물 양이온과 함께 첨가될 수 있는 할로겐화물 음이온과 같은 추가의 음이온으로 제조될 수 있다. 할로겐화물 음이온은 퍼옥시드 리간드와 반응하여 Cl_2 , Br_2 또는 I_2 와 같은 할로겐 분자를 형성할 수 있다. 할로겐화물 음이온과의 반응은 퍼옥시드 농도를 첨가되는 퍼옥시드 양에 대하여 온건한 양으로 감소시킨다.

- [0045] 퍼옥시드계 리간드는 촉합에 대하여 조성물을 안정화시킨다. 특히, 비교적 높은 퍼옥시드계 리간드 농도에서, 촉합된 금속 산화물 또는 금속 수산화물의 형성 없이 조성물로부터 유의적인 양의 물을 제거할 수 있다. 이러한 안정화 특성의 발견에 기초하여, 고농도의 방사선 감수성 리간드로 코팅을 형성하는 편리한 가공을 유지하면서 양호한 저장 안정성을 갖는 용액을 형성할 수 있다. 특히 주목되는 방사선 감수성 리간드는 퍼옥시드기 $-O-O-$ 를 가진다. 도 1의 맥락에서 상기 개시한 바와 같이, 흡수된 방사선으로부터의 에너지는 산소-산소 결합을 깰 수 있다. 퍼옥시드기가 깨질 때, 조성물이 $M-O-M$ 결합(여기서, M 은 금속 원자임)을 형성하면서 촉합되므로 상응하는 안정 상태가 소실된다. 따라서, 촉합은 방사선으로 제어될 수 있다. 높은 방사선 감수성 리간드 농도를 갖는 조성물은 자발적인 촉합의 회피에 있어서 매우 안정할 수 있다.
- [0046] 화학적으로 가장 간단한 리간드 조성물은 물에 가용성인 과산화수소, H_2O_2 이다. 추가의 퍼옥시드계 리간드는 예컨대 유기 조성물 및/또는 무기 조성물을 포함한다. 일부 구체예에서, 탄소는 많은 소자에서 분리할 수 있으므로 무기 퍼옥시드계 리간드가 바람직할 수 있다. 방사선 감수성 리간드로서 무기 퍼옥시드를 사용하는 경우, 방사선 감수성 리간드로 인한 탄소 오염의 위험이 회피된다. 적당한 무기 퍼옥시드 리간드는 예컨대 과옥시황산염(SO_5H), 과옥시아황산염($\text{S}_2\text{O}_8^{2-}$), 과옥시염소산염(ClO_5H) 등 또는 여의 조합을 포함한다. 전구체 조성물은 일반적으로 금속 양이온 농도의 적어도 약 2배, 추가의 구체예에서 적어도 약 3배, 다른 구체예에서 적어도 약 4배, 추가의 구체예에서 약 5배 내지 약 25배의 리간드 농도를 포함한다.
- [0047] 일반적으로, 소정 화합물을 용해시켜 수용액을 형성한다. 용액의 성분들이 용해되고 합쳐진 후, 수화 및 퍼옥시드계 리간드 결합의 결과 화학종들의 특성이 변화될 수 있다. 본 명세서에서 용액의 조성이 언급되는 경우, 용액 중의 화학종의 성질은 잘 알 수 없으므로 상기 언급은 용액에 첨가되는 성분들에 대한 것이다.
- [0048] 일부 구체예에서, 합쳐져 전구체 용액을 형성할 수 있는 별도의 용액들을 형성하는 것이 바람직할 수 있다. 특히, 금속 아산화물 양이온, 임의의 추가의 금속 양이온, 퍼옥시드계 리간드 및 다원자 음이온 중 하나 이상을 포함하는 별도의 용액들을 형성할 수 있다. 다수의 금속 양이온을 도입하는 경우, 다수의 금속 양이온은 동일한 용액으로 및/또는 별도의 용액으로 도입될 수 있다. 일반적으로, 별도의 용액들을 잘 혼합할 수 있다. 일부 구체예에서, 퍼옥시드계 리간드가 금속 양이온과 공액될 수 있도록 금속 양이온 용액을 퍼옥시드계 리간드 용액과 혼합한다. 생성되는 용액은 안정화된 금속 양이온 용액이라 할 수 있다. 일부 구체예에서, 안정화된 금속 양이온은 추가의 가공 전에 약 5분 이상 이상, 추가의 구체예에서 약 15분 이상 동안 안정화될 수 있다. 중합체 음이온 용액을 안정화된 금속 양이온 용액에 첨가하여 안정화된 전구체 용액을 형성할 수 있다. 이 순서로 용액을 합치면 전구체 용액의 일부 구체예에서 더 바람직한 결과를 유도할 수 있다. 양호한 혼합을 달성하기 위하여 적절한 속도에서 적절한 혼합 조건 하에 용액을 합할 수 있다.
- [0049] 전구체 용액 중의 화학종의 농도는 용액의 소정 특성을 달성하도록 선택될 수 있다. 특히, 농도가 낮으면 대체로 스펀 코팅과 같은 특정 코팅법에 바람직한 용액 특성을 얻을 수 있고, 적합한 코팅 매개변수를 이용하여 더 얇은 코팅을 달성할 수 있다. 일반적으로, 농도는 선택된 코팅법에 적절하도록 선택될 수 있다. 상기 개시된 바와 같이, 금속 양이온에 대하여 비교적 큰 비율의 퍼옥시드계 리간드를 사용하여 전구체 용액을 크게 안정화시킬 수 있다. 전구체 용액의 안정성은 처음 용액에 대한 변화로 평가될 수 있다. 특히, 큰 폴 입자의 생성으로 상분리가 일어나는 경우, 용액은 안정성을 잃는다. 본 명세서에 개시된 개선된 안정화법에 기초하여, 용액은 추가의 혼합 없이 약 2시간 이상 동안, 추가의 구체예에서 약 1일 이상 동안, 다른 구체예에서 약 5일 이상, 추가의 구체예에서 약 25일 이상 안정할 수 있다. 당업자라면 추가 범위의 안정화 시간이 고려되고 본 개시내용에 포함됨을 인식할 것이다. 용액은 적절한 저장 수명을 갖고 유통될 수 있기에 충분한 안정화 시간을 갖도록 조제될 수 있다.

[0050] 코팅 물질

- [0051] 코팅 물질은 선택된 기재에 전구체 용액을 침착시킴으로써 형성된다. 기재는 일반적으로 코팅 물질이 침착될 수 있는 표면을 가지며, 복수의 층을 포함할 수 있는데, 여기서 표면은 최상층을 의미한다. 코팅 물질의 부착을 위한 표면을 준비하기 위하여 기재 표면을 처리할 수 있다. 표면의 준비 전에, 적절할 경우 표면을 세정 및/또는 평활화할 수 있다. 적당한 기재 표면은 이의 적합한 물질을 포함할 수 있다. 특히 주목되는 일부 표면은 예컨대 규소 웨이퍼, 실리콘 기재, 기타 무기 물질, 유기 중합체와 같은 중합체 기재, 이의 복합물 및 이의 조합을 표면에 걸쳐 및/또는 표면층에 포함한다. 비교적 얇은 원통형 구조와 같은 웨이퍼가 편리할 수 있으나, 임의의 적합한 구형 구조를 사용할 수 있다. 중합체 기재 또는 비중합체 구조 위에 중합체층을 갖는 기재가 저비용 및 용동성에 기반한 특정 제품에 바람직할 수 있으며, 적당한 중합체는 본 명세서에 개시된 패터닝 가능한 무기 물질의 가공에 사용될 수 있는 비교적 낮은 가공 온도에 기초하여 선택될 수 있다. 적당한 중합체는 예컨대 폴리 카르보네이트, 폴리아미드, 폴리에스테르, 폴리아렌, 이들의 공중합체 및 이들의 혼합물을 포함할 수 있다. 일반적으로, 이것은 평평한 표면을 갖는 기판, 특히 고해상 제품에 바람직하다.
- [0052] 종래의 유기 레지스트는 비극성 용매에 가용성이며 소수성 표면에 침착된다. 표면을 소수성화하고 중합체 레지스트의 부착을 촉진하기 위하여 표면을 헥사메틸디실란(HMDS)과 같은 화합물로 처리할 수 있다. 대조적으로, 본 명세서에 개시된 무기 패터닝가능한 코팅 물질은 수용액을 베이스로 하므로, 기판 표면에 적용하기 위하여 용액이 친수성 표면에 도포하는 것이 바람직할 수 있다. 표면이 처음에 바람직한 정도로 친수성이 아닐 경우, 기판이 친수성이 되도록 하는 특정 기판 조성물에 적당한 방법을 사용할 수 있다. 규소 기판의 경우, 염기성 세제에 침지, 산소 플라즈마 처리, UV 오존 처리, 퍼라나 에칭제(농축 $\text{H}_2\text{SO}_4(\text{aq})$ 및 30 중량%의 $\text{H}_2\text{O}_2(\text{aq})$ 의 3:1 혼합물)에 침지, 및 디메틸설폭사이드(DMSO)에 의한 처리 및 이어서 약 5분까지 동안 약 225°C 내지 약 275°C에서 가열하는 것을 포함하나 이에 한정되지 않는 다양한 방법을 이용하여 표면을 친수성으로 할 수 있다.
- [0053] 일반적으로, 임의의 적당한 코팅 방법을 이용하여 기판에 전구체 용액을 전달할 수 있다. 적당한 코팅 방법은 예컨대 스핀 코팅, 분무 코팅, 침지 코팅, 나이프 에지 코팅, 잉크젯 인쇄 및 스크린 인쇄와 같은 인쇄법 등을 포함할 수 있다. 이들 코팅법 중 일부는 코팅 공정 동안 코팅 물질의 패턴을 형성하나, 현재 인쇄 등으로부터 이용가능한 해상도는 본 명세서에 개시된 바와 같은 방사선에 기초한 패터닝으로부터 이용가능한 것보다 현저히 낮은 수준의 해상도를 가진다. 코팅 물질은 코팅 공정을 더 잘 제어할 수 있도록 다수의 코팅 단계로 도포될 수 있다. 예컨대, 다량의 스핀 코팅을 수행하여 원하는 최종 코팅 두께를 얻을 수 있다. 이하에 개시된 열처리라는 각 코팅 단계 후 또는 복수의 코팅 단계 후 적용될 수 있다.
- [0054] 방사선을 이용하여 패터닝을 수행할 경우, 스핀 코팅은 에지 효과가 있을 수 있으나 기판을 비교적 균일하게 커버하기에 바람직한 방법일 수 있다. 일부 구체예에서, 웨이퍼는 약 500 rpm 내지 약 10,000 rpm, 추가의 구체예에서 약 1000 rpm 내지 약 7500 rpm, 추가의 구체예에서 약 2000 rpm 내지 약 6000 rpm의 속도로 스피닝될 수 있다. 스피닝 속도를 조절하여 소정의 코팅 두께를 얻을 수 있다. 스핀 코팅은 약 5초 내지 약 5분, 추가의 구체예에서 약 15초 내지 약 2분의 시간 동안 수행될 수 있다. 처음에 예컨대 50 rpm 내지 250 rpm의 저속 스핀을 이용하여 기판에 걸쳐 조성물의 초기 벌크 확산을 수행할 수 있다. 물 또는 기타 적당한 세정액으로 씻면 세정, 에지링 제거 단계 등을 수행하여 임의의 에지 비드를 제거할 수 있다. 당업자라면 상기 명시 범위에 속하는 추가 범위의 스핀 코팅 매개변수가 고려되며 본 발명의 개시내용을 인식할 것이다.
- [0055] 코팅의 두께는 일반적으로 전구체 용액 농도, 점도 및 스핀 속도의 함수일 수 있다. 다른 코팅 방법에서, 두께는 또한 일반적으로 코팅 매개변수의 선택에 의하여 조절될 수 있다. 일부 구체예에서, 작은 고해상의 피치의 형성을 촉진하기 위하여 얇은 코팅을 사용하는 것이 바람직할 수 있다. 일부 구체예에서, 코팅 물질의 평균 두께는 약 1 마이크로 이하, 추가의 구체예에서 약 250 나노미터(nm) 이하, 추가의 구체예에서 약 1 나노미터(nm) 내지 약 50 nm, 다른 구체예에서 약 1 nm 내지 약 40 nm, 일부 구체예에서 약 1 nm 내지 약 25 nm일 수 있다. 당업자라면 상기 명시 범위에 속하는 추가 범위의 두께가 고려되며 본 발명의 개시내용을 인식할 것이다. 두께는 필름의 광학 특성에 기초한 타원계측법 및/또는 x-선 반사의 비접촉법을 이용하여 평가할 수 있다.
- [0056] 많은 코팅 공정이 증발을 자극하는 용액의 이동 및 큰 표면적을 갖는 액적 또는 다른 형태의 코팅 물질을 형성 하므로 코팅 공정 자체로 용매의 일부가 증발될 수 있다. 용매가 손실되면 물질 중의 화학종의 농도가 증가하므로 코팅 물질의 점도가 증가되는 경향이 있다. 일반적으로, 방사선 노광 전에 코팅 물질을 가열하여 용매를 더 제거하여 코팅 물질의 치밀화를 촉진할 수 있다. 열처리 및 코팅 물질 치밀화 결과, 코팅 물질은 파옥시드기의 열분해 결과 유의적인 콘트라스트 손실 없이 방사선 흡수 및 내화성 지수 증가를 나타낼 수 있다.
- [0057] 코팅 공정 동안의 목적은 용매를 충분히 제거하여 코팅 물질을 추가 처리를 위하여 안정화시키는 것일 수 있다. 용매 제거 공정은 코팅 물질 중에 잔존하는 특정량의 용매를 양적으로 제어할 수 없고 일반적으로 생성되는 코

팅 물질 특성에 대한 실험적인 평가를 수행하여 패터닝 공정에 효과적인 처리 조건을 선택할 수 있다. 공정의 성공적인 적용에 가열이 필요한 것은 아니나, 처리 속도를 높이고/높이거나 공정의 재현성을 증가시키기 위하여 코팅 물질을 가열하는 것이 바람직할 수 있다. 용매를 제거하기 위하여 가열이 적용되는 구체예에서, 코팅 물질을 약 45℃ 내지 약 150℃, 추가의 구체예에서 약 50℃ 내지 약 130℃, 다른 구체예에서 약 60℃ 내지 약 110℃의 온도에서 가열할 수 있다. 용매 제거를 위한 가열은 일반적으로 약 0.1분 이상 동안, 추가의 구체예에서, 약 0.5분 내지 약 30분 동안, 추가의 구체예에서 약 0.75분 내지 약 10분 동안 수행될 수 있다. 당업자라면 상기 명시 범위에 속하는 추가 범위의 가열 온도 및 시간이 고려되며 본 발명의 개시내용을 인식할 것이다.

[0058] 패터닝된 노광 및 패터닝된 코팅 물질

[0059] 코팅 물질은 방사선을 이용하여 미세하게 패터닝될 수 있다. 상기 개시한 바와 같이, 전구체 용액의 조성 및 이에 따른 코팅 물질의 농도는 소정 형태의 방사선을 충분히 흡수하도록 설계될 수 있다. 방사선의 흡수는 피옥시드제 리간드의 적어도 일부가 물질의 안정화에 더이상 이용될 수 없도록 피옥시드 -O-O- 결합을 깨는 에너지를 전달한다. 충분한 양의 방사선의 흡수로, 노광된 코팅 물질은 축합된다. 방사선은 일반적으로 선택된 패턴에 따라 전달될 수 있다. 방사선 패턴은 조사 영역 및 미조사 영역을 갖는 코팅 물질 층의 해당 패턴 또는 잠상으로 전달된다. 조사 영역은 축합된 코팅 물질을 포함하며, 미조사 영역은 일반적으로 형성된대로의 코팅 물질을 포함한다. 아래 개시되는 바와 같이, 미조사 코팅 물질의 제거에 의한 코팅 물질의 현상시 매우 선풍한 에너지가 형성될 수 있다.

[0060] 방사선은 일반적으로 마스크를 통해 코팅 기판으로 전달할 수 있거나 또는 방사선 빔은 기판에 거쳐 제어 스캐닝될 수 있다. 일반적으로, 방사선은 전자기 방사선, 전자빔(메타 방사선) 또는 다른 적당한 방사선을 포함할 수 있다. 일반적으로, 전자기 방사선은 가시 방사선, 자외 방사선 또는 x-선 방사선과 같은 소정 파장 또는 파장 범위를 가질 수 있다. 방사선 패턴에 이용할 수 있는 방사선은 일반적으로 방사선 파장에 의존하며, 고해상도 패턴은 일반적으로 단파장 방사선으로 달성될 수 있다. 따라서, 자외광, x-선 방사선 또는 전자빔을 이용하여 특히 높은 해상도 패턴을 달성하는 것이 바람직할 수 있다.

[0061] 본 명세서에 참고로 포함된 국제 표준 ISO 21348 (2007)에 따르면, 자외광은 100 nm 이상 400 nm 미만의 파장 범위에 존재한다. 크립톤 불화물 레이저가 248 nm 자외광을 위한 공급원으로서 사용할 수 있다. 자외광 범위는 10 nm 이상 121 nm 미만의 극자외선(EUV) 및 122 nm 이상 200 nm 미만의 원자외선(FUV)과 같은 허용되는 표준 하에 몇가지 방식으로 나뉘어질 수 있다. 아르곤 불화물 레이저로부터의 193 nm 선을 FUV에서의 방사선 공급원으로서 사용할 수 있다. EUV광은 13.5 nm에서 리소그래피에 사용되어 왔고, 이 광은 방전 펄스 또는 고에너지 레이저를 이용하여 여기되는 Xe 또는 Sn 플라스마로부터 발생된다. 소프트 x-선은 0.1 nm 이상 10 nm 미만에서 취득될 수 있다.

[0062] 전자기 방사선의 양은 노광 시간에 걸쳐 통합 방사선 플럭스에 의하여 취득되는 영향력 또는 용량을 특징으로 할 수 있다. 적당한 방사선 선속은 약 1 mJ/cm² 내지 약 150 mJ/cm², 추가의 구체예에서 약 2 mJ/cm² 내지 약 100 mJ/cm², 추가의 구체예에서 약 3 mJ/cm² 내지 약 50 mJ/cm²일 수 있다. 당업자라면 상기 명시 범위에 속하는 추가 범위의 방사선 선속이 고려되며 본 발명의 개시내용을 인식할 것이다.

[0063] 전자빔 리소그래피에서, 일반적으로 전자빔은 일반적으로 조사 물질을 변형시키는 2차 전자를 유도한다. 해상도는 적어도 부분적으로 물질 층의 2차 전자 범위의 함수일 수 있으며, 일반적으로 2차 전자 범위가 짧을수록 해상도가 높아진다고 믿어진다. 본 명세서에 개시된 무기 코팅 물질을 이용하여 전자 리소그래피로 달성될 수 있는 고해상에 기초하여, 무기 물질에서 2차 전자의 범위는 제한된다. 전자빔은 빔 에너지를 특징으로 할 수 있으며, 적당한 에너지는 약 5 eV 내지 약 200 keV 범위, 추가의 구체예에서 약 7.5 eV 내지 약 100 keV 범위일 수 있다. 30 keV에서 근사치 보정된 빔 용량은 약 0.1 μC/cm² 내지 약 5 μC/cm², 추가의 구체예에서 약 0.5 μC/cm² 내지 약 1 μC/cm², 다른 구체예에서 약 1 μC/cm² 내지 약 100 μC/cm² 범위일 수 있다. 당업자라면 본 명세서의 교시에 기초하여 다른 빔 에너지에서 해당 용량을 계산할 수 있고 상기 명시 범위에 속하는 추가 범위의 전자빔 특성이 고려되며 본 발명의 개시내용을 인식할 것이다.

[0064] 방사선 노광 후, 코팅 물질은 조사 영역 및 미조사 영역으로 패터닝된다. 도 2 및 3을 참조하면, 기판(102), 얇은 필름(103) 및 패터닝된 코팅 물질(104)을 포함하는 패터닝된 구조(100)가 도시된다. 패터닝된 코팅 물질(104)은 조사 코팅 물질의 축합 영역(10, 112, 114, 116) 및 미조사 코팅 물질의 비축합 영역(118, 120)을 포함한다. 축합 영역(110, 112, 114, 116) 및 비축합 영역(118, 120)에 의하여 형성된 패터닝은 코팅 물질에 잠상을 나타낸다.

- [0065] 무기 코팅 물질의 디자인에 기초하여, 축합된 코팅 물질을 갖는 조사 영역 및 미조사 비축합 코팅 물질 사이에 큰 물질 특성 대비가 존재한다. 놀랍게도, 일부 구체예에서 조사후 열처리 없이 만족스러운 결과가 달성될 수 있으나, 조사후 열처리로 콘트라스트가 개선될 수 있음을 발견하였다. 노광후 열처리하는 피옥시드의 열분해에 기초하여 코팅 물질의 미조사 영역을 유익적으로 축합하는 일 없이 조사된 코팅 물질을 어닐링하여 축합을 개선시키는 것으로 보인다. 열처리가 이용되는 구체예에서, 후조사 열처리는 약 45°C 내지 약 150°C, 추가의 구체예에서 약 50°C 내지 약 130°C, 추가의 구체예에서 약 60°C 내지 약 110°C의 온도에서 수행될 수 있다. 용매 제거를 위한 가열은 일반적으로 약 0.1분 이상 동안, 추가의 구체예에서, 약 0.5분 내지 약 30분 동안, 추가의 구체예에서 약 0.75분 내지 약 10분 동안 수행될 수 있다. 당업자라면 상기 명시 범위에 속하는 추가 범위의 후조사 가열 온도 및 시간이 고려되며 본 발명의 개시내용을 인식할 것이다. 코팅 물질 특성에서 이렇게 높은 콘트라스트는 이하의 섹션에서 개시되는 바와 같이 현상 후 패턴에서 선명한 선의 형성을 더 촉진한다.
- [0066] 현상 및 패터닝된 구조
- [0067] 화상의 현상은 현상제 조성물에 잠상을 포함하는 패터닝된 코팅 물질을 접촉시켜 미조사 코팅 물질을 제거하는 것을 수반한다. 도 4 및 5를 참조하면, 도 2 및 3에 도시된 구조의 잠상을 현상제와의 접촉을 통해 현상하여 패터닝된 구조 (130)를 형성한다. 화상의 현상 후, 기관 (102)은 개구부 (132, 134)를 통해 튜브면을 따라 노광된다. 개구부 (132, 134)는 각각 비축합 영역 (118, 120)의 위치에 존재한다.
- [0068] 일반적으로, 현상제는 수성 산 또는 염기일 수 있다. 일반적으로, 수성 염기를 사용하여 더 선명한 화상을 얻을 수 있다. 현상제로부터의 오염을 감소시키기 위하여, 금속 원자를 갖지 않는 현상제를 이용하는 것이 바람직할 수 있다. 따라서, 테트라에틸암모늄 히드록사이드, 테트라프로필암모늄 히드록사이드, 테트라부틸암모늄 히드록사이드 또는 이들의 조합과 같은 4급 암모늄 히드록사이드 조성물이 현상제로서 바람직하다. 일반적으로, 특히 주목되는 4급 암모늄 히드록사이드는 화학식 R_4NOH (여기서, R = 메틸기, 에틸기, 프로필기, 부틸기 또는 이의 조합)으로 표시될 수 있다. 무기 코팅 물질은 일반적으로 현재 중합체 레지스트, 특히 테트라메틸 암모늄 히드록사이드 (TMAH)에 통상적으로 사용되는 동일한 현상제로 현상될 수 있다. 시판되는 TMAH는 2.38 중량%에서 이용될 수 있으며, 이 농도는 본 명세서에 개시된 가공에 사용될 수 있다. 그러나, 무기 물질의 현상에 대한 일부 구체예에서, 현상제는 25 중량% TMAH와 같은 유기 레지스트의 현상에 일반적으로 사용되는 농도보다 높은 농도로 전달될 수 있다. 또한, 혼합 4급 테트라알킬암모늄 히드록사이드를 선택하여 실험적 평가에 기초하여 개선된 라인 에지 프로필을 제공할 수 있다. 일반적으로, 현상제는 약 2 내지 약 40 중량%, 추가의 구체예에서 약 3 내지 약 35 중량%, 다른 구체예에서 약 4 내지 약 30 중량%의 테트라알킬암모늄 히드록사이드를 포함할 수 있다. 당업자라면 상기 명시 범위에 속하는 추가 범위의 현상제 농도가 고려되며 본 발명의 개시내용을 인식할 것이다.
- [0069] 주요 현상제 조성물 외에, 현상제는 현상 공정을 촉진하기 위하여 추가의 조성물을 포함할 수 있다. 적당한 첨가제는 예컨대 임프늄, d-블록 금속 양이온 (하프늄, 지르코늄, 탄탈륨 등), f-블록 금속 양이온 (세륨, 루테튬 등), p-블록 금속 양이온 (알루미늄, 주석 등), 알칼리 금속 (리튬, 나트륨, 칼륨 등), 및 이의 조합으로 이루어지는 군에서 선택된 양이온, 및 불화물, 염화물, 브롬화물, 요오드화물, 질산염, 황산염, 인산염, 규산염, 붕산염, 피옥시드, 부옥시드, 포름산염, 에틸렌디아민-테트라아세트산 (EDTA), 텅스텐산염, 폴리브덴산염 등 및 이의 조합으로 이루어지는 군에서 선택되는 음이온을 갖는 용해된 염을 포함한다. 임의의 첨가제가 존재하는 경우, 현상제는 약 10 중량% 이하의 첨가제, 추가의 구체예에서 약 5 중량% 이하의 첨가제를 포함할 수 있다. 당업자라면 상기 명시 범위에 속하는 추가 범위의 첨가제 농도가 고려되며 본 발명의 개시내용을 인식할 것이다. 첨가제는 콘트라스트, 감도 및 선측 거칠기를 개선시키도록 선택될 수 있다. 현상제 중의 첨가제는 또한 $\text{HfO}_2/\text{ZrO}_2$ 입자의 형성 및 침전을 억제할 수 있다.
- [0070] 더 약한 현상제, 예컨대 더 낮은 농도의 현상제에서는, 공정의 속도를 증가시키기 위하여 더 교온의 현상 공정을 이용할 수 있다. 더 강한 현상제에서는, 현상 공정의 온도를 낮추어 속도를 감소시키고/감소시키거나 현상의 카이네틱스를 제어할 수 있다. 일반적으로, 현상 온도는 수성 용매의 적절한 값 사이에서 조절될 수 있다. 또한, 현상제-코팅 계면 근처에서 용해된 무기 코팅을 갖는 현상제는 현상 동안 초음파로 분산될 수 있다.
- [0071] 현상제는 임의의 적합한 방법을 이용하여 패터닝된 코팅 물질에 도포될 수 있다. 예컨대, 현상제는 패터닝된 코팅 물질에 분무될 수 있다. 또한, 스핀 코팅에 이용될 수 있다. 자동화된 가공에서는, 경자 포맷에서 코팅 물질에 현상제를 부어 넣는 것을 수반하는 퍼즐법이 이용될 수 있다. 필요에 따라, 스핀 세정 및/또는 건조를 이용하여 현상 공정을 완료할 수 있다. 적당한 세정 용액은 예컨대 초순수, 메틸 알콜, 에틸 알콜, 프로필 알콜 및 이의 조합을 포함한다. 화상을 현상한 후, 코팅 물질을 패턴으로서 기관에 배치한다.
- [0072] 현상 단계의 완료 후, 코팅 물질을 열처리하여 물질을 더 축합하고 더 탈수할 수 있다. 추가의 패터닝을 촉진하

기 위하여 코팅 물질의 안정화가 바람직할 경우 무기 코팅 물질이 레지스트로서 사용되고 궁극적으로 제거되는 일부 구체에에서 열처리를 수행하는 것이 바람직할 수 있으나, 이러한 열처리는 무기 코팅 물질이 최종 소자에 포함되는 구체에에 특히 바람직할 수 있다. 특히, 패터닝된 코팅 물질의 소성은 패터닝된 코팅 물질이 바람직한 수준의 애칭 선택성을 나타내는 조건 하에 수행될 수 있다. 일부 구체에에서, 패터닝된 코팅 물질은 약 150°C 내지 약 600°C, 추가의 구체에에서 약 175°C 내지 약 500°C, 추가의 구체에에서 약 200°C 내지 약 400°C의 온도로 가열될 수 있다. 가열은 약 1분 이상 동안, 다른 구체에에서 약 2분 내지 약 1시간 동안, 추가의 구체에에서 약 2.5분 내지 약 25분 동안 수행될 수 있다. 당업자라면 상기 명시 범위에 속하는 추가 범위의 열처리 온도 및 시간이 고려되며 본 발명의 개시내용을 인식할 것이다.

- [0073] 유기 레지스트의 경우, 구조의 종횡비, 폭으로 나눈 높이가 지나치게 커지면 구조는 패턴 붕괴하기 쉽다. 패턴 붕괴는 높은 종횡비 구조의 기계적 불안정성과 연관될 수 있어, 가공 단계와 관련된 예컨대 표면 장력과 같은 힘이 구조 요소를 변형시킨다. 낮은 종횡비 구조는 잠재 변형력에 있어서 더 안정하다. 본 명세서에 개시된 패터닝 가능한 무기 물질을 사용할 경우, 더 얇은 코팅 물질층을 갖는 구조체를 효과적으로 가공하는 능력으로 인하여, 높은 종횡비 패터닝된 코팅 물질이 필요 없이 개선된 패터닝이 달성될 수 있다. 따라서, 패터닝된 코팅 물질 층의 높은 종횡비 피치가 손실되지 않고 매우 높은 해상도의 피치가 형성되었다.
- [0074] 생성되는 구조는 매우 낮은 선폭 거칠기를 갖는 선명한 애치를 가질 수 있다. 특히, 선폭 거칠기 감소는 외에, 높은 콘트라스트는 또한 매우 잘 해상된 2차원 패턴(예컨대 선명한 코너) 형성능 및 피치간 공간 및 작은 피치의 형성을 허용할 수 있다. 따라서, 일부 구체에에서, 이웃하는 구조의 인접 선형 세그먼트는 약 60 nm 이하, 일부 구체에에서 약 50 nm 이하, 추가의 구체에에서 약 40 nm 이하의 평균 피치를 가질 수 있다. 피치는 디자인으로 평가될 수 있고 역상 화상에 의해서와 같이 주사 전자 현미경(SEM)으로 확인할 수 있다. 본 명세서에서 사용될 때, 피치는 공간적인 주기 또는 반복 구조 요소의 중심-대-중심 거리를 의미한다. 패턴의 피치 치수는 또한 일반적으로 모서리 등으로부터 평가되는 피치의 평균 폭으로 개시될 수 있다. 또한, 피치는 물질 요소간 및/또는 물질 요소까지의 겹을 의미할 수 있다. 일부 구체에에서, 평균 폭은 약 30 nm 이하, 추가의 구체에에서 약 25 nm 이하, 추가의 구체에에서 약 20 nm 이하일 수 있다. 평균 선폭 거칠기는 약 2.25 nm 이하, 추가의 구체에에서 약 1.2 nm 내지 약 2.0 nm일 수 있다. 선폭 거칠기 평가는 평균 선폭으로부터 3σ 편차를 유도하는 표준 SEM 이미지의 분석으로 수행된다. 평균은 고주파수 및 저주파수 거칠기, 즉 각각 짧은 상관(correlation) 길이 및 긴 상관 길이를 모두 포함한다. 유기 레지스트의 선폭 거칠기는 주로 긴 상관 길이를 특징으로 하는 반면, 본 발명 무기 코팅 물질은 유의적으로 더 짧은 상관 길이를 나타낸다. 패턴 전사 공정에서, 짧은 보정 거칠기는 애칭 공정 동안 평활화되어 산뢰성이 훨씬 더 높은 패턴을 생성할 수 있다. 당업자라면 상기 명시 범위에 속하는 추가 범위의 피치, 평균폭 및 선폭 거칠기가 고려되며 본 발명의 개시내용을 인식할 것이다.
- [0075] 패터닝된 코팅 물질의 추가 가공
- [0076] 패터닝된 코팅 물질의 형성 후, 코팅 물질을 더 가공하여 선택된 소자의 형성을 용이하게 할 수 있다. 또한, 일반적으로 추가의 물질 침착 및/또는 패터닝을 수행하여 구조를 완료할 수 있다. 코팅 물질은 최종적으로 제거되거나 제거되지 않을 수 있다. 패터닝된 코팅 물질의 품질은 임의의 경우 더 작은 공간 치수 등을 갖는 소자와 같은 개선된 소자의 형성에 긍정적인 수 있다.
- [0077] 패터닝된 코팅 물질은 도 4 및 5의 실시예에 도시된 바와 같이 하부 기판에 개구부를 형성한다. 종래의 레지스트와 같이, 패터닝된 코팅 물질은 패턴을 전사하여 하부 박막을 선택적으로 제거하는 데 이용될 수 있는 애칭 마스크를 형성한다. 도 6을 참조하면, 하부 박막(103)은 축합 영역(110, 112, 114) 아래 각각 패터닝된 남은 피쳐(152, 154, 156)이다. 종래의 중합체 레지스트에 비하여, 본 명세서에 개시된 물질은 유의적으로 더 큰 애칭 내성을 제공할 수 있다.
- [0078] 대안으로 또는 추가로, 추가 물질의 침착은 하부 구조의 특성을 바꿀 수 있고/있거나 하부 구조에 접촉을 제공할 수 있다. 추가의 코팅 물질은 물질의 소정 특성을 기초로 선택될 수 있다. 또한, 패터닝된 무기 코팅 물질의 밀도가 높은 주입 내성을 제공할 수 있으므로 이온이 하부 구조에 선택적으로 주입될 수 있다. 일부 구체에에서, 추가의 침착 물질은 유전체, 반도체, 도체 또는 다른 적당한 물질일 수 있다. 추가의 침착 물질은 용액 배이스법, 화학 증기 증착(CVD), 스퍼터링, 물리적 증기 증착(PVD) 또는 다른 적당한 방법과 같은 적당한 방법을 이용하여 침착시킬 수 있다.
- [0079] 일반적으로, 복수의 추가층을 침착시킬 수 있다. 복수의 층의 침착과 함께, 추가의 패터닝을 수행할 수 있다. 수행할 경우, 임의의 추가의 패터닝은 본 명세서에 개시된 추가량의 코팅 물질, 중합체 레지스트로, 다른 패터닝법으로 또는 이의 조합으로 수행될 수 있다.

- [0080] 상기 개시된 바와 같이, 패터닝 후 코팅 물질의 층을 제거하거나 제거하지 않을 수 있다. 층을 제거하지 않을 경우, 패터닝된 코팅 물질을 구조에 포함시킨다. 패터닝된 코팅 물질을 구조에 포함시킨 구체예에서, 코팅 물질의 특성은 구조 내에 소정 패터닝 특성 및 물질 특성을 제공하도록 선택될 수 있다.
- [0081] 패터닝된 코팅 물질을 제거하는 것이 바람직한 경우, 코팅 물질은 레지스트로서 기능한다. 패터닝된 코팅 물질을 이용하여 추후 침착되는 물질을 레지스트/코팅 물질의 제거 전에 패터닝하고/하거나 축합된 코팅 물질 층의 스페이스를 통해 기판을 선택적으로 에칭한다. 적당한 에칭 공정을 이용하여 코팅 물질을 제거할 수 있다. 특히, 축합 코팅 물질을 제거하기 위하여, 예컨대 BCl_3 플라스마, Cl_2 플라스마, HBr 플라스마, Ar 플라스마 또는 다른 적절한 공정 가스를 이용한 플라스마에 의하여 건식 에칭을 수행할 수 있다. 대안으로 또는 추가로, 예컨대 HF(aq) 또는 완충 HF(aq) / NH_4F 를 이용한 습식 에칭을 이용하여 패터닝된 코팅 물질을 제거할 수 있다. 도 7을 참조하면, 코팅 물질의 제거 후 도 6의 구조가 도시된다. 에칭된 구조 (150)는 기판 (102) 및 피치 (152, 154, 156)를 포함한다.
- [0082] 코팅 물질은 종래의 레지스트에 대하여 일반적으로 문헌 (P. Zimmerman, J. Photopolym. Sci. Technol., Vol. 22, No. 5, 2009, p. 625)에 개시된 바와 같이 열적 동결 공정을 이용하는 다중 패터닝을 수행하는 데 특히 편리하다. "열적 동결"을 이용한 중 패터닝 공정은 도 8에 개략적으로 도시된다. 제1 단계에서, 코팅 물질은 도 4 및 5와 관련하여 개시된 리소그래피 공정 및 현상을 이용하여 기판 (162) 상의 패턴 (60)에 형성된다. 가열 단계 (164)를 수행하여 코팅 물질을 탈수한다. 이러한 가열 단계는 상기 현상 섹션에 개시된 현상 후 가열 단계와 동일하다. 이러한 "열적 동결" 공정으로 인하여 코팅 물질은 후속되는 제2 코팅 물질층의 침착에 불용성이 된다. 제2 리소그래피 및 현상 단계 (166)를 수행하여 기판 (162)에 이중 패터닝 구조 (168)를 형성한다. 에칭 단계 (170) 후, 생성물인 이중 패터닝 구조 (172)가 형성된다. 이 공정을 다회 코팅 및 패턴 단계로 확장하는 것이 간단한데, 이러한 확장은 고려되고 본 발명 개시 내용에 속한다. 다회 패터닝과 관련하여, 본 명세서에 개시된 무기 코팅 물질 및 종래의 유기 레지스트 사이의 유의적인 차이는 유기 레지스트가 열소성 후에도 종래의 레지스트 캐스팅 용매에 여전히 가용성이라는 것이다. 본 명세서에 개시된 레지스트 물질은 수용성이 아니도록 열소성으로 탈수된 후 후속 코팅층이 도포될 수 있다.

도면의 간단한 설명

- [0083] 도 1은 방사선으로부터의 에너지 흡수에 의하여 유발되는 축합 반응을 거치는 리간드에 결합된 금속 양이온을 도시한 개략도로서, 여기서 M은 금속 원자이고 0는 산소 원자이다.
- 도 2는 잠상을 포함하는 방사선 패터닝된 구조체의 개략적인 사시도이다.
- 도 3은 도 2의 구조체의 측면도이다.
- 도 4는 미조사 코팅 물질을 제거하여 패터닝된 구조체를 형성하는 잠상 현상 후의 도 2의 구조체의 개략적인 사시도이다.
- 도 5는 도 4의 패터닝된 구조체의 측면도이다.
- 도 5는 하층의 에칭 후 도 4 및 5의 패터닝된 구조체의 측면도이다.
- 도 7은 에칭하여 패터닝된 축합 코팅 물질을 제거한 후 도 6의 구조체의 측면도이다.
- 도 8은 "열적 동결 (thermal freeze)" 이중 패터닝 공정 흐름의 측면도이다. 도 2-4에 도시된 공정은 제1층이 제2층에 불용성이 되도록 하는 소성 후에 반복된다.
- 도 9는 약 100 nm 높이의 스텝과 Hf계 코팅 물질을 이용한 금속 게이트 라인 상의 스텝 커버리지의 주사 전자 현미경 사진이다.
- 도 10은 20 mJ/cm^2 의 용량 수준에서 193 nm 파장 간섭 리소그래피를 통해 패터닝된 Zr계 코팅 물질 층의 120 nm 피치 라인의 주사 전자 현미경 사진이다.
- 도 11은 전자빔 리소그래피를 통해 패터닝된 Hf계 코팅 물질 층의 36 nm 피치 라인의 주사 전자 현미경 사진이다.
- 도 12는 도 11에 도시된 패턴의 일부의 확대도이다.
- 도 13A는 2.38%의 TMAH에서 현상된 e-빔에 의해 패터닝된 36 nm 피치 포스트의 주사 전자 현미경 사진이다.

도 13B는 25%의 TMAH에서 현상된 e-빔에 의해 패터닝된 36 nm 피치 포스트의 주사 전자 현미경 사진이다.

도 14는 거칠기 1.6-1.8 nm의 라인을 갖는 현상된 패턴의 일부의 주사 전자 현미경 사진이다.

도 15는 본 명세서에 개시된 바와 같은 코팅 물질과 e-빔 리소그래피를 이용하여 형성된 이중 패터닝된 구조체의 주사 전자 현미경 사진이다.

도 16은 도 15에 도시된 패턴의 일부의 확대도이다.

도 17은 폭 40 nm의 예정된 규소 나노필러의 주사 전자 현미경 사진이다. 필러는 Hf계 코팅 물질로 형성된 하드 마스크에 의한 이온-에칭을 통해 제조되었다.

도 18A-D는 25% TMAH에서 현상되고 본 명세서에 개시된 Hf계 코팅 물질로 수행된 EUV 리소그래피의 주사 전자 현미경 사진이다. 각 경우, 도면은 주어진 피치의 라인 및 스페이스를 나타내는데, 여기서 라인은 언급된 피치의 대략 반의 폭을 가진다: A) 32 nm 피치 라인 및 스페이스, B) 30 nm 피치 라인 및 스페이스, C) 28 nm 피치 라인 및 스페이스, D) 26 nm 피치 라인 및 스페이스.

발명을 실시하기 위한 구체적인 내용

[0084] 실시예

[0085] 실시예 1: 전구체 용액의 제조

[0086] 이 실시예는 hafnium (Hf) 및/또는 zirconium (Zr)을 배이스로 하는 금속 아산화물 양이온을 포함하는 전구체 용액의 제조에 사용될 방법을 개시한다.

[0087] 전구체 용액의 성분을 위하여 별도의 수용액을 제조하였다. 명명의 편의를 위하여, 각각의 용액을 금속 아산화물 양이온에 대하여 파트 A로, 퍼옥시드계 리간드 용액에 대하여 파트 B로, 다원자 음이온을 포함하는 용액에 대하여 파트 C로 일컬을 수 있다. 용액 파트 A1은 500 mL의 초순수(18-MΩ·cm 전기 저항)와 조합된 0.5 mol $ZrOCl_2 \cdot 8H_2O$ (161.125, Alfa Aesar 99.9%)의 용액을 여과하여 제조하였다. 용액 파트 A2는 500 mL의 초순수(18-MΩ·cm 전기 저항)와 조합된 0.5 mol $HfOCl_2 \cdot 8H_2O$ (204.76g, Alfa Aesar 98%)의 용액을 여과하여 제조하였다. 이하 개시되는 바와 같이, 파트 A1을 이용하여 193 nm 리소그래피 패터닝을 위한 전구체 용액을 형성하고, 파트 A2를 이용하여 13 nm (극UV 또는 EUV로도 공지됨) 또는 전자빔 리소그래피 패터닝을 위한 전구체 용액을 형성하였다. 초순수로 H_2O_2 (aq) (30% w/w, Mallinckrodt Baker)를 희석하여 6-8% w/w H_2O_2 (aq) 용액을 얻음으로써 파트 B 용액을 제조하였다. 파트 C 용액은 공인된 농도 (Fischer Scientific, 10 N)로 수득되거나 초순수에 의하여 농축 용액으로부터 희석된 (98% H_2SO_4 , Mallinckrodt Baker) 2-5 M H_2SO_4 (aq)를 포함하였다.

[0088] 193 nm 리소그래피 패터닝을 위하여, Zr계 전구체 용액을 제조하였다. EUV 또는 전자빔 리소그래피 패터닝을 위하여, Hf계 전구체 용액을 제조하였다. 전구체 용액의 제조에 사용되는 방법은 Zr계 전구체 용액이 파트 A1으로 제조되고 Hf계 전구체 용액이 파트 A2로 제조되는 것을 제외하고 동일하였다. 선택된 비율의 성분 용액 파트 A1 또는 파트 A2, 파트 B, 및 파트 C를 개개의 미리세정된 폴리에틸렌 병으로 측정하여 넣었다. 표적 최종 금속 농도를 얻기 위하여 충분한 양의 초순수를 파트 C 성분 용액에 첨가하였다. 이후 파트 A1 또는 파트 A2 성분 용액을 파트 B 성분 용액에 부어 병 안의 성분들을 합하고, 5분 기다린 후, 파트 C를 파트 A1 또는 파트 A2 및 파트 B를 합한 것에 붓고 다시 5분 기다렸다. 이러한 특정의 혼합 순서가 입자 성장을 제한한다고 발견되었다.

[0089] 상기 개시된 방법을 이용하여, 4.8 mL의 파트 A1 용액 (Zr), 1.8 mL의 파트 B 용액 (H_2O_2), 2.16 mL의 파트 C 용액 (H_2SO_4 (aq)), 및 21.24 mL의 초순수를 합함으로써, 0.16 M의 최종 zirconium 농도를 갖는 Zr계 전구체 용액 제제 30 mL를 얻었다. 상기 개시된 방법을 이용하여, 4.5 mL의 파트 A2 용액 (Hf), 16.875 mL의 파트 B 용액 (H_2O_2), 1.8 mL의 파트 C 용액 (H_2SO_4 (aq)), 및 6.825 mL의 초순수를 합함으로써, 0.15 M의 최종 hafnium 농도를 갖는 Hf계 전구체 용액 제제 30 mL를 얻었다.

[0090] 실시예 2: 코팅 물질의 제조 및 침착

[0091] 이 실시예는 실시예 1에 따라 제조된 전구체 용액을 이용한 패터닝 가능한 코팅 물질의 침착 및 기판 표면의 제조를 개시한다.

[0092] 기판으로 5인치 규소 웨이퍼를 사용하였다. 규소 웨이퍼 표면을 열기성 세제, 산성 세제, O_2 플라즈마, 자외선, 피라나 에칭 용액 또는 DMSO로 미리 처리한 다음 225°C 내지 275°C의 온도로 가열하여 표면을 친수성이 되게 하였다. 선택된 전구체 용액을 표준 리소그래피 스핀 코팅 트랙에서 코팅하였다. 웨이퍼를 스핀 코팅가에 로

닝하고, 전구체 용액을 웨이퍼 중심에 분산시켰다. 분산된 전구에 용액의 양은 소정 코팅 두께 및 웨이퍼의 크기를 기초로 선택하였다. 스핀 코팅기를 100 RPM에서 5초간 스피닝하여 웨이퍼에 걸쳐 레지스트를 확산시킨 다음 3000 RPM에서 30-60초간 스피닝하여 레지스트막을 캐스팅하였다. 웨이퍼를 40-200℃에서 0.1-5분 동안 미리 노광 소성하였다.

[0093] 이 방법은 또한 스텝으로 웨이퍼를 코팅하는 데 이용되었다. 도 9는 박막 트랜지스터(TFT) 게이트 유전체 제품에서 약 100 nm 스텝을 이용한 웨이퍼 상에서의 Hf계 코팅 물질의 커버리지를 도시한다. 5개의 연속 침착된 층으로부터 코팅을 제조하여 스텝 커버리지가 가능함을 입증하였다. 더 날카로운 스텝 상의 적절한 커버리지가 관찰되었다.

[0094] 실시예 3: Zr계 코팅 물질의 193-nm 리소그래피 패터닝

[0095] 이 실시예는 Zr 아산화물계 코팅 물질의 패터닝에 사용된 방법을 개시한다.

[0096] ZrO_2 -계 코팅 조성물을 사용하여 실시예 2의 방법에 따라 코팅 물질을 제조하였다. 코팅 물질을 10-50 nm의 두께로 침착하였다. Zr계 코팅 물질을 ArF 레이저 공급원과 마스크 또는 생성된 간섭 패턴을 갖는 리소그래피 처리 시스템을 이용하여 패터닝된 193 nm (원UV) 광으로 조사하였다. 조사 후, 웨이퍼를 웨이퍼 트렉으로 되돌리고 40℃ 내지 200℃에서 1-5분간 후노광 소성하였다. 193 nm UV광으로 노광하여 패터닝된 코팅 물질을 얻었다. 패터닝된 코팅 물질을 피들 현상 공정을 이용하여 2.38 중량% TMAH으로 현상하였다. TMAH를 20초간 코팅 물질과 접촉시킨 다음 기판을 물로 세정하고 건조시켰다. 도 10을 참조하면, 현상제를 사용하여 교해상 패턴을 생성하였다. 도 10은 20 mJ/cm²의 용량에서 193 nm 리소그래피에 의하여 생성된 Zr계 코팅 물질 층의 120-nm 피치 라인(약 60 nm 라인 및 스페이스)의 패턴이다.

[0097] 실시예 4: Hf계 코팅 물질의 전자빔 및 EUV 리소그래피 패터닝

[0098] 이 실시예는 Hf 아산화물계 코팅 물질의 패터닝에 사용된 방법을 개시한다.

[0099] HfO_2 -계 코팅 조성물을 사용하여 실시예 2의 방법에 따라 코팅 물질을 제조하고 침착시켰다. 한 구체예에서, Hf계 코팅 조성물을 30 keV 및 약 78 $\mu\text{C}/\text{cm}^2$ 에서 전자빔으로 노광시켰다. 생성된 패터닝된 코팅 물질을 침지법을 이용하여 2.38 내지 25 중량% TMAH으로 현상하였다. 현상제를 20초간 웨이퍼와 접촉시켰다. 이후, 웨이퍼를 물로 세정하고 건조시켰다. 현상제와 접촉시켜 도 11, 12, 13A 및 13B에 도시된 바와 같은 패턴을 얻는다. 교해상 패턴이 생성되었다. 도 11은 Hf계 코팅 물질 층의 36 nm 피치 라인을 도시한다. 36 nm 피치를 갖는 다른 패턴이 도 12에 도시된다. 이 패턴은 244 $\mu\text{C}/\text{cm}^2$ 의 e-빔 용량으로 발생되었다.

[0100] 도 13A 및 13B는 전자빔 방사선으로 패터닝된 Hf계 코팅 물질 층의 36 nm 피치 포스트를 도시한다. 도 13A에 도시된 샘플을 2.38 중량% TMAH 농도로 현상한 반면, 도 13B에 도시된 샘플은 25 중량% TMAH 농도로 현상하였다. 25 중량% TMAH 농도 현상으로 더 정확하게 정의된 포스트가 얻어졌으나 이들 샘플은 약 8 $\times$ 초과의 전자빔 용량을 수반하였다. 1.6 내지 1.8 nm 선폭 거칠기를 갖는 패턴은 60 nm 피치에서 21 nm 선폭을 갖는 패턴에 대하여 도 14에 도시된다.

[0101] 이중 패터닝된 구조가 도 15 및 16에 도시된다. 패터닝은 500 $\mu\text{C}/\text{cm}^2$ 의 용량을 사용하여 30 keV 전자빔으로 수행되었다. 제1층을 패터닝한 후, 코팅을 220℃에서 소성한 후 제2 코팅을 도포하였다. 더 교해상의 관찰은 도 16에 도시된다. 양호한 해상도의 균일한 30 nm 접촉홀을 도 16에서 볼 수 있다.

[0102] 현상 후 이 실시예에 개시된 바와 같은 Hf계 코팅 물질로 형성된 하드 마스크를 통해 이온 에칭을 수행하였다. 코팅 물질은 이온 에칭을 위한 마스크로서 기능하였다. 규모 나노필러의 주사 전자 현미경 사진을 도 17에 나타낸다. 이온 에칭 후 패터닝된 구조는 40 nm의 필러 폭을 가졌다. 마스크는 이온 에칭에 대한 우수한 내성을 보였다.

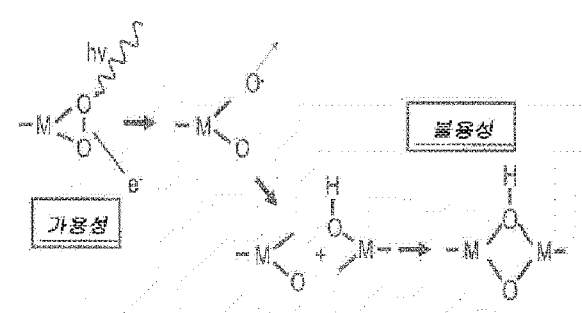
[0103] EUV 화상은 13 nm에서 작동하는 0.25의 수치 구경을 갖는 투명 리소그래피를 이용하여 얻었다. 레지스트를 스핀 코팅에 의하여 규소 웨이퍼 상에 20 nm의 두께로 도포한 다음 50℃에서 도포후 소성하였다. 약 80 mJ/cm²에서 노광 후, 25% TMAH에서 현상 전에 75℃의 노광후 소성을 이용하였다. 현상된 패턴을 도 18A-B에 도시한다. 도 18에 도시된 패턴은 A) 32 nm, B) 30 nm, C) 28 nm 및 D) 26 nm의 피치를 가진다.

[0104] 상기 구체예는 예시의 의도이지 제한의 의도는 아니다. 추가의 구체예는 청구범위에 속한다. 또한, 특정 구체예를 참조하여 본 발명을 개시하였으나, 당업자라면 본 발명의 사상 및 범위에서 이탈하지 않는 한 형태 및 세부사항의 변경이 가능함을 이해할 것이다. 참고문헌으로서 상기 문헌들의 임의의 인용은 본 명세서의 명시

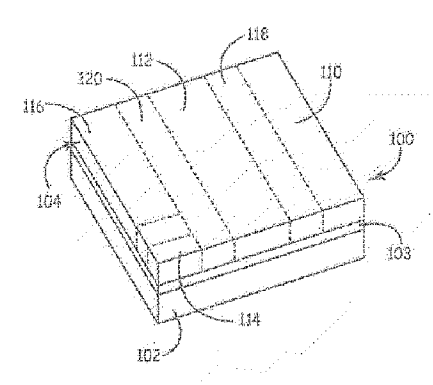
된 개시 내용에 반하는 주제가 포함되지 않도록 제한된다.

도면

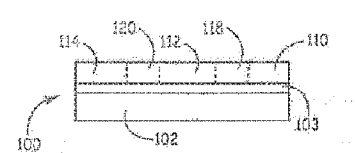
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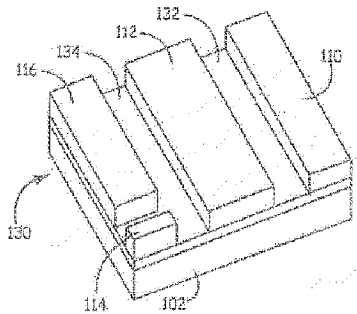
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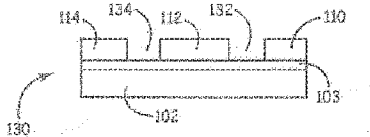
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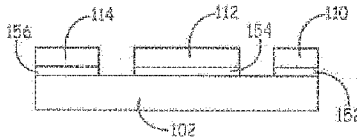
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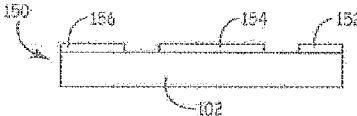
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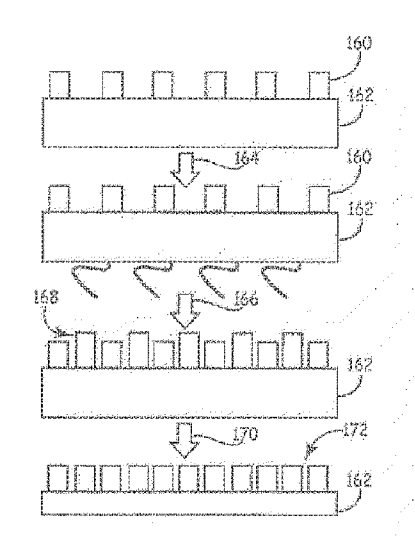
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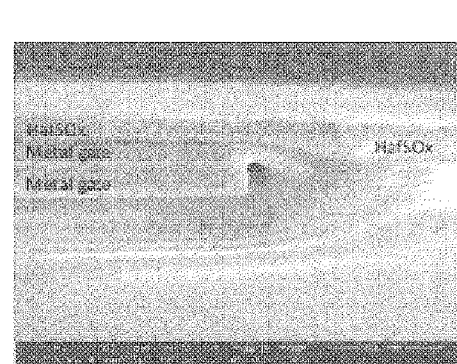
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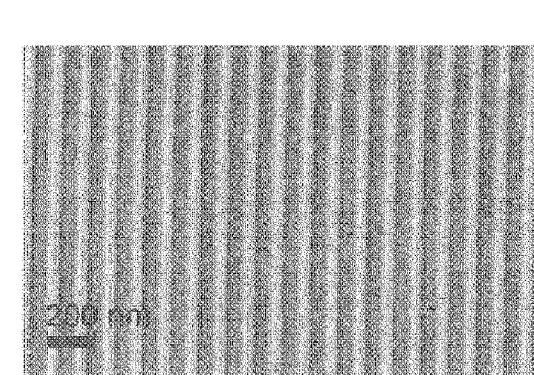
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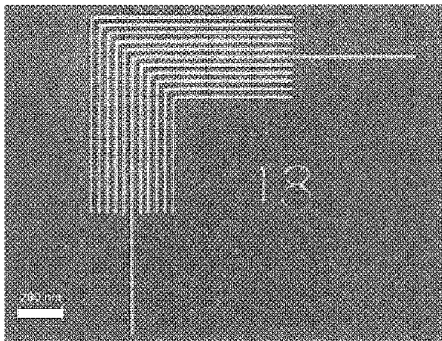
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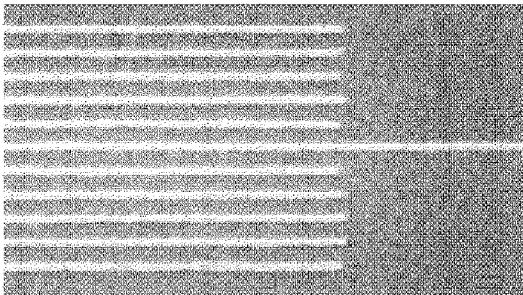
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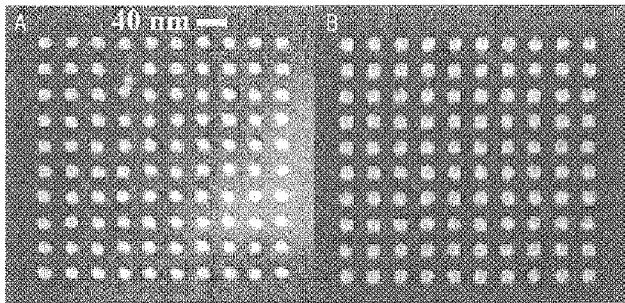
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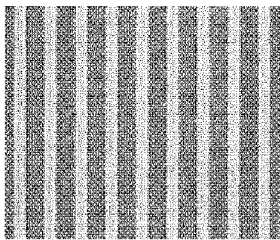
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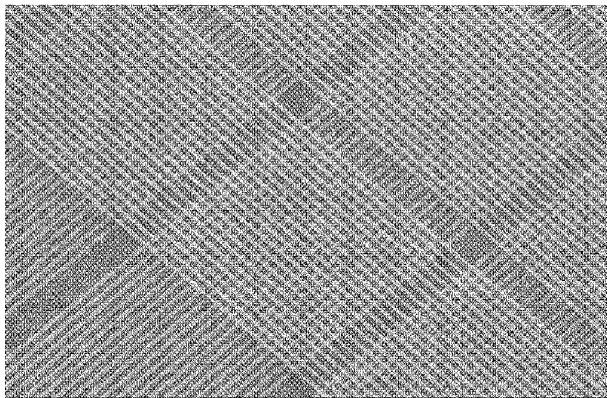
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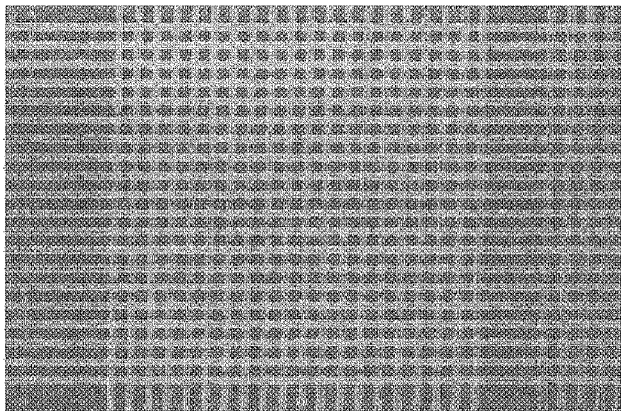
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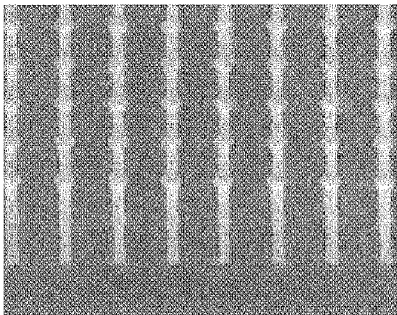
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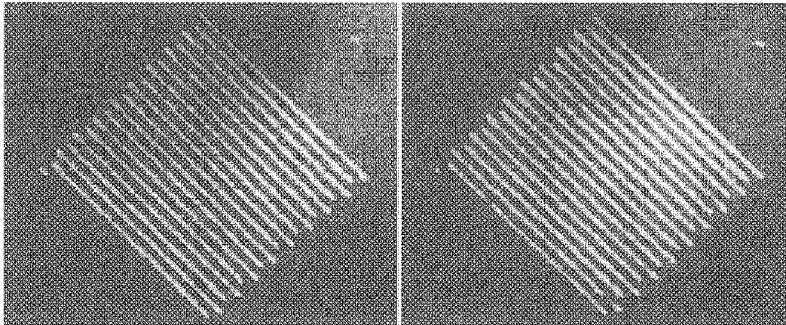
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도면17

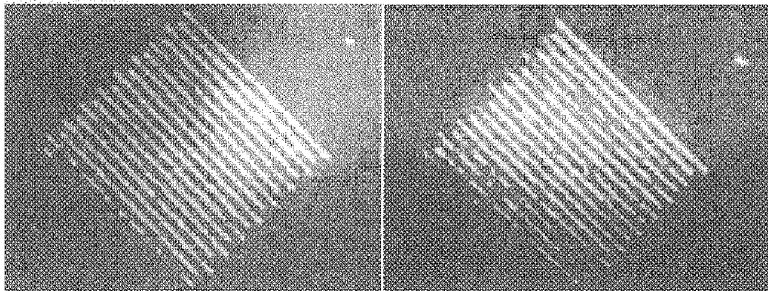


도면18



A

B



C

D

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(57) Abstract: The present invention relates to high purity monoalkyltin compounds, more specifically to alkyltin compound compositions containing monoalkyltin as major compound, and minor quantities of di- and/or trialkyltin compounds. The present invention also relates to the preparation processes of such high purity monoalkyltin compounds, as well as to the uses of said monoalkyltin compounds as chlorine-containing polymer-stabilisers, glass coating chemicals and catalysts, as well as articles comprising at least one polymer matrix and a high purity monoalkyltin compound.

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HIGH PURITY MONOALKYLTIN COMPOUNDS AND USES THEREOF

Field of the invention

[0001] The present invention relates to high purity monoalkyltin compounds, more specifically to alkyltin compound compositions containing monoalkyltin as major compound, and minor quantities of di- and/or trialkyltin compounds.

[0002] The present invention also relates to the preparation processes of such high purity monoalkyltin compounds, as well as to the uses of said monoalkyltin compounds, such as chlorine-containing polymer-stabilisers, glass coating chemicals and catalysts, and the like.

Prior art and Technical problem

[0003] Tin-based stabilisers are widely known and used in chlorine-containing polymers and co-polymers, such as for example poly(vinyl chloride) (PVC) polymers and PVC-based copolymers. Such uses of tin-based stabilisers are for example described in the Kirk Othmer "Encyclopedia of Chemical Technology", 4th Edition, (1994), vol. 12, Heat Stabilisers, pp. 1071-1091.

[0004] These known tin-based stabilisers are used as mixtures of mono-alkyltin with di-alkyltin compounds. For example widely used tin-based compounds in PVC polymers and copolymers are mixtures of mono- and di-methyltin compounds, mono- and di-butyltin compounds or mono- and di-octyltin compounds, such as those sold under the name Thermolite® by Arkema.

[0005] However, tri-alkyltin compounds are known to be toxic compounds, and di-alkyltin compounds have recently been classified as toxic compounds. Toxicity of tin compounds is known to be linked to mono-, di- and tri-alkyl tin compound contents, particularly toxicity is increasing from mono-, to di- and to tri-alkyl tin compound contents. Therefore it is nowadays highly relevant to develop mono-alkyltin compounds, with low levels of di- and tri-alkyl tin compounds, in order to avoid toxicity issues.

[0006] Attempts to the production of high purity mono-alkyltin chlorides have been conducted, for example through redistribution of tetra-alkyltin and tri-alkyltin compounds with tin tetrachloride followed by fractional distillation: mono-alkyltin chlorides were obtained in relatively pure form but di-alkyltin chlorides were always co-produced in significant quantities rendering these routes less attractive from an industrial perspective.

[0007] Recently developed technology as disclosed in EP-A-0 1225 177 and EP-A-1 743 898 allows the more selective production of mono-alkyltin chlorides without producing significant amount of di- and tri-alkyltin species as by-products. These technologies provide access to high purity monoalkyltin compounds through relatively short purification procedures.

[0008] Therefore an objective of the present invention is to provide non-toxic or less toxic tin-based compounds or compositions for stabilising polymers, more specifically chlorine-containing polymers, e.g. PVC polymers and copolymers.

[0009] Another objective of the present invention is to provide high purity monoalkyltin compounds, i.e. compositions with a major content of monoalkyltin compound and minor contents, and preferably only traces of, and even more preferably no di- and tri-alkyltin compounds, for use as stabilisers for chlorine-containing polymers, especially PVC polymers, post-chlorinated PVC and copolymers thereof, as well as for uses as a catalyst, or in glass coating compositions.

Brief description of the invention

[0010] The inventors have now discovered that high purity monoalkyltin trihalides can be converted to other mono-alkyltin derivatives that are of interest for several existing applications. The technology developed thus provides high purity mono-alkyltin compounds on an industrial scale as more benign alternatives to currently applied mixtures of mono- and di-alkyltin compounds.

[0011] The inventors have also discovered that high purity mono-alkyltin compounds, when used for example as stabilisers for chlorine-containing polymers and copolymers, provide to said polymers and copolymers remarkable and unexpected stability properties, more specifically thermal properties, long term colorhold retention properties, transparency properties (specifically for polymer films of variable thickness), among others.

Detailed description of the invention

[0012] In a first aspect, the present invention relates to a composition comprising:

- from 85 wt% to 99.999 wt%, preferably from 90 wt% to 99.999 wt%, more preferably from 95 wt% to 99.99 wt%, still more preferably from 97 wt% to 99.99 wt% (limits included) of at least one monoalkyltin compound of formula $R\text{Sn}(T)_3$, in which R is linear, branched or cyclic C_1 - C_{20} alkyl, preferably C_1 - C_{10} alkyl, and T is a ligand;
- from 0.001 wt% to 10 wt%, preferably from 0.001 wt% to 1 wt%, more preferably from 0.01 wt% to 0.5 wt%, most preferably from 0.01 wt% to 0.1 wt%, of at least one di-alkyltin compound of formula $R_2\text{Sn}(T)_2$, in which R and T are as defined above;
- from 0.001 wt% to 5 wt%, preferably from 0.005 wt% to 1 wt%, more preferably from 0.01 wt% to 0.5 wt%, most preferably from 0.01 wt% to 0.1 wt%, of at least one tri-alkyltin compound of formula $R_3\text{Sn}(T)$, in which R and T are as defined above; and
- from 0 wt% to 5 wt%, more preferably from 0 wt% to 1 wt%, still more preferably from 0 wt% to 0.2 wt% of one or more impurities.

[0013] According to another aspect, the composition of the present invention comprises a weight ratio of (mono-alkyltin compound)/(di-alkyltin compound) of not less than 90/10, preferably of not less than 95/5, most preferably of not less than 97/3.

[0014] According to still another preferred aspect, the composition of the present invention comprises a weight ratio of (mono-alkyltin compound)/(tri-alkyltin compound) of not less than 99/1, preferably of not less than 99.5/0.5, more preferably of not less than 99.7/0.3.

[0015] Still according to another aspect, the composition of the present invention comprises an amount of tri-alkyltin compound(s) of less than 1 wt%, preferably of less than 0.5 wt%, most preferably the composition comprises traces, expressed as parts per million (ppm), and even parts per billion (ppb) of tri-alkyltin compound(s).

[0016] Impurities that may be found in the composition of the present invention are any and all impurities that may be found as residues (or traces) from the preparation process of the composition, such as ligand precursors, ligand precursor-hydrolysed by-products, tin halides, solvents, alkenes, alkyl halides, catalysts or catalyst components, decomposed catalysts or catalyst components, water, neutralization salts, and the like.

[0017] In the composition of the present invention, R is a linear, branched or cyclic alkyl radical having from 1 to 20 (C₁-C₂₀ alkyl), preferably from 1 to 10 carbon atoms (C₁-C₁₀ alkyl), and preferably R is methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, cyclopentyl, cyclohexyl, cycloheptyl. The R radical may also comprise one or more unsaturations in the form of double and/or triple bond(s), and in such cases R may be chosen from among propenyl, butenyl, butadienyl, pentenyl, octenyl, octadienyl, cyclohexenyl, phenyl, and the like.

[0018] According to a preferred embodiment, R is chosen from among ethyl, *n*-propyl, *iso*-propyl, *n*-butyl, *iso*-butyl, *n*-pentyl, *n*-hexyl, *n*-heptyl, *n*-octyl, 2-ethylhexyl, *iso*-octyl, and decyl. More preferably R is methyl, *n*-butyl, 2-ethylhexyl, *n*-octyl, or *n*-decyl.

[0019] As regards the ligand T, it is any ligand known in the art, for example as disclosed in EP 0 010 008 or EP 0 501 780. More preferably, T is a ligand the precursor of which being H-T. H-T compounds may advantageously be chosen from among H-SCH₂CH₂OH, H-SCH₂-CH(OH)-CH₃, H-SCH₂COOR¹, H-SCH₂CH₂O-COR², H-SR², H-OH, H-OOCR², and H-OOCR³-COOR², wherein R¹ represents C₁-C₁₂ alkyl, R² represents C₆-C₁₈ alkyl, aryl or alkaryl, R³ represents -CH=CH-; or -CH₂-R⁴-CH₂-, with R⁴ representing C₂-C₆ alkylene.

[0020] According to a preferred embodiment, T is chosen from among thioglycolate esters, 2-ethylhexylthioglycolate esters, *iso*-octylthioglycolates, *iso*-butylthioglycolates, thioglycolate itself, hydroxyl, carboxylates, maleates, diketonates, alcoholates, more preferably T is 2-ethylhexylmercaptoacetate (EHMA).

[0021] In the formula $RSn(T)_3$, each T may be identical or different from the others. According to still a preferred embodiment, all three ligands T are identical.

[0022] Preferred compounds of formula $RSn(T)_3$ are $RSn[\text{tris}(2\text{-ethylhexylmercaptoacetate})]$, and among them the preferred ones are chosen from among monomethyltin[tris(2-ethylhexylmercaptoacetate)], mono-*n*-butyltin[tris(2-ethylhexylmercaptoacetate)], mono-*n*-octyl[tris(2-ethylhexylmercaptoacetate)], and mixtures thereof. Advantageously, the composition of the present invention comprises mono-*n*-octyl[tris(2-ethylhexylmercaptoacetate)] as major compound.

[0023] According to another aspect, the present invention relates to the process of preparation of the above-described tin-based compositions. High purity monoalkyltin-based compounds of formula $RSn(T)_3$, in which R and T are as defined above, are advantageously prepared from the corresponding monoalkyltin trihalides of formula $RSn(\text{Hal})_3$, in which R is as defined above and Hal is chosen from chlorine, bromine and iodine.

[0024] Some monoalkyltin trihalide preparations are already known from the prior art, and among them may be cited distillation of monoalkyltin halides from thermal redistribution mixtures containing mono-, di- and tri-alkylhalides. However, on an industrial point of view, distillation is less preferred when co-produced di- and/or tri-alkyltin compounds are not desired, since extensive distillation fractionation is often necessary to yield mono-alkyltin compounds of high purity, and particularly with a weight ratio of (mono-alkyltin) to (di-alkyltin) compounds greater than 90/10, preferably greater than 95/5, more preferably greater than 97/3.

[0025] Catalytic platinum-catalysed redistribution of di-alkyltin dihalides with tin tetrachloride is one of the few general methods for the selective production of mono-alkyltin species from higher alkyltins, but tin(II) halide is however formed as a by-product in substantial amounts. The only other selective preparation process leading to monoalkyltin halides involves palladium-catalysed hydrostannylation of 1-alkenes in the presence of tin(II) dihalide and hydrogen halide and is disclosed in patent application WO 07/006783.

[0026] Other known methods for the selective production of mono-alkyltin trihalides generally suffer from poor yields due to the use of harsh reaction conditions, are limited to $RSn(\text{Hal})_3$ compounds, wherein R represents methyl or unsaturated hydrocarbyl, or use non-economical amounts of catalyst or alkylating agent (EP-A-1 225 177; S.H.L. Thoonen, *J. Organomet. Chem.*, **689**, (2004), 2145-2157).

[0027] Selectively produced mono-alkyltin trihalides have been found to be easily converted to mono-alkyltin compounds of formula $RSn(T)_3$ by reacting mono-alkyltin halides $RSn(\text{Hal})_3$ with a compound of formula H-T in the presence of a suitable base. Alternatively compounds of formula $RSn(T)_3$ can be prepared by reaction of $RSn(\text{Hal})_3$ to

alkylstannoic acid RSn(O)OH using a hydroxide base, followed by contacting the alkylstannoic acid with a compound of formula H-T under elimination of water.

[0028] The present invention therefore provides a very easy, cost-effective and industrial process of preparation of the above-described and claimed composition, i.e. of mono-alkyltin compounds of high purity of formula RSn(T)_3 , wherein R and T are as defined above, said process comprising:

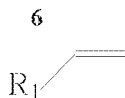
- α) hydrostannylation of a 1-alkene to the corresponding mono-alkyltin trihalide RSn(Hal)_3 in the presence of a transition metal catalyst, tin(II) dihalide and hydrogen halide; and
- β) converting the mono-alkyltin trihalide RSn(Hal)_3 to RSn(T)_3 by contacting the mono-alkyltin trihalide RSn(Hal)_3 with a compound of formula H-T in the presence of a suitable base or, alternatively, by reacting RSn(Hal)_3 to alkylstannoic acid RSn(O)OH using a hydroxide base followed by contacting the alkylstannoic acid with a compound of formula H-T under elimination of water.

[0029] More precisely, the process of preparation of mono-alkyltin compounds of high purity of formula RSn(T)_3 , wherein R and T are as defined above, comprises the steps of:

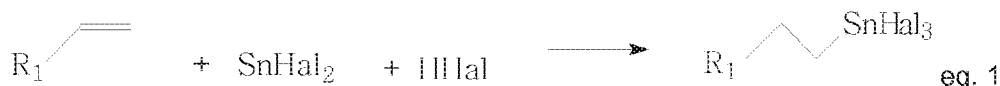
- a) preparing a solution of stannous halide SnHal_2 in a solvent, together with a transition metal-based catalyst;
- b) reacting the obtained solution with a molar excess (1.5 to 2 molar equivalents relative to the stannous halide) of the corresponding alkene or cycloalkene precursor of the R radical, at a temperature ranging between room temperature to 200°C , in the presence of hydrogen halide (H-Hal) and optionally metallic tin (Sn);
- c) optionally removing the solvent of the reaction medium, for example stripping or vacuum-distillation of the solvent;
- d) optionally filtering the crude reaction medium;
- e) adding a 2- to 5-fold molar excess (relative to the obtained monoalkyltin trihalide) of H-T, and water, under stirring;
- f) neutralising the reaction medium, for example with alkali or alkaline-earth hydroxide, e.g. sodium hydroxide;
- g) separating the water layer from the organic layer; and
- h) removing the solvent from the organic layer, and optionally filtering to recover RSn(T)_3 of high purity.

[0030] In a specific embodiment of the above process, Hal is chloride. This means that the stannous halide is SnCl_2 and hydrogen halide is HCl. Stannous bromide and stannous iodide may also be used.

[0031] As regards the alkene or cycloalkene precursor (sometimes called olefin) of the R radical, it can be described, by way of example, with the following formula :



and the reaction route as follows (eq 1):



5 in which R_1 is H or is defined as an alkyl (linear or branched or substituted), having from 1 to 18 carbon atoms.

[0032] The alkene, but also cycloalkene, has advantageously from 2 to 20 carbon atoms. In a specific embodiment the alkene also can be described as $\text{R}_1(\text{R}_2)\text{C}=\text{C}(\text{R}_3)(\text{R}_4)$ with R_1 - R_4 being any alkyl group (branched or linear or substituted) or hydrogen, R_1 , R_2 , R_3 and/or
 10 R_4 being optionally linked to any of the other R groups, for example R_1 or R_2 being linked to R_3 or R_4 , or R_1 being linked to R_2 , and the number of carbon atoms in R_1 - R_4 ranging from 0 to 18.

[0033] The olefin can contain functions and/or substituents. Advantageously this hydrocarbon has 4 to 8 carbon atoms. Especially 1-butene and 1-octene are relevant to
 15 produce industrially important organotins.

[0034] As regards stannous halide, it can be SnHal_2 or any precursor. Mention may be made, by way of examples, of Sn/SnHal_4 blends and HHal/Sn . The precursor also relates to $\text{SnHal}_2/\text{Sn}/\text{SnHal}_4$ blends. The stannous halide is preferably anhydrous but also their aqua complexes can be used. The stannous halide SnHal_2 can be produced *in situ*.
 20 According to a specific embodiment, SnHal_2 can be partly or totally replaced by an Sn/SnHal_4 blend (1/1 ratio) producing SnHal_2 *in situ*.

[0035] As regards the hydrogen halide, it can be the hydrogen halide itself as gas or solution in a solvent or any precursor or any blend thereof. The precursor can be $[\text{HN}(\text{alkyl})_3]\text{Hal}$, another ammonium salt or other Lewis base adduct of hydrogen halide.
 25 When used as gas the hydrogen halide may be diluted with another gas. In a preferred embodiment of the invention the hydrogen halide can be HCl or $[\text{HN}(\text{C}_2\text{H}_5)_3]\text{Cl}$. In another preferred embodiment, Hal is chloride, the stannous halide is SnCl_2 and hydrogen halide is HCl.

[0036] As regards the catalyst, in its broadest form the catalyst is a transition metal-based
 30 catalyst, such as a palladium-based catalyst, supported or not, as commonly used in the art. Examples of such catalysts are widely described in WO 2007/006783. Preferably, the complex is $\text{M}(\text{PPh}_3)_4$, wherein M is chosen from among Pt, Pd and/or Ni, preferably M is Pd.

[0037] Support for the catalyst may be of any type known in the art and is preferably
 35 carbon.

[0038] As regards the solvent, in general organic, aprotic or even protic solvents are preferred, especially aromatic solvents, chloroaromatic solvents, alkanes, ethers and alcohols. In particular tetrahydrofuran (THF), ethanol and 1,2-dimethoxyethane (DME) are suitable solvents.

5 **[0039]** As regards the operating conditions and the proportions, the reaction is made continuously or in batch. The batch process is preferred. Temperature can be, by way of example, from ambient to 200°C. A range from 20°C to 130°C is advantageous, preferably from 20°C to the boiling point of the solvent.

[0040] As regards the pressure, no pressure is necessary except to maintain the alkene, 10 when it has a low boiling point, and hydrogen halide in the reaction medium. However, to speed up the reaction higher pressures may be advantageous.

[0041] Preferred reaction times range from a few seconds to 48 hours. The molar ratio of olefin to SnHal_2 falls within the range 0.1/1 to 200/1, more advantageously 1/1 to 100/1. The molar ratio of HHal to SnHal_2 falls within the range 0.01/1 to 100/1.

15 **[0042]** The catalyst loading (molar percentage of M) based on the number of moles of SnHal_2 can be 0.001 to 5 %, more preferred 0.1 to 1.5%. Should a solvent be used, any proportion is convenient.

[0043] The reaction is carried out in any usual apparatus. The reaction can be checked by taking samples and conventional analysis. According to an embodiment, the 20 monoalkyltin trihalides can be separated from the reaction medium by any means such as, by way of examples, distillation, solvent extraction, crystallisation, and the like.

[0044] For the compositions of the present invention comprising at least one monomethyltin compound, the monomethyltin trihalide may advantageously be prepared according to the process disclosed in EP-A-1 225 177.

25 **[0045]** The present invention also relates to the mono-alkyltin compounds, composition containing the same, as well as precursors thereof, as mentioned above, prepared starting from raw materials of renewable origin, i.e. starting from raw materials of nonfossil origin.

[0046] More precisely, by raw materials of renewable origin, one preferably understands the raw materials which include at least one carbon atom, preferably more than one, more 30 preferably all carbon atoms, of renewable origin.

[0047] Compared to materials obtained from fossil raw materials, the compounds prepared from raw materials of renewable origin contain the isotope 14 of carbon (^{14}C). All carbon samples drawn from living organisms (animals or vegetables) are in fact a mixture of 3 isotopes: ^{12}C (accounting for approximately 98.892%), ^{13}C (approximately 1.108%) and 35 ^{14}C (traces: approximately $1.2 \times 10^{-12}\%$).

[0048] The $^{14}\text{C}/^{12}\text{C}$ ratio in living organisms is identical to that of the atmosphere. In the environment, ^{14}C exists in two dominating forms: mineral form, i.e. carbon dioxide (CO_2) and organic form, i.e. of carbon integrated in organic molecules.

[0049] In a living organism, the $^{14}\text{C}/^{12}\text{C}$ ratio is maintained constant by the metabolism because carbon is continuously exchanged with the environment. The proportion of ^{14}C being constant in the atmosphere, it is the same in the organism, as long as it is alive, since it absorbs ^{14}C as it absorbs ^{12}C . The proportion of ^{14}C and ^{12}C did not change significantly during last thousands of years and the average ratio of $^{14}\text{C}/^{12}\text{C}$ is equal to approximately 1.2×10^{-12} .

[0050] The ^{12}C isotope is stable, i.e. the number of atoms of ^{12}C in a given sample is constant in the course of time. The ^{14}C isotope is radioactive (each gram of carbon from a living organism contains sufficient ^{14}C isotope to give 13.6 disintegrations per minute) and the content of ^{14}C in a sample decreases during a period of time (T) according to the following equation:

$$n = n_0 e^{-at}$$

wherein

- n_0 is the original number of ^{14}C atoms (at the time of death of the animal or plant),
- n is the number of ^{14}C atoms remaining after the time period t ,
- a is the disintegration constant (or radioactive constant), related to the half-life.

[0051] The half-life (or period), is the duration at the end of which an unspecified number of radioactive cores or unstable particles of a given species, is reduced by two-fold by disintegration; the half-life $T_{1/2}$ is related to the disintegration constant a according to the formula $aT_{1/2} = \ln 2$. The half-life of ^{14}C is approximately 5730 years.

[0052] Given the half-life ($T_{1/2}$) of the ^{14}C isotope, one considers that the content of ^{14}C is constant since the extraction of the raw materials of renewable origin until the preparation of the compounds, compositions and precursors thereof, and even until the end of their uses.

[0053] According to the present invention, mono-alkyltin compounds, composition containing the same, as well as precursors thereof, can easily be obtained, in whole or in part, from raw materials of renewable origin. For example, the alkyl group of the alkyltin compounds may be prepared starting from alkenes, or corresponding alcohols, of biological origin (e.g. extraction from living organisms, plants, wood, animals, fish, or extraction from sugars, enzymatic preparation, bacterial fermentation, and the like).

[0054] Thus, mono-alkyltin compounds, composition containing the same, as well as precursors thereof according to the present invention, when they are prepared entirely or partly starting from raw materials of renewable origin, are characterized by the fact that they contain a quantity of isotope 14 of carbon higher than that of the same compounds,

compositions or precursors thereof prepared exclusively starting from raw materials of fossil origin.

[0055] At present, there are at least two different techniques for measurement of the content of ^{14}C in a sample:

- 5 - by spectrometry with liquid scintillation: this method consists in numbering the 'beta' (β) particles resulting from the disintegration of the ^{14}C isotope; the β -radiation resulting from a sample of known mass (a known number of atoms ^{12}C) is measured during a certain time; this 'radioactivity' is proportional to the number of ^{14}C atoms, which can therefore be determined; the ^{14}C isotope present in the sample emits β -radiations, which, in contact with
10 a scintillating liquid (scintillator), give rise to photons; these photons have different energies (between 0 keV and 156 keV) and form what is named a spectrum of ^{14}C ; according to alternatives of this method, the analysis is based either on the carbon dioxide produced beforehand by the carbonaceous sample in an appropriate absorbing solution, or on benzene after preliminary conversion of the carbonaceous sample into benzene;
- 15 - by mass spectrometry: the sample is turned to graphite or to gaseous carbon dioxide, analyzed in a mass spectrometer; this technique uses an accelerator and a mass spectrometer to separate the ^{14}C ions from the ^{12}C ions and thus to determine the ratio of the two isotopes.

[0056] All these methods aiming at measuring the content of ^{14}C in the alkyltin
20 compounds, compositions containing them and precursors thereof, are described in the ASTM D 6866 standard (in particular ASTM D 6866 06 of January 2006) and in ASTM D 7026 standard (in particular ASTM D 7026-04). The measurement method preferentially used in the field of the present invention is the mass spectrometry method described in ASTM D 6866 06 standard ("Radiocarbon and Isotope Ratio Mass Spectroscopy
25 Analysis").

[0057] The alkyltin compounds, compositions containing them and precursors thereof prepared from at least one raw material of renewable origin are new and are therefore also part of the present invention. These compounds, compositions and precursors, are characterized by a ^{14}C content strictly greater than 0, more precisely a ratio $^{14}\text{C}/^{12}\text{C}$ strictly
30 greater than 0 and lower or equal to approximately 1.2×10^{-12} , the value '0' indicating a compound which is exclusively obtained starting from carbon species of fossil origin, the value 1.2×10^{-12} indicating a alkyltin compounds, compositions and precursors thereof prepared exclusively from carbon species of renewable origin.

[0058] The invention also relates to the use of the claimed composition mainly comprising
35 monoalkyltin-based compounds as stabilisers for chlorine-containing polymers, glass coating chemicals and catalysts, and the like.

[0059] As stabiliser for chlorine-containing polymers, the composition of the present invention is of particular interest when the mono-alkyltin compound as major component is RSn(EHMA)_3 , wherein R is chosen from among methyl, *n*-butyl, *iso*-octyl and *n*-octyl, preferably wherein R is *n*-octyl, and EHMA is 2-ethylhexyl-mercaptoacetate.

5 **[0060]** As catalyst, the composition of the present invention is of particular interest when the mono-alkyltin compound as major component is mono-alkyltin oxide/hydroxide, i.e. the reaction product of mono-alkyltin trihalide with T-H, wherein T is OH.

[0061] More specifically the claimed composition is useful as a stabiliser for chlorine-containing polymers. As chlorine-containing polymers, mention may be made of:

- 10 • homopolymers and copolymers of vinyl chloride (PVC) and of vinylidene chloride (PVDC), vinyl resins comprising vinyl chloride units in their structure, such as copolymers of vinyl chloride, and vinyl esters of aliphatic acids, especially vinyl acetate, copolymers of vinyl chloride with esters of acrylic and methacrylic acid and with acrylonitrile, copolymers of vinyl chloride with diene compounds and unsaturated
15 dicarboxylic acids or their anhydrides, such as copolymers of vinyl chloride with diethyl maleate, diethyl fumarate or maleic anhydride, post-chlorinated polymers and copolymers of vinyl chloride, copolymers of vinyl chloride and vinylidene chloride with unsaturated aldehydes, ketones and others, such as acrolein, crotonaldehyde, vinyl methyl ketone, vinyl methyl ether, vinyl isobutyl ether and the like; polymers of
20 vinylidene chloride and its copolymers with vinyl chloride and other polymerizable compounds;
- polymers of vinyl chloroacetate and dichlorodivinyl ether; chlorinated polymers of vinyl carboxylate, such as vinyl acetate, vinyl propionate, vinyl butyrate, chlorinated polymeric esters of acrylic acid and of α -substituted acrylic acid, such as methacrylic
25 acid, of nitriles, amides, alkyl esters such as acrylonitrile, (meth)acrylamide, methyl (meth)acrylate, butyl acrylate, ethyl acrylate, 2-ethylhexyl acrylate;
- polymers of vinyl aromatic derivatives, such as styrene, dichlorostyrene; chlorinated rubbers;
- chlorinated polymers of olefin, such as ethylene, propene, 1-butene, (2.2.1)bicyclo
30 heptene-2, (2.2.1)bicyclo hepta-diene-2,5;
- polymers and post-chlorinated polymers of chlorobutadiene and copolymers thereof with vinyl chloride, chlorinated natural and synthetic rubbers, and also mixtures of these polymers with one another or with other polymerizable compounds.

35 **[0062]** In the context of this invention, PVC also embraces copolymers with polymerizable compounds such as acrylonitrile, vinyl acetate or ABS, which can be suspension, bulk or emulsion polymers. Preference is given to PVC homopolymers and copolymers, optionally post-chlorinated, alone or in combination with polyacrylates.

[0063] Also included are graft polymers of PVC with EVA, ABS and MBS. Preferred substrates are also mixtures of the abovementioned homo- and copolymers, especially vinyl chloride homopolymers, with other thermoplastic and/or elastomeric polymers, especially blends with homo- or copolymers as ABS (acrylonitrile-butadiene-styrene), MBS (methylmethacrylate-butadiene-styrene), NBR (nitrile butadiene rubber), SAN (styrene-acrylonitrile), EVA (ethylene-vinyl acetate), CPE (chlorinated polyethylene), MBAS(methylmethacrylate-butadiene-acrylonitrile-styrene), PMA (polymethyl acrylate) , PMMA (polymethylmethacrylate), EPDM (ethylene-propene-diene monomer) and polylactones.

[0064] These polymers (resins) can be thermoplastic and/or elastomeric. Examples of such components are compositions of (i) 20-80 parts by weight of a vinyl chloride homopolymer (PVC) and (ii) 80-20 parts by weight of at least one thermoplastic copolymer based on styrene and acrylonitrile, in particular from the group ABS, NBR, NAR, SAN and EVA. The abbreviations used for the copolymers are familiar to the person skilled in the art and have the following meanings: ABS: acrylonitrile-butadiene-styrene; SAN: styrene-acrylonitrile; NBR: acrylonitrile- butadiene; NAR: acrylonitrile-acrylate; EVA: ethylene-vinyl acetate.

[0065] Also suitable in particular are acrylate-based styrene-acrylonitrile copolymers (ASA). Preferred components in this context are polymer compositions comprising as components (i) and (ii) a mixture of 25-75% by weight PVC and 75-25% by weight of the abovementioned copolymers. Examples of such compositions are: 24-50% by weight PVC and 75-50% by weight copolymers of 40-75% by weight PVC and 60-25% by weight copolymers. Preferred copolymers are ABS, SAN and modified EVA, especially ABS, NBR, NAR and EVA are also particularly suitable.

[0066] It is possible for one or more of the abovementioned copolymers to be present. Particularly important components are compositions comprising (i) 100 parts by weight of PVC and (ii) 0-300 parts by weight of ABS and/or SAN-modified ABS and 0-80 parts by weight of the copolymers NBR, NAR and/or EVA, and especially EVA.

[0067] For stabilisation in the context of this invention, further suitable polymers are, in particular, recyclates of chlorine-containing polymers, these polymers being the polymers described in more detail above that have also undergone damage through processing, use or storage. PVC recyclate is particularly preferred. The recyclates may also include small amounts of extraneous substances, such as, for example, paper, pigments, adhesives, which are often difficult to remove. These extraneous substances may also arise from contact with various materials in the course of use or reprocessing, examples being residues of fuel, fractions of coating material, traces of metal and residues of initiator.

[0068] Preferably chlorine-containing polymers stabilised with the composition of the present invention are chosen from among polymers or mixtures of polymers chosen from among homopolymer vinyl halides such as polyvinyl chloride, polyvinylidene chloride, chlorinated polyvinyl chloride, post-chlorinated polyvinyl chloride and copolymers formed by the polymerisation of a vinyl halide monomer with up to 40% of a comonomer such as vinyl acetate, vinyl butyrate, vinylidene chloride, propylene, methylmethacrylate and the like.

[0069] The invention also includes chlorine-containing polymers containing other polymers such as chlorinated polyethylene; terpolymers of acrylonitrile, butadiene, styrene; terpolymers of methylmethacrylate, butadiene, styrene; polyacrylate resins; polymethylmethacrylate resins and terpolymer of alkyl acrylate, methylmethacrylate, butadiene.

[0070] As hereinbefore described, known tin-based stabilisers are mixtures of mono- and di-alkyltin compounds, since it is known that monoalkyltin species provide a very good early colour to chlorine-containing polymers and dialkyltin species confer a good long term stability (colorhold) to these polymers.

[0071] It has now surprisingly been found that the composition of the present invention comprising a very high monoalkyltin compound content, ensures both early colour and colour retention, in chlorine-containing polymers.

[0072] The content of the claimed composition within the chlorine-containing polymers (resin) may vary in great proportions and is generally comprised between about 0.01 parts by weight and 10 parts by weight, preferably between about 0.1 and 7, more preferably from about 0.1 to about 5 and still more preferably between 0.4 and 2.5, parts by weight for 100 parts by weight of polymer(s).

[0073] One or more stabilising composition(s) of the present invention may be added to polymers or copolymers according to any procedure known in the art, and, by way of non limiting examples: as an emulsion or dispersion (e.g. in the form of a paste-like mixture), as a dry mix in the course of the mixing of additional stabilisers and/or polymer mixtures and/or additives, by direct addition to the processing apparatus (e.g. calenders, mixers, compounders, extruders and the like), or as a solution or melt or as flakes or pellets in dust-free form as a one-pack product.

[0074] Preferably, the composition(s) of the present invention is(are) added to the chlorine-containing polymer(s) according to the dry-blending method.

[0075] One or more stabilising composition(s) of the present invention may be added to the chlorine-containing polymers alone or as a formulation together with one or more other co-stabilisers known in the art, especially PVC co-stabilisers, and/or one or more additive(s). Alternatively, the composition of the present invention, co-stabiliser(s) and/or

additives may be added concomitantly or sequentially into the above defined chlorine-containing polymer(s).

[0076] Co-stabilisers which may be present within said formulation, or more generally within the chlorine-containing polymer(s) together with the composition of the present invention may be for example chosen from among epoxysised soy bean oil, dihydropyridine compounds such as those described in FR 2 429 806, EP 0 027 439 or WO 2002/092686, and especially dihydropyridine and polydihydropyridine derivatives, more especially dihydro-1,4-dimethyl-2,6-dicarbododecyloxy-3,5-pyridine (Stavinor® D507, Arkema, referred to as "DHP" in the following description) or thiodiethanolbis-(5-methoxy-carbonyl-2,6-dimethyl-1,4-dihydropyridine-3-carboxylate (Synesal® M, Lagor), α -phenylindole, polyols, disaccharide alcohols, perchlorate compounds, glycidyl compounds, layered lattice compounds (hydrotalcite), zeolite compounds, phosphite compounds, β -diketones, β -ketoesters, mercaptocarboxylic esters, metal soaps, amino- and/or thiouracils, hydrazides, and the like and mixtures thereof.

[0077] Such co-stabilisers are well known to the skilled artisan and a detailed list of particularly advantageous co-stabilisers may be found in WO 2006/058789.

[0078] Examples of suitable polyols and disaccharide alcohols are pentaerythritol, dipentaerythritol, tripentaerythritol, trimethylolethane, bistrimethylolpropane, inositol (cyclitols), polyvinyl alcohol, bis-trimethylolethane, trimethylolpropane, sorbitol (hexitols), maltitol, isomaltitol, cellobiitol, lactitol, lycasine, mannitol, lactose, leucrose, tris(hydroxyethyl) isocyanurate, tris(hydroxypropyl) isocyanurate, palatinitol, tetramethylolcyclohexanol, tetramethylolcyclopentanol, tetramethylolcyclopyranol, xylitol, arabinitol (pentitols), tetritols, glycerol, diglycerol, polyglycerol, thiodiglycerol or 1-O- α -D-glycopyranosyl-D-mannitol dihydrate. Of these, preference is given to the disaccharide alcohols.

[0079] Mention may also be made of polyol syrups, such as sorbitol, mannitol and maltitol syrup. The polyols and/or disaccharide compounds can be employed in an amount of, for example, from 0.01 to 20, judiciously from 0.1 to 20 and, in particular, from 0.1 to 10 parts by weight per 100 parts by weight of chlorine-containing polymers and resins, such as PVC.

[0080] Examples of perchlorate compounds are those of formula $M(\text{ClO}_4)_n$, in which M is Li, Na, K, Mg, Ca, Sr, Ba, Zn, Al, La or Ce. Depending on the valency of M, the index n is 1, 2 or 3. The perchlorate salts can be present as solutions or may be in the form of complexes with alcohols (polyols, cyclodextrins) or ether alcohols or ester alcohols. The ester alcohols also include the polyol partial esters. In the case of polyhydric alcohols or polyols, their dimers, trimers, oligomers and polymers are also suitable, such as di-, tri-,

tetra- and polyglycols and also di-, tri- and tetrapentaerythritol or polyvinyl alcohol in various degrees of polymerisation.

[0081] Other suitable solvents are phosphate esters and also cyclic and acyclic carbonates. In this context, the perchlorate salts can be employed in various common forms of presentation; for example, as a salt or solution in water or an organic solvent as such, or adsorbed on a support material such as PVC, Ca silicate, zeolites or hydrotalcites, or bound by chemical reaction into a hydrotalcite or into another layered lattice compound. As polyol partial ethers, preference is given to glycerol monoethers and glycerol monothioethers. Further embodiments are described in EP 0 394 547, EP 0 457 471 and WO 94/24200.

[0082] Perchlorates can be employed in an amount of, for example, from 0.001 to 5, judiciously from 0.01 to 3, and, with particular preference, from 0.01 to 2 parts by weight per 100 parts by weight of chlorine-containing polymers and resins, such as PVC.

[0083] Glycidyl compounds that may be used as co-stabilisers are preferably those containing a glycidyl group directly bonded to carbon, oxygen, nitrogen or sulphur atoms. Examples are:

- Glycidyl esters and β -methylglycidyl esters obtainable by reacting a compound having at least one carboxyl group in the molecule with epichlorohydrin or glyceroldichlorohydrin or β -methylepichlorohydrin, wherein the reaction advantageously takes place in the presence of bases.

As compounds having at least one carboxyl group in the molecule, mention may be made of aliphatic carboxylic acids, such as glutaric, adipic, pimelic, suberic, azelaic and sebacic acid or dimerised or trimerised linoleic acid, acrylic and methacrylic acid, caproic, caprylic, lauric, myristic, palmitic, stearic and pelargonic acid. Mention may also be made of cycloaliphatic carboxylic acids, such as, for example, cyclohexanecarboxylic, tetrahydrophthalic, 4-methyltetrahydrophthalic, hexahydrophthalic and 4-methylhexahydrophthalic acids. Aromatic carboxylic acids can also be used, examples being benzoic, phthalic, isophthalic, trimellitic and pyromellitic acid. It is likewise possible to make use of carboxyl-terminated adducts of, for example, trimellitic acid with polyols, such as glycerol or 2,2-bis(4-hydroxycyclohexyl)propane. Other epoxide compounds which can be used in the context of this invention are given in EP 0 506 617.

- Glycidyl ethers or β -methylglycidyl ethers obtainable by reacting a compound having at least one free alcoholic hydroxyl group and/or phenolic hydroxyl group with an appropriately substituted epichlorohydrin under alkaline conditions or in the presence of an acidic catalyst with subsequent alkali treatment.

Ethers of this type are derived, for example, from acyclic alcohols, such as ethylene

glycol, diethylene glycol and higher poly(oxyethylene) glycols, propane-1,2- diol, or poly(oxypropylene)glycols, propane-1,3-diol, butane-1,4-diol, poly(oxytetramethylene)glycols, pentane-1,5-diol, hexane-1,6-diol, hexane-2,4,6-triol, glycerol, 1,1,1-trimethylolpropane, bis(tri-methylol)propane, pentaerythritol, sorbitol, and from polyepichlorohydrins, butanol, amyl alcohol, pentanol, and from monofunctional alcohols such as isooctanol, 2-ethylhexanol, isodecanol and also C₇-C₉-alkanol and C₉-C₁₁-alkanol mixtures. They are also derived, however, for example, from cycloaliphatic alcohols, such as 1,3- or 1,4-dihydroxycyclohexane, bis(4-hydroxycyclohexyl)methane, 2,2-bis-(4-hydroxycyclohexyl)propane or 1,1-bis(hydroxymethyl)cyclohex-3-ene, or they possess aromatic nuclei, such as N,N-bis(2-hydroxyethyl)aniline or p,p'-bis(2-hydroxyethylamino)diphenylmethane.

The epoxide compounds can also be derived from mononuclear phenols, such as, for example, from phenol, resorcinol or hydroquinone; or, they are based on polynuclear phenols, such as, for example, on bis(4-hydroxyphenyl)methane, 2,2-bis(4-hydroxyphenyl)propane, 2,2-bis(3,5-dibromo-4-hydroxyphenyl)-propane, on 4,4'-dihydroxydiphenyl sulphone or on condensates of phenols with formaldehyde obtained under acidic conditions, such as phenol novolacks. Examples of further possible terminal epoxides are: glycidyl-1-naphthyl ether, glycidyl 2-phenylphenyl ether, 2-biphenyl glycidyl ether, N-(2,3-epoxypropyl)phthalimide and 2,3-epoxypropyl 4-methoxyphenyl ether.

- N-Glycidyl compounds obtainable by dehydrochlorination of the reaction products of epichlorohydrin with amines containing at least one amino hydrogen atom. These amines are, for example, aniline, N-methylaniline, toluidine, n-butylamine, bis(4-aminophenyl)methane, m-xylylenediamine or bis(4-methylaminophenyl)methane, and also N,N,O-triglycidyl-m-aminophenol or N,N,O-triglycidyl-p-aminophenol. However, the N-glycidyl compounds also include N,N'-di-, N,N',N"-tri- and N,N',N",N"-tetraglycidyl derivatives of cycloalkyleneureas, such as ethyleneurea or 1,3-propyleneurea and N,N'-diglycidyl derivatives of hydantoins, such as of 5,5-dimethylhydantoin or glycoluril and triglycidyl isocyanurate.
- S-Glycidyl compounds such as di-S-glycidyl derivatives derived from dithiols, such as ethane-1,2-dithiol or bis(4-mercaptomethylphenyl) ether, for example.
- Epoxy compounds are for example, (3'-4'-epoxy-6'-methylcyclohexyl)methyl-3,4-epoxy-6-methylcyclohexanecarboxylate. Examples of suitable terminal epoxides are: a) liquid bisphenol A diglycidyl ethers, such as Araldit® GY 240, Araldit® GY 250, Araldit® GY 260, Araldit® GY 266, Araldit® GY 2600, Araldit® MY 790; b) solid bisphenol A diglycidyl ethers, such as Araldit® GT 6071, Araldit® GT 7071, Araldit® GT 7072, Araldit® GT 6063, Araldit® GT 7203, Araldit® GT 6064, Araldit® GT 7304,

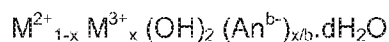
Araldit® GT 7004, Araldit® GT 6084, Araldit® GT 1999, Araldit® GT 7077, Araldit® GT 6097, Araldit® GT 7097, Araldit® GT 7008, Araldit® GT 6099, Araldit® GT 6608, Araldit® GT 6609, Araldit® GT 6610; c) liquid bisphenol F diglycidyl ethers, such as Araldit® GY 281, Araldit® PY 302, Araldit® PY 306; d) solid polyglycidyl ethers of tetraphenylethane, such as CG Epoxy Resin 0163; e) solid and liquid polyglycidyl ethers of phenol-formaldehyde novolack, such as EPN 1 138, EPN 1 139, GY 1180, PY 307; f) solid and liquid polyglycidyl ethers of o-cresol-formaldehyde novolack, such as ECN 1235, ECN 1273, ECN 1280, ECN 1299; g) liquid glycidyl ethers of alcohols, such as Shell Glycidyl ether 162, Araldit® DY 0390, Araldit® DY 0391; h) liquid glycidyl ethers of carboxylic acids, such as Shell Cardura® E terephthalic acid ester, trimellitic acid ester, Araldit® PY 284; i) solid heterocyclic epoxy resins (triglycidyl isocyanurate), such as Araldit® PT 810; j) liquid cycloaliphatic epoxy resins such as Araldit® CY 179; k) liquid N,N,O-triglycidyl ethers of p-aminophenol, such as Araldit® MY 0510; l) tetraglycidyl-4,4'-methylenediamine or N,N,N',N'-tetraglycidyl-diamino-phenylmethane, such as Araldit® MY 720, and Araldit® MY 721. Preference is given to the use of epoxy compounds having two functional groups. In principle, however, it is also possible to employ epoxy compounds having one, three or more functional groups. Use is made predominantly of epoxy compounds, especially diglycidyl compounds, having aromatic groups.

If desired, it is also possible to employ a mixture of different epoxy compounds. Particular preference is given as terminal epoxy compounds to diglycidyl ethers based on bisphenols, such as on 2,2-bis(4-hydroxyphenyl)propane (bisphenol A), bis(4-hydroxyphenyl)methane or mixtures of bis(ortho/para-hydroxyphenyl)methane (bisphenol F), for example.

The terminal epoxy compounds can be employed in an amount of preferably at least 0.1 part, for example from 0.1 to 50, judiciously from 1 to 30 and in particular, from 1 to 25 parts by weight, per 100 parts by weight of chlorine-containing polymers and resins, such as PVC.

[0084] Examples of hydrotalcites that may be used as co-stabilisers are compounds known to the person skilled in the art, for example, from DE 384 35 81, EP 0 062 813 and WO 1993/20135.

[0085] Compounds from the series of the hydrotalcites can be described by the following general formula:



wherein

M^{2+} represents one or more metals from the group Mg, Ca, Sr, Zn and Sn, M^{3+} represents Al or B,

An is an anion having the valency n,

b is a number from 1-2,

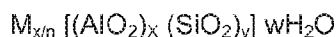
$0 < x < 0.5$

m is a number from 0-20 and

- 5 d is a number in the range from 0 to 300, preferably in the range from 0.5 to 30. Preferably An is OH^- , ClO_4^- , HCO_3^- , CH_3COO^- , $\text{C}_6\text{H}_5\text{COO}^-$, CO_3^{2-} , $(\text{CHOHCOO})_2^{2-}$, $(\text{CH}_2\text{COO})_2^{2-}$, $\text{CH}_3\text{CHOHCOO}^-$, HPO_3^- or HPO_4^{2-} .

[0086] Examples of hydrotalcites are $\text{Al}_2\text{O}_3 \cdot 6\text{MgO} \cdot \text{CO}_2 \cdot 12\text{H}_2\text{O}$ (i), $\text{Mg}_{4.5}\text{Al}_2(\text{OH})_{13}\text{CO}_2 \cdot 3.5\text{H}_2\text{O}$ (ii), $4\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CO}_2 \cdot 9\text{H}_2\text{O}$ (iii), $4\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CO}_2 \cdot 6\text{H}_2\text{O}$,
 10 $\text{ZnO} \cdot 3\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CO}_2 \cdot 8-9\text{H}_2\text{O}$ and $\text{ZnO} \cdot 3\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CO}_2 \cdot 5-6\text{H}_2\text{O}$. Very particular preference is given to types i, ii and iii.

[0087] Zeolite co-stabilisers may be all kinds of zeolites known in the art, such as those described by the following general formula :



15 in which n is the charge of the cation M;

M is an element from the first or second main group, such as Li, Na, K, Mg, Ca, Sr or Ba;

y:x is a number from 0.8 to 15, preferably from 0.8 to 1.2;

and w is a number from 0 to 300, preferably from 0.5 to 30.

Examples of zeolites are sodium aluminosilicates of the following types: zeolite A, sodalite,
 20 zeolite Y, zeolite X, zeolite LSX; or the zeolites preparable by complete or partial replacement of the Na atoms by Li, K, Mg, Ca, Sr or Zn atoms.

[0088] Preferred zeolites are zeolite A, sodalite; zeolite Y, zeolite X; and those X zeolites having an Si/Al ratio of about 1 :1 called LSX for Low Silica X, or the zeolites preparable by complete or partial replacement of the Na atoms by Li, K, Mg, Ca, Sr, Ba or Zn atoms. The
 25 zeolites indicated can also be lower in water content, or anhydrous.

[0089] Further suitable zeolites are zeolite P, zeolite MAP or the zeolites preparable by complete or partial replacement of the Na atoms by Li, K and/or H atoms, such as zeolite K-F, zeolite D, as described for instance in Barrer *et al.*, *J. Chem. Soc.*, (1952), 1561-71, and in U.S. Pat. No. 2,950,952; also suitable are the following zeolites: K offretite, zeolite
 30 R, zeolite LZ-217, Ca-free zeolite LZ-218, zeolite T, zeolite LZ-220, zeolite L, zeolite LZ-211, zeolite LZ-212, zeolite O, zeolite LZ-217, zeolite LZ-219, zeolite Rho, zeolite LZ-214, zeolite ZK-19, zeolite W (K-M), zeolite ZK-5, zeolite Q. Particular preference is given to zeolite P grades of the above formula in which x is from 2 to 5 and y is from 3.5 to 10, and very particular preference is given to zeolite MAP of the standard formula in which x is 2
 35 and y is from 3.5 to 10. In particular, the zeolite concerned is zeolite Na-P, i.e. M is Na. This zeolite generally occurs in the variants Na-P-1, Na-P-2 and Na-P-3, which differ in their cubic, tetragonal or orthorhombic structure (see R. M. Barrer, B. M. Munday, *J. Chem.*

Soc. A, (1971), 2909-14). The above literature reference also describes the preparation of zeolite P-1 and P-2. According to that reference, Zeolite P-3 is very rare and is therefore of virtually no practical interest. The structure of the zeolite P-1 corresponds to the gismondite structure known from the abovementioned "Atlas of Zeolite Structures". In EP-A-0 384 070, a distinction is made between cubic (zeolite B or Pc) and tetragonal (zeolite P1) zeolites of the P type. Also mentioned therein are zeolites of the P type having Si:Al ratios below 1.07:1. These are zeolites having the designation MAP or MA-P, for "Maximum Aluminium P".

[0090] Depending on the preparation process, zeolite P may also include small fractions of other zeolites. Highly pure zeolite P has been described in WO 1994/26662. Within the scope of the invention, it is also possible to use those finely divided, water-insoluble sodium aluminosilicates which have been precipitated and crystallised in the presence of water-soluble organic or inorganic dispersants. These can be introduced into the reaction mixture in any desired manner, prior to or during the precipitation and crystallization.

[0091] Very particular preference is given to Na zeolite A and Na zeolite P. The hydrotalcites and/or zeolites can be employed in amounts, for example, from 0.1 to 20, judiciously from 0.1 to 10 and, in particular, from 0.1 to 5 parts by weight per 100 parts by weight of chlorine-containing polymers and resins, such as PVC.

[0092] As examples of phosphites (phosphorous triesters), thiophosphites and thiophosphates, mention may be made of triphenyl phosphite, diphenyl alkyl phosphites, phenyl dialkyl phosphites, tris(nonylphenyl) phosphite, trilauryl phosphite, trioctadecyl phosphite, distearyl pentaerythritol diphosphite, tris(2,4-di-*tert*-butylphenyl) phosphite, diisodecyl pentaerythritol diphosphite, bis(2,4-di-*tert*-butylphenyl) pentaerythritol diphosphite, bis(2,6-di-*tert*-butyl-4-methylphenyl) pentaerythritol diphosphite, bisisodecyloxy-pentaerythritol diphosphite, bis(2,4-di-*tert*-butyl-6-methylphenyl) pentaerythritol diphosphite, bis(2,4,6-tri-*tert*-butylphenyl) pentaerythritol diphosphite, tristearyl sorbitol triphosphite, bis(2,4-di-*tert*-butyl-6-methylphenyl) methylphenyl methyl phosphite, bis(2,4-di-*tert*-butyl-6-methylphenyl) ethyl phosphite.

[0093] Particularly suitable are trioctyl, tridecyl, tridodecyl, tritetradecyl, tristearyl, trioleyl, triphenyl, tricresyl, tris- p-nonylphenyl or tricyclohexyl phosphite and, with particular preference, the aryl dialkyl and alkyl diaryl phosphites, examples being phenyl didecyl, 2,4-di-*tert*-butylphenyl didodecyl phosphite, 2,6-di-*tert*-butylphenyl didodecyl phosphite and the dialkyl and diaryl pentaerythritol diphosphites, such as distearyl pentaerythritol diphosphite, and also non-stoichiometric triaryl phosphites whose composition is, for example, $(\text{H}_{19}\text{C}_9\text{-C}_6\text{H}_4)\text{O}_{1.5}\text{P}(\text{OC}_{12,13}\text{-H}_{25,27})_{1.5}$ or $(\text{H}_8\text{C}_{17}\text{-C}_6\text{H}_4)\text{O}_2\text{P}(\text{i-C}_8\text{H}_{17}\text{O})$ or $(\text{H}_{19}\text{C}_9\text{-C}_6\text{H}_4)\text{O}_{1.5}\text{P}(\text{OC}_{9,11}\text{-H}_{19,23})_{1.5}$.

[0094] Preferred organic phosphites are distearyl pentaerythritol diphosphite, trisnonylphenyl phosphite and phenyl didecyl phosphite. Other suitable phosphites are phosphorous diesters (with abovementioned radicals) and phosphorous monoesters (with abovementioned radicals), possibly in the form of their alkali metal, alkaline earth metal, zinc or aluminium salts. It is also possible for these phosphorous esters to have been applied to an alumo salt compound; in this regard see also DE-A-403 18 18.

[0095] The organic phosphites can be employed in an amount of, for example, from 0.01 to 10, judiciously from 0.05 to 5 and, in particular, from 0.1 to 3 parts by weight per 100 parts by weight of chlorine-containing polymers and resins, such as PVC.

[0096] By thiophosphites and thiophosphates are meant compounds of the general type $(RS)_3P$, $(RS)_3P=O$ and $(RS)_3P=S$, respectively, as are described, for instance, in patents DE 2 809 492, EP 0 090 770 and EP 0 573 394. Examples of these compounds are trithiohexyl phosphite, trithio-octyl phosphite, trithiolauryl phosphite, trithiobenzyl phosphite, trithiophosphorous acid tris(carbo-*iso*-octyloxy)methyl ester, trithiophosphorous acid tris(carbotrimethylcyclohexyloxy)methyl ester, trithiophosphoric acid S,S,S-tris(carbo-*iso*-octyloxy)methyl ester, trithiophosphoric acid S,S,S-tris(carbo-2-ethylhexyloxy)methyl ester, trithiophosphoric acid S,S,S-tris-1-(carbohexyloxy)ethyl ester, trithiophosphoric acid S,S,S-tris-1-(carbo-2-ethylhexyloxy)ethyl ester and trithiophosphoric acid S,S,S-tris-2-(carbo-2-ethylhexyloxy)ethyl ester.

[0097] Among the β -diketones and β -keto esters that may be used, mention may be made of 1,3-dicarbonyl compounds, which can be linear or cyclic dicarbonyl compounds. Preference is given to the use of dicarbonyl compounds of the following formulae: $R'_1COCHR'_2COR'_3$ in which R'_1 is C_1 - C_{22} -alkyl, C_5 - C_{10} -hydroxyalkyl, C_2 - C_{18} -alkenyl, phenyl, OH-, C_1 - C_4 -alkyl-, C_1 - C_4 -alkoxy- or halogen- substituted phenyl, C_7 - C_{10} -phenylalkyl, C_5 - C_{12} -cycloalkyl, C_1 - C_4 -alkyl-substituted C_5 - C_{12} -cycloalkyl or a group $-R'_5-S-R'_6$ or $-R'_5-O-R'_6$, R'_2 is hydrogen, C_1 - C_8 -alkyl, C_2 - C_{12} -alkenyl, phenyl, C_7 - C_{12} -alkylphenyl, C_7 - C_{10} -phenylalkyl or a group $-CO-R'_4$, R'_3 is as defined for R'_1 or is C_1 - C_{18} -alkoxy, R'_4 is C_1 - C_4 -alkyl or phenyl, R'_5 is C_1 - C_{10} -alkylene and R'_6 is C_1 - C_{12} -alkyl, phenyl, C_7 - C_{18} -alkylphenyl or C_7 - C_{10} -phenylalkyl.

[0098] These include the hydroxyl-containing diketones of EP 0 346 279 and the oxa and thia diketones of EP 0 307 358, as well as the keto esters based on isocyanic acid of U.S. 4,339,383.

[0099] R'_1 and R'_3 as alkyl can in particular be C_1 - C_{18} -alkyl, such as, for example methyl, ethyl, n-propyl, isopropyl, n-butyl, *tert*-butyl, pentyl, hexyl, heptyl, octyl, decyl, dodecyl or octadecyl. R'_1 and R'_3 as hydroxyalkyl are in particular a group $-(CH_2)_n-OH$, in which n is 5, 6 or 7.

[0100] R'_1 and R'_3 as alkenyl can for example be vinyl, allyl, methallyl, 1-butenyl, 1-hexenyl or oleyl, preferably allyl. R'_1 and R'_3 as OH-, alkyl-, alkoxy- or halogen-substituted

phenyl can for example be tolyl, xylyl, *tert*-butylphenyl, methoxyphenyl, ethoxyphenyl, hydroxyphenyl, chlorophenyl or dichlorophenyl. R₁ and R₃ as phenylalkyl are in particular benzyl. R₂ and R₃ as cycloalkyl or alkylcycloalkyl are, in particular, cyclohexyl or methylcyclohexyl. R₂ as alkyl can in particular be C₁-C₄-alkyl. R₂ as C₂-C₁₂-alkenyl can in particular be allyl. R₂ as alkylphenyl can in particular be tolyl. R₂ as phenylalkyl can in particular be benzyl.

[0101] Preferably, R₂ is hydrogen. R₃ as alkoxy can for example be methoxy, ethoxy, butoxy, hexyloxy, octyloxy, dodecyloxy, tridecyloxy, tetradecyloxy or octadecyloxy. R₅ as C₁-C₁₀-alkylene is, in particular, C₂-C₄-alkylene. R₆ as alkyl is, in particular, C₄-C₁₂-alkyl, such as, for example butyl, hexyl, octyl, decyl or dodecyl. R₆ as alkylphenyl is in particular tolyl. R₆ as phenylalkyl is in particular benzyl.

[0102] Examples of 1,3-dicarbonyl compounds of the above formula and their alkali metal, alkaline earth metal and zinc chelates are acetylacetone, butanoylacetone, heptanoylacetone, steroylacetone, palmitoylacetone, lauroylacetone, 7-*tert*-nonylthio-2,4-heptanedione, benzoylacetone, dibenzoylmethane, lauroylbenzoylmethane, palmitoylbenzoylmethane, stearylbenzoylmethane, isooctylbenzoylmethane, 5-hydroxycapronyl-benzoylmethane, tribenzoylmethane, bis(4-methylbenzoyl)methane, benzoyl-*p*-chlorobenzoylmethane, bis(2-hydroxybenzoyl)methane, 4-methoxybenzoylbenzoylmethane, bis(4-methoxybenzoyl)methane, 1-benzoyl-1-acetylnonane, benzoylacetylphenylmethane, stearyl-4-methoxybenzoylmethane, bis(4-*tert*-butylbenzoyl)methane, benzoylformylmethane, benzoylphenylacetyl methane, biscyclohexanoylmethane, di-pivaloylmethane, 2-acetylcyclopentanone, 2-benzoylcyclopentanone, methyl, ethyl and allyl diacetoacetate, methyl and ethyl benzoyl-, propionyl- and butyrylacetate, triacetyl methane, methyl, ethyl, hexyl, octyl, dodecyl or octadecyl acetate, methyl, ethyl, butyl, 2-ethylhexyl, dodecyl or octadecyl benzoylacetate, and also C₁-C₁₆-alkyl propionylacetates and butyrylacetates; ethyl, propyl, butyl, hexyl or octyl stearylacetate, and also polycyclic .beta.-keto esters, as described in EP 0 433 230, and dehydraacetic acid, and the zinc, magnesium or alkali metal salts thereof.

[0103] Preference is given to 1,3-diketo compounds of the above formula in which R₁ is C₁-C₁₆-alkyl, phenyl, OH-, methyl- or methoxy-substituted phenyl, C₇-C₁₀-phenylalkyl or cyclohexyl, R₂ is hydrogen and R₃ is as defined for R₁. The 1,3-diketo compounds can be employed in amount of, for example, from 0.01 to 10, judiciously from 0.01 to 3 and, in particular, from 0.01 to 2 parts by weight per 100 parts by weight of chlorine-containing polymers and resins, such as PVC C (post-chlorinated polyvinyl chloride).

[0104] Examples of mercaptocarboxylic esters includes esters of thioglycolic acid, thiomalic acid, mercaptopropionic acid, mercaptobenzoic acids and thiolactic acid,

mercaptoethyl stearate and mercaptoethyl oleate, as are described in FR 2 459 816, EP 0 090 748, FR 2 552 440 and EP 0 365 483. The generic mercaptocarboxylic esters also embrace polyol esters and partial esters thereof, and also thioethers derived from them. These molecules may also be latent-mercaptides as described in EP 0 945 485.

5 **[0105]** Metal soaps for use as co-stabilisers in the present invention include , as examples, primarily metal carboxylates of preferably relatively long-chain carboxylic acids. Familiar examples are stearates and laurates, and also oleates and salts of shorter-chain alkanecarboxylic acids. Alkylbenzoic acids are also said to be included under metal soaps.

[0106] Metals that may be mentioned are Li, Na, K, Mg, Ca, Sr, Ba, Zn, Al, La, Ce and
10 rare earth metals. Use is often made of what are known as synergistic mixtures, such as barium/zinc, magnesium/zinc, calcium/zinc or calcium/magnesium/zinc stabilisers. The metal soaps can be employed individually or in mixtures. A review of common metal soaps is given in Ullmann's Encyclopedia of Industrial Chemistry, 5th Ed., Vol. A16 (1985), p. 361 sqq.). It is judicious to use organic metal soaps from the series of the aliphatic saturated
15 C₂-C₂₂ carboxylates, the aliphatic unsaturated C₃-C₂₂ carboxylates, the aliphatic C₂-C₂₂ carboxylates substituted by at least one OH group, the cyclic and bicyclic carboxylates having 5-22 carbon atoms, the unsubstituted benzenecarboxylates substituted by at least one OH group and/or by C₁-C₁₆-alkyl, the unsubstituted naphthalenecarboxylates substituted by at least one OH group and/or by C₁-C₁₆-alkyl, the phenyl-C₁-C₁₆-
20 alkylcarboxylates, the naphthyl-C₁-C₁₆-alkylcarboxylates or the unsubstituted or C₁-C₁₂-alkyl-substituted phenolates, tallates and resinates.

[0107] Named examples which may be mentioned are the zinc, calcium, magnesium or barium salts of monovalent carboxylic acids such as acetic, propionic, butyric, valeric, hexanoic, enanthoic, octanoic, neodecanoic, 2-ethylhexanoic, pelargonic, decanoic,
25 undecanoic, dodecanoic, tridecanoic, myristic, palmitic, isostearic, stearic, 12-hydroxystearic, behenic, benzoic, *p-tert*-butylbenzoic, 3,5-di-*tert*-butyl-4-hydroxybenzoic, toluic, dimethylbenzoic, ethylbenzoic, *n*-propylbenzoic, salicylic, *p-tert*-octylsalicylic and sorbic acid; calcium, magnesium and zinc salts of the monoesters of divalent carboxylic acids such as oxalic, malonic, succinic, glutaric, adipic, fumaric, pentane-1,5-dicarboxylic,
30 hexane-1,6-dicarboxylic, heptane-1,7-dicarboxylic, octane-1,8-dicarboxylic, phthalic, isophthalic, terephthalic and hydroxyphthalic acid; and of the di- or triesters of tri- or tetra-valent carboxylic acids such as hemimellitic, trimellitic, pyromellitic and citric acid.

[0108] Preference is given to calcium, magnesium and zinc carboxylates of carboxylic acids having 7 to 18 carbon atoms (metal soaps in the narrow sense), such as, for
35 example, benzoates or alkanoates, preferably stearate, oleate, laurate, palmitate, behenate, hydroxystearates, dihydroxystearates or 2-ethylhexanoate. Particular preference is given to stearate, oleate and *p-tert*-butylbenzoate. Overbased carboxylates, such as

overbased zinc octoate, are also preferred. Preference is likewise given to overbased calcium soaps. If desired, it is also possible to employ a mixture of carboxylates of different structures. Preference is given to compositions, as described, comprising an organozinc and/or organocalcium compound.

5 **[0109]** Other named examples of metal soaps or metal salts which may be mentioned are dimetallic salts of dicarboxylic acids such as dilithium, disodium or dipotassium salts of divalent carboxylic acids such as of oxalic, malonic, succinic, glutaric, adipic, fumaric, pentane-1,5-dicarboxylic, hexane-1,6-dicarboxylic, heptane-1,7-dicarboxylic, octane-1,8-dicarboxylic, phthalic, isophthalic and terephthalic. Preference is given to disodium adipate.

10 **[0110]** In addition to the compounds mentioned, organoaluminum compounds are also suitable, as are compounds analogous to those mentioned above, especially aluminium tristearate, aluminium distearate and aluminium monostearate, and also aluminium acetate and basic derivatives derived therefrom. Further information on the aluminium compounds, which can be used and are preferred is given in US 4,060,512 and US 3,243,394.

15 **[0111]** Also suitable in addition to the compounds already mentioned are organic rare earth compounds, especially compounds analogous to those mentioned above. The term rare earth compound means especially compounds of the elements cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium, lanthanum and yttrium; mixtures, especially with cerium, being preferred. Further preferred rare earth compounds can be found in
20 EP 0 108 023.

[0112] It is possible if desired to employ a mixture of zinc, alkali metal, alkaline earth metal, aluminium, cerium, lanthanum or lanthanoid compounds of different structure. It is also possible for organozinc, organoaluminum, organocerium, organo-alkali metal, organo-alkaline earth metal, organolanthanum or organolanthanoid compounds to be coated on an
25 alumo salt compound; in this regard see also DE 403 18 18.

[0113] The metal soaps and/or mixtures thereof can be employed in an amount of, for example, from 0.001 to 10 parts by weight, judiciously from 0.01 to 8 parts and, with particular preference, from 0.05 to 5 parts by weight per 100 parts by weight of chlorine-
30 containing polymers and resins, such as PVC. The same applies to the further metal stabilisers.

[0114] As regards further metal stabilisers, mention may be made of the organometallic stabilisers and in particular of the organotin stabilisers. These can be the carboxylates, maleates, mercaptides and sulphides, in particular.
35 Examples of suitable compounds are described in US 4,743,640, US 2,567,651, US 2,598,936, US 2,567,652, US 6,174,941, US 5,925,696, US 6,156,830, US 6,084,013, US 6,194,494, US 4,105,627, US 4,352,903, DE 2,427,853.

[0115] Further customary additives can also optionally be added in addition to the composition of the present invention in chlorine-containing polymers. As these additives, mention may be made of stabilisers, auxiliaries and processing aids, examples being alkali metal compounds and alkaline earth metal compounds, lubricants, plasticisers, pigments, fillers, epoxidized fatty acid esters, antioxidants, UV absorbers and light stabilisers, optical brighteners, impact modifiers and processing aids, gelling agents, antistats, biocides, metal passivators, flame retardants, blowing agents, anti-fog agents, compatibilisers and anti plate-out agents, and the like, as well as mixtures thereof. Such additives are commonly known in the art, and disclosed, for example in "Handbook of PVC Formulating" by E. J. Wickson, John Wiley & Sons, New York, (1993).

[0116] Examples of such additives are as follows:

- Fillers and reinforcing agents are, for example, calcium carbonate, dolomite, wollastonite, magnesium oxide, magnesium hydroxide, silicates, china clay, talc, glass fibres, glass beads, wood flour, mica, metal oxides, or metal hydroxides, carbon black, graphite, rock flour, heavy spar, glass fibres, talc, kaolin and chalk. The fillers can be employed in an amount of for example, from 5 to 80, judiciously from 10 to 40 and, in particular, from 10 to 20 parts by weight per 100 parts by weight of chlorine-containing polymers and resins, such as PVC.
- Alkali metal and alkaline earth metal compounds. By these are meant principally the carboxylates of the above-described metal soaps, but also corresponding oxides and/or hydroxides or carbonates. Also suitable are mixtures thereof with organic acids. Examples are LiOH, NaOH, KOH, CaO, Ca(OH)₂, MgO, Mg(OH)₂, Sr(OH)₂, Al(OH)₃, CaCO₃ (also basic carbonates, such as magnesia alba and hutite), and also Na and K salts of fatty acids. In the case of alkaline earth metal and Zn carboxylates it is also possible to employ their adducts with MO or M(OH)₂ (M = Ca, Mg, Sr or Zn), known as "overbased" compounds. In addition to the stabiliser combination of the invention it is preferred to employ alkali metal carboxylates, alkaline earth metal carboxylates and/or aluminium carboxylates.
- Lubricants, examples of which are montan wax, fatty acid esters, PE waxes, amide waxes, chlorinated paraffins, glycerol esters or alkaline earth metal soaps. Lubricants which can be used are also described in "Kunststoffadditive", R. Gächter ; H. Müller, Carl Hanser Verlag, 3rd Ed., (1989), pages 478-488. Mention may also be made of fatty ketones (as described in DE 42 04 887) and of silicone-based lubricants (as described in EP 0 225 261) or combinations thereof, as set out in EP 0 259 783. Calcium stearate is preferred. The lubricants can also be applied to an alumo salt compound; in this regard see also DE 403 18 18.

- Plasticisers, and examples of suitable organic plasticisers are those from the following groups: A) Phthalates: examples of such plasticisers are dimethyl, diethyl, dibutyl, dihexyl, di-2-ethylhexyl, di-n-octyl, di-iso-octyl, di-iso-nonyl, di-iso-decyl, di-iso-tridecyl, dicyclohexyl, dimethylcyclohexyl, dimethylglycol, dibutylglycol, benzyl butyl and diphenyl phthalates, and also mixtures of phthalates, such as C₇-C₉- and C₉-C₁₁-alkyl phthalates obtained from predominantly linear alcohols, C₆-C₁₀-n-alkyl phthalates and C₈-C₁₀-n-alkyl phthalates. Of these preference is given to dibutyl, dihexyl, di-2-ethylhexyl, di-n-octyl, di-iso-octyl, di-iso-nonyl, di-iso-decyl, di-iso-tridecyl and benzyl butyl phthalate, and the stated mixtures of alkyl phthalates. Particular preference is given to di-2-ethylhexyl, di-isononyl and di-iso-decyl phthalate, which are also known by the common abbreviations DOP (dioctyl phthalate, di-2-ethylhexyl phthalate), DINP (di-iso-nonyl phthalate) and DIDP (diisodecyl phthalate); B) Esters of aliphatic dicarboxylic acids, especially esters of adipic, azelaic and sebacic acid: examples of such plasticisers are di-2-ethylhexyl adipate, diisooctyl adipate (mixture), di-iso-nonyl adipate (mixture), diisodecyl adipate (mixture), benzyl butyl adipate, benzyl octyl adipate, di-2-ethylhexyl azelate, di-2-ethylhexyl sebacate and diisodecyl sebacate (mixture), di-2-ethylhexyl adipate and di-iso-octyl adipate being preferred; C) Trimellitates, examples being tri-2-ethylhexyl trimellitate, tri-iso-decyl trimellitate (mixture), tri-iso-tridecyl trimellitate, tri-iso-octyl trimellitate (mixture) and also tri-C₆-C₈-alkyl, tri-C₆-C₁₀-alkyl, tri-C₇-C₉-alkyl- and tri-C₉-C₁₁-alkyl trimellitates. The latter trimellitates are formed by esterification of trimellitic acid with the corresponding alkanol mixtures. Preferred trimellitates are tri-2-ethylhexyl trimellitate and the abovementioned trimellitates from alkanol mixtures. Customary abbreviations are TOTM (trioctyl trimellitate, tri-2-ethylhexyl trimellitate), TIDTM (tri-iso-decyl trimellitate) and TITDTM (tri-iso-tridecyl trimellitate); D) Epoxy plasticisers: these are primarily epoxidized unsaturated fatty acids, such as epoxidized soybean oil; E) Polymer plasticisers: a definition of these plasticisers and examples of them are given in "Kunststoffadditive", R. Gächter ; H. Müller, Carl Hanser Verlag, 3rd ed., (1989), section 5.9.6, pages 412-415, and also in "PVC Technology", W. V. Titow, 4th ed., Elsevier Publ., (1984), pages 165-170. The most common starting materials for preparing the polyester plasticisers are dicarboxylic acids, such as adipic, phthalic, azelaic and sebacic acids; diols, such as 1,2-propanediol, 1,3-butanediol, 1,4-butanediol, 1,6-hexanediol, *neo*-pentyl glycol and diethylene glycol; F) Phosphoric esters: a definition of these esters is given in the abovementioned "Taschenbuch der Kunststoffadditive" section 5.9.5, pp. 408-412. Examples of such phosphoric esters are tributyl phosphate, tri-2-ethylbutyl phosphate, tri-2-ethylhexyl phosphate, trichloroethyl phosphate, 2-ethylhexyl diphenyl phosphate, cresyl diphenyl phosphate;

triphenyl phosphate, tricresyl phosphate and trixylenyl phosphate. Preference is given to tri-2-ethylhexyl phosphate and to Reofos(R) 50 and 95 (Ciba Spezialitätenchemie); G) Chlorinated hydrocarbons (paraffins); H) Hydrocarbons; I) Monoesters, e.g., butyl oleate, phenoxyethyl oleate, tetrahydrofurfuryl oleate and alkylsulphonic esters; J) Glycol esters, e.g., diglycol benzoates. Definitions and examples of plasticizers of groups G) to J) are given in the following handbooks: "Kunststoffadditive", R. Gachter/H. Muller, Carl Hanser Verlag, 3rd ed., 1989, section 5.9.14.2, pp. 422-425, (group G), and section 5.9.14.1, p. 422, (group H). <11>PVC Technology", W. V. Titow, 4th ed., Elsevier Publishers, 1984, section 6.10.2, pages 171-173, (group G), section 6.10.5 page 174, (group H), section 6.10.3, page 173, (group I) and section 6.10.4, pages 173-174 (group J). It is also possible to use mixtures of different plasticizers. The plasticizers can be employed in an amount of, for example, from 5 to 20 parts by weight, judiciously from 10 to 20 parts by weight, per 100 parts by weight of chlorine-containing polymers and resins, such as PVC. Rigid or semi rigid PVC contains preferably up to 10%, with particular preference up to 5% of plasticiser, or no plasticiser.

[0117] As other additives, pigments may be used, suitable substrates of which are known to the person skilled in the art. Examples of inorganic pigments are TiO_2 , zirconium oxide-based pigments, BaSO_4 , zinc oxide (zinc white) and lithopones (zinc sulphide/barium sulphate), carbon black, carbon black/titanium dioxide mixtures, iron oxide pigments, Sb_2O_3 , $(\text{Ti}, \text{Ba}, \text{Sb})\text{O}_2$, Cr_2O_3 , spinels, such as cobalt blue and cobalt green, $\text{Cd}(\text{S}, \text{Se})$, ultramarine blue. Organic pigments are, for example, azo pigments, phthalocyanine pigments, quinacridone pigments, perylene pigments, diketopyrrolopyrrole pigments and anthraquinone pigments. Preference is also given to TiO_2 in micronised form.

[0118] Epoxidized fatty acid esters and other epoxy compounds may also be used as additives to the chlorine-containing polymers together with the stabilising composition of the invention. Particularly suitable such esters are those of fatty acids from natural sources (fatty acid glycerides), such as soybean oil or rapeseed oil. It is, however, also possible to employ synthetic products such as epoxidized butyl oleate. Epoxidized polybutadiene and polyisoprene can also be used, as they are or in partially hydroxylated form, or else homo- or copolymeric glycidyl acrylate and glycidyl methacrylate can be used. These epoxy compounds can also have been applied to an alumo salt compound; in this regard see also DE 031 818.

[0119] Customary antioxidants may also be used as additives, alone or in combination. Examples of suitable antioxidants are alkylated monophenols, for example, 2,6-di-*tert*-butyl-4-methylphenol, 2-*tert*-butyl-4,6-dimethylphenol, 2,6-di-*tert*-butyl-4-ethylphenol, 2,6-di-*tert*-butyl-4-n-butylphenol, 2,6-di-*tert*-butyl-4-*iso*-butylphenol, 2,6-di-cyclopentyl-4-

methylphenol, 2-(α -methylcyclohexyl)-4,6-dimethylphenol, 2,6-di-octadecyl-4-methylphenol, 2,4,6-tricyclohexylphenol, 2,6-di-*tert*-butyl-4-methoxymethylphenol, 2,6-dinonyl-4-methylphenol, 2,4-dimethyl-6-(1'-methylundec-1'-yl)phenol, 2,4-dimethyl-6-(1'-methylheptadec-1'-yl)phenol, 2,4-dimethyl-6-(1'-methyltridec-1'-yl)phenol, octylphenol, 5 nonylphenol, dodecylphenol and mixtures thereof.

[0120] Other examples are alkylthiomethylphenols, such as 2,4-dioctylthiomethyl-6-*tert*-butylphenol, 2,4-dioctylthiomethyl-6-methylphenol, 2,4-dioctylthiomethyl-6-ethylphenol, and 2,6-didodecylthiomethyl-4-nonylphenol; alkylated hydroquinones, such as 2,6-di-*tert*-butyl-4-methoxyphenol, 2,5-di-*tert*-butylhydroquinone, 2,5-di-*tert*-amylhydroquinone, 2,6-10 diphenyl-4-octadecyloxyphenol, 2,6-di-*tert*-butylhydroquinone, 2,5-di-*tert*-butyl-4-hydroxyanisole, 3,5-di-*tert*-butyl-4-hydroxyanisole, 3,5-di-*tert*-butyl-4-hydroxyphenyl stearate, bis(3,5-di-*tert*-butyl-4-hydroxyphenyl) adipate; hydroxylated thiodiphenyl ethers, such as 2,2'-thiobis(6-*tert*-butyl-4-methylphenol), 2,2'-thiobis(4-octylphenol), 4,4'-thiobis(6-*tert*-butyl-3-methylphenol), 4,4'-thiobis(6-*tert*-butyl-2-methylphenol), 4,4'-thiobis-(3,6-di-sec-15 amylphenol)-4,4'-bis-(2,6-dimethyl-4-hydroxyphenyl)disulphide; alkylidenebisphenols, such as 2,2'-methylenebis(6-*tert*-butyl-4-methylphenol), 2,2'-methylenebis(6-*tert*-butyl-4-ethylphenol), 2,2'-methylene bis-[4-methyl-6-(α -methylcyclohexyl)phenol], 2,2'-methylenebis(4-methyl-6-cyclohexylphenol), 2,2'-methylenebis(6-nonyl-4-methylphenol), 2,2'-methylenebis-(4,6-di-*tert*-butylphenol), 2,2'-ethylidenebis(4,6-di-*tert*-butylphenol), 2,2'-ethylidenebis(6-*tert*-butyl-4-isobutylphenol), 2,2'-methylenebis[6-(α -methylbenzyl)-4-nonylphenol], 2,2'-methylenebis[6-(α,α -dimethylbenzyl)-4-nonylphenol], 4,4'-methylene bis(2,6-di-*tert*-butylphenol), 4,4'-methylene bis-(6-*tert*-butyl-2-methylphenol), 1,1-bis-(5-*tert*-butyl-4-hydroxy-2-methylphenyl)butane, 2,6-bis-(3-*tert*-butyl-5-methyl-2-hydroxybenzyl)-4-methylphenol, 1,1,3-tris-(5-*tert*-butyl-4-hydroxy-2-methyl-phenyl)butane, 1,1-bis-(5-*tert*-25 butyl-4-hydroxy-2-methylphenyl)-3-n-dodecylmercaptobutane, ethylene glycol bis[3,3-bis-(3'-*tert*-butyl-4'-hydroxyphenyl)butyrate], bis(3-*tert*-butyl-4-hydroxy-5-methyl-phenyl)dicyclopentadiene, bis[2-(3'-*tert*-butyl-2'-hydroxy-5'-methylbenzyl)-6-*tert*-butyl-4-methylphenyl]terephthalate, 1,1-bis-(3,5-dimethyl-2-hydroxyphenyl)butane, 2,2-bis-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propane, 2,2-bis(4-hydroxyphenyl)propane, 2,2-bis-(5-*tert*-butyl-4-hydroxy-2-methylphenyl)-4-n-dodecylmercaptobutane, 1,1,5,5-tetra-(5-*tert*-butyl-4-hydroxy-2-methylphenyl)pentane; benzyl compounds, such as 3,5,3',5'-tetra-*tert*-butyl-4,4'-dihydroxy-dibenzyl ether, octadecyl 4-hydroxy-3,5-dimethylbenzyl-mercaptoacetate, tris(3,5-di-*tert*-butyl-4-hydroxybenzyl)amine, bis(4-*tert*-butyl-3-hydroxy-2,6-dimethylbenzyl)-dithioterephthalate, bis(3,5-di-*tert*-butyl-4-hydroxybenzyl) sulphide, isooctyl 3,5-di-*tert*-butyl-35 4-hydroxybenzyl-mercaptoacetate; hydroxybenzylated malonates, for example, di-octadecyl 2,2-bis(3,5-di-*tert*-butyl-2-hydroxybenzyl)malonate, di-oactadecyl 2-(3-*tert*-butyl-4-hydroxy-5-methylbenzyl)malonate, di-dodecyl mercapto-ethyl-2,2-bis(3,5-di-*tert*-butyl-4-

hydroxybenzyl)malonate, di-[4-(1,1,3,3-tetramethylbutyl)-phenyl]-2,2-bis(3,5-di-*tert*-butyl-4-hydroxybenzyl)malonate; aromatic hydroxybenzyl compounds, for example, 1,3,5-tris(3,5-di-*tert*-butyl-4-hydroxybenzyl)-2,4,6-trimethylbenzene, 1,4-bis(3,5-di-*tert*-butyl-4-hydroxybenzyl)-2,3,5,6-tetramethylbenzene, 2,4,6-tris(3,5-di-*tert*-butyl-4-hydroxybenzyl)phenol; triazine compounds, such as 2,4-bis(octylmercapto-6-(3,5-di-*tert*-butyl-4-hydroxyanilino)-1,3,5-triazine, 2-octylmercapto-4,6-bis-(3,5-di-*tert*-butyl-4-hydroxyanilino)-1,3,5-triazine, 2-octylmercapto-4,6-bis-(3,5-di-*tert*-butyl-4-hydroxyphenoxy)-1,3,5-triazine, 2,4,6-tris(3,5-di-*tert*-butyl-4-hydroxyphenoxy)-1,2,3-triazine, 1,3,5-tris(3,5-di-*tert*-butyl-4-hydroxybenzyl)isocyanurate, 1,3,5-tris-(4-*tert*-butyl-3-hydroxy-2,6-dimethylbenzyl)isocyanurate, 2,4,6-tris-(3,5-di-*tert*-butyl-4-hydroxyphenylethyl)-1,3,5-triazine, 1,3,5-tris(3,5-di-*tert*-butyl-4-hydroxyphenylpropionyl)hexahydro-1,3,5-triazine, 1,3,5-tris-(3,5-dicyclohexyl-4-hydroxybenzyl) isocyanurate; phosphates and phosphonites, for example, dimethyl-2,5-di-*tert*-butyl-4-hydroxybenzylphosphonate, diethyl-3,5-di-*tert*-butyl-4-hydroxybenzylphosphonate, dioctadecyl-3,5-di-*tert*-butyl-4-hydroxybenzylphosphonate, dioctadecyl-5-*tert*-butyl-4-hydroxy-3-methylbenzylphosphonate, calcium salt of monoethyl 3,5-di-*tert*-butyl-4-hydroxybenzylphosphonate, tetrakis-(2,4-di-*tert*-butylphenyl)-4,4'-biphenylenediphosphonite, 6-isooctyloxy-2,4,8,10-tetra-*tert*-butyl-12*H*-dibenzo-[d,g]-1,3,2-dioxaphosphocine, 6-fluoro-2,4,8,10-tetra-*tert*-butyl-12-methyl-dibenzo-[d,g]-1,3,2-dioxaphosphocine; acylaminophenols, such as 4-hydroxylauranilide, 4-hydroxystearanilide, octyl N-(3,5-di-*tert*-butyl-4-hydroxyphenyl)carbamate; esters of β -(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, *neo*-pentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, dipentaerythritol, tris(hydroxyethyl) isocyanurate, N,N'-bis(hydroxyethyl)oxalamide, 3-thia-undecanol, 3-thia-pentadecanol, trimethylhexanediol, trimethylolpropane, ditrimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane; esters of β -(5-*tert*-butyl-4-hydroxy-3-methylphenyl)propionic acid with mono- or polyhydric alcohols, for example, with methanol, ethanol, octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol *neo*-pentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxy)ethyl isocyanurate, N,N'-bis(hydroxyethyl)oxalamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane; esters of β -(3,5-dicyclohexyl-4-hydroxyphenyl)propionic acid with mono- or polyhydric alcohols, for example, with methanol, ethanol, octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxy)ethyl isocyanurate, N,N'-bis(hydroxyethyl)oxalamide, 3-thia-undecanol, 3-

thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane; esters of 3,5-di-*tert*-butyl-4-hydroxyphenylacetic acid with mono- or polyhydric alcohols, for example, with methanol, ethanol, octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxy)ethyl isocyanurate, N,N'-bis(hydroxyethyl)oxalamide, 3-thia-undecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane; amides of β -(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionic acid, such as, for example, N,N'-bis(3,5-di-*tert*-butyl-4-hydroxyphenylpropionyl)hexamethylenediamine, N,N'-bis(3,5-di-*tert*-butyl-4-hydroxyphenylpropionyl)trimethylenediamine, N,N'-bis(3,5-di-*tert*-butyl-4-hydroxyphenylpropionyl)hydrazine; vitamin E (tocopherol) and derivatives.

[0121] As antioxidants, preference is given to 2,2-bis(4-hydroxyphenyl)propane, esters of 3,5-di-*tert*-butyl-4-hydroxyphenylpropionic acid with octanol, octadecanol or pentaerythritol or tris(2,4-di-*tert*-butylphenyl) phosphite. It is also possible, if desired, to employ a mixture of antioxidants of different structures.

[0122] The antioxidants can be employed in an amount of, for example, from 0.01 to 10 parts by weight judiciously from 0.1 to 10 parts by weight and in particular, from 0.1 to 5 parts by weight per 100 parts by weight of PVC.

[0123] Other additives may be UV absorbers and light stabilisers, examples of which are 2-(2'-hydroxyphenyl)benzotriazoles, such as, for example 2-(2'-hydroxy-5'-methylphenyl)benzotriazole, 2-(3',5'-di-*tert*-butyl-2'-hydroxyphenyl)benzotriazole, 2-(5'-*tert*-butyl-2'-hydroxyphenyl)benzotriazole, 2-(2'-hydroxy-5'-(1,1,3,3-tetramethylbutyl)phenyl)benzotriazole, 2-(3',5'-di-*tert*-butyl-2'-hydroxyphenyl)-5-chlorobenzotriazole, 2-(3'-*tert*-butyl-2'-hydroxy-5'-methylphenyl)-5-chlorobenzotriazole, 2-(3'-*sec*-butyl-5'-*tert*-butyl-2'-hydroxyphenyl)benzotriazole, 2-(2'-hydroxy-4'-octoxyphenyl)benzotriazole, 2-(3',5'-di-*tert*-amyl-2'-hydroxyphenyl)benzothiazole, 2-(3',5'-bis(α,α -dimethylbenzyl)-2'-hydroxyphenyl)benzothiazole, mixtures of 2-(3'-*tert*-butyl-2'-hydroxy-5'-(2-octyloxycarbonylethyl)phenyl)-5-chlorobenzotriazole, 2-(3'-*tert*-butyl-5'-[2-(2-ethylhexyloxy)carbonylethyl]-2'-hydroxyphenyl)-5-chlorobenzotriazole, 2-(3'-*tert*-butyl-2'-hydroxy-5'-(2-methoxycarbonylethyl)phenyl)-5-chlorobenzotriazole, 2-(3'-*tert*-butyl-2'-hydroxy-5'-(2-methoxycarbonylethyl)phenyl)benzotriazole, 2-(3'-*tert*-butyl-2'-hydroxy-5'-(2-octyloxycarbonylethyl)phenyl)benzotriazole, 2-(3'-*tert*-butyl-5'-[2-(2-ethylhexyloxy)carbonylethyl]-2'-hydroxyphenyl)benzotriazole, 2-(3'-dodecyl-2'-hydroxy-5'-methylphenyl)benzotriazole and 2-(3'-*tert*-butyl-2'-hydroxy-5'-(2-isooctyloxycarbonylethyl)phenyl)benzotriazole, 2,2'-methylenebis[4-(1,1,3,3-tetramethylbutyl)-6-benzotriazol-2-ylphenol]; the transesterification product of 2-[3'-*tert*-

butyl-5'-(2-methoxycarbonyl-ethyl)-2'-hydroxyphenyl]benzotriazole with polyethylene glycol 300; where R = 3'-*tert*-butyl-4'-hydroxy-5'-2*H*-benzotriazol-2-yl-phenyl; 2-hydroxybenzophenones, for example the 4-hydroxy-, 4-methoxy-, 4-octyloxy-, 4-decyloxy, 4-dodecyloxy-, 4-benzyloxy, 4,2',4'-trihydroxy-, 2'-4,4'-dimethoxy-derivatives; esters of substituted or unsubstituted benzoic acids, for example 4-*tert*-butylphenyl salicylate, phenyl salicylate, octylphenyl salicylate, dibenzoylresorcinol, bis(4-*tert*-butylbenzoyl)resorcinol, benzoylresorcinol, 2,4-di-*tert*-butylphenyl 3,5-di-*tert*-butyl-4-hydroxybenzoate, hexadecyl-3,5-di-*tert*-butyl-4-hydroxybenzoate, octadecyl 3,5-di-*tert*-butyl-4-hydroxybenzoate, 2-methyl-4,6-di-*tert*-butylphenyl 3,5-di-*tert*-butyl-4-hydroxy-benzoate; acrylates, for example ethyl- α -cyano- β , β -diphenylacrylate or isooctyl-ethyl- α -cyano- β , β -diphenylacrylate, methyl- α -carbo-methoxycinnamate, methyl- α -cyano- β -methyl-*para*-methoxycinnamate or butyl- α -cyano- β -methyl-*para*-methoxycinnamate, methyl- α -carbomethoxy-*para*-methoxycinnamate, N-(β -carbomethoxy-cyanovinyl)-2-methylindoline; nickel compounds, for example nickel complexes of 2,2'-thiobis[4-(1,1,3,3-tetramethylbutyl)phenol], such as the 1:1 or 1:2 complex, with or without additional ligands such as n-butylamine, triethanolamine or N-cyclohexyldiethanolamine, nickel dibutyldithiocarbamate, nickel salts of monoalkyl esters such as the methyl or ethyl ester, of 4-hydroxy-3,5-di-*tert*-butylbenzylphosphonic acid, nickel complexes of ketoximes, such as of 2-hydroxy-4-methylphenylundecylketoxime, nickel complexes of 1-phenyl-4-lauroyl-5-hydroxypyrazole, with or without additional ligands; oxalamides, for example 4,4'-dioctyloxyoxanilide, 2,2'-dioctyloxy-5,5'-di-*tert*-butyl-oxanilide, 2,2'-didodecyloxy-5,5'-di-*tert*-butyl-oxanilide, 2-ethoxy-2'-ethyl-oxanilide, N,N'-bis(3-dimethylaminopropyl)oxalamide, 2-ethoxy-5-*tert*-butyl-2'-ethyloxyanilide and its mixture with 2-ethoxy-2'-ethyl-5,4'-di-*tert*-butyl-oxanilide, mixtures of *ortho*- and *para*-methoxy and of *ortho*- and *para*-ethoxy-di-substituted oxanilides; 2-(2-hydroxyphenyl)-1,3,5-triazines, for example 2,4,6-tris(2-hydroxy-4-octyloxyphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-octyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2,4-dihydroxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2,4-bis(2-hydroxy-4-propyloxyphenyl)-6-(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-octyloxyphenyl)-4,6-bis(4-methylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-dodecyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-3-butyloxypropoxy)phenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-3-octyloxypropoxy)phenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine; sterically hindered amines, for example bis(2,2,6,6-tetramethyl-piperidin-4-yl) sebacate, bis(2,2,6,6-tetramethylpiperidin-4-yl)succinate, bis(1,2,2,6,6-pentamethylpiperidin-4-yl)sebacate, bis(1-octyloxy-2,2,6,6-tetramethylpiperidin-4-yl)sebacate, bis(1,2,2,6,6-pentamethylpiperidyl) n-butyl-3,5-di-*tert*-butyl-4-hydroxybenzylmalonate; the condensate of 1-hydroxyethyl-2,2,6,6-tetramethyl-4-hydroxypiperidine and succinic acid, linear or cyclic condensates of N,N'-bis(2,2,6,6-

tetramethyl-4-piperidyl)hexamethylenediamine and 4-*tert*-octylamino-2,6-dichloro-1,3,5-s-triazine, tris(2,2,6,6-tetramethyl-4-piperidyl)nitrilotriacetate, tetrakis(2,2,6,6-tetramethyl-4-piperidyl)-1,2,3,4-butanetetracarboxate, 1,1'-(1,2-ethanediyl)-bis(3,3,5,5-tetramethylpiperazinone), 4-benzoyl-2,2,6,6-tetramethylpiperidine, 4-stearyloxy-2,2,6,6-tetramethylpiperidine, bis(1,2,2,6,6-pentamethylpiperidyl), 2-n-butyl-2(2-hydroxy-3,5-di-*tert*-butylbenzyl)malonate, 3-n-octyl-7,7,9,9-tetramethyl-1,3,8-triazaspiro[4.5]decane-2,4-dione, bis(1-octyloxy-2,2,6,6-tetramethylpiperidyl)sebacate, bis(1-octyloxy-2,2,6,6-tetramethylpiperidyl)succinate, linear or cyclic condensates of N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine and 4-morpholino-2,6-dichloro-1,3,5-triazine; the
 10 condensate of 2-chloro-4,6-di-(4-n-butylamino-2,2,6,6-tetramethylpiperidyl)-1,3,5-triazine and 1,2-bis(3-aminopropylamino)ethane, the condensate of 2-chloro-4,6-di-(4-n-butylamino-1,2,2,6,6-pentamethylpiperidyl)-1,3,5-triazine and 1,2-bis(3-aminopropylamino)ethane, 8-acetyl-3-dodecyl-7,7,9,9-tetramethyl-1,3,8-triazaspiro[4.5]decane-2,4-dione, 3-dodecyl-1-(2,2,6,6-tetramethyl-4-piperidyl)pyrrolidone-2,5-dione, 3-dodecyl-1-(1,2,2,6,6-pentamethyl-
 15 4-piperidyl)pyrrolidine-2,5-dione, mixtures of 4-hexadecyloxy- and 4-stearyloxy-2,2,6,6-tetramethylpiperidine; the condensate of N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine and 4-cyclohexylamino-2,6-dichloro-1,3,5-triazine, the condensate of 1,2-bis(3-aminopropylamino)ethane and 2,4,6-trichloro-1,3,5-triazine, and also 4-butylamino-2,2,6,6-tetramethylpiperidine (CAS Reg. No. [136504-96-6]); N-(2,2,6,6-tetramethyl-4-piperidyl)-n-dodecylsuccinimide, N-(1,2,2,6,6-pentamethyl-4-piperidyl)-n-dodecylsuccinimide, 2-undecyl-7,7,9,9-tetramethyl-1-oxa-3,8-diaza-4-oxo-spiro[4.5]decane; 1,1-bis(1,2,2,6,6-pentamethyl-4-piperidyl)oxycarbonyl-2-(4-methoxyphenyl)ethene, N,N'-bisformyl-N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine, the diester of 4-methoxymethylenemalononic acid with 1,2,2,6,6-pentamethyl-4-hydroxypiperidine,
 25 poly[methylpropyl-3-oxy-4-(2,2,6,6-tetramethyl-4-piperidyl)]siloxane; the reaction product of maleic anhydride- α -olefin copolymer and 2,2,6,6-tetramethyl-4-aminopiperidine or 1,2,2,6,6-pentamethyl-4-aminopiperidine.

[0124] Still as additives, mention may be made of blowing agents, examples thereof being organic azo and hydrazo compounds, tetrazoles, oxazines, isatoic anhydride, and
 30 also sodium carbonate and sodium bicarbonate. Preference is given to azodicarboxamide and sodium bicarbonate and mixtures thereof.

[0125] Still other additives may be used in the context of the present invention, and among them, mention may be made of impact modifiers, thermal modifiers, processing aids, gelling agents, antistatic agents, biocides, fungicides, metal passivators, optical
 35 brighteners, flame retardants, antifogging agents and compatibilisers, which are described in "Kunststoffadditive", R. Gächter ; H. Müller, Carl Hanser Verlag, 3rd ed., 1989, and in the "Handbook of Polyvinyl Chloride Formulating" E. J. Wickson, J. Wiley & Sons, 1993, and in

"Plastics Additives" G. Pritchard, Chapman & Hall, London, 1st ed., 1998. Impact modifiers are also described in detail in "Impact Modifiers for PVC", J. T. Lutz/D. L. Dunkelberger, John Wiley & Sons, 1992.

[0126] The compositions of the present invention can also contain other stabilisers such as amino-uracils and particularly 6-aminouracils disclosed for instance in US 6,174,941 B1 and/or thiouracils and particularly 4-amino-6-hydroxy-2-mercapto-pyrimidine.

[0127] Hydrazides and hydrazide systems may also be used as additives. Preferred hydrazides are selected among one or more hydrazides compounds of formula $R^{11}-CO-NH-R^{12}$, in which

* R^{11} is chosen from among:

C_1-C_{30} linear or branched alkyl and C_2-C_{30} mono- or poly-unsaturated hydrocarbon, each of these groups possibly containing one or more heteroatoms, and possibly being substituted with one or more phenyl groups (substituted or not), epoxy groups, cycloaliphatic or heterocyclic group, halogen atom(s), hydroxy and/or alkoxy,

phenyl, benzyl, naphthyl, toluyl group, optionally substituted by -OH, -Cl, -alkoxy, -alkyl, -cycloalkyl, -COOR" or OCOR" (where R" is C_1-C_{12} alkyl), thienyl, -CH=CH-CO-NH-NH- R^{21} , -X-CO-NH-NH₂, -CH=CH-CO- R^{14} , -(CH₂)_n-C₆H₅ (with n varying from 1 to 5), -NH-NH₂;

* R^{12} is chosen from hydrogen and the group -CO- R^{13} ;

* R^{13} and R^{14} , which may be the same or different are chosen from among C_1-C_{30} linear or branched alkyl and C_2-C_{30} mono- or poly-unsaturated hydrocarbon, each of these groups possibly containing one or more heteroatoms, and possibly being substituted with one or more phenyl groups (substituted or not), epoxy groups, cycloaliphatic or heterocyclic group, halogen atom(s), hydroxy and/or alkoxy; phenyl, benzyl, naphthyl, toluyl group, optionally substituted by -OH, -Cl, -alkoxy, -alkyl, -cycloalkyl, -COOR" or OCOR" (where R" is C_1-C_{12} alkyl);

* X is chosen from among C_1-C_{30} linear or branched alkylene and C_2-C_{30} mono- or poly-unsaturated bivalent hydrocarbon, each of these groups possibly containing one or more heteroatoms, and possibly being substituted with one or more phenyl groups (substituted or not), epoxy groups, cycloaliphatic or heterocyclic group, halogen atom(s), hydroxy and/or alkoxy,

phenylene, benzylenes, naphthylene, toluylene group, optionally substituted by -OH, -Cl, -alkoxy, -alkyl, -cycloalkyl, -COOR" or OCOR" (where R" is C_1-C_{12} alkyl);

* R^{11} and R^{12} also possibly be linked by a covalent bond when $R^{11} = -CH=CH-$ and $R^{12} = -CO-$ (ketonic function).

[0128] Preferred hydrazides are those for which at least one hydrazide is such as R^{11} is C^1-C^{17} alkyl group (e.g. methyl, butyl, octyl, ethyl-2-hexyl, stearyl, lauryl); -X-CO-NH-NH₂ where X is C_1-C_{17} alkyl (e.g. methyl, butyl, octyl, ethyl-2-hexyl, stearyl, lauryl), or 1,3-phenyl

group substituted or not; *ortho*-substituted phenol, benzenic cycle, isophthalic group, naphthol, cyclo-S-pentadiene-2,4, $C_6H_5-CH_2-$ and R^{12} is H, COR^{13} with R^{13} being preferably chosen from among C_1-C_{17} alkyl (e.g. methyl, butyl, octyl, ethyle-2-hexyle, stearyl, lauryl) and a benzenic ring).

5 **[0129]** Particularly preferred co-stabilisers and additives are chosen from among epoxydised soy bean oil, hydrotalcite, zeolite, dihydropyridine-based compounds as described hereinbefore, α -phenylindole, β -diketones, phosphates, polyols, THEIC (isocyanurate), metallic salts (especially Zn, Mg, or Ca stearate(s)), acetylacetonate (acac) salts such as $Ca(acac)_2$, perchlorate-based compounds (such as sodium or potassium
10 perchlorates), and the like, as well as mixtures thereof.

[0130] According to another embodiment of the present invention, preferred co-stabilisers are chosen from among dihydropyridine compounds. Particularly valuable compositions of the invention comprise dihydro-1,4-dimethyl-2,6-dicarbododecyloxy-3,5-pyridine (Stavinor® D507, Arkema, or "DHP") as co-stabiliser. Particularly advantageous mixtures of
15 co-stabiliser and additive may be for example mixtures of DHP with sodium perchlorate.

[0131] Therefore, according to another aspect, the present invention relates to a formulation comprising at least one composition of the invention as disclosed above, i.e. a composition mainly comprising at least one monoalkyltin-based compound as a major compound, and at least one dihydropyridine-based compound, preferably dihydro-1,4-
20 dimethyl-2,6-dicarbododecyloxy-3,5-pyridine, and optionally at least one perchlorate compound, preferably sodium perchlorate.

[0132] Still according to another embodiment of the present invention, preferred co-stabilisers are chosen from among metal soaps or metals salts of carboxylic acids. Particularly valuable compositions of the invention comprise disodium diadipate as co-
25 stabiliser.

[0133] Still other conventional additives may be added to the composition according to the invention, and to the optional co-stabiliser(s). This additive may be all and any additives used in the domain of application and the nature of which will be evident for the skilled artisan.

30 **[0134]** The present invention also relates to chlorine-containing polymers comprising at least one composition as defined above, and optionally at least one co-stabiliser, such as defined above, preferably a dihydropyridine-based compound, such as DHP, and/or one or more additive(s), such as previously described, preferably a perchlorate compound, such as sodium perchlorate.

35 **[0135]** Because of the high content of mono-alkyltin species, and the low content of the di-alkyltin species, and the very low (traces) of tri-alkyltin species within the compositions of the present invention, said compositions present a low to very low toxicity versus di- and/or

tri-alkyltin compound compositions. More particularly the compositions of the present invention are less toxic than (and even non toxic according to the regulations when compared to) the known and used compositions containing both mono- and di-alkyltin species, wherein the weight ratio of mono- to di-alkyltin species is less than 90/10.

5 **[0136]** According to another embodiment, the composition of the present invention may be used to stabilise chlorine-containing polymers as defined above (matrix), said chlorine-containing polymers being processed by any method known in the art, such as, for example, extrusion, calendaring, injection, injection-moulding, to prepare articles based on the said matrix.

10 **[0137]** According to a preferred embodiment, the amount of composition within the chlorine-containing polymers ranges from 0.2 to 5 phr and preferably 0.5 to 3 phr (the term "phr" means per hundred of resin). Still according to another preferred embodiment, the thermal stability may even be increased by adding a friction or shear rate controlling agent, a viscosity controlling agent, or mixtures thereof, and particularly a viscosity reducing agent
15 and/or a friction or shear rate decreasing agent. Friction or shear rate controlling, and particularly reducing, agents are well known in the art, as are the viscosity controlling, and particularly reducing agents. Friction or shear rate can also be decreased by processing conditions, according to known techniques of the art. Similarly viscosity can also be reduced by modifying the structure of the halogenated resin, for example when the
20 chlorine-containing polymers is a copolymer, again according to techniques well known in the art

[0138] The stabilised polymers in accordance with the invention can be prepared in a manner known *per se* using devices known *per se* such as the abovementioned processing apparatus to mix the stabilising composition of the invention and any further additives with
25 the polymers. In this case, the stabilisers can be added individually or as a mixture or else in the form of so-called master batches.

[0139] The stabilised polymers in accordance with the present invention can be brought into the desired form by known methods. Examples of such methods are milling, calendaring, extruding, injection moulding or spinning, and also extrusion blow moulding.
30 The stabilised polymers can also be processed to foam materials.

[0140] Stabilised polymers in accordance with the invention are suitable, for example, for the manufacture of hollow articles (bottles), packaging films (thermoform sheets), blown films, pipes, foam materials, heavy profiles (window frames), transparent-wall profiles, construction profiles, sidings, fittings, office films, and apparatus enclosures (computers,
35 domestic appliances). Preference is given to rigid or semi-rigid PVC films (opaque or transparent), PVC rigid foam articles and PVC pipes for drinking water or wastewater, pressure pipes, gas pipes, cable-duct and cable protection pipes, pipes for industrial

pipelines, seepage pipes, flow-off pipes, guttering pipes and drainage pipes. For further details on this subject see "Kunststoffhandbuch PVC", Vol. 2/2, W. Becker / H. Braun, 2nd ed., (1985), Carl Hanser Verlag, pages 1236-1277.

[0141] The present invention also relates to articles comprising at least one polymer matrix and at least one composition according to the present invention, and optionally one or more additive(s) and/or co-stabiliser(s), as hereinbefore described.

[0142] According to a preferred embodiment of the invention, the article is a rigid or semi-rigid, opaque or transparent film, especially those chosen from among rigid or semi-rigid, opaque or transparent films, shrink-films, adhesive films, sheets, fittings, profiles (window, in-door), edge-bands.

[0143] Preferably, the article is an opaque or transparent rigid or semi-rigid film, which may be advantageously used for thermoforming (or not) and preparing food-packaging, pharmaceutical blisters, plastic cards (such as credit cards), furniture films and technical packaging films, and generally all kinds of opaque and transparent films.

[0144] The present invention is now illustrated with the following examples, which do not aim at limiting the sought scope of protection, which is defined by the annexed claims.

Examples:

PART 1: Preparation of monoalkyltin compounds

Example 1:

Distillation of mono-octyltin trichloride from a thermal redistribution mixture of octyltin chlorides.

[0145] A mixture (928 g) consisting of mono-octyltin trichloride (59.0%), di-octyltin dichloride (39.5%), tin tetrachloride (1.2%) and tri-octyltin chloride (0.3%) that resulted from a thermal redistribution of tetra-octyltin and SnCl₄ (1:2 molar ratio), was fractionally distilled at 8 mbar. The distillate (520 g) collected at a vapour temperature of 145°C, consisted of mono-octyltin trichloride (99.3%), di-octyltin dichloride (0.5%) and tin tetrachloride (0.2%) according to GC analysis after ethylation with excess EtMgCl.

Example 2:

Mono-octyltin tris((2-ethylhexyl)mercaptoacetate)

[0146] 2-Ethylhexylmercaptoacetate (371 g; 1.82 mol) and water (102 g) were added under stirring to 200 g (0.589 mol) of mono-octyltin trichloride obtained from Example 1. Then 290 g (1.81 mol) of a 25% solution of sodium hydroxide (NaOH) in water was added in ca. 1.5 hours at a reaction temperature of 50°C.

[0147] After the reaction the pH of the water layer was adjusted to pH = 5-6 and the two phases were allowed to separate. The water layer was drained and volatiles were removed

by distillation (10 mbar) up to a pot temperature of 110°C. The product was filtered through 8 µm filter paper using Dicalcel as filter aid to afford 462 g (93%) of the final product.

[0148] GC analysis after ethylation with excess EtMgCl indicated that the purity of this product was > 99.5% with less than 0.5% di-octyltin bis(2-ethylhexylmercaptoacetate) being present. Tri-organotin species were not detectable (< 0.1%).

Example 3:

Re-distillation of mono-octyltin trichloride obtained from thermal redistribution

[0149] Re-distillation of mono-octyltin trichloride (at 8 mbar, 145°C) that had been obtained from the procedure described in Example 1, afforded mono-octyltin trichloride in 99.7 % purity (by GC analysis after ethylation with excess EtMgCl) with only a small quantity of di-octyltin dichloride (0.03 %).

Example 4:

Mono-octyltin tris((2-ethylhexylmercaptoacetate)

[0150] 2-Ethylhexylmercaptoacetate (744 g; 3.64 mol) and 204 g of water were added under stirring to 400 g (1.18 mol) of mono-octyltin trichloride from Example 3. Then 567 gram (3.54 mol) of a 25% solution of NaOH in water was added in ca. 2 hours at a reaction temperature of 50°C.

[0151] After the reaction the pH of the water layer was adjusted to pH = 5-6 and the two phases were allowed to separate. The water layer was drained and volatiles were removed by distillation (10 mbar) up to a pot temperature of 110°C. The product was filtered through 8 µm filter paper using Dicalcel as filter aid to afford 985 gram (98%) of the final product.

[0152] GC analysis after ethylation with excess EtMgCl, indicated that the purity of this product was 97.9 % with minor amounts of other species being present: tin tetrakis(2-ethyl hexyl mercaptoacetate) (0.26%), di-octyltin bis(2-ethylhexylmercaptoacetate) (< 0,1%), tri-octyltin (2-ethylhexylmercaptoacetate) (< 0,01%).

Example 5:

Mono-octyltin trichloride from 1-octene, HCl and SnCl₂.

[0153] A reaction vessel equipped with magnetic stirring, was brought under inert atmosphere and charged with 0.55 g of Pd(PPh₃)₄ (0.46 mmol). Next, 110 mL of a 0.80 M solution of anhydrous SnCl₂ in THF (88 mmol) were added, followed by 220 mL of 1-octene (1.40 mol). The vessel was placed in an oil bath and heated to 50°C. Subsequently, 332 mL of a 0.25 M HCl solution in THF (83 mmol) were added and the resulting pale yellow solution was stirred for 1.5 hours at 50°C.

[0154] Volatiles were removed in vacuum (80°C, 70 mbar) and hexane (100 mL) was added to the resulting suspension. Filtration followed by concentration in vacuum afforded 24.5 g of a yellow-orange liquid that, according to GC-analysis (after alkylation with excess EtMgCl), consisted of mono-octyltin trichloride (89.7%), di-octyltin dichloride (0.09%), tri-octyltin chloride (< 0,01%) and residual solvent.

Example 6:

Mono-octyltin tris((2-ethylhexylmercaptoacetate)

[0155] 2-ethylhexylmercaptoacetate (37.0 g; 0.181 mol) and 8.90 g of water were added under stirring to 20.64 g (0.058 mol) of mono-octyltin trichloride obtained from Example 5. Then 26.5 g (0.17 mol) of a 25% solution of NaOH in water was added in ca. 2 hours at a reaction temperature of 50°C.

[0156] After the reaction the pH of the water layer was adjusted to pH = 5-6 and the two phases were allowed to separate. The water layer was drained and volatiles were removed by distillation (9 mbar) up to a pot temperature of 110°C. The product was filtered through 8 µm filter paper using Dicacel as filter aid to afford 41.6 g of the final product.

[0157] GC analysis after ethylation with excess EtMgCl, indicated that this product consisted of mono-octyltin tris((2-ethylhexylmercaptoacetate) (95.4%) and di-octyltin bis(2-ethylhexylmercaptoacetate) (< 0,1%). Residual solvent as measured by measuring the weight loss on drying at 50°C (3.0%) and residual 2-ethylhexylmercaptoacetate (not quantified) accounted for the remaining weight of the sample. A sample of this compound was tested for PVC stabilisation.

PART 2: Application examples

[0158] In the following examples, the term "phr" means per hundred of poly(vinyl chloride) (PVC) resin (e.g.: 0.2 phr means 0.2 g per 100 g of PVC). All parts are given by weight.

Example A

Comparative study of monoalkyltin- vs. dialkyltin compounds on long term colorhold retention in PVC transparent rigid films

[0159] A PVC formulation typical for transparent rigid film (amounts of each component in phr are given below) is evaluated using a Collin two-roll mill, the rolls of which are heated to 200°C. The rotational speeds of the two cylinders are respectively adjusted to 20 rpm and 24 rpm, providing sufficient friction to gelate PVC and sufficient heat to thoroughly study the thermal stabilisation efficiency of stabilisers. The gap between the cylinders is adjusted to 0.5 mm. Samples are withdrawn from the cylinders at regular time intervals, their coloration being recorded.

[0160] The components of the various PVC formulations and their amounts are the following:

- PVC (Lacovyl RB8010, Arkema, kW = 57) : 100
- Epoxydised soybean oil (Ecepo PB3, Arkema) 1
- 5 • Hydrogenated castor oil (Loxiol G15, Henkel) 0.6
- Oxidized PE wax (A-C 316A, Honeywell) 0.12
- Process aid (Plastistrength 551, Arkema) 0.6
- Antisticking process aid (Plastistrength 770, Arkema) 1
- MBS impact modifier (Clearstrength 320, Arkema) 8
- 10 • Stabiliser (cf. list below) 1.3

[0161] The various stabilisers are the following:

- Stab 1 = Composition of Example 6 comprising high purity mono-octyltin-(2-ethylhexylmercaptoacetate);
- Stab 2 = 30% mono octyl tin (2-ethylhexylmercaptoacetate) and 70% di-octyltin-(2-ethylhexylmercaptoacetate);
- 15 • Stab 3 = 60% mono octyl tin (2-ethylhexylmercaptoacetate) and 40% di-octyltin-(2-ethylhexylmercaptoacetate).

[0162] The b^* value in Hunter $L^*a^*b^*$ scale (b^* , ASTM Standard E 313) is measured on each sample withdrawn and the results are reported in Table 1 below:

20

-- Table 1 --

<i>t (min.)</i>	<i>Stab 1 (according to the invention)</i>	<i>Stab 2 (comparative)</i>
2	7.1	7
3	7.8	7.8
4	8.4	9.2
5	9.4	10.5
6	9.9	13.3
7	10.1	14.6
8	12.1	16.9
9	13.0	18.0
10	15.7	21.1
12	22.2	26.5
15	43.6	53.7

[0163] The results listed in Table 1 above show the efficiency of the stabiliser containing a high content of mono-alkyltin compound, i.e. high purity mono-alkyltin compound as described in the present invention, not only on the initial colour of the PVC formulation but

also on the long term colorhold retention compared to formulations containing both mono- and di-alkyltin compounds.

Example B

5 **Comparative study of mono-alkyltin vs. di-alkyltin compounds on long term colorhold retention in PVC used in film calendaring production**

[0164] A PVC formulation containing a copolymer widely used in film calendaring production (amounts of each component in phr are given below) is evaluated using a Collin two-roll mill, the rolls of which are brought to 190°C. The rotational speeds of the two
10 cylinders are respectively adjusted to 20 rpm and 24 rpm, providing sufficient friction to gelate PVC and sufficient heat to thoroughly study the thermal stabilisation efficiency of stabilisers. The gap between the cylinders is adjusted to 0.5 mm. Samples are withdrawn from the cylinders at regular time intervals, their coloration being recorded.

[0165] The components of the PVC formulation and their amounts are the following:

- | | | |
|----|--|------------|
| 15 | • PVC (Lacovyl SO71, Arkema, kW = 57): | 60 |
| | • Copolymer vinyl chloride – vinyl acetate
(Lacovyl GA 7701H, Arkema KW = 57) | 40 |
| | • Epoxysided soybean oil (Ecepoxy PB3, Arkema) | 1 |
| | • Glycerol mono-oleate (Loxiol G10, Henkel) | 0.7 |
| 20 | • Pentaerythritol adipate stearate (Loxiol G70S, Henkel) | 0.4 |
| | • Process aid (Plastistrength 550, Arkema) | 1 |
| | • Antisticking process aid (Plastistrength 770, Arkema) | 0.7 |
| | • MBS impact modifier (Clearstrength 303H, Arkema) | 8 |
| | • Stabiliser (see list below) | 1.5 or 1.7 |

25 **[0166]** The same stabilisers Stab 1, Stab 2 and Stab 3 as defined above are tested. Stab 2 and 3 are used at 1.5 phr and Stab 1 at 1.7 phr to compare formulations at equal tin content.

[0167] The b* value in Hunter L*a*b* scale (b*, ASTM Standard E 313) is measured on each sample withdrawn and the results are reported in Table 2 below:

30

-- Table 2 --

<i>t (min.)</i>	<i>Stab 1 (according to the invention)</i>	<i>Stab 2 (comparative)</i>	<i>Stab 3 (comparative)</i>
2	7.5	8	7.7
3	8.1	9.4	9.1
4	8.8	11	10
5	8.6	12	11
6	9.3	13	11
7	8.9	14	11
8	10	14	12
9	10	15	12
10	11	17	14
12	13	20	16
15	17	41	30
20	40	65	61

[0168] As in previous Example A above, the results listed in Table 2 show the efficiency of the stabiliser containing mono-alkyltin compound of high purity as described in the present invention not only on the initial colour of the PVC formulation but also on the long term colorhold retention compared to formulations with a much higher di-alkyltin compound content, i.e. mixtures of mono- and di-alkyltin compounds as known in the art.

Example C

Comparative study on long term colorhold retention of thin- and thick- PVC films used in film calendaring production, each containing mono-alkyltin- and/or di-alkyltin compounds

[0169] Each PVC formulation used in example B containing a copolymer widely used in film calendaring production is milled during 5 minutes at 180°C (Collin two-roll mill with rolls brought to 180°C, rotational speeds of the two cylinders are respectively adjusted to 20 rpm and 24 rpm) to obtain a thin film of 0.5 mm thickness.

[0170] Measurement of colour is made, as well as on a thicker film obtained from the thin film pressed under a plate press at a temperature of 190°C, during 5 minutes. This thicker film is 4 mm thick and colour (b*) is recorded as described above.

[0171] The results are reported in Table 3 below:

-- Table 3 --

B* value	<i>Stab 1 (according to the invention)</i>	<i>Stab 2 (comparative)</i>	<i>Stab 3 (comparative)</i>
Thin film (0.5 mm)	7.8	9.6	8.3
Thick film (4 mm)	35	51	47

- 5 **[0172]** Early colour provided by very high purity mono octyl tin stabiliser is excellent compared to current technology also in thick films.

Example D

Comparative Haze study of thin- and thick- PVC films used in film calendering production,

- 10 each containing monoalkyltin- or dialkyltin compounds

[0173] The PVC formulation used in Example A widely used in film calendering production is milled during 5 minutes at 180°C (Collin two-roll mill with rolls heated to 180°C, rotational speeds of the two cylinders respectively adjusted to 20 rpm and 24 rpm) to obtain a thin film of 0.5 mm thickness.

- 15 **[0174]** Measurement of optical properties such as haze in a PVC sample is made, on both thin and thicker film obtained from the thin film pressed under a plate press at a temperature of 190°C, during 5 minutes. This thicker film is 4 mm thick and haze is recorded.

- [0175]** The haze value is measured on a Hazemeter according to ASTM D1003 on each
20 sample and the results are reported in Table 4 below:

-- Table 4 --

Haze value (%)	<i>Stab 1 (according to the invention)</i>	<i>Stab 2 (comparative)</i>
Thin film (0.5 mm)	0.76	0.74
Thick film (4 mm)	7.9	10

[0176] Very high purity mono-alkyltin stabiliser is able to decrease the haze and then gives to the finished film an excellent level of transparency.

Example E

Comparative colour study of PVC films containing a monoalkyltin-compound and an organic co-stabiliser

[0177] The advantageous use of a co-stabiliser together with a high purity mono-alkyltin stabiliser is illustrated: the formulation described below is evaluated using a Collin two-roll mill, the rolls of which are heated to 190°C. The rotational speeds of the two cylinders are respectively adjusted to 20 rpm and 24 rpm, providing sufficient friction to gelate PVC and sufficient heat to thoroughly study the thermal stabilisation efficiency of stabilisers.

[0178] The gap between the cylinders is adjusted to 0.5 mm. Samples are withdrawn from the cylinders at regular time intervals, their coloration being recorded.

[0179] The tested formulations are the following:

- PVC (Lacovyl RB8010, Arkema, kW = 57) 100
- Epoxysided soybean oil (Ecepoxy PB3, Arkema) 1
- Hydrogenated castor oil (Loxiol G15, Henkel) 0.6
- Oxidized PE wax (A-C 316A, Honeywell) 0.12
- Process aid (Plastistrength 551, Arkema) 0.6
- Antisticking process aid (Plastistrength 770, Arkema) 1
- MBS impact modifier (Clearstrength 320, Arkema) 8
- Stab 1 1.3
- Dihydro-1,4-dimethyl-2,6 dicarbododecyloxy-3,5-pyridine
(‘DHP’; CAS 36265-41-5; Stavisor® D507, Arkema) 0 to 0.2

[0180] The b^* value in Hunter $L^*a^*b^*$ scale (b^* , ASTM Standard E 313) is measured on each sample withdrawn and the results are reported in Table 5 below:

-- Table 5 --

<i>T (min.)</i>	<i>Stab 1</i>	<i>Stab 1 + 0.05 phr DHP</i>	<i>Stab 1 + 0.1 phr DHP</i>
2	7.4	7.1	7.1
4	8.3	7.8	7.8
6	9.1	8.4	7.9
8	10	9.1	8.2
10	11	10.1	9.1
12	12.9	12	10.6
14	14.7	13.7	11.7
16	17.3	16.5	14.1
18	20.3	23.8	17.5
20	26.9	28	17.6

[0181] It is well known that dihydropyridine-based compounds alone, such as DHP alone, give poor results in this test. However, when combined with a highly pure mono-alkyltin stabiliser according to the invention, the co-stabilising effect is drastically improved in terms of initial colour and colour hold during a dynamic thermal stability test.

5 **[0182]** This is the evidence of a synergistic effect resulting from the use of dihydropyridine-based compounds together with high purity mono-alkyltin compounds.

[0183] A good effect of initial colour may also be evidenced by preparing first a film on two roll mill (190°C, 5 minutes) and then pressing several sheets until a thickness of 4 mm (plate press at 190°C during 10 minutes with pressure: 30 bars, during 60 sec., 200 bars
10 during 40 sec., 300 bars during 180 sec.). Yellow index (YI) and L* value in Hunter L*a*b* scale (b*, ASTM Standard E 313) is given in table 6 below:

-- Table 6 --

	<i>Stab 1</i>	<i>Stab 1 + 0.05 phr DHP</i>	<i>Stab 1 + 0.1 phr DHP</i>	<i>Stab 1 + 0.2 phr DHP</i>
YI	35.5	27.7	25.5	24
L*	79.3	81.3	82.1	81.6

[0184] Yellow index decreases with adding a dihydropyridine-based compound with the
15 composition of the invention (highly pure mono-alkyltin compound) and L* value increases attesting a higher whiteness.

Example F

Comparative colour study of PVC films containing a monoalkyltin-compound and another
20 organic co-stabiliser based on disodium adipate

[0185] The advantageous use of another co-stabiliser together with a high purity mono-alkyltin stabiliser is illustrated: the formulation described below is evaluated using a Collin two-roll mill, the rolls of which are heated to 195°C. The rotational speeds of the two cylinders are respectively adjusted to 20 rpm and 24 rpm, providing sufficient friction to
25 gelate PVC and sufficient heat to thoroughly study the thermal stabilisation efficiency of stabilisers.

[0186] The gap between the cylinders is adjusted to 0.5 mm. Samples are withdrawn from the cylinders at regular time intervals, their coloration being recorded.

[0187] The tested formulations are the following:

- | | | |
|----|---|------|
| 30 | • PVC (Lacovyl SO71, Arkema, kW = 57) | 100 |
| | • Epoxysed soybean oil (Ecepoxy PB3, Arkema) | 1 |
| | • Oxidized PE wax (A-C 316A, Honeywell) | 0.12 |
| | • Process aid (Plastistrength 551, Arkema) | 1.2 |
| | • Antisticking process aid (Plastistrength 770, Arkema) | 1 |

- MBS impact modifier (Clearstrength 303H, Arkema) 8
- Glycerol monostearate (Loxiol G12, Henkel) 1.2
- Adipate stearate pentaerythritol (Loxiol G70S, Henkel) 1.2
- Stab 1 1.1 to 1.4
- 5 • Disodium adipate ('DSA', Reapak NAD) 0 to 0.4

[0188] The b^* value in Hunter $L^*a^*b^*$ scale (b^* , ASTM Standard E 313) is measured on each sample withdrawn and the results are reported in Table 7 below:

-- Table 7 --

<i>T (min.)</i>	<i>Stab 1 1.1 phr</i>	<i>Stab 1 1.4 phr</i>	<i>Stab 1 1.1phr + DSA 0.4 phr</i>
2	13.5	13.2	15.2
4	14.5	14.0	15.2
6	16.2	14.8	18.8
8	18.9	16.1	21.6
10	24.2	18.4	24.2
12	34.3	22.2	28
14	49.1	26.5	31.6
16	70.9	35.6	37.1
18	88.5	49.4	43.7
20	101	68.3	50.5
22	107	82.4	51.7
24		96.6	57.9

- 10 **[0189]** Disodium adipate when combined with a highly pure mono-alkyltin stabiliser according to the invention improves the co-stabilising effect especially in terms of colour hold during a dynamic thermal stability test.

[0190] This is the evidence of a synergistic effect resulting from the use of disodium adipate together with high purity mono-alkyltin compounds.

15

PART 3: Reproduction/Developmental Toxicity Study(according to OECD 421 guideline)

Example AA: 14-day oral (diet) dose-range toxicity study (preliminary study for the reproduction/developmental study)

[0191] The aim of this study is to select appropriate dose-levels for the main study.

- 20 **[0192]** Materials and methods:

- Groups: one control group and four test groups (4 males and 4 female per group) administered with different dose levels of the test substance;
- Housing: 2 rats/sex/cage, macrolon cages;

- Species: rat, Wistar outbred, Charles River Wiga GmbH, 9-10 weeks of age at start;
- Carrier: Commercial rodent diet (Rat & Mouse No. 3 Breeding diet, RM3), *ad libitum*;
- 5 • Treatment: Administration via the diet during 14 consecutive days; one batch of test diets is prepared shortly before initiation of treatment and stored in a freezer/refrigerator; the feed in the animal feeders is refreshed twice per week;
- Clinical observations: general observations (all rats): daily; morbidity is checked again in the afternoon;
- 10 • Body weight: at least once pretest, twice per week from the start of treatment (for the last time, on the day of scheduled necropsy);
- Food consumption: twice weekly per cage (2 rats/cage) from the start of treatment;
- Water consumption: visual inspection of the drinking bottles;
- Pathology: - macroscopic examination (all rats);
- 15 - weighing the following organs of all the surviving rats: kidneys, liver, spleen, testes, thymus;
- preservation: the weighed organs are preserved in formalin and discarded when the results of the subsequent 90-day study indicate non need for microscopy on tissues from the 14-day study;
- 20 **[0193]** On each day of analysis, calibration solutions are prepared by spiking rodent diet with a stock solution of the organotin compound followed by derivatisation with sodium tetraethyl borate, in order to derivatise the octyltin compounds to the corresponding octyltin-ethyl compounds, with simultaneous extraction of the derivatised compounds into hexane.
- 25 **[0194]** The concentration of the test substance in diet is then determined by GC-MS of the hexane extracts.

Example AB

Reproduction/Developmental toxicity screening test (according to OECD 421 guideline)

- 30 **[0195]** The objective of this study is to assess whether octyltin tris (2-ethylhexylmercaptoacetate) causes adverse effects on reproduction and/or development of wistar rats. This study was preceded by a dose-range finding study (see Example AA).
- [0196]** Materials and methods:
- Groups: one control group and three test groups (12 males and 12 female per group) administered with different dose levels of the test substance;
- 35

- Housing: Pre-mating (PM): 4 rats/sex/cage, macrolon cages;
Mating (M): 1 male and 1 female per cage;
Gestation (G) and lactation: 1 rat/sex/cage, macrolon cages;
- Species: rat, Wistar outbred, Charles River Wiga GmbH, 9-10 weeks of age at start;
- Carrier: Commercial rodent diet (Rat & Mouse No. 3 Breeding diet, RM3), *ad libitum*;
- Treatment: Administration via the diet during 14 consecutive days premating; during 14 consecutive days mating, gestation and lactation up to 4 days (males are given the test substance in the diet until sacrifice at the end of the mating period);
one or two batches of test diets are prepared shortly before initiation of treatment and stored in a freezer/refrigerator; the feed in the animal feeders is refreshed once per week;
- Clinical observations: general clinical observations (all rats): daily; morbidity is checked again in the afternoon;
- Body weight: at least once pretest, males and females, premating and mating weekly;
- Food consumption: males and females, premating and mating weekly; for female during gestation: GD 0, 7, 14 and 21 during lactation; PN 1 and 4;
- Pups: sex, body, weight, number of live and dead pups, clinical signs PN 1 and 4;
- Water consumption: visual inspection of the drinking bottles;
- Pathology: - macroscopic examination (all rats);
- count: number of implantations (uterus) and *corpora lutea* (ovaria);
weighing the following organs of all the surviving rats: testes (males), epididymes (females), thymus;
- preservation all animals): testes, epididymes, seminal vesicles, prostate, ovaries, uterus, thymus and organs and tissues showing macroscopic abnormalities; the organs are preserved in formalin and discarded when the results of the OECD 421 study indicate non need for microscopy;
- Histopathology: preserved tissues for control and high level only (low and mid dose groups only).

[0197] On each day of analysis, calibration solutions are prepared by spiking rodent diet with a stock solution of the organotin compound followed by derivatisation with sodium tetraethyl borate, in order to derivatise the octyltin compounds to the corresponding octyltin-ethyl compounds, with simultaneous extraction of the derivatised compounds into hexane.

[0198] The concentration of the test substance in diet is then determined by GC-MS of the hexane extracts.

Results of the toxicity tests of Examples AA and AB

5 **[0199]** In the preliminary study (example AA), no clinical abnormalities were observed as well as no change in body weight and food consumption. Furthermore no abnormalities were observed at necropsy and no effects were observed on organ weights. In the main reproduction and developmental toxicity screening study in rats (example AB), the oral administration of octyltin tris (2-ethylexylmercaptoacetate) at 200, 500 and 1250 mg/kg diet
10 was well tolerated at all dose-levels. No effects were observed on reproduction organs or on pre- and post-natal development. The no adverse effect level (NOAEL) for parental toxicity, fertility and development is 1250 mg/kg diet (aproximatly 72 and 96 mg octyltin tris (2-ethylexylmercaptoacetate)/kg body weight/day for male and female animals respectively.

[0200] The results of these new studies with high purity monooctyltin compound as
15 defined above in Examples AA and AB indicate that the composition of the present invention that contains a high amount of mono-alkyltin compounds has no target organ effects and particularly no effects on fertility and reproduction. These results on the pure monooctyltin are different for the available published results performed on mixture on mono- and dialkyltin compounds, which have shown severe effects on fertility and
20 reproduction. Mono-alkyltin compounds of high purity are much less toxic than compositions comprising less pure mono-alkyltin compounds, and particularly the known compositions containing both mono- and di-alkyltin compounds in almost or substantially almost comparable content.

25

CLAIMS

1. Composition comprising:
- 5 • from 85 wt% to 99.999 wt%, preferably from 90 wt% to 99.999 wt%, more preferably from 95 wt% to 99.99 wt%, still more preferably from 97 wt% to 99.99 wt% (limits included) of at least one monoalkyltin compound of formula RSn(T)_3 , in which R is linear, branched or cyclic $\text{C}_1\text{-C}_{20}$ alkyl, preferably $\text{C}_1\text{-C}_{10}$ alkyl, and T is a ligand;
 - from 0.001 wt% to 10 wt%, preferably from 0.001 wt% to 1 wt%, more preferably from
10 0.01 wt% to 0.5 wt%, most preferably from 0.01 wt% to 0.1 wt%, of at least one dialkyltin compound of formula $\text{R}_2\text{Sn(T)}_2$, in which R and T are as defined above;
 - from 0.001 wt% to 5 wt%, preferably from 0.005 wt% to 1 wt%, more preferably from 0.01 wt% to 0.5 wt%, most preferably from 0.01 wt% to 0.1 wt%, of at least one trialkyltin compound of formula $\text{R}_3\text{Sn(T)}$, in which R and T are as defined above; and
 - 15 • from 0 wt% to 5 wt%, more preferably from 0 wt% to 1 wt%, still more preferably from 0 wt% to 0.2 wt% of one or more impurities.
2. Composition according to claim 1, wherein the weight ratio of (mono-alkyltin compound)/(di-alkyltin compound) is not less than 90/10, preferably not less than 95/5,
20 most preferably not less than 97/3.
3. Composition according to claim 1 or claim 2, wherein the weight ratio of (mono-alkyltin compound)/(di-alkyltin compound) is not less than 99/1, preferably not less than 99.5/0.5, most preferably not less than 99.7/0.3.
- 25 4. Composition according to any of claims 1 to 3, wherein R is chosen from among methyl, ethyl, *n*-propyl, *iso*-propyl, *n*-butyl, *iso*-butyl, *n*-pentyl, *n*-hexyl, *n*-heptyl, *n*-octyl, 2-ethylhexyl, *iso*-octyl, and decyl, preferably R is methyl, *n*-butyl, 2-ethylhexyl, *n*-octyl, or *n*-decyl.
- 30 5. Composition according to any of claims 1 to 4, wherein T is chosen from among thioglycolate esters, 2-ethylhexylthioglycolate esters, *iso*-octylthioglycolates, *iso*-butylthioglycolates, thioglycolate itself, hydroxyl, carboxylates, maleates, diketonates and alcoholates, preferably T is 2-ethylhexylmercaptoacetate.
- 35 6. Composition according to any of claims 1 to 5, wherein RSn(T)_3 is $\text{RSn[tris(2-ethylhexylmercaptoacetate)]}$, preferably RSn(T)_3 is chosen from among

monomethyltin[tris(2-ethylhexylmercaptoacetate)], mono-*n*-butyltin[tris(2-ethylhexylmercaptoacetate)], mono-*n*-octyl[tris(2-ethylhexylmercaptoacetate)], and mixtures thereof.

7. Process of preparation of a composition according to any of claims 1 to 6, comprising:

- α) hydrostannylation of a 1-alkene to the corresponding mono-alkyltin trihalide $\text{RSn}(\text{Hal})_3$ in the presence of a transition metal catalyst, tin(II) dihalide and hydrogen halide; and
- β) converting the mono-alkyltin trihalide $\text{RSn}(\text{Hal})_3$ to $\text{RSn}(\text{T})_3$ by contacting the mono-alkyltin trihalide $\text{RSn}(\text{Hal})_3$ with a compound of formula H-T in the presence of a suitable base or, alternatively, by reacting $\text{RSn}(\text{Hal})_3$ to alkylstannoic acid $\text{RSn}(\text{O})\text{OH}$ using a hydroxide base followed by contacting the alkylstannoic acid with a compound of formula H-T under elimination of water, wherein R and T are as defined in any of claims 1 to 6.

8. Process of preparation of a composition according to any of claims 1 to 6, comprising the steps of:

- a) preparing a solution of stannous halide SnHal_2 in a solvent, together with a transition metal-based catalyst;
- b) reacting the obtained solution with a molar excess (1.5 to 2 molar equivalent relative to the stannous halide) of the corresponding alkene or cycloalkene precursor of the R radical, at a temperature ranging between room temperature to 200°C , in the presence of hydrogen halide (H-Hal) and optionally metallic tin (Sn);
- c) optionally removing the solvent of the reaction medium, for example stripping or vacuum-distillation of the solvent;
- d) optionally filtering the crude reaction medium;
- e) adding a 2- to 5-fold molar excess (relative to the obtained monoalkyltin trihalide) of H-T, and water, under stirring;
- f) neutralising the reaction medium, for example with alkali or alkaline-earth hydroxide, e.g. sodium hydroxide;
- g) separating the water layer from the organic layer; and
- h) removing the solvent from the organic layer, and optionally filtering to recover $\text{RSn}(\text{T})_3$ of high purity,

wherein R and T are as defined in any of claims 1 to 6.

9. Process according to claim 7 or claim 8, wherein stannous halide is SnCl_2 and hydrogen halide is HCl.

10. Process according to any of claims 7 to 9, wherein R is chosen from among methyl, *n*-butyl, *iso*-octyl and *n*-octyl.
- 5 11. Process according to any of claims 7 to 10, wherein T is 2-ethylhexyl mercaptoacetate or T is OH.
12. Use of a composition according to any of claims 1 to 6, as stabiliser for chlorine-containing polymers, glass coating chemical or as catalyst.
- 10 13. Use according to claim 12, wherein the chlorine-containing polymer is chosen from among polymers or mixtures of polymers chosen from among homopolymer vinyl halides such as polyvinyl chloride, polyvinylidene chloride, chlorinated polyvinyl chloride, post-chlorinated polyvinyl chloride and copolymers formed by the polymerisation of a vinyl halide
15 monomer with up to 40% of a comonomer such as vinyl acetate, vinyl butyrate, vinylidene chloride, propylene, methylmethacrylate and the like, as well as chlorine-containing polymers containing other polymers such as chlorinated polyethylene, terpolymers of acrylonitrile, butadiene, styrene, terpolymers of methylmethacrylate, butadiene, styrene; polyacrylate resins, polymethylmethacrylate resins and terpolymer of alkyl acrylate,
20 methylmethacrylate, butadiene, preferably the chlorine-containing polymer is polyvinyl chloride or post-chlorinated polyvinyl chloride.
14. Use according to any of claim 12 or 13, wherein the content of the composition according to any of claims 1 to 6 within the chlorine-containing polymers (resin) is
25 comprised between about 0.01 parts by weight and 10 parts by weight, preferably between about 0.1 and 7, more preferably from about 0.1 to about 5 and still more preferably between 0.4 and 2.5, parts by weight for 100 parts by weight of polymer(s).
15. Formulation comprising at least one composition according to any of claims 1 to 6
30 together with at least one co-stabiliser and/or at least one additive.
16. Formulation according to claim 15, wherein the co-stabiliser is chosen from among epoxydised soy bean oil, dihydropyridine-based compounds, α -phenylindole, polyols, disaccharide alcohols, perchlorate-based compounds, glycidyl compounds, layered lattice
35 compounds (hydrotalcite), zeolite compounds, phosphite compounds, β -diketones, β -ketoesters, mercaptocarboxylic esters, metal soaps, amino- and/or thiouracils, hydrazides, and the like and mixtures thereof.

17. Formulation according to claim 15 or claim 16, comprising at least one composition according to any of claims 1 to 6, and at least one dihydropyridine-based compound, preferably dihydro-1,4-dimethyl-2,6-dicarbododecyloxy-3,5-pyridine, and optionally at least one perchlorate compound, preferably sodium perchlorate.
18. Formulation according to any of claims 15 to 17, wherein the additive is chosen from among stabilisers, auxiliaries and processing aids, lubricants, plasticizers, pigments, fillers, epoxidized fatty acid esters, antioxidants, UV absorbers and light stabilisers, optical brighteners, impact modifiers and processing aids, gelling agents, antistats, biocides, metal passivators, flame retardants, blowing agents, antifog agents, compatibilisers and anti plate-out agents, and the like, as well as mixtures thereof.
19. Chlorine-containing polymer comprising at least one composition according to any of claims 1 to 6, optionally together with at least one co-stabiliser, and/or one or more additive(s).
20. Article comprising at least one polymer matrix and at least one composition according to any of claims 1 to 6, and optionally one or more additive(s) and/or co-stabiliser(s).
21. Article according to claim 20, wherein the matrix is a chlorine-containing polymer, preferably the matrix is PVC polymer or copolymer.
22. Article according to any of claims 20 or 21, which is a hollow article, a packaging film, a blown film, a pipe, a foamed material, a heavy profile, a transparent-wall profile, a construction profile, a siding, a fitting, an office film, an apparatus enclosure, preferably a rigid or semi-rigid opaque or transparent PVC film, a PVC rigid foamed article, or a PVC pipe for drinking water or wastewater, a pressure pipe, a gas pipe, a cable-duct and a cable protection pipe, a pipe for industrial pipelines, a seepage pipe, a flow off pipe, a guttering pipe or a drainage pipe, more preferably, the article is a rigid or semi-rigid, opaque or transparent film, especially those chosen from among rigid or semi-rigid, opaque or transparent films, shrink-films, adhesive films, sheets, fittings, profiles (window, in-door), edge-bands.

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2009/055868

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07F7/22 C08K5/58

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C07F C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	NL 7 811 090 A (HAAGEN CHEMIE B. V., NETH.) 12 May 1980 (1980-05-12) Tinstab A to D. page 6 - page 10; claims 1-5; table A	1-6, 12-22
Y	BATT, JOHN, M.: "The organotin industry rises to the HPV challenge" APPLIED ORGANOMETALLIC CHEMISTRY, vol. 19, no. 4, 2005, pages 458-464, XP002488410 page 462; table 2	1-6, 12-22
X	ANONYMOUS: "Strem Chemicals for Research Metals, Inorganics and Organometallics: Tin(Compounds)" STREM CATALOG, no. 20, 2004, - 2006 pages 288-295, XP002488411 the whole document	1
-/-		

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2009/055868

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	FR 1 320 473 A (KONINK IND MIJ VOORHEEN NOURY) 8 March 1963 (1963-03-08) example 22	1-6, 12-22
Y	DATABASE CA [Online] CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; "Sulfur-containing organotin compounds" XP002488412 retrieved from STN Database accession no. 1983:160948 abstract & JP 57 188598 A (TOKYO FINE CHEMICAL CO., LTD., JAPAN) 19 November 1982 (1982-11-19)	1-6, 12-22
Y	EP 1 743 898 A (ARKEMA VLISSINGEN B V [NL]) 17 January 2007 (2007-01-17) cited in the application paragraph [0015] - paragraph [0027]	7,9-11
Y	DE 10 2004 037369 A1 (ARTEMIS RES GMBH & CO KG [DE]) 23 March 2006 (2006-03-23) paragraph [0104]; claims 13-15	17
Y	claims 32-35	21,22
Y	EP 1 389 620 A (CROMPTON GMBH [DE]) 18 February 2004 (2004-02-18) claims 2,12; examples 1-8	1-6, 12-22
Y	paragraph [0031] - paragraph [0032]; claim 11	7,9-11
Y	DE 11 2005 001194 T5 (BAERLOCHER ITALIA S P A [IT]) 12 April 2007 (2007-04-12) examples 2-15	1
Y	DE 26 39 086 A1 (CINCINNATI MILACRON CHEM) 31 March 1977 (1977-03-31) examples 4,6,8,12,14,15,27,28	1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP2009/055868

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers allsearchable claims.
2. ☒ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-7, 12-22 partially 9-11

Composition, preparation of the composition, use and final products

2. claims: 8, partially 9-11

Alternative preparation for the composition according to claim 1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2009/055868

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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61/077,024 30 June 2008 (30.06.2008) US(71) Applicants (for all designated States except US): **INTERUNIVERSITAIR MICROELEKTRONICA CENTRUM** [BE/BE]; Kapeldreef 75, B-3001 Leuven (BE). **UNIVERSITEIT HASSELT** [/BE]; Campus Diepenbeek, Agoralaan Geb. D, B-3590 Diepenbeek (BE).

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Declarations under Rule 4.17:

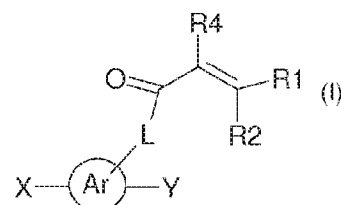
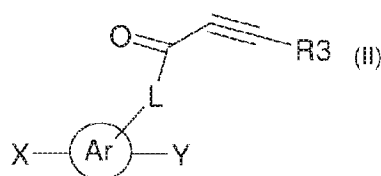
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(54) Title: POLYMERISABLE COMPOUNDS FOR MAKING OPTO-ELECTRONIC DEVICES

(57) Abstract: This invention provides monomeric compounds represented by the structural formula (I) or the structural formula (II) which can be polymerized into crosslinkable polymers useful for producing opto-electronic devices.



WO 2010/000504 A1

POLYMERISABLE COMPOUNDS FOR MAKING OPTO-ELECTRONIC DEVICES

Field of the invention

The present invention relates to aromatic polymerisable compounds, as well as conjugated polymers made therefrom having either p-type or n-type properties, blends of such polymers with n-type or p-type compounds respectively, and opto-electronic devices made by cross-linking such blends preferably in the absence of a photoinitiator. The present invention also relates to methods for producing and polymerising such aromatic polymerisable compounds, and methods for crosslinking blends of such polymers and n-type or p-type compounds.

Background of the invention

Photosensitive polymers with photo-crosslinkable groups have gained a considerable interest in recent years owing to a wide variety of applications in the field of photoresist, photocurable coatings, microlithography, etc.

Also in the field of organic semi-conducting materials, the interest in crosslinkable materials is increasing, notably for electroluminescent devices and the application of the active layer in a direct structured manner, avoiding then the use of shadow masks.

An approach has been proposed in U.S. Pat. 2007/0290194 in which a crosslinking process using oxetane-functionalized organic semiconductors and conductors is proposed. In this procedure the crosslinking reaction is initiated by UV irradiation in the presence of at least one added onium compound as photoinitiator.

Another approach has been proposed in WO 2008/001051A2 wherein the active layer of the organic based device (mainly OLED, PLED, organic capacities touch sensor and bi-layer photovoltaics) is a semi-conducting polymer made from a polymerisable ink formulation comprising a liquid formed from a UV reactive resin monomer (monomer), a UV reactive thinner (oligomer) and a photoinitiator: the ink is configured for polymerization by UV exposure into a (semi-conducting) polymer film.

However the disadvantage of an admixed electronically active compound such as a photoinitiator is that it cannot be removed from the film after crosslinking and therefore can act as an impurity, adversely affecting the film composition, the film morphology and then affecting the functioning of the organic device. This is even more true for organic devices such as organic bulk hetero-junction solar cells in which the nano-morphology of the active layer is very sensitive to any parameter change (during the fabrication process but also during time after fabrication) and then to the power efficiency of the cell.

Other methods towards crosslinkable semi-conducting polymers, mainly polythiophenes, have been reported in which no photoinitiator is used, but they show many drawbacks:

- G. Zotti in *Synthetic Metals* (1999) 105:135 has polymerized by electrochemistry an acrylated monomer giving a totally insoluble polymer;
- B. de Ruiter in *Synthetic Metals*, (1996) 79:215-218 has polymerized by oxidative polymerization an acrylated monomer but this method shows interference between the acrylate chemistry and the radical chain process leading to a very difficult control of the polymer fabrication (e.g. linear polymer chain are difficult to reach, with high polydispersity values even for very short reaction times).
- Zhu et al. in *Journal of Macromolecular Science* (2004) 41:1467-1487 reports the synthesis of epoxy-functionalized polythiophene derivatives. A slow degradation of cells made from poly(3-hexylthiophene) and a fullerene derivative of butyric acid methyl ester was observed due to a change of phase morphology.

Summary of the invention

It is an object of the present invention to provide new crosslinkable semi-conductive materials suitable for use in opto-electronic devices as well as opto-electronic devices comprising such materials.

It is an advantage of some embodiments of the present invention that crosslinkable semi-conducting materials can be produced that permit to stabilise in time the nano-morphology of an active layer comprising said

crosslinkable semi-conducting materials. For instance, an active layer in organic bulk heterojunction solar cells comprising a semi-conducting material according to an embodiment of the present invention can have its nano-morphology stabilised upon cross-linking of said material.

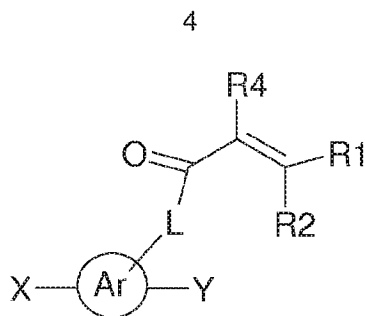
5 It is another advantage of some embodiments of the present invention that the stabilisation of the morphology is accompanied by a stabilisation of the performances of the device, such as for instance the stabilisation of the power efficiency and/or the short circuit current of a bulk heterojunction solar cell.

10 It is another advantage of some embodiments of the present invention that the stabilisation of the morphology is accompanied by an increase in the lifetime to predetermined performance levels of the devices, in particular solar cells.

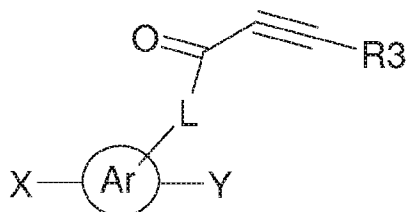
It is another advantage of some embodiments of the present invention
15 that the stability in time of the power efficiency of the solar cells may be linked to the stability in time of the active layer. This active layer may be processed as a thin film from an organic solvent in which both p- and n-type components are soluble, and may be made from a blend of a p-type semi-conducting polymer and a n-type material (for example a C60 fullerene derivative or a n-
20 type semi-conducting polymer) which would tend to de-mix with time if not properly stabilised according to the teachings of this invention.

It is an object of the present invention to provide a stable active layer based on a blend of p-type and n-type materials for bulk heterojunction solar cell applications. This blend may be made of a p-type semi-conducting
25 material containing specific crosslinkable functions as side chains and a n-type material mixed together in various ratios and processed e.g. as a thin film from solution. The n-type material included in such blends can be any previously known small molecule, oligomer or polymer optionally containing known crosslinkable functions as side chains.

30 In a first aspect, the present invention provides a class of monomeric compounds represented by the structural formula (I)



and a class of monomeric compounds represented by the structural formula (II)



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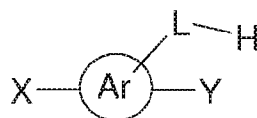
wherein:

- Ar is a homocyclic or heterocyclic aromatic group selected from the group consisting of thienyl, phenyl, naphthyl, pyrrolyl, pyridyl, carbazolyl, fluorenyl and benzothiazolyl;
- 10 - L is selected from the group consisting of $-O-$, $-\text{CH}(\text{CH}_3)-O-$, $-(\text{CH}_2)_q-O-$, $-NH-$, $-\text{CH}(\text{CH}_3)-NH-$, $-(\text{CH}_2)_q-NH-$, $-S-$, $-\text{CH}(\text{CH}_3)-S-$ and $-(\text{CH}_2)_q-S-$, the oxygen atom of said $-\text{CH}(\text{CH}_3)-O-$ or $-(\text{CH}_2)_q-O-$, being adjacent to the carbonyl group, the NH group of said $-\text{CH}(\text{CH}_3)-NH-$ or $-(\text{CH}_2)_q-NH-$, being adjacent to the carbonyl group and the sulphur atom of said $-\text{CH}(\text{CH}_3)-S-$ or $-(\text{CH}_2)_q-S-$, being adjacent to the carbonyl group;
- 15 - q is 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 or 12;
- R_1 and R_2 are independently selected from the group consisting of hydrogen, C_{1-12} alkyl and phenyl, wherein said phenyl is optionally substituted with one or more substituents independently selected from the group consisting of hydroxyl, halogen, metonym, C_{2-4} -alkoxy and trifluoromethyl;
- 20 - R_3 is selected from the group consisting of hydrogen, C_{1-12} -alkyl and phenyl;
- R_4 is hydrogen, methyl or C_{2-4} -alkyl; and
- 25 - X and Y are independently selected from the group consisting of hydrogen, chloro, bromo, iodo, boronic acid, boronic esters and organotin, provided

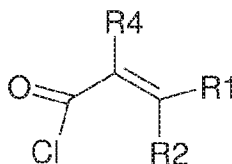
that X and Y are not both hydrogen. In a preferred embodiment of the first aspect L is selected from the group consisting of $-O-$, $-\text{CH}(\text{CH}_3)-O-$, $-(\text{CH}_2)_q-O-$, $-\text{NH}-$ or $-\text{S}-$, the oxygen atom of said $-\text{CH}(\text{CH}_3)-O-$ or $-(\text{CH}_2)_q-O-$, being adjacent to the carbonyl group.

5 In a second aspect, the present invention provides conjugated polymers comprising one or more repeating units derived from the above-defined monomeric compounds represented by the structural formula (I) or the structural formula (II), and optionally one or more repeating units derived from a co-monomer copolymerisable with said monomeric compound, the latter
 10 repeating units comprising a divalent homocyclic or heterocyclic aromatic group Ar' optionally substituted with one or more substituents independently selected from the group consisting of C_{1-20} -alkyl, C_{1-20} -alkoxy, C_{1-20} -alkylsulfate, phenyl, benzyl, and functional crosslinkable groups.

In a third aspect, the present invention provides methods for producing
 15 an above-defined monomeric compounds represented by the structural formula (I) or the structural formula (II), comprising reacting a hydroxyl-substituted homocyclic or heterocyclic aromatic compound represented by the structural formula (III)

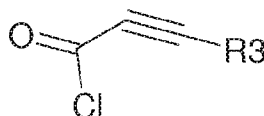


20 wherein Ar, X, Y and L are as defined above, with an ethylenically unsaturated carbonyl chloride represented by the structural formula (IV)



wherein R_1 , R_2 and R_4 are as defined above, or the corresponding carboxylic anhydride,

25 or with an acetylenically unsaturated carbonyl chloride represented by the structural formula (V)



wherein R_3 is as defined above.

In a fourth aspect, the present invention provides a method for producing the above-described polymer comprising polymerising a compound represented for formula (I) or formula (II) by reductive coupling.

5 In a fifth aspect, the present invention provides a method for producing the above-described polymer comprising copolymerising by reductive coupling a compound according to formula (I) or formula (II) and one or more co-monomers.

In a sixth aspect, the present invention provides a process for preparing
10 a polymer comprising the following steps: copolymerization of a monomer post-functionalizable to a compound represented by structural formula (I) or structural formula (II) as defined above with a co-monomer copolymerizable therewith, said co-monomer being a divalent homocyclic or heterocyclic aromatic group Ar' optionally substituted with one or more substituents
15 independently selected from the group consisting of C_{1-20} -alkyl, C_{1-20} -alkoxy, C_{1-20} -alkylsulfate, phenyl and benzyl, to produce a post-functionalizable copolymer; and post-functionalizing said post-functionalizable copolymer to produce the polymer of the fifth aspect. Examples of monomers post-functionalizable to a compound represented by structural formula (I) are esters
20 of 3-(2-hydroxyethyl)thiophene e.g. 3-(2-acetoxyethyl)thiophene.

In a seventh aspect, the present invention provides blends of a n-type or p-type compound and a conjugated polymer or conjugated copolymer derived from a monomeric compound represented by the structural formula (I) or the structural formula (II).

25 In an eighth aspect, the present invention provides crosslinked polymer materials, and methods for producing the same, being irradiated, e.g. UV-irradiated, blends as mentioned before preferably in the absence of a photoinitiator.

In yet another aspect, the present invention provides opto-electronic
30 devices such as, but not limited to, solar cells comprising a crosslinked polymer material as defined above, i.e. obtained from irradiated blends of a n-type or p-type compound and a conjugated polymer or copolymer derived from an above-defined monomeric compound.

Brief description of the drawings

Fig. 1 shows the UV spectrum of an irradiation lamp used to operate cross-linking in an embodiment of the present invention.

Fig. 2 shows a TEM picture of a comparative blend (film A) as deposited.

5 Fig. 3 shows a TEM picture of a comparative blend (film A) after heat treatment.

Fig. 4 shows an electron diffraction pattern measured on the comparative blend (Fig. 3) after heat treatment.

10 Fig. 5 shows a TEM picture of a comparative blend (film A) after heat treatment. The magnification is larger than in the TEM picture of Fig. 3.

Fig. 6 shows a TEM picture of a blend according to an embodiment of the present invention (film B) as deposited.

Fig. 7 shows a TEM picture of a blend according to an embodiment of the present invention (film B) after heat treatment.

15 Fig. 8 shows a TEM picture of a blend according to an embodiment of the present invention (film B) after heat treatment. The magnification is smaller than for Fig. 7.

Fig. 9 shows a TEM picture of a blend according to an embodiment of the present invention (film B) after UV curing and heat treatment.

20 Fig. 10 shows a TEM picture of a blend according to an embodiment of the present invention (film B) after UV curing and heat treatment. The magnification is smaller than for Fig. 9.

25 Fig. 11 is a graph of the current density versus the voltage as measured on a bulk heterojunction solar cell having an active layer made from a blend according to an embodiment of the present invention.

Fig. 12 is a graph of the relative Fill Factor versus time as measured on a bulk heterojunction solar cell having an active layer made from a comparative blend (Cell A) and on a bulk heterojunction solar cell having an active layer made from a P3/PCBM blend according to an embodiment of the present invention (Cell B) at 80°C.

30 Fig. 13 is a graph of the relative open circuit voltage versus time as measured on a bulk heterojunction solar cell having an active layer made from a comparative blend (Cell A) and on a bulk heterojunction solar cell having an

active layer made from a **P3**/PCBM blend according to an embodiment of the present invention (Cell B) at 80 °C.

Fig. 14 is a graph of the relative short-circuit current density versus time as measured on a bulk heterojunction solar cell having an active layer made from a comparative blend (Cell A) and on a bulk heterojunction solar cell having an active layer made from a **P3**/PCBM blend according to an embodiment of the present invention (Cell B) at 80 °C.

Fig. 15 is a graph of the relative power efficiency versus time as measured on a bulk heterojunction solar cell having an active layer made from a comparative blend (Cell A) and on a bulk heterojunction solar cell having an active layer made from a **P3**/PCBM blend according to an embodiment of the present invention (Cell B) at 80 °C.

Fig. 16 is a graph of the relative Fill Factor versus time as measured on a bulk heterojunction solar cell having an active layer made from a comparative blend (Cell A) and on a bulk heterojunction solar cell having an active layer made from a **P3**/PCBM blend according to an embodiment of the present invention (Cell B) at 100 °C.

Fig. 17 is a graph of the relative open circuit voltage versus time as measured on a bulk heterojunction solar cell having an active layer made from a comparative blend (Cell A) and on a bulk heterojunction solar cell having an active layer made from a **P3**/PCBM blend according to an embodiment of the present invention (Cell B) at 100 °C.

Fig. 18 is a graph of the relative short-circuit current density versus time as measured on a bulk heterojunction solar cell having an active layer made from a comparative blend (Cell A) and on a bulk heterojunction solar cell having an active layer made from a **P3**/PCBM blend according to an embodiment of the present invention (Cell B) at 100 °C.

Fig. 19 is a graph of the relative power efficiency versus time as measured on a bulk heterojunction solar cell having an active layer made from a comparative blend (Cell A) and on a bulk heterojunction solar cell having an active layer made from a **P3**/PCBM blend according to an embodiment of the present invention (Cell B) at 100 °C.

Fig. 20 is a graph of the relative Fill Factor versus time as measured on a bulk heterojunction solar cell having an active layer made from a comparative blend (Cell A) and on a bulk heterojunction solar cell having an active layer made from a blend according to an embodiment of the present invention (Cell B) at 150 °C.

Fig. 21 is a graph of the relative open circuit voltage versus time as measured on a bulk heterojunction solar cell having an active layer made from a comparative blend (Cell A) and on a bulk heterojunction solar cell having an active layer made from a **P3**/PCBM blend according to an embodiment of the present invention (Cell B) at 150 °C.

Fig. 22 is a graph of the relative short-circuit current density versus time as measured on a bulk heterojunction solar cell having an active layer made from a comparative blend (Cell A) and on a bulk heterojunction solar cell having an active layer made from a **P3**/PCBM blend according to an embodiment of the present invention (Cell B) layer made from a blend according to an embodiment of the present invention at 150 °C.

Fig. 23 is a graph of the relative power efficiency versus time as measured on a bulk heterojunction solar cell having an active layer made from a comparative blend (Cell A) and on a bulk heterojunction solar cell having an active layer made from a **P3**/PCBM blend according to an embodiment of the present invention (Cell B) at 150 °C.

Fig. 24 is a graph of the relative Fill Factor versus time as measured on a bulk heterojunction solar cell having an active layer made from a comparative blend (Cell A) and on a bulk heterojunction solar cell having an active layer made from a **P3**/PCBM blend according to an embodiment of the present invention (Cell B) and on a bulk heterojunction solar cell having an active layer made from a **P6**/PCBM blend according to an embodiment of the present invention (Cell C) at 125 °C.

Fig. 25 is a graph of the relative open circuit voltage versus time as measured on a bulk heterojunction solar cell having an active layer made from a comparative blend (Cell A) and on a bulk heterojunction solar cell having an active layer made from a **P3**/PCBM blend according to an embodiment of the present invention (Cell B) and on a bulk heterojunction solar cell having an

active layer made from a **P6**/PCBM blend according to an embodiment of the present invention (Cell C) at 125°C.

Fig. 26 is a graph of the relative short-circuit current density versus time as measured on a bulk heterojunction solar cell having an active layer made from a comparative blend (Cell A) and on a bulk heterojunction solar cell having an active layer made from a **P3**/PCBM blend according to an embodiment of the present invention (Cell B) and on a bulk heterojunction solar cell having an active layer made from a **P6**/PCBM blend according to an embodiment of the present invention (Cell C) at 125°C.

Fig. 27 is a graph of the relative power efficiency versus time as measured on a bulk heterojunction solar cell having an active layer made from a comparative blend (Cell A), on a bulk heterojunction solar cell having an active layer made from a **P3**/PCBM blend according to an embodiment of the present invention (Cell B) and on a bulk heterojunction solar cell having an active layer made from a **P6**/PCBM blend according to an embodiment of the present invention (Cell C) at 125°C.

Definitions

As used herein with respect to a substituting group, and unless otherwise stated, the term "C₁₋₁₂ alkyl" refers to a straight (non-branched) or branched chain saturated acyclic hydrocarbon monovalent group having from 1 to 4 carbon atoms such as, for example, methyl, ethyl, propyl, n-butyl, 1-methylethyl (isopropyl), 2-methylpropyl (isobutyl), and 1,1-dimethylethyl (*tert*-butyl). Similarly, the term "C₁₋₂₀ alkyl" refers to straight (non-branched) or branched chain groups having from 1 to 20 carbon atoms such as, for example, pentyl, hexyl, heptyl, octyl, nonyl, decyl, dodecyl, tetradecyl, hexadecyl, octadecyl and the like.

As used herein with respect to a substituting group, and unless otherwise stated, the terms "homocyclic aromatic" or "aryl" designate any mono- or polycyclic aromatic monovalent hydrocarbon group having from 6 to 15 carbon atoms such as, but not limited to, phenyl, naphthyl, anthracenyl, phenanthracenyl, fluoranthenyl, chrysenyl, pyrenyl, biphenyl, terphenyl, picenyl, indenyl, biphenyl, indacenyl, tetrahydropyrenyl, benzocyclobutenyl,

benzocyclooctenyl and the like, including fused benzo-C₄₋₈ cycloalkyl groups such as, for instance, indanyl, tetrahydronaphthyl, fluorenyl and the like, all of the said groups being optionally substituted with one or more substituents (preferably 1 to 3 substituents) independently selected from the group
5 consisting of halogen, C₁₋₁₂ alkyl, nitro, trifluoromethoxy, trifluoromethyl and C₁₋₁₂ alkoxy (all of such substituents being such as herein defined, including individual species and sub-groups thereof), such as, but not limited to, 4-fluorophenyl, 4-chlorophenyl, 3,4-dichlorophenyl, 2,6-dichlorophenyl, 2-fluorophenyl, 3-chlorophenyl, 3,5-dichlorophenyl, trifluoromethylphenyl, 3,4-
10 dimethoxyphenyl, iodophenyl, and bromophenyl.

As used herein with respect to a substituting group, and unless otherwise stated, the terms "heterocyclic aromatic" or "heteroaryl" means a mono- or polycyclic, polyunsaturated, monovalent hydrocarbon group having from 4 to 12 carbon atoms and including one or more heteroatoms in one or more
15 heterocyclic rings, each of said rings having 5 or 6 atoms (and optionally further including one or more heteroatoms attached to one or more carbon atoms of said ring, for instance in the form of a carbonyl, and/or to one or more heteroatoms of said ring, for instance in the form of a N-oxide), each of said heteroatoms being independently nitrogen or sulfur, also including groups
20 wherein a heterocyclic ring is fused to one or more aromatic homocyclic rings for instance in the form of benzo-fused, dibenzo-fused and naphtho-fused heterocyclic groups; within this definition are included heteroaryl groups such as, but not limited to, thienyl, pyrrolyl, pyridyl, carbazolyl and benzothiazolyl.

As used herein with respect to a substituting atom, and unless otherwise
25 stated, the term "halogen" means any atom selected from the group consisting of fluorine, chlorine, bromine and iodine.

As used herein with respect to a substituting group, and unless otherwise stated, the term "C₁₋₁₂ alkoxy" refers to substituents wherein a carbon atom of a C₁₋₂₀ alkyl group (such as defined herein above, including sub-groups
30 thereof), is attached to an oxygen atom through a single bond, including methoxy, ethoxy, propoxy, n-butoxy, isopropoxy, sec-butoxy, and tert-butoxy.

As used herein with respect to a substituting group, and unless otherwise stated, the term "C₁₋₂₀ alkylsulfate" refers to substituents wherein a carbon

atom of a C₁₋₂₀ alkyl group (such as defined herein above, including subgroups thereof), is attached to an oxygen atom of a sulfate group through a single bond such as, but not limited to methylsulfate (methoxysulfonyloxy), ethylsulfate (ethoxysulfonyloxy), n-butylsulfate (n-butoxysulfonyloxy), *tert*-butylsulfate (*tert*-butoxysulfonyloxy), undecylsulfate (undecyloxysulfonyloxy), and the like.

As used herein, and unless otherwise stated, the term "arylene" designates any divalent group derived from aryl (such as above defined) by abstracting a hydrogen atom.

As used herein, and unless otherwise stated, the term "heteroarylene" designates any divalent group derived from heteroaryl (such as above defined) by abstracting a hydrogen atom.

As used herein, and unless otherwise stated, "crosslinkable" refers to the capacity of being irreversibly cured or polymerized, thereby forming a material that cannot be reshaped or reformed.

As used herein with respect to a substituting group, and unless otherwise stated, the term "functional crosslinkable" group designates moieties containing one or more functionalities selected from the group consisting of double bond, triple bond, or precursors thereof, or addition-polymerisable groups known in the art. Suitable crosslinkable groups include vinyl, allyl, or may be derived from acrylates, methacrylates, vinyl ethers, 1-propenyl ethers, arylene containing one or more substituents independently selected from the group consisting of benzocyclobutane, azide, di(hydrocarbyl)amino, cyanate, ester, hydroxyl, glycidyl ether, C₁₋₂₀ alkyl acrylates, C₁₋₂₀ alkyl methacrylates, alkenyl, alkenyloxy, alkynyl, maleimide, vinylbenzyl, allyloxy, p-ethenylphenyl, perfluoroethenyl, perfluoroethenyloxy, coumaroyl, and halogenated derivatives thereof.

As used herein with respect to organic devices, and unless otherwise stated, the term "active layer" designates an organic layer which includes an organic semiconductor material exhibiting one type of electronic conductivity and possibly a second semiconductor material having the same or opposite type conductivity.

As used herein with respect to an active, and unless otherwise stated, the term "stable" refers to the adequate nano-morphology of the active layer which does not change in time at room temperature or even at higher temperature under inert atmosphere.

5 As used herein, and unless otherwise stated, the term "boronic ester" refers to a boronic acid derivative wherein hydrogen is replaced by any organic residue, preferably a hydrocarbonyl group, and which can be obtained by condensation with alcohols or diols, including but not limited to dioxaborolanes and dioxaborinanes.

10 As used herein, and unless otherwise stated, the term "organotin" refers to a group represented by the structural formula $\text{SnR}_9\text{R}_{10}\text{R}_{11}$ wherein each of R_9 , R_{10} and R_{11} is independently selected from the group consisting of halogen, C_{1-20} alkyl, C_{3-10} cycloalkyl, aryl, benzyl and C_{2-7} alkenyl, provided that R_9 , R_{10} and R_{11} are not simultaneously halogen; such organotin groups
 15 may be derived from tin compounds including, but not limited to, di-*n*-butyltin dibromide, di-*n*-butyltin dichloride, di-*tert*-butyltin dichloride, dimethyltin dibromide, dimethyltin dichloride, dimethyltin difluoride, dimethyltin diiodide, diphenyltin dichloride, diphenyltin dibromide, diphenyltin difluoride, diphenyltin diiodide, tributyltin fluoride, tributyltin chloride, tributyltin bromide, tributyltin
 20 iodide, phenyltin tribromide, phenyltin trichloride, tricyclohexyltin chloride, triethyltin bromide, triethyltin chloride, triethyltin iodide, vinyltributyltin, tetrabutyltin, butyltin trichloride, *n*-butylvinyltin dichloride, diallyldibutyltin, diallyldiphenyltin, dibutylvinyltin bromide, dibutylvinyltin chloride, dichlorodi-*m*-tolylstannane, diethyldiisoamyltin, diethyldiisobutyltin, diethyldiphenyltin,
 25 diethylisoamyltin bromide, diethylisoamyltin chloride, diethylisobutyltin bromide, diethyl-*n*-propyltin bromide, diethyl-*n*-propyltin chloride, diethyl-*n*-propyltin fluoride, diethyltin dibromide, diethyltin dichloride, diethyltin difluoride, diethyltin diiodide, diisoamyltin dibromide, diisoamyltin dichloride, diisoamyltin diiodide, diisobutyltin dichloride, diisobutyltin diiodide, diisopropyltin dichloride,
 30 diisopropyltin dibromide, dimethyldiethyltin, dimethyldiisobutyltin, dimethyldioctyltin, dimethyldivinyltin, dimethylethylpropyltin, dimethylethyltin iodide, dimethyldivinyltin, dimethylvinyltin bromide, dimethylvinyltin iodide, diphenyldivinyltin, dipropyltin difluoride, dipropyltin diiodide, dipropyltin

dichloride, dipropyltin dibromide, di-*o*-tolyltin dichloride, di-*p*-tolyltin dichloride, ditriphenyl-stannylmethane, divinylbutyltin chloride, divinyltin dichloride, ethyldiisoamyltin bromide, ethyldiisobutyltin bromide, ethylmethylpropyltin iodide, ethyl-*n*-propyldiisoamyltin, ethylpropyltin dichloride, ethyltin tribromide, 5 ethyltin triiodide, ethyltri-*n*-butyltin, ethyltri-*n*-propyltin, methyltin tribromide, methyltin trichloride, methyltin triiodide, methyltri-*n*-butyltin, methyltri-*n*-propyltin, phenylbenzyltin dichloride, phenyltribenzyltin, propyltin triiodide, propyltri-*n*-amyltin, tetra-*n*-amyltin, tetra-*n*-butyltin, tetrabenzyltin, tetracyclohexyltin, tetraethyltin, tetra-*n*-heptyltin, tetra-*n*-hexyltin, 10 tetraisoamyltin, tetraisobutyltin, tetralauryltin, tetramethyltin, tetra-*n*-octyltin, tetraphenyltin, tetrapropyltin, tetra-*o*-tolyltin, tetra-*m*-tolyltin, tetra-*p*-tolyltin, tetravinyltin, tetra-*m*-xylyltin, tetra-*p*-xylyltin, *o*-tolyltin trichloride, *p*-tolyltin trichloride, *m*-tolyltrichlorostannane, triallylbutyltin, tri-*n*-amyltin bromide, tribenzylethyltin, tribenzyltin chloride, tribenzyltin iodide, tri-*n*-butyltin bromide, 15 tri-*n*-butylvinyltin, triethyl-*n*-amyltin, triethylisoamyltin, triethylisobutyltin, triethylphenyltin, triethyl-*n*-propyltin, triisoamyltin bromide, triisoamyltin chloride, triisoamyltin fluoride, triisoamyltin iodide, triisobutylethyltin, triisobutylisoamyltin, triisobutyltin bromide, triisobutyltin chloride, triisobutyltin fluoride, triisobutyltin iodide, triisopropyltin bromide, triisopropyltin iodide, 20 trimethyldecyltin, trimethyldodecyltin, trimethylethyltin, trimethyltin bromide, trimethyltin chloride, trimethyltin fluoride, trimethyltin iodide, triphenylallyltin, triphenylbenzyltin, triphenylbutyltin, triphenylethyltin, triphenylmethyltin, triphenyl- α -naphthyltin, triphenyltin bromide, triphenyltin chloride, triphenyltin fluoride, triphenyltin iodide, triphenyl-*p*-tolyltin, triphenyl-*p*-xylyltin, tri-*n*-propyl- 25 *n*-butyltin, tri-*n*-propylethyltin, tri-*n*-propylisobutyl tin, tri-*n*-propyltin chloride, tri-*n*-propyltin fluoride, tri-*n*-propyltin iodide, tri-*o*-tolyltin bromide, tri-*p*-tolyltin bromide, tri-*o*-tolyltin chloride, tri-*m*-tolyltin chloride, tri-*p*-tolyltin chloride, tri-*p*-tolyltin fluoride, tri-*o*-tolyltin iodide, tri-*p*-tolyltin iodide, triphenylstannylmethane, trivinyldecyltin, trivinylhexyltin, trivinyl-octyltin, 30 trivinyltin chloride, vinyltin trichloride, tri-*p*-xylyltin bromide, tri-*p*-xylyltin chloride, tri-*p*-xylyltin fluoride, tri-*p*-xylyltin iodide and tri-*m*-xylyltin fluoride.

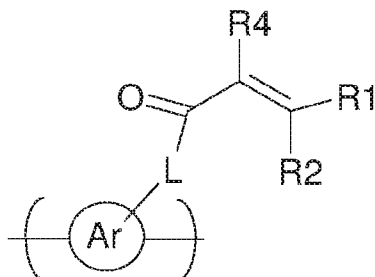
Detailed description of the invention

Within the first aspect of this invention, as described in the Summary of the Invention, the following more specific embodiments are of particular importance:

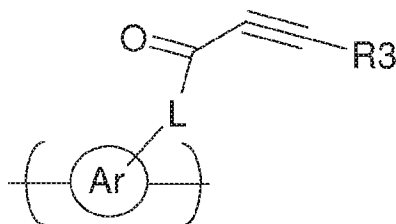
- 5 - compounds represented by the structural formula (I) or the structural formula (II) wherein L is adjacent to X or Y;
- compounds represented by the structural formula (I) wherein R₁ and R₂ are both hydrogen, and R₄ is methyl, which may be derived from methacryloyl chloride, as explained below with regard to the third aspect of the
10 invention;
- compounds represented by the structural formula (I) wherein R₁ and R₄ are hydrogen, and wherein R₂ is methyl or ethyl or *n*-propyl or *n*-butyl, or R₂ is phenyl optionally mono-substituted with fluoro, chloro, hydroxyl, methoxy, trifluoromethyl or C₂₋₄-alkoxy; such compounds may be derived from
15 crotonyl chloride, pent-2-enoyl chloride, hex-2-enoyl chloride, hept-2-enoyl chloride, phenylprop-2-enoyl chloride, cinnamoyl chloride, 2-chlorocinnamoyl chloride, 4-fluorocinnamoyl chloride, 4-methoxycinnamoyl chloride, or analogs thereof as explained below with regard to the third aspect of the invention;
- 20 - compounds represented by the structural formula (I) wherein R₁, R₂ and R₄ are hydrogen, which may be derived from acryloyl chloride, as explained below with regard to the third aspect of the invention; and
- compounds represented by the structural formula (II) wherein R₃ is hydrogen, methyl, ethyl, *n*-propyl or phenyl, which may be derived from
25 propiolic acid chloride and analogs thereof, as explained below with regard to the third aspect of the invention.

Within the second aspect of this invention, as described in the Summary of the Invention, a more specific embodiment of particular importance consists of functionalized semi-conducting materials (conjugated materials), being
30 oligomers, polymers or copolymers, containing one or more monomeric groups or repeating units represented by the structural formula (IA):

16



and/or represented by the structural formula (IIA):



- 5 wherein Ar, L, R₁, R₂, R₃ and R₄ are as defined with respect to structural formulae (I) and (II), and optionally one or more monomeric groups or repeating units comprising a divalent group Ar' wherein Ar' may be arylene or heteroarylene, said Ar' being optionally substituted with one or more substituents independently selected from the group consisting of C₁₋₂₀-alkyl, C₁₋₂₀-alkoxy, C₁₋₂₀-alkylsulfate, aryl, benzyl, and functional crosslinkable groups known in the art.

More specifically Ar' may be 2,5-thienylene optionally substituted with one or more substituents independently selected from the group consisting of C₁₋₂₀-alkyl, C₁₋₂₀-alkoxy, C₁₋₂₀-alkylsulfate, phenyl, benzyl, and functional crosslinkable groups known in the art, e.g. 3-*n*-hexyl-2,5-thienylene or 3-*n*-octyl-2,5-thienylene.

The aromatic homocyclic or heterocyclic group Ar and the optionally substituted arylene or heteroarylene divalent group Ar' may be the same, e.g. they may be both 2,5-thienylene, or may be different.

- 20 In one embodiment, when said semi-conducting conjugated material is a copolymer containing one or more monomeric groups or repeating units represented by the structural formula (IA), wherein Ar is thienyl, and one or more monomeric groups or repeating units comprising a divalent group Ar' wherein Ar' is 3-C₁₋₂₀-alkyl-2,5-thienylene, then R₁ and R₂ are not both hydrogen.

In another embodiment, when said semi-conducting conjugated material is a copolymer containing one or more monomeric groups or repeating units represented by the structural formula (IA), wherein Ar is fluorenyl, and one or more monomeric groups or repeating units comprising a divalent group Ar' wherein Ar' is 2,7-fluorenylene, then R₁ and R₂ are not both hydrogen.

In another embodiment, the weight average molecular weight Mw (measured against a polystyrene standard) of the polymer or copolymer of this invention may be in the range from about 10,000 to about 1,000,000 Dalton, e.g. from about 40,000 to 75,000 Dalton;

In another embodiment, the polydispersity index (PD = Mw/Mn) of the polymer or copolymer of this invention may be comprised between 1.05 and about 5.0, e.g. between 1.1 and 3.0, or between about 1.3 and 2.5.

In a particular embodiment of this second aspect of the invention, the arylene or heteroarylene divalent group Ar' present in the recurring units of the co-monomer may be selected from the group consisting of 1,4-phenylene; 2,6-naphthalenediyl; 1,4-naphthalenediyl; 1,4-anthracenediyl; 2,6-anthracenediyl; 9,10-anthracenediyl; 2,5-thienylene; 2,5-furandiyl; 2,5-pyrrolediyl; 1,3,4-oxadiazole-2,5-diyl; 1,3,4-thiadiazole-2,5-diyl; 2,3-benzo[c]thienylene; thieno[3,2-b]thiophene-2,5-diyl; pyrrolo[3,2-b]pyrrole-2,5-diyl; pyrene-2,7-diyl; 4,5,9,10-tetrahydropyrene-2,7-diyl; 4,4'-bi-phenylene; phenantrene-2,7-diyl; 9,10-dihydrophenantrene-2,7-diyl; dibenzo-furane-2,7-diyl; dibenzothiophene-2,7-diyl; 2,5-selenophenylene; isothianaphthylene; 2,7-silafluorenylene; 3,6-carbazolediyl; pyridinediyl; 2,2'-dipyridinediyl; pyridopyrazinediyl; quinoxalinediyl; thieno[3,4-c]pyridinediyl; thieno[3,4-b]pyridinediyl; thieno[3,4-b]pyrazinediyl; benzothiadiazolediyl; 4H-cyclopenta[2,1-b;3,4-b']dithienylene; silacyclopentadienediyl; and anthrazolinediyl. More specific examples of suitable co-monomers of this type are given below, together with literature references relating to their polymerisation techniques.

In a particular embodiment of this second aspect of the invention, the co-monomer comprising a divalent group Ar' may represent at least 0.5 % by mole of the copolymer, e.g. at least 50 % by mole of the copolymer, or at least 85 % by mole of the copolymer. In another particular embodiment of this second aspect of the invention, the co-monomer comprising a divalent group

Ar' may represent at most 99.5 % by mole of the copolymer, e.g. at most 98 % by mole of the copolymer, or at most 15 % by mole of the copolymer.

Within the third aspect of this invention, as described in the Summary of the Invention, the following more specific embodiments are of particular importance:

- the ethylenically unsaturated carbonyl chloride represented by the structural formula (IV) may be selected from the group consisting of crotonyl chloride, acryloyl chloride, methacryloyl chloride, pent-2-enoyl chloride, hex-2-enoyl chloride, hept-2-enoyl chloride, cinnamoyl chloride, 2-chlorocinnamoyl chloride, 4-fluorocinnamoyl chloride, and 4-methoxycinnamoyl chloride;
- the acetylenically unsaturated carbonyl chloride represented by the structural formula (V) may be selected from the group consisting of propiolic acid chloride, phenylpropionic acid chloride, 2-butyneic acid chloride, 2-pentyneic acid chloride, and 2-hexyneic acid chloride;
- the hydroxyl-substituted homocyclic or heterocyclic aromatic compound represented by the structural formula (III) may be selected from the group consisting of 2,5-dibromo-3-hydroxyethyl thiophene, 2,5-dibromo-3-hydroxymethyl thiophene, 2,5-dibromophenol, 2-bromophenol, 3-bromophenol, 4-bromophenol, 2,5-dibromo-1-(2-hydroxyethyl)benzene, 2-bromobenzyl alcohol, 3-bromobenzyl alcohol, 4-bromobenzyl alcohol, 4-hydroxyphenylboronic acid, 4-(hydroxymethyl)phenylboronic acid, 3-(hydroxymethyl)phenylboronic acid, 2,6-dibromo-4-(2-hydroxyethyl)-pyridine, 2,6-dibromo-3-(2-hydroxyethyl)pyridine, (S)-2,6-dibromo-4-(1-hydroxyethyl)pyridine, (R)-2,6-dibromo-4-(1-hydroxyethyl)pyridine, 2,6-dibromo-4-(hydroxymethyl)-pyridine, 2,6-dibromo-3-(hydroxymethyl)-pyridine, 2,6-dibromo-3-(3-hydroxypropyl)-pyridine, 3,6-dibromo-9H-2-hydroxycarbazole, 3,6-dibromo-9H-4-hydroxycarbazole, 2,7-dibromo-9-hydroxyfluorene, 2,7-dibromo-9-hydroxymethylfluorene, 1,4-dibromo-2-naphthol, 1,4-dibromo-2-naphthalenemethanol and 4,7-dibromo-2-hydroxybenzothiazole ; when such a homocyclic or heterocyclic aromatic compound represented by the structural formula (III) is not commercially available, it may be produced by inserting the X and/or Y substituent onto

a readily available hydroxyl-containing compound with the structural formula Ar-LH, e.g. through chlorination, bromination, iodination or boronation, using synthetic procedures known in the art.

In a preferred embodiment of the present invention, the polymers and
5 copolymers of this invention may be produced via a reductive coupling reaction such as, but not limited to, Rieke coupling (e.g. following a procedure analog to the one disclosed in *T.-A.Chen, R. D. Rieke, J. Am. Chem. Soc. (1992) 114, 10087*), McCullough coupling (e.g. following a procedure analog to the one disclosed in *R. D. McCullough et al., J. Chem. Soc., Chem.*
10 *Commun., 1992, 70* or U.S. Pat. No. 6,166,172), Stille coupling (e.g. following a procedure analog to the one disclosed in *Milstein, D.; Stille, J. K. J. Am. Chem. Soc. 1978, 100, 3636* or *D. Milstein, J. K. Stille, J. Am. Chem. Soc., 1979, 101, 4992.*), Suzuki coupling (e.g. following a procedure analog to the one disclosed in *N. Miyaura, T. Yanagi, A. Suzuki, Synth. Commun., 1981, 11,*
15 *513*) or Yamamoto coupling (e.g. following a procedure analog to the one disclosed in *T. Yamamoto, A. Morita, Y. Miyazaki, T. Maruyama, H. Wakayama, Z. H. Zhou, Y. Nakamura, T. Kanbara, S. Sasaki and K. Kubota, Macromolecules, 1992, 25, 1214*).

In a particular embodiment of the invention, the polymers according to
20 the second aspect of this invention include homopolymers containing monomeric groups or repeating units represented by the structural formula (IA) or the structural formula (IIA), and copolymers comprising two or more different recurring units, including a divalent group Ar', in a random or block arrangement type, which may include the same or a different aromatic
25 homocyclic or heterocyclic group.

Suitable co-monomers that can be co-polymerised with the crosslinkable monomers according to different embodiments of the present invention, especially as represented by the structural formula (I) or the structural formula (II), include monomers, preferably conjugated monomers, comprising two
30 reactive groups selected from the group consisting of halogen (e.g. I, Br or Cl), boronic acid, boronic esters, organotin, and other groups known by the person skilled in the art be useful in reductive coupling reactions. Those co-monomers includes monomers such as among others fluorene derivatives

(such as but not limited to 2,7-dibromo-9,9-dialkylfluorene or 2,7-dibromo-9,9-diarylfluorenes (see e.g. C. Ego et al, *Adv. Mater.* 14 (2002) 809-811)) , indenofluorene derivatives (see e.g. S. Setayesh, *Macromolecules* (2000)33:2016), phenylene or ladder-type phenylene derivatives (see e.g. J. Grimme et al., *Adv. Mat.* (1995) 7 ,292), aniline derivatives, thiophene derivatives (such as 2,5-dibromothiophenes and 2,5-dibromo-3-C₁₋₂₀ alkylthiophenes), fluorenone derivatives (such as but not limited to 2,7-dibromofluorenone), naphthalene derivatives (such as but not limited to 2,6-dibromonaphthalene and 1,4-dibromonaphthalene); anthracene derivatives (such as, but not limited to, 1,4-dibromoanthracene, 2,6-dibromoanthracene and 9,10-dibromoanthracene); furane derivatives (such as, but not limited to, 2,5-dibromofurane); pyrrole derivatives such as, but not limited to, 2,5-dibromopyrrole); 1,3,4-oxadiazole-2,5-diyl derivatives; 1,3,4-thiadiazole-2,5-diyl derivatives; 2,3-benzo[c]thienylene derivatives; thieno[3,2-b]thiophene-2,5-diyl derivatives; pyrrolo[3,2-b]pyrrole-2,5-diyl derivatives; pyrene derivatives such as, but not limited to, 2,7-dibromopyrene and 2,7-dibromo-4,5,9,10-tetrahydropyrene; 4,4'-bi-phenylene derivatives; phenanthrene derivatives (such as, but not limited to, 2,7-dibromo phenanthrene; 3,6-dibromophenanthrene and 2,7-dibromo-,9,10-dihydrophenanthrene); dibenzofurane-2,7-diyl derivatives; dibenzo-thiophene-2,7-diyl derivatives, and perylene derivatives (see C. Ego et al, *J. Am. Chem. Soc.* 125(2) (2003) 437-443).

A monomer or co-monomer involved in the polymerisation process in a Rieke or Yamamoto coupling polymerisation comprises preferably two identical (i.e. X = Y) reactive halogens (e.g. I, Br or Cl).

The monomer or co-monomers involved in a polymerisation process in a Suzuki coupling polymerisation preferably comprise:

- (a) two identical (i.e. X = Y) reactive halogens (e.g. I, Br or Cl) for one molar half of the comonomers involved and two identical reactive groups selected from the group consisting of boronic acid and boronic esters for another molar half of the comonomers involved, or

(b) one reactive halogen (e.g. I, Br or Cl) and another reactive group (i.e. X and Y are different) selected from the group consisting of boronic acid or boronic esters.

The monomer or co-monomers involved in the polymerisation process in
5 a Stille coupling polymerisation preferably comprise:

- (a) two identical (i.e. $X = Y$) reactive halogens (e.g. I, Br or Cl) for one molar half of the comonomers involved and two identical reactive organotin groups for another molar half of the comonomers involved, or
- (b) each one reactive halogen (e.g. I, Br or Cl) and another reactive (i.e. X and
10 Y are different) organotin group.

The nature of the end groups resulting from the polymerisation process is usually difficult to determined in view of the large molecular mass of the polymer produced but it is usually accepted that they are either of the same nature as one of the leaving groups present on the starting monomer (e.g.
15 halogen (e.g. I, Br or Cl), boronic acid, boronic ester or organotin, or hydrogen.

Methods to introduce alternative end-groups into the (co)polymer are well known to the person skilled in the art. A first method (a so-called "one pot" method) involves the addition of ending molecules together with the monomer
20 or co-monomers into the reaction mixture right from the start of the polymerisation. A second method involves a first step of producing the (co)polymer as described in the previous paragraphs, and a second step of reacting this (co)polymer with the ending molecules. In both methods the ending molecules preferably comprise only one reactive halogen (e.g. I, Br or
25 Cl), boronic acid, boronic ester, organotin or other group known by the person skilled in the art be useful in reductive coupling and are otherwise analog to the co-monomers described above.

An example of end-group introduction according to the first method is disclosed in *C. Ego et al, J. of the Am. Chem. Soc. 125(2) (2003), 437-443*.

30 According to a ninth aspect of the present invention the polymers according to the invention are suitable for use in active layer of organic devices and more particularly bulk heterojunction solar cells. The invention

further relates to an active layer, which comprises the polymers according to the invention.

In order to be used as active layers, the polymers according to the invention are generally applied in the form of a thin film to a substrate by know
5 methods familiar to the person skilled in the art, such as dipping, spin coating, inkjet printing, screen printing, etc.

The invention likewise relates to organic solar cells having one or more active layers, where at least one of these active layers comprises one or more polymers according to the invention.

10 The invention likewise relates to organic solar cells having one or more active layers, where at least one of these active layers is made from a blend of one or more polymers according to the invention having one type of electronic conductivity and a second semi-conducting material (small molecule as for example C60 derivatives or polymers as semi-conducting polymers) having
15 the opposite type conductivity.

In a particular embodiment the second semi-conducting material having the opposite type conductivity may be or may not be a polymer according to the invention, i.e. with crosslinkable side groups.

Polymers according to the invention are furthermore suitable for organic
20 based devices, for example but not limited to, for use in light emitting diodes, optical storage media, as photorefractive, for nonlinear-optical applications, in organic transistors such as Field effect transistors (FET), in photovoltaic cells (bi-layers, bulk heterojunction, tandem cells, dye-sensitized, organic/organic, organic/polymer, organic/inorganic, etc), in chemo- and bio-sensors.

25 According to another aspect of the present invention there is provided a method for stabilizing the nano-morphology of an active layer, which comprises one or more polymers according to the invention. The invention relates to a "stable" active layer, which comprises one or more polymers according to the invention. The nano-morphology of the active layer becomes
30 stable after UV curing.

In a particular embodiment, UV lamps with shortwave (200-280 nm, typically 254 nm), midrange (280-315 nm, typically 302 nm) or long-wave (315-380 nm, typically 365 nm) are suitable for the UV-curing process which is

carried out in inert atmosphere. The plurality of parameters of the UV light (for example but not limited to UV peak intensity and dosage) is controlled to ensure optimum curing of the layer. A low irradiation for a relatively long period is not equivalent to a higher irradiation for a shorter period, even if the overall energies are equal.

According to a fourth aspect of the present invention there is provided a time-stable organic solar cell comprising one or more "stable" active layer.

Organic solar cells with active layers containing one or more polymers according the invention are fabricated using state-of-the-art procedures as described in literature (especially relating to parameters such as substrates, electrodes, p-type/n-type ratios, solvents, concentration, etc). The active layer is preferably subject to an annealing step at a temperature dependent upon the copolymer ratio used in the copolymer, before the top electrode is applied. The choice of top electrode (cathode), e.g. 20nm Ca and 80 nm Al or 100 nm Ytterbium, has little effect upon the ageing characteristics of the solar cell, but affects the absolute value of the initial power efficiency. The solar cell is then exposed to UV light under inert atmosphere for a defined time to induce the crosslinking of the active layer and therefore the stabilization of the nano-morphology of the active layer.

In a particular embodiment, UV lamps with short-wave (200-280 nm, typically 254 nm), Midrange (280-315 nm, typically 302 nm) or long-wave (315-380 nm, typically 365 nm) are suitable for the UV-curing process which is carried out in inert atmosphere.

Preferred irradiation conditions are: Wavelength: 253.7 nm; Intensity: 250 $\mu\text{W}/\text{cm}^2$ at 15 cm & 14 mW/cm^2 at 2 cm with a distance lamp/device during irradiation of 2 cm.

The following examples are given for illustrative purposes and, although explained in details with reference to various schemes showing 2,5-thienyl as the Ar or Ar' group, can easily translated by the skilled person to other Ar groups such as phenyl, naphthyl, pyrrolyl, pyridyl, carbazolyl, fluorenyl and benzothiazolyl, by mere analogy to the teaching incorporated therein.

General Experimental Materials and methods

All chemicals were used as obtained from commercial sources, unless stated otherwise. THF and diethylether were distilled after drying with sodium wire and benzophenone until a blue colour appeared. 3-Bromothiophene was purified using short path distillation. NMR spectra were recorded on a Varian Inova 300 spectrometer at 300 MHz for ^1H and at 75 MHz for ^{13}C NMR using a 5 mm probe. Deuterated CHCl_3 was obtained from Cambridge Isotope Laboratories, Inc. ^1H and ^{13}C chemical shifts were reported downfield from tetramethylsilane (TMS) using the peak of residual CHCl_3 as an internal standard at $\delta=7.24$ ppm. UV-Vis spectra were recorded using films dropcast from a CHCl_3 solution on a quartz substrate on a Varian CARY 500 UV-Vis-NIR spectrophotometer from 200 to 800 nm at 600 nm/min. Fourier transform infrared (FT-IR) was performed on a Perkin Elmer Spectrum One FT-IR spectrometer with a nominal resolution of 4 cm^{-1} . Samples for the FTIR were pellets in KBr or films dropcast from a CHCl_3 solution. Gas chromatography/mass spectrometry (GC-MS) was carried out on TSQ-70 and Voyager mass spectrometers. Size exclusion chromatography (SEC) was performed on a 1wt% polymer solution, which was filtered with a $0.45\mu\text{m}$ pore PTFE syringe filter. A Spectra series P100 (Spectra Physics) pump equipped with two mixed-B columns ($10\mu\text{m}$, $2\times 30\text{cm}$, Polymer Labs) and a refractive index detector (Shodex) at 40°C in THF at a flow rate of 1.0 ml/min were used. Molecular weight distributions were measured relative to polystyrene standards. Toluene was used as a flow rate marker.

The morphology of thin films, prepared analogously to the active layer of the solar cells, was studied with a transmission electron microscope (TEM) (Philips CM12-STEM). Thin freestanding films were used as TEM samples and obtained by spincoating a blend on a Silicon plate, covered with a thin layer of silicon oxide. These blends were separated from the silicon substrate by dissolving the oxide layer in HF and placed on a copper grid.

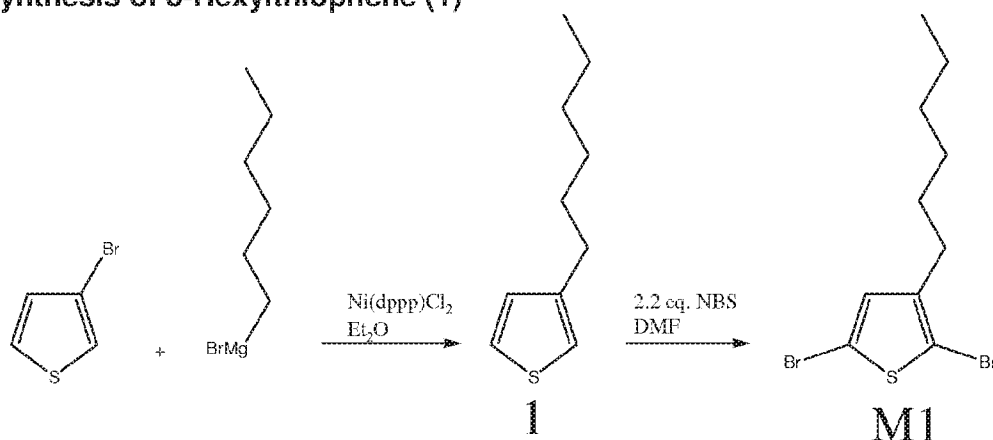
For every accelerated lifetime measurement, a new substrate with 4 solar cells was used. The displayed J_{sc} was the averaged J_{sc} of the 4 solar cells. To obtain a continuous degradation curve, outliers were removed. The influence of a prolonged thermal treatment on the photovoltaic performance of

the devices was measured in a set-up that measured Solar cell characteristics (J_{sc} , V_{oc} , FF , Eff) was measured every 30 minutes. Illumination was done with a White 5500K LED (Lamina) while the samples were kept under continuous annealing. In between the measurements, the samples were kept in the dark.

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MONOMER SYNTHESIS

Synthesis of 3-Hexylthiophene (1)



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Starting from the commercially available products 3-bromothiophene (3-BT) and hexylmagnesiumbromide, **1** was produced using a Ni catalyst. In a three-necked flask, 100ml (1 eq, 166.0 g, 1.018 mol) of bromothiophene is stirred under nitrogen atmosphere with 0.01 equivalent of $Ni(dppp)Cl_2$ (5.19 g, 0.0102 mol) and 300ml dry diethylether. 1.2 equivalent (0.611 l of a 2.0M solution in diethyl ether, 1.22 mol) of hexylmagnesiumbromide was added dropwise at a temperature of 0°C. The reaction was stirred overnight at room temperature before neutralisation by addition of a 1M HCl solution. After extraction with diethyl ether, washing with a saturated $NaHCO_3$ solution and drying over $MgSO_4$ a brown liquid was obtained. This liquid was purified by short path distillation to obtain **1** in a yield of 95.6% (163.73g, 0.973mol) at $p=7.10^{-3}$ mbar and $T=81-84^\circ C$.

Characterization: TLC (hexane): $R_f = 0.81$; ^1H NMR (300MHz, $CDCl_3$): δ 7.23(s, H), 6.95 (d, H), 6.92 (d, H), 2.63 (t, CH_2), 1.63 (q, CH_2), 1.32 (m, 3 CH_2), 0.90 (t, CH_3); ^{13}C NMR (75MHz, $CDCl_3$): δ 142.8, 130.8, 110.2, 107.2, 31.5, 29.4, 29.3, 28.7, 22.5, 14.0; GC/MS (m/z): 168 $[M]^+$, 153 $[M-CH_3]^+$, 139 $[M-CH_2CH_3]^+$, 125 $[M-(CH_2)_2CH_3]^+$, 111 $[M-(CH_2)_3CH_3]^+$, 97 $[M-$

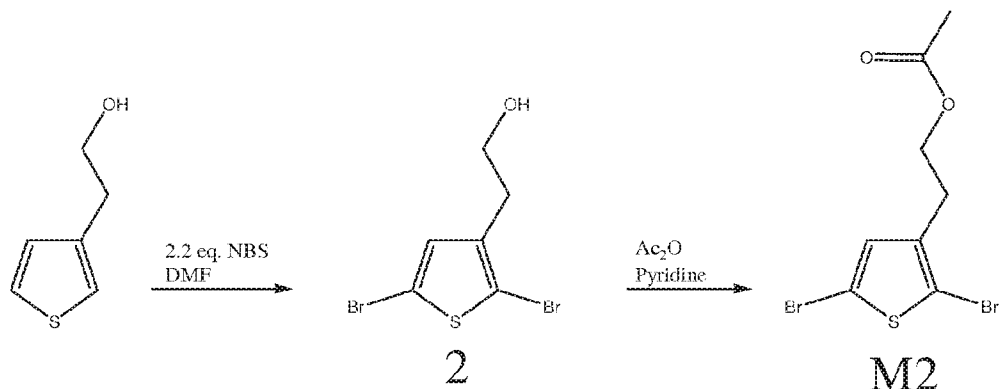
$(\text{CH}_2)_4\text{CH}_3]^+$, 85 $[\text{M} - (\text{CH}_2)_5\text{CH}_3]^+$; FT-IR: 3000- 2800 cm^{-1} (C-H stretch alkyl), 1600-1500 cm^{-1} (C=C stretch aromatic ring).

Synthesis of 2,5-dibromo-3-hexylthiophene (M1)

5 A solution of NBS (2.2 eq, 23.26 g, 0.130 mol) in 100ml DMF was added dropwise to a solution of **1** (10g, 0.059 mol) in 100ml DMF and stirred in the dark at 0°C. When addition was complete, the reaction was allowed to warm to room temperature. After stirring for 48h, the solution was added to 100ml of an ice cooled 2.5M NaOH solution and stirred before extraction with 3 x 100ml
10 diethyl ether. The organic phase was washed using 100ml of 2.5M NaOH solution, H₂O and NaCl_{sat} and dried with MgSO₄ to obtain a yellow liquid that was purified using short path distillation to yield 81% (15.50 g, 0.048mol) of a colourless liquid.

Characterization ¹H NMR (300 MHz, CDCl₃): δ 6.76 (s, H), 2.49 (t, CH₂),
15 1.53 (q, CH₂), 1.29 (m, 3 CH₂), 0.89 (t, CH₃); GC/MS (m/z): 326 [M]⁺, 255 [M - (CH₂)₄CH₃]⁺, 247 [M - Br]⁺, 177 [M - Br, (CH₂)₄CH₃]⁺, 111 [M - (CH₂)₃CH₃]⁺, 95 [M - 2Br, (CH₂)₄CH₃]⁺. FT-IR: 3000- 2800 cm^{-1} (C-H stretch alkyl); 1600-1500 cm^{-1} (C=C stretch aromatic ring).

20 2,5-dibromo-3-ethanolthiophene (2)



2 Was obtained by dibromination of 3-ethanolthiophene using NBS in an analogous procedure to that used for **M1**. 2.2 eq of NBS (32.93g, 0.185mol) was dissolved in 100ml DMF and added dropwise to 3-ethanolthiophene (1
25 eq, 10.75 g, 0.084 mol) in 100ml DMF at 0°C. The reaction was allowed to warm to room temperature and stirred for 48h. The solution was added to

100ml of an ice cooled 2.5M NaOH solution and stirred before extraction with 3 x 100ml diethyl ether. The organic phase was washed with 100ml of a 2.5M NaOH solution, H₂O and NaCl_{sat.} and dried with MgSO₄. The yellow liquid obtained was purified using short path distillation to isolate a colourless liquid
 5 (18.66g, 73.5 mmol, 95%) at $p = 4 \cdot 10^{-3}$ mbar, $T = 107^\circ\text{C}$. ¹H-NMR (300MHz; CDCl₃): δ 6.82 (s, 1H), 3.72 (t, 2H), 2.73 (t, 2H), 2.52 (s, 1 H); ¹³C-NMR (75MHz, CDCl₃): δ 139.0, 131.2, 110.7, 109.3, 61.5, 32.2; GC/MS m/z 288, 286, 284 [M]⁺ 257, 255, 253 [M - CH₂OCH]⁺ 257,255,253 [M - CH₂OC(O)CH₃]⁺ 189,187 [M - Br, OCOCH₃]⁺

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2,5-dibromo-3-acetyethanolthiophene (M2)

M2 was obtained after stirring **2** (1 eq, 36.2g, 0.143 mol) under reflux with 1.3 eq. (18.93 g, 0.185 mol) of acetic anhydride and 140 ml of pyridine for 5 hours. The mixture was neutralised by adding HCl, extracted with 3x100ml
 15 diethyl ether and washed with 3x100ml H₂O. The extract was dried over MgSO₄, filtered and evaporated. The mixture was purified with short path distillation to provide 36.2g (113 mmol, 78%) of **M2** at $p = 1 \cdot 10^{-3}$ mbar and $T = 95^\circ\text{C}$.

Characterization: TLC (hexane:diethyl ether, 8:2) $R_f = 0.81$, ¹H-NMR
 20 (300MHz, CDCl₃): δ 6.79 (s, 1H), 4.17 (t, 2 H), 2.82 (t, 2H), 2.02 (s, 3H); ¹³C-NMR (75MHz, CDCl₃): δ 170.7, 138.1, 130.8, 110.7, 109.6, 62.8, 28.7, 20.8; GC/MS (m/z) 330,328,326 [M]⁺ 270, 268, 266 [M - OCOCH₃]⁺ 257, 255, 253 [M - CH₂OC(O)CH₃]⁺ 205, 207 [M - Br]⁺ 187,189 [M - Br, OCOCH₃]⁺ 176, 174 [M - Br, CH₂OC(O)CH₃]⁺ 108 [M - 2Br, CH₂OC(O)CH₃]⁺, 95 M - 2Br, CH₂CH₂OC(O)CH₃]⁺ $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$
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POLYMER SYNTHESIS

Example 1 (comparative) - synthesis of poly(3-hexyl-thiophene) (P3HT)

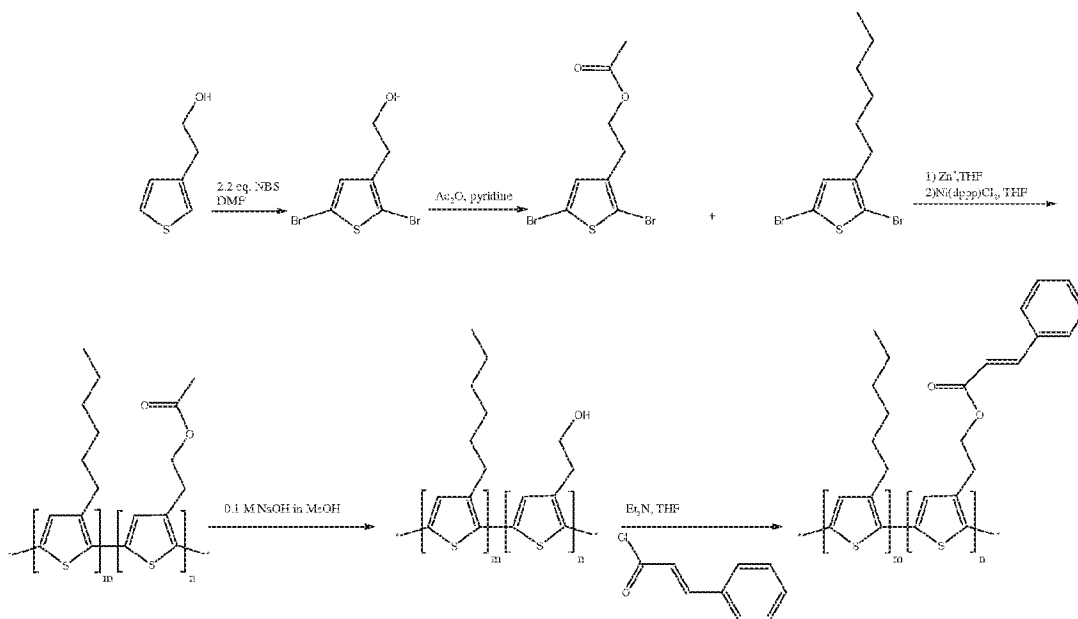
30 P3HT for use in a solar cell as a reference system was synthesized using the Rieke method for the production of highly regioregular poly(3-alkylthiophene)s. A solution of **M1** (1 eq, 10.04 g, 0.031 mol) in 80ml THF was added to active Zinc at -78°C . The organozinc solution formed was added

to a solution of 0.002 eq (0.035 g, $6.4 \cdot 10^{-5}$ mol) Ni(dppp)Cl₂ in 40ml THF and stirred under inert atmosphere at 60°C for 18h. The crude polymer was precipitated in a MeOH/ 2M HCl (2/1, v/v) mixture and purified by solid phase extraction with methanol and hexane. The purified polymer was extracted with

5 chloroform and precipitated in MeOH before filtration and drying, yielding 3.63g (67%) of conjugated polymer.

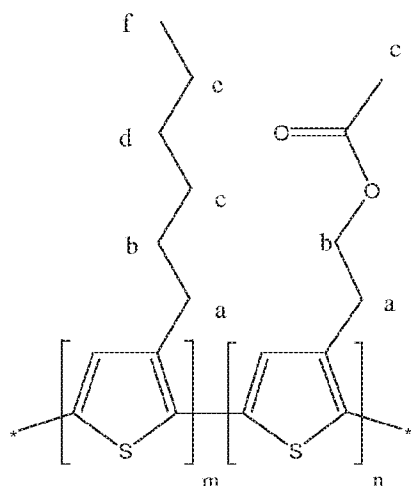
- GPC (THF): $M_n = 27,800$; $M_w = 53,500$; polydispersity index, $D = 1.9$;

10 **Example 2 - synthesis of random copolymers of 3-hexylthiophene (M1) and 3-(2-acetoxyethyl)thiophene (M2) (P1), random copolymers of 3-hexylthiophene and 3-hydroxyethylthiophene (P2), and random copolymers with a 9:1 molar ratio of 3-hexylthiophene and 3-cinnamoyloxyethylthiophene (P3)**



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a) **synthesis of poly-3-hexylthiophene-co-3-(2-acetoxyethyl)thiophene (P1).**

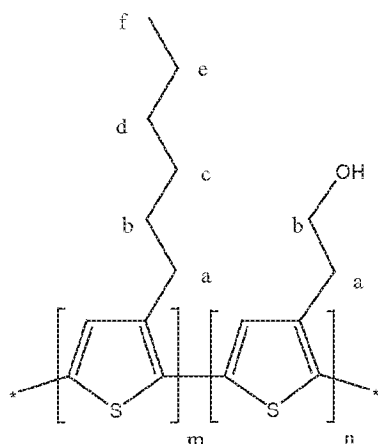


(P1)

A solution of a mixture of 2,5-dibromo-3-(2-acetoxyethyl)thiophene (**M2**) (10 % molar) (1.05 g, 0.003 mol) and 2,5-dibromo-3-hexylthiophene (**M1**) (90 % molar) (9.41 g, 0.029 mol) in THF was added to active zinc at -78 °C to form an organozinc solution which was then polymerised in the presence of a Ni(dppp)Cl₂ catalyst. After reaction, the co-polymer was precipitated in a mixture of MeOH and 2M HCl (2/1). The crude co-polymer was purified using a soxhlet extraction with methanol and pentane. The purified poly-3-hexylthiophene-co-3-(2-acetoxyethyl)thiophene (**P1**) was extracted with chloroform and precipitated again in MeOH, before filtration and drying to obtain 3.18 g of a 9/1 copolymer in 61% yield, which was characterised as follows:

- GPC (THF): $M_n = 34,400$; $M_w = 65,500$; polydispersity index, $D = 1.9$ giving an average of 207 repeating units/chain;
- ¹H-NMR (CDCl₃): $\delta = 7.00$ (1H_{arom,AcET}, s), 6.96 ppm (1H_{arom,3HT}, s), 4.35 ppm (2H_{b,AcET}, t), 3.14 ppm (2H_{a,AcET}, t), 2.79 ppm (2 H_{a,3HT}, t), 2.05 ppm (3H_{c,AcET}, s) 1.70 ppm (2 H_{b,3HT}, t), 1.45 ppm (2 H_{c,3HT}, m), 1.40 ppm (2 H_{d,3HT}, m), 1.35 ppm (2 H_{e,3HT}, m), and 0.90 ppm (3 H_{f,3HT}, t);
- UV/Vis: λ_{max} at 555 nm; sh at 600 nm;
- infrared spectrum: see Table 1 below.

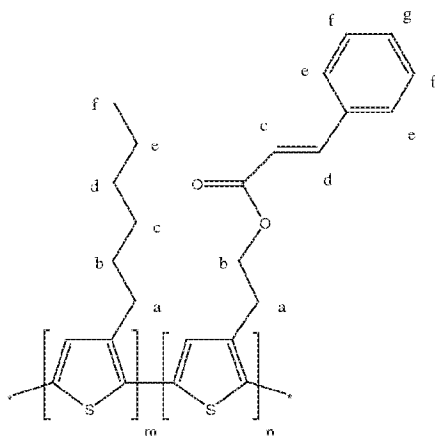
b) synthesis of poly-3-hexylthiophene-co-3-(2-hydroxyethyl)thiophene (P2)

**P2**

1.04 g Polymer (**P1**) was refluxed under an inert atmosphere with 100 mL of 0.1 M NaOH solution in MeOH to yield **P2** in 100% yield, which was characterised as follows:

- GPC (THF): $M_n = 31,300$, $M_w = 68,100$, $D = 2.2$ giving an average of 190 repeating units/chain;
- $^1\text{H-NMR}$ (CDCl_3): $\delta = 7.03$ ($1\text{H}_{\text{arom,ET}}$, s), 6.96 ppm ($1\text{H}_{\text{arom,3HT}}$, s), 3.94 ppm ($2\text{H}_{\text{b,ET}}$, t), 3.09 ppm ($2\text{H}_{\text{a,ET}}$, t), 2.79 ppm ($2\text{H}_{\text{a,3HT}}$, t), 1.70 ppm ($2\text{H}_{\text{b,3HT}}$, t), 1.45 ppm ($2\text{H}_{\text{c,3HT}}$, m), 1.40 ppm ($2\text{H}_{\text{d,3HT}}$, m), 1.25 ppm ($2\text{H}_{\text{e,3HT}}$, m), and 0.90 ppm ($3\text{H}_{\text{f,3HT}}$, t);
- UV/Vis: λ_{max} at 551 nm, sh, at 600 nm;
- infrared spectrum: see Table 1 below.

c) synthesis of poly-co-(3-hexylthiophene-co-3-cinnamoyloxyethylthiophene (**P3**))



P3

- 0.61 g **P3** was obtained in 95% yield by reacting 0.60 g poly-3-hexylthiophene-co-3-(2-hydroxyethyl)thiophene (**P2**) with 0.62 g (0.004 mol) cinnamoyl chloride in THF in the presence of 0.37 g (0.004 mol) triethylamine, and was purified using soxhlet extraction with methanol and acetone before characterisation as follows:
- GPC (THF): $M_n = 33,100$, $M_w = 74,500$, $D = 2.2$ giving an average of 193 repeating units/chain;
 - $^1\text{H-NMR}$ (CDCl_3): $\delta = 7.67$ ppm ($1\text{H}_{\text{d, cin}}$, d), 7.47 ppm ($2\text{H}_{\text{e, cin}}$, m), 7.32 ppm ($2\text{H}_{\text{f, cin}}$, m), 7.05 ppm ($1\text{H}_{\text{g, cin}}$, m), 6.96 ppm ($1\text{H}_{\text{arom, 3HT and cin}}$, s), 6.42 ppm ($1\text{H}_{\text{c, cin}}$, d), 4.49 ppm ($2\text{H}_{\text{b, cin}}$, t), 3.23 ppm ($2\text{H}_{\text{a, cin}}$, t), 2.79 ppm ($2\text{H}_{\text{a, 3HT}}$, t), 1.70 ppm ($2\text{H}_{\text{b, 3HT}}$, m), 1.40 ppm ($2\text{H}_{\text{c, 3HT}}$, m), 1.35 ppm ($2\text{H}_{\text{d, 3HT}}$, m), 1.25 ppm ($2\text{H}_{\text{e, 3HT}}$, m), and 0.90 ppm ($3\text{H}_{\text{f, 3HT}}$, t); and integrations originating from the **M2** monomer unit corresponded to about 10% of a comparable integration originating from the **M1** monomer unit, indicating that 1 out of 10 monomer units has a functionalized side chain. Disappearance of the methyl group in the acetyler of the **P1** side chain at $\delta = 2.05$ ppm proved hydrolysis was completed. The complete functionalisation was also illustrated by a change in chemical shift of CH_2 – proton signals in **P3** because of a different ester.
 - Appearance of double bond and aromatic proton signals in the functionalized polymer confirmed the presence of the cinnamoyl ester in the side chain.
 - UV/Vis: λ_{max} at 275 nm and 551 nm, sh. at 600 nm. λ_{max} at 275 nm of polymer films dropcast from chloroform solutions was due to the presence of the cinnamic acid ester in the copolymer side chain. In the absorption region of the conjugated polymer, the shoulder at 600 nm had a higher intensity, but was less sharply pronounced. After 2 hours UV-exposure of such a film of **P3** the intensity of the 275 nm peak decreased ca. 10% indicating that some cinnamoyl moieties had disappeared due to photo-initiated [2+2] cyclo-addition. With an average of about 200 monomer units in a polymer chain, there were thus an average of 2 side chains that were linked to another chain, which accounted for the immobilization and enhanced thermal stability after such exposure;
 - infrared spectrum: see Table 1 below.

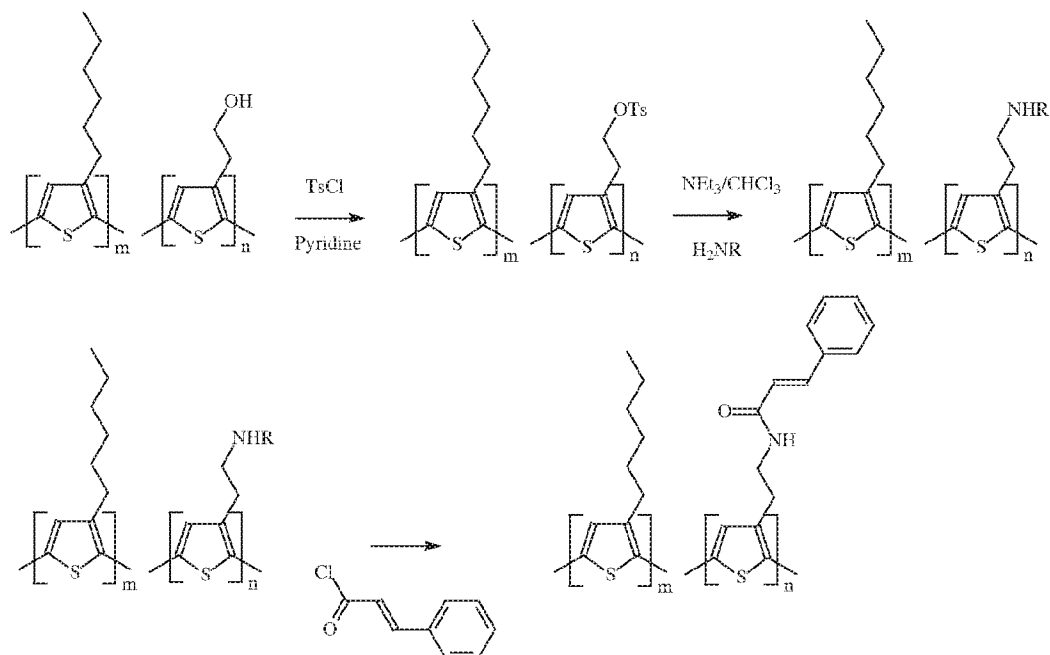
Table 1 - wavenumber (cm^{-1}) of absorptions observed in FT-IR

Absorption:	P3HT homopolymer (3)	10% ester functionalised copolymer (P1)	10% ethanol functionalised copolymer (P2)	10% cinnamon functionalised copolymer (P3)
C-H stretch on aromatic ring	2953	2952	2952	2950
C-H stretch in aliphatic chain	2923	2922	2922	2923
C-H stretch in aliphatic chain	2853	2853	2852	2853
C=O stretch ester bond	-	1742	-	1715
Conjugated system	1635	1635	1640	1635
C=C asymmetric ring stretch	1508	1507	1508	1505
C=C symmetric ring stretch	1454	1452	1455	1449
methyl deformation	1376	1376	1376	1375
C-O stretch	-	1225	1262	1259
C-H in plane bending of 2,3,5 substituted thiophene	1088	1032	1046	1075
C-H out of plane bending of 2,3,5 substituted thiophene or C-S stretching	820	819	821	818
methyl rock	724	723	723	721

- 5 The C=O ester absorption at around 1740 cm^{-1} in **P1** disappeared upon its hydrolysis to **P2**. Upon functionalisation of **P2** to **P3** a peak at around 1715 cm^{-1} appeared due to the C=O bond of the cinnamic ester group.

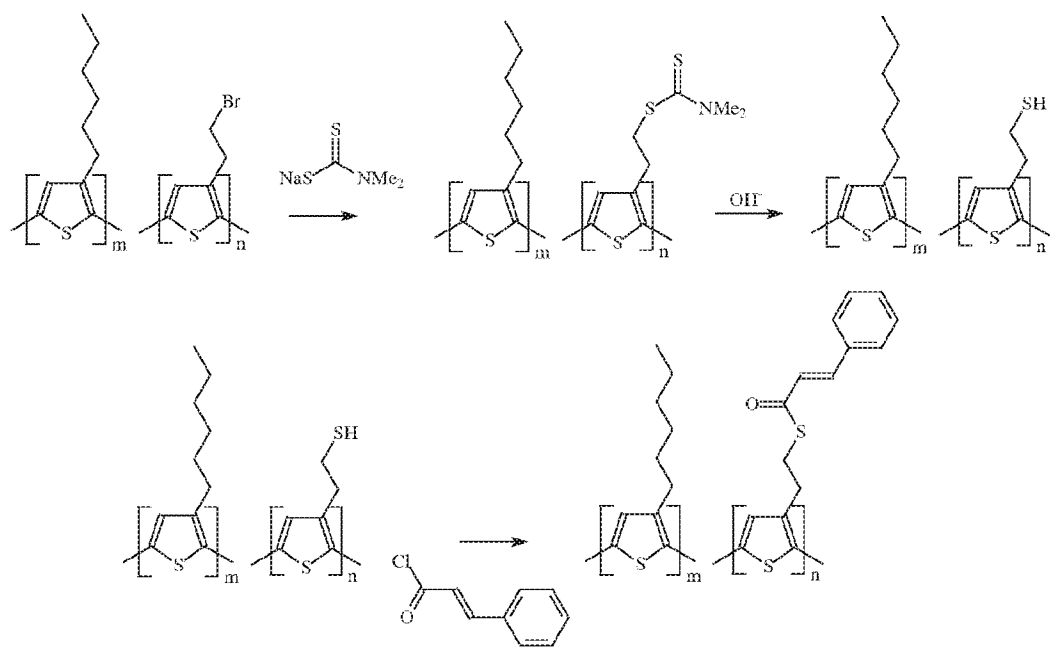
Example 3 – synthesis of random copolymers of 3-hexylthiophene and 3-cinnamoylaminoethylthiophene (P4).

- 10 The synthesis proceeds according to the following scheme and provides a copolymer comprising recurrent units from a monomer represented by the structural formula (I) wherein L is NH.



Example 4 – synthesis of random copolymers of 3-hexylthiophene and 3-cinnamoylthioethylthiophene (P5).

- 5 The synthesis proceeds according to the following scheme and provides a copolymer comprising recurrent units from a monomer represented by the structural formula (I) wherein L is S.



Example 5 - Fabrication and comparative study of the nano-morphology of two active layers made respectively of a comparative semi-conducting polymer P3HT (3) and a n-type material (fullerene derivative) for Film A, and the random copolymer (P3) of example 2 and a n-type material (fullerene derivative) for "Film B"

In the TEM pictures of Fig. 7-8, a phase separation in the thin film B was observed after 2 hours at 110°C. This phase separation was similar to these observed for the film A heated in the same conditions (Fig. 3 and 5). This phase separation was prevented when the thin film B was preliminarily UV cured: the nano-morphology of the film was then stable (Fig. 9-10). Film A and Film B as deposited, i.e. before heat treatment, are shown in Fig. 2 and 6 respectively for comparison purpose. Figure 4 shows an electron diffraction of a black spot as visible in Fig. 3. The diffraction pattern indicates that the black spots are PCBM crystals.

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Example 6 - Fabrication and study of the power efficiency of organic bulk heterojunction solar cells having the random copolymer (P3) of example 2 as p-type material in the active layer.

Solar cells were prepared on glass ITO-patterned substrates. The substrates were cleaned with sonicating in soapy water, Milli-Q water, acetone and heated in isopropanol before a UV/O₃ treatment. A 30 nm thick PEDOT:PSS (Baytron P) layer was spincoated from aqueous dispersion on the ITO electrode. This was dried for 15 minutes at 130°C. A ca. 250 nm thick 1/1 (w/w) blend of the copolymer (P3) of example 2, containing 10% by moles of a cinnamic acid ester functionalised monomer, with PCBM active layer was spincoated from chlorobenzene solution and annealed for 10 minutes on a hotplate at 130°C. Then the Ytterbium top electrode was evaporated on the active layer in vacuum ($1 \cdot 10^{-6}$ mbar) until the electrode reached a thickness of 100 nm. The active surface of each solar cell was 3 mm². After clearing the ITO contacts, I-V measurements were performed in a nitrogen atmosphere under AM 1.5G simulation, using an Oriel simulator equipped with a 150W Xenon short arc lamp. These cells displayed a Fill Factor of 0.60. The Short Circuit Current (J_{sc}) reached 8.74 mA/cm². Together with an Open Circuit

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Voltage (V_{oc}) of 0.59V: this leads to a power efficiency of 3.22% comparable to a value of 3.95% with the P3HT/PCBM-blend. Fig. 11 displays the I-V curve and Table 2 compares the initial device characteristics for P3HT/PCBM- and P3/PCBM-blends.

5

Table 2:

Blend [1:1 w/w]	J_{sc} [mA/cm ²]	V_{oc} [V]	FF	Power efficiency [%]
P3HT/PCBM	10.93	0.60	0.60	3.95
P3 /PCBM	8.87	0.59	0.62	3.22

Then the cell was UV-cured for 2 hours in a nitrogen atmosphere with UV-light ($\lambda = 254$ nm), whose spectrum is shown in Fig. 1, in a Lawtronics ME5 exposure unit and the power efficiency was measured again: a value of 3.22% was then measured indicating that UV curing had no influence on the power efficiency of the cell.

Example 7 - Fabrication and comparative study of the power efficiency, open circuit voltage, Fill factor and short-circuit current versus time of two organic bulk heterojunction solar cells having respectively P3HT for "cell A" and the random copolymer P3 of example 2 for "cell B" as p-type material in their active layer.

Accelerated lifetime measurements were performed on solar cells with 1:1 (w/w) blends of P3HT and the 10 % cinnamic acid ester functionalized copolymer of example 2 (**P3**) with PCBM, after 2 hours exposure in the Lawtronics ME5 exposure unit used in Example 6 in the case of the **P3**/blend, and kept at temperatures of 80,100 and 150°C in a specially developed heating chamber for at least 100 hours. The top electrode used was typically 20 nm Ca and 80 nm Al. The device was kept in the dark between measurements. The relative values for a given parameter are given as the ratio of the value at time t to the initial value at time t_0 . In these experiments, the performances of the solar cells with P3HT/PCBM- and **P3**/PCBM -blends were clearly different.

The relative open circuit voltages (V_{oc}), Fill Factors (FF), short-circuit current (J_{sc}) values and power efficiencies of the solar cells with 1:1 (w/w) P3HT/PCBM-blends and **P3**/PCBMblends as a function of time are shown in Fig. 12 to Fig. 15 for a temperature of 80°C, Fig. 16 to Fig. 19 for a temperature of 100°C and Fig. 20 to Fig. 23 for a temperature of 150°C. Note the different timescales at different temperatures.

At temperatures of 100°C or less, the decline in efficiency of J_{sc} proceeded according to a pseudo-linear behaviour for P3HT. This decline in efficiency was more marked than with solar cells with a crosslinked **P3**/PCBM active layer.

Figures 12 to 15 show that at a temperature of 80°C, the relative FF decreased very slightly and pseudo-linearly with time for the blend with **P3**, whereas the blend with P3HT exhibited slightly lower relative FF values in a pseudo-linear decrease for the first 400 hours after which the deviation in FF for the blend with P3HT increased strongly with time, the relative V_{oc} values for both blends first decreased and then the relative V_{oc} value for the **P3**-blend declined slightly linearly whereas the relative V_{oc} value for the P3HT-blend first decreased slightly more strongly up to 500 hours before increasing and at 800 hours exceeded the value for the **P3**-blend, and the relative J_{sc} value for the **P3**-blend first increased and then decreased pseudo-linearly passing the initial value after about 800 hours whereas the relative J_{sc} value for the P3HT-blend decreased pseudo-linearly by about 20% after 800 hours. The resulting relative power efficiency values mirrored the relative J_{sc} -time characteristics with a reduction in relative power efficiency after 800 hours of about 7% with the P3/PCBM-blend and about 25% with the P3HT/PCBM-blend.

Fig. 16 to 19 show that at a temperature of 100°C, the relative FF value for the **P3**-blend initially rose slightly and then decreased linearly very slightly, whereas for the P3HT-blend there is a strong pseudo-linear decline of 12.5% after 100 hours, the relative V_{oc} -value for the **P3**-blend rose slightly and then stabilized over 100 hours whereas although the initial relative V_{oc} -value for the P3HT-blend was slightly higher there was a pseudo-linear decline of 15% after 100 hours, the relative short circuit current of Cell B (according to an embodiment of the present invention) was stable over time (more than 110

hours) whereas that for cell A (comparative) declined pseudo-linearly by 15% after 100 hours, and the relative power efficiency of Cell B was also stable over time (more than 110 hours) whereas that for Cell A (comparative) decreased pseudo-linearly by ca. 38% after 100 hours.

5

Figures 20 to 23 show that at a temperature of 150°C the relative FF value decreased slightly and linearly with time for the blend with **P3**, whereas the blend with P3HT showed a pronounced exponential decrease in relative FF value from comparable start values, the relative V_{oc} -values also decreased with time with again a much reduced pseudo-linear decrease with the blend with **P3** compared with a pronounced exponential decrease in the case of the blend with P3HT, and the relative J_{sc} value for the blend with **P3** exhibited a slight increase whereas the value for the blend with P3HT showed a pronounced exponential decrease to about 53% of the initial value after 40 hours, and the relative power efficiency for the blend with **P3** increased by about 10% and then exhibited a linear back to the initial value after 50 hours whereas the power efficiency value for the blend with P3HT showed a pronounced exponential decline by about 78% of the initial value after 40 hours.

20 An estimate of the likely lifetime of solar cells on the basis of **P3**/PCBM- and P3HT/PCBM-blends at operating temperatures of 25°C and 50°C was made using the activation energy values derived from the data at 80, 100 and 150°C i.e. 0.95 eV for both the P3HT/PCBM and **P3**/PCBM blends yielded the lifetimes to a particular decrease in short-circuit current given in Table 3
25 below.

Table 3:

Maximum permissible decrease in J_{sc}	Cell A with P3HT/PCBM-blend [comparative]		Cell B with P3 /PCBM-blend [present invention]	
	Lifetime at 25 °C [years]	Lifetime at 50 °C [years]	Lifetime at 25 °C [years]	Lifetime at 50 °C [years]
10%	10.9	0.6	49.3	2.8

20%	21.7	1.2	98.6	5.6
25%	27.1	1.6	123.2	7.1
50%	54.3	3.1	246.5	14.1

The lifetime estimates are considerably longer for solar cell B with the P3/PCBM blend, according to the present invention, than for solar cell A with the P3HT/PCBM blend (comparative example) both at 25°C and 50°C.

5

Example 8 - synthesis of random copolymers of 3-hexylthiophene (M1) and 3-(2-acetoxyethyl)thiophene (M2), random copolymers of 3-hexylthiophene and 3-hydroxyethylthiophene (P2), and random copolymers with a 7:3 molar ratio of 3-hexylthiophene and 3-cinnamoyloxyethylthiophene (P6).

10

The random copolymers with a 7:3 molar ratio of 3-hexylthiophene and 3-cinnamoyloxyethylthiophene (P6) was prepared entirely analogously to P3 except that the molar ratio of the 3-hexyl thiophene to 2,5-dibromo-3-acetylanthiophene (M2), 2,5-dibromo-3-ethanolthiophene (2) and cinnamoylthiophene respectively was 7:3.

15

Example 9 - fabrication and comparative study of the power efficiency of two organic bulk heterojunction solar cells having respectively P3HT for "cell A", the random copolymer P3 of example 2 for "cell B" as p-type material in their active layer and the random copolymer P6 of example 8 for "cell C" as p-type material.

20

The solar cells of Example 9 were produced as described for Example 6 except that in addition to solar cells of with a 1:1 (w/w) P3HT/PCBM-blend and solar cells with a 1:1 (w/w) P3/PCBM-blend solar cells were also produced with a 1:1 (w/w) P6/PCBM-blend. The solar cells were kept at temperatures of 125 and 150°C for at least 100 hours, but in the case of P3/PCBM- and P6/PCBM-blends after the solar cells were irradiated 2 hours with the UV-lamp used in Example 6. In these experiments, the performances of the solar cells made with these polymer blends were clearly different.

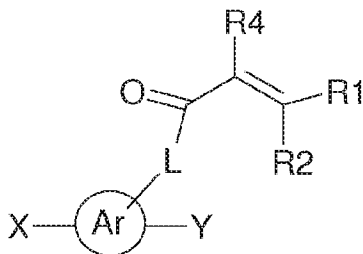
25

The relative open circuit voltages (V_{oc}), Fill Factors (FF), short-circuit current (J_{sc}) values and efficiencies of the solar cells of P3HT, **P3** and **P6** with PCBM (1/1) as a function of time are shown in Fig. 24 to Fig. 27 for a temperature of 125 °C. The relative power efficiency with the blend of

5 **P6**/PCBM-blend initially increased strongly to 200% of the initial value reflecting strong initial increases in Fill Factor and open-circuit current and even after 150 hours was still ca. 50% above its initial value, whereas the relative power efficiency in the case of the **P3**/PCBM-blend exhibited a pseudo-linear decline to about 75% of its initial value.

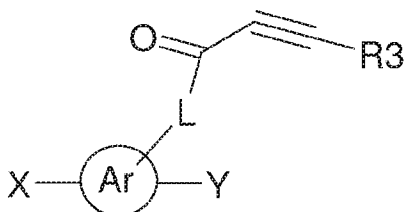
CLAIMS

1. A compound represented by the structural formula (I)



5

or the structural formula (II)



10

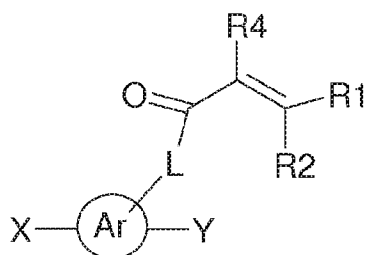
wherein:

- Ar is a homocyclic or heterocyclic aromatic group selected from the group consisting of thienyl, phenyl, naphthyl, pyrrolyl, pyridyl, carbazolyl, fluorenyl and benzothiazolyl;
- L is selected from the group consisting of $-O-$, $-CH(CH_3)-O-$ and $-(CH_2)_q-O-$, $-NH-$, $-CH(CH_3)-NH-$, $-(CH_2)_q-NH-$, $-S-$, $-CH(CH_3)-S-$ and $-(CH_2)_q-S-$, the oxygen atom of said $-CH(CH_3)-O-$ or $-(CH_2)_q-O-$ being adjacent to the carbonyl group, the NH group of said $-CH(CH_3)-NH-$ or $-(CH_2)_q-NH-$ being adjacent to the carbonyl group and the sulphur atom of said $-CH(CH_3)-S-$ or $-(CH_2)_q-S-$ being adjacent to the carbonyl group
- L is selected from the group consisting of $-O-$, $-CH(CH_3)-O-$ and $-(CH_2)_q-O-$, NH and S, the oxygen atom of said $-CH(CH_3)-O-$ or $-(CH_2)_q-O-$ being adjacent to the carbonyl group;
- q is 1, 2 or 3;
- R_1 and R_2 are hydrogen;
- R_3 is selected from the group consisting of hydrogen, C_{1-4} -alkyl and phenyl;
- R_4 is methyl; and

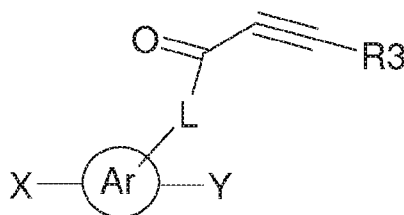
25

- X and Y are independently selected from the group consisting of hydrogen, chloro, bromo, iodo, boronic acid, boronic esters and organotin, provided that X and Y are not both hydrogen.

5 2. A compound represented by the structural formula (I)



or the structural formula (II)



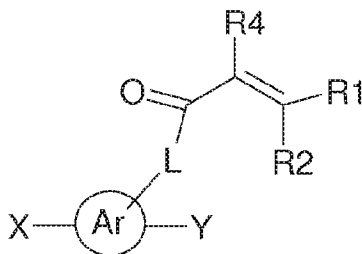
wherein:

- Ar is a homocyclic or heterocyclic aromatic group selected from the group consisting of thienyl, phenyl, naphthyl, pyrrolyl, pyridyl, carbazolyl, fluorenyl and benzothiazolyl;
- L is selected from the group consisting of $-O-$, $-\text{CH}(\text{CH}_3)-O-$ and $-(\text{CH}_2)_q-O-$, $-\text{NH}-$, $-\text{CH}(\text{CH}_3)-\text{NH}-$, $-(\text{CH}_2)_q-\text{NH}-$, $-\text{S}-$, $-\text{CH}(\text{CH}_3)-\text{S}-$ and $-(\text{CH}_2)_q-\text{S}-$, the oxygen atom of said $-\text{CH}(\text{CH}_3)-O-$ or $-(\text{CH}_2)_q-O-$ being adjacent to the carbonyl group, the NH group of said $-\text{CH}(\text{CH}_3)-\text{NH}-$ or $-(\text{CH}_2)_q-\text{NH}-$ being adjacent to the carbonyl group and the sulphur atom of said $-\text{CH}(\text{CH}_3)-\text{S}-$ or $-(\text{CH}_2)_q-\text{S}-$ being adjacent to the carbonyl group;
- q is 1, 2 or 3;
- R_1 is hydrogen;
- R_2 is methyl or ethyl or *n*-propyl or *n*-butyl, or phenyl optionally mono-substituted with fluoro, chloro or methoxy;
- R_3 is selected from the group consisting of hydrogen, C_{1-4} -alkyl and phenyl;

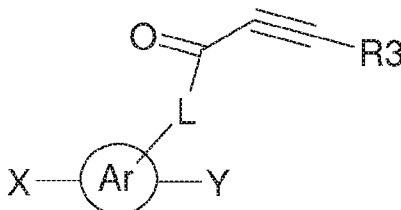
- R₄ is hydrogen; and
- X and Y are independently selected from the group consisting of hydrogen, chloro, bromo, iodo, boronic acid, boronic esters and organotin, provided that X and Y are not both hydrogen.

5

3. A compound represented by the structural formula (I)



10 or the structural formula (II)

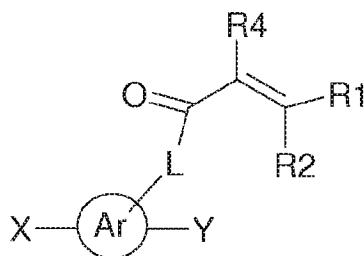


wherein:

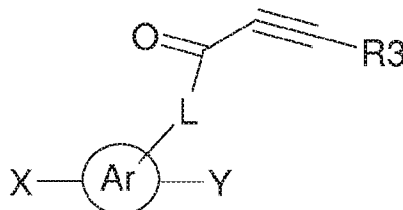
- Ar is a homocyclic or heterocyclic aromatic group selected from the group consisting of thienyl, phenyl, naphthyl, pyrrolyl, pyridyl, carbazolyl, fluorenyl and benzothiazolyl;
- L is selected from the group consisting of O, -CH(CH₃)-O- and -(CH₂)_q-O-, -NH-, -CH(CH₃)-NH-, -(CH₂)_q-NH-, -S-, -CH(CH₃)-S- and -(CH₂)_q-S-, the oxygen atom of said -CH(CH₃)-O- or -(CH₂)_q-O- being adjacent to the carbonyl group, the NH group of said -CH(CH₃)-NH- or -(CH₂)_q-NH- being adjacent to the carbonyl group and the sulphur atom of said -CH(CH₃)-S- or -(CH₂)_q-S- being adjacent to the carbonyl group;
- q is 1, 2 or 3;
- R₁ and R₂ are hydrogen;
- R₃ is selected from the group consisting of hydrogen, C₁₋₄-alkyl and phenyl;
- R₄ is hydrogen; and

- X and Y are independently selected from the group consisting of hydrogen, chloro, bromo, iodo, boronic acid, boronic esters and organotin, provided that X and Y are not both hydrogen.

- 5 4. A polymer comprising one or more repeating units derived from a compound represented by the structural formula (I)



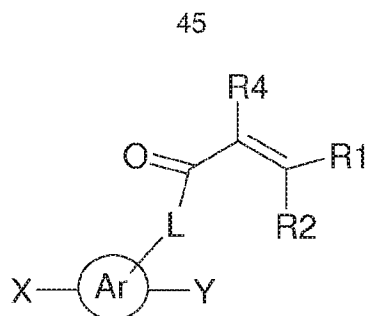
- 10 or the structural formula (II)



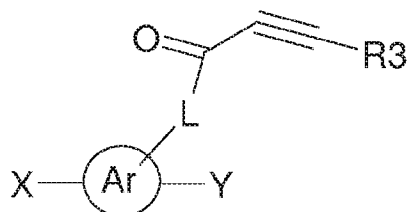
wherein:

- Ar is a homocyclic or heterocyclic aromatic group selected from the group consisting of thienyl, phenyl, naphthyl, pyrrolyl, pyridyl, carbazolyl, fluorenyl and benzothiazolyl;
- L is selected from the group consisting of -O-, -CH(CH₃)-O- and -(CH₂)_q-O-, -NH-, -CH(CH₃)-NH-, -(CH₂)_q-NH-, -S-, -CH(CH₃)-S- and -(CH₂)_q-S-, the oxygen atom of said -CH(CH₃)-O- or -(CH₂)_q-O- being adjacent to the carbonyl group, the NH group of said -CH(CH₃)-NH- or -(CH₂)_q-NH- being adjacent to the carbonyl group and the sulphur atom of said -CH(CH₃)-S- or -(CH₂)_q-S- being adjacent to the carbonyl group;
- q is 1, 2 or 3;

- R₁ and R₂ are independently selected from the group consisting of hydrogen, C₁₋₄ alkyl and phenyl, wherein said phenyl is optionally substituted with one or more substituents independently selected from the group consisting of halogen and methoxy;
 - 5 - R₃ is selected from the group consisting of hydrogen, C₁₋₄-alkyl and phenyl;
 - R₄ is hydrogen or methyl; and
 - X and Y are independently selected from the group consisting of hydrogen, chloro, bromo, iodo, boronic acid, boronic esters and organotin, provided that X and Y are not both hydrogen.
 - 10
5. The polymer according to claim 4, further comprising one or more repeating units derived from a co-monomer copolymerisable with said compound according to claim 1, said repeating units comprising a
- 15 divalent homocyclic or heterocyclic aromatic group Ar' optionally substituted with one or more substituents independently selected from the group consisting of C₁₋₂₀-alkyl, C₁₋₂₀-alkoxy, C₁₋₂₀-alkylsulfate, phenyl and benzyl.
- 20 6. The polymer according to claim 5, wherein said co-monomer comprises the same homocyclic or heterocyclic aromatic group Ar' as the group Ar in said compound according to claim 1.
- 25 7. The polymer according to claim 6, wherein Ar and Ar' are both 2,5-thienylene.
8. The polymer according to any one of claims 5 to 7, wherein said co-monomer represents from 0.5 % to 99.5% by mole of said polymer.
- 30 9. A method for producing a compound represented by the structural formula (I)



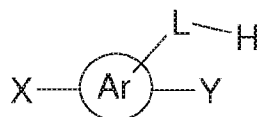
or the structural formula (II)



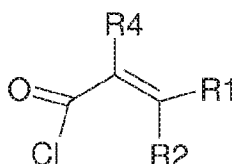
wherein:

- Ar is a homocyclic or heterocyclic aromatic group selected from the group consisting of thienyl, phenyl, naphthyl, pyrrolyl, pyridyl, carbazolyl, fluorenyl and benzothiazolyl;
- L is selected from the group consisting of $-O-$, $-\text{CH}(\text{CH}_3)-O-$ and $-(\text{CH}_2)_q-O-$, $-\text{NH}-$, $-\text{CH}(\text{CH}_3)-\text{NH}-$, $-(\text{CH}_2)_q-\text{NH}-$, $-\text{S}-$, $-\text{CH}(\text{CH}_3)-\text{S}-$ and $-(\text{CH}_2)_q-\text{S}-$, the oxygen atom of said $-\text{CH}(\text{CH}_3)-O-$ or $-(\text{CH}_2)_q-O-$ being adjacent to the carbonyl group, the NH group of said $-\text{CH}(\text{CH}_3)-\text{NH}-$ or $-(\text{CH}_2)_q-\text{NH}-$ being adjacent to the carbonyl group and the sulphur atom of said $-\text{CH}(\text{CH}_3)-\text{S}-$ or $-(\text{CH}_2)_q-\text{S}-$ being adjacent to the carbonyl group;
- q is 1, 2 or 3;
- R_1 and R_2 are independently selected from the group consisting of hydrogen, C_{1-4} -alkyl and phenyl, wherein said phenyl is optionally substituted with one or more substituents independently selected from the group consisting of halogen and methoxy;
- R_3 is selected from the group consisting of hydrogen, C_{1-4} -alkyl and phenyl;
- R_4 is hydrogen or methyl; and
- X and Y are independently selected from the group consisting of hydrogen, chloro, bromo, iodo, boronic acid, boronic esters and organotin, provided that X and Y are not both hydrogen,

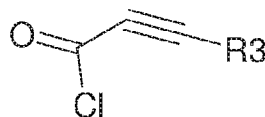
said method, comprising reacting a hydroxyl-substituted homocyclic or heterocyclic aromatic compound represented by the structural formula (III)



- 5 with an ethylenically unsaturated carbonyl chloride represented by the structural formula (IV)



or the corresponding carboxylic anhydride, or an acetylenically unsaturated carbonyl chloride represented by the structural formula (V)



10

10. The method according to claim 9, wherein said ethylenically unsaturated carbonyl chloride represented by the structural formula (IV) is selected from the group consisting of crotonyl chloride, acryloyl chloride, methacryloyl chloride, pent-2-enoyl chloride, hex-2-enoyl chloride, hept-2-enoyl chloride, cinnamoyl chloride, 2-chlorocinnamoyl chloride, 4-fluorocinnamoyl chloride, and 4-methoxycinnamoyl chloride.
- 15
11. The method according to claim 9, wherein said acetylenically unsaturated carbonyl chloride represented by the structural formula (V) is selected from the group consisting of propiolic acid chloride, phenylpropionic acid chloride, 2-butyric acid chloride, 2-pentynoic acid chloride, and 2-hexynoic acid chloride.
- 20
12. The method according to any one of claims 9 to 11, wherein said hydroxyl-substituted homocyclic or heterocyclic aromatic compound represented by the structural formula (III) is selected from the group
- 25

consisting of 2,5-dibromo-3-hydroxyethyl thiophene, 2,5-dibromo-3-hydroxymethyl thiophene, 2,5-dibromophenol, 2-bromophenol, 3-bromophenol, 4-bromophenol, 2,5-dibromo-1-(2-hydroxyethyl)benzene, 2-bromobenzyl alcohol, 3-bromobenzyl alcohol, 4-bromobenzyl alcohol, 4-hydroxyphenylboronic acid, 4-(hydroxymethyl)phenylboronic acid, 3-(hydroxymethyl)phenylboronic acid, 2,6-dibromo-4-(2-hydroxyethyl)-pyridine, 2,6-dibromo-3-(2-hydroxyethyl)pyridine, (S)-2,6-dibromo-4-(1-hydroxyethyl)pyridine, (R)-2,6-dibromo-4-(1-hydroxyethyl)pyridine, 2,6-dibromo-4-(hydroxymethyl)-pyridine, 2,6-dibromo-3-(hydroxymethyl)-pyridine, 2,6-dibromo-3-(3-hydroxypropyl)-pyridine, 3,6-dibromo-9H-2-hydroxycarbazole, 3,6-dibromo-9H-4-hydroxycarbazole, 2,7-dibromo-9-hydroxyfluorene, 2,7-dibromo-9-hydroxymethylfluorene, 1,4-dibromo-2-naphthol, 1,4-dibromo-2-naphthalenemethanol and 4,7-dibromo-2-hydroxybenzothiazole.

15

13. A method for producing a polymer according to claim 4, comprising polymerising a compound represented by formula (I) or formula (II) by reductive coupling.
- 20 14. A method for producing a copolymer according to claim 5, comprising copolymerising by reductive coupling a compound represented by formula (I) or formula (II) and one or more co-monomers.
- 25 15. A process for preparing a polymer comprising the following steps:
 - copolymerization of a monomer post-functionalisable to a compound represented by structural formula (I) or structural formula (II) in claim 4 with a co-monomer copolymerisable therewith, said co-monomer being a divalent homocyclic or heterocyclic aromatic group Ar' optionally substituted with one or more substituents independently selected from the group consisting of C₁₋₂₀-alkyl, C₁₋₂₀-alkoxy, C₁₋₂₀-alkylsulfate, phenyl and benzyl, to produce a post-functionalisable copolymer; and post-functionalizing said post-functionalisable copolymer to produce a polymer according to claim 5.
- 30

16. The process according to claim 15, wherein said copolymerization is by reductive coupling.
- 5 17. A blend comprising:
- a polymer according to any one of claims 4 to 8, and
 - a n-type or p-type compound.
- 10 18. A method for producing a crosslinked polymer material, comprising the step of irradiating a blend according to claim 17 with ultra-violet light.
19. The method for producing a crosslinked polymer material according to claim 18, wherein said step is performed in the absence of a photoinitiator.
- 15 20. An opto-electronic device comprising a crosslinked polymer material, obtained by irradiating a blend according to claim 17.
- 20 21. The opto-electronic device according to claim 20, being a solar cell.

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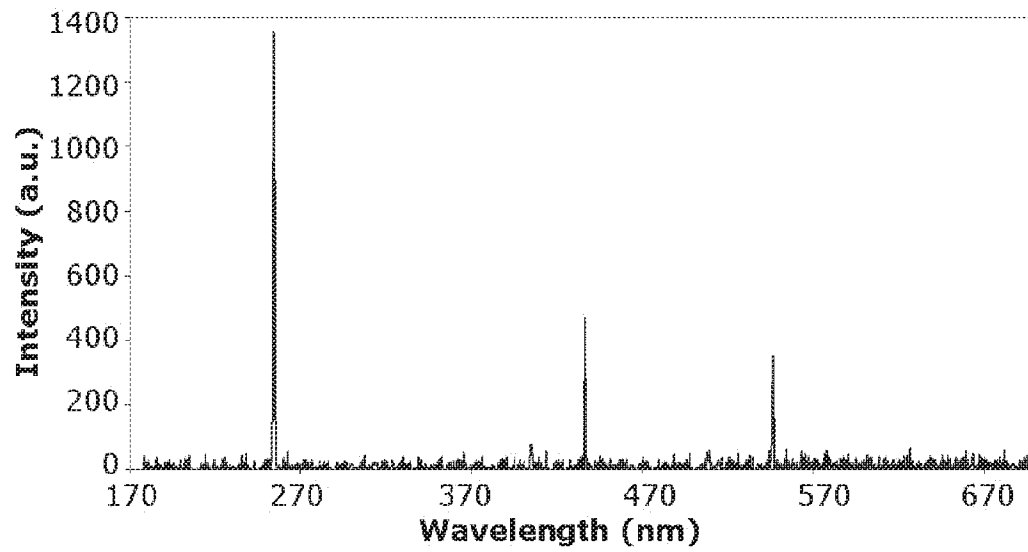


FIG. 1

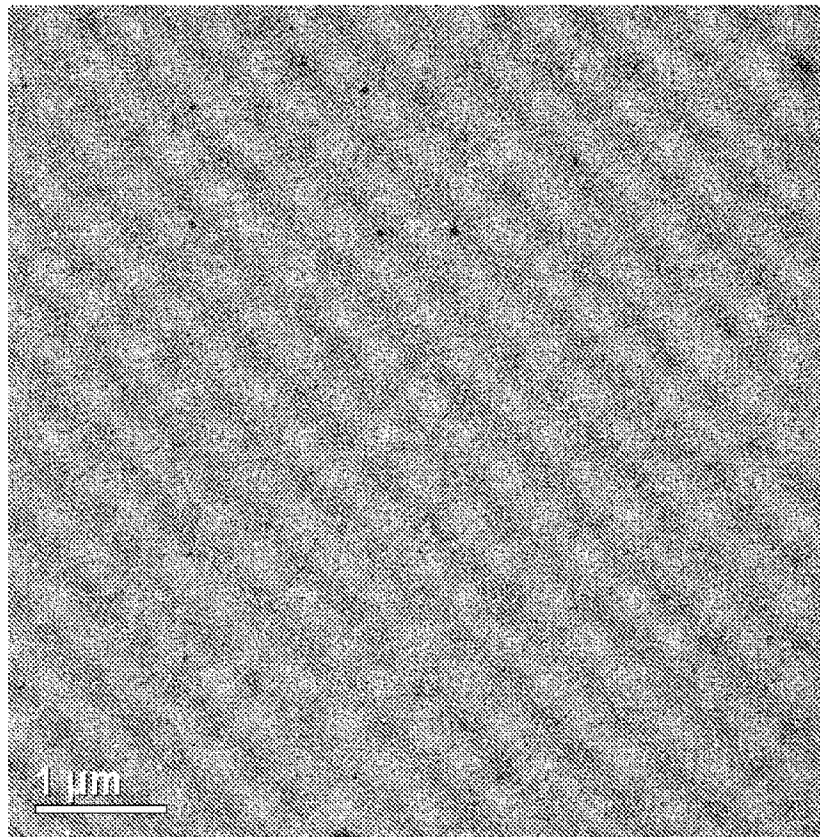


FIG. 2

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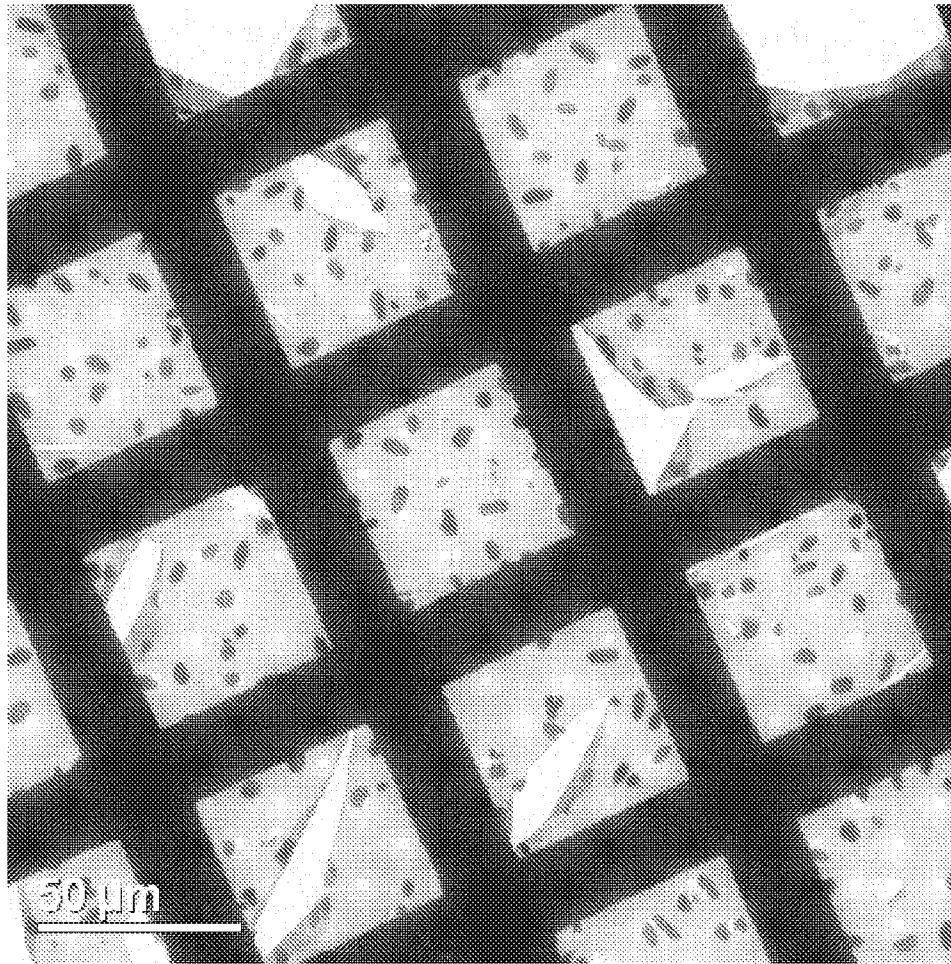


FIG. 3

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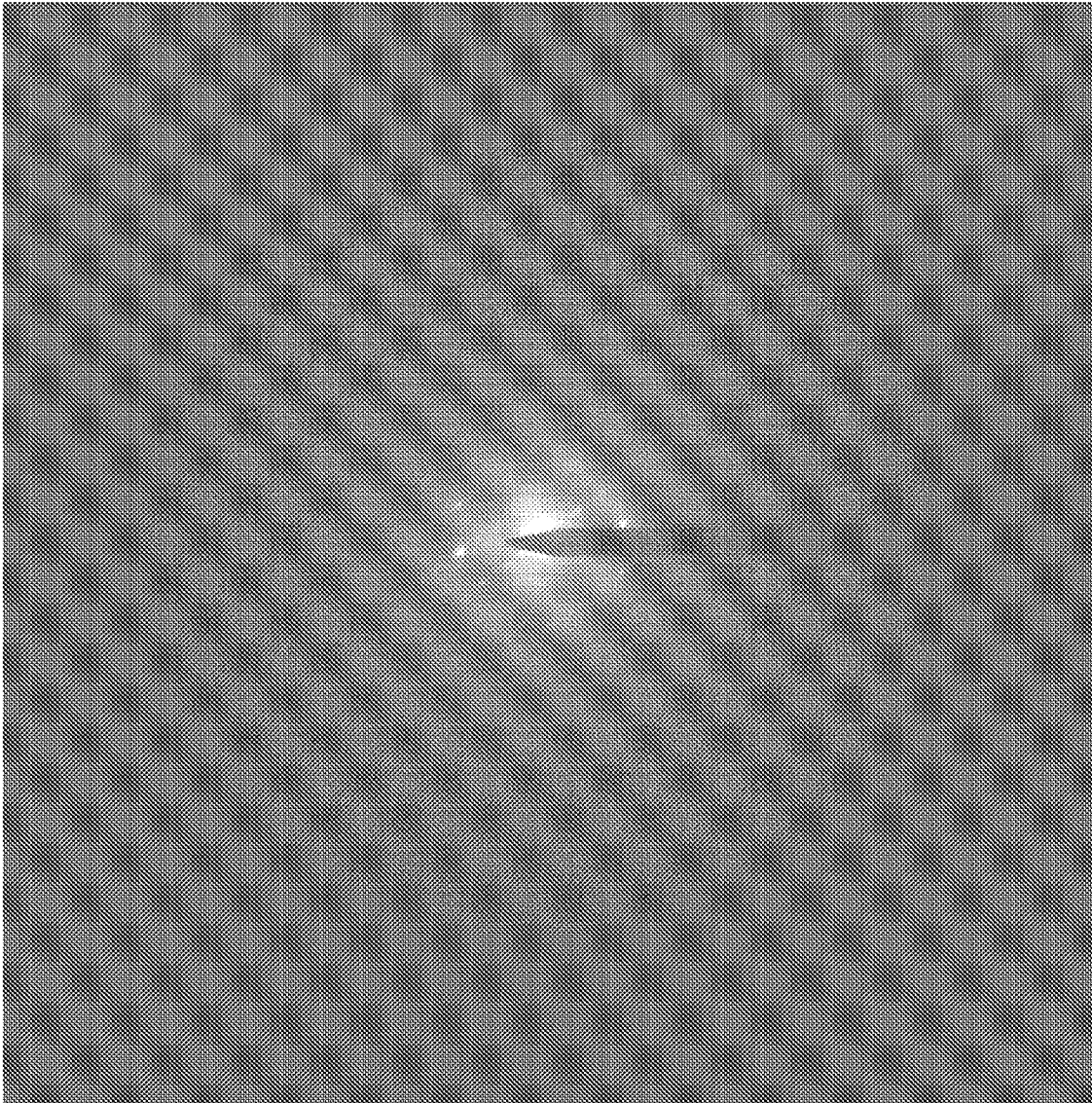


FIG. 4

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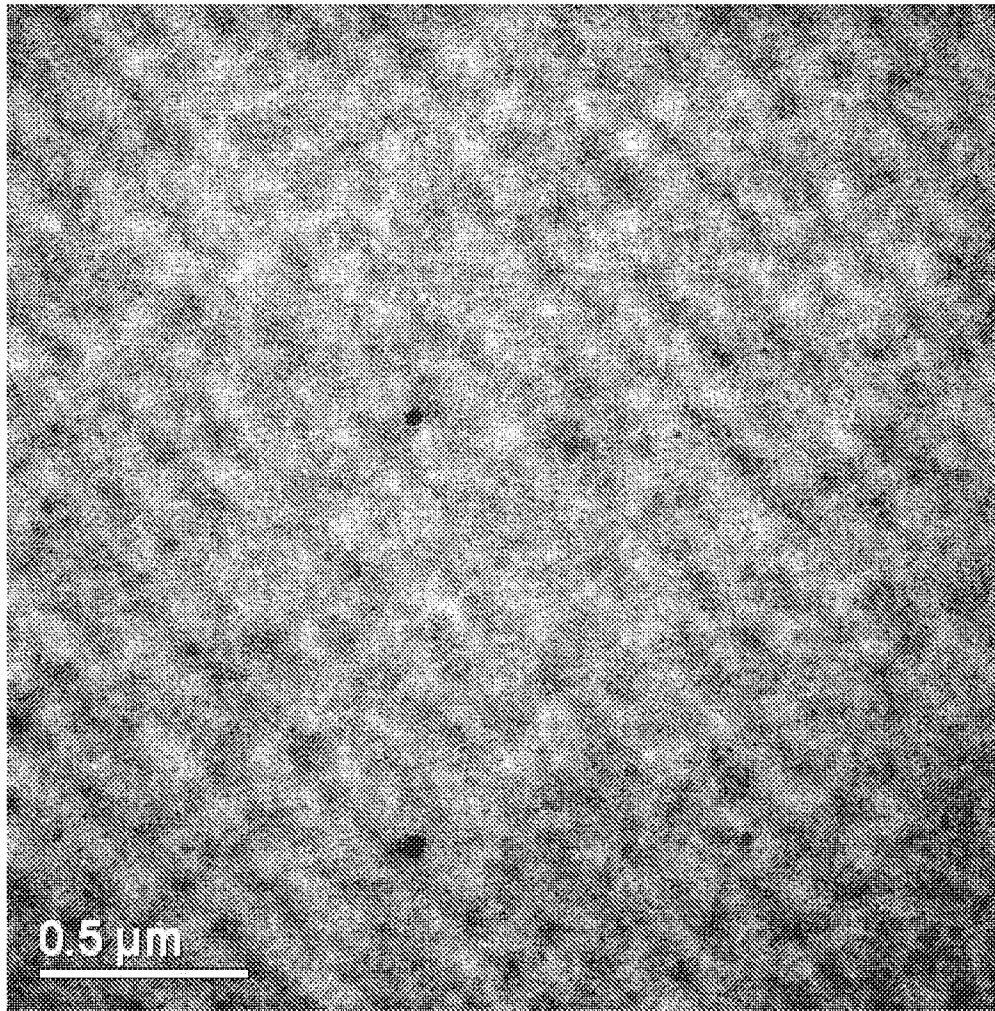


FIG. 5

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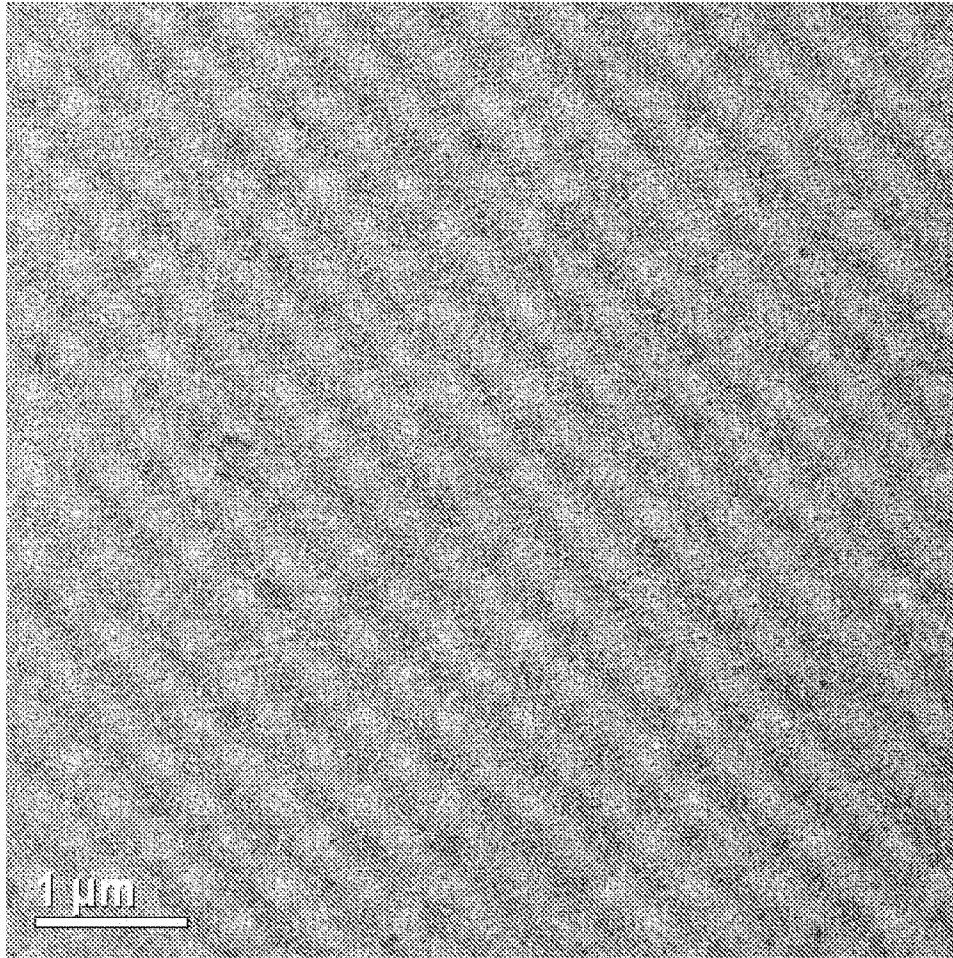


FIG. 6

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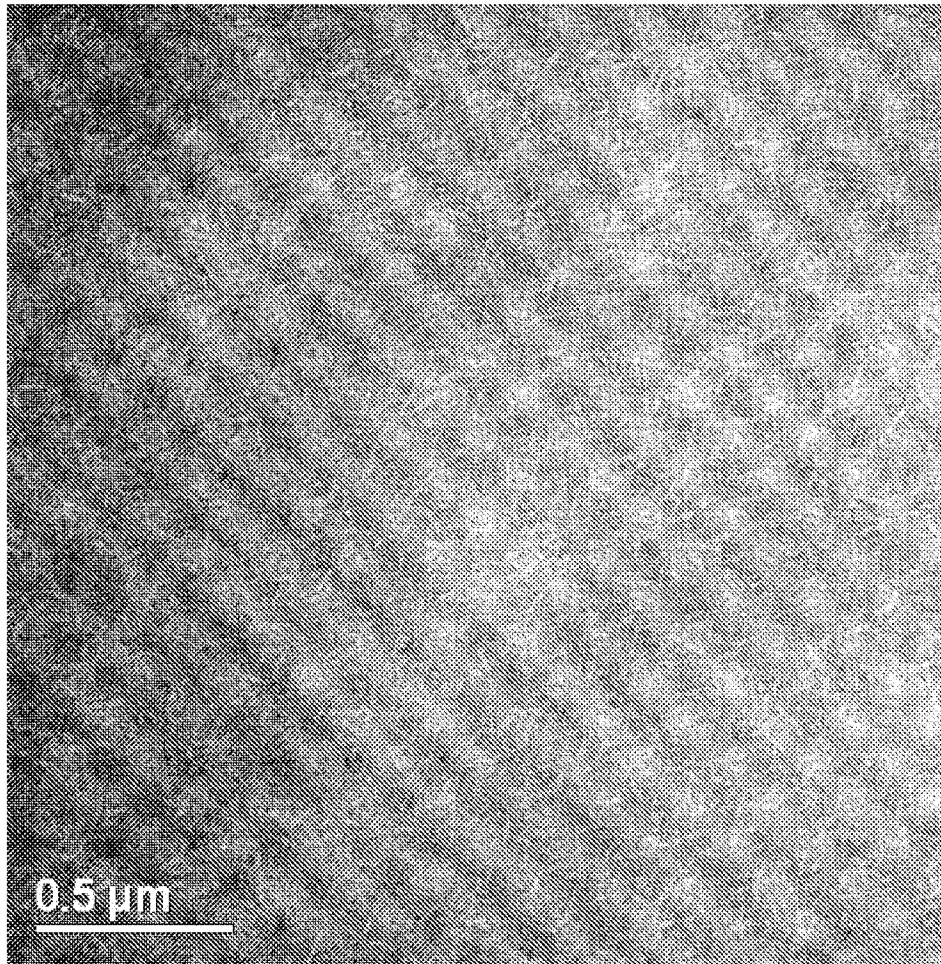


FIG. 7

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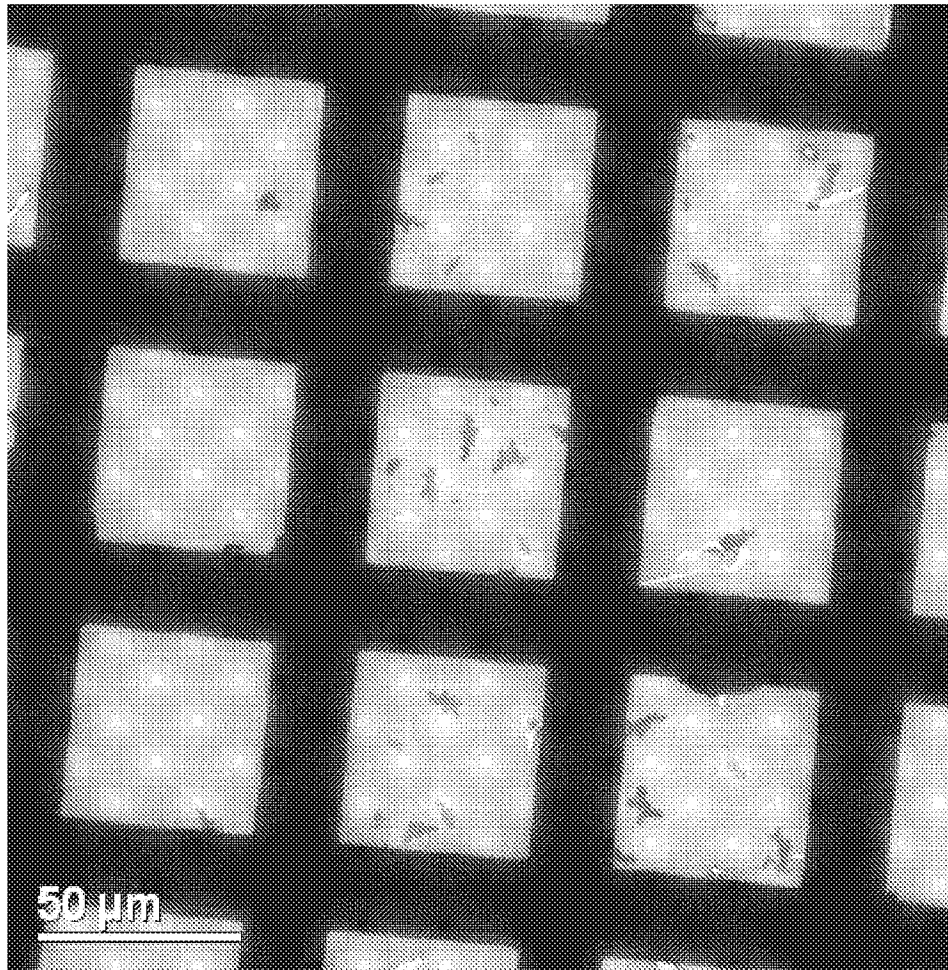


FIG. 8

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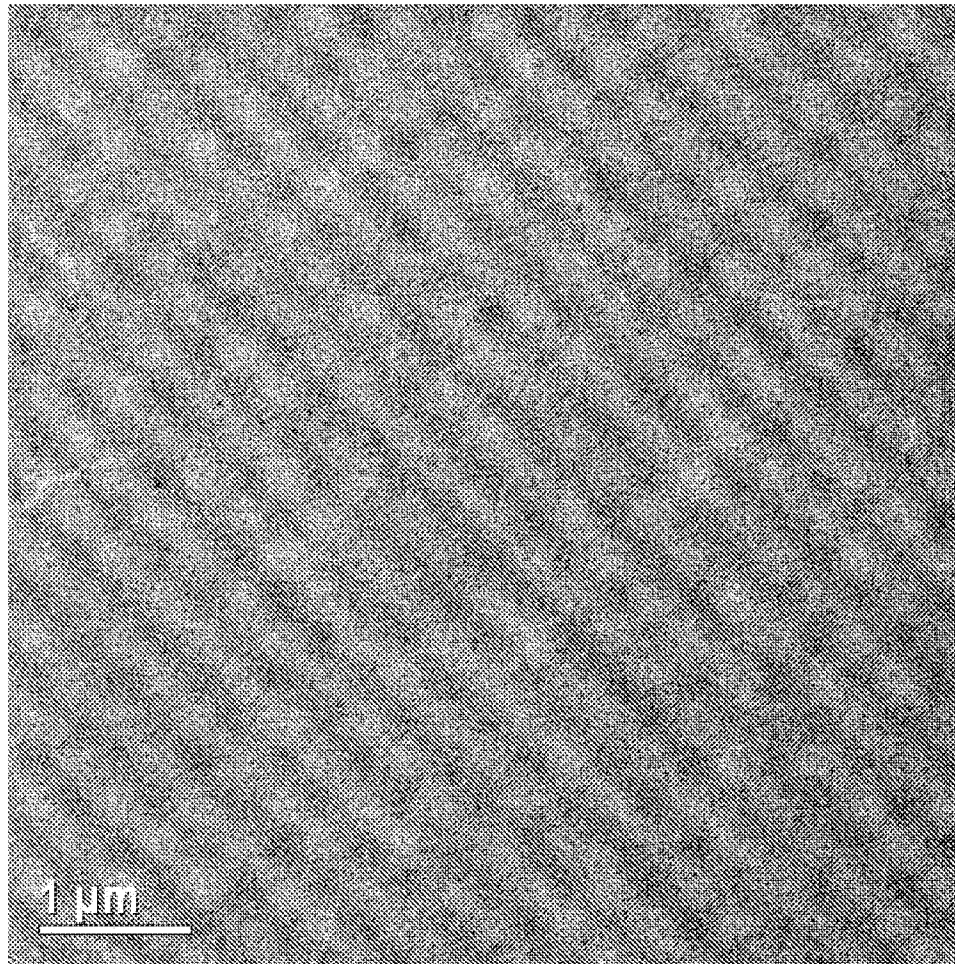


FIG. 9

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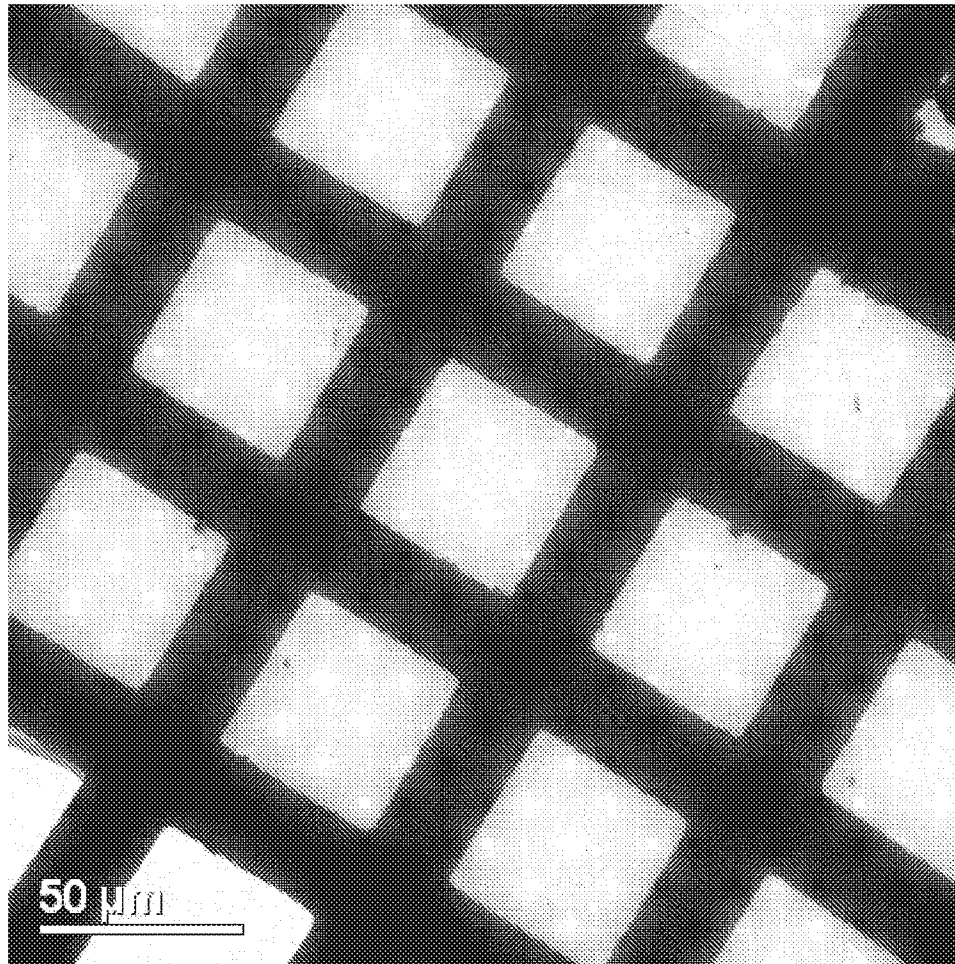


FIG. 10

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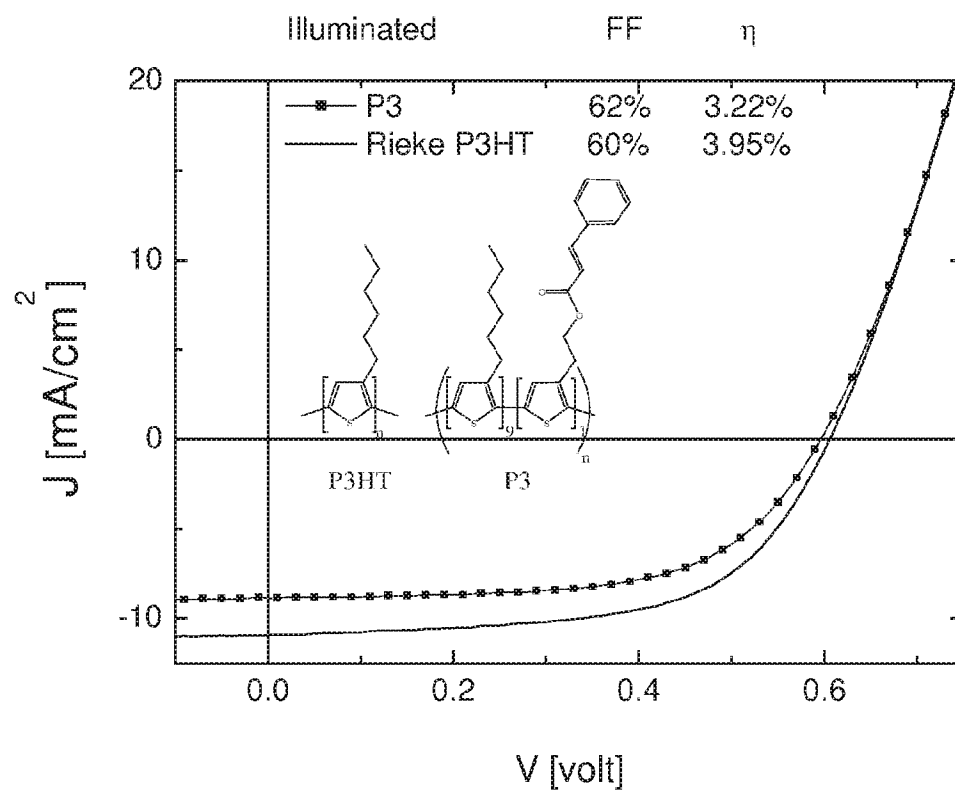


FIG. 11

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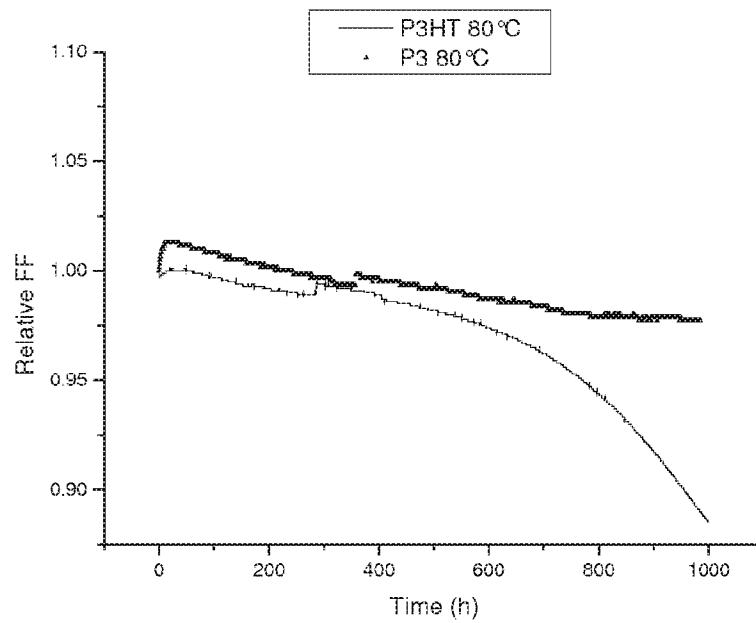


FIG. 12

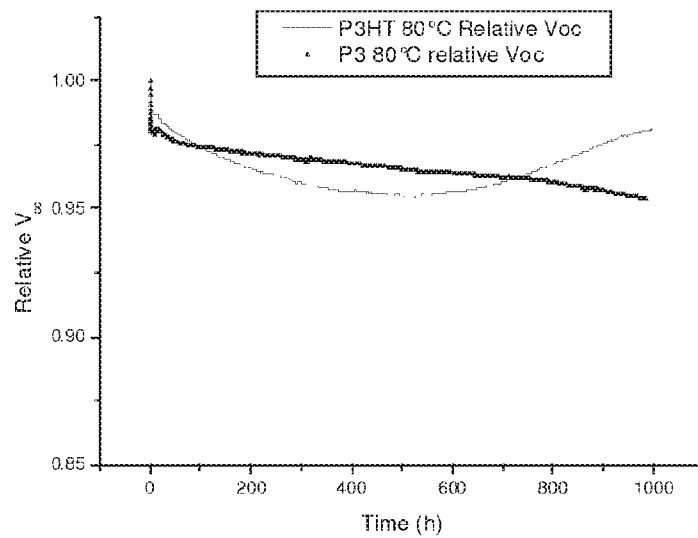


FIG. 13

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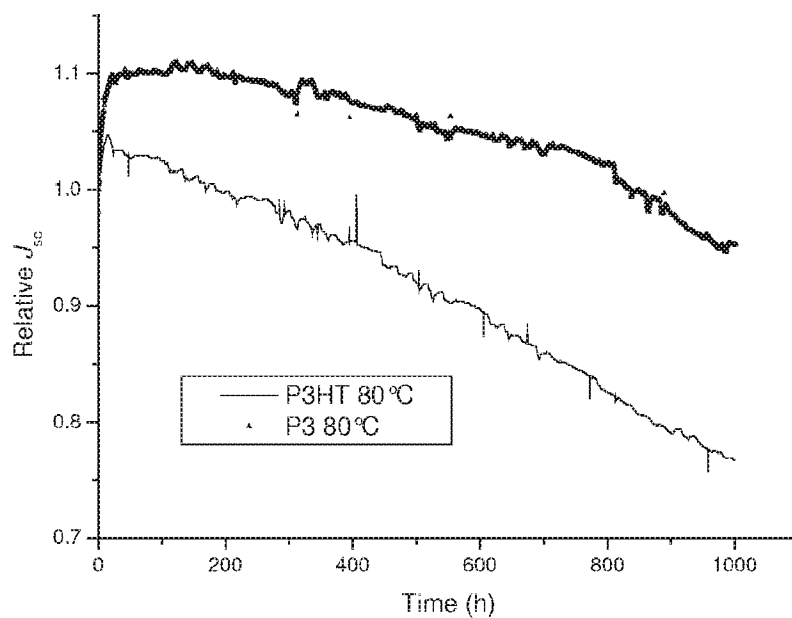


FIG. 14

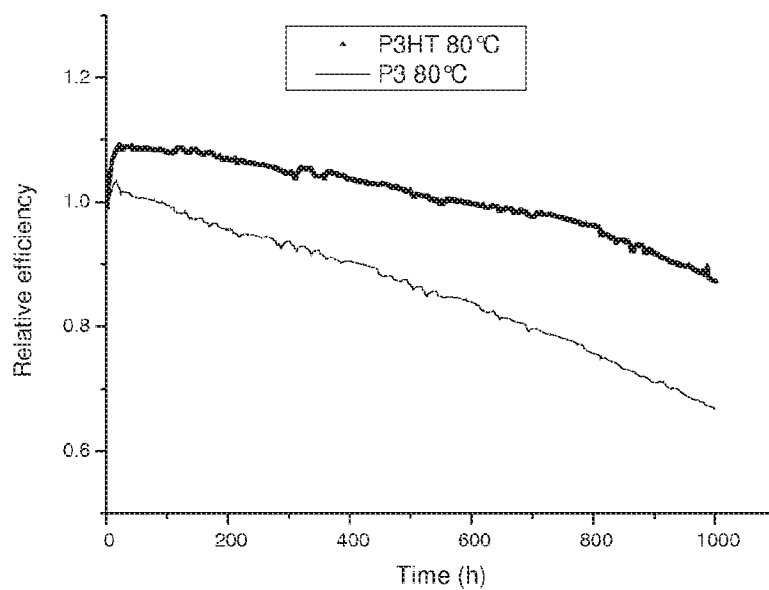


FIG. 15

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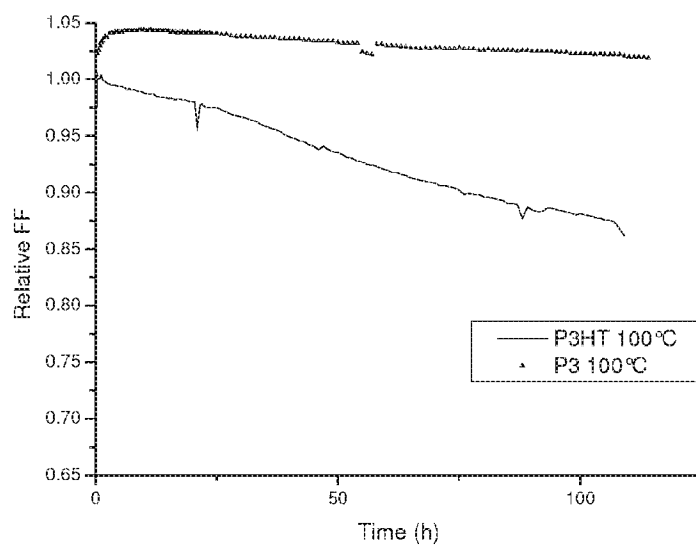


FIG. 16

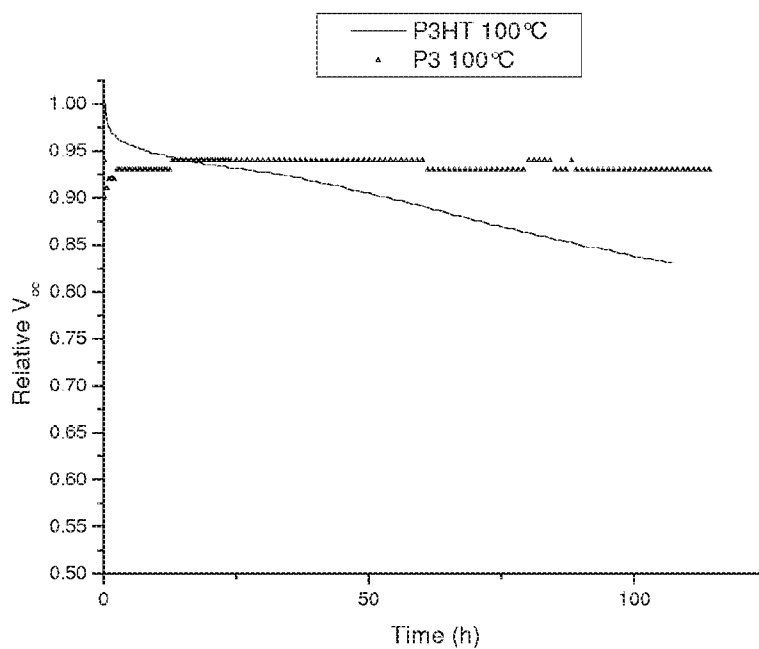


FIG. 17

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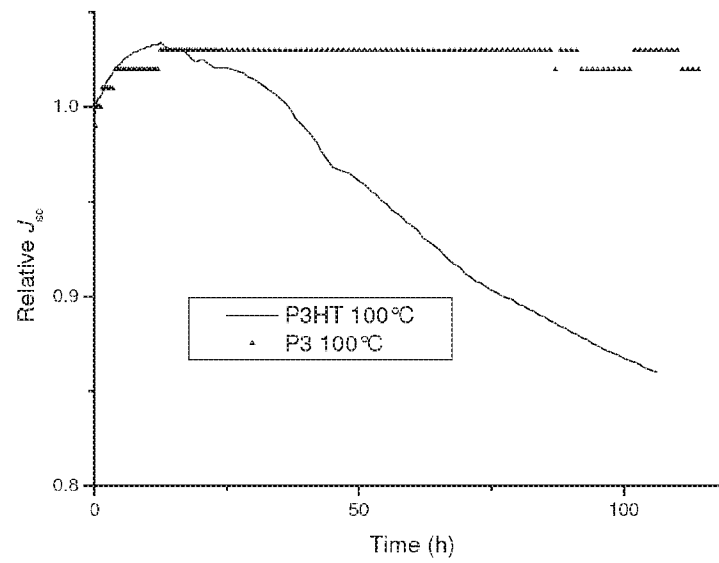


FIG. 18

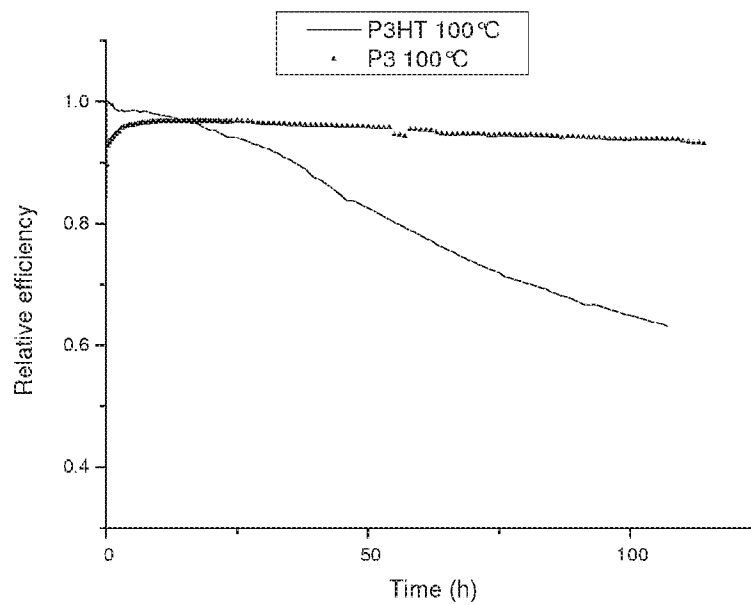


FIG. 19

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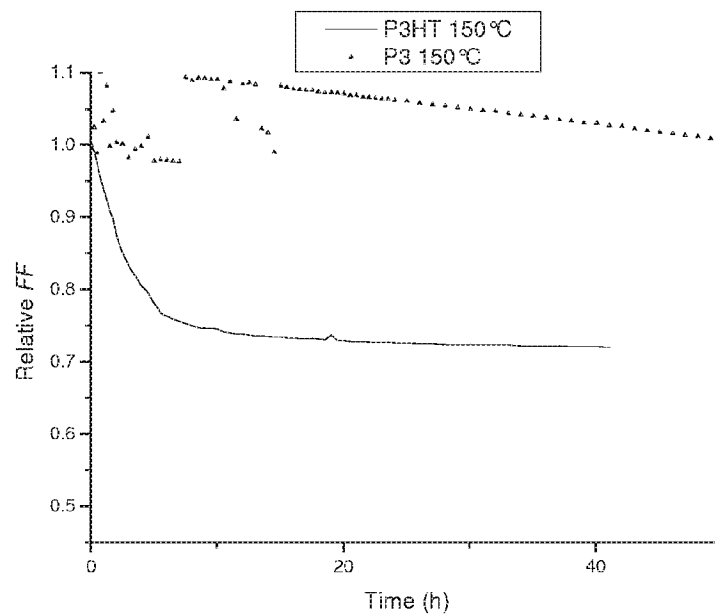


FIG. 20

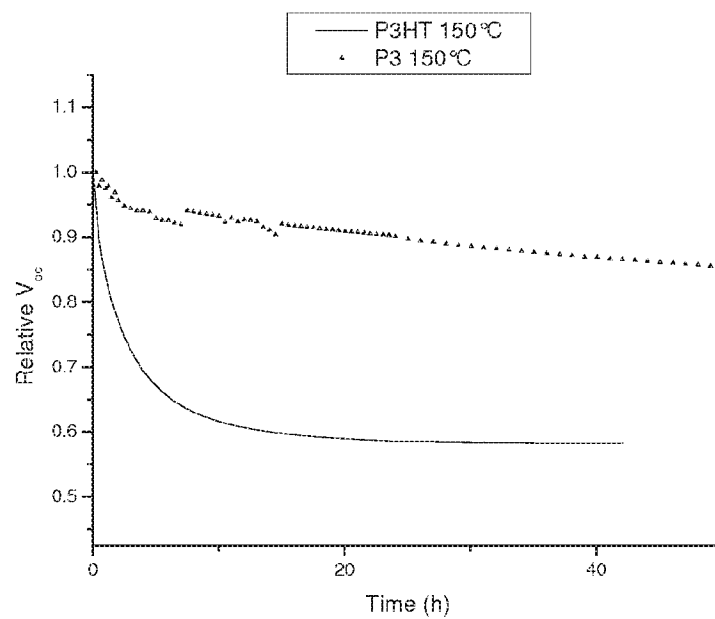


FIG. 21

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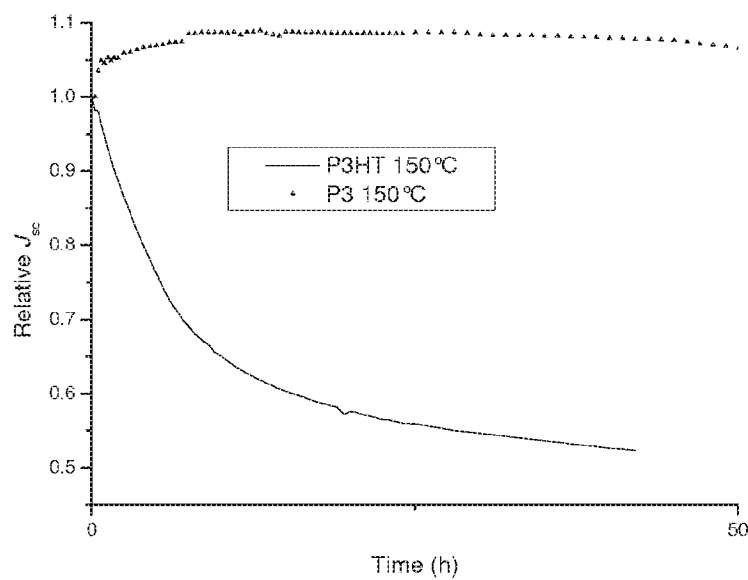


FIG. 22

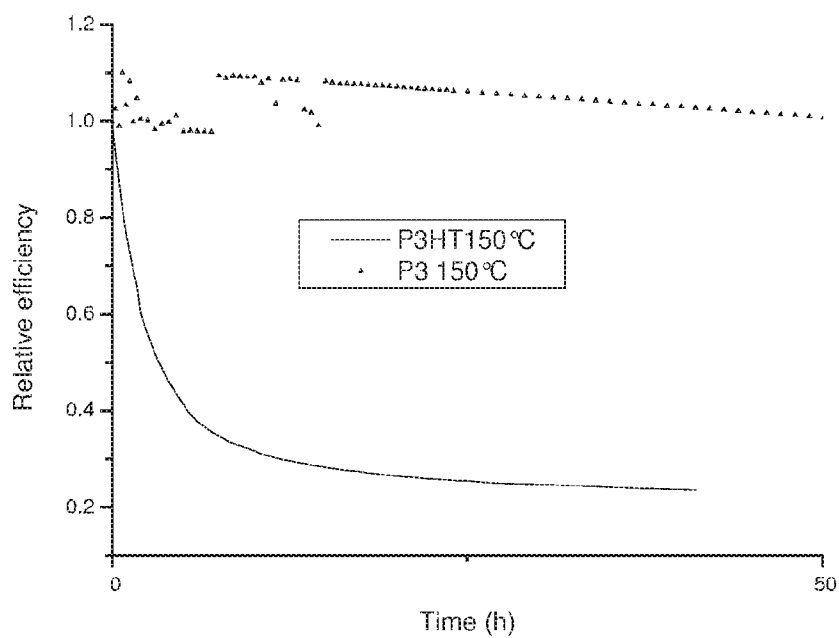


FIG. 23

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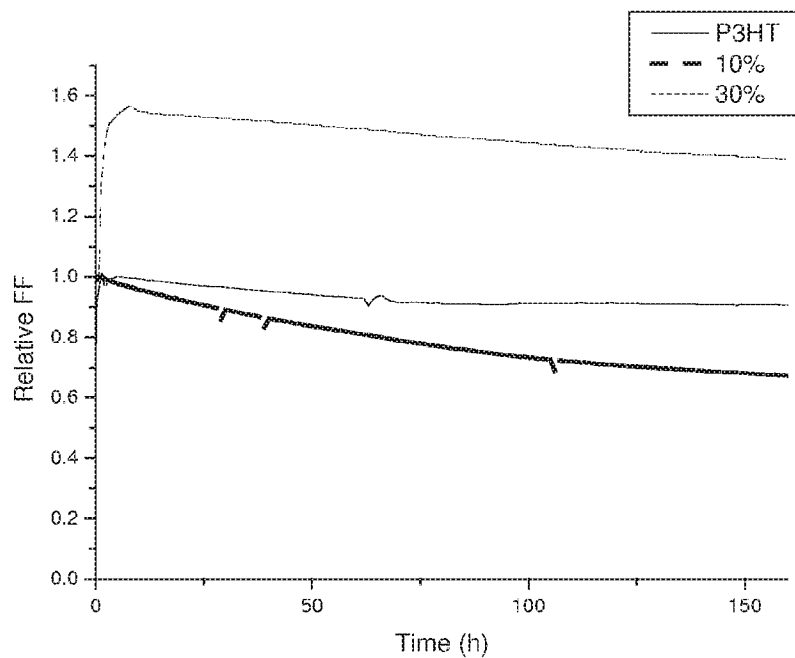


FIG. 24

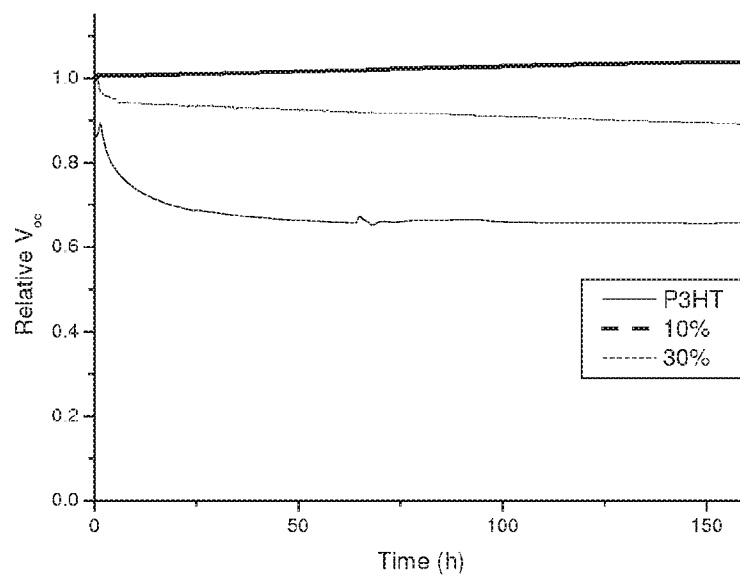


FIG. 25

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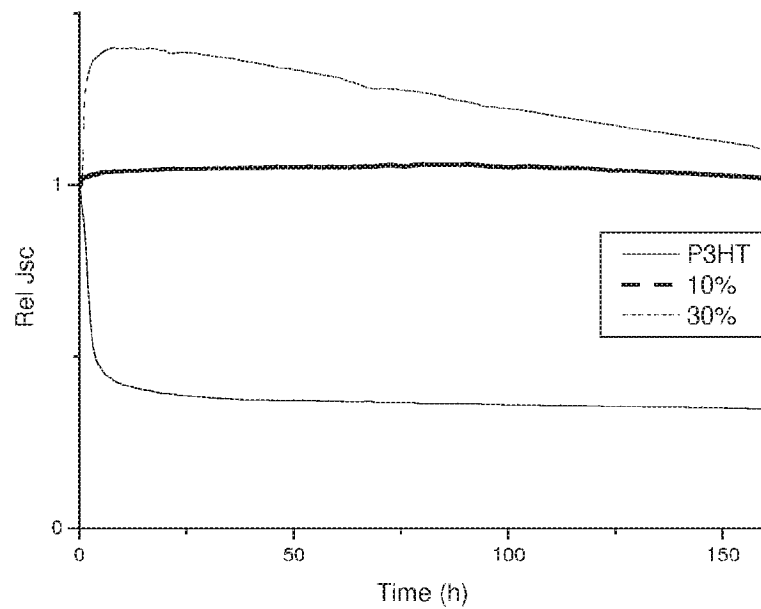


FIG. 26

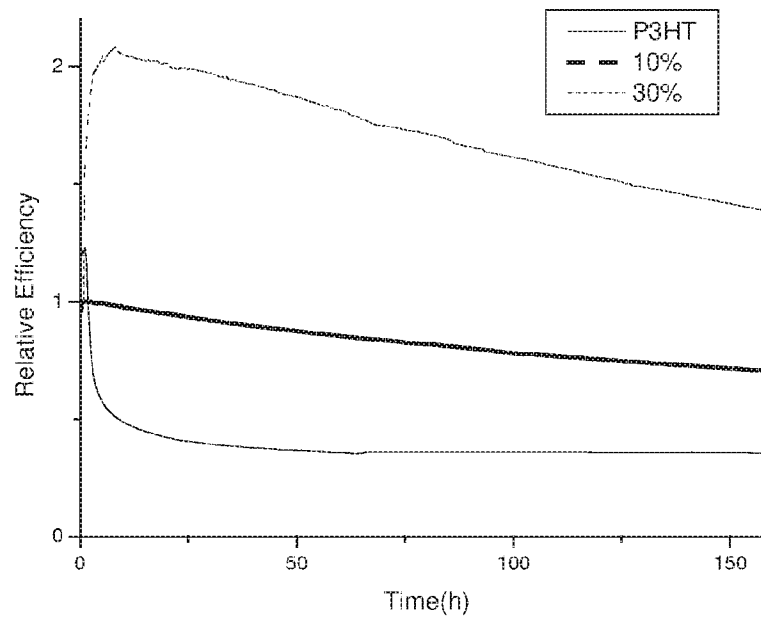


FIG. 27

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2009/054056

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07D333/28 C08G61/12 H01L51/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C07D C08G H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, CHEM ABS Data, BEILSTEIN Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2008/053158 A (CHROMA THERAPEUTICS LTD [GB]; MOFFAT DAVID FESTUS CHARLES [GB]; PINTAT) 8 May 2008 (2008-05-08) scheme 4, reagent of stage 3 page 29	3
X	US 3 097 230 A (MILLER LEE A) 9 July 1963 (1963-07-09) column 4; example 3	1-3, 9, 11

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *Z* document member of the same patent family

Date of the actual completion of the international search

28 July 2009

Date of mailing of the international search report

27/08/2009

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European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
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Fax: (+31-70) 340-3016

Authorized officer

Brandstetter, T

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2009/054056

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	MATSUDA TATSUHIITO ET AL: "Novel thiophene methacrylates for materials of high refractive index" JOURNAL OF MACROMOLECULAR SCIENCE : PART A - CHEMISTRY, MARCEL DEKKER, NEW YORK, NY, US, vol. A36, no. 9, 1 August 1999 (1999-08-01), pages 1271-1288, XP008092069 ISSN: 0022-233X page 15; table 3; compound DIBROMOTHIOPHENEMETHACRYLATES	1
X	DATABASE WPI Week 1988 Thomson Scientific, London, GB; AN 1988-136356 XP002538792 *New (di)bromo-2-methacrylic:oxy:methyl:thiophe ne(s) - useful as optical plastics etc., prepd. e.g. by reaction of brominated 2-halo:methyl:thiophene with methacrylic acid salts" & JP 63 077872 A (NIPPON SHOKUBAI KAGAKU KOGYO CO LTD) 8 April 1988 (1988-04-08) scheme on page 2 compounds II, III abstract; compounds RN117802-54-7, RN117802-55-8	1
X	SYBILLE ALLARD ET AL: "Oligothiophenes for pattern formation by stamping" MACROMOL. CHEM. PHYS., vol. 204, no. 1, 2003, pages 63-75, XP002538791 page 69, column 2, lines 25-57; compounds 4, 10 scheme 3 on page 72	1, 9, 10, 12
X	JP 2008 047855 A (TORAY INDUSTRIES) 28 February 2008 (2008-02-28) scheme on page 17 paragraph [0033]	1-14
Y	paragraphs [0001], [0033], [0037], [0039]	15-21
Y	Z. ZHU ET AL: "Stabilization of Film Morphology in Polymer-Fullerene Heterojunction Solar Cells" JOURNAL OF MACROMOLECULAR SCIENCE; PART A - PURE AND APPLIED CHEMISTRY, vol. 41, no. 12, 2004, pages 1467-1487, XP009120745 scheme 4 on page 1476 and scheme 5 on page 1477	15-21

Form PCT/ISA/210 (continuation of second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2009/054056

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 2008053158	A	08-05-2008	NONE	
US 3097230	A	09-07-1963	NONE	
JP 63077872	A	08-04-1988	NONE	
JP 2008047855	A	28-02-2008	NONE	

Form PCT/ISA/210 (patent family annex) (April 2005)



(51) International Patent Classification:

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C08G 59/14 (2006.01) C08G 63/91 (2006.01)

(21) International Application Number:

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kind of national protection available): AE, AG, AL, AM,

AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

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kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

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— of inventorship (Rule 4.17(iv))

Published:

— with international search report (Art. 21(3))

WO 2014/150411 A1

(54) Title: CURABLE COMPOSITIONS

(57) Abstract: A multi-component curable composition which is reactive upon admixing of the components and which is the reaction product of (i) a polyester epoxy block or graft copolymer having acetoacetoxyl functionality; and (ii) a crosslinking component. The crosslinking component may include at least one imine functional compound having an average of at least two imine groups per molecule which are reactive with acetoacetoxyl functionality.

CURABLE COMPOSITIONS

FIELD OF THE INVENTION

[0001] The present invention generally relates to curable coating compositions suitable for use over metal substrates and to flexible, ambient cure coatings for metal substrates.

DETAILED DESCRIPTION OF THE INVENTION

[0002] According to one embodiment of the present invention a curable composition comprises:

- (a) a polyester epoxy block or graft copolymer having acetoacetoxy functionality; and
- (b) a crosslinking component.

[0003] Acetoacetoxy functional polymers may be being obtained by partially or completely reacting a mono or polyepoxide with a carboxylic acid functional polycaprolactone polyester polyol to form a hydroxyl functional epoxy-polyester block copolymer, with subsequent reaction of hydroxyl groups on the epoxy-polyester adduct with one or more acetoacetic acid derivatives. The reaction with the acetoacetic acid derivatives is carried out as an esterification or transesterification reaction or as ring opening reaction with diketene.

[0004] According to another embodiment of the invention, the polymer containing acetoacetate groups may be a block copolymer comprising polyester and epoxy blocks and having one or more functionalities selected from epoxy and hydroxyl functionalities.

[0005] The crosslinking component may comprise an isocyanate crosslinker.

[0006] In another embodiment, the crosslinking component may comprise at least one imine functional compound having an average of at least two imine groups per molecule which are reactive with acetoacetoxy functionality.

[0007] The curable compositions described herein are particularly suited for use in the preparation of paints and coatings for a variety of substrates, and are particularly

suited for metal substrates, and more particularly, for aluminum substrates, including both chrome and non-chrome treated pretreated aluminum substrates.

[0008] Examples of suitable epoxy compounds which may be employed in preparation of the hydroxyl functional epoxy-polyester copolymer may include monoepoxides, polyepoxides and blends thereof. Representative useful monoepoxides include the monoglycidyl ethers of aliphatic or aromatic alcohols such as butyl glycidyl ether, octyl glycidyl ether, nonyl glycidyl ether, decyl glycidyl ether, dodecyl glycidyl ether, p-tertbutylphenyl glycidyl ether, o-cresyl glycidyl ether, and 3-glycidoxypropyl trimethoxysilane. Monoepoxy esters such as the glycidyl ester of versatic acid (commercially available as CARDURA® from Momentive) or the glycidyl esters of other acids such as tertiary-nonanoic acid, tertiary-decanoic acid, tertiary-undecanoic acid, etc. are also useful. Similarly, if desired, unsaturated monoepoxy esters such as glycidyl acrylate, glycidyl methacrylate or glycidyl laurate could be used. Additionally, monoepoxidized oils can also be used.

[0009] Other useful monoepoxies include styrene oxide, cyclohexene oxide, 1,2-butene oxide, 2,3-butene oxide, 1,2-pentene oxide, 1,2-heptene oxide, 1,2-octene oxide, 1,2-nonene oxide, 1,2-decene oxide, and the like.

[0010] Useful polyepoxides may include polyepoxy-functional novalac, bisphenol and cycloaliphatic epoxies. Exemplary polyepoxides may have a number average molecular weight less than about 2,000. Polyepoxides may include the di- or polyglycidyl ethers of (cyclo)aliphatic or aromatic hydroxy compounds, such as ethylene glycol, glycerol or cyclohexanediol (or the epoxides as mentioned in the introduction), or cycloaliphatic epoxy compounds such as epoxidized styrene or divinylbenzene which may subsequently be hydrogenated; glycidyl esters of fatty acids, containing for example from 6-24 carbon atoms; glycidyl (meth)acrylate; epoxy compounds containing an isocyanurate group; an epoxidized polyalkadiene such as, for example, epoxidized polybutadiene; hydantoin epoxy resins; epoxy resins obtained by epoxidation of aliphatic and/or cycloaliphatic alkenes, such as, for example, dipentene dioxide, dicyclopentadiene dioxide and vinylcyclohexene dioxide, and resins containing glycidyl groups, for example polyesters or polyurethanes containing one or more glycidyl groups per molecule, or mixtures of the abovementioned epoxy resins. The epoxy resins are known to those skilled in the art and require no further description here.

[0011] Difunctional bisphenol A/epichlorohydrin derived polyepoxides (commercially available as EPON® from Momentive) are particularly useful.

[0012] Other suitable epoxide compounds may include polyglycidyl ethers based on polyhydric, preferably dihydric, alcohols, phenols, hydrogenation products of these phenols and/or novolacs (reaction products of mono- or polyhydric phenols with aldehydes, in particular formaldehyde, in the presence of acidic catalysts). The epoxide equivalent weights of these epoxide compounds (epoxy resins) are between 100 and 5000, preferably between 160 and 4000. Examples of polyhydric phenols are: resorcinol, hydroquinone, 2,2-bis(4-hydroxyphenyl)propane (bisphenol A), isomer mixtures of dihydroxydiphenylmethane (bisphenol-F), tetrabromobisphenol A, 4,4'-dihydroxydiphenylcyclohexane, 4,4'-dihydroxy-3,3'-dimethyldiphenylpropane, 4,4'-dihydroxybiphenyl, 4,4'-dihydroxybenzophenone, 1,1-bis(4-hydroxyphenyl)ethane, 1,1-bis(4-hydroxyphenyl)isobutane, 2,2-bis(4-hydroxy-tert-butylphenyl)propane, bis(2-hydroxynaphthyl)methane, 1,5-dihydroxynaphthalene, tris(4-hydroxyphenyl)methane, bis(4-hydroxyphenyl) ether, bis(4-hydroxyphenyl) sulfone etc. and the products of chlorination and bromination of the abovementioned compounds. Bisphenol A and bisphenol F are particularly preferred in this respect.

[0013] Also suitable are the polyglycidyl ethers of polyhydric alcohols. Examples of such polyhydric alcohols are ethylene glycol, diethylene glycol, triethylene glycol, 1,2-propylene glycol, polyoxypropylene glycols (n=1-10), 1,3-propylene glycol, 1,4-butylene glycol, 1,5-pentanediol, 1,6-hexanediol, 1,2,6-hexanetriol, glycerol and 2,2-bis(4-hydroxycyclohexyl)propane.

[0014] Polyglycidyl esters of polycarboxylic acids can also be used, which are obtained by reacting epichlorohydrin or similar epoxy compounds with an aliphatic, cycloaliphatic or aromatic polycarboxylic acid, such as oxalic acid, succinic acid, adipic acid, glutaric acid, phthalic acid, terephthalic acid, hexahydrophthalic acid, 2,6-naphthalenedicarboxylic acid and dimerized linolenic acid. Examples are diglycidyl adipate, diglycidyl phthalate and diglycidyl hexahydrophthalate.

[0015] These polyepoxide compounds can also be used in mixtures with one another and, if appropriate, in mixtures with monoepoxides. Examples of suitable monoepoxides are: epoxidized monounsaturated hydrocarbons (butylene oxide, cyclohexene oxide,

styrene oxide), epoxide ethers of monohydric phenols (phenol, cresol and other o- or p-substituted phenols), and glycidyl esters of saturated and unsaturated carboxylic acids.

[0016] Further suitable epoxides for the reaction may include those containing amide or urethane groups, for example triglycidyl isocyanurate or glycidyl-blocked hexamethylene diisocyanate.

[0017] Further suitable epoxide compounds may be derived from unsaturated fatty acids, for example from linoleic acids or linolenic acids. Examples of suitable epoxidized fatty acid derivatives are those from linseed oil, soya bean oil, alkyl esters of ricinene fatty acid, soya bean oil or linoleic fatty acid, oleic or arachidonic acid, and oligomeric fatty acids and their esters, and epoxidized alkyl esters having two or more ester groups are also suitable. Epoxidized linseed oil and soya bean oil are preferred.

[0018] Plasticized epoxy resins with terminal epoxy groups are particularly preferred, which are prepared by partial reaction of the epoxy groups of epoxy resins containing at least two epoxy groups with OH- and COOH-containing substances, such as polyhydric alcohols, for example the abovementioned diols or phenols, polycarboxylic acids or polyesters containing carboxyl or OH groups, or by reaction with polyamines.

[0019] Possible epoxides containing hydroxyl groups, within the meaning of the present invention, are also reaction products of compounds having at least two 1,2-epoxide groups per molecule and epoxide equivalent weights of from 160 to 600, and aromatic dicarboxylic acids or mixtures thereof with compounds from the group comprising (cyclo)aliphatic dicarboxylic acids, monocarboxylic acids and/or monohydric phenols, and optionally cyclic anhydrides. Products of this type are described in EP-0 387 692, to which reference is made here. For the preparation of these reaction products it is possible to use all the epoxy compounds mentioned in the introduction.

[0020] According to one embodiment of the present invention, an epoxy-polyester copolymer containing acetoacetate functionality may be obtained by partially or completely reacting the epoxy groups of a mono or polyepoxide (as described above) with a carboxylic acid functional polycaprolactone polyester polyol, with subsequent reaction of this reaction product with one or more acetoacetic acid derivatives.

[0021] Acid functional polyesters polyols, which may be useful in the present invention, may be made by the lactone or polycaprolactone ring opening polymerization

initiated by hydroxy-functional acid. In general such polyesters will also have a terminal hydroxyl group or groups.

[0022] For example, the ring opening polymerization of caprolactone initiated by 2,2'-bis(hydroxymethyl) propionic acid (also referred to as dimethylol propionic acid or DMPA) provides a useful way to make a monoacid functional polyester. Another useful reaction is between dimethylolbutyric acid and caprolactone to form a carboxyl modified polycaprolactone, in particular a polycaprolactone polyester diol with a pendant carboxylic functional group. Other hydroxy-functional carboxylic acids and lactones may also be used to form useful acid functional polyesters. Without being limited to any particular theory, the extent of caprolactone modification believed to be most useful is by having a resulting number average molecular weight measured by gel permeation chromatography using polystyrene as a standard ("GPC") of over about 500, for example, about 500 to about 4000. The use of these polyesters has the advantage of providing hydroxyl groups on the side chains for subsequent reaction with acetoacetic acid derivatives. Examples of commercially available acid functional polycaprolactone polyester diols include CAPA polyester diols available from Perstorp and DICAP polyester diols available from GEO Specialty Chemicals. Polyesters of caprolactone using 2-ethylhexanol as the initiating alcohol and dibutyl tin dilaurate as the catalyst reacted with a cyclic anhydride to form a terminal acid group may also be useful in the present invention.

[0023] In another useful embodiment, an acid functional polycaprolactone polyester diol may be modified by capping one or both hydroxyl groups using one or more mono-functional acids, R-COOH. In one useful embodiment, R may have about 4 to about 18, for example, about 11 to about 12 carbon atoms. Examples of useful mono-functional carboxylic acids include lauric acid, caprylic acid, capric acid, myristic acid, palmitic acid, stearic acid, oleic acid, elaidic acid (9-octadecenoic acid), linoleic acid, linolenic acid, stearic acid, soya fatty acid or other fatty acids. In one useful embodiment, two moles of such a mono-functional acid may react with the hydroxyl groups of the polyester to form a mono-acid functional polyester, where both hydroxyl groups are capped by the ester chains.

[0024] By controlling the molar ratios of acid groups on the polyester to epoxy groups in the reaction mixture, the product of the epoxide and the acid functional

polycaprolactone polyester polyol reaction described above may include epoxy functionality and/or primary and secondary hydroxyl functionality. Accordingly, in one embodiment, a useful epoxy-polyester block copolymer may be formed as a reaction product of the aforementioned components having an acid/epoxy molar ratio of 0.8 to about 1.1, and in another embodiment, of about 1.8 to about 2.1.

[0025] In one useful embodiment, the reaction product may be a polyester epoxy diblock copolymer (adduct) formed as the reaction product of the acid functional polycaprolactone polyester polyol and a monofunctional epoxide or the reaction product of a polyepoxide with an appropriate molar ratio of the acid functional polycaprolactone polyester polyol to ensure unreacted epoxy groups. In another useful embodiment, the reaction product may be a polyester epoxy polyester triblock copolymer, formed as the reaction product of a difunctional epoxide with an appropriate molar ratio of the acid functional polycaprolactone polyester polyol to ensure opening of substantially all of the epoxy groups. In either case, the reaction product will preferably have free hydroxyl groups, contributed by the polyester polyol or resulting from the epoxide ring opening, which may be subsequently reacted directly with acetoacetic acid derivatives. While the present invention characterizes the reaction product of the acid functional polyester and epoxy as a block co-polymer, it will be recognized that the reaction product, in some embodiments, may be characterized as polyester grafted epoxy copolymer, particularly in embodiments comprising acid functional polyesters and bisphenol F-type epoxies.

[0026] The subsequent esterification of the hydroxyl groups of the epoxide-polyester adduct to give acetoacetates is carried out as a rule by reaction with monomeric acetoacetic acid esters such as, for example, methyl, ethyl or tert-butyl acetoacetate. The degree of esterification of the hydroxyl groups can be varied here over a wide range, depending on the properties desired in the end product.

[0027] The transesterification is carried out by heating both components together at boiling and slowly, if appropriate under vacuum, distilling off the lower-boiling alcohol which is formed.

[0028] However, the esterification of the hydroxyl groups can also be carried out with equivalents of acetoacetic acid, such as for example, diketene or 2,2,6-trimethyl-1,3-dioxan-4-one.

[0029] By selection, particularly of the molar ratios of reaction components, the product of the acetoacetate acid derivative and the epoxide-polyester adduct may include acetoacetoxy functionality in addition to one or more of epoxy functionality and primary and secondary hydroxyl functionality.

[0030] **CROSSLINKERS**

[0031] Isocyanates

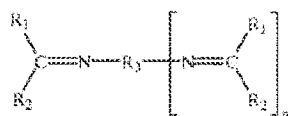
[0032] Provided there are free hydroxyl groups on the acetoacetoxy functionalized epoxy-polyester copolymers, the acetoacetoxy functionalized epoxy-polyester copolymers described above may be crosslinked using a suitable isocyanate crosslinker. The hydroxyls may be primary or secondary.

[0033] Polyisocyanates useful for reaction with the acetoacetoxy functionalized copolymers according to the preferred configuration have an average of at least two isocyanate groups per molecule. Representative polyisocyanates include the aliphatic compounds such as ethylene, trimethylene, tetramethylene, pentamethylene, hexamethylene, 1,2-propylene, 1,2-butylene, 2,3-butylene, 1,3-butylene, ethylidene and 1,2-butyldiene diisocyanates; the cycloalkylene compounds such as 3-isocyanatomethyl-3,5,5-trimethylcyclohexylisocyanate, and the 1,3-cyclopentane, 1,3-cyclohexane, and 1,2-cyclohexane diisocyanates; the aromatic compounds such as m-phenylene, p-phenylene, 4,4-diphenyl, 1,5-naphthalene and 1,4-naphthalene diisocyanates; the aliphatic-aromatic compounds such as 4,4-diphenylene methane, 2,4- or 2,6-toluene or mixtures thereof, 4,4'-toluidine, and 1,4-xylylene diisocyanates; the nuclear substituted aromatic compounds such as dianisidine diisocyanate, 4,4'-diphenylether diisocyanate and chlorodiphenylene diisocyanate; the triisocyanates such as triphenyl methane-4,4',4"-triisocyanate toluene; and the tetraisocyanates such as 4,4'-diphenyl-dimethyl methane - 2,2',5,5'-tetraisocyanate; the polymerized polyisocyanates such as dimers and trimers, and other various polyisocyanates containing biuret, urethane, and/or allophanate linkages.

[0034] Imine Compounds

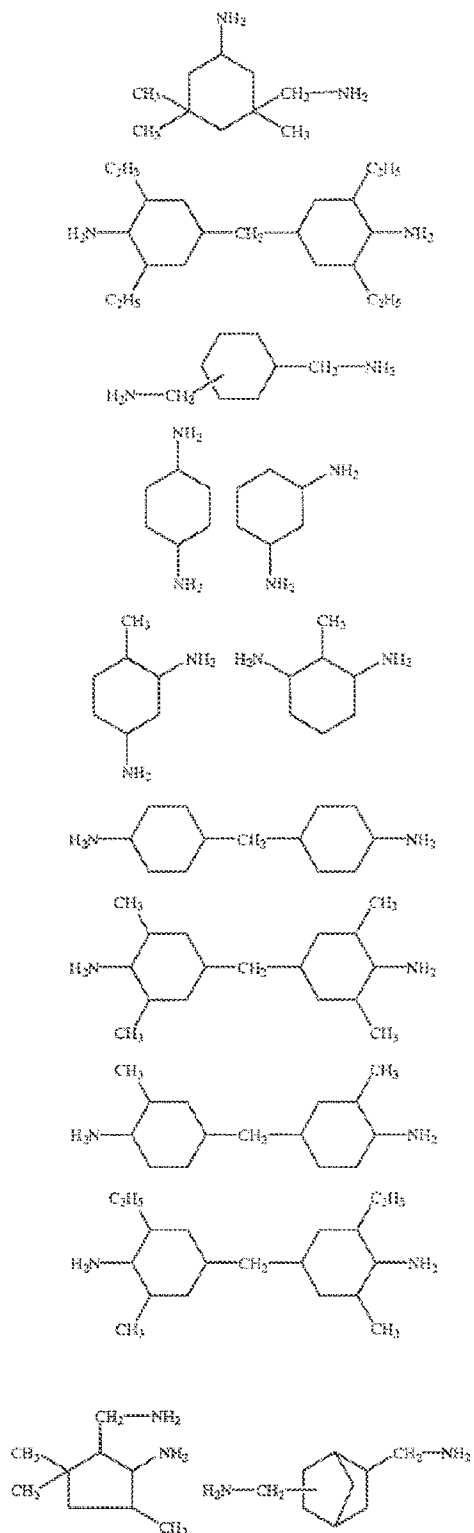
[0035] In another embodiment, the acetoacetoxy functionalized epoxy-polyester copolymers may be crosslinked by means of a crosslinking component comprising at least one imine functional compound having an average of at least two imine groups per molecule which are reactive with acetoacetoxy functionality.

[0036] The imine compounds which are useful in the present invention may be generally represented by the formula:



wherein n is 1 to 30, and preferably n is 1 to 5; R₁ and R₂ are hydrogen, an alkyl, aryl, cycloaliphatic, or substituted alkyl, aryl, or cycloaliphatic group; and R₁ and R₂ may be the same or different; and R₃ is an aliphatic, aromatic, arylaliphatic or cycloaliphatic group which may also contain heteroatoms such as O, N, S, or Si.

[0037] These imine compounds are typically prepared by the reaction of certain carbonyl compounds such as aldehydes and ketones with amines. Representative carbonyl compounds which may be used to form the imine include ketones such as acetone, methyl ethyl ketone, methyl isopropyl ketone, methyl isobutyl ketone, diethyl ketone, benzyl methylketone, diisopropyl ketone, cyclopentanone, and cyclohexanone, and aldehydes such as acetaldehyde, formaldehyde, propionaldehyde, isobutyraldehyde, n-butyraldehyde, heptaldehyde and cyclohexyl aldehydes. Representative amines which may be used to form the imine include ethylene diamine, ethylene triamine, propylene diamine, tetramethylene diamine, 1,6-hexamethylene diamine, bis(6-aminoethyl)ether, tricyclodecane diamine, N,N'-dimethyldiethyltriamine, cyclohexyl-1,2,4-triamine, cyclohexyl-1,2,4,5-tetraamine, 3,4,5-triaminopyran, 3,4-diaminofuran, and cycloaliphatic diamines such as those having the following structures:



[0038] The imines are conveniently prepared by reacting a stoichiometric excess of the ketone or aldehyde with the polyamine in an azeotropic solvent and removing water

as it is formed. In order to minimize side reactions, and to avoid delays due to prolonged processing, it is frequently desirable to avoid the prolonged heating necessary to remove all of the excess ketone or aldehyde and unreacted starting materials, provided that their presence does not adversely affect the performance of the final product.

[0039] One preferred type of imine compound for reaction with acetoacetoxymethyl functional materials in the practice of this invention is an adduct obtained by reacting an imine having an additional reactive group other than an imine, such as a hydroxyl group or, preferably, an amine group with a compound, such as an isocyanate, or an epoxide, having one or more chemical groups or sites capable of reaction with the additional reactive group. For example, an imine obtained from the reaction of two moles of an aldehyde or ketone with a triamine having two primary and one secondary amine groups, such as diethylene triamine, will have an unreacted secondary amine group which could be subsequently reacted with a mono and/or polyepoxide, or a mono or polyisocyanate to produce the imine functional adduct. One especially preferred commercial imine having an additional reactive group is Shell Epicure 3501 and KT22 from Air Products which is the reaction product of diethylene triamine and methyl isobutyl ketone.

[0040] Polyisocyanates useful for reaction with the hydroxyl or amine group of the imine in the preferred configuration may include those identified as crosslinkers above.

[0041] For reaction with the imines having unreacted amine groups, representative useful monoepoxides include many of those cited above, such as the monoglycidyl ethers of aliphatic or aromatic alcohols such as butyl glycidyl ether, octyl glycidyl ether, nonyl glycidyl ether, decyl glycidyl ether, dodecyl glycidyl ether, p-tertbutylphenyl glycidyl ether, o-cresyl glycidyl ether, and 3-glycidoxypropyl trimethoxysilane. Monoepoxy esters such as the glycidyl ester of versatic acid (commercially available as CARDURA ® from Momentive, or the glycidyl esters of other acids such as tertiary-nonanoic acid, tertiary-decanoic acid, tertiary-undecanoic acid, etc. are also useful. Similarly, if desired, unsaturated monoepoxy esters such as glycidyl acrylate, glycidyl methacrylate or glycidyl laurate could be used. Additionally, monoepoxidized oils can also be used.

[0042] Other useful monoepoxies include styrene oxide, cyclohexene oxide, 1,2-butene oxide, 2,3-butene oxide, 1,2-pentene oxide, 1,2-heptene oxide, 1,2-octene oxide, 1,2-nonene oxide, 1,2-decene oxide, and the like.

[0043] Especially preferred as the poly-functional epoxy compounds, due to their reactivity and durability, are the polyepoxy-functional novalac, bisphenol and cycloaliphatic epoxies. Preferably, the polyepoxies will have a number average molecular weight less than about 2,000 to minimize the viscosity of the adduct. It is particularly preferred for some applications to utilize a combination of both an imine adduct prepared by reaction of an imine having a secondary amine group and a polyepoxide and an imine adduct obtained by reaction of an imine having a secondary amine group and a monoepoxide.

[0044] The curable coating compositions according to the invention may optionally contain a diluent, such as conventional inert organic solvents. Examples are: halogenated hydrocarbons, ethers, such as, diethyl ether, 1,2-dimethoxyethane, tetrahydrofuran or dioxane; ketones, such as, for example, methyl ethyl ketone, acetone, cyclohexanone and the like; alcohols, such as methanol, ethanol, propanol, methoxypropanol, butanol and benzyl alcohol, (cyclo)aliphatic and/or aromatic solvents in the boiling range from about 150° to 180° C or esters, such as butyl acetate. The solvents can be employed individually or in a mixture.

[0045] Conventional additives which may be present in the coating compositions according to the invention are--depending on the particular intended use--the conventional coating additives such as pigments, pigment pastes, antioxidants, leveling and thickening agents, flow assistants, antifoams and/or wetting agents, fillers, catalysts, additional curing agents and additional curable compounds, etc. These additives can if appropriate be added to the mixture only immediately prior to processing.

[0046] One useful pigment package comprises at least one metal phosphate compound, such as Zn, Al, Ca, Fe, preferably aluminum polyphosphate modified by a metal compound, including but not limited to calcium, strontium, zinc, or manganese, or at least one metal compound modified polyphosphate combined with an ion exchanged inorganic pigment, such as calcium ion exchanged silica.

[0047] In one useful embodiment, the present invention may comprise about 5 to about 80 parts by weight, for example about 15 to about 40 parts by weight of polymeric binder, and about 2 to about 36 parts by weight, for example about 6 to about 20 parts by weight of metal modified aluminum polyphosphate pigment. The remainder of the coating composition may comprise components generally known to those of ordinary

skill in the art. The coating may optionally include about 0.1 to about 20 parts by weight, for example, about 0.5 to about 15 parts by weight of one or more ion exchanged inorganic pigments.

[0048] Various metal modified aluminum polyphosphates are commercially available such as zinc aluminum phosphate sold by Tayca as K-WHITE® 105 and K-WHITE® 108 or by SNCZ as NOVINOX™ PAZ. Strontium aluminum polyphosphate is also available from Huebach as HUECOPHAS™ SRPP and SAPP, or from SNCZ as NOVINOX™ PAS. Manganese aluminum polyphosphate is also available from SNCZ as NOVINOX™ PAM. Ion exchanged inorganic pigments are available from WR Grace under the tradename SHIELDEX® AC5 or AC3, which is a cation exchanged calcium ion exchanged silica. An example of an anion exchanged inorganic pigment is HALOX® 430, available from Halox.

[0049] A preferred area of application for the acetoacetoxy functionalized epoxy-polyester copolymers according to the invention is in coating preparations. In this respect, coatings comprising the acetoacetoxy functionalized epoxy-polyester copolymers and a crosslinker as described above are useful. It is noted however that coatings comprising resin blends comprising the acetoacetoxy functionalized epoxy-polyester copolymers described herein with one or more other acetoacetoxy functionalized polymers, including without limitation acetoacetoxy functionalized acrylics, epoxies, alkyds, and polyesters may be useful.

[0050] Compositions according to the invention can be used in the production of final and/or intermediate coatings on a wide variety of substrates, for example on those of organic or inorganic nature, such as, for example, wood, textiles, plastics, glass, ceramics or building materials, but in particular on metal, and more particularly Alodine 1200 and 1000 — chrome pretreated aluminum and non-chrome pretreatment aluminum. Furthermore the mixtures according to the invention can be employed as constituents of paints and coatings for coating industrial articles and domestic appliances, such as, for example, refrigerators, washing machines, electrical devices, windows and doors. Application can be carried out by, for example, brushing, spraying, dipping etc.

[0051] The coatings obtained are notable for improved flexibility.

[0052] EXAMPLES

[0053] The invention is described further by the following example, which is intended to be illustrative and by no means limiting.

[0054] Preparation of AcAc functional polyester epoxy resins

[0055] Example 1

[0056] To a four-necked reactor equipped with an overhead stirrer, temperature controller, horizontal condenser and nitrogen inlet, 130.6 grams of a carboxylic acid functional polyester polycaprolactone polyol (Dicap 1000), 326.5 grams of a monofunctional epoxide (Cardura E10), 146.5 grams dimethylolpropionic Acid (DMPA) and 0.70 grams n-methylimidazole were charged. The mixture was heat to 135°C under nitrogen and was held for 4 hours at which the acid value reached 0.34 mg KOH/g solid. The reactor was cooled to 100°C. 396.5 grams of tertiary butyl acetoacetate and 0.70 grams of tertiary butyl stannous acid were then added to the reactor. The reaction temperature was gradually increased to 145°C while collecting distillate. The mixture was cooled and 175.0 grams methylamyl ketone was added before the solution was discharged. The resulting resin had an NVM of 80.5%, a weight per gallon of 8.69 lb/gal, a Gardner-Holdt viscosity of C, a number average molecular weight of 796, and a weight average molecular weight of 1191.

[0057] Example 2

[0058] To a four-necked reactor equipped with an overhead stirrer, temperature controller, horizontal condenser and nitrogen inlet, Dicap 1000 (104.0 grams), 413.5 grams of a difunctional epoxide (Epon 828), DMPA (116.7 grams) and n-methylimidazole (0.67 grams) were charged. The mixture was heat to 135°C under nitrogen and was held until the acid value reached 2.8 mg KOH/g solid. The reactor was cooled to 100°C. Tertiary butyl acetoacetate (315.8 grams) and tertiary butyl stannous acid (0.67 grams) were then added to the reactor. The reaction temperature was gradually increased to 135°C while collecting distillate. The mixture was cooled and methylamyl ketone (166.30 grams) was added before the solution was discharged. The resulting resin had an NVM of 78.5%, a weight per gallon of 9.12 lb/gal, a Gardner-Holdt viscosity of U, a number average molecular weight of 1650, and a weight average molecular weight of 1980.

[0059] Preparation of paint formulations

[0060] Example 3

[0061] Preparation of mill base. A mixture of 105.27 grams of the resin from Example 1, 39.71 grams of a dispersing agent (DisperByk 103 available from BYK), 8.20 grams of an epoxy silane (from Dow Corning), 21.06 grams propylene glycol methyl ether acetate and 37.91 grams n- butyl acetate were mixed for 15 minutes. 3.25 grams carbon black , 98.24 grams talc, 77.58 grams Kaolin clay, 120.20 grams titanium oxide and 230.30grams Barium Sulfate were sifted into the mixture and grind to 7 Hegman grind. 20.90 grams MAK, 100.00 grams Epon 1001-B-80 and 16.52 grams acetone were then added.

[0062] Admixture with hardener and reducer. 120.00 grams of the above described mill base dispersion was mixed thoroughly with 22.60 grams of a ketone and ester solvent blend (US-3 solvent available from The Sherwin-Williams Company), 14.07 grams proprietary ketimine epoxy adduct crosslinker (NH77 available from The Sherwin-Williams Company) hardener, inducted for 30 minutes. The admixture showed 3 hours pot life. The admixture was sprayed by Devilbiss HVLP gun at 55 psi on clean 2024T3 clad substrate with Alodine 1000 pretreatment.

[0063] Results. After 7 days ambient cure, the coating has the following properties: dry film thickness around 1.0 mil, dry adhesion rated 10 per Boeing BSS7225. Wet adhesion after 7 days water immersion was rated 10 with few blisters per Boeing BSS7225 . MEK double rub was 82. Both direct impact and reverse impact rated 60 in-lb. No cracks showed in conical mandrel testing. 3000 hour ASTM B117 salt fog average scribe creepage rated 5 per ASTM D1654 with few No.8 blisters per ASTM D714. 1000 hour filiform (top coated with SW JetGlo Express CMO 480103) scribe creepage rated 6 per ASTM D1654.

[0064] **Example 4**

[0065] Preparation of mill base. A mixture of 105.27 grams of the resin from Example 1, 39.71 grams DisperByk 103, 8.20 grams epoxy silane, 21.06 grams propylene glycol methyl ether acetate and 37.91 grams n- butyl acetate were mixed for 15 minutes. 1.98 grams carbon black , 98.07 grams K-White 108, 53.76 grams Shieldex AC-5, 59.73 grams talc, 47.17 grams Kolin clay, 73.09 grams titanium oxide and 140.03grams Barium Sulfate were sifted into the mixture and grind to 7 Hegman grind. 20.90 grams MAK, 100.00 grams Epon 1001-B-80 and 16.52 grams acetone were then added.

[0066] Admixture with hardener and reducer. 120.00 grams of the above described mill base dispersion was mixed thoroughly with 24.108 grams US-3 solvent, 15.01 grams NH77 hardener, inducted for 30 minutes. The admixture showed 4 hours pot life. The admixture was sprayed by Devilbiss HVLP gun at 55 psi on clean 2024T3 clad substrate with Alodine 1000 pretreatment.

[0067] Results. After 7 days ambient cure, the coating has the following properties: dry film thickness around 1.0 mil, dry adhesion rated 10 per Boeing BSS7225. Wet adhesion after 7 days water immersion was rated 10 per Boeing BSS7225. MEK double rub was 133. Both direct impact and reverse impact rated 60 in-lb. No cracks showed in conical mandrel testing. 3000 hour ASTM B117 salt fog average scribe creepage rated 8 per ASTM D1654 and no blisters. 1000 hour filiform (top coated with SW JetGlo Express CMO 480103) scribe creepage rated 7 per ASTM D1654.

[0068] While the invention has been explained in relation to its preferred embodiments, it is to be understood that various modifications thereof will become apparent to those skilled in the art upon reading the specification. Therefore, it is to be understood that the invention disclosed herein is intended to cover such modifications as fall within the scope of the appended claims.

I CLAIM:

1. A curable composition comprising the reaction product of:
 - (a) an acetoacetoxy functional polyester epoxy block or graft copolymer; and
 - (b) a crosslinking component.
2. The curable composition of claim 1, wherein the acetoacetoxy functional polyester epoxy copolymer comprises the reaction product of:
 - (a) an epoxy functional agent, and
 - (b) an acid functional polyester polyol.
3. The curable composition of claim 2, wherein the epoxy functional agent is a monoepoxide.
4. The curable composition of claim 2, wherein the epoxy functional agent is a polyepoxide having two or more epoxy functionalities.
5. The curable composition of claim 4, wherein the acetoacetoxy functional polyester epoxy block copolymer is a diblock copolymer.
6. The curable composition of claim 4, wherein the acetoacetoxy functional polyester epoxy block copolymer is a triblock copolymer.
7. The curable composition of claim 4, wherein the acetoacetoxy functional polyester epoxy copolymer is a graft copolymer.
8. The curable composition of claim 1, wherein the crosslinking component is an isocyanate functional crosslinker.
9. The curable composition of claim 1, wherein the crosslinking component comprises at least one imine functional compound having an average of at least two imine groups per molecule which are reactive with acetoacetoxy functionality.
10. The curable composition of claim 8, further comprising at least one other acetoacetoxy functional polymer selected from the group consisting of acetoacetoxy functional acrylics, epoxies, polyesters and alkyds.
11. The curable composition of claim 10, further comprising a metal modified aluminum polyphosphate pigment.

INTERNATIONAL SEARCH REPORT

International application No

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A. CLASSIFICATION OF SUBJECT MATTER

INV. C08K9/02 C08G59/14 C08G59/40 C08G63/91
ADD.

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B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C08K C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2008/089410 A1 (3M INNOVATIVE PROPERTIES CO [US]; GOEB SIEGFRIED [DE]; HASENBERG DIRK) 24 July 2008 (2008-07-24) page 5, line 15 - page 6, line 27 claim 1 -----	1-11
A	US 4 816 528 A (DERVAN ANDREW H [US] ET AL) 28 March 1989 (1989-03-28) claim 1 -----	1-11
A	WO 94/17111 A1 (VALSPAR CORP [US]) 4 August 1994 (1994-08-04) claim 1 -----	1-11



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

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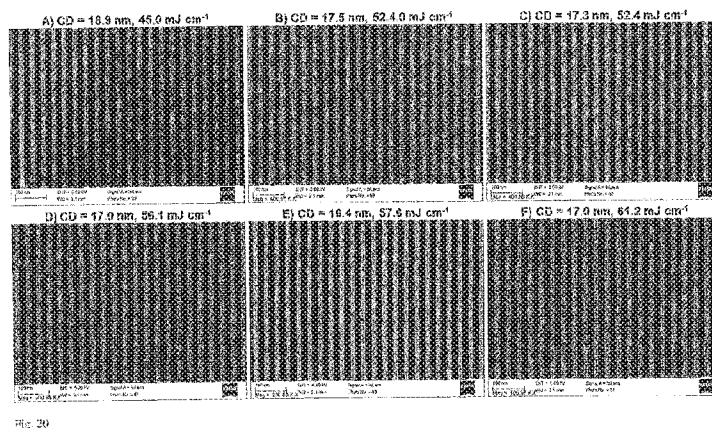
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(54) Title: ORGANOMETALLIC SOLUTION BASED HIGH RESOLUTION PATTERNING COMPOSITIONS AND CORRESPONDING METHODS



(57) Abstract: Organometallic radiation resist compositions are described based on tin ions with alkyl ligands. Some of the compositions have branched alkyl ligands to provide for improved patterning contrast while maintaining a high degree of solution stability. Blends of compounds with distinct alkyl ligands can provide further improvement in the patterning. High resolution patterning with a half-pitch of no more than 25 nm can be achieved with a line width roughness of no more than about 4.5 nm. Synthesis techniques have been developed that allow for the formation of alkyl tin oxide hydroxide compositions with very low metal contamination.

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ORGANOMETALLIC SOLUTION BASED HIGH RESOLUTION PATTERNING COMPOSITIONS AND CORRESPONDING METHODS

CROSS REFERENCE TO RELATED APPLICATIONS

5 This application claims priority to U.S. Provisional Application No. 62/067,552 filed on October 23, 2014 to Meyers et al., entitled "Organo-Tin Compounds for Forming High Resolution Radiation Patternable Films, Precursor Compounds and Solutions, and Corresponding Methods," and to U.S. Provisional Application No. 62/119,972 filed on February 24, 2015 to Meyers et al., entitled "Organo-Tin Compounds for Forming High
10 Resolution Radiation Patternable Films, Precursor Formulations and Solutions, and Corresponding Methods," both of which are incorporated herein by reference.

FIELD OF THE INVENTION

15 The invention relates to radiation-based methods for the performance of patterning materials using an organometallic coating composition. The invention further relates to precursor solutions that can be deposited to form organometallic coatings that can be patterned with very high resolution with radiation and to the coated substrates and coatings formed with the precursor solutions before and after patterning.

BACKGROUND OF THE INVENTION

20 For the formation of semiconductor-based devices as well as other electronic devices or other complex fine structures, materials are generally patterned to integrate the structure. Thus, the structures are generally formed through an iterative process of sequential deposition and etching steps through which a pattern is formed of the various materials. In this way, a
25 large number of devices can be formed into a small area. Some advances in the art can involve that reduction of the footprint for devices, which can be desirable to enhance performance.

 Organic compositions can be used as radiation patterned resists so that a radiation pattern is used to alter the chemical structure of the organic compositions corresponding with the pattern. For example, processes for the patterning of semiconductor wafers can entail
30 lithographic transfer of a desired image from a thin film of organic radiation-sensitive material. The patterning of the resist generally involves several steps including exposing the resist to a selected energy source, such as through a mask, to record a latent image and then developing and removing selected regions of the resist. For a positive-tone resist, the exposed regions are

transformed to make such regions selectively removable, while for a negative-tone resist, the unexposed regions are more readily removable.

Generally, the pattern can be developed with radiation, a reactive gas, or liquid solution to remove the selectively sensitive portion of the resist while the other portions of the resist act as a protective etch-resistant layer. Liquid developers can be particularly effective for developing the latent image. The substrate can be selectively etched through the windows or gaps in the remaining areas of the protective resist layer. Alternatively, desired materials can be deposited into the exposed regions of the underlying substrate through the developed windows or gaps in the remaining areas of the protective resist layer. Ultimately, the protective resist layer is removed. The process can be repeated to form additional layers of patterned material. The functional inorganic materials can be deposited using chemical vapor deposition, physical vapor deposition or other desired approaches. Additional processing steps can be used, such as the deposition of conductive materials or implantation of dopants. In the fields of micro- and nanofabrication, feature sizes in integrated circuits have become very small to achieve high-integration densities and improve circuit function.

SUMMARY OF THE INVENTION

In a first aspect, the invention pertains to a coating solution comprising an organic solvent and a first organometallic compound represented by the formula $\text{RSnO}_{(3/2-x/2)}(\text{OH})_x$ where $(0 < x < 3)$ with from about 0.0025M to about 1.5M tin in the solution, where R is an alkyl group or cycloalkyl group with 3-31 carbon atoms, where the alkyl or cycloalkyl group is bonded to the tin at a secondary or tertiary carbon atom.

In a further aspect, the invention pertains to a coating solution comprising an organic solvent, a first organometallic compound represented by the formula $\text{RSnO}_{(3/2-x/2)}(\text{OH})_x$ where $(0 < x < 3)$, where R is an alkyl group or cycloalkyl group with 3-31 carbon atoms, where the alkyl or cycloalkyl group is bonded to the tin at a secondary or tertiary carbon atom, and a second organometallic compound distinct from the first organometallic compound and represented by the formula $\text{R}'\text{SnO}_{(3/2-x/2)}(\text{OH})_x$ where $(0 < x < 3)$, where R' is a linear or branched alkyl or cycloalkyl group and wherein R and R' are not the same.

In another aspect, the invention pertains to a method for patterning a film on a substrate, the method comprising:

exposing the film with EUV doses of no more than about 80 mJ/cm^2 ; and
developing the film to form features at half-pitch no more than about 25 nm and linewidth roughness no more than about 5 nm.

exposing the organometallic film to EUV radiation at a dose-to-gel value of no more than about 15 mJ/cm² to obtain a contrast of at least about 6.

10 In a further aspect, the invention pertains to a solution comprising a solvent and a compound represented by the formula $\text{RSnO}_{(3/2-x/2)}(\text{OH})_x$ where $(0 < x < 3)$, where R is an alkyl, cycloalkyl or substituted alkyl moiety having from 1 to 31 carbon atoms, the solution having individual concentrations of contaminant metals of no more than about 1 ppm by weight.

hydrolyzing a precursor composition having the formula $R\text{SnX}_3$, where X represents a halide atom (F, Cl, Br or I), or amido group(s), or combinations thereof wherein the hydrolysis is performed with sufficient water to effectuate the hydrolysis, wherein the hydrolysis product has individual concentrations of metals other than tin of no more than about 1 ppm by weight.

Fig. 1 is a schematic perspective view of a radiation patterned structure with a latent image.

Fig. 3 is a schematic perspective view of the structure of Fig. 1 after development of the latent image to remove un-irradiated coating material to form a patterned structure.

Fig. 5 is a schematic perspective view of the structure of Fig. 1 after development of
30 the latent image to remove irradiated coating material to form a patterned structure.

Fig. 7 is a side plan view of the patterned structure of Figs. 3 and 4 following etching of the underlayer.

Fig. 9 is a side plan view of a "thermal freeze" double patterning process flow. The process shown in Figs. 1-3 is repeated after a bake that renders the first layer insoluble to the second layer.

Fig. 11 is a plot of mass spectral analysis as a function of sample temperature performed in combination with the thermogravimetric analysis of Fig. 10.

Fig. 13 is a plot of a representative time correlation function from the dynamic light scattering measurement used to obtain particle size distributions such as that of Fig. 12.

Fig. 15 is a representative ^1H NMR spectrum of a solution of compound 1 as described in Example 3.

Fig. 17 is a plot of contrast as a function of dose-to-gel for three different coating compositions having distinct alkyl ligands (n-butyl, iso-propyl and t-butyl).

25 Fig. 19 is a scanning electron micrograph of a silicon wafer patterned with iso-propyl tin oxide hydroxide following exposure using 13.5-nm wavelength EUV radiation in a bright-field pattern of 22-nm contact holes on a 44 nm pitch with a +20% bias and following development.

Fig. 21 is a plot of dose-to-size plotted as a function of coating composition for formulations A-F used to obtain the micrographs in Fig. 20.

Fig. 22 is a ^1H NMR spectrum of $i\text{-PrSn}(\text{NMe}_2)_3$ prepared as described in Example 7.

Fig. 23 is a ^{119}Sn NMR spectrum of $i\text{-PrSn}(\text{NMe}_2)_3$ prepared as described in Example 7.

Fig. 24 is plot of weight as a function of temperature in a thermogravimetric analysis of a sample of isopropyl tin oxide hydroxide prepared by Method 1 in Example 7.

Fig. 25 is a mass spectral analysis performed in conjunction with the thermogravimetric analysis of Fig. 24.

Fig. 26 is plot of weight as a function of temperature in a thermogravimetric analysis of a sample of isopropyl tin oxide hydroxide prepared by Method 2 in Example 7.

Fig. 27 is an SEM micrograph of a silicon wafer patterned with isopropyl tin oxide hydroxide synthesized using Method 1 of Example 7 following exposure to EUV radiation at an imaging dose of 60 mJ cm^{-2} , with resulting 14.5 nm resist lines patterned on a 34 nm pitch with an LWR of 2.9 nm..

Fig. 28 is a plot of weight as a function of temperature in a thermogravimetric analysis of a sample of isopropyl tin oxide hydroxide formed using the process of Example 10.

Fig. 29 is a mass spectral analysis performed in conjunction with the thermogravimetric analysis of Fig. 28.

Fig. 30 is a ^1H NMR spectrum of $t\text{-AmylSn}(\text{C}\equiv\text{CPh})_3$ synthesized by the method of Example 11.

Fig. 31 is a ^{119}Sn NMR spectrum of $t\text{-AmylSn}(\text{C}\equiv\text{CPh})_3$ synthesized by the method of Example 11.

Fig. 32 is a ^{119}Sn NMR spectrum of $t\text{-amyl tin oxide hydroxide}$ synthesized as described in Example 11.

Fig. 33 is a ^1H NMR spectrum of $t\text{-amyl tin oxide hydroxide}$ synthesized as described in Example 11.

Fig. 34 is a set of SEM micrographs of silicon wafers with isopropyl tin oxide hydroxide (right images) or $t\text{-butyl tin oxide hydroxide}$ (left images) exposed to 30-keV electron beam and developed at a pitch of 32-nm (top) and 28-nm (bottom).

Fig. 35 is a set of two SEM micrographs of a silicon wafer patterned with isopropyl tin oxide hydroxide following exposure to EUV radiation and development for positive tone imaging with 100-nm (a) pitch and 60-nm (b) pitch.

DETAILED DESCRIPTION OF THE INVENTION

It has been discovered that organo-tin compounds with bonds to alkyl groups, especially branched alkyl groups (including cyclic ligands), can be used as improved radiation patterned precursor film forming compounds. Films formed with the compounds can be patterned with desirable doses of radiation to achieve very high resolution patterns. The ligand structure for the organo-tin compounds provides for good precursor solution stability and good radiation sensitivity upon forming a coating. While alkyl-tin compounds with branched alkyl ligands have been found to provide for particularly improved patterning at lower radiation doses, use of a mixture of alkyl ligands provides for further potential improvement through the engineering of several features of the resulting coatings facilitating patterning. Desirable features of coatings formed with the organometallic precursor solutions provide for large radiation absorption and superior direct patterning for the formation of a patterned metal oxide coating. Precursor solutions with low metal contamination, distinct from the metal, for example, tin, or combination of metals comprising the organometallic coating composition, provide for coating formation useful for applications where metal contamination can be unsuitable for the associated materials and devices. Appropriate processing techniques for the formation of low contaminant precursor solutions are described. Precursor solutions can be coated using appropriate techniques. Radiation patterning and development of the latent image can be performed to achieve images with a high degree of resolution and low line width roughness with very small pattern features.

Exposure to radiation alters the composition of the irradiated organometallic coating material, disrupting the structure defined by the alkyl ligands and permitting further condensation and reaction with moisture from any source, such as ambient moisture. On the basis of these chemical changes dissolution rates may vary substantially between irradiated and non-irradiated portions of the film with selection of appropriate developer compositions, facilitating either negative tone patterning or positive tone patterning with the same coating in some embodiments. In negative patterning, exposure to radiation and potential subsequent condensation converts the irradiated coating material into a material that is more resistant to removal with organic solvent-based developer compositions relative to the non-irradiated coating material. In positive patterning, exposure sufficiently changes the polarity of the exposed coating material, e.g., increasing the polarity, such that the exposed coating material can be selectively removed with an aqueous solvent or other sufficiently polar solvent. Selective removal of at least a portion of the coating material can leave a pattern where regions of coating have been removed to expose the underlying substrate. After development of the

coating following irradiation, the patterned oxide materials can be used for facilitating processing in device formation with excellent pattern resolution. The coating materials can be designed to be sensitive to selected radiation, such as extreme ultraviolet light, ultraviolet light and/or electron beams. Furthermore, the precursor solutions can be formulated to be stable with an appropriate shelf life for commercial distribution.

The metal ions generally also are further bound to one or more oxo-ligands, i.e., M-O and/or hydroxo-ligands, i.e., M-O-H, in addition to the organic ligands. The alkyl ligands and the oxo/hydroxo ligands provide desirable features to precursor solution and corresponding coating by providing significant control over the condensation process to a metal oxide with resulting significant processing, patterning, and coating advantages. The use of organic solvents in the coating solutions supports the stability of the solution, while the non-aqueous solution based processing maintains the ability to selectively develop the resulting coating following the formation of a latent image with excellent development rate contrast, for both positive tone patterning and negative tone patterning due to the change in solubility of the exposed regions relative to the unexposed regions. Desirable precursor solutions with dissolved alkyl-stabilized metal ions provide for convenient solution based deposition to form a coating that can have high radiation sensitivity and excellent contrast with respect to etch resistance to allow for fine structure formation. The design of the precursor composition can provide for the formation of a coating composition with a high sensitivity to a particular radiation type and/or energy/wavelength.

The ligand structure of the precursor organometallic compositions are believed to provide the observed desirable stability of the precursor solutions as well as the radiation patterning function. In particular, it is believed that the absorption of radiation can provide for the disruption of the bonds between the metal and the organic ligands to create a differentiation of the composition at the irradiated and non-irradiated sections of the coated material. This differentiation can be further amplified by suitable processing of the exposed film prior to development, after development, or both. Thus, the compositional changes to form the improved precursor solutions also provide for improved development of the image. In particular, the irradiated coating material may result in a stable inorganic metal oxide material with a tunable response to the developer.

Through proper developer selection either positive or negative-tone images can be developed. In some embodiments, suitable developers include, for example, 2.38% TMAH, i.e., the semiconductor industry standard. The coating layers can be made thin without pattern loss during development from removing the coating material from regions where the coating

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within a single ligand structure: e.g., stability, solubility, radiation sensitivity, size, etc. Thus the formulation of mixed metal ions with distinct alkyl ligands in the precursor compositions may provide the basis for a range of improved performance parameters, including the desirable patterning dose and line-width roughness values demonstrated in a subsequent example.

5 The use of organo-metal compounds for radiation resist coatings is described generally in published U.S. patent application 2015/0056542 to Meyers et al. ("the '542 application"), entitled "Organometallic Solution Based High Resolution Patterning Compositions," incorporated herein by reference. The '542 application exemplifies n-butylSnOOH and di-
10 vinylSn(OH)₂ compositions for the formation of a radiation sensitive patterning layer, and describes the desirability of alkyl ligands involving compounds with tin, indium, antimony or a combination thereof. These general compositions are relevant for appropriate embodiments described herein. It has been discovered that branched alkyl ligands, such as tert-butyl, isopropyl, or tert-amyl (1,1-dimethylpropyl) attached to tin, and branched at the carbon of tin attachment (α -carbon branched), can be effectively used as radiation patterning resists with
15 lower radiation doses than those containing unbranched ligands. Similarly, other alkyl and cyclo-alkyl ligands branched at the α -carbon, including 2-butyl, cyclohexyl, cyclopentyl, cyclobutyl, cyclopropyl, 1-adamantyl, and 2-adamantyl are contemplated, and within the scope of the present disclosure along with mixtures of compounds with alkyl ligands as describe herein. In other words, the resists with branched organic ligands contain alkyl or cycloalkyl
20 ligands bonded to the Sn atom via secondary or tertiary carbon atoms, $\text{RSnO}_{(3/2-x/2)}(\text{OH})_x$, ($0 < x < 3$), where R is a secondary or tertiary alkyl or cycloalkyl group with 3 to 31 carbon atoms. Alternatively, this composition may be expressed as $\text{R}_1\text{R}_2\text{R}_3\text{CSnO}_{(3/2-x/2)}(\text{OH})_x$, ($0 < x < 3$), where R₁ and R₂ are independently an alkyl group with 1-10 carbon atoms, R₃ is hydrogen or an alkyl group with 1-10 carbon atoms in which R₁, R₂ can form a cyclic carbon chain as well
25 as R₃ optionally also in a cyclic carbon structure where the ranges of carbon atoms are additive if a cyclic structure. A person of ordinary skill in the art will recognize that the order of the R₁, R₂ and R₃ is essentially arbitrary, so that a comparison of groups in different compounds can take into account an arbitrary reordering and does not change the compound or associated comparison of the compound. In the same concept, a compound does not avoid the scope of
30 this formula through the arbitrary assignment of an H to R₁ or R₂ rather than R₃ since the formula instructs the association of a single H with R₃. While not wanting to be limited by theory, it is believed that the structure of these branched alkyl ligands facilitates cleavage of the Sn-C bond during exposure, thereby increasing the sensitivity of the resist to radiation.

This facilitation may be attributable to the increased stability of secondary and tertiary alkyl radical or carbocation intermediates relative to related primary alkyl moieties. While not directly documented in Sn-C radiolysis studies, similar properties are evident in tabulated C-H bond-dissociation energies. Thus, the improved compositions described herein provide for significant commercial advantages through lower radiation processing to achieve high resolution patterns with low line width roughness. High resolution patterns with low line width roughness can thus be achieved with lower radiation doses for processing improvements relative to similar superior resolution and low line with roughness achieved with metal oxide based photoresists with peroxide based ligands, as described in the '000 patent cited above.

The new precursor solutions have been formulated with improved stability and control of network formation and precipitation relative to inorganic resist materials with peroxide based ligands. Characterization of ligands as radiation sensitive in this case refers to the lability of the metal-ligand bond following absorption of radiation, so that radiation can be used to induce a chemical change in the material. In particular, alkyl ligands stabilize the precursor solutions while also providing control over the processing of the materials, and selection of the ratio of alkyl ligands to metal ions can be adjusted to control properties of the solution and the resulting coatings.

The precursor compositions comprising a mixture with different alkyl ligands can comprise mixtures of two alkyl-tin compounds with different organic ligands, three alkyl-tin compounds with different organic ligands, or more than three alkyl-tin compounds with different alkyl ligands. Generally, for binary or tertiary mixtures, the mixture comprises at least about 8 mole percent of each component with distinct alkyl ligands, in some embodiments at least about 12 mole percent and in further embodiments at least about 25 mole percent of each component with distinct alkyl ligands. A person of ordinary skill in the art will recognize that additional ranges of mixture components within the explicit ranges above are contemplated and are within the present disclosure.

The alkyl ligands, especially branched alkyl ligands, stabilize the metal cation with respect to condensation in the absence of exposure. In particular, at appropriate concentrations of alkyl-based ligands, unintended formation of condensed metal oxides or metal hydroxides and related agglomerates are very slow if they spontaneously occur at all at room temperature. Based on the discovery of this stabilization property, solutions can be formed with high concentrations of radiation sensitive ligands that have good shelf stability while retaining convenient processing to form coatings. Energy from absorbed radiation can break the metal-alkyl ligand bond. As these bonds are broken, the corresponding stabilization with respect to

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The processing approaches that allow for the formation of low metal contaminant precursors avoid the use of reactants, such as bases (e.g., NaOH), that introduce contaminant metals into the compositions. Alternative bases that can provide low metal contamination include, for example, tetramethyl ammonium hydroxide and other quaternary ammonium hydroxides. Also, water can be directly used for the hydrolysis in an organic solvent with the water provided from the atmosphere or added in a controlled amount. Given the very low trace-metal levels specified in semiconductor device manufacturing (generally < 10 ppb for resist compositions), if even modest amounts of contaminant metals are introduced, techniques have not been identified to adequately remove the contaminant metals from a formulated alkyltin oxide hydroxide resist. Thus, appropriately hydrolysable ligands, e.g., halides or amides, are replaced with oxo-hydroxo ligands through alternative hydrolysis reactions that do not contribute substantial concentrations of non-tin metals. The hydrolysate can be purified to remove reaction byproducts through appropriate approaches, such as precipitation, washing, and recrystallization and/or redissolving in a suitable solvent.

Generally, the precursor coating solution can comprise sufficient radiation sensitive alkyl ligands such that the solution has a molar concentration ratio of radiation sensitive ligands to metal cations from about 0.1 to about 2. Ligand ratios in this range may be prepared by hydrolysis of SnX_4 , RSnX_3 or R_2SnX_2 precursors in the appropriate stoichiometry, subject to the constraints of precursor stability and solubility. The coating formed from the precursor solution is influenced by the ligand structure of the ions in the precursor solution and may be an equivalent ligand structure around the metal upon drying or the ligand structure can be altered during the coating and/or drying process. The coating generally is also influenced by exposure to the radiation to enable the patterning function. In general, the coating can be represented by the formulation $(\text{R})_z\text{SnO}_{2-z/2-x/2}(\text{OH})_x$ ($0 < (x+z) < 4$), where R is an alkyl group or cycloalkyl group with 3-31 carbon atoms, where the alkyl or cycloalkyl group is bonded to the tin at a secondary or tertiary carbon atom. For unirradiated coating, the value of z can be the same or close to the coating solution value, while the irradiated coating generally has a lower value of z, which can be driven close to 0 by further heating and/or irradiation, such as following patterning. In particular, the alkyl ligand concentrations provide for a surprisingly large improvement in the precursor stability and control in network formation with solutions formed with organic solvents, generally polar organic solvents. While not wanting to be limited by theory, a radiation sensitive, low polarity ligand concentration in the appropriate range evidently reduces unintended condensation and agglomeration of the metal cations with corresponding oxo-ligands and/or hydroxo-ligands, to stabilize the solution. Thus, the

precursor coating solution can be stable relative to settling of solids without further stirring for at least one week and possibly for significantly longer periods of time, such as greater than a month. Due to the long stability times, the alkyltin oxide hydroxide precursors have increased versatility with respect to potential commercial uses. The overall molar concentration can be selected to achieve a desired coating thickness and desired coating properties, which can be obtained consistent with desired stability levels.

The polyatomic metal oxo/hydroxo cations with alkyl ligands can be selected to achieve the desired radiation absorption. In particular, tin based coating materials exhibit good absorption of far ultraviolet light at a 193 nm wavelength and extreme ultraviolet light at a 13.5 nm wavelength. Table 1 lists optical constants (n=index of refraction and k=extinction coefficient) at selected wavelengths for a coating material formed from monobutyltin oxide hydrate and baked at 100°C.

TABLE 1

Wavelength (nm)	n	k
193	1.75	0.211
248	1.79	0.0389
365	1.63	0
405	1.62	0
436	1.61	0

To correspondingly provide a high absorption of radiation generally used for patterning, it is desirable to include Sn, In and Sb metals in the precursor solutions, although these metals can be combined with other metals to adjust the properties, especially the radiation absorption. Hf provides good absorption of electron beam material and extreme UV radiation and In and Sb provide strong absorption of extreme ultraviolet light at 13.5 nm. For example, one or more metal compositions comprising Ti, V, Mo, or W or combinations thereof can be added to the precursor solution to form a coating material with an absorption edge moved to longer wavelengths, to provide, for example, sensitivity to 248 nm wavelength ultraviolet light. These other metal ions may or may not involve an alkyl ligand, and suitable salts for the metal ions without alkyl ligands for use in the precursor compositions described herein may include, for example, organic or inorganic salts, amides, alkoxides, or the like that are soluble in the solvent for the coating precursor solution. For the determination of metal contaminants, clearly specifically added functional metals are not considered as contaminants, and these metals can generally be identified by a presence in the precursor solutions at a level greater than 100 ppm

by weight, and such metals can be selected to avoid undesirable contamination for a particular application.

In general, the desired hydrolysate can be dissolved in an organic solvent, e.g., alcohols, esters or combinations thereof to form the precursor solution. The concentrations of the species
5 in the coating solutions can be selected to achieve desired physical properties of the solution. In particular, lower concentrations overall can result in desirable properties of the solution for certain coating approaches, such as spin coating, that can achieve thinner coatings using reasonable coating parameters. It can be desirable to use thinner coatings to achieve ultrafine patterning as well as to reduce material costs. In general, the concentration can be selected to
10 be appropriate for the selected coating approach. Coating properties are described further below.

The precursor solutions can be deposited generally with any reasonable coating or printing technique as described further below. The coating generally is dried, and heat can be applied to stabilize or partially condense the coating prior to irradiation. Generally, the coatings
15 are thin, such as with an average thickness of less than 10 microns, and very thin submicron coatings, for example, no more than about 100 nanometers (nm), can be desirable to pattern very small features. To form high resolution patterns, radiation sensitive organic compositions can be used to introduce patterns, and the compositions can be referred to as resists since portions of the composition are processed to be resistant to development/etching such that
20 selective material removal can be used to introduce a selected pattern. The dried coating can be subjected to appropriate radiation, e.g., extreme ultraviolet light, e-beam or ultraviolet light, with the selected pattern or the negative of the pattern to form a latent image with developer resistant regions and developer dissolvable regions. After exposure to appropriate radiation, and prior to developing, the coating can be heated or otherwise reacted to further differentiate
25 the latent image from non-irradiated areas. The latent image is contacted with the developer to form a physical image, i.e., a patterned coating. The patterned coating can be further heated to stabilize the remaining coating patterned on the surface. The patterned coating can be used as a physical mask to perform further processing, e.g., etching of the substrate and/or deposition of additional materials according to the pattern. At appropriate points of the processing after
30 using the patterned resist as desired, the remaining patterned coating can be removed, although the patterned coating can be incorporated into the ultimate structure. Very fine features can be accomplished effectively with the patterning compositions described herein.

In some embodiments, the resulting patterned material can be incorporated into the structure following appropriate stabilization through at least some condensation into an

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Precursor Solutions

The precursor solutions for forming the resist coatings generally comprise tin cations with appropriate alkyl stabilizing ligands in a solvent, generally an organic solvent. The precursor solutions and the ultimate resist coatings are based on metal oxide chemistry, and the organic solutions of metal polycations with alkyl ligands provide stable solutions with good resist properties. Branched alkyl ligands in particular provide improved patterning capability.

The ligands provide the radiation sensitivity, and the particular selection of ligands can influence the radiation sensitivity. Also, the precursor solutions can be designed to achieve desired levels of radiation absorption for a selected radiation based on the selection of the metal cations as well as the associated ligands. The concentration of ligand stabilized metal cations in the solution can be selected to provide suitable solution properties for a particular deposition approach, such as spin coating. The precursor solutions have been formulated to achieve very high levels of stability such that the precursor solutions have appropriate shelf lives for commercial products. As described in the following section, the precursor solutions can be applied to a substrate surface, dried and further processed to form an effective radiation resist. The precursor solutions are designed to form a coating composition upon at least partial solvent removal and ultimately an inorganic solid dominated by tin oxides upon irradiation and/or thermal treatment, exposure to a plasma, or similar processing.

The precursor solutions generally comprise one or more tin cations. In aqueous solutions, metal cations are hydrated due to interactions with the water molecules, and hydrolysis can take place to bond oxygen atoms to the metal ion to form hydroxide ligands or oxo bonds with the corresponding release of hydrogen ions. The nature of the interactions is generally pH dependent. As additional hydrolysis takes place in aqueous solutions, the solutions can become unstable with respect to precipitation of the metal oxide or with respect to gelation. Ultimately, it is desirable to form the oxide material, but this progression can be controlled better with the precursor solutions based on organic solvents with alkyl ligand stabilized metal cations. If placed over an atmosphere with water vapor, the solvent may comprise some dissolved water in equilibrium with the partial pressure of water in contact with the solvent, and the examples demonstrate the use of dissolved water to effect controlled hydrolysis of hydrolysable ligands. With the precursor solutions based on alkyl-stabilization ligands and an organic solvent, progression to the oxide can be controlled as part of the procedure for processing the solution first to a coating material and then to the ultimate metal oxide composition with organic ligands. As described herein, alkyl ligands, especially

branched alkyl ligands and/or combinations of alkyl ligands, can be used to provide significant control to the processing of the solution to an effective radiation resist composition.

In general, the precursor compounds can be represented by the formula $\text{RSnO}_{(3/2-x/2)}(\text{OH})_x$, ($0 < x < 3$) where R is a linear or branched (i.e., secondary or tertiary at the metal bonded carbon atom) alkyl group. R generally has from 1 to 31 carbon atoms with 3 to 31 carbon atoms for the branched embodiments. In particular, branched alkyl ligands are desirable where the compound can be represented in another representation by $\text{R}_1\text{R}_2\text{R}_3\text{CSnO}_{(3/2-x/2)}(\text{OH})_x$, ($0 < x < 3$) where R_1 and R_2 are independently an alkyl group with 1-10 carbon atoms, and R_3 is hydrogen or an alkyl group with 1-10 carbon atoms. In some embodiments R_1 and R_2 can form a cyclic alkyl moiety, and R_3 may also join the other groups in a cyclic moiety. Precursor solutions may also comprise blends of compositions with different alkyl ligands. Exemplified branched alkyl ligands include isopropyl (R_1 and R_2 are methyl and R_3 is hydrogen), tert-butyl (R_1 , R_2 and R_3 are methyl), sec-butyl (R_1 is methyl, R_2 is $-\text{CHCH}_3$, and R_3 is hydrogen) and tert-amyl (R_1 and R_2 are methyl and R_3 is $-\text{CHCH}_3$). Preliminary experiments with cyclic alkyl ligands have shown promising results. Examples of suitable cyclic groups include, for example, 1-adamantyl ($-\text{C}(\text{CH}_2)_3(\text{CH})_3(\text{CH}_2)_3$ or tricyclo(3.3.1.1^{3,7}) decane bonded to the metal at tertiary carbon) and 2-adamantyl ($-\text{CH}(\text{CH})_2(\text{CH}_2)_4(\text{CH})_2(\text{CH}_2)$ or tricyclo(3.3.1.1^{3,7}) decane bonded to the metal at a secondary carbon). Thus, the solutions of the metal cations are poised for further processing. In particular, it can be desirable to use as an added component of the precursor solution, a polynuclear tin oxo/hydroxo cation that can poise the solution further toward a tin oxide composition. In general, the precursor solution comprises from about 0.01M to about 1.4M metal polynuclear oxo/hydroxo cation, in further embodiments from about 0.05M to about 1.2M, and in additional embodiments from about 0.1M to about 1.0M. A person of ordinary skill in the art will recognize that additional ranges of tin polynuclear oxo/hydroxo cations within the explicit ranges above are contemplated and are within the present disclosure.

The precursor compositions comprising a mixture with different organic ligands can comprise mixtures of two alkyl-tin compounds with different alkyl ligands, three alkyl-tin compounds with different alkyl ligands, or more than three alkyl-tin compounds with different alkyl ligands. Generally, for binary or tertiary mixtures, the mixture comprises at least about 8 mole percent of each component with distinct alkyl ligands, in some embodiments at least about 12 mole percent and in further embodiments at least about 25 mole percent of each component with distinct alkyl ligands. A person of ordinary skill in the art will recognize that

The metal generally significantly influences the absorption of radiation. Tin provides strong absorption of extreme ultraviolet light at 13.5 nm. In combination with alkyl ligands, the cations also provide good absorption of ultraviolet light at 193 nm wavelength. Tin also provides good absorption of electron beam radiation. The energy absorbed is modulated by the metal-organic interactions, which can result in the rupturing of the metal-ligand and the desired control over the material properties.

The alkyl ligands stabilize the composition with respect to unintended spontaneous condensation and agglomeration of the hydrolysate. In particular, at high relative concentration of alkyl ligands, formation of condensed metal oxides or metal hydroxides are very slow if the condensation spontaneously occurs at all at room temperature. Based on the discovery of this stabilization property, hydrolysate solutions can be formed with high concentrations of radiation sensitive ligands that have good shelf stability while retaining convenient processing to form coatings. Radiation sensitive ligands include alkyl moieties forming a tin-carbon bond. Energy from absorbed radiation can break the tin-alkyl ligand bond. As these bonds are broken, the corresponding stabilization with respect to condensation is reduced or lost. The composition can change through formation of M--OH or through condensation to form M--O--M bonds, where M represents a metal atom. Thus, chemical changes can be controlled with radiation. Compositions with high radiation sensitive ligand concentrations can be highly stable with respect to the avoidance of spontaneous formation of hydroxide and condensation.

Some suitable metal compositions with desired ligand structures can be purchased from commercial sources, such as Alfa Aesar (MA, USA) and TCI America (OR, USA), see Examples below, and other metal-ligand compositions can be synthesized as described below. Low metal contaminant precursor compositions are synthesized using the methods described herein.

In general, alkyl ligands can be, for example, methyl, ethyl, propyl, butyl, and branched alkyl. Suitable branched alkyl ligands can be, for example, isopropyl, tert-butyl, tert-amyl, 2-butyl, cyclohexyl, cyclopentyl, cyclobutyl, cyclopropyl, 1-adamantyl or 2-adamantyl. Improved patterning results have been obtained using branched alkyl ligands. But fuller advantage of ligand selection has been achieved through the use of mixed alkyl ligands, as separately advantageous patterning properties such as dose and line-width-roughness imparted by different ligands may be obtained through the teachings herein through blending of multiple alkyl ligands as illustrated in the examples provided.

As described herein, processing approaches have been developed that provide for reduction of metal contamination. Thus, the precursor solutions can be formulated that have very low levels of non-tin metal. In general, the non-tin metal concentrations can all be individually reduced to values of no more than about 1 part per million by weight (ppm) in further embodiments, no more than about 200 parts per billion by weight (ppb), in additional embodiments no more than about 50 ppb, and in other embodiments no more than about 10 ppb. In some embodiments, it may be desirable to add other metal elements to influence processing, and generally these can be identified by levels of at least about 1 weight percent and in some embodiments at least about 2 weight percent, and can thus be distinguished from contaminant metals, if appropriate. Metal contaminants to be decreased in particular include alkali metals and alkaline earth metals, Au, Ag, Cu, Fe, Pd, Pt, Co, Mn, and Ni. A person of ordinary skill in the art will recognize that additional ranges of metal levels within the explicit levels above are contemplated and are within the present disclosure.

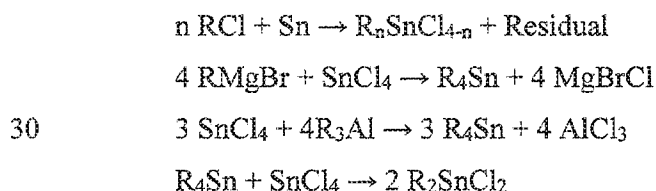
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be performed in a non-aqueous solvent or with an aqueous solvent where the product compounds immediately precipitate. In some embodiments, water can be introduced in just a sufficient amount to hydrolyse the hydrolysable ligands to form the desired alkyl tin oxide hydroxide compound.

5 With respect to the oxo/hydroxo ligands for the metal ions, these ligands can be formed during processing through hydrolysis. In some embodiments, the hydrolysis can involve replacement of hydrolysable ligands to form oxo (O) and/or hydroxo (-OH) ligands. For example, halide ligands can be hydrolysed in a basic aqueous solution with subsequent transfer to an organic solvent. However, for the production of precursor compositions with low metal
10 contamination, performing the hydrolysis using alternative reactions has been found to be desirable. Specific examples are presented below.

In some embodiments, a composition comprising the tin ions with organic stabilizing ligands and hydrolysable ligands are dissolved in an organic solvent, which is then contacted with a basic aqueous solution, whereupon substitution of the hydrolysable ligands with hydroxo
15 ligands may occur. After providing enough time to form hydroxo ligands, the aqueous solution can be separated from the organic phase assuming that the organic liquid is not soluble in the aqueous liquid. In some embodiments, the oxo/hydroxo ligands can be formed through hydrolysis from atmospheric water. The hydrolysable metal ion composition can be heated in the presence of atmospheric moisture so that the oxo/hydroxo ligands form directly in the
20 coating material, which can be relatively facile due to the high surface area. An example of hydrolysis from atmospheric water is also described below. In additional or alternative embodiments, sufficient water to effectuate the hydrolysis is dissolved into an organic solvent along with the precursor compound with the hydrolysable ligands.

To form the precursor compound with the alkyl ligands and hydrolysable ligands, M-C
25 bonds can also be formed in a solution phase substitution reaction. The following reactions are representative suitable reactions for the substitution reactions to form Sn-C bonds:



where R represents an alkyl ligand. Generally, different suitable halides can be substituted in the above reactions. The reactions can be carried out in a suitable organic solvent in which the reactants have reasonable solubility.

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contaminants or other components that do not appropriately dissolve. In some embodiments, it may be desirable to form separate solutions that can be combined to form the precursor solution from the combination. Specifically, separate solutions can be formed comprising one or more of the following: the metal polynuclear oxo/hydroxo cations, any additional metal cations, and the organic ligands. If multiple metal cations are introduced, the multiple metal cations can be introduced into the same solution and/or in separate solutions. Generally, the separate solutions or the combined solutions can be well mixed. In some embodiments, the metal cation solution is then mixed with the organic-based ligand solution such that the organic-based ligand can conjugate with the metal cations. The resulting solution can be referred to as a stabilized metal cation solution. In some embodiments, the stabilized metal cation solution is allowed to react for a suitable period of time to provide for stable ligand formation, which may or may not also involve cluster formation in solution, whether or not mixed metal ions are introduced. In some embodiments, the reaction or stabilization time for the solution can be for at least about five minutes, in other embodiments at least about 1 hour, and in further embodiments from about 2 hours to about 48 hours prior to further processing. A person of ordinary skill in the art will recognize that additional ranges of stabilization periods are contemplated and are within the present disclosure.

The concentrations of the species in the precursor solutions can be selected to achieve desired physical properties of the solution. In particular, lower concentrations overall can result in desirable properties of the solution for certain coating approaches, such as spin coating, that can achieve thinner coatings using reasonable coating parameters. It can be desirable to use thinner coatings to achieve ultrafine patterning as well as to reduce material costs. In general, the concentration can be selected to be appropriate for the selected coating approach. Coating properties are described further below.

Stability of the precursor solutions can be evaluated with respect to changes relative to the initial solution. Specifically, a solution has lost stability if phase separation occurs with the production of large sol particles or if the solution loses its ability to perform desired pattern formation. Based on the improved stabilization approaches described herein, the solutions can be stable for at least about a week without additional mixing, in further embodiments at least about 2 weeks, in other embodiments at least about 4 weeks. A person of ordinary skill in the art will recognize that additional ranges of stabilization times are contemplated and are within the present disclosure. The solutions can be formulated with sufficient stabilization times that the solutions can be commercially distributed with appropriate shelf lives.

Coating Material

A coating material is formed through the deposition and subsequent processing of the precursor solution onto a selected substrate. A substrate generally presents a surface onto which the coating material can be deposited, and the substrate may comprise a plurality of layers in which the surface relates to an upper most layer. In some embodiments, the substrate surface can be treated to prepare the surface for adhesion of the coating material. Also, the surface can be cleaned and/or smoothed as appropriate. Suitable substrate surfaces can comprise any reasonable material. Some substrates of particular interest include, for example, silicon wafers, silica substrates, other inorganic materials such as ceramic materials, polymer substrates, such as organic polymers, composites thereof and combinations thereof across a surface and/or in layers of the substrate. Wafers, such as relatively thin cylindrical structures, can be convenient, although any reasonable shaped structure can be used. Polymer substrates or substrates with polymer layers on non-polymer structures can be desirable for certain applications based on their low cost and flexibility, and suitable polymers can be selected based on the relatively low processing temperatures that can be used for the processing of the patternable materials described herein. Suitable polymers can include, for example, polycarbonates, polyimides, polyesters, polyalkenes, copolymers thereof and mixtures thereof. In general, it is desirable for the substrate to have a flat surface, especially for high resolution applications. However, in specific embodiments the substrate may possess substantial topography, where the resist coating is intended to fill or planarize features for particular patterning applications. Such a function of the resist material is described in published U.S. patent application 2015/0253667A1 to Bristol et al., entitled "Pre-Patterned Hard Mask for Ultrafast Lithographic Imaging," incorporated herein by reference.

In general, any suitable coating process can be used to deliver the precursor solution to a substrate. Suitable coating approaches can include, for example, spin coating, spray coating, dip coating, knife edge coating, printing approaches, such as inkjet printing and screen printing, and the like. Some of these coating approaches form patterns of coating material during the coating process, although the resolution available currently from printing or the like has a significantly lower level of resolution than available from radiation based patterning as described herein. The coating material can be applied in multiple coating steps to provide greater control over the coating process. For example, multiple spin coatings can be performed to yield an ultimate coating thickness desired. The heat processing described below can be applied after each coating step or after a plurality of coating steps.

If patterning is performed using radiation, spin coating can be a desirable approach to cover the substrate relatively uniformly, although there can be edge effects. In some embodiments, a wafer can be spun at rates from about 500 rpm to about 10,000 rpm, in further embodiments from about 1000 rpm to about 7500 rpm and in additional embodiments from about 2000 rpm to about 6000 rpm. The spinning speed can be adjusted to obtain a desired coating thickness. The spin coating can be performed for times from about 5 seconds to about 5 minutes and in further embodiments from about 15 seconds to about 2 minutes. An initial low speed spin, e.g., at 50 rpm to 250 rpm, can be used to perform an initial bulk spreading of the composition across the substrate. A back side rinse, edge bead removal step or the like can be performed with water or other suitable solvent to remove any edge bead. A person or ordinary skill in the art will recognize that additional ranges of spin coating parameters within the explicit ranges above are contemplated and are within the present disclosure.

The thickness of the coating generally can be a function of the precursor solution concentration, viscosity and the spin speed for spin coating. For other coating processes, the thickness can generally also be adjusted through the selection of the coating parameters. In some embodiments, it can be desirable to use a thin coating to facilitate formation of small and highly resolved features in the subsequent patterning process. For example, the coating materials after drying can have an average thickness of no more than about 10 microns, in other embodiments no more than about 1 micron, in further embodiments no more than about 250 nanometers (nm), in additional embodiments from about 1 nanometers (nm) to about 50 nm, in other embodiments from about 2 nm to about 40 nm and in some embodiments from about 3 nm to about 25 nm. A person of ordinary skill in the art will recognize that additional ranges of thicknesses within the explicit ranges above are contemplated and are within the present disclosure. The thickness can be evaluated using non-contact methods of x-ray reflectivity and/or ellipsometry based on the optical properties of the film. In general, the coatings are relatively uniform to facilitate processing. In some embodiments, the variation in thickness of the coating varies by no more than $\pm 50\%$ from the average coating thickness, in further embodiments no more than $\pm 40\%$ and in additional embodiments no more than about $\pm 25\%$ relative to the average coating thickness. In some embodiments, such as high uniformity coatings on larger substrates, the evaluation of coating uniformity may be evaluated with a 1 centimeter edge exclusion, i.e., the coating uniformity is not evaluated for portions of the coating within 1 centimeter of the edge. A person of ordinary skill in the art will recognize that additional ranges within the explicit ranges above are contemplated and are within the present disclosure.

The coating process itself can result in the evaporation of a portion of the solvent since many coating processes form droplets or other forms of the coating material with larger surface areas and/or movement of the solution that stimulates evaporation. The loss of solvent tends to increase the viscosity of the coating material as the concentration of the species in the material increases. An objective during the coating process can be to remove sufficient solvent to stabilize the coating material for further processing. These species may condense during coating or subsequent heating to forming a hydrolysate coating material. In general, the coating material can be heated prior to radiation exposure to further drive off solvent and promote densification of the coating material. The dried coating material may generally form a polymeric metal oxo/hydroxo network based on the oxo-hydroxo ligands to the metals in which the metals also have some alkyl ligands, or a molecular solid comprised of polynuclear metal oxo/hydroxo species with alkyl ligands.

The solvent removal process may or may not be quantitatively controlled with respect to specific amounts of solvent remaining in the coating material, and empirical evaluation of the resulting coating material properties generally can be performed to select processing conditions that are effective for the patterning process. While heating is not needed for successful application of the process, it can be desirable to heat the coated substrate to speed the processing and/or to increase the reproducibility of the process. In embodiments in which heat is applied to remove solvent, the coating material can be heated to temperatures from about 45°C to about 250°C and in further embodiments from about 55°C to about 225°C. The heating for solvent removal can generally be performed for at least about 0.1 minute, in further embodiments from about 0.5 minutes to about 30 minutes and in additional embodiments from about 0.75 minutes to about 10 minutes. A person of ordinary skill in the art will recognize that additional ranges of heating temperature and times within the explicit ranges above are contemplated and are within the present disclosure. As a result of the heat treatment and densification of the coating material, the coating material can exhibit an increase in index of refraction and in absorption of radiation without significant loss of contrast.

Patterned Exposure and Patterned Coating Material

The coating material can be finely patterned using radiation. As noted above, the composition of the precursor solution and thereby the corresponding coating material can be designed for sufficient absorption of a desired form of radiation. The absorption of the radiation results in energy that can break the bonds between the metal and alkyl ligands so that at least some of the alkyl ligands are no longer available to stabilize the material. Radiolysis products,

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With electron beam lithography, the electron beam generally induces secondary electrons which generally modify the irradiated material. The resolution can be a function at least in part of the range of the secondary electrons in the material in which a higher resolution is generally believed to result from a shorter range of the secondary electrons. Based on high resolution achievable with electron lithography using the inorganic coating materials described herein, the range of the secondary electrons in the inorganic material is limited. Electron beams can be characterized by the energy of the beam, and suitable energies can range from about 5 V to about 200 kV (kilovolt) and in further embodiments from about 7.5 V to about 100 kV. Proximity-corrected beam doses at 30 kV can range from about 0.1 microcoulombs per centimeter squared to about 5 millicoulombs per centimeter squared (mC/cm^2), in further embodiments from about $0.5 \mu\text{C}/\text{cm}^2$ to about $1 \text{ mC}/\text{cm}^2$ and in other embodiments from about $1 \mu\text{C}/\text{cm}^2$ to about $100 \mu\text{C}/\text{cm}^2$. A person of ordinary skill in the art can compute corresponding doses at other beam energies based on the teachings herein and will recognize that additional ranges of electron beam properties within the explicit ranges above are contemplated and are within the present disclosure.

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Following exposure with radiation, the coating material is patterned with irradiated regions and un-irradiated regions. Referring to Figs. 1 and 2, a patterned structure 100 is shown comprising a substrate 102, a thin film 103 and patterned coating material 104. Patterned coating material 104 comprises regions 110, 112, 114, 116 of irradiated coating material and uncondensed regions 118, 120, 122 of un-irradiated coating material. The patterned formed by condensed regions 110, 112, 114, 116 and uncondensed regions 118, 120, 122 represent a latent image in to the coating material, and the development of the latent image is discussed in the following section.

Development of the image involves the contact of the patterned coating material including the latent image to a developer composition to remove either the un-irradiated coating material to form the negative image or the irradiated coating to form the positive image. Using the resist materials described herein, effective negative patterning or positive patterning can be performed with desirable resolution using appropriate developing solutions, generally based on the same coating. In particular, the irradiated regions are at least partially condensed to increase the metal oxide character so that the irradiated material is resistant to dissolving by organic solvents while the un-irradiated compositions remain soluble in the organic solvents. Reference to a condensed coating material refers to at least partial condensation in the sense of increasing the oxide character of the material relative to an initial material. On the other hand, the un-irradiated material is less soluble in weak aqueous bases or acids due to the hydrophobic nature of the material so that aqueous bases can be used to remove the irradiated material while maintaining the non-irradiated material for positive patterning.

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With respect to negative tone imaging, referring to Figs. 3 and 4, the latent image of the structure shown in Figs. 1 and 2 has been developed through contact with a developer to form patterned structure 130. After development of the image, substrate 102 is exposed along the top surface through openings 132, 134, 135. Openings 132, 134, 135 are located at the positions of uncondensed regions 118, 120, 122 respectively. With respect to positive tone imaging, referring to Figs. 5 and 6, the latent image of the structure shown in Figs. 1 and 2 has been developed to form patterned structure 140. Patterned structure 140 has the conjugate image of patterned structure 130. Patterned structure 140 has substrate 102 exposed at positions of irradiated regions 110, 112, 114, 116 that are developed to form openings 142, 144, 146, 148.

For the negative tone imaging, the developer can be an organic solvent, such as the solvents used to form the precursor solutions. In general, developer selection can be influenced by solubility parameters with respect to the coating material, both irradiated and non-irradiated, as well as developer volatility, flammability, toxicity, viscosity and potential chemical interactions with other process material. In particular, suitable developers include, for example, aromatic compounds (e.g., benzene, xylenes, toluene), esters (e.g., propylene glycol monomethyl ester acetate, ethyl acetate, ethyl lactate, n-butyl acetate, butyrolactone), alcohols (e.g., 4-methyl-2-pentanol, 1-butanol, isopropanol, 1-propanol, methanol), ketones (e.g., methyl ethyl ketone, acetone, cyclohexanone, 2-heptanone, 2-octanone), ethers (e.g., tetrahydrofuran, dioxane, anisole) and the like. The development can be performed for about 5 seconds to about 30 minutes, in further embodiments from about 8 seconds to about 15 minutes and in addition embodiments from about 10 seconds to about 10 minutes. A person of ordinary skill in the art will recognize that additional ranges within the explicit ranges above are contemplated and are within the present disclosure.

For positive tone imaging, the developer generally can be aqueous acids or bases. In some embodiments, aqueous bases can be used to obtain sharper images. To reduce contamination from the developer, it can be desirable to use a developer that does not have metal atoms. Thus, quaternary ammonium hydroxide compositions, such as tetraethylammonium hydroxide, tetrapropylammonium hydroxide, tetrabutylammonium hydroxide or combinations thereof, are desirable as developers. In general, the quaternary ammonium hydroxides of particular interest can be represented with the formula R_4NOH , where R = a methyl group, an ethyl group, a propyl group, a butyl group, or combinations thereof. The coating materials described herein generally can be developed with the same developer commonly used presently for polymer resists, specifically tetramethyl ammonium

hydroxide (TMAH). Commercial TMAH is available at 2.38 weight percent, and this concentration can be used for the processing described herein. Furthermore, mixed quaternary tetraalkyl- ammonium hydroxides can be used. In general, the developer can comprise from about 0.5 to about 30 weight percent, in further embodiments from about 1 to about 25 weight percent and in other embodiments from about 1.25 to about 20 weight percent tetra-alkylammonium hydroxide or similar quaternary ammonium hydroxides. A person of ordinary skill in the art will recognize that additional ranges of developer concentrations within the explicit ranges above are contemplated and are within the present disclosure.

In addition to the primary developer composition, the developer can comprise additional compositions to facilitate the development process. Suitable additives include, for example, dissolved salts with cations selected from the group consisting of ammonium, d-block metal cations (hafnium, zirconium, lanthanum, or the like), f-block metal cations (cerium, lutetium or the like), p-block metal cations (aluminum, tin, or the like), alkali metals (lithium, sodium, potassium or the like), and combinations thereof, and with anions selected from the group consisting of fluoride, chloride, bromide, iodide, nitrate, sulfate, phosphate, silicate, borate, peroxide, butoxide, formate, oxalate, ethylenediamine-tetraacetic acid (EDTA), tungstate, molybdate, or the like and combinations thereof. Other potentially useful additives include, for example, molecular chelating agents, such as polyamines, alcohol amines, amino acids, carboxylic acids, or combinations thereof. If the optional additives are present, the developer can comprise no more than about 10 weight percent additive and in further embodiments no more than about 5 weight percent additive. A person of ordinary skill in the art will recognize that additional ranges of additive concentrations within the explicit ranges above are contemplated and are within the present disclosure. The additives can be selected to improve contrast, sensitivity and line width roughness. The additives in the developer can also inhibit formation and precipitation of metal oxide particles.

With a weaker developer, e.g., lower concentration aqueous developer, diluted organic developer or compositions in which the coating has a lower development rate, a higher temperature development process can be used to increase the rate of the process. With a stronger developer, the temperature of the development process can be lower to reduce the rate and/or control the kinetics of the development. In general, the temperature of the development can be adjusted between the appropriate values consistent with the volatility of the solvents. Additionally, developer with dissolved coating material near the developer-coating interface can be dispersed with ultrasonication during development.

The developer can be applied to the patterned coating material using any reasonable approach. For example, the developer can be sprayed onto the patterned coating material. Also, spin coating can be used. For automated processing, a puddle method can be used involving the pouring of the developer onto the coating material in a stationary format. If
5 desired spin rinsing and/or drying can be used to complete the development process. Suitable rinsing solutions include, for example, ultrapure water, methyl alcohol, ethyl alcohol, propyl alcohol and combinations thereof for negative patterning and ultrapure water for positive patterning. After the image is developed, the coating material is disposed on the substrate as a pattern.

10 After completion of the development step, the coating materials can be heat treated to further condense the material and to further dehydrate, densify, or remove residual developer from the material. This heat treatment can be particularly desirable for embodiments in which the oxide coating material is incorporated into the ultimate device, although it may be desirable to perform the heat treatment for some embodiments in which the coating material is used as a
15 resist and ultimately removed if the stabilization of the coating material is desirable to facilitate further patterning. In particular, the bake of the patterned coating material can be performed under conditions in which the patterned coating material exhibits desired levels of etch selectivity. In some embodiments, the patterned coating material can be heated to a temperature from about 100°C to about 600°C, in further embodiments from about 175°C to
20 about 500°C and in additional embodiments from about 200°C to about 400°C. The heating can be performed for at least about 1 minute, in other embodiment for about 2 minutes to about 1 hour, in further embodiments from about 2.5 minutes to about 25 minutes. The heating may be performed in air, vacuum, or an inert gas ambient, such as Ar or N₂. A person of ordinary skill in the art will recognize that additional ranges of temperatures and time for the heat
25 treatment within the explicit ranges above are contemplated and are within the present disclosure. Likewise, non-thermal treatments, including blanket UV exposure, or exposure to an oxidizing plasma such as O₂ may also be employed for similar purposes.

With conventional organic resists, structures are susceptible to pattern collapse if the aspect ratio, height divided by width, of a structure becomes too large. Pattern collapse can be
30 associated with mechanical instability of a high aspect ratio structure such that forces, e.g., surface tension, associated with the processing steps distort the structural elements. Low aspect ratio structures are more stable with respect to potential distorting forces. With the patternable coating materials described herein, due to the ability to process effectively the structures with thinner layers of coating material, improved patterning can be accomplished without the need

The resulting structures can have sharp edges with very low line-width roughness. In particular, in addition to the ability to reduce line-width roughness, the high contrast also allows for the formation of small features and spaces between features as well as the ability to form very well resolved two-dimensional patterns (e.g., sharp corners). Thus, in some embodiments, adjacent linear segments of neighboring structures can have an average pitch (half-pitch) of no more than about 60 nm (30 nm half-pitch), in some embodiments no more than about 50 nm (25 nm half-pitch) and in further embodiments no more than about 34 nm (17 nm half-pitch).

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After forming a patterned coating material, the coating material can be further processed to facilitate formation of the selected devices. Furthermore, further material deposition, etching and/or patterning generally can be performed to complete structures. The

The patterned coating material forms openings to the underlying substrate, as shown for example in Figs. 3 and 4. As with conventional resists, the patterned coating material forms an etch mask which can be used to transfer the pattern to selectively remove an underlying thin film. Referring to Fig. 7, underlying thin film 103 (see Fig. 6) is patterned leaving features 152, 154, 156 respectively on substrate 102 under condensed regions 110, 112, 114. Compared with conventional polymer resists, the materials described herein can provide significantly greater etch resistance. Similar processing can be undertaken with the mask pattern shown in Figs. 5 and 6 with corresponding shifting of the patterned structures that follow directly from the alternative mask pattern.

In general, a plurality of additional layers can be deposited. In conjunction with the deposition of a plurality of layers, additional patterning can be performed. Any additional patterning, if performed, can be performed with additional quantities of the coating materials described herein, with polymer-based resists, with other patterning approaches or a combination thereof.

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If it is desired to remove the patterned coating material, the coating material functions as a conventional resist. The patterned coating material is used to pattern a subsequently deposited material prior to the removal of the resist/coating material and/or to selectively etch the substrate through the spaces in the condensed coating material. The condensed coating material can be removed using a suitable etching process. Specifically, to remove the condensed coating material, a dry etch can be performed, for example, with a BCl_3 plasma, Cl_2 plasma, HBr plasma, Ar plasma or plasmas with other appropriate process gases. Alternatively or additionally, a wet etch with, for example, an aqueous acid or base, such as $\text{HF}(\text{aq})$, or buffered $\text{HF}(\text{aq})/\text{NH}_4\text{F}$ or oxalic acid can be used to remove the patterned coating material. Referring to Fig. 8, the structure of Fig. 8 is shown after removal of the coating material. Etched structure 150 comprises substrate 102 and features 152, 154, 156.

The metal oxo/hydroxo based coating materials are particularly convenient for performing multiple patterning using a thermal freeze process, as described generally with conventional resists in P. Zimmerman, J. Photopolym. Sci. Technol., Vol. 22, No. 5, 2009, p. 625. A double patterning process with a "thermal freeze" is outlined in Fig. 9. In the first step, the coating material is formed into a pattern 160 on substrate 162 using a lithographic process and development as described with respect to Figs. 3 and 4. A heating step 164 is performed to remove solvent and condense the coating material, which may or may not involve full oxide formation. This heating step is equivalent to the post-development heating step described in the Development section above. This "thermal freeze" process makes the coating material insoluble to a subsequent deposition of a second layer of the coating material. A second lithographic and development step 166 is performed to form a double patterned structure 168 on substrate 162. After an etch step 170, the product double patterned structure 172 is formed. Note that it is straightforward to extend this process to multiple coat and pattern steps, and such extensions are contemplated and are within the present disclosure. With respect to multiple patterning, a significant difference between the inorganic coating materials described herein and conventional organic resists is that organic resists remain soluble in conventional resist casting solvents even after a thermal bake. The resist materials described herein can be condensed with a thermal bake such that they are not soluble in organic solvents and subsequent coating layers can be applied.

EXAMPLES

Example 1 – Hydrolysate of $\text{t-BuSn}(\text{NEt}_2)_3$

A hydrolysate oxide hydroxide product with the nominal formula $t\text{-BuSnO}_{(3/2-x/2)}(\text{OH})_x$, (where $0 > x < 3$) (1) was prepared from *t*-butyl tris(diethylamido)tin (2), which was synthesized according to the method reported in Hänssgen, D.; Puff, H.; Beckerman, N. *Journal of Organometallic Chemistry*, 293, 1985, 191-195, which is incorporated herein by reference. A gas-tight syringe was used to steadily ($\sim 125 \mu\text{L/s}$) add 4.4 g of *t*-butyl tris(diethylamido) tin to 150 mL of DI H_2O (18 M Ω), forming an immediate precipitate that was allowed to stand for 5 minutes. The resulting slurry was stirred for 30 minutes and then suction filtered through no. 1 filter paper (Whatman). The resulting solid was rinsed 3 times with 50-mL portions of DI H_2O . Solids retained after filtration and rinsing were dried under vacuum (~ 5 torr) for 8 h at room temperature to yield 1.9 g of powdered solid of hydrolysate 1.

Example 2 – Hydrolysate of i-PrSnCl₃

The hydrolysate oxide hydroxide product ($i\text{-PrSnO}_{(3/2-x/2)}(\text{OH})_x$, where $0 < x < 3$) (**3**) of *i*-propyltin trichloride (**4**, $i\text{-PrSnCl}_3$, Gelest) was prepared by rapidly adding 6.5 g of compound **4** to 150 mL of 0.5-M NaOH (aq) with vigorous stirring, immediately producing a precipitate. The resulting mixture was stirred for 1 h at room temperature and then filtered with suction through no. 1 filter paper (Whatman). The retained solids were washed three times with ~25-mL portions of DI H₂O and then dried for 12 h under vacuum (~5 torr) at room temperature.

Elemental analysis (18.04% C, 3.76% H, 1.38% Cl; Microanalysis, Inc.; Wilmington, DE) of the dried powder, hydrolysate of i-propyltin trichloride, indicated substantial removal of chloride ions occurs upon hydrolysis of i-propyltin trichloride and an approximate hydrolysate empirical formula of $i\text{-PrSnO}_{(3/2-x/2)}(\text{OH})_x$ where $x \approx 1$. (Calculated for $\text{C}_3\text{H}_8\text{O}_2\text{Sn}$: 18.50% C, 4.14% H, 0.00% Cl). The results are consistent with the approximate empirical formula $(\text{C}_3\text{H}_7)\text{SnOOH}$ for hydrolysate of i-propyltin trichloride.

Example 3 – Preparation of Photoresist Solutions

This example describes the preparation of photoresist solutions from the hydrolysate precursors.

A solution of compound 1 (Example 1) was prepared by adding 0.1 g of dry powder to 10 mL of methanol (ACS, 99.8%) while stirring to form a mixture with a Sn concentration of ~ 0.05 M. After stirring for 24 h, the mixture was filtered through a $0.45\text{-}\mu\text{m}$ PTFE syringe filter to remove insoluble material. Dynamic light scattering (DLS) analysis of the resulting precursor solution, performed using a Möbius instrument (Wyatt Technology), is consistent with a unimodal mass weighted distribution of clusters with a mean diameter of ~ 1.9 nm, as shown in Fig. 12. A representative time correlation function providing such a particle size distribution is shown in Fig. 13.

Nuclear Magnetic Resonance (NMR) spectroscopy was performed on similar solutions prepared in d_4 -methanol using a Bruker Avance-III-HD 600 MHz Spectrometer equipped with a Bruker Prodigy[™] CryoProbe. A representative ^{119}Sn spectrum is shown in Fig. 14, and a representative ^1H spectrum is shown in Fig. 15. Two primary sets of proton resonances are observed, each consisting of a stronger (1.58, 140 ppm) and weaker (1.55, 1.37 ppm) resonance. These locations and integrated intensities are approximately consistent with the expected chemical shift of the methyl protons on $-\text{C}(\text{CH}_3)_3$ ligands bound to five- and six-coordinate tin atoms in a closo-type dodecameric cluster $[(t\text{-BuSn})_{12}\text{O}_{14}(\text{OH})_6]^{+2}$ or closely related chemical environment. Resonances centered at 3.33, and 4.90 ppm are attributed to methanol CH_3 and OH protons. Two sets of closely-spaced ^{119}Sn resonances are observed at -333.86 and -336.10 ppm, and at -520.33 and -521.48 ppm. These results similarly approximate expected shifts for the two tin environments in the cationic dodecamer clusters, as described for $(n\text{-BuSn})_{12}$ clusters by Eychenne-Baron, et al., *Organometallics* 19, 2000, 1940-1949., incorporated herein by reference.

Electrospray Ionization Mass Spectroscopy (ESI-MS) was used to characterize methanol solutions of the same hydrolysate. Representative positive-ion mode mass spectra

are presented in Fig. 16. Two primary cationic species are observed in the spectra. One, at a mass to charge (m/z) ratio of 1219, and a second, stronger signal at $m/z = 2435$. These m/z ratios are attributed to the presence of a doubly charged ($[(t\text{-BuSn})_{12}\text{O}_{14}(\text{OH})_6]^{+2}$ calculated $m/z = 1218$) and singly charged (deprotonated, $[(t\text{-BuSn})_{12}(\text{O}_{15}(\text{OH})_5)]^+$ $m/z = 2435$) cationic dodecameric species in the methanol solutions of the hydrolysate. Surrounding the peak at m/z 2436 are a number of shoulder and satellite peaks, that may represent the presence of methoxo and solvated or hydrated derivatives of the primary dodecameric species, and are presumed to correspond to the closely related ^{119}Sn and ^1H resonances observed via NMR.

A solution of compound 3 (Example 2) was prepared by adding 0.16 g of dry powder to 10 mL of 4-methyl-2-pentanol (Alfa-Aesar, 99%) while stirring to form a mixture with a Sn concentration of ~ 0.08 M. After stirring for 2 h, the mixture was dried overnight with activated 4Å molecular sieves to remove residual water, and then filtered through a 0.45 μm PTFE syringe filter to remove insoluble material.

Example 4 – Resist coating, Film Processing, Negative Tone Imaging

This example demonstrates the formation of a resist pattern based on negative tone imaging with extreme ultraviolet radiation exposure. Branched alkyltin oxide hydroxide photoresists were coated on silicon wafers and negative-tone characteristic contrast curves generated using EUV radiation.

Silicon wafers (100-mm diameter) with a native-oxide surface were used as substrates for thin-film deposition. Si substrates were treated with a hexamethyldisilazane (HMDS) vapor prime prior to resist deposition. Silicon wafers (100-mm diameter) with a native-oxide surface were used as substrates for thin-film deposition. Si substrates were treated with a hexamethyldisilazane (HMDS) vapor prime prior to resist deposition. *i*-Propyl and *t*-butyl tin oxide hydroxide photoresist solutions were prepared as described in Example 3, and diluted to ~ 0.06 and 0.05 M, respectively. Precursor solutions of an *n*-butyltin oxide hydroxide ($n\text{-BuSnO}_{(3/2-x/2)}(\text{OH})_x$) resist solutions (0.057 M Sn) were prepared as described in the '524 application cited above. Precursor solutions were spin-coated on Si substrates and baked for 2 minutes at the indicated rpm / temperature to form alkyltin oxide hydroxide resist thin films: 1500 rpm / 80°C (*i*Pr-); 1800 rpm / 100°C (*n*Bu-); 2000 rpm / 100°C (*t*Bu-).

A linear array of 50 circular pads ~ 500 μm in diameter were projected on the wafer using EUV light (Lawrence Berkeley National Laboratory Micro Exposure Tool, MET). Pad exposure times were modulated to deliver an increasing EUV dose (7% exponential step) to each pad. Resist and substrate were then subjected to a post-exposure bake (PEB) on a hotplate

for 2 min at 100-200 °C. The exposed films were dipped in 2-heptanone for 15 seconds and rinsed an additional 15 seconds with the same developer to form a negative tone image, i.e., unexposed portions of the coating were removed. n-Butyltin oxide hydroxide resist films were further rinsed 30s in DI H₂O. A final 150°C, 2 minutes hotplate bake was performed to complete the process. Residual resist thicknesses of the exposed pads were measured using a J. A. Woollam M-2000 Spectroscopic Ellipsometer. The measured thicknesses were normalized to the maximum measured resist thickness and plotted versus the logarithm of exposure dose to form characteristic curves for each resist at a series of PEB temperatures. The maximum slope of the normalized thickness vs log dose curve is defined as the photoresist contrast (γ) and the dose value at which a tangent line drawn through this point equals 1 is defined as the photoresist dose-to-gel, (D_g). In this way common parameters used for photoresist characterization may be approximated following Mack, C. *Fundamental Principles of Optical Lithography*, John Wiley & Sons, Chichester, U.K; pp 271-272, 2007, incorporated herein by reference.

By plotting γ versus D_g for each resist, a clear relationship between decreasing dose and contrast is illustrated as the PEB temperature is increased for each resist (Fig. 17). It is found that both branched alkyltin oxide hydroxide resists tested here have better contrast than the n-butyltin oxide hydroxide-based resist, and preserve equivalent or better contrast at lower dose (as modulated by PEB) when developed in 2-heptanone.

The improved sensitivity and contrast obtained from branched alkyltin oxide hydroxide photoresists were similarly used to generate high-resolution patterns by exposure to EUV radiation. The solution of compound 1 from Example 3 was diluted with methanol to ~0.03 M Sn then spin-coated on the substrate at 2000 rpm and baked on a hotplate for 2 minutes at 100°C. Film thickness following coating and baking was measured via ellipsometry to be ~23 nm.

The coated substrate was exposed to extreme ultraviolet radiation (Lawrence Berkeley National Laboratory Micro Exposure Tool). A pattern of 17-nm lines on a 34-nm pitch was projected onto the wafer using 13.5-nm wavelength radiation, dipole illumination, and a numerical aperture of 0.3 at an imaging dose of 43 mJ/cm². The patterned resist and substrate were then subjected to a post-exposure bake (PEB) on a hotplate for 2 minutes at 175°C. The exposed film was then dipped in 2-heptanone for 15 seconds, rinsed an additional 15 seconds with the same developer, and finally rinsed for 30 seconds with DI H₂O to form a negative tone image, i.e., unexposed portions of the coating were removed. A final 5-minute hotplate bake at 150°C was performed after development. Fig. 18 exhibits SEM images of the resulting 15.4-

nm resist lines patterned on a 34-nm pitch with a calculated line-width roughness (LWR) of 4.6 nm.

The solution of $i\text{-PrSnO}_{(3/2-x/2)}(\text{OH})_x$ (compound 3 from Example 2) was used in a similar way to realize high-resolution patterning via EUV exposure. Solution of 3 from Example 3 was diluted in 4-methyl-2-pentanol to ~0.06 M Sn, and spin-coated on a second Si substrate at 1500 rpm and baked on a hotplate for 2 minutes at 80°C. Film thickness following coating and baking was measured via ellipsometry to be ~19 nm. A bright-field pattern of 22-nm contact holes on a 44 nm pitch with a +20% bias was projected onto the wafer using quadrupole illumination at an imaging dose of 36 mJ/cm². The patterned resist and substrate were then subjected to a PEB for 2 minutes at 150°C. The exposed film was then dipped in 2-octanone for 15 seconds and rinsed with 2-octanone for an additional 15 seconds to form a negative tone image with unexposed portions of the coating removed, leaving a pattern of contact holes. A final 5-minute hotplate bake at 150°C was performed after development. Fig. 19 exhibits SEM images of the resulting 22-nm holes patterned on a 44-nm pitch.

Example 5 – Preparation of Photoresist Solutions With Mixed Alkyl Ligands

This Example describes the formulation of precursor solutions comprising mixed alkyl ligands, and the effectiveness of these formulations for patterning are described in the following example.

A t-butyltin oxide hydroxide hydrolysate (1) was prepared from t-butyl tris(diethylamido)tin following the method described above in Example 1. A gas-tight syringe was used to add 4.4 g (11 mmol) of t-butyl tris(diethylamido)tin to 150 mL of DI H₂O (18 MΩ), forming an immediate precipitate that was allowed to stand for 5 minutes. The resulting slurry was stirred for 30 minutes and then suction filtered through no. 1 filter paper (Whatman) and rinsed 3 times with 60-mL portions of DI H₂O. Solids retained after filtration and rinsing were dried under vacuum (~5 torr) for 17 hours at room temperature to yield 1.85 g of powdered solid of hydrolysate t-butyltin oxide hydroxide (1).

An i-propyltin oxide hydroxide hydrolysate (3) was similarly prepared by the method described above in Example 2. A 9.65 g (36 mmol) quantity of i-propyltin trichloride ($i\text{-PrSnCl}_3$, Gelest) was rapidly added to 220 mL of 0.5-M NaOH (aq) while stirring vigorously, immediately producing a precipitate. The resulting mixture was stirred for 1.25 hours at room temperature and then filtered with suction through two no. 5 filter papers (Whatman). The retained solids were washed 3 times with ~30-mL portions of DI H₂O and then then dried for 16 hours under vacuum (~5 torr) at room temperature.

Separate solutions of t-butyltin oxide hydroxide hydrolysate (1) and i-propyltin oxide hydroxide hydrolysate (3) were prepared from the respective powders. A 1.04 g quantity of dried powder t-butyltin oxide hydroxide hydrolysate was added to 100 mL methanol (ACS, 99.8%) and stirred for 24 hours, whereupon the mixture was syringe filtered through a 0.45-
 5 um PTFE filter to remove insoluble particles. The residual mass of a sample following solvent evaporation and subsequent thermal decomposition of the residual solids at 700°C in air was consistent with an initial Sn concentration of 0.035 M assuming stoichiometric conversion to SnO₂. A solution of i-propyltin oxide hydroxide hydrolysate (3) was prepared by adding 3.129 g of dry powder to 80 mL of 4-methyl-2-pentanol (Alfa-Aesar, 99%) while stirring. After
 10 stirring for 6 hours, the mixture was dried 60 hours over activated 4Å molecular sieves, then vacuum filtered through a 0.2-um PTFE membrane filter to remove insoluble material. The Sn concentration of the solution was found to be 0.16 M via thermal decomposition to the oxide.

Photoresist formulations A-F (Table 2) were prepared by mixing the methanol solution of t-butyl tin oxide hydroxide hydrolysate (1) with the 4-methyl-2-pentanol solution of i-propyl
 15 tin oxide hydroxide hydrolysate (3), and diluting the resulting mixture with pure solvents according to the volumes specified in Table 2. The resulting solutions are characterized as a blend of i-PrSnO_(3/2-x/2)(OH)_x and t-BuSnO_(3/2-x/2)(OH)_x hydrolysates, where the fraction of t-BuSnO_(3/2-x/2)(OH)_x is expressed relative to the total Sn concentration.

TABLE 2

Formulation n	Volume Added (mL)				t-Bu-Sn relative to Total Sn (%)
	Methan ol	4-methyl 2- pentanol	Solution 3	Solution 1	
A	0	0	0	5	100
B	0	0.75	0.5	3.75	62
C	0	0.45	0.8	3.75	50
D	1.033	0.517	1.15	2.3	30
E	0	1.5	1.5	2	22
F	0	2.75	2.25	0	0

Example 6 -- Resist coating, Film Processing, Negative Tone Imaging With Mixed Alkyl Ligand Precursors

25 Mixed-ligand organotin oxide hydroxide photoresists were used to generate negative-tone patterns by exposure to extreme ultraviolet radiation. This Example explores patterning using the precursor solutions from Example 5 having mixed alkyl ligands.

Silicon wafers (100-mm diameter) with a native-oxide surface were used as substrates for thin-film deposition. Si substrates were treated with a hexamethyldisilazane (HMDS) vapor prime prior to resist deposition. Resist formulations A-F from Example 5 were spin-coated on substrates at 2000-2500 rpm and baked on a hotplate for 2 minutes at 100°C. Film thickness following coating and baking was measured via ellipsometry to be ~ 30 nm. The coated substrates were exposed to extreme ultraviolet radiation (Lawrence Berkeley National Laboratory Micro Exposure Tool). A pattern of 17-nm lines and spaces on a 34-nm pitch was projected onto the wafer using 13.5-nm wavelength radiation, dipole illumination, and a numerical aperture of 0.3. The patterned resist and substrate were then subjected to a post-exposure bake (PEB) on a hotplate for 2 minutes at 170°C. The exposed film was then dipped in 2-heptanone for 15 seconds and rinsed an additional 15 seconds with the same developer to form a negative tone image, i.e., unexposed portions of the coating were removed. A final 5-minute hotplate bake at 150°C was performed after development.

Fig. 20 exhibits SEM images of the resulting resist lines patterned on a 34-nm pitch. SuMMIT analysis software (EUV Technology Corporation) was used to extract resist critical dimension (CD) and line-width-roughness (LWR) from SEM images of 17 hp lines patterned using resist formulation A-F. A plot of LWR and Dose to size (E_{size}) for each formulation is shown in Fig. 21. A clear trend of decreasing dose (circular dots) is observed across the formulations as the fraction of $t\text{-BuSnO}_{(3/2-x/2)}(\text{OH})_x$ is increased. Moreover, LWR (triangular dots) in Fig. 21 for blended formulations are substantially lower than pure $t\text{-BuSnO}_{(3/2-x/2)}(\text{OH})_x$ and $i\text{-PrSnO}_{(3/2-x/2)}(\text{OH})_x$ formulations A and F, respectively.

Example 7 -- Preparation of an Iso-propyltin Hydroxide Oxide Hydrolysate via an Iso-propyl Tris(dimethylamido)tin Precursor

A water-reactive precursor, isopropyl tris(dimethylamido)tin, ($i\text{-PrSn}(\text{NMe}_2)_3$), was synthesized under inert atmosphere and subsequently hydrolysed by two methods using 1) atmospheric moisture and 2) liquid H_2O , to form an $i\text{-PrSnO}_{(3/2-x/2)}(\text{OH})_x$ hydrolysate.

Under argon, a 1L Schlenk-adapted round bottom flask was charged with LiNMe_2 (81.75 g, 1.6 mol, Sigma-Aldrich) and anhydrous hexanes (700 mL, Sigma-Aldrich) to form a slurry. A large stir bar was added and the vessel sealed. An addition funnel under positive argon pressure was charged with $i\text{-PrSnCl}_3$ (134.3 g, 0.5 mol, Gelest) via syringe and attached to the reaction flask. The flask was cooled to -78°C and the $i\text{-PrSnCl}_3$ added dropwise over a period of 2 hours. The reaction was allowed to come to room temperature overnight while stirring, and the solid precipitates allowed to settle. After settling, the reaction solution was filtered

under positive argon pressure through an in-line cannula filter. The solvent was removed under vacuum and the residue distilled under reduced pressure (50-52°C, 1.4 mmHg) to give a pale yellow liquid (110 g, 75 % yield). ^1H and ^{119}Sn NMR spectra of the distillate in a C_6D_6 solvent collected on a Bruker DPX-400 (400 MHz, BBO probe) spectrometer are shown in Figs. 22 and 23, respectively. Observed ^1H resonances, as shown in Fig. 22, (s, 2.82 ppm, $-\text{N}(\text{CH}_3)_2$; d 1.26 ppm, $-\text{CH}_3$; m, 1.60 ppm, $-\text{CH}$) match the predicted spectra for $^i\text{PrSn}(\text{NMe}_2)_3$. The primary ^{119}Sn resonance, as shown in Fig. 23, at -65.4 ppm is consistent with a major product with a single tin environment, with a chemical shift comparable to reported monoalkyltin amido compounds.

An *i*-propyltin oxide hydroxide hydrolysate was prepared from the *i*-propyl tris(dimethylamido) tin, (*i*-PrSn(NMe₂)₃), via H₂O hydrolysis using two different methods.

Method 1:

A gas-tight syringe was used to add 23.4 g (79.6 mmol) of *i*-propyl tris(dimethylamido) tin, (*i*-PrSn(NMe₂)₃) to 150 mL of *n*-hexanes (HPLC Grade, >99.5 % Hexanes, > 95% *n*-Hexane), forming an opaque suspension that was stirred for 5 minutes in air, then poured in equal volumes into six 150 mm diameter petri dishes. The suspensions were allowed to react with atmospheric moisture while the solvent evaporated in air for 1.5 hours, leaving a crude solid that was collected, combined, and dried under vacuum for 15 hours to yield 15.8 g of solid hydrolysate (compound 3, Example 2). Elemental analyses (UC Berkeley Microanalytical Facility) of a hydrolysate powder prepared by the same procedure returned a composition of 18.91% C, 4.24% H, and 0.51% N (mass), consistent with substantial hydrolysis of dimethylamido ligands and evaporation of the resultant alkyl amine. The results are consistent with calculated values for $\text{C}_3\text{H}_8\text{O}_2\text{Sn}$: 18.50% C, 4.14% H, 0.00% N, and 60.94% Sn, mass). Thermogravimetric analysis (Fig. 24) of the same sample in dry air is indicative of a Sn composition of ~60% (mass) based on the residual weight at 500°C (75.9%) assuming complete decomposition to SnO_2 . The mass spectral analysis of the same decomposition (Fig. 25) indicates the presence of $-\text{C}_3\text{H}_6$. Taken together, these results agree with an empirical composition of $^i\text{PrSnSnO}_{(3/2-x/2)}(\text{OH})_x$ where $x \approx 1$, and the possible presence of a small amount of residual dimethyl amido.

Method 2:

A gas-tight syringe was used to rapidly add 1.0 g (3.4 mmol) of *i*-propyl tris(dimethylamido) tin, (*i*-PrSn(NMe₂)₃) directly to 15 mL DI H₂O (18.2 MΩ) with vigorous

stirring to form a slurry that was stirred for an additional 60 minutes. This slurry was then vacuum filtered through a 0.7- μ m filter and the retained solids washed with 10 mL DI H₂O. The solid was then collected and dried under vacuum for 16 hours to yield 0.7g of solid hydrolysate. Thermogravimetric analyses, performed in dry air on hydrolysate powders prepared by the same procedure (Fig. 26), are similarly consistent with the empirical composition of 3 (Example 2), i-PrSnSnO_(3/2-x/2)(OH)_x where $x \approx 1$. Weight losses attributed to stepwise dehydration (50-175°C, ~95.7% residual weight) and dealkylation/combustion (200-500°C, ~77% residual weight) are observed as expected on the basis of complete decomposition of 3 to SnO₂.

Example 8 – Trace-metals Analysis of Organotin Oxide Hydroxide Photoresist Solutions

A resist precursor solution was prepared by adding 15.8 g of dried powder, prepared according to Method 1 in the preceding example, to 810 mL 4-methyl-2-pentanol (High Purity Products), and stirring for 24 h. Following stirring, the mixture was suction filtered through a 0.22- μ m PTFE filter to remove insoluble material. The residual mass of a sample following solvent evaporation and subsequent calcination of the solid at 700°C in air was consistent with an initial Sn concentration of 0.072 M assuming stoichiometric conversion to SnO₂.

Trace-metal concentrations in the resist precursor solution above were evaluated relative to a hydrolysate prepared using aqueous sodium hydroxide and i-propyltin trichloride.

The 0.072-M solution prepared above, was further diluted to 0.042 M (Sn) with 4-methyl-2-pentanol. A second i-propyltin oxide hydroxide precursor solution was prepared by hydrolysis of i-PrSnCl₃ with aqueous NaOH as described in Example 2, and diluted to 0.42 M Sn with the same high-purity 4-methyl-2-pentanol. Aliquots of both solutions were analyzed using inductively coupled plasma mass spectroscopy (ICP-MS, Balazs Nanoanalysis, Fremont, CA) to determine the concentration of 22 metals with a lower detection limit (LDL) of 10 parts per billion (ng/g). The results of these analyses are presented in Table 3. In both cases the concentration of all analyzed metals except sodium (Na) was < 10 ppb. The resist solution (A) containing the hydrolysate prepared with NaOH (aq) was found to contain 34,000 ppb residual sodium, even after three washings with 18 M Ω DI H₂O. In contrast, the resist solution (B) prepared from the hydrolysate of i-propyl (tris)dimethylamido tin was found to contain < 10 ppb Na, as anticipated by the alkali-free hydrolysis.

Trace metal concentrations in i-PrSnSnO_(3/2-x/2)(OH)_x photoresist precursor solutions as measured by ICP-MS with an LDL of 10 ppb are shown in Table 3.

TABLE 3

		Concentration, ppb (ng/g)	
Metal		Resist	Resist
		Precursor A	Precursor B
		i-PrSnCl ₃	/ i-PrSn(NMe ₂) ₃
		NaOH	/ Air
Aluminum	(Al)	< 10	< 10
Arsenic	(As)	< 10	< 10
Barium	(Ba)	< 10	< 10
Cadmium	(Cd)	< 10	< 10
Calcium	(Ca)	< 10	< 10
Chromium	(Cr)	< 10	< 10
Cobalt	(Co)	< 10	< 10
Copper	(Cu)	< 10	< 10
Gold	(Au)	< 10	< 10
Iron	(Fe)	< 10	< 10
Lithium	(Li)	< 10	< 10
Magnesium	(Mg)	< 10	< 10
Manganese	(Mn)	< 10	< 10

Nickel	(Ni)	< 10	< 10
Palladium	(Pd)	< 10	< 10
Potassium	(K)	< 10	< 10
Silver	(Ag)	< 10	< 10
Sodium	(Na)	34,000	< 10
Titanium	(Ti)	< 10	< 10
Tungsten	(W)	< 10	< 10
Vanadium	(V)	< 10	< 10
Zinc	(Zn)	< 10	< 10

Example 9 – Film Coating, Processing, and Negative Tone Imaging of a Photoresist with Low Trace-Metal Contamination

Silicon wafers (100-mm diameter) with a native-oxide surface were used as substrates for thin-film deposition. Si substrates were treated with a hexamethyldisilazane (HMDS) vapor prime prior to resist deposition. The 0.072 M resist solution from Example 8 was dispensed through a 0.45 μ m syringe filter onto a substrate, spin-coated at 1500 rpm, and baked on a hotplate for 2 min at 100°C. Film thickness following coating and baking was measured via ellipsometry to be ~ 25 nm. The coated substrate was exposed to extreme ultraviolet radiation (Lawrence Berkeley National Laboratory Micro Exposure Tool). A pattern of 17-nm lines and spaces on a 34-nm pitch was projected onto the wafer using 13.5-nm wavelength radiation, dipole illumination, and a numerical aperture of 0.3. The patterned resist and substrate were then subjected to a post-exposure bake (PEB) on a hotplate for 2 min at 180°C. The exposed film was then dipped in 2-heptanone for 15 seconds and rinsed an additional 15 seconds with the same developer to form a negative tone image, i.e., unexposed portions of the coating were removed. A final 5-minute hotplate bake at 150 °C was performed after development. Fig.

27 shows an SEM image of the resulting resist line/space pattern on the substrate defined with an imaging dose of 60 mJ cm^{-2} , 14.5 nm resist lines patterned on a 34 nm pitch with an LWR of 2.9 nm.

5 Example 10 – Preparation of an i-Propyltin Hydrolysate via Hydrolysis of Iso-propyltin Trichloride with an Aqueous Organic Base

A hydrolysate of i-PrSnCl_3 was prepared by rapidly adding 6.5 g (24 mmol) of compound 4 i-PrSnCl_3 to 150 mL of 0.5-M aqueous tetramethyl ammonium hydroxide (TMAH) while stirring vigorously, immediately producing a precipitate. TMAH is free of metal cations in the formula so that it can be introduced with low metal contamination. The resulting mixture was stirred for 1 hour at room temperature and then filtered with suction through no. 1 filter paper (Whatman). The retained solids were washed three times with ~25-mL portions of DI H_2O and then then dried for 12 hours under vacuum (~5 torr) at room temperature. Elemental analysis (18.67% C, 4.22% H, 0.03% N, 0.90% Cl; Microanalysis, Inc.; Wilmington, DE) of the dried powder hydrolysate, was consistent with substantial removal of chloride ions upon hydrolysis and rinsing, and again in agreement with the general stoichiometry $\text{i-PrSnSnO}_{(3/2-x/2)}(\text{OH})_x$ where $x \approx 1$. (Calculated for $\text{C}_3\text{H}_3\text{O}_2\text{Sn}$: 18.50% C, 4.14% H, 0.00% N, 0.00% Cl). TGA-MS analyses, (dry air) of hydrolysate powders prepared by the same procedure (Figs. 28 and 29), are likewise consistent with the same. Weight losses attributed to stepwise dehydration (50-175°C, ~97.0% residual weight) and dealkylation/combustion (200-500°C, ~77.5% residual weight) are observed as expected on the basis of complete decomposition of to SnO_2 . While this experiment was not conducted to specifically test for low metal contamination, the experiment is designed to indicate the capability for the product t-amyltin oxide hydroxide to be synthesized with low metal contamination as demonstrated in companion examples herein.

Example 11 – Preparation of an Alkyltin Hydroxide Oxide Hydrolysate Via Aqueous Hydrolysis of an Alkyltin tris(alkynide)

A t-amyl tin hydroxide oxide hydrolysate, $\text{t-AmylSnO}_{(3/2-x/2)} (0 < x < 3)$ (compound 6), was prepared via aqueous hydrolysis of (1,1-dimethylpropyl) tin tris(phenylacetylide), $\text{t-AmylSn}(\text{C}\equiv\text{CPh})_3$ (compound 7)

Tin tetra(phenylacetylide), $\text{Sn}(\text{C}\equiv\text{CPh})_4$, compound 8 was synthesized as reported in Levashov, A.S.; Andreev, A. A.; Konshin, V. V. *Tetrahedron Letters*, 56, 2015, 56, 1870-1872, incorporated herein by reference. Compound 7 was then prepared via transmetalation of

compound 8 by a modification of the method of Jaumier, et al. (Jaumier P.; Jousseau, B.; Lahcini, M. *Angewandte Chemie, International Edition*, 38, 1999, 402-404, incorporated herein by reference): In a 150-mL flask, $\text{Sn}(\text{C}\equiv\text{CPh})_4$ (9.53 g/19.33 mmol) was dissolved in anhydrous toluene (80 mL). Nitrogen was then bubbled through the solution for 10 min, and the solution cooled in an ice bath. 1,1-dimethylpropylmagnesium bromide solution in ether (30 mL/1 N) was then added dropwise. The solution was allowed to warm to room temperature and stirred for two hours. The reaction mixture was then filtered through silica and condensed under vacuum. The resulting solid was sonicated in anhydrous hexanes, filtered, and the supernatant condensed under vacuum. The resulting waxy solid was then recrystallized from 20% aqueous methanol (v/v) at -10°C over the course of ~ 2 hours. Representative ^{119}Sn and ^1H NMR spectra for compound t-Amyl $\text{Sn}(\text{C}\equiv\text{CPh})_3$ synthesized by this method are found in Figs. 30 and 31. Fig. 30 depicts the ^1H NMR spectrum. Fig. 31 depicts the ^{119}Sn NMR spectrum.

tert-Amyltin hydroxide oxide, t-Amyl $\text{SnO}_{(3/2-x/2)}(\text{OH})_x$, where $0 < x < 3$ (compound 6), was prepared via hydrolysis of t-Amyl $\text{Sn}(\text{C}\equiv\text{CPh})_3$ with H_2O through an adaptation of the method Jaumier, et al. describe for unbranched alkyltin alkynides. *Chemical Communications*, 1998, 369-370, incorporated herein by reference. In a 50 mL flask, t-Amyl $\text{Sn}(\text{C}\equiv\text{CPh})_3$ was dissolved in tetrahydrofuran (20 mL/2 % water) and 0.5 mL water. The solution was stirred at room temperature for two days and the precipitate collected and dissolved in chloroform. The resulting solution was filtered through a 0.2 μm PTFE filter, and the solvent removed under vacuum. Representative ^{119}Sn (Fig. 32) and ^1H NMR spectra (Fig. 33) were collected in CDCl_3 . Observed ^{119}Sn resonances at -340.65 and -489.29 ppm are characteristic of the respective five and six-coordinate tin atoms in closo-type dodecameric clusters of the form $[(\text{RSn})_{12}\text{O}_{14}(\text{OH})_6](\text{OH})_2$. ^1H resonances are likewise indicative of the presence of 1,1-dimethylpropyl ligands in the two chemical environments, and importantly only very weak phenyl resonances (7.29-7.60 ppm) are observed relative to Figs. 32 and 33, indicating near-complete hydrolysis and removal of phenylacetylide ligands. While this experiment was not conducted to specifically test for low metal contamination, the experiment provides a synthetic approach that allows the product t-amyltin oxide hydroxide to be synthesized with low metal contamination as demonstrated in companion examples herein.

Example 12 – Resist coating, Film Processing, Negative Tone Imaging with Electron Beam Exposure

t-Bu $\text{SnO}_{(3/2-x/2)}(\text{OH})_x$ and i-Pr $\text{SnSnO}_{(3/2-x/2)}(\text{OH})_x$ resist precursor solutions were prepared as described in Example 3. The solutions were spin-coated and patterned using

electron-beam lithography with the process parameters summarized in Table 4. Silicon wafers (25x25 mm²) with a native-oxide surface were used as substrates for thin-film deposition. Substrates were ashed for 1 min in a 25 W O₂ plasma at 15 mTorr prior to resist coating. Precursor solutions were dispensed through a 0.45 nm syringe filter onto a substrate, spin-coated for 30 s at the indicated rpm, and baked on a hotplate for 2 min (post-apply bake, PAB) at the indicated temperature. Film thickness following coating and baking was measured via ellipsometry. The coated substrates were exposed to a 30-keV electron-beam rastered to form a line / space pattern at the designated dose. The patterned resist and substrate were then subjected to a post-exposure bake (PEB) on a hotplate for 2 min at the temperature shown in Table 4. The exposed film was then dipped in developer for 15 seconds and rinsed an additional 15 seconds with the same developer to form a negative tone image, i.e., unexposed portions of the coating were removed. A final 5-minute hotplate bake at 150°C was performed after development. Fig. 34 exhibits an SEM image of the resulting resist line/space patterns on the substrates at a pitch of 32-nm (top) and 28-nm (bottom).

TABLE 4

Resist Precursor Formulation	t-BuSnO _(3/2-x/2) (OH) _x	i-PrSnSnO _(3/2-x/2) (OH) _x
Solvent	methanol	4-methyl-2-pentanol
Coating Speed (rpm)	1500	2500
PAB temperature (°C)	100	80
Resist Film Thickness (nm)	40	31
PEB Temperature (°C)	170	120
Developer	2-heptanone	2-octanone
Imaging Dose (μC cm ⁻²)	1022	696

32 / 28 nm Pitch Resist Line Critical 15.2 / 13.5

16.2 / 15.1

Dimension (nm)

Example 13 – Positive Tone Imaging with EUV Exposure

A branched-alkyltin oxide hydroxide resist was used to generate positive tone images using EUV radiation. An $i\text{-PrSnO}_{(3/2-x/2)}(\text{OH})_x$ hydrolysate (compound 3) was prepared using Method 1 described in Example 7, and dissolved in 4-methyl-2-pentanol to produce ~0.07M Sn precursor solution. Silicon wafers (100 mm diameter) with a native-oxide surface were used as substrates for thin-film deposition. A hexamethyldisilazane (HMDS) vapor prime was performed on the wafers prior to coating. The precursor solutions were dispensed via pipet onto the substrate, spin-coated for 30 s at 1500 rpm, and baked on a hotplate for 2 min at 100°C. Film thickness following coating and baking was measured via ellipsometry to be ~23 nm. EUV exposures were carried out on the Berkeley MET. A series of line and space patterns at varying pitches were projected onto the wafer using 13.5-nm wavelength radiation and annular illumination at a numerical aperture of 0.3 and imaging dose of 25 mJ cm⁻². Immediately following exposure, the resist and substrate were baked a hotplate for 2 min at 150°C in air.

The exposed film was dipped in a 0.52 M solution of aqueous NaOH for 15 seconds and rinsed 15 seconds with H₂O to develop a positive tone image, i.e., exposed portions of the coating were removed. A final 5-minute hotplate bake at 150°C was performed after development. SEM images of positive-tone resist lines patterned on a 100-nm, (a) and 60-nm (b) pitch are found in Fig. 35.

The embodiments above are intended to be illustrative and not limiting. Additional embodiments are within the claims. In addition, although the present invention has been described with reference to particular embodiments, those skilled in the art will recognize that changes can be made in form and detail without departing from the spirit and scope of the invention. Any incorporation by reference of documents above is limited such that no subject matter is incorporated that is contrary to the explicit disclosure herein.

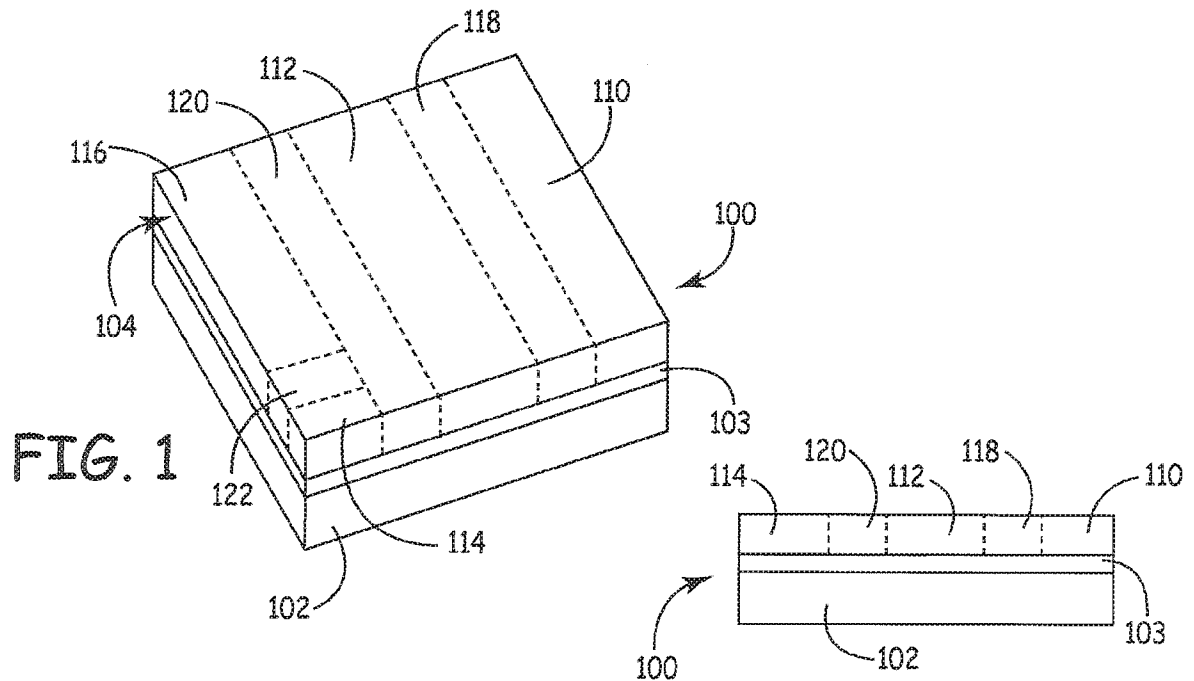
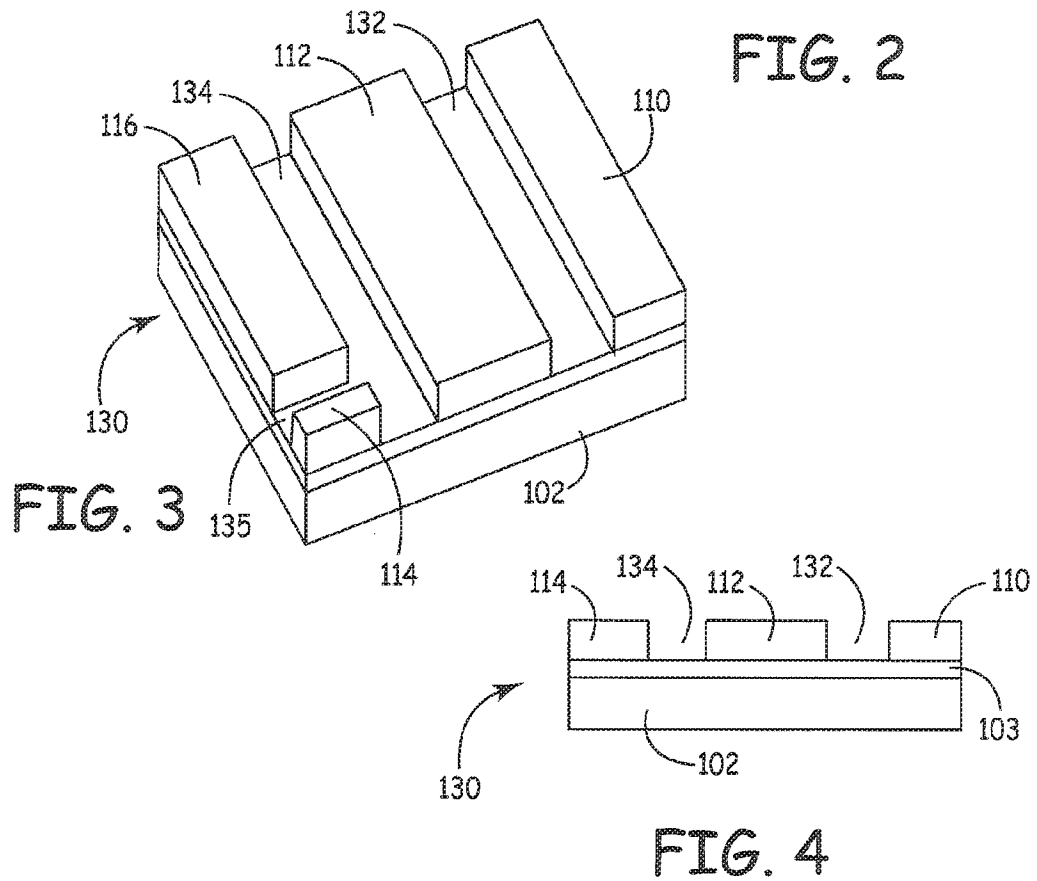
What is claimed is:

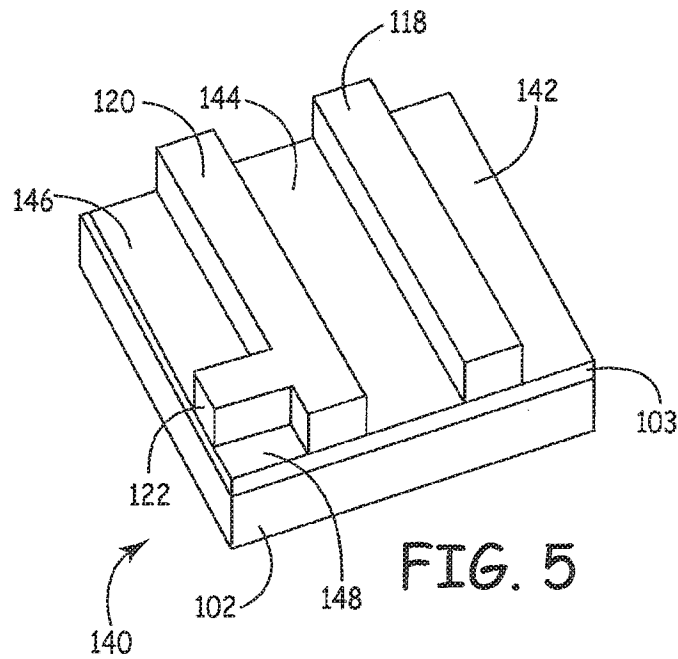
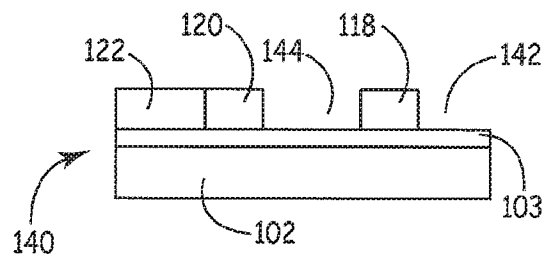
1. A coating solution comprising an organic solvent and a first organometallic compound represented by the formula $\text{RSnO}_{(3/2-x/2)}(\text{OH})_x$ where $(0 < x < 3)$ with from about 0.0025M to about 1.5M tin in the solution, where R is an alkyl group or cycloalkyl group with 3-31 carbon atoms, where the alkyl or cycloalkyl group is bonded to the tin at a secondary or tertiary carbon atom.
2. The coating solution of claim 1 wherein the first organometallic compound comprises tert-butyl tin oxide hydroxide ($\text{R} = -\text{C}(\text{CH}_3)_3$), iso-propyl tin oxide hydroxide ($\text{R} = -\text{CH}(\text{CH}_3)_2$), tert-amyl tin oxide hydroxide ($\text{R} = -\text{C}(\text{CH}_2\text{CH}_3)(\text{CH}_3)_2$) or mixtures thereof.
3. The coating solution of claim 1 or claim 2 further comprising a second organometallic compound distinct from the first organometallic compound and represented by the formula $\text{R}'\text{SnO}_{(3/2-x/2)}(\text{OH})_x$ where $(0 < x < 3)$ and R' is a linear or branched alkyl or cycloalkyl group.
4. The coating solution of any one of claims 1-3 wherein the organic solvent comprises an alcohol.
5. The coating solution of any one of claims 1-4 having a viscosity from about 0.5 centipoises (cP) to about 150cP and a tin concentration from about 0.01M to about 1.0M.
6. A coating solution comprising an organic solvent, a first organometallic compound represented by the formula $\text{RSnO}_{(3/2-x/2)}(\text{OH})_x$ where $(0 < x < 3)$, where R is an alkyl group or cycloalkyl group with 3-31 carbon atoms, where the alkyl or cycloalkyl group is bonded to the tin at a secondary or tertiary carbon atom, and a second organometallic compound distinct from the first organometallic compound and represented by the formula $\text{R}'\text{SnO}_{(3/2-x/2)}(\text{OH})_x$ where $(0 < x < 3)$, where R' is a linear or branched alkyl or cycloalkyl group and wherein R and R' are not the same.
7. The coating solution of claim 6 wherein the first organometallic compound comprises tert-butyl tin oxide hydroxide ($\text{R} = -\text{C}(\text{CH}_3)_3$), iso-propyl tin oxide hydroxide ($\text{R} = -\text{CH}(\text{CH}_3)_2$), or tert-amyl tin oxide hydroxide ($\text{R} = -\text{C}(\text{CH}_2\text{CH}_3)(\text{CH}_3)_2$).

8. The coating solution of claim 6 or claim 7 wherein R and R' are each independently branched alkyl or cycloalkyl groups.
9. The coating solution of any one of claims 6-8 wherein the second organometallic compound represents at least about 10 weight percent of the organometallic compounds in the coating solution.
10. The coating solution of any one of claims 6-9 further comprising a third distinct organometallic compound represented by the formula $R''SnO_{(3/2-x/2)}(OH)_x$ where $(0 < x < 3)$, where R'' is a linear or branched alkyl or cycloalkyl group wherein the third organometallic compound represents at least about 10 weight percent of the organometallic compounds in the coating solution.
11. The coating solution of any one of claims 6-10 wherein the solvent comprises an alcohol and wherein the organometallic compounds result in a tin ion concentration from about 0.0025M to about 1.5M.
12. A method for patterning a film on a substrate, the method comprising:
exposing the film with EUV doses of no more than about 80 mJ/cm²; and
developing the film to form features at half-pitch no more than about 25 nm and linewidth roughness no more than about 5 nm.
13. The method of claim 12 wherein the EUV dose is from about 12 mJ/cm² to about 75 mJ/cm².
14. The method of claim 12 or claim 13 wherein the half-pitch is no more than about 18 nm.
15. The method of any one of claims 12-14 wherein the organometallic film comprises a first organometallic compound represented by the formula $RSnO_{(3/2-x/2)}(OH)_x$ where $(0 < x < 3)$ where R is an alkyl group or cycloalkyl group with 3-31 carbon atoms, where the alkyl or cycloalkyl group is bonded to the tin at a secondary or tertiary carbon.

16. The method of any one of claims 12-15 further comprising developing the film following exposure to form a negative image through the removal of unexposed portions of film.
17. The method of any one of claims 12-15 further comprising developing the film following exposure to form a positive image through the removal of exposed portions of film.
18. A method for patterning an organometallic film on a substrate, the method comprising:
exposing the organometallic film to EUV radiation at a dose-to-gel value of no more than about 15 mJ/cm² to obtain a contrast of at least about 6.
19. A patterned structure comprising a substrate having a surface and a coating associated with the surface wherein at least portions of the coating are represented by the formulation $(R)_z\text{SnO}_{2-z/2-x/2}(\text{OH})_x$ ($0 < (x+z) < 4$), where R is an alkyl group or cycloalkyl group with 3-31 carbon atoms, where the alkyl or cycloalkyl group is bonded to the tin at a secondary or tertiary carbon atom.
20. The patterned structure of claim 19 wherein z is less than about 1.
21. The patterned structure of claim 19 wherein z is less than about 1 and the ratio $(2-z/2-x/2):x$ is greater than about 1.
22. The patterned structure of any one of claims 19-21 wherein the substrate comprises a polymer sheet, elemental silicon and/or a ceramic material.
23. The patterned structure of any one of claims 19-22 wherein the coating has an average thickness of no more than about 50 nm.
24. The patterned structure of any one of claims 19-23 wherein the coating forms a pattern at least a portion of which form features with a half-pitch of no more than about 25 nm.

25. A solution comprising a solvent and a compound represented by the formula $\text{RSnO}_{(3/2-x/2)}(\text{OH})_x$ where $(0 < x < 3)$, where R is an alkyl, cycloalkyl or substituted alkyl moiety having from 1 to 31 carbon atoms, the solution having individual concentrations of contaminant metals of no more than about 1 ppm by weight.
26. The solution of claim 25 wherein R is an alkyl group or cycloalkyl group with 3-31 carbon atoms, where the alkyl or cycloalkyl group is bonded to the tin at a secondary or tertiary carbon atom.
27. The solution of claim 25 or claim 26 having concentrations of individual contaminant metals of no more than about 500 ppb by weight, wherein contaminant metals have a concentration of less than 100 ppm by weight.
28. The solution of any one of claims 25-27 having concentrations of individual alkali and alkaline earth metals no more than about 100 ppb by weight.
29. A method for synthesizing a compound represented by the formula RSnOOH or $\text{RSnO}_{(3/2-x/2)}(\text{OH})_x$ $(0 < x < 3)$, where R is an alkyl or cycloalkyl moiety having from 1 to 31 carbon atoms, the method comprising:
hydrolyzing a precursor composition having the formula RSnX_3 , where X represents a halide atom (F, Cl, Br or I), or amido group(s), or combinations thereof wherein the hydrolysis is performed with sufficient water to effectuate the hydrolysis, wherein the hydrolysis product has individual concentrations of metals other than tin of no more than about 1 ppm by weight.
30. The method of claim 29 wherein the hydrolysis is performed with a quaternary ammonium hydroxide.
31. The method of claim 29 wherein the hydrolysis is performed in an organic solvent with sufficient water to effectuate the hydrolysis in a controlled reaction.
32. The method of claim 31 wherein the water is added to the organic solvent in a measured quantity.
33. The method of claim 31 wherein the water is absorbed from the ambient.





3 / 18

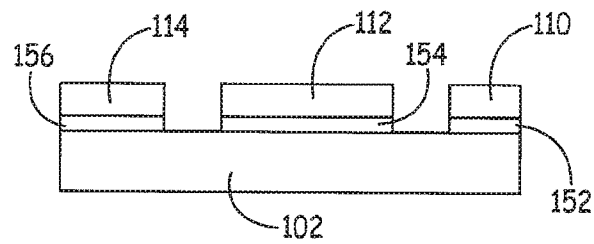


FIG. 7

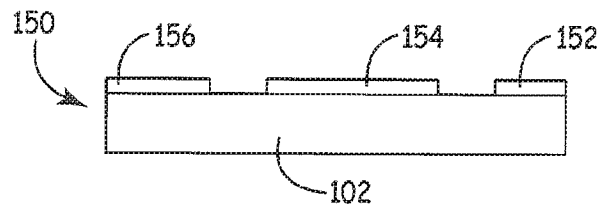


FIG. 8

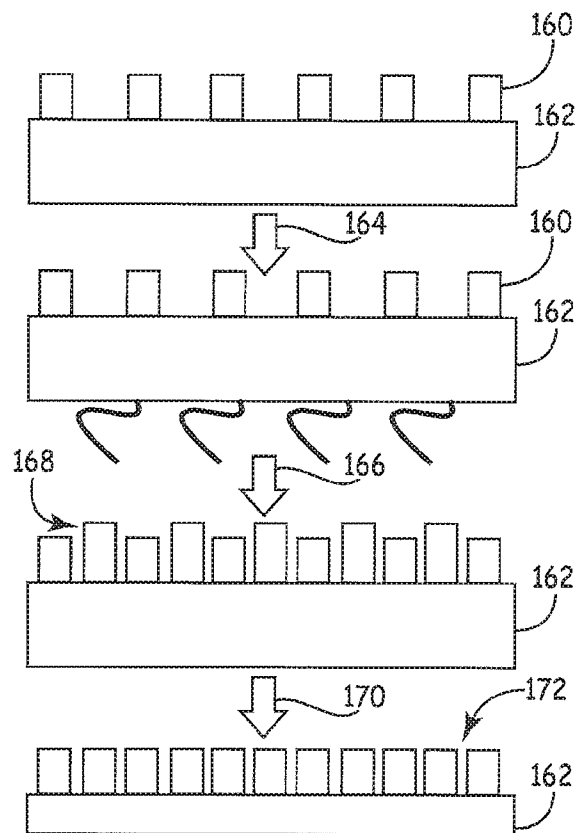


FIG. 9

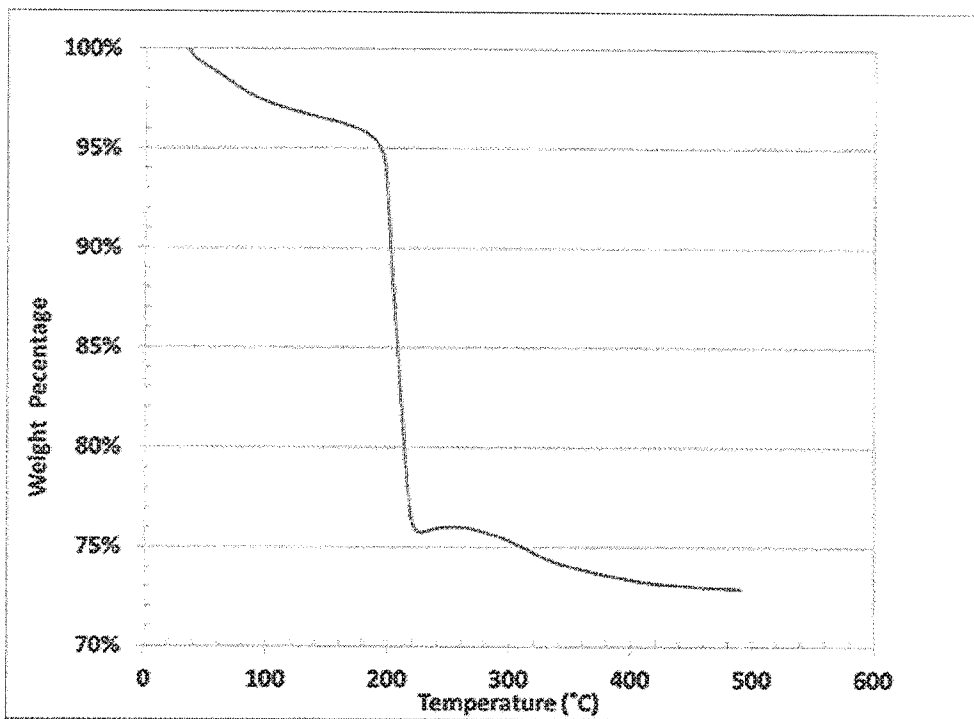


Fig. 10

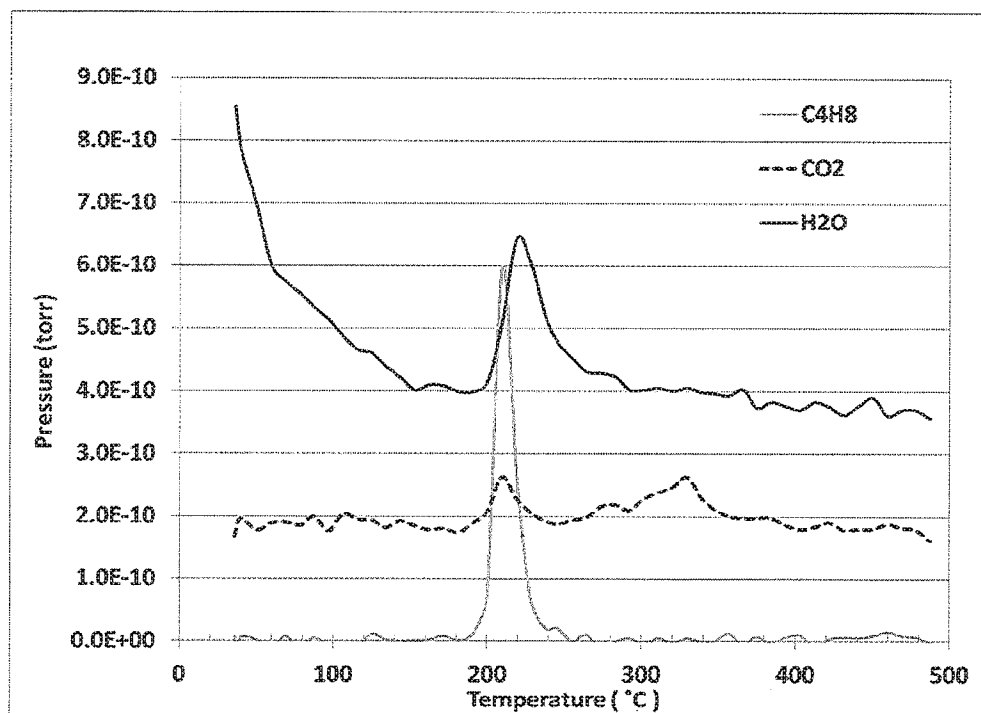


Fig. 11

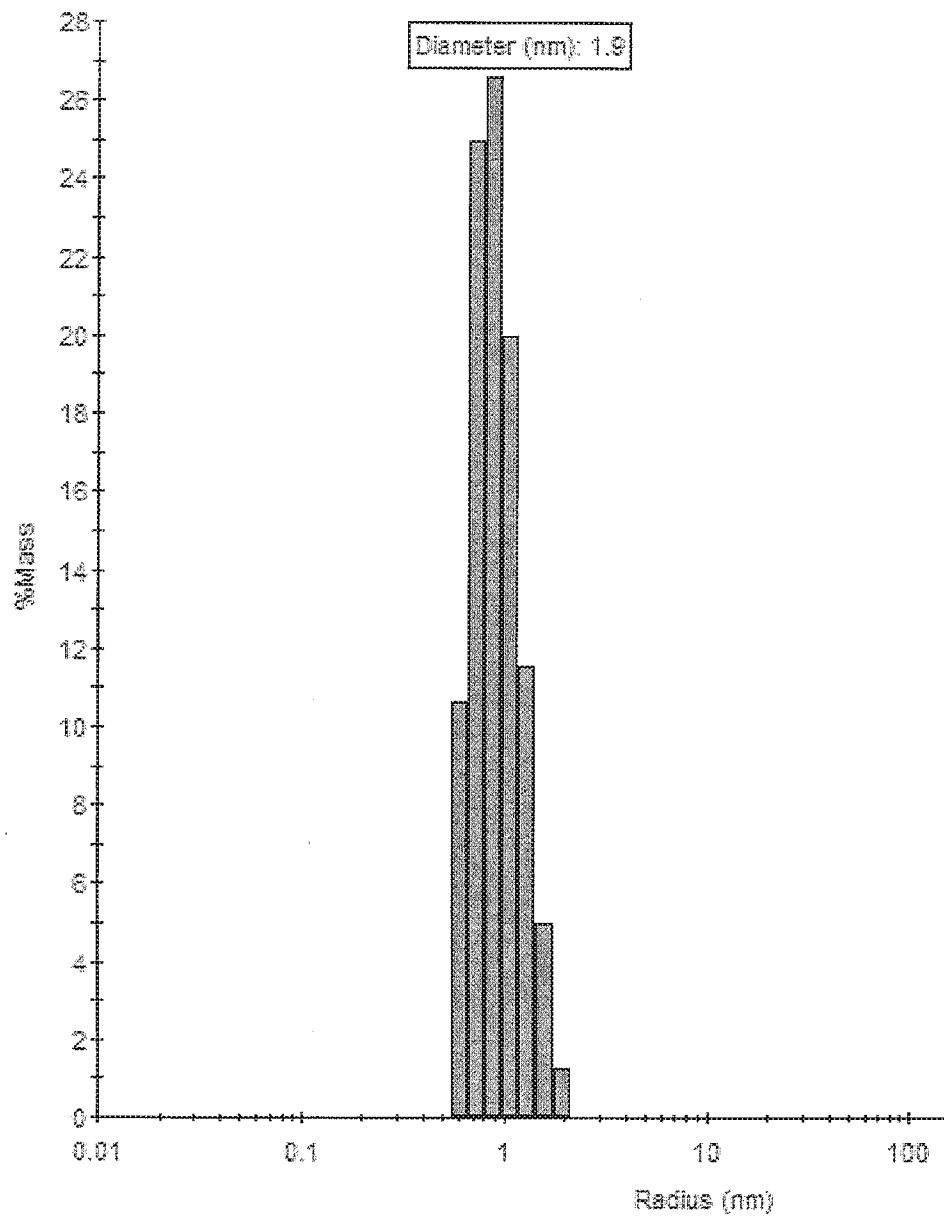


Fig. 12

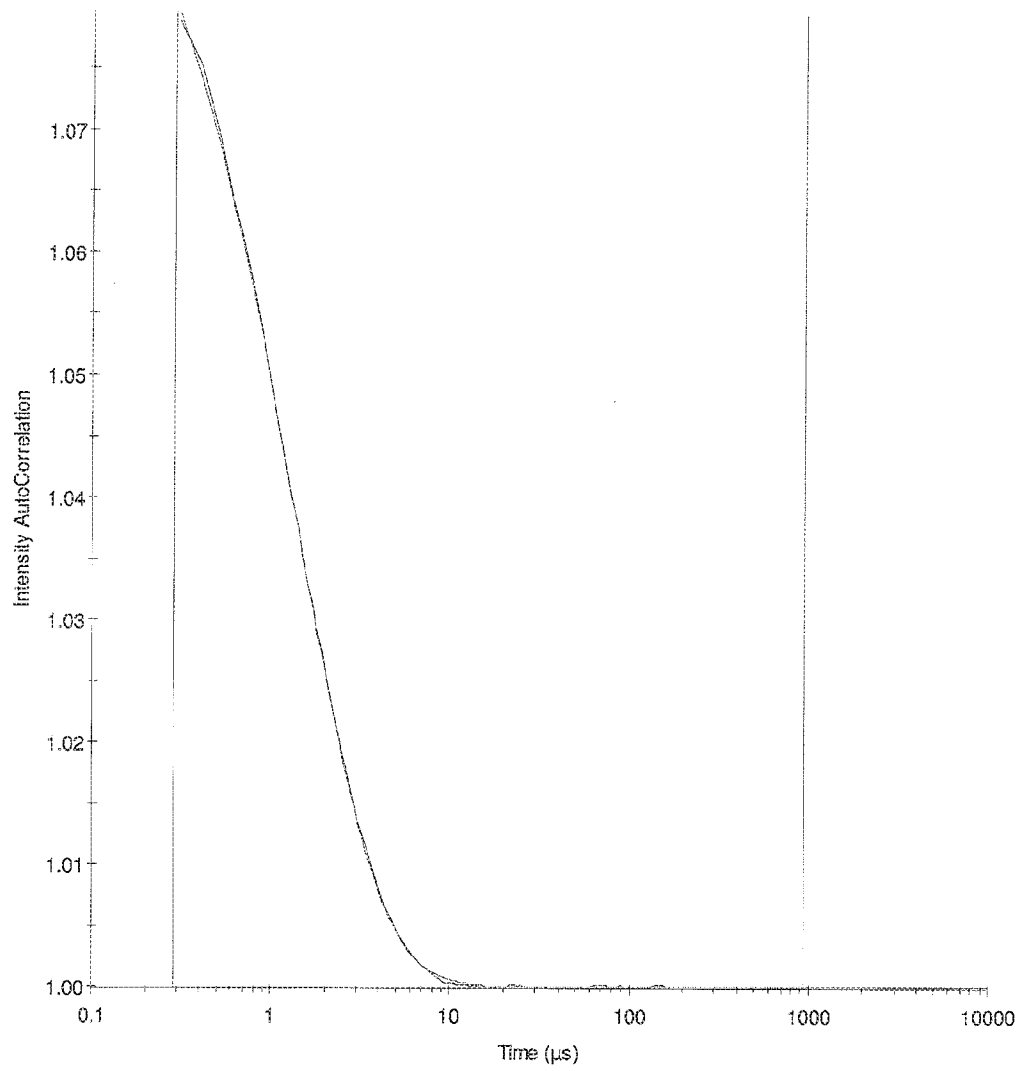


Fig. 13

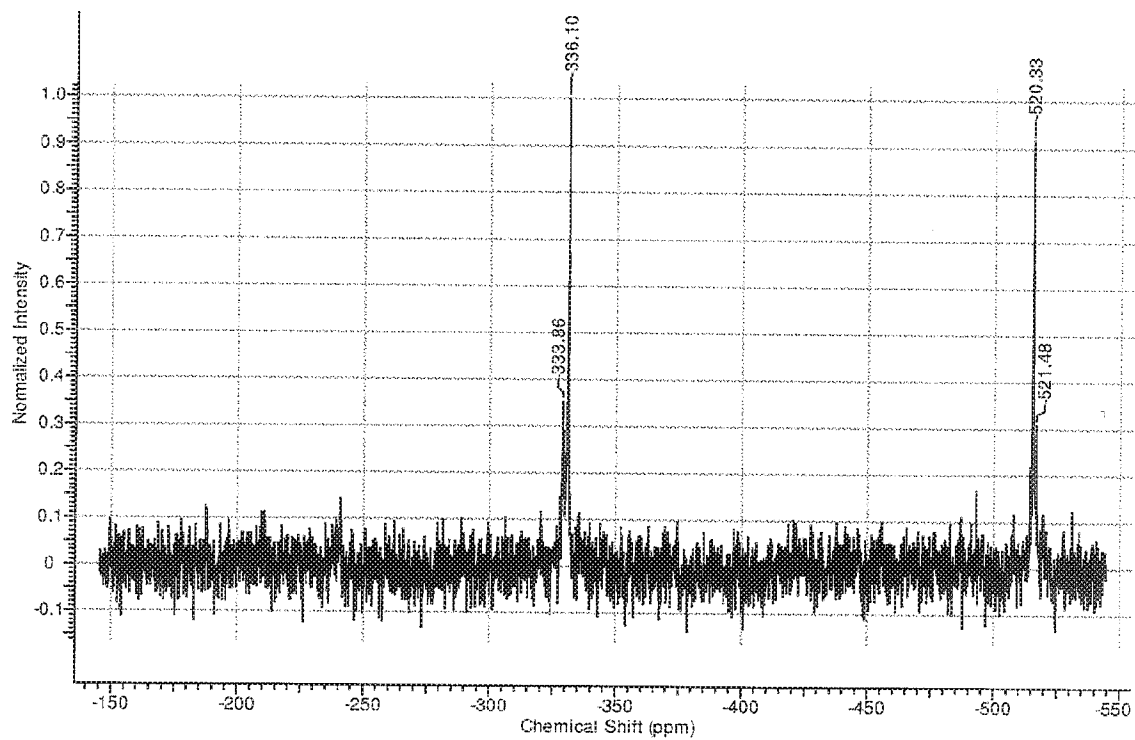


Fig. 14

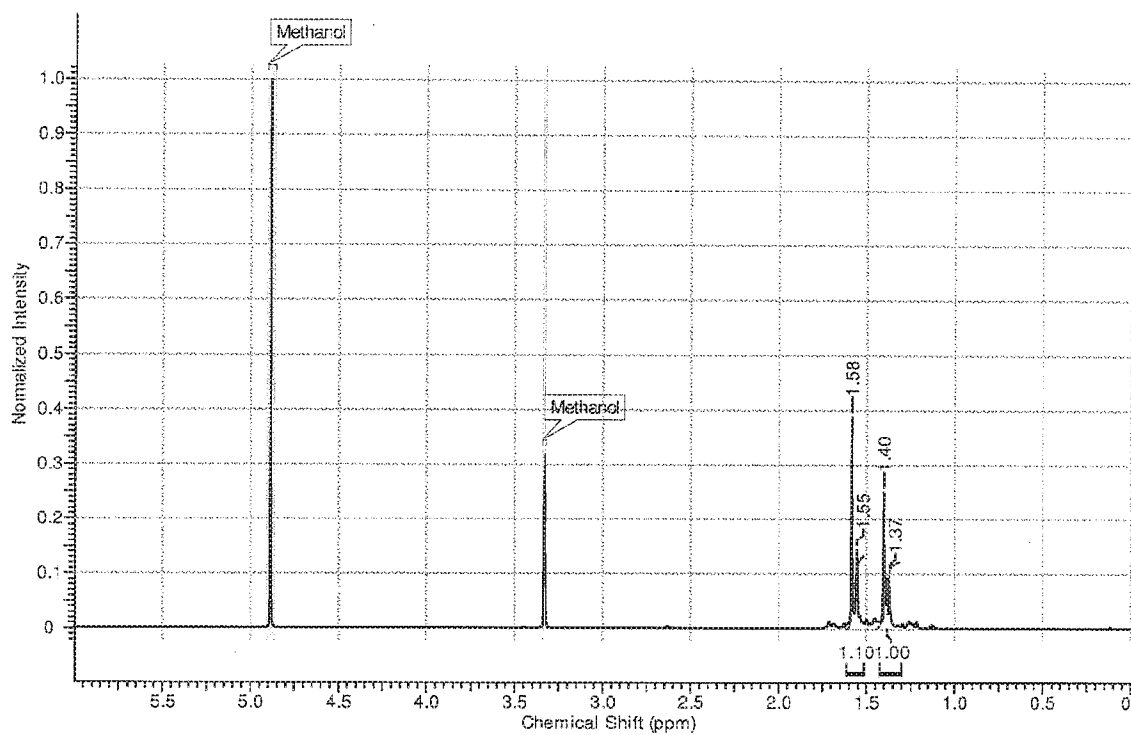


Fig. 15

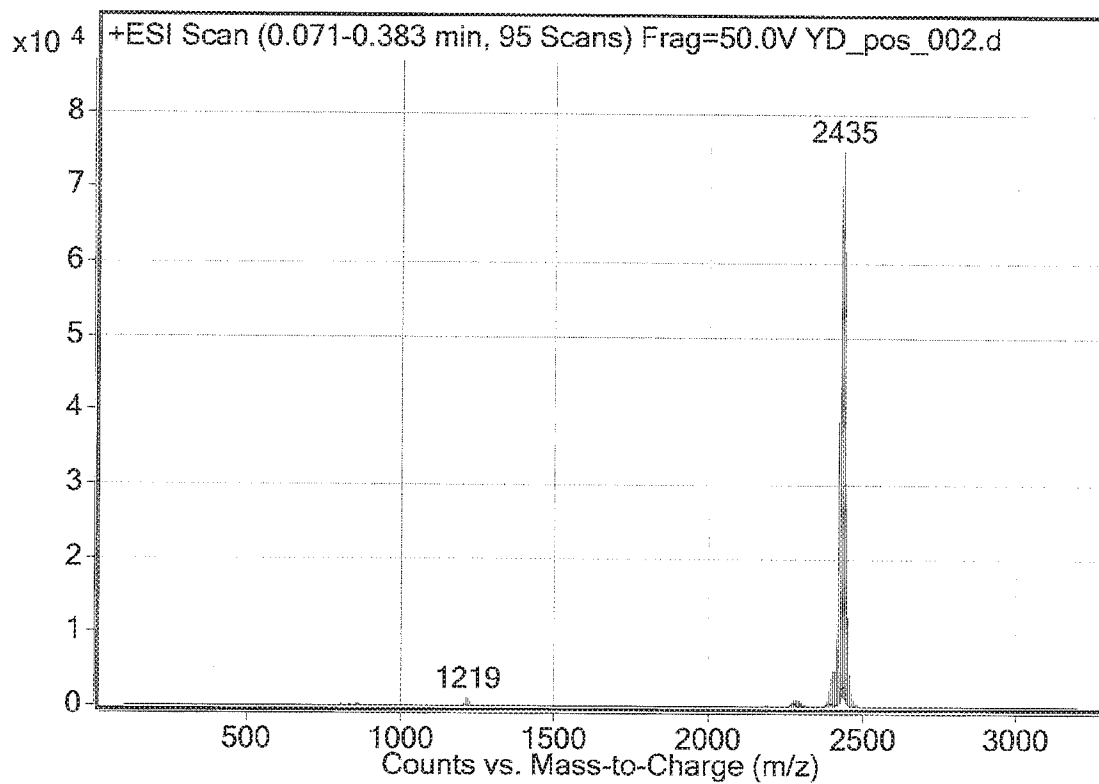


Fig. 16

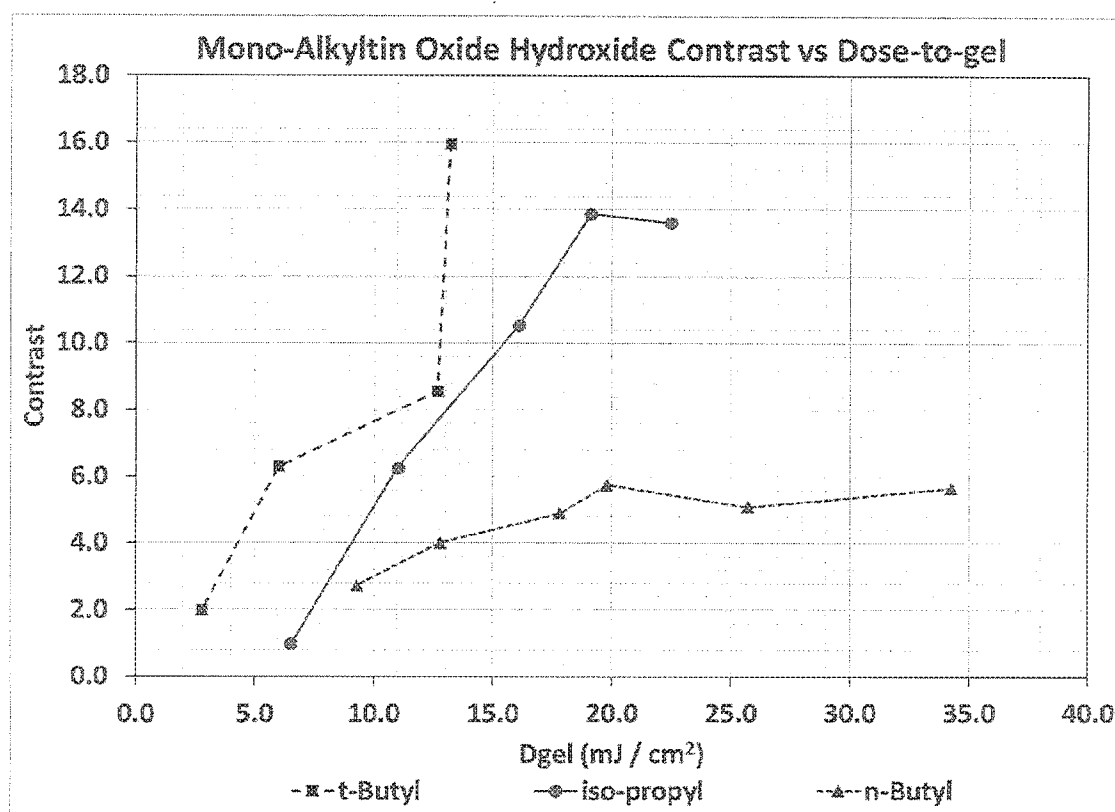


Fig. 17

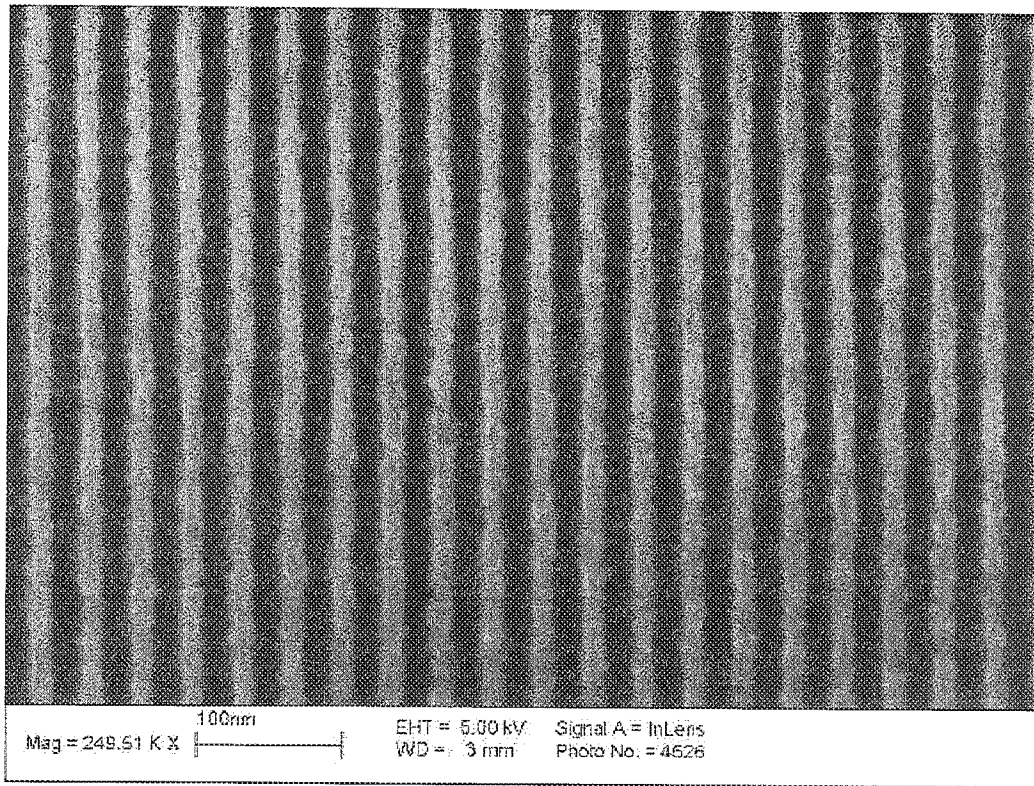


Fig. 18

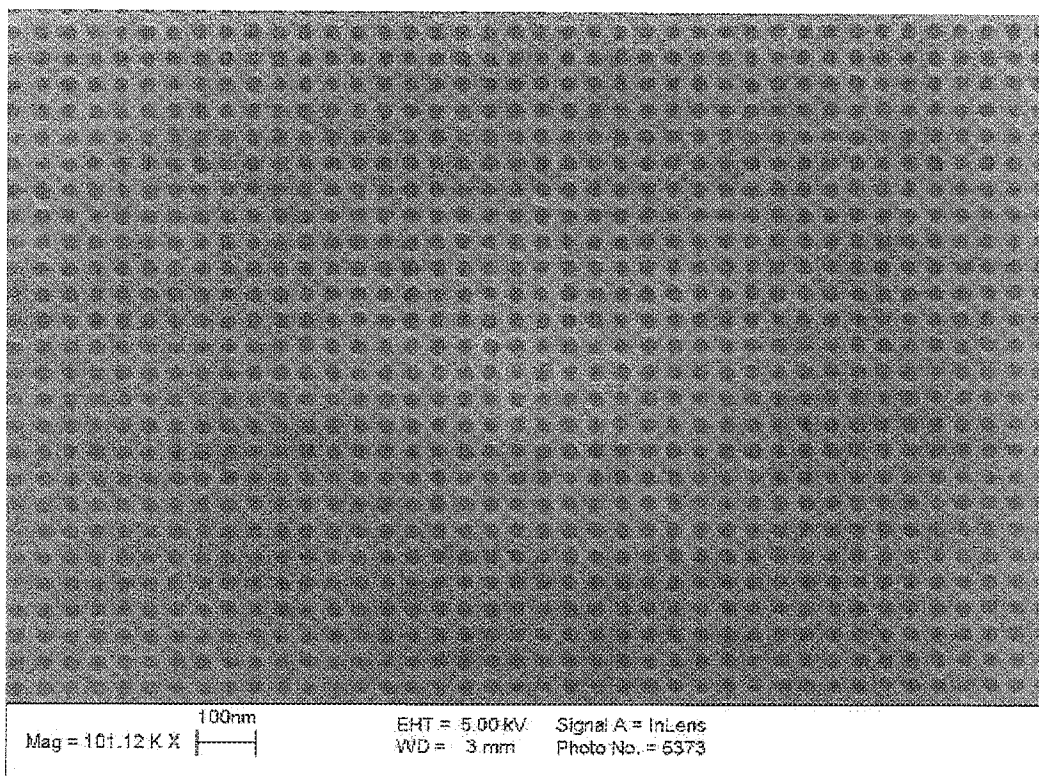


Fig. 19

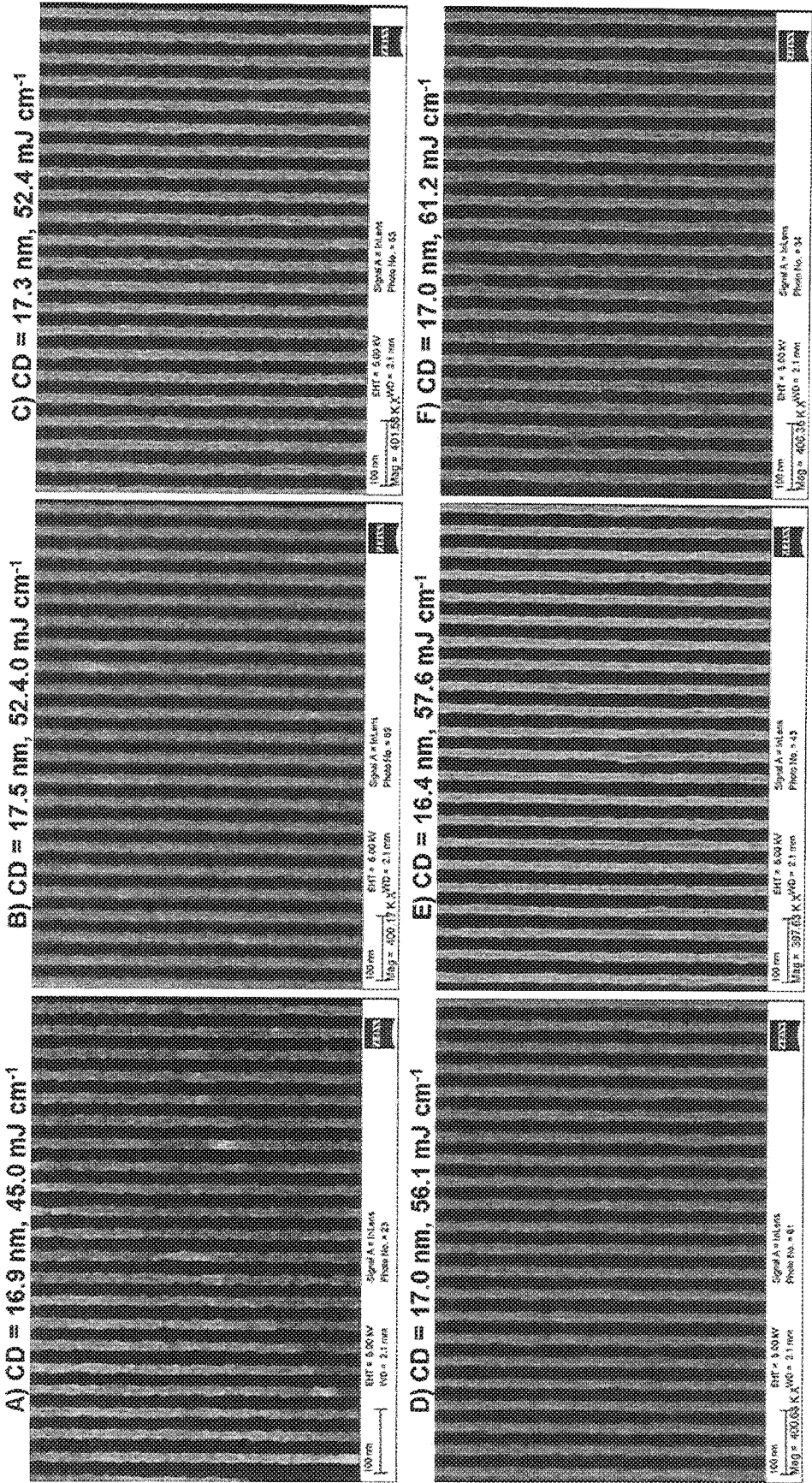


Fig. 20

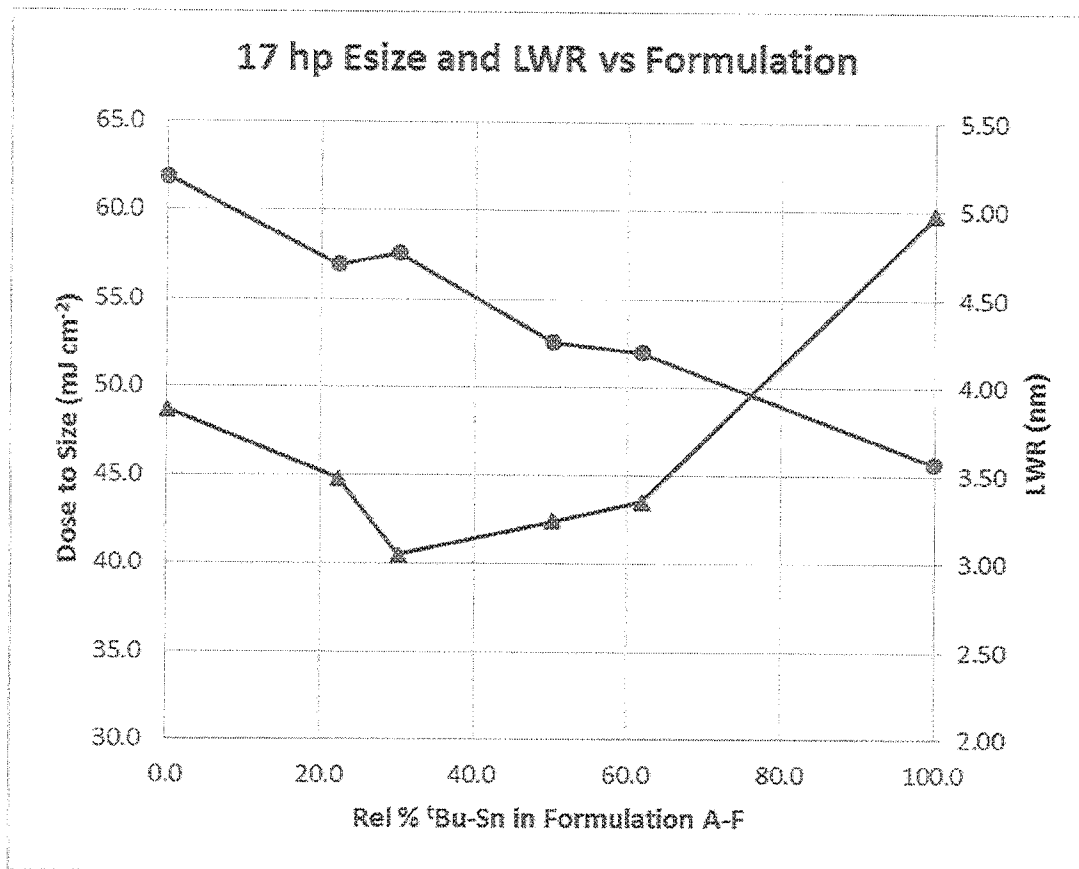


Fig. 21

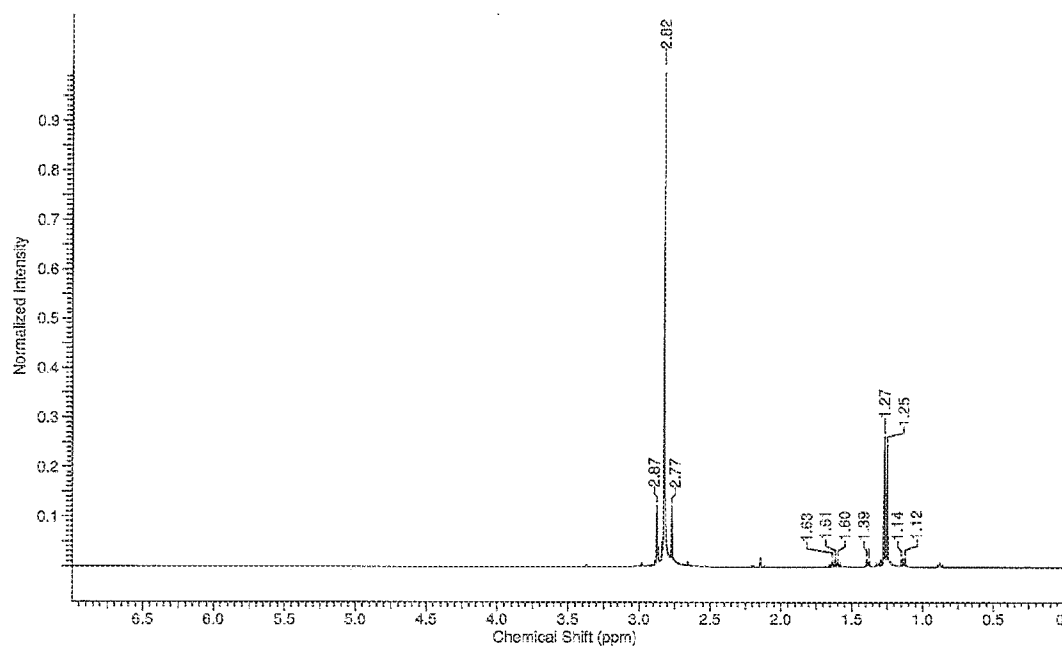


Fig. 22

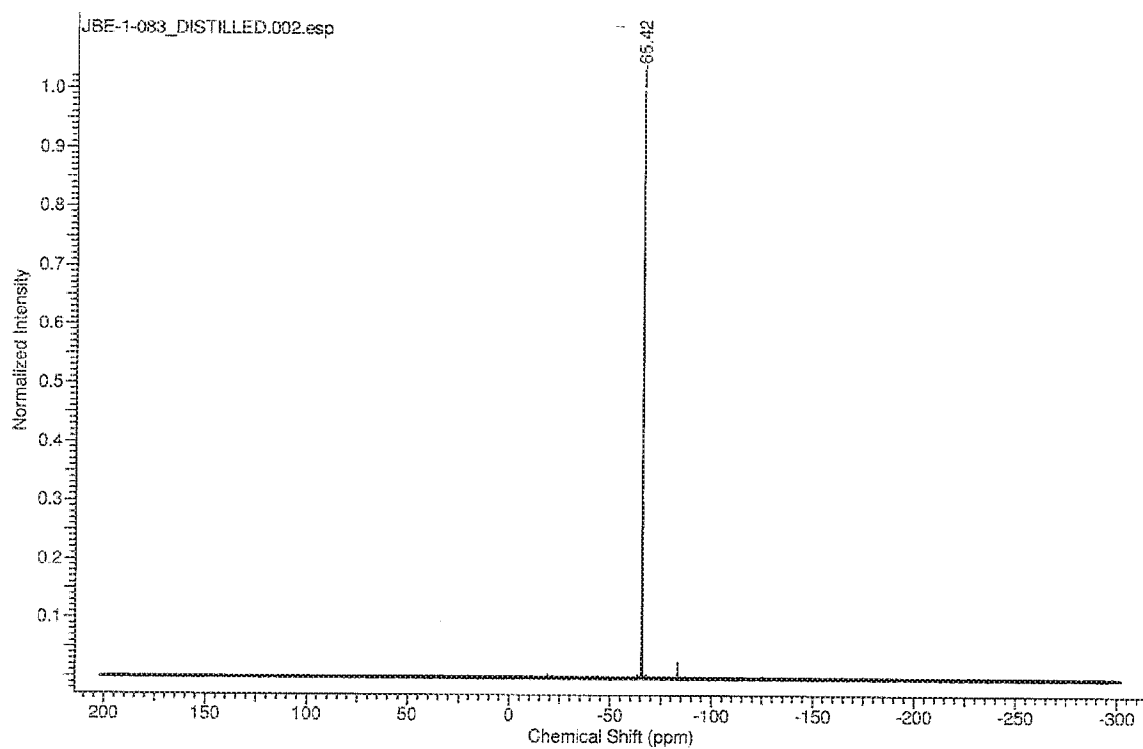


Fig. 23

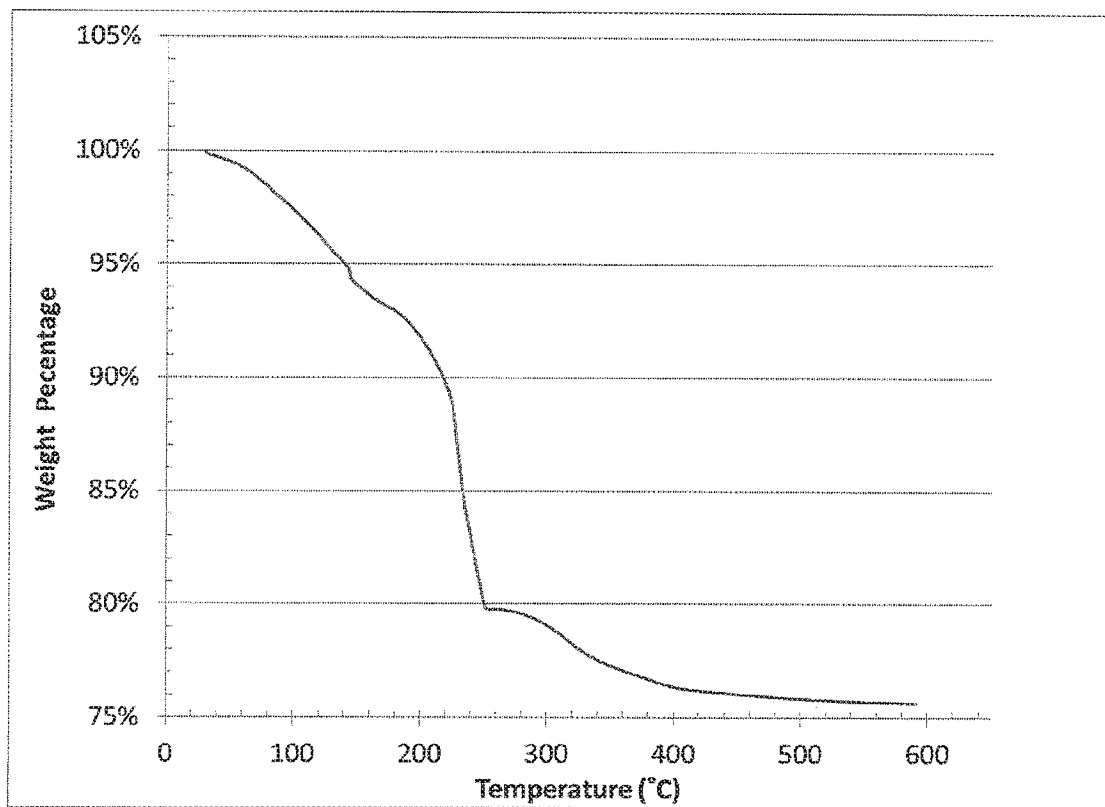


Fig. 24

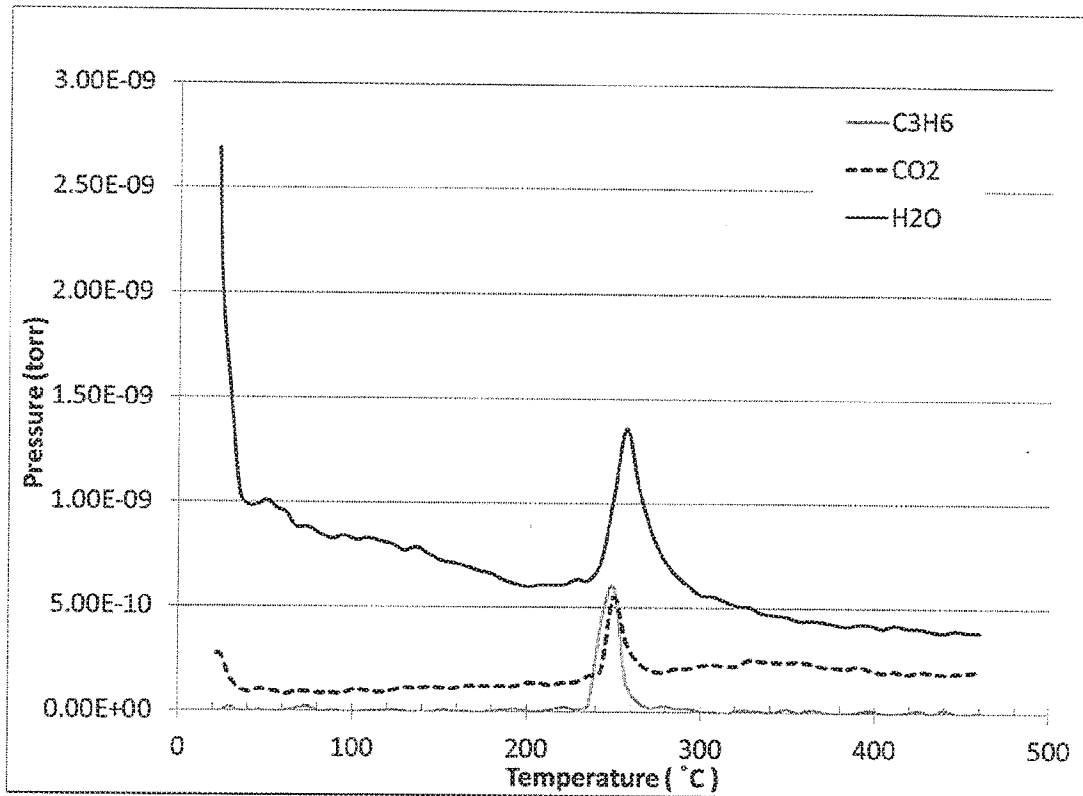


Fig. 25

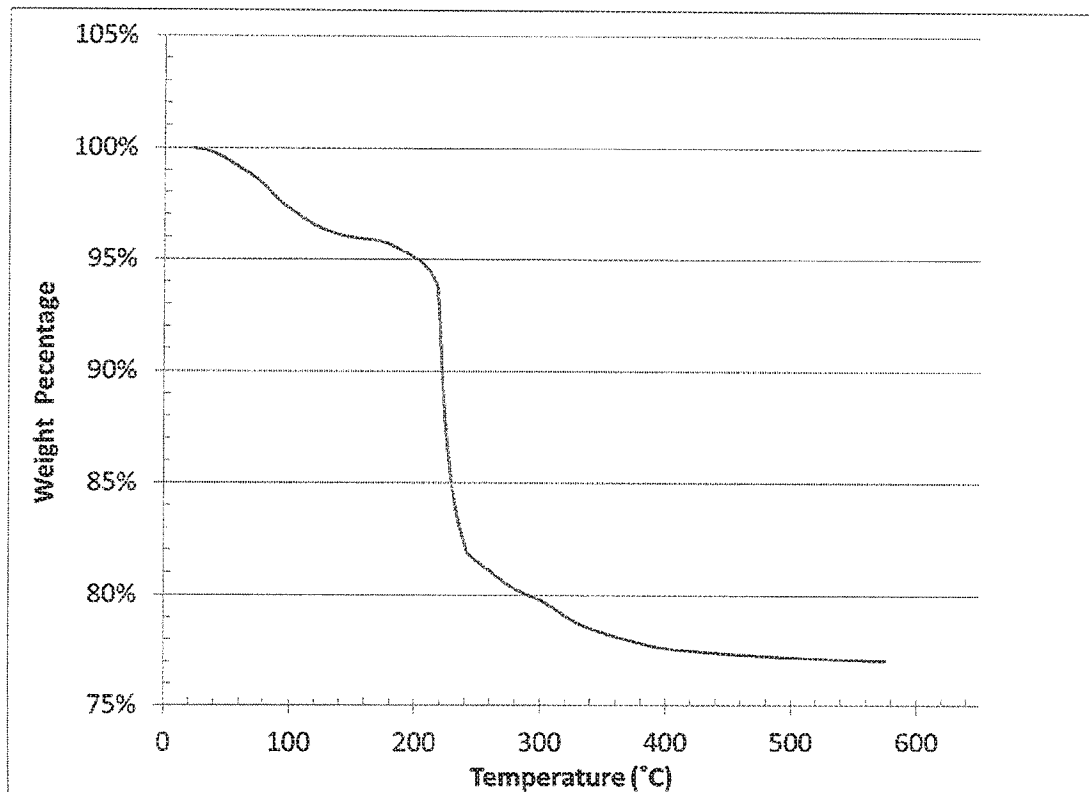


Fig. 26

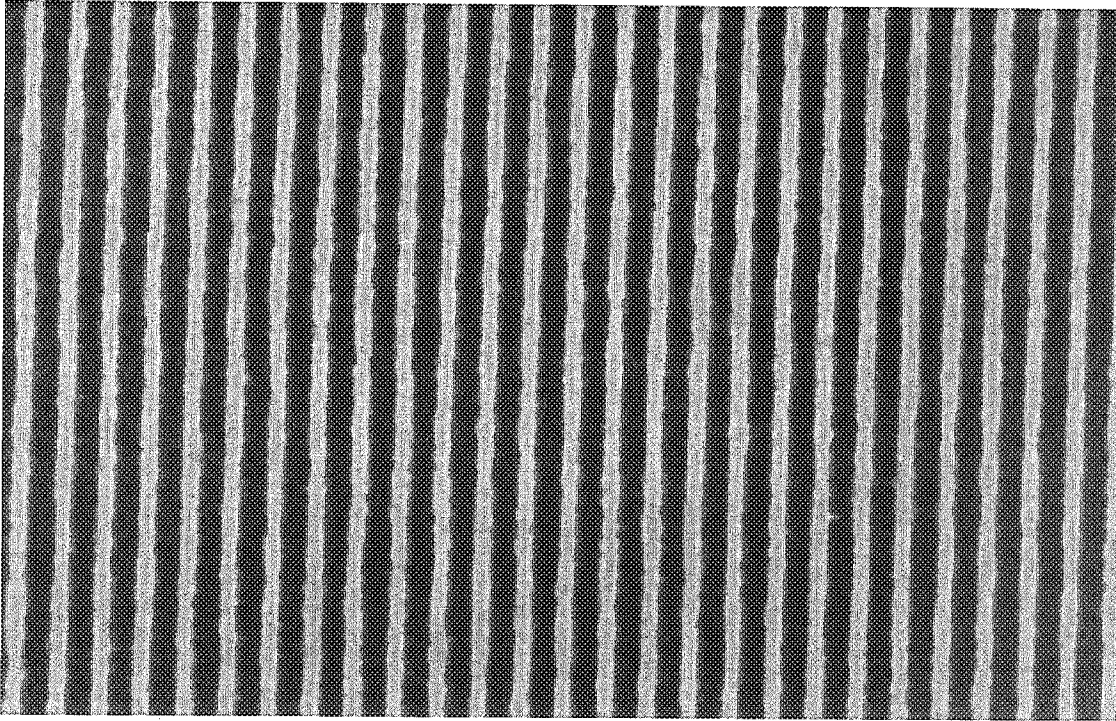


Fig. 27

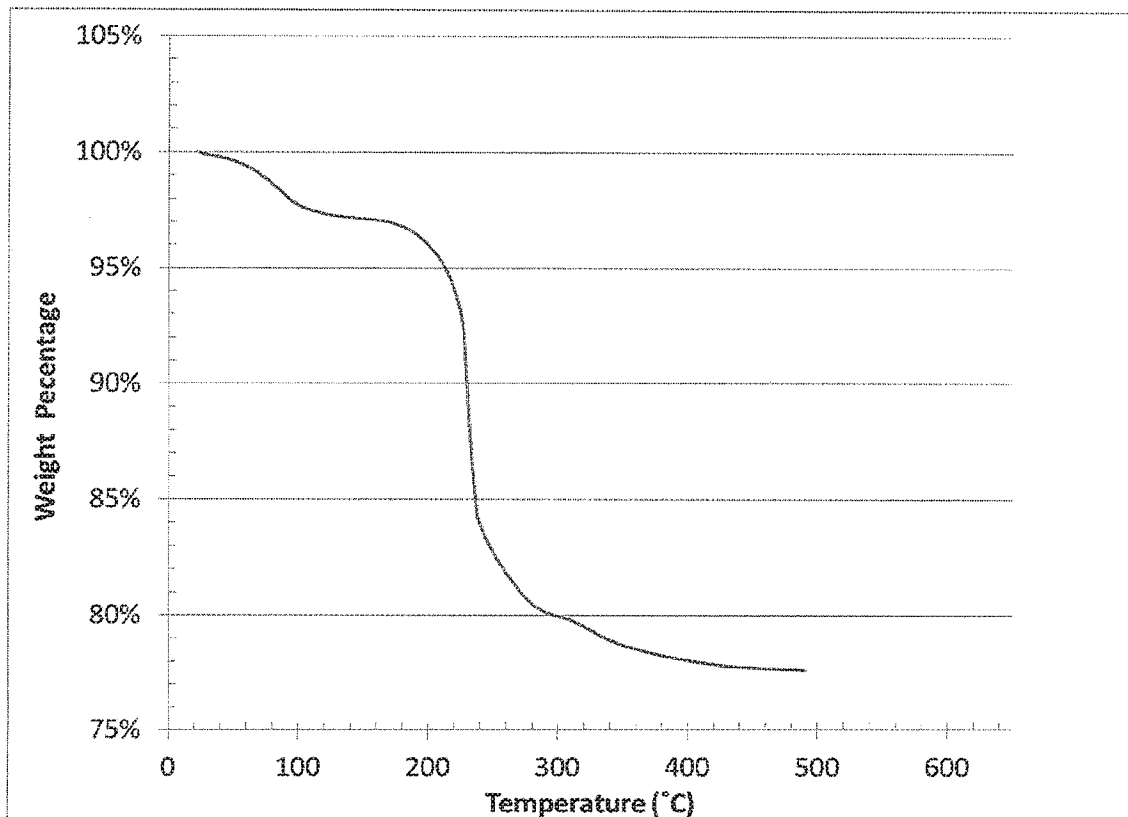


Fig. 28

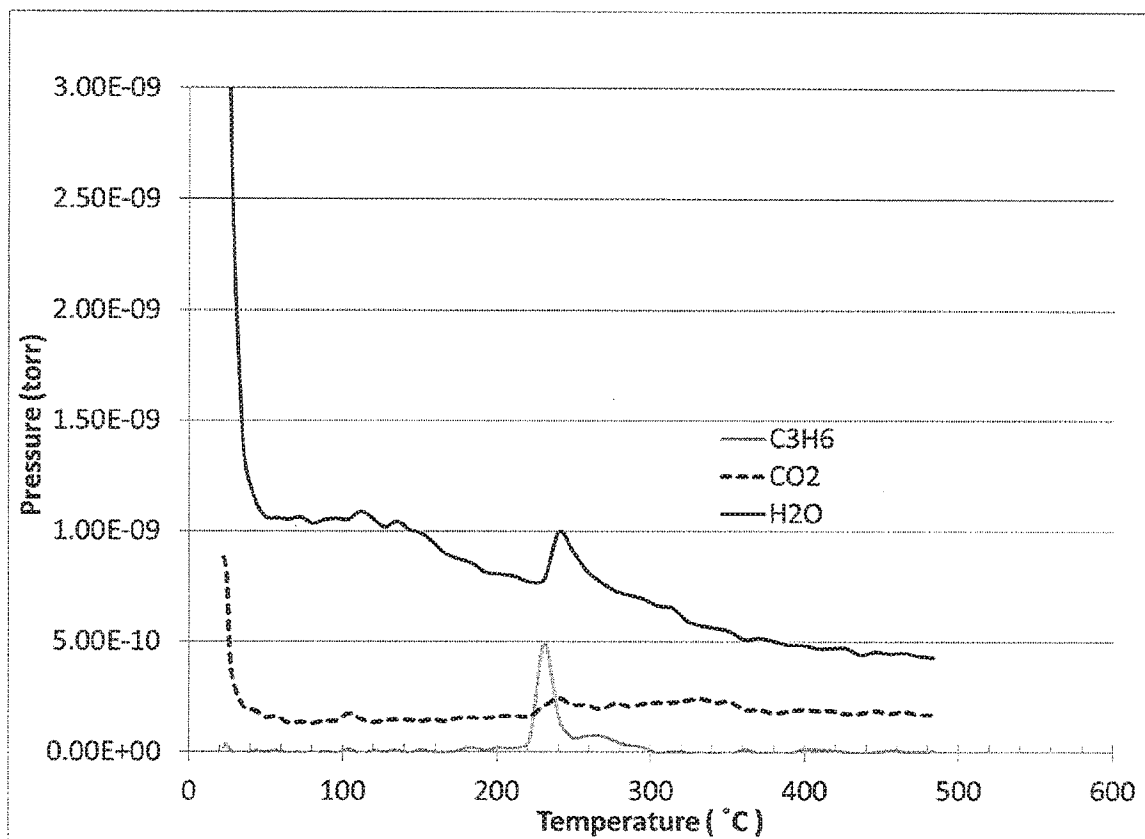


Fig. 29

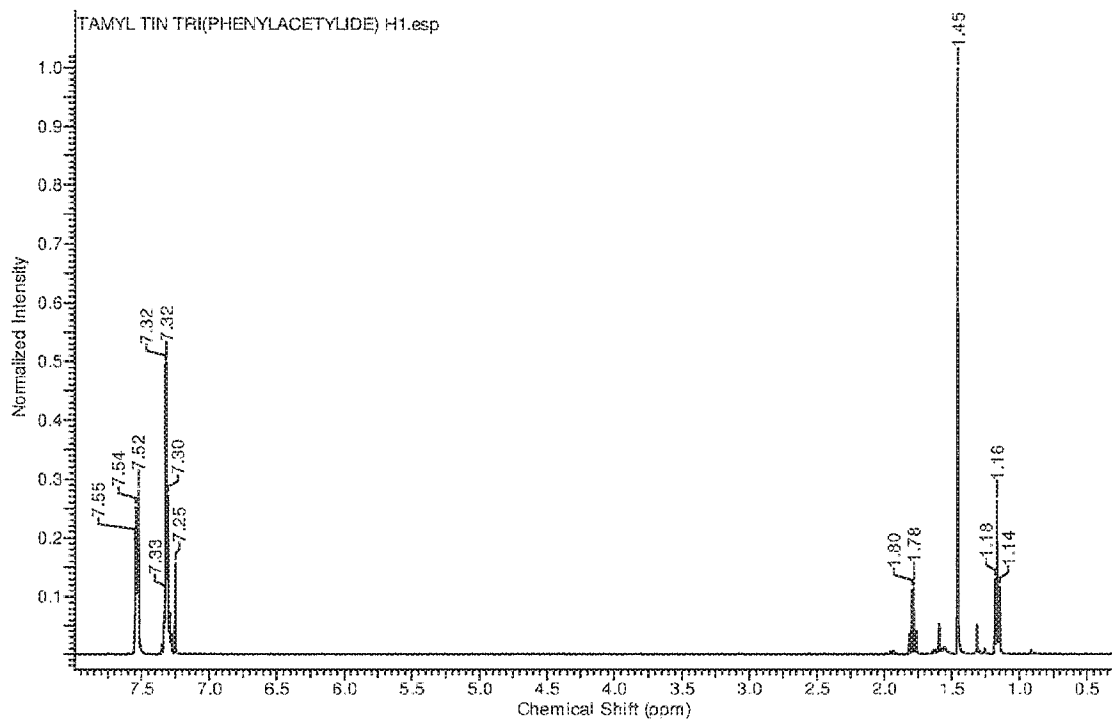


Fig. 30

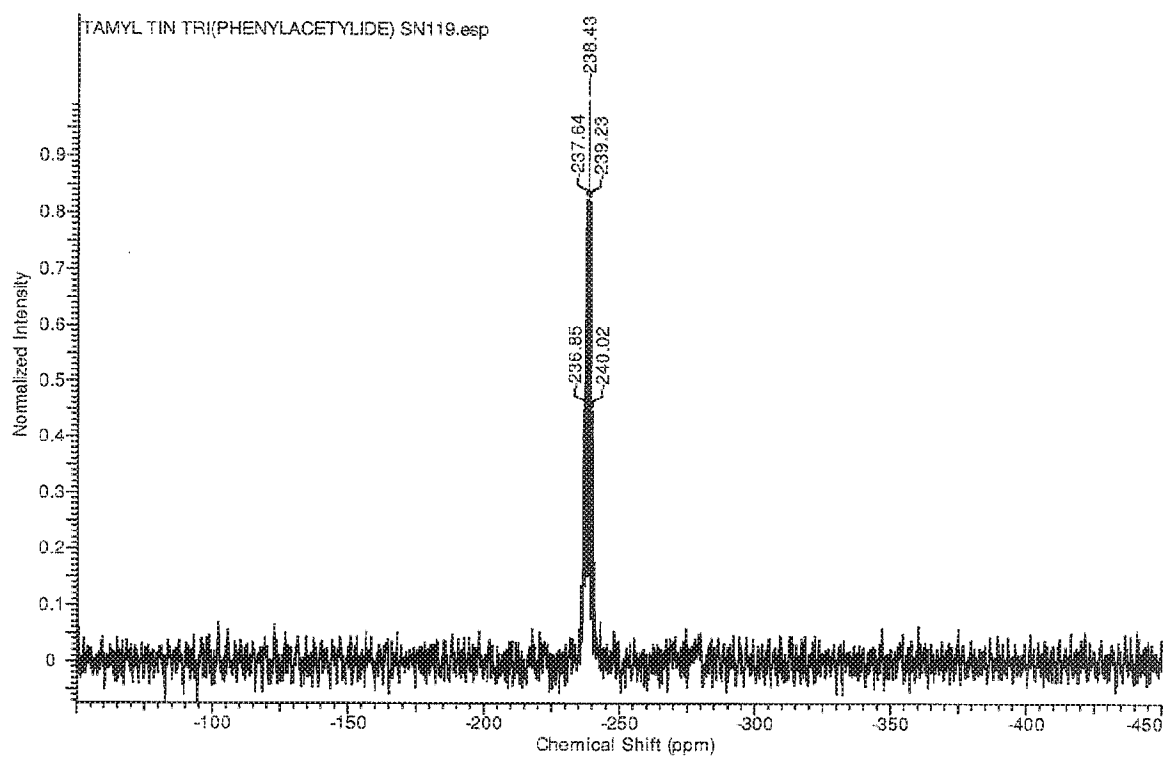


Fig. 31

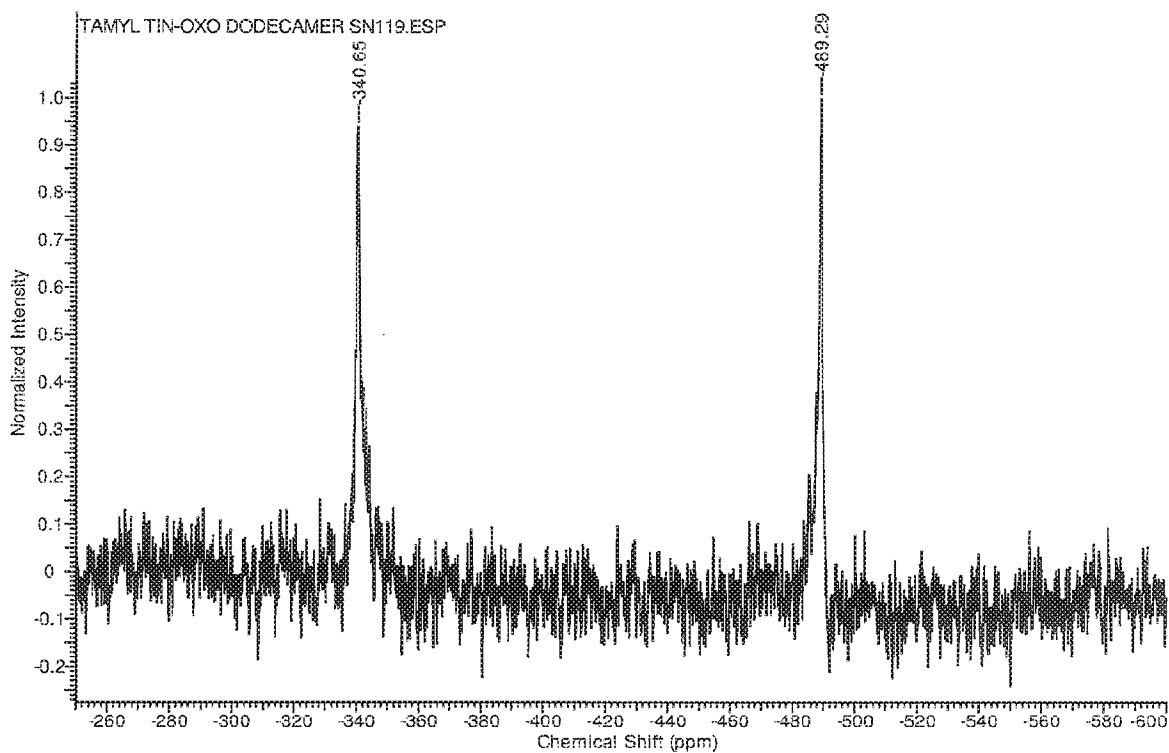


Fig. 32

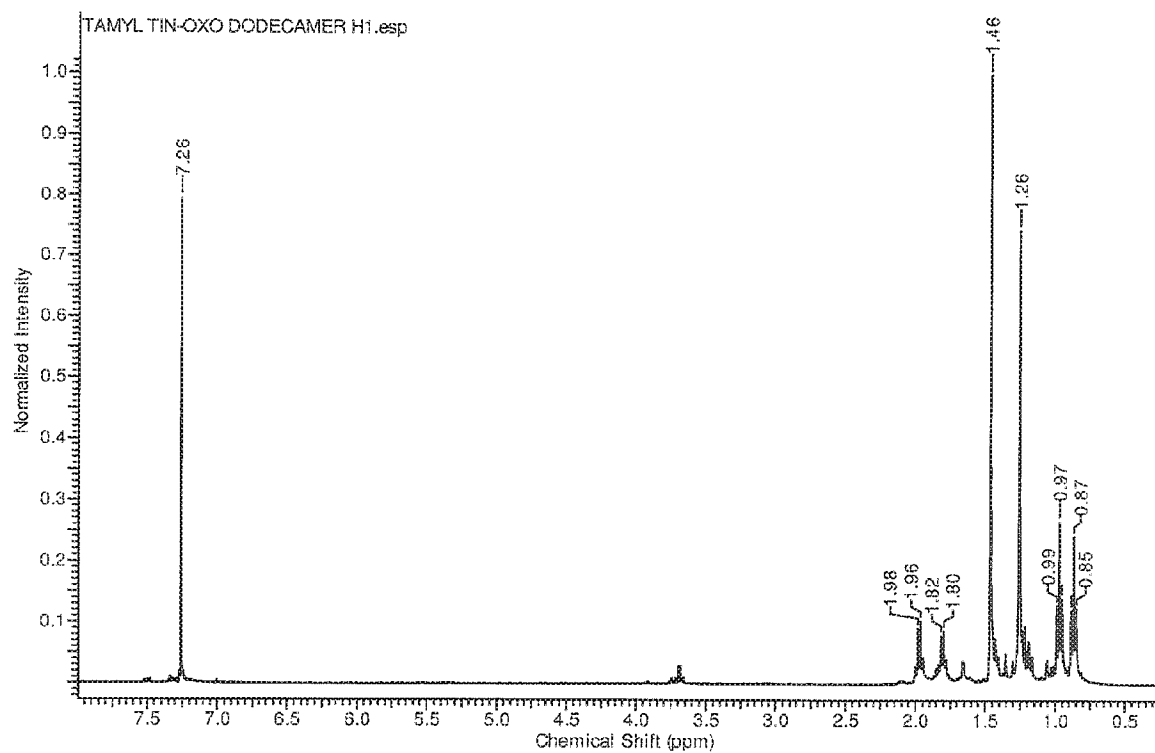


Fig. 33

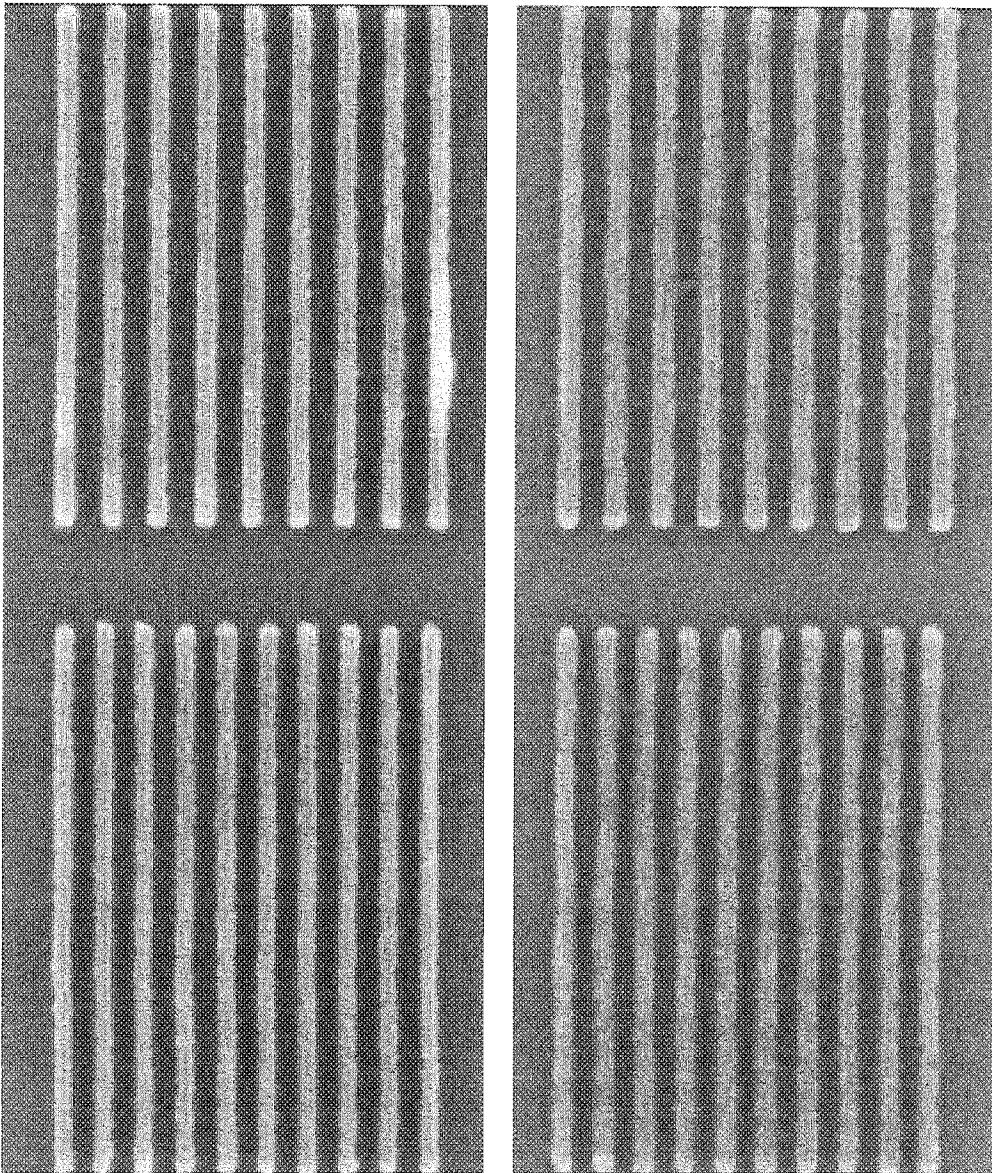


Fig. 34

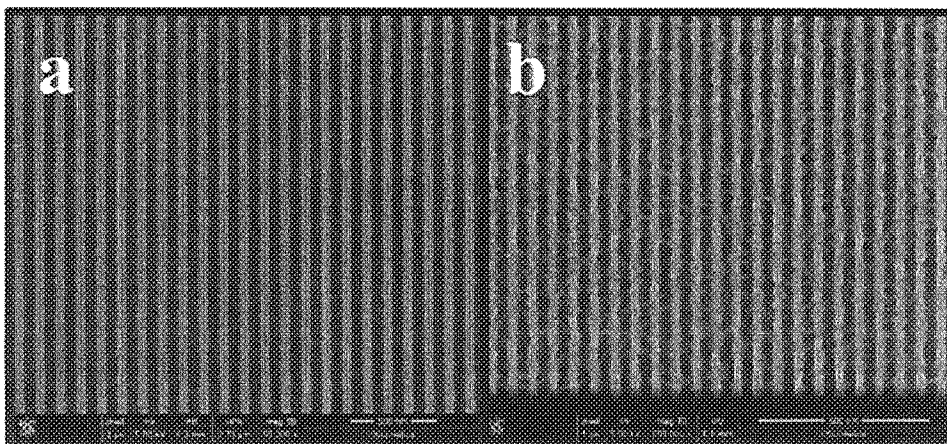


Fig. 35

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 15/56865

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - C07F 7/22; G03F 7/004; H05K 3/02 (2016.01)

CPC - C07F7/2232; H01L21/314

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC(8): C07F 7/22; G03F 7/004; H05K 3/02 (2016.01)

CPC: C07F 7/2232; H01L 21/314

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC: 556/89; 430/270.1; 430/313 (key word limited; see search terms below)

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

PatBase, Google Patents, Google Scholar

Search terms used: organotin oxide, hydroxide, tert-butyl, isopropyl, coating, radiation, resist, photoresist

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2014/150411 A1 (THE SHERWIN-WILLIAMS COMPANY) 25 September 2014 (25.09.2014); para [0007], [0044], [0056]	1-2
Y		3, 6-8, 25-27
Y	US 3,635,683 A (STAMM) 18 January 1972 (18.01.1972); col 2 ln 63-72	3, 6-8
Y	US 2011/0166268 A1 (DEELMAN et al.) 07 July 2011 (07.07.2011); para [0001], [0012]	25-27
A	WO 1998/015559 A1 (E. I. DUPONT DE NEMOURS AND COMPANY) 16 April 1998 (16.04.1998); entire document	1-2

☐ Further documents are listed in the continuation of Box C.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

26 January 2016

Date of mailing of the international search report

05 FEB 2016

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents

P.O. Box 1450, Alexandria, Virginia 22313-1450

Facsimile No. 571-273-8300

Authorized officer:

Lee W. Young

PCT Helpdesk: 571-272-4300

PCT OSP: 571-272-7774

Form PCT/ISA/210 (second sheet) (January 2015)

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 15/66865

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 4-5, 9-11, 15-17, 23-24 and 28
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:
--Please see attached sheet--

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1-3, 6-8 and 25-27

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

Form PCT/ISA/210 (continuation of first sheet (2)) (January 2015)

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 15/56865

Attachment to Box.No.III:

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1.

Group I: Claims 1-3, 6-8 and 25-27, directed to a coating solution comprising an organic solvent and an organometallic compound represented by the formula $\text{RSnO}(3/2-x/2)(\text{OH})_x$ where $(0 < x < 3)$, where R is an alkyl group or cycloalkyl group with 3-31 carbon atoms, where the alkyl or cycloalkyl group is bonded to the tin at a secondary or tertiary carbon atom.

Group II: Claims 12-14 and 18-22, directed to a method for patterning a film on a substrate, comprising exposing the film to EUV radiation at the specified doses and a patterned structure comprising a surface and a coating associated with the surface wherein at least portions of the coating are represented by the formulation $(\text{R})_z\text{SnO}_2-z/2-x/2(\text{OH})_x$ $(0 < (x+z) < 4)$, where R is an alkyl group or cycloalkyl group with 3-31 carbon atoms, where the alkyl or cycloalkyl group is bonded to the tin at a secondary or tertiary carbon atom.

Group III: Claims 29-33, directed to a method for synthesizing a compound represented by the formula RSnOOH or $\text{RSnO}(3/2-x/2)(\text{OH})_x$ $(0 < x < 3)$, where R is an alkyl or cycloalkyl moiety having from 1 to 31 carbon atoms,

The groups of inventions listed above do not relate to a single general inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons:

Special Technical Features:

Group I includes the technical feature of a coating solution comprising a solvent and an organometallic compound, not required by Groups II and III.

Group II includes the technical feature of a method of patterning an organometallic film on a substrate and a patterned structure containing an organometallic formulation, not required by Groups I and III.

Group III includes the technical feature of a method of synthesizing an organometallic compound, not required by Groups I and II.

Common technical features:

Groups I-III share the technical feature of an organotin compound.

Groups I and II further share the technical feature of a coating formulation containing an organotin compound.

Groups I and III further share the technical feature of a compound of the formula, $\text{RSnO}(3/2-x/2)(\text{OH})_x$ $(0 < x < 3)$, where R is an alkyl or cycloalkyl moiety having from 1 to 31 carbon atoms.

These shared technical features, however, do not provide a contribution over the prior art, as being anticipated by WO 2014/150411 A1 to Ding et al. published on 25 September 2014 (hereinafter Ding).

Regarding claim 1, Ding discloses a coating solution (para [0007]: "the curable compositions described herein are particularly suited for use in the preparation of paints and coatings for a variety of substrates") comprising an organic solvent (para [0044]: "the curable coating compositions according to the invention may optionally contain a diluent, such as conventional inert organic solvents") and an organometallic compound represented by the formula $\text{RSnO}(3/2-x/2)(\text{OH})_x$ where $(0 < x < 3)$ where R is an alkyl group bonded to the tin at a tertiary carbon atom (para [0056]: tertiary-butyl stannic acid).

As said composition was known in the art at the time of the invention, these cannot be considered special technical features, that would otherwise unify the inventions of Groups I-III.

The inventions of Groups I-III, therefore, lack unity under PCT Rule 13.

Note reg item 4: Claims 4-5, 9-11, 15-17, 23-24 and 28 are unsearchable because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a). These claims are, therefore, not included in the above analysis.

Electronic Patent Application Fee Transmittal

Application Number:	15784258			
Filing Date:	16-Oct-2017			
Title of Invention:	RADIATION BASED PATTERNING METHODS			
First Named Inventor/Applicant Name:	Jason K. Stowers			
Filer:	Diane Elizabeth Bennett/Michelle Douglas			
Attorney Docket Number:	5063.02US05			
Filed as Large Entity				
Filing Fees for Utility under 35 USC 111(a)				
Description	Fee Code	Quantity	Amount	Sub-Total in USD(\$)
Basic Filing:				
Pages:				
Claims:				
Miscellaneous-Filing:				
Petition:				
Patent-Appeals-and-Interference:				
Post-Allowance-and-Post-Issuance:				
Extension-of-Time:				

Description	Fee Code	Quantity	Amount	Sub-Total in USD(\$)
Miscellaneous:				
RCE- 1ST REQUEST	1801	1	1300	1300
Total in USD (\$)				1300

Electronic Acknowledgement Receipt

EFS ID:	39408885
Application Number:	15784258
International Application Number:	
Confirmation Number:	9576
Title of Invention:	RADIATION BASED PATTERNING METHODS
First Named Inventor/Applicant Name:	Jason K. Stowers
Customer Number:	62274
Filer:	Diane Elizabeth Bennett
Filer Authorized By:	
Attorney Docket Number:	5063.02US05
Receipt Date:	11-MAY-2020
Filing Date:	16-OCT-2017
Time Stamp:	22:23:26
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	yes
Payment Type	CARD
Payment was successfully received in RAM	\$ 1300
RAM confirmation Number	E20205AM23481493
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Authorized User	

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File Listing:					
Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Request for Continued Examination (RCE)	RCETransmittal-1st.pdf	29815	no	2
			a0f168599d1d5da0fb4a04027d1c47f312c5d14b		
Warnings:					
This is not a USPTO supplied RCE SB30 form.					
Information:					
2	Information Disclosure Statement (IDS) Form (SB08)	IDS_Form_SB_08a-signed.pdf	1036143	no	6
			19049617521fd3c8df651f14ca31d010cc853b40		
Warnings:					
Information:					
3	Foreign Reference	CN1457504A_EAO.pdf	12841757	no	85
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Warnings:					
Information:					
4	Foreign Reference	EP1992665A1.pdf	6407989	no	37
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Warnings:					
Information:					
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Warnings:					
Information:					
Total Files Size (in bytes):			77026209		

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New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

PATENT APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the application of:

Attorney Docket No.: 5063.02US05

Stowers et al.

Confirmation No.: 9576

Application No.: 15/784,258

Examiner: Chanceity N. Robinson

Filed: October 16, 2017

Group Art Unit: 1722

For: RADIATION BASED PATTERNING METHODS

AMENDMENT

Mail Stop Amendment
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

INTRODUCTORY COMMENTS

In response to the Office Action of February 4, 2020, please enter the following amendments and consider the following remarks. This Amendment includes the following sections:

- A. Amendments to the Claims
- B. Remarks

Please grant any extension of time necessary for entry; charge any fee due to Deposit Account No. 60-1363.

CERTIFICATE OF ELECTRONIC TRANSMISSION

I hereby certify that this paper is being transmitted electronically to the U.S. Patent and Trademark Office on the date shown below.

May 11, 2020
Date

/Diane Bennett/
Diane E. Bennett, Ph.D., Reg. #63,240

AMENDMENTS TO THE CLAIMS

A detailed listing of all claims that are, or were, in the present application, irrespective of whether the claim(s) remains under examination in the application are presented below. The claims are presented in ascending order and each includes one status identifier. Those claims not cancelled or withdrawn but amended by the current amendment utilize the following notations for amendment: 1. deleted matter is shown by strikethrough for six or more characters and double brackets for five or less characters; and 2. added matter is shown by underlining.

1. (Currently Amended) A method for forming a patterned structure comprising a substrate and a patterned coating material on a surface of the substrate, the method comprising:

irradiating along a selected pattern, a layer of coating material on the surface of the substrate having an average thickness from ~~about~~ 5 nm to ~~about~~ 30 nm with ~~UV radiation~~ ~~or~~ EUV radiation at a dose of no more than about 100 mJ/cm²; and

contacting the irradiated layer with a developing composition to dissolve un-irradiated material to form a patterned coating material according to the selected pattern.

2. (Original) The method of claim 1 wherein the irradiation is performed with EUV at a dose of no more than about 90 mJ/cm².

3. (Previously Presented) The method of claim 1 wherein the selected pattern has a pitch of no more than about 60 nm.

4. (Original) The method of claim 1 wherein the developing composition comprises tetramethyl ammonium hydroxide.

5. (Original) The method of claim 1 wherein following exposure an exposed coating region is insoluble in an aqueous base.

6. (Original) The method of claim 1 wherein following exposure an exposed coating region is soluble in an organic solvent.

7. (Original) The method of claim 1 further comprising heating the coated substrate after irradiation to a temperature of at least about 45°C prior to contacting the irradiated layer with the developing composition.
8. (Original) The method of claim 1 further comprising heating the substrate with the patterned coating material to a temperature from about 150°C to about 600°C for from one minute to 25 minutes to form a post-patterning condensed structure.
9. (Original) The method of claim 8 further comprising performing a second patterning using the post-patterning condensed structure to form a double patterned structure.
10. (Currently Amended) The method of claim 1 wherein the coating material prior to irradiation comprises metal ions with radiation sensitive ligands and wherein interaction of the coating material with EUV ~~and/or e-beam radiation~~ alters the chemical properties of the coating material creating a structure with differential dissolution rates.
11. (Original) The method of claim 10 wherein the metal of the metal ions comprises Cu, Al, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, Y, Zr, Nb, Mo, In, Sn, Sb, Hf, Ta, W, Ir, Pt, La, Ce, Pr, Nb, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu or a combination thereof.
12. (Original) The method of claim 10 wherein the radiation sensitive ligands comprise peroxide ligands, and wherein the coating material further comprises metal suboxide cations.
13. (Currently Amended) The method of claim 12 wherein the coating material further comprises inorganic polyatomic anions and wherein the peroxide ligand to metal ion ratio is at least about 2.
14. (Currently Amended) A method for forming a patterned inorganic material on a substrate, the method comprising:

irradiating a coated substrate with a pattern of radiation wherein the coated substrate comprises a coating with a radiation patternable coating material comprising metal suboxide cations, ligands comprising a peroxide group and inorganic polyatomic anions and wherein irradiation creates a differential dissolution rate between irradiated and un-irradiated locations, wherein the coating material is formed by removing solvent from a deposited precursor solution wherein the peroxide ligand to metal suboxide cation[[ion]] ratio is at least about 2; and

heating the coated substrate after irradiation to a temperature of at least about 45°C prior to contacting the coating with a developing composition.

15. (Original) The method of claim 14 further comprising contacting the coated substrate after heating with a developing composition to remove un-irradiated coating material to form the patterned inorganic material.

16. (Original) The method of claim 15 wherein the patterned inorganic material has edges with an average line-width roughness no more than about 2.25 nm at a pitch of no more than about 60 nm or for individual features having an average width of no more than about 30 nm.

17. (Original) The method of claim 14 wherein the metal suboxide cations comprise Cu, Al, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, Y, Zr, Nb, Mo, In, Sn, Sb, Hf, Ta, W, Ir, Pt, La, Ce, Pr, Nb, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu or a combination thereof.

18. (Original) The method of claim 14 wherein the irradiating step comprises irradiation with extreme ultraviolet light at a dose of no more than about 100 mJ/cm² or with an electron beam at a dose equivalent to no more than about 300 μ C/cm² at 30 kV.

19. (Original) The method of claim 14 wherein the coating has an average thickness of about 5 nm to about 30 nm.

REMARKS

Claims 1-19 are pending. By this Amendment, claims 1, 10, 13, and 14 are amended. Specifically, claim 1 is amended to remove reference to UV radiation and the term "about" from the recited average layer thickness range. Claim 10 is amended to remove the references to electron beam radiation. Claim 13 is amended to correct a typographical error by adding the word "comprises" after the word "further". Claim 14 is amended to clarify that the "metal ion" recited is the "metal suboxide cation" as recommended by the Examiner. No new matter is introduced.

Allowable Subject Matter

The Examiner stated that claims 12 and 13 would be allowable if rewritten in independent form including all of the limitations of the base claim and any intervening claims.

Claim Objections

Claim 14

The Examiner objected to claim 14 over an asserted informality in the recitation of the term "metal ion" in independent claim 14. In order to advance prosecution, Applicant amends the claim to recite "metal suboxide cation" as suggested by the Examiner. However, the Applicant does not believe the amendment is necessary. Applicant respectfully requests withdrawal of the objection to claim 14.

Claims 15 and 16

The Examiner objected to claims 15 and 16 over an asserted informality in the recitation of the term "the patterned inorganic material". Claims 15 and 16 depend from claim 14. Applicant notes that the preamble of claim 14 recites "A method for forming a patterned inorganic material on a substrate." Claim 15 recites an additional step to the method of claim 14. Thus, the additional step of claim 15 is also directed to a method for **forming a patterned inorganic material** on a substrate. The recitation of "to form the patterned inorganic material" in line 3 of claim 15 is consistent with the method of both claims 14 and 15. In order to read claim 15 as a whole, one must read claim 14. Appellant asserts that there are no informalities in claim 15 when read as a whole. Rather, it is clear that claim 15 is reciting the forming of a patterned inorganic material.

Respectfully, Applicant believes that the Examiner's suggestion to amend the claim to "the patterned coating material" is not appropriate since the claimed invention is directed to a method for forming a patterned inorganic material on a substrate. In addition, there is no antecedent basis for the suggested "the patterned coating material" in either claim 14 or claim 15. Applicant respectfully requests withdrawal of the objections to claims 15 and 16.

Claims 17-19

The Examiner objected to claims 17-19 as being dependent on claims 14 and 15, which were objected to for informalities. For clarity of the record, Applicant notes that claims 17-19 do not depend on claim 15. Claim 14 has been amended, making the objections to claims 17-19 presently moot. Applicant respectfully requests withdrawal of the objections to claims 17-19.

Rejection Under 35 U.S.C. 103(a) Over Guerrero

The Examiner rejected claims 1-6, 8, 10, and 11 under pre-AIA 35 U.S.C. 103(a) as being unpatentable over Guerrero et al. (U.S. 8,257,910, hereinafter "Guerrero"). Claims 2-6, 8, 10, and 11 depend from claim 1. The Examiner acknowledges that Guerrero does not explicitly recite a layer of coating material having an average thickness from about 5 nm to about 30 nm as instantly recited. In as such, Applicant respectfully maintains that the cited reference does not teach all of the features of Applicant's claimed invention. The Examiner asserts that the term "about" is not defined by the claim or the specification. Applicant notes that claims are construed from the perspective of a person of ordinary skill in the art. Applicant strenuously and unwaveringly disagrees with the Examiner's position regarding claim construction. Nevertheless, to advance prosecution, Applicant has amended claim 1 to remove the "about" from the recitation of the average thickness range. The claim as amended recites a layer of coating material having an average thickness from 5 nm to 30 nm. Respectfully, the Examiner's rejections of claim 1 are no longer on point.

Since the cited reference does not teach all of the features of amended claim 1, the cited reference does not render Applicant's claimed invention *prima facie* obvious. Applicant respectfully requests withdrawal of the rejection of claims 1-6, 8, 10, and 11 under 35 U.S.C. 103(a) as being unpatentable over Guerrero. While Applicant does not acquiesce with respect to specific assertions in the rejection directed to the features of the dependent claims, Applicant does

not comment further on these in view of the comments and amendments above relating to independent claim 1 that are dispositive.

Rejection Under 35. U.S.C. 103(a) Over Guerrero and Ando

The Examiner rejected claim 9 under pre-AIA 35 U.S.C. 103(a) as being unpatentable over Guerrero et al. (U.S. 8,257,910, hereinafter "Guerrero") as applied to claims 1-6, 8, 10, and 11 above, and further in view of Ando (U.S. 2010/0167271 A1). Claim 9 depends from claim 1, which has been amended. The deficiencies of Guerrero were described above. Ando was cited for teaching a double patterning process. Ando does not make up for the deficiencies of Guerrero. Thus, the combined teachings of Guerrero and Ando do not render Applicant's claimed invention *prima facie* obvious.

While Applicant does not acquiesce with respect to the specific assertions in the rejection directed to the features of dependent claim 9, Applicant does not comment further on these issues here since the arguments directed to claim 1 are dispositive. Applicant respectfully requests withdrawal of the rejection of claim 9 under 35 U.S.C. 103(a) as being unpatentable over Guerrero in view of Ando.

Rejection Under 35. U.S.C. 103(a) Over Guerrero and Cheng

The Examiner rejected claims 1-6 and 8-11 under pre-AIA 35 U.S.C. 103(a) as being unpatentable over Guerrero et al. (U.S. 8,257,910, hereinafter "Guerrero") in view of Cheng et al. (U.S. 2009/0214823 A1, hereinafter "Cheng-1"). Claims 2-6 and 8-11 depend from claim 1.

Claims 2-6 and 8-11 depend from claim 1. The deficiencies of the teachings of Guerrero et al. with respect to claim 1 are presented in detail above. Cheng et al. does not make up for the deficiencies of Guerrero et al. with respect to the presently claimed method. In particular, instant claim 1 is directed to a method which involves irradiating a layer of coating with EUV radiation. Cheng-1 is not directed to patterning a layer of coating material with EUV radiation. Rather, Cheng-1 is directed to a method that uses two or more immiscible polymers with different affinities for the sidewall of a substructure to enable pattern formation through polymer segregation. See, for example, the Abstract, Fig. 3, and the examples of Cheng-1. One of ordinary skill in the art would not look to Cheng-1 to modify the average thickness of the coating of Guerrero.

Thus, the combined teachings of Guerrero and Cheng-1 do not render Applicant's claimed invention *prima facie* obvious. While Applicant does not acquiesce with respect to the specific assertions in the rejection directed to the features of the dependent claims, Applicant does not comment further on these issues here since the arguments directed to claim 1 are dispositive. Applicant respectfully requests withdrawal of the rejection of claims 1-6 and 8-11 under 35 U.S.C. 103(a) as being unpatentable over Guerrero in view of Cheng-1.

Rejection Under 35. U.S.C. 103(a) Over Guerrero and Cheng

The Examiner rejected claim 7 under pre-AIA 35 U.S.C. 103(a) as being unpatentable over Guerrero et al. (U.S. 8,257,910, hereinafter "Guerrero") as applied to claims 1-6, 8, 10, and 11 above, and further in view of Cheng et al. (U.S. 8,828,493 B2, hereinafter "Cheng-2"). Claim 7 depends from claim 1, which has been amended. Cheng-2 was cited for teaching a pre-irradiation heating step. Cheng-2 does not make up for the deficiencies of Guerrero with respect to Applicant's claimed invention. The combined teachings of Guerrero and Cheng-2 do not render Applicant's claimed invention *prima facie* obvious.

While Applicant does not acquiesce with respect to the specific assertions in the rejection directed to the features of dependent claim 7, Applicant does not comment further on these issues here since the above arguments directed to claim 1 are dispositive. Applicant respectfully requests withdrawal of the rejection of claim 7 under 35 U.S.C. 103(a) as being unpatentable over Guerrero as applied to claims 1-6, 8, 10, and 11 above and further in view of Cheng-2.

Rejection Under 35. U.S.C. 103(a) Over Guerrero, Cheng, and Cheng, Joy

The Examiner rejected claim 7 under pre-AIA 35 U.S.C. 103(a) as being unpatentable over Guerrero et al. (U.S. 8,257,910, hereinafter "Guerrero") in view of Cheng-1 as applied to claims 1-6 and 8-11 above, and further in view of Cheng-2. Claim 7 depends from claim 1, which has been amended. It is respectfully not clear why the Examiner provided separate rejections of claim 7 over Guerrero and Cheng-2 and over Guerrero, Cheng-1 and Cheng-2 since Cheng-1 is not mentioned in the second rejection. In any case, the arguments above with respect to the combination of Guerrero and Cheng-2 apply equally here with respect to Guerrero, Cheng-1 and Cheng-2.

While Applicant does not acquiesce with respect to the specific assertions in the rejection

directed to the features of dependent claim 7, Applicant does not comment further on these issues here since the above arguments directed to claim 1 are dispositive. Applicant respectfully requests withdrawal of the rejection of claim 7 under 35 U.S.C. 103(a) over Guerrero in view of Cheng-1 as applied to claims 1-6 and 8-11 above and further in view of Cheng-2.

Rejection Under 35. U.S.C. 103(a) Over Guerrero and Fedynyshyn

The Examiner rejected claims 1-8 and 10-11 under pre-AIA 35 U.S.C. 103(a) as being unpatentable over Guerrero et al. (U.S. 8,257,910, hereinafter "Guerrero") in view of Fedynyshyn et al. (U.S. 8,158,338 B2, herein after "Fedynyshyn").

Claims 2-8 and 10-11 depend from claim 1, which has been amended. The deficiencies of the teachings of Guerrero with respect to claim 1 are presented in detail above. Fedynyshyn does not make up for the deficiencies of Guerrero et al. with respect to the presently claimed method. While Fedynyshyn mentions EUV, the focus of this reference is on UV at longer wavelengths. No EUV doses are cited. Thus, Fedynyshyn does not make up for the deficiencies of Guerrero.

Guerrero does not teach or suggest the claimed range of layer thickness. Fedynyshyn does not remedy the deficiencies of Guerrero. Thus, the combined teachings of Guerrero and Fedynyshyn do not render Applicant's claimed invention *prima facie* obvious. While Applicant does not acquiesce with respect to the specific assertions in the rejection directed to the features of the dependent claims, Applicant does not comment further on these issues here since the arguments directed to claim 1 are dispositive. Applicant respectfully requests withdrawal of the rejection of claims 1-8 and 10-11 under 35 U.S.C. 103(a) as being unpatentable over Guerrero in view of Fedynyshyn.

CONCLUSION

In view of the foregoing, it is submitted that this application is in condition for allowance. Favorable consideration and prompt allowance of the application are respectfully requested.

The Examiner is invited to telephone the undersigned if the Examiner believes it would be useful to advance prosecution.

Respectfully submitted,

/Diane Bennett/

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INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)	Application Number	15784258
	Filing Date	2017-10-16
	First Named Inventor	Jason K. Stowers
	Art Unit	1722
	Examiner Name	Chanceity N. Robinson
	Attorney Docket Number	5063.02US05

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	2	6387012		2002-05-14	Mitamura	
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(Not for submission under 37 CFR 1.99)

Application Number	15784258
Filing Date	2017-10-16
First Named Inventor	Jason K. Stowers
Art Unit	1722
Examiner Name	Chanceity N. Robinson
Attorney Docket Number	5063.02US05

3	20110244403		2011-10-06	Carcasi et al.
4	20120202349	A1	2012-08-09	Sun
5	20130253161		2013-09-26	Amako et al.
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	1	CHANDRASEKHAR ET AL., "Organotin Assemblies Containing SN-O Bonds," Coordination Chemistry Reviews 235:1-52 (2002).	
	2	EYCHENNE-BARON ET AL., "New Synthesis Of The Nanobuilding Block {(BuSn)12O14(OH)6 }2+ And Exchange Properties Of {(BuSn)12O14(OH)6}(O3SC6H4CH3)2," Journal Of Organometallic Chemistry, 567:137-142 (1998).	

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	Art Unit	1722	
	Examiner Name	Chanceity N. Robinson	
	Attorney Docket Number	5063.02US05	

3	EYCHENNE-BARON ET AL., "Reaction Of Butyltin Hydroxide Oxide With p-Toluenesulfonic Acid: Synthesis, X-ray Crystal Analysis, And Multinuclear NMR Characterization Of {(BuSn)12O14(OH)6}{4-CH3C6H4SO3}2," Organometallics, 19:1940-1949 (2000).
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	Filing Date		2017-10-16
	First Named Inventor	Jason K. Stowers	
	Art Unit	1722	
	Examiner Name	Chanceity N. Robinson	
	Attorney Docket Number	5063.02US05	

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Please see 37 CFR 1.97 and 1.98 to make the appropriate selection(s):

That each item of information contained in the information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(1).

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See attached certification statement.

The fee set forth in 37 CFR 1.17 (p) has been submitted herewith.

☒ A certification statement is not submitted herewith.

SIGNATURE

A signature of the applicant or representative is required in accordance with CFR 1.33, 10.18. Please see CFR 1.4(d) for the form of the signature.

Signature	/Diane Bennett/	Date (YYYY-MM-DD)	2020-05-28
Name/Print	Diane E. Bennett, Ph.D.	Registration Number	63,240

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EFS ID:	39559966
Application Number:	15784258
International Application Number:	
Confirmation Number:	9576
Title of Invention:	RADIATION BASED PATTERNING METHODS
First Named Inventor/Applicant Name:	Jason K. Stowers
Customer Number:	62274
Filer:	Diane Elizabeth Bennett
Filer Authorized By:	
Attorney Docket Number:	5063.02US05
Receipt Date:	28-MAY-2020
Filing Date:	16-OCT-2017
Time Stamp:	12:14:17
Application Type:	Utility under 35 USC 111(a)

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1722

DATE MAILED: 06/04/2020

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
15/784,258	10/16/2017	Jason K. Stowers	5063.02US05	9576

TITLE OF INVENTION: RADIATION BASED PATTERNING METHODS

APPLN. TYPE	ENTITY STATUS	ISSUE FEE DUE	PUBLICATION FEE DUE	PREV. PAID ISSUE FEE	TOTAL FEE(S) DUE	DATE DUE
nonprovisional	UNDISCOUNTED	\$1000	\$0.00	\$0.00	\$1000	09/04/2020

THE APPLICATION IDENTIFIED ABOVE HAS BEEN EXAMINED AND IS ALLOWED FOR ISSUANCE AS A PATENT. PROSECUTION ON THE MERITS IS CLOSED. THIS NOTICE OF ALLOWANCE IS NOT A GRANT OF PATENT RIGHTS. THIS APPLICATION IS SUBJECT TO WITHDRAWAL FROM ISSUE AT THE INITIATIVE OF THE OFFICE OR UPON PETITION BY THE APPLICANT. SEE 37 CFR 1.313 AND MPEP 1308.

THE ISSUE FEE AND PUBLICATION FEE (IF REQUIRED) MUST BE PAID WITHIN THREE MONTHS FROM THE MAILING DATE OF THIS NOTICE OR THIS APPLICATION SHALL BE REGARDED AS ABANDONED. THIS STATUTORY PERIOD CANNOT BE EXTENDED. SEE 35 U.S.C. 151. THE ISSUE FEE DUE INDICATED ABOVE DOES NOT REFLECT A CREDIT FOR ANY PREVIOUSLY PAID ISSUE FEE IN THIS APPLICATION. IF AN ISSUE FEE HAS PREVIOUSLY BEEN PAID IN THIS APPLICATION (AS SHOWN ABOVE), THE RETURN OF PART B OF THIS FORM WILL BE CONSIDERED A REQUEST TO REAPPLY THE PREVIOUSLY PAID ISSUE FEE TOWARD THE ISSUE FEE NOW DUE.

HOW TO REPLY TO THIS NOTICE:

I. Review the ENTITY STATUS shown above. If the ENTITY STATUS is shown as SMALL or MICRO, verify whether entitlement to that entity status still applies.

If the ENTITY STATUS is the same as shown above, pay the TOTAL FEE(S) DUE shown above.

If the ENTITY STATUS is changed from that shown above, on PART B - FEE(S) TRANSMITTAL, complete section number 5 titled "Change in Entity Status (from status indicated above)".

For purposes of this notice, small entity fees are 1/2 the amount of undiscounted fees, and micro entity fees are 1/2 the amount of small entity fees.

II. PART B - FEE(S) TRANSMITTAL, or its equivalent, must be completed and returned to the United States Patent and Trademark Office (USPTO) with your ISSUE FEE and PUBLICATION FEE (if required). If you are charging the fee(s) to your deposit account, section "4b" of Part B - Fee(s) Transmittal should be completed and an extra copy of the form should be submitted. If an equivalent of Part B is filed, a request to reapply a previously paid issue fee must be clearly made, and delays in processing may occur due to the difficulty in recognizing the paper as an equivalent of Part B.

III. All communications regarding this application must give the application number. Please direct all communications prior to issuance to Mail Stop ISSUE FEE unless advised to the contrary.

IMPORTANT REMINDER: Maintenance fees are due in utility patents issuing on applications filed on or after Dec. 12, 1980. It is patentee's responsibility to ensure timely payment of maintenance fees when due. More information is available at www.uspto.gov/PatentMaintenanceFees.

PART B - FEE(S) TRANSMITTAL

Complete and send this form, together with applicable fee(s), by mail or fax, or via EFS-Web.

By mail, send to: Mail Stop ISSUE FEE
Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450

By fax, send to: (571)-273-2885

INSTRUCTIONS: This form should be used for transmitting the ISSUE FEE and PUBLICATION FEE (if required). Blocks 1 through 5 should be completed where appropriate. All further correspondence including the Patent, advance orders and notification of maintenance fees will be mailed to the current correspondence address as indicated unless corrected below or directed otherwise in Block 1, by (a) specifying a new correspondence address; and/or (b) indicating a separate "FEE ADDRESS" for maintenance fee notifications.

CURRENT CORRESPONDENCE ADDRESS (Note: Use Block 1 for any change of address)

Note: A certificate of mailing can only be used for domestic mailings of the Fee(s) Transmittal. This certificate cannot be used for any other accompanying papers. Each additional paper, such as an assignment or formal drawing, must have its own certificate of mailing or transmission.

62274 7590 06/04/2020
CHRISTENSEN, FONDER, DARDI & HERBERT PLLC
33 South Sixth Street
Suite 4540
Minneapolis, MN 55402

Certificate of Mailing or Transmission

I hereby certify that this Fee(s) Transmittal is being deposited with the United States Postal Service with sufficient postage for first class mail in an envelope addressed to the Mail Stop ISSUE FEE address above, or being transmitted to the USPTO via EFS-Web or by facsimile to (571) 273-2885, on the date below.

(Typed or printed name)
(Signature)
(Date)

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
15/784,258	10/16/2017	Jason K. Stowers	5063.02US05	9576

TITLE OF INVENTION: RADIATION BASED PATTERNING METHODS

APPLN. TYPE	ENTITY STATUS	ISSUE FEE DUE	PUBLICATION FEE DUE	PREV. PAID ISSUE FEE	TOTAL FEE(S) DUE	DATE DUE
nonprovisional	UNDISCOUNTED	\$1000	\$0.00	\$0.00	\$1000	09/04/2020

EXAMINER	ART UNIT	CLASS-SUBCLASS
ROBINSON, CHANCEITY N	1722	430-270100

1. Change of correspondence address or indication of "Fee Address" (37 CFR 1.363).

☐ Change of correspondence address (or Change of Correspondence Address form PTO/SB/122) attached.

☐ "Fee Address" indication (or "Fee Address" Indication form PTO/SB/47; Rev 03-09 or more recent) attached. **Use of a Customer Number is required.**

2. For printing on the patent front page, list

(1) The names of up to 3 registered patent attorneys or agents OR, alternatively,

1 _____

(2) The name of a single firm (having as a member a registered attorney or agent) and the names of up to 2 registered patent attorneys or agents. If no name is listed, no name will be printed.

2 _____

3 _____

3. ASSIGNEE NAME AND RESIDENCE DATA TO BE PRINTED ON THE PATENT (print or type)

PLEASE NOTE: Unless an assignee is identified below, no assignee data will appear on the patent. If an assignee is identified below, the document must have been previously recorded, or filed for recordation, as set forth in 37 CFR 3.11 and 37 CFR 3.81(a). Completion of this form is NOT a substitute for filing an assignment.

(A) NAME OF ASSIGNEE

(B) RESIDENCE: (CITY and STATE OR COUNTRY)

Please check the appropriate assignee category or categories (will not be printed on the patent) : ☐ Individual ☐ Corporation or other private group entity ☐ Government

4a. Fees submitted: ☐ Issue Fee ☐ Publication Fee (if required) ☐ Advance Order - # of Copies _____

4b. Method of Payment: (Please first reapply any previously paid fee shown above)

☐ Electronic Payment via EFS-Web ☐ Enclosed check ☐ Non-electronic payment by credit card (Attach form PTO-2038)

☐ The Director is hereby authorized to charge the required fee(s), any deficiency, or credit any overpayment to Deposit Account No. _____

5. Change in Entity Status (from status indicated above)

☐ Applicant certifying micro entity status. See 37 CFR 1.29

☐ Applicant asserting small entity status. See 37 CFR 1.27

☐ Applicant changing to regular undiscounted fee status.

NOTE: Absent a valid certification of Micro Entity Status (see forms PTO/SB/15A and 15B), issue fee payment in the micro entity amount will not be accepted at the risk of application abandonment.

NOTE: If the application was previously under micro entity status, checking this box will be taken to be a notification of loss of entitlement to micro entity status.

NOTE: Checking this box will be taken to be a notification of loss of entitlement to small or micro entity status, as applicable.

NOTE: This form must be signed in accordance with 37 CFR 1.31 and 1.33. See 37 CFR 1.4 for signature requirements and certifications.

Authorized Signature _____

Date _____

Typed or printed name _____

Registration No. _____



UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
15/784,258	10/16/2017	Jason K. Stowers	5063.02US05	9576
62274	7590	06/04/2020	EXAMINER	
CHRISTENSEN, FONDER, DARDI & HERBERT PLLC			ROBINSON, CHANCEITY N	
33 South Sixth Street			ART UNIT	
Suite 4540			PAPER NUMBER	
Minneapolis, MN 55402			1722	

DATE MAILED: 06/04/2020

Determination of Patent Term Adjustment under 35 U.S.C. 154 (b) (Applications filed on or after May 29, 2000)

The Office has discontinued providing a Patent Term Adjustment (PTA) calculation with the Notice of Allowance.

Section 1(h)(2) of the AIA Technical Corrections Act amended 35 U.S.C. 154(b)(3)(B)(i) to eliminate the requirement that the Office provide a patent term adjustment determination with the notice of allowance. See Revisions to Patent Term Adjustment, 78 Fed. Reg. 19416, 19417 (Apr. 1, 2013). Therefore, the Office is no longer providing an initial patent term adjustment determination with the notice of allowance. The Office will continue to provide a patent term adjustment determination with the Issue Notification Letter that is mailed to applicant approximately three weeks prior to the issue date of the patent, and will include the patent term adjustment on the patent. Any request for reconsideration of the patent term adjustment determination (or reinstatement of patent term adjustment) should follow the process outlined in 37 CFR 1.705.

Any questions regarding the Patent Term Extension or Adjustment determination should be directed to the Office of Patent Legal Administration at (571)-272-7702. Questions relating to issue and publication fee payments should be directed to the Customer Service Center of the Office of Patent Publication at 1-(888)-786-0101 or (571)-272-4200.

OMB Clearance and PRA Burden Statement for PTOL-85 Part B

The Paperwork Reduction Act (PRA) of 1995 requires Federal agencies to obtain Office of Management and Budget approval before requesting most types of information from the public. When OMB approves an agency request to collect information from the public, OMB (i) provides a valid OMB Control Number and expiration date for the agency to display on the instrument that will be used to collect the information and (ii) requires the agency to inform the public about the OMB Control Number's legal significance in accordance with 5 CFR 1320.5(b).

The information collected by PTOL-85 Part B is required by 37 CFR 1.311. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 30 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, Virginia 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, Virginia 22313-1450. Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

Privacy Act Statement

The Privacy Act of 1974 (P.L. 93-579) requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C. 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether disclosure of these records is required by the Freedom of Information Act.
2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.
3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.
4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).
5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.
6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).
7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.
8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspection or an issued patent.
9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency if the USPTO becomes aware of a violation or potential violation of law or regulation.

Notice of Allowability	Application No. 15/784,258	Applicant(s) Stowers et al.	
	Examiner CHANCEITY N ROBINSON	Art Unit 1722	AIA (FITF) Status No

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address--

All claims being allowable, PROSECUTION ON THE MERITS IS (OR REMAINS) CLOSED in this application. If not included herewith (or previously mailed), a Notice of Allowance (PTOL-85) or other appropriate communication will be mailed in due course. **THIS NOTICE OF ALLOWABILITY IS NOT A GRANT OF PATENT RIGHTS.** This application is subject to withdrawal from issue at the initiative of the Office or upon petition by the applicant. See 37 CFR 1.313 and MPEP 1308.

1. ☒ This communication is responsive to 05/11/2020.
☐ A declaration(s)/affidavit(s) under **37 CFR 1.130(b)** was/were filed on _____.

2. ☐ An election was made by the applicant in response to a restriction requirement set forth during the interview on _____; the restriction requirement and election have been incorporated into this action.

3. ☒ The allowed claim(s) is/are 1-19. As a result of the allowed claim(s), you may be eligible to benefit from the **Patent Prosecution Highway** program at a participating intellectual property office for the corresponding application. For more information, please see http://www.uspto.gov/patents/init_events/pph/index.jsp or send an inquiry to PPHfeedback@uspto.gov.

4. ☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).

Certified copies:

a) ☐ All b) ☐ Some *c) ☐ None of the:

1. ☐ Certified copies of the priority documents have been received.

2. ☐ Certified copies of the priority documents have been received in Application No. _____.

3. ☐ Copies of the certified copies of the priority documents have been received in this national stage application from the International Bureau (PCT Rule 17.2(a)).

* Certified copies not received: _____.

Applicant has THREE MONTHS FROM THE "MAILING DATE" of this communication to file a reply complying with the requirements noted below. Failure to timely comply will result in ABANDONMENT of this application.
THIS THREE-MONTH PERIOD IS NOT EXTENDABLE.

5. ☐ CORRECTED DRAWINGS (as "replacement sheets") must be submitted.
☐ including changes required by the attached Examiner's Amendment / Comment or in the Office action of Paper No./Mail Date _____.

Identifying indicia such as the application number (see 37 CFR 1.84(c)) should be written on the drawings in the front (not the back) of each sheet. Replacement sheet(s) should be labeled as such in the header according to 37 CFR 1.121(d).

6. ☐ DEPOSIT OF and/or INFORMATION about the deposit of BIOLOGICAL MATERIAL must be submitted. Note the attached Examiner's comment regarding REQUIREMENT FOR THE DEPOSIT OF BIOLOGICAL MATERIAL.

Attachment(s)

1. ☐ Notice of References Cited (PTO-892)	5. ☐ Examiner's Amendment/Comment
2. ☒ Information Disclosure Statements (PTO/SB/08), Paper No./Mail Date _____.	6. ☒ Examiner's Statement of Reasons for Allowance
3. ☐ Examiner's Comment Regarding Requirement for Deposit of Biological Material _____.	7. ☐ Other _____.
4. ☐ Interview Summary (PTO-413), Paper No./Mail Date. _____.	

/CHANCEITY N ROBINSON/ Primary Examiner, Art Unit 1722	
---	--

DETAILED ACTION

Notice of Pre-AIA or AIA Status

1. The present application is being examined under the pre-AIA first to invent provisions.

Continued Examination Under 37 CFR 1.114

2. A request for continued examination under 37 CFR 1.114 was filed in this application after appeal to the Patent Trial and Appeal Board, but prior to a decision on the appeal. Since this application is eligible for continued examination under 37 CFR 1.114 and the fee set forth in 37 CFR 1.17(e) has been timely paid, the appeal has been withdrawn pursuant to 37 CFR 1.114 and prosecution in this application has been reopened pursuant to 37 CFR 1.114. Applicant's submission filed on 05/11/2020 has been entered.

3. The following is an examiner's statement of reasons for allowance: Claims 1-19 are allowed. No prior art teaches a method for forming a patterned structure comprising a substrate and a patterned coating material on a surface of the substrate, the method comprising : irradiating along a selected pattern, a layer of coating material on the surface of the substrate having an average thickness from 5 nm to 30 nm with EUV radiation at a dose of no more than about 100 mJ/cm² or wherein the coating material is formed by removing solvent from a deposited precursor solution wherein the peroxide ligand to metal suboxide cation ratio is at least about and heating the coated substrate after irradiation to a temperature of at least about 45°C prior to contacting the coating with a developing composition as instantly claimed.

Any comments considered necessary by applicant must be submitted no later than the payment of the issue fee and, to avoid processing delays, should preferably accompany the issue fee. Such submissions should be clearly labeled "Comments on Statement of Reasons for Allowance."

Conclusion

Any inquiry concerning this communication or earlier communications from the examiner should be directed to CHANCEITY N ROBINSON whose telephone number is (571)270-3786. The examiner can normally be reached on Monday-Friday (5:30 am-10:00 pm; IFP; PHP).

Examiner interviews are available via telephone, in-person, and video conferencing using a USPTO supplied web-based collaboration tool. To schedule an interview, applicant is encouraged to use the USPTO Automated Interview Request (AIR) at <http://www.uspto.gov/interviewpractice>.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Cynthia Kelly can be reached on 571-272-1526. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.

Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see <https://ppair-my.uspto.gov/pair/PrivatePair>. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free). If you would like assistance from a USPTO Customer Service Representative or access to the automated information system, call 800-786-9199 (IN USA OR CANADA) or 571-272-1000.

/CHANCEITY N ROBINSON/
Primary Examiner, Art Unit 1722

Search Notes 	Application/Control No. 15/784,258	Applicant(s)/Patent Under Reexamination Stowers et al.
	Examiner CHANCEITY N ROBINSON	Art Unit 1722

CPC - Searched*		
Symbol	Date	Examiner
G03F 7/00	01/05/2019	CR

CPC Combination Sets - Searched*		
Symbol	Date	Examiner

US Classification - Searched*			
Class	Subclass	Date	Examiner

* See search history printout included with this form or the SEARCH NOTES box below to determine the scope of the search.

Search Notes		
Search Notes	Date	Examiner
East and IDS Search	01/05/2019	CR
East Search Updated	01/28/2020	CR

Interference Search			
US Class/CPC Symbol	US Subclass/CPC Group	Date	Examiner
G03F	7/00	05/27/2020	CR

/CHANCEITY N ROBINSON/ Primary Examiner, Art Unit 1722	
---	--

Issue Classification 	Application/Control No. 15/784,258	Applicant(s)/Patent Under Reexamination Stowers et al.
	Examiner CHANCEITY N ROBINSON	Art Unit 1722

CPC						
Symbol					Type	Version
G03F	/	7	/	0043	F	2013-01-01
G03F	/	7	/	0042	I	2013-01-01
G03F	/	7	/	20	I	2013-01-01
G03F	/	7	/	327	I	2013-01-01
Y10T	/	428	/	24355	A	2015-01-15

CPC Combination Sets					
Symbol				Type	Set

NONE (Assistant Examiner) (Date)		Total Claims Allowed: 19	
/CHANCEITY N ROBINSON/ Primary Examiner, Art Unit 1722 (Primary Examiner) (Date)		27 May 2020 O.G. Print Claim(s)	O.G. Print Figure 1

Issue Classification 	Application/Control No. 15/784,258	Applicant(s)/Patent Under Reexamination Stowers et al.
	Examiner CHANCEITY N ROBINSON	Art Unit 1722

INTERNATIONAL CLASSIFICATION			
CLAIMED			
G03F	/	7	/ 00
NON-CLAIMED			
	/		/

US ORIGINAL CLASSIFICATION	
CLASS	SUBCLASS

CROSS REFERENCES(S)						
CLASS	SUBCLASS (ONE SUBCLASS PER BLOCK)					

NONE		Total Claims Allowed:	
(Assistant Examiner)	(Date)	19	
/CHANCEITY N ROBINSON/ Primary Examiner, Art Unit 1722 (Primary Examiner)	27 May 2020 (Date)	O.G. Print Claim(s) 1	O.G. Print Figure 1

Issue Classification 	Application/Control No. 15/784,258	Applicant(s)/Patent Under Reexamination Stowers et al.
	Examiner CHANCEITY N ROBINSON	Art Unit 1722

☒ Claims renumbered in the same order as presented by applicant ☐ CPA ☒ T.D. ☐ R.1.47															
CLAIMS															
Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original

NONE	Total Claims Allowed:	
(Assistant Examiner)	(Date)	19
/CHANCEITY N ROBINSON/ Primary Examiner, Art Unit 1722	27 May 2020	O.G. Print Claim(s)
(Primary Examiner)	(Date)	1

<i>Index of Claims</i> 	Application/Control No. 15/784,258	Applicant(s)/Patent Under Reexamination Stowers et al.
	Examiner CHANCEITY N ROBINSON	Art Unit 1722

✓	Rejected	-	Cancelled	N	Non-Elected	A	Appeal
=	Allowed	÷	Restricted	I	Interference	O	Objected

CLAIMS										
☒ Claims renumbered in the same order as presented by applicant ☐ CPA ☒ T.D. ☐ R.1.47										
CLAIM			DATE							
Final	Original		01/28/2020							
1	1	=								
2	2	=								
3	3	=								
4	4	=								
5	5	=								
6	6	=								
7	7	=								
8	8	=								
9	9	=								
10	10	=								
11	11	=								
12	12	=								
13	13	=								
14	14	=								
15	15	=								
16	16	=								
17	17	=								
18	18	=								
19	19	=								

Doc code: IDS

PTO/SB/08a (03-15)

Doc description: Information Disclosure Statement (IDS) Filed

Approved for use through 07/31/2016. OMB 0651-0031

U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)

Application Number	15784258
Filing Date	2017-10-16
First Named Inventor	Jason K. Stowers
Art Unit	1722
Examiner Name	Chanceity N. Robinson
Attorney Docket Number	5063.02US05

U.S.PATENTS

Remove

Examiner Initial*	Cite No	Patent Number	Kind Code ¹	Issue Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1	4639208	A	1983-01-18	Okunaka et al.	
	2	4601917		1986-07-22	Russo et al.	Corresponds to JPS61-000586
	3	4851481		1989-01-25	Kuriyama et al.	Corresponds to JPS63-241061
	4	6566276		2003-05-20	Maloney et al.	Corresponds to CN1457504
ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /C.N.R/						

If you wish to add additional U.S. Patent citation information please click the Add button.

Add

U.S.PATENT APPLICATION PUBLICATIONS

Remove

Examiner Initial*	Cite No	Publication Number	Kind Code ¹	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1	20110166268	A1	2011-07-07	Deelman et al.	
	2	20160116839	A1	2016-04-28	Meyers et al.	Corresponds to JP2018-502173.
ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /C.N.R/						

If you wish to add additional U.S. Published Application citation information please click the Add button.

Add

FOREIGN PATENT DOCUMENTS

Remove

**INFORMATION DISCLOSURE
STATEMENT BY APPLICANT**
(Not for submission under 37 CFR 1.99)

Application Number		15784258
Filing Date		2017-10-16
First Named Inventor	Jason K. Stowers	
Art Unit		1722
Examiner Name	Chanceity N. Robinson	
Attorney Docket Number		5063.02US05

Examiner Initial*	Cite No	Foreign Document Number ³	Country Code ²	Kind Code ⁴	Publication Date	Name of Patentee or Applicant of cited Document	Pages, Columns, Lines where Relevant Passages or Relevant Figures Appear	T ⁵
	1	1457504	CN	A	2003-11-19	EKC Technology	English Abstract Only	
	2	1992665	EP	A1	2008-11-19	Kaneka Corporation		
	3	S63-241061	JP	A	1988-10-06	Sunstar Engineering Inc.	English Abstract Only	
	4	2003-218118	JP	A	2003-07-31	Samsung Electronics Co., Ltd.	English Abstract Only	
	5	2008-091215	JP	A	2008-04-17	Nitto Kasei Co., Ltd.	English Abstract Only	
	6	2009-533521	JP	A	2009-09-17	LG Chemical Ltd.	English Abstract Only	
	7	2010-094583	JP	A	2010-04-30	Nippon Soda Co.	English Abstract Only	
	8	2016-530565	JP	A	2016-09-29	Inpria Corporation	English Abstract Only	
	9	10-2003-0007904	KR		2003-01-23	EKC Technology, Inc.	English Abstract Only	
	10	10-2011-0132288	KR		2011-12-07	Inpria Corporation	English Abstract Only	

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)

Application Number		15784258
Filing Date		2017-10-16
First Named Inventor	Jason K. Stowers	
Art Unit	1722	
Examiner Name	Chanceity N. Robinson	
Attorney Docket Number	5063.02US05	

11	2009-138474	WO	A1	2009-11-19	Arkema France		
12	2010-000504	WO	A1	2010-01-07	Centrum		
13	2016-065120	WO	A1	2016-04-28	Inpria Corporation		
14	2001-81560	JP	A	2001-03-27	Air Products & Chemicals, Inc.		
15	2018-502173	JP	A	2018-01-25	Inpria Corporation	English Abstract Only	
16	2014-150411	WO	A1	2014-09-25	The Sherwin Williams Company		
ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /C.N.R/							

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NON-PATENT LITERATURE DOCUMENTS

Examiner Initials*	Cite No	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc), date, pages(s), volume-issue number(s), publisher, city and/or country where published.	T ⁵
	1		

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EXAMINER SIGNATURE

Examiner Signature	/CHANCEITY N ROBINSON/	Date Considered	05/27/2020
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*EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through a citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

**INFORMATION DISCLOSURE
STATEMENT BY APPLICANT**
(Not for submission under 37 CFR 1.99)

Application Number		15784258
Filing Date		2017-10-16
First Named Inventor	Jason K. Stowers	
Art Unit		1722
Examiner Name	Chanceity N. Robinson	
Attorney Docket Number		5063.02US05

¹ See Kind Codes of USPTO Patent Documents at www.USPTO.GOV or MPEP 901.04. ² Enter office that issued the document, by the two-letter code (WIPO Standard ST.3). ³ For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. ⁴ Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. ⁵ Applicant is to place a check mark here if English language translation is attached.

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	15784258
Filing Date	2017-10-16
First Named Inventor	Jason K. Stowers
Art Unit	1722
Examiner Name	Chanceity N. Robinson
Attorney Docket Number	5063.02US05

CERTIFICATION STATEMENT

Please see 37 CFR 1.97 and 1.98 to make the appropriate selection(s):

That each item of information contained in the information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(1).

OR

☐ That no item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the person signing the certification after making reasonable inquiry, no item of information contained in the information disclosure statement was known to any individual designated in 37 CFR 1.56(c) more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(2).

See attached certification statement.

The fee set forth in 37 CFR 1.17 (p) has been submitted herewith.

☒ A certification statement is not submitted herewith.

SIGNATURE

A signature of the applicant or representative is required in accordance with CFR 1.33, 10.18. Please see CFR 1.4(d) for the form of the signature.

Signature	/Diane Bennett/	Date (YYYY-MM-DD)	2020-05-11
Name/Print	Diane E. Bennett, Ph.D.	Registration Number	63,240

This collection of information is required by 37 CFR 1.97 and 1.98. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 1 hour to complete, including gathering, preparing and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. **DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

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9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

Bibliographic Data

Application No: 15/784,258

Foreign Priority claimed: ☐ Yes ☒ No

35 USC 119 (a-d) conditions met: ☐ Yes ☐ No

☐ Met After Allowance

Verified and Acknowledged:

/CHANCEITY N
ROBINSON/

CR

Examiner's Signature

Initials

Title:

RADIATION BASED PATTERNING METHODS

FILING or 371(c) DATE	CLASS	GROUP ART UNIT	ATTORNEY DOCKET NO.
10/16/2017	430	1722	5063.02US05
RULE			

APPLICANTS

Inpria Corporation, Corvallis, OR, UNITED STATES

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CONTINUING DATA

This application is a DIV of 14858612 09/18/2015 PAT 9823564

14858612 is a CON of 12850867 08/05/2010 PAT 9176377

12850867 has PRO of 61350103 06/01/2010

FOREIGN APPLICATIONS

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EAST Search History

EAST Search History (Prior Art)

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	Time Stamp
		S67 and S69	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/05/27 11:19
L1	1	("20050242330").PN.	US-PGPUB; USPAT; USOCR	OR	OFF	2020/05/27 11:20
L2	56466	EUV or (extreme adj ultraviolet)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/05/27 11:20
L3	0	L1 and L2	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/05/27 11:20
L4	6	((("4639208") or ("4601917") or ("4851481") or ("6566276") or ("20110166268") or ("20160116839")).PN.	US-PGPUB; USPAT; USOCR	OR	OFF	2020/05/27 11:21
L5	6	L4	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/05/27 11:21

L6	6	4 and 5	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/05/27 11:21
L7	1	4 and 2	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/05/27 11:21
S1	7	"12850867"	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/01/05 16:41
S2	3847446	(method or process) with (substrate or support)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2019/01/05 18:44
S3	367748	(EUV or UV or ultraviolet) with radiation	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2019/01/05 18:45
S4	155899	heat\$3 with (coat\$3) with (support or substrate)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2019/01/05 18:45

S5	5772464	irraditat\$4 or expos\$4	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2019/01/05 18:45
S6	24187	(EUV or UV or ultraviolet) with (dosage or dose)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2019/01/05 18:45
S7	1271	S2 and S3 and S4 and S5 and S6	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2019/01/05 18:45
S8	1189	S7 and thickness	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2019/01/05 18:46
S9	691	S8 and (developer or developing)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2019/01/05 18:46
S10	54733	(TMAH or (tetramethylammonium adj hydroxide))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2019/01/05 18:47

S11	528	S9 and S10	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2019/01/05 18:47
S12	527	S11 and pattern\$3	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2019/01/05 18:47
S13	20	S12 and ligands and (metal adj (ion or cation))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2019/01/05 18:47
S14	20	S13 AND ((G03F7/0042 OR G03F7/0043 OR G03F7/20 OR G03F7/325 OR G03F7/327 OR G03F7/022 OR G03F7/032 OR G03F7/033 OR G03F7/0382 OR G03F7/0385 OR G03F7/0392 OR G03F7/0397 OR G03F7/32 OR G03F7/322 OR G03F7/09 OR G03F7/2002 OR G03F7/2037 OR G03F7/30 OR G03F7/2004 OR G03F7/162 OR G03F7/168 OR G03F7/40 OR Y10T428/24355 OR H01M10/0525 OR H01M2004/021 OR H01M2004/025 OR H01M2004/027 OR H01M4/045 OR H01M4/049 OR H01M4/134 OR H01M4/1391 OR H01M4/1395 OR H01M4/48 OR H01M4/60 OR H01M4/66 OR H01M4/665 OR H01M4/667 OR H01M4/668 OR Y02E60/122 OR Y02P70/54 OR Y02T10/7011).CPC.)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2019/01/05 18:48

S15	1	("8415000").PN.	US-PGPUB; USPAT; USOCR	OR	OFF	2019/06/09 21:42
S16	2	"15784258"	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/06/09 21:50
S17	2	"8158338"	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2020/01/27 19:05
S18	4	((("8158338") or ("8828493") or ("8785113") or ("8124319")).PN.	US-PGPUB; USPAT; USOCR	OR	OFF	2020/01/27 19:05
S19	99753	(forming adj pattern)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 08:07
S20	4415	(EUV or UV) with dosage	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 08:07
S21	1630	dosage with mJ	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 08:07

S22	14	S19 and S20 and S21	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 08:08
S23	15186	(EUV or UV) with dose	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 08:15
S24	14182	dose with mJ	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 08:15
S25	5103	S23 and S24	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 08:15
S26	477	S19 and S25	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 08:15
S27	110	S26 and pitch	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 08:15

S28	87	(pitch with nm) and S26	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 08:16
S29	67	S28 and EUV	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 08:16
S30	36	S29 and (double adj patterning)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 09:02
S31	504274	metal adj (ion or cation or suboxide)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 09:11
S32	59	peroxide adj ligand	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 09:11
S33	33	S31 and S32	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 09:11

S34	0	S19 and S33	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 09:12
S35	16	pattern and S33	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 09:12
S36	18	"4877718"	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 09:42
S37	9	S36 and thickness	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 09:42
S38	1	"20080020291".pn. and thickness	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 09:49
S39	0	"825710".pn. and thickness	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 09:57

S40	2	"8257910".pn. and thickness	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 09:58
S41	2	"8257910".pn. and pattern	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 10:00
S42	1	"8257910".pn. and pitch	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 10:52
S43	0	"8257910".pn. and suboxide	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 11:21
S44	0	"8257910".pn. and peroxide	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 11:21
S45	0	"8257910".pn. and double	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 11:22

S46	22142	negative adj photoresist	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 11:22
S47	20232	negative adj resist	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 11:22
S48	39675	S46 or S47	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 11:23
S49	108	S20 and S48	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 11:23
S50	953433	(heat\$3 or bak\$3) with (substrate)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 11:23
S51	36	S49 and S50	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 11:24

S52	36	S51 and thickness	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 11:24
S53	2	S52 and (double adj patterning)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 11:42
S54	91	(EUV with (dosage or dose)) and (double adj patterning)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 11:43
S55	77	S50 and S54	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 11:43
S56	65	S55 and (thickness with (nm or nanometer))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 11:43
S57	2	"20090214823".pn. and pattern	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 12:16

S58	4	((("8158338") or ("8828493") or ("8785113") or ("8124319"))).PN.	US-PGPUB; USPAT; USOCR	OR	OFF	2020/01/28 12:20
S59	4	S58	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 12:20
S60	16439977	S59 adn (heat\$3)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 12:20
S61	4	S59 and (heat\$3)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 12:20
S62	10	(peroxide adj ligand) and (metal adj suboxide)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 12:46
S63	600	(peroxide a) and (metal adj suboxide)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 12:46
S64	116	(peroxide) and (metal adj suboxide)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO;	OR	ON	2020/01/28 12:46

			DERWENT; IBM_TDB			
S65	2	"15784258"	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2020/01/29 10:17
S66	1	S65 and (coated adj substrate) and substrate	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2020/01/29 10:17
S67	6	((("4639208") or ("4601917") or ("4851481") or ("6566276") or ("20110166268") or ("20160116839")).PN.	US-PGPUB; USPAT; USOCR	OR	OFF	2020/05/27 09:47
S68	1	("20050242330").PN.	US-PGPUB; USPAT; USOCR	OR	OFF	2020/05/27 10:04
S69	56466	EUV or (extreme adj ultraviolet)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/05/27 10:17
S70	950	(EUV or (extreme adj ultraviolet)) with (dose or dosage)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/05/27 10:17
S71	117532	(pattern\$5 adj (structure or material or device))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO;	OR	ON	2020/05/27 10:18

			DERWENT; IBM_TDB			
S72	193	S70 and S71	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/05/27 10:18
S73	10182	(developer or developing) with (TMAH or (tetramethyl adj ammonium adj hydroxide))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/05/27 10:19
S74	131446	unirradiated or unexposed or nonexposed or non-exposed	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/05/27 10:19
S75	84857	pattern with pitch	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/05/27 10:19
S76	5168	S74 and S75	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/05/27 10:19
S77	1274	S73 and S76	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO;	OR	ON	2020/05/27 10:19

			DERWENT; IBM_TDB			
S78	27	S72 and S77	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/05/27 10:19
S79	27	S78 and (thickness)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/05/27 10:20
S80	24	S79 AND ((G03F7/0042 OR G03F7/0043 OR G03F7/20 OR G03F7/325 OR G03F7/32 OR G03F7/322 OR G03F7/09 OR G03F7/2002 OR G03F7/2037 OR G03F7/30 OR G03F7/327 OR G03F7/2004 OR G03F7/039 OR G03F7/0392 OR G03F7/38 OR G03F7/422 OR G03F7/162 OR G03F7/168 OR G03F7/40).CPC.)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/05/27 10:34
S81	1129491	(developer or developing) and "18"	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/05/27 10:48

EAST Search History (Interference)

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	Time Stamp
		"1" and "3"	US-PGPUB; USPAT	OR	ON	2020/05/27 11:19

S82	841	(EUV or (extreme adj ultraviolet)) with (dose or dosage)	US-PGPUB; USPAT	OR	ON	2020/05/27 10:47
S83	95558	unirradiated or unexposed or nonexposed or non-exposed	US-PGPUB; USPAT	OR	ON	2020/05/27 10:47
S84	65637	pattern with pitch	US-PGPUB; USPAT	OR	ON	2020/05/27 10:48
S85	152	S82 and S83 and S84	US-PGPUB; USPAT	OR	ON	2020/05/27 10:48
S86	841	(EUV or (extreme adj ultraviolet)) with (dose or dosage)	US-PGPUB; USPAT	OR	ON	2020/05/27 10:48
S87	131	S85 and (thickness)	US-PGPUB; USPAT	OR	ON	2020/05/27 10:49

5/27/2020 11:22:03 AM

C:\Users\crobinson4\Documents\EAST\Workspaces\15784258.wsp



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APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
15/784,258	10/16/2017	Jason K. Stowers	5063.02US05	9576

62274 7590 08/06/2020
CHRISTENSEN, FONDER, DARDI & HERBERT PLLC
33 South Sixth Street
Suite 4540
Minneapolis, MN 55402

EXAMINER

ROBINSON, CHANCEITY N

ART UNIT	PAPER NUMBER
----------	--------------

1722

NOTIFICATION DATE	DELIVERY MODE
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08/06/2020

ELECTRONIC

Please find below and/or attached an Office communication concerning this application or proceeding.

The time period for reply, if any, is set in the attached communication.

Notice of the Office communication was sent electronically on above-indicated "Notification Date" to the following e-mail address(es):

docket@cfid-ip.com
patents@cfid-ip.com

Corrected Notice of Allowability	Application No. 15/784,258	Applicant(s) Stowers et al.	
	Examiner CHANCEITY N ROBINSON	Art Unit 1722	AIA (FITF) Status No

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address--

All claims being allowable, PROSECUTION ON THE MERITS IS (OR REMAINS) CLOSED in this application. If not included herewith (or previously mailed), a Notice of Allowance (PTOL-85) or other appropriate communication will be mailed in due course. **THIS NOTICE OF ALLOWABILITY IS NOT A GRANT OF PATENT RIGHTS.** This application is subject to withdrawal from issue at the initiative of the Office or upon petition by the applicant. See 37 CFR 1.313 and MPEP 1308.

1. ☒ This communication is responsive to 05/28/2020.
☐ A declaration(s)/affidavit(s) under **37 CFR 1.130(b)** was/were filed on ____.

2. ☐ An election was made by the applicant in response to a restriction requirement set forth during the interview on ____; the restriction requirement and election have been incorporated into this action.

3. ☒ The allowed claim(s) is/are 1-19. As a result of the allowed claim(s), you may be eligible to benefit from the **Patent Prosecution Highway** program at a participating intellectual property office for the corresponding application. For more information, please see http://www.uspto.gov/patents/init_events/pph/index.jsp or send an inquiry to PPHfeedback@uspto.gov.

4. ☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).

Certified copies:

a) ☐ All b) ☐ Some *c) ☐ None of the:

1. ☐ Certified copies of the priority documents have been received.

2. ☐ Certified copies of the priority documents have been received in Application No. ____.

3. ☐ Copies of the certified copies of the priority documents have been received in this national stage application from the International Bureau (PCT Rule 17.2(a)).

* Certified copies not received: ____.

Applicant has THREE MONTHS FROM THE "MAILING DATE" of this communication to file a reply complying with the requirements noted below. Failure to timely comply will result in ABANDONMENT of this application.
THIS THREE-MONTH PERIOD IS NOT EXTENDABLE.

5. ☐ CORRECTED DRAWINGS (as "replacement sheets") must be submitted.
☐ including changes required by the attached Examiner's Amendment / Comment or in the Office action of Paper No./Mail Date ____.

Identifying indicia such as the application number (see 37 CFR 1.84(c)) should be written on the drawings in the front (not the back) of each sheet. Replacement sheet(s) should be labeled as such in the header according to 37 CFR 1.121(d).

6. ☐ DEPOSIT OF and/or INFORMATION about the deposit of BIOLOGICAL MATERIAL must be submitted. Note the attached Examiner's comment regarding REQUIREMENT FOR THE DEPOSIT OF BIOLOGICAL MATERIAL.

Attachment(s)

1. ☐ Notice of References Cited (PTO-892)

2. ☒ Information Disclosure Statements (PTO/SB/08), Paper No./Mail Date ____.

3. ☐ Examiner's Comment Regarding Requirement for Deposit of Biological Material ____.

4. ☐ Interview Summary (PTO-413), Paper No./Mail Date. ____.

5. ☐ Examiner's Amendment/Comment

6. ☐ Examiner's Statement of Reasons for Allowance

7. ☐ Other ____.

/CHANCEITY N ROBINSON/
 Primary Examiner, Art Unit 1722

Issue Classification 	Application/Control No. 15/784,258	Applicant(s)/Patent Under Reexamination Stowers et al.
	Examiner CHANCEITY N ROBINSON	Art Unit 1722

CPC						
Symbol					Type	Version
G03F	/	7	/	0043	F	2013-01-01
G03F	/	7	/	0042	I	2013-01-01
G03F	/	7	/	20	I	2013-01-01
G03F	/	7	/	327	I	2013-01-01
Y10T	/	428	/	24355	A	2015-01-15

CPC Combination Sets					
Symbol				Type	Version
/	/	/	/		

NONE (Assistant Examiner) _____ (Date) _____		Total Claims Allowed: 19	
/CHANCEITY N ROBINSON/ Primary Examiner, Art Unit 1722 (Primary Examiner) _____ (Date) 04 August 2020		O.G. Print Claim(s) 1	O.G. Print Figure 1

Issue Classification 	Application/Control No. 15/784,258	Applicant(s)/Patent Under Reexamination Stowers et al.
	Examiner CHANCEITY N ROBINSON	Art Unit 1722

INTERNATIONAL CLASSIFICATION			
CLAIMED			
G03F	/	7	/ 00
NON-CLAIMED			
	/		/

US ORIGINAL CLASSIFICATION	
CLASS	SUBCLASS

CROSS REFERENCES(S)						
CLASS	SUBCLASS (ONE SUBCLASS PER BLOCK)					

NONE	Total Claims Allowed:	
(Assistant Examiner)	(Date)	19
/CHANCEITY N ROBINSON/ Primary Examiner, Art Unit 1722	04 August 2020	O.G. Print Claim(s)
(Primary Examiner)	(Date)	1
		O.G. Print Figure
		1

Issue Classification 	Application/Control No. 15/784,258	Applicant(s)/Patent Under Reexamination Stowers et al.
	Examiner CHANCEITY N ROBINSON	Art Unit 1722

☒ Claims renumbered in the same order as presented by applicant ☐ CPA ☒ T.D. ☐ R.1.47															
CLAIMS															
Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original

NONE	Total Claims Allowed:	
(Assistant Examiner)	(Date)	19
/CHANCEITY N ROBINSON/ Primary Examiner, Art Unit 1722	04 August 2020	O.G. Print Claim(s)
(Primary Examiner)	(Date)	1
		O.G. Print Figure
		1

<i>Search Notes</i> 	Application/Control No. 15/784,258	Applicant(s)/Patent Under Reexamination Stowers et al.
	Examiner CHANCEITY N ROBINSON	Art Unit 1722

CPC - Searched*		
Symbol	Date	Examiner
G03F 7/00	01/05/2019	CR

CPC Combination Sets - Searched*		
Symbol	Date	Examiner

US Classification - Searched*			
Class	Subclass	Date	Examiner

* See search history printout included with this form or the SEARCH NOTES box below to determine the scope of the search.

Search Notes		
Search Notes	Date	Examiner
East and IDS Search	01/05/2019	CR
East Search Updated	01/28/2020	CR
IDS Search	08/04/2020	CR

Interference Search			
US Class/CPC Symbol	US Subclass/CPC Group	Date	Examiner
G03F	7/00	05/27/2020	CR

/CHANCEITY N ROBINSON/ Primary Examiner, Art Unit 1722	
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<i>Index of Claims</i> 	Application/Control No. 15/784,258	Applicant(s)/Patent Under Reexamination Stowers et al.
	Examiner CHANCEITY N ROBINSON	Art Unit 1722

✓	Rejected	-	Cancelled	N	Non-Elected	A	Appeal
=	Allowed	÷	Restricted	I	Interference	O	Objected

CLAIMS										
☒ Claims renumbered in the same order as presented by applicant ☐ CPA ☒ T.D. ☐ R.1.47										
CLAIM			DATE							
Final	Original		01/28/2020							
1	1	=								
2	2	=								
3	3	=								
4	4	=								
5	5	=								
6	6	=								
7	7	=								
8	8	=								
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10	10	=								
11	11	=								
12	12	=								
13	13	=								
14	14	=								
15	15	=								
16	16	=								
17	17	=								
18	18	=								
19	19	=								

Doc code: IDS

PTO/SB/08a (03-15)

Doc description: Information Disclosure Statement (IDS) Filed

Approved for use through 07/31/2016. OMB 0651-0031

U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

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INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)

Application Number	15784258
Filing Date	2017-10-16
First Named Inventor	Jason K. Stowers
Art Unit	1722
Examiner Name	Chanceity N. Robinson
Attorney Docket Number	5063.02US05

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Examiner Initial*	Cite No	Patent Number	Kind Code ¹	Issue Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1	4104292		1978-08-01	Dworkin et al.	
	2	6387012		2002-05-14	Mitamura	
	3	8426107		2013-04-23	Takashi et al.	
	4	9310684		2016-04-12	Meyers et al.	
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	1	20110135823		2011-06-09	Lee et al.	
	2	20110206599		2011-08-25	Keszler et al.	

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INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)

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Filing Date	2017-10-16
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Art Unit	1722
Examiner Name	Chanceity N. Robinson
Attorney Docket Number	5063.02US05

3	20110244403		2011-10-06	Carcasi et al.
4	20120202349	A1	2012-08-09	Sun
5	20130253161		2013-09-26	Amako et al.
6	20140303283	A1	2014-10-09	Ding et al.

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	1							

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Examiner Initials*	Cite No	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc), date, pages(s), volume-issue number(s), publisher, city and/or country where published.	T ⁵
	1	CHANDRASEKHAR ET AL., "Organotin Assemblies Containing SN-O Bonds," Coordination Chemistry Reviews 235:1-52 (2002).	
	2	EYCHENNE-BARON ET AL., "New Synthesis Of The Nanobuilding Block {(BuSn)12O14(OH)6 }2+ And Exchange Properties Of {(BuSn)12O14(OH)6}(O3SC6H4CH3)2," Journal Of Organometallic Chemistry, 567:137-142 (1998).	

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /C.N.R/

**INFORMATION DISCLOSURE
STATEMENT BY APPLICANT**
(Not for submission under 37 CFR 1.99)

Application Number	15784258
Filing Date	2017-10-16
First Named Inventor	Jason K. Stowers
Art Unit	1722
Examiner Name	Chanceity N. Robinson
Attorney Docket Number	5063.02US05

3

EYCHENNE-BARON ET AL., "Reaction Of Butyltin Hydroxide Oxide With p-Toluenesulfonic Acid: Synthesis, X-ray Crystal Analysis, And Multinuclear NMR Characterization Of $\{(\text{BuSn})_{12}\text{O}_{14}(\text{OH})_6\}(\text{4-CH}_3\text{C}_6\text{H}_4\text{SO}_3)_2$," *Organometallics*, 19:1940-1949 (2000).
ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /C.N.R/

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EXAMINER SIGNATURE

Examiner Signature	/CHANCEITY N ROBINSON/	Date Considered	08/04/2020
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*EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through a citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

¹ See Kind Codes of USPTO Patent Documents at www.USPTO.GOV or MPEP 901.04. ² Enter office that issued the document, by the two-letter code (WIPO Standard ST.3). ³ For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. ⁴ Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. ⁵ Applicant is to place a check mark here if English language translation is attached.

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	15784258
Filing Date	2017-10-16
First Named Inventor	Jason K. Stowers
Art Unit	1722
Examiner Name	Chanceity N. Robinson
Attorney Docket Number	5063.02US05

CERTIFICATION STATEMENT

Please see 37 CFR 1.97 and 1.98 to make the appropriate selection(s):

That each item of information contained in the information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(1).

OR

☐ That no item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the person signing the certification after making reasonable inquiry, no item of information contained in the information disclosure statement was known to any individual designated in 37 CFR 1.56(c) more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(2).

See attached certification statement.

The fee set forth in 37 CFR 1.17 (p) has been submitted herewith.

☒ A certification statement is not submitted herewith.

SIGNATURE

A signature of the applicant or representative is required in accordance with CFR 1.33, 10.18. Please see CFR 1.4(d) for the form of the signature.

Signature	/Diane Bennett/	Date (YYYY-MM-DD)	2020-05-28
Name/Print	Diane E. Bennett, Ph.D.	Registration Number	63,240

This collection of information is required by 37 CFR 1.97 and 1.98. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 1 hour to complete, including gathering, preparing and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. **DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

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5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.
6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).
7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.
8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspections or an issued patent.
9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

EAST Search History

EAST Search History (Prior Art)

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	Time Stamp
L2	10	((("4104292") or ("6387012") or ("8426107") or ("9310684") or ("20110135823") or ("20110206599") or ("20110244403") or ("20120202349") or ("20130253161") or ("20140303283")).PN.	US-PGPUB; USPAT; USOCR	OR	OFF	2020/08/04 10:44
L3	37,697	"1" and (EUV)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/08/04 10:47
L4	1	2 and (EUV)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/08/04 10:47
S1	7	"12850867"	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/01/05 16:41
S2	3,847,446	(method or process) with (substrate or support)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2019/01/05 18:44
S3	367,748	(EUV or UV or ultraviolet) with radiation	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2019/01/05 18:45

S4	155,899	heat\$3 with (coat\$3) with (support or substrate)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2019/01/05 18:45
S5	5,772,464	irraditat\$4 or expos\$4	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2019/01/05 18:45
S6	24,187	(EUV or UV or ultraviolet) with (dosage or dose)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2019/01/05 18:45
S7	1,271	S2 and S3 and S4 and S5 and S6	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2019/01/05 18:45
S8	1,189	S7 and thickness	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2019/01/05 18:46
S9	691	S8 and (developer or developing)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2019/01/05 18:46
S10	54,733	(TMAH or (tetramethylammonium adj hydroxide))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2019/01/05 18:47

S11	528	S9 and S10	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2019/01/05 18:47
S12	527	S11 and pattern\$3	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2019/01/05 18:47
S13	20	S12 and ligands and (metal adj (ion or cation))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2019/01/05 18:47
S14	20	S13 AND ((G03F7/0042 OR G03F7/0043 OR G03F7/20 OR G03F7/325 OR G03F7/327 OR G03F7/022 OR G03F7/032 OR G03F7/033 OR G03F7/0382 OR G03F7/0385 OR G03F7/0392 OR G03F7/0397 OR G03F7/32 OR G03F7/322 OR G03F7/09 OR G03F7/2002 OR G03F7/2037 OR G03F7/30 OR G03F7/2004 OR G03F7/162 OR G03F7/168 OR G03F7/40 OR Y10T428/24355 OR H01M10/0525 OR H01M2004/021 OR H01M2004/025 OR H01M2004/027 OR H01M4/045 OR H01M4/049 OR H01M4/134 OR H01M4/1391 OR H01M4/1395 OR H01M4/48 OR H01M4/60 OR H01M4/66 OR H01M4/665 OR H01M4/667 OR H01M4/668 OR Y02E60/122 OR Y02P70/54 OR Y02T10/7011).CPC.)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2019/01/05 18:48
S15	1	("8415000").PN.	US-PGPUB; USPAT; USOCR	OR	OFF	2019/06/09 21:42
S16	2	"15784258"	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO;	OR	OFF	2019/06/09 21:50

			DERWENT; IBM_TDB			
S17	2	"8158338"	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2020/01/27 19:05
S18	4	((("8158338") or ("8828493") or ("8785113") or ("8124319"))).PN.	US-PGPUB; USPAT; USOCR	OR	OFF	2020/01/27 19:05
S19	99,753	(forming adj pattern)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 08:07
S20	4,415	(EUV or UV) with dosage	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 08:07
S21	1,630	dosage with mJ	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 08:07
S22	14	S19 and S20 and S21	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 08:08
S23	15,186	(EUV or UV) with dose	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 08:15
S24	14,182	dose with mJ	US-PGPUB; USPAT;	OR	ON	2020/01/28 08:15

			USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB			
S25	5,103	S23 and S24	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 08:15
S26	477	S19 and S25	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 08:15
S27	110	S26 and pitch	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 08:15
S28	87	(pitch with nm) and S26	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 08:16
S29	67	S28 and EUV	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 08:16
S30	36	S29 and (double adj patterning)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 09:02
S31	504,274	metal adj (ion or cation or suboxide)	US-PGPUB; USPAT; USOCR;	OR	ON	2020/01/28 09:11

			FPRS; EPO; JPO; DERWENT; IBM_TDB			
S32	59	peroxide adj ligand	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 09:11
S33	33	S31 and S32	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 09:11
S34	0	S19 and S33	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 09:12
S35	16	pattern and S33	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 09:12
S36	18	"4877718"	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 09:42
S37	9	S36 and thickness	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 09:42
S38	1	"20080020291".pn. and thickness	US-PGPUB; USPAT; USOCR; FPRS; EPO;	OR	ON	2020/01/28 09:49

			JPO; DERWENT; IBM_TDB			
S39	0	"825710".pn. and thickness	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 09:57
S40	2	"8257910".pn. and thickness	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 09:58
S41	2	"8257910".pn. and pattern	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 10:00
S42	1	"8257910".pn. and pitch	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 10:52
S43	0	"8257910".pn. and suboxide	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 11:21
S44	0	"8257910".pn. and peroxide	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 11:21
S45	0	"8257910".pn. and double	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO;	OR	ON	2020/01/28 11:22

			DERWENT; IBM_TDB			
S46	22,142	negative adj photoresist	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 11:22
S47	20,232	negative adj resist	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 11:22
S48	39,675	S46 or S47	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 11:23
S49	108	S20 and S48	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 11:23
S50	953,433	(heat\$3 or bak\$3) with (substrate)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 11:23
S51	36	S49 and S50	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 11:24
S52	36	S51 and thickness	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO;	OR	ON	2020/01/28 11:24

			DERWENT; IBM_TDB			
S53	2	S52 and (double adj patterning)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 11:42
S54	91	(EUV with (dosage or dose)) and (double adj patterning)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 11:43
S55	77	S50 and S54	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 11:43
S56	65	S55 and (thickness with (nm or nanometer))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 11:43
S57	2	"20090214823".pn. and pattern	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 12:16
S58	4	((("8158338") or ("8828493") or ("8785113") or ("8124319")).PN.	US-PGPUB; USPAT; USOCR	OR	OFF	2020/01/28 12:20
S59	4	S58	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 12:20
S60	16,439,977	S59 adn (heat\$3)	US-PGPUB; USPAT;	OR	ON	2020/01/28 12:20

			USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB			
S61	4	S59 and (heat\$3)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 12:20
S62	10	(peroxide adj ligand) and (metal adj suboxide)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 12:46
S63	600	(peroxide a) and (metal adj suboxide)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 12:46
S64	116	(peroxide) and (metal adj suboxide)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 12:46
S65	2	"15784258"	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2020/01/29 10:17
S66	1	S65 and (coated adj substrate) and substrate	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2020/01/29 10:17
S67	6	(("4639208") or ("4601917") or ("4851481") or ("6566276") or	US-PGPUB; USPAT; USOCR	OR	OFF	2020/05/27 09:47

		("20110166268") or ("20160116839")).PN.				
S68	1	("20050242330").PN.	US-PGPUB; USPAT; USOCR	OR	OFF	2020/05/27 10:04
S69	56,466	EUV or (extreme adj ultraviolet)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/05/27 10:17
S70	950	(EUV or (extreme adj ultraviolet)) with (dose or dosage)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/05/27 10:17
S71	117,532	(pattern\$5 adj (structure or material or device))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/05/27 10:18
S72	193	S70 and S71	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/05/27 10:18
S73	10,182	(developer or developing) with (TMAH or (tetramethyl adj ammonium adj hydroxide))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/05/27 10:19
S74	131,446	unirradiated or unexposed or nonexposed or non-exposed	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/05/27 10:19
S75	84,857	pattern with pitch	US-PGPUB; USPAT;	OR	ON	2020/05/27 10:19

			USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB			
S76	5,168	S74 and S75	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/05/27 10:19
S77	1,274	S73 and S76	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/05/27 10:19
S78	27	S72 and S77	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/05/27 10:19
S79	27	S78 and (thickness)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/05/27 10:20
S80	24	S79 AND (G03F7/0042 OR G03F7/0043 OR G03F7/20 OR G03F7/325 OR G03F7/32 OR G03F7/322 OR G03F7/09 OR G03F7/2002 OR G03F7/2037 OR G03F7/30 OR G03F7/327 OR G03F7/2004 OR G03F7/039 OR G03F7/0392 OR G03F7/38 OR G03F7/422 OR G03F7/162 OR G03F7/168 OR G03F7/40).CPC.)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/05/27 10:34
S81	1,129,491	(developer or developing) and "18"	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/05/27 10:48

S88	1	("20050242330").PN.	US-PGPUB; USPAT; USOCR	OR	OFF	2020/05/27 11:20
S89	56,466	EUV or (extreme adj ultraviolet)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/05/27 11:20
S90	0	S88 and S89	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/05/27 11:20
S91	6	((("4639208") or ("4601917") or ("4851481") or ("6566276") or ("20110166268") or ("20160116839")).PN.	US-PGPUB; USPAT; USOCR	OR	OFF	2020/05/27 11:21
S92	6	S91	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/05/27 11:21
S93	6	S91 and S92	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/05/27 11:21
S94	1	S91 and S89	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/05/27 11:21

EAST Search History (Interference)

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	Time Stamp
L1	14	"4104292"	US-PGPUB; USPAT	OR	ON	2020/08/04 10:43

S82	841	(EUV or (extreme adj ultraviolet)) with (dose or dosage)	US-PGPUB; USPAT	OR	ON	2020/05/27 10:47
S83	95,558	unirradiated or unexposed or nonexposed or non-exposed	US-PGPUB; USPAT	OR	ON	2020/05/27 10:47
S84	65,637	pattern with pitch	US-PGPUB; USPAT	OR	ON	2020/05/27 10:48
S85	152	S82 and S83 and S84	US-PGPUB; USPAT	OR	ON	2020/05/27 10:48
S86	841	(EUV or (extreme adj ultraviolet)) with (dose or dosage)	US-PGPUB; USPAT	OR	ON	2020/05/27 10:48
S87	131	S85 and (thickness)	US-PGPUB; USPAT	OR	ON	2020/05/27 10:49

8/4/2020 10:48:09 AM

C:\Users\crobinson4\Documents\EAST\Workspaces\15784258.wsp

Document Description: Issue Fee Payment (PTO-85B)

Issue Fee Transmittal Form

Application Number	Filing Date	First Named Inventor	Atty. Docket No.	Confirmation No.
15784258	16-Oct-2017	Jason Stowers	5063.02US05	9576

TITLE OF INVENTION :

RADIATION BASED PATTERNING METHODS

Entity Status	Application Type	Art Unit	Class - Subclass	EXAMINER
Regular Undiscounted	Utility under 35 USC 111(a)	1722	270100	CHANCEITY ROBINSON
Issue Fee Due	Publication Due	Total Fee(s) Due	Date Due	Prev. Paid Fee
\$1000	\$0	\$1000	04-Sep-2020	\$0

1.Change of Correspondence Address and/or Indication Of Fee Address (37 CFR 1.33 & 1.363)

Current Correspondence Address:	Current Indicated Fee Address :
62274 CHRISTENSEN, FONDER, DARDI & HERBERT PLLC 33 South Sixth Street Suite 4540 Minneapolis MN 55402 UNITED STATES 612 315 4100 docket@cfp-ip.com	
☐ Change of correspondence address requested, system generated AIA/122-EFS form attached	☐ Fee Address indication requested, system generated SB/47-EFS form attached

2.Entity Status

Change in Entity Status

- ☐

Applicant certifying micro entity status; system generated Micro Entity certification form attached. See 37 CFR 1.29.
Note: Absent a valid certification of micro entity status, issue fee payment in the micro entity amount will not be accepted at the risk of application abandonment.
If this box is checked, you will be prompted to choose a micro entity status on the gross income basis (37 CFR 1.29(a)) or the institution of higher education basis (37 CFR 1.29(d)), and make the applicable certification online.
- ☐

Applicant asserting small entity status. See 37 CFR 1.27.
Note: If the application was previously under micro entity status, checking this box will be taken to be a notification of loss of entitlement to micro entity status.
- ☒

Applicant changing to regular undiscounted fee status.
Note: Checking this box will be taken to be a notification of loss of entitlement to small or micro entity status, as applicable.

Document Description: Issue Fee Payment (PTO-85B)

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☒ Issue Fee

☐ I authorize USPTO to apply my previously paid issue fee to the current fees due

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The **issue fee must be submitted** with this form. **If payment of the issue fee does not accompany this form, checking this box and providing a deposit account number will NOT be effective to satisfy full payment of the fee(s) due.**

4.Firm and/or Attorney Names To Be Printed

NOTE: If no name is listed, no name will be printed
For printing on the patent front page, list to be displayed as entered

1. Christensen, Fonder, Dardi
2. Diane E. Bennett, Ph.D.
3. Peter S. Dardi, Ph.D.

5.Assignee Name(s) and Residence Data To Be Printed

PLEASE NOTE: Unless an assignee is identified below, no assignee data will appear on the patent. If an assignee is identified below, the document has been filed for recordation as set forth in 37 CFR 3.11. Completion of this form is NOT a substitute for filing an assignment.

Name	City	State	Country	Category
Inpria Corporation	Corvallis	OREGON	united states	corporation

6.Signature

I certify, in accordance with 37 CFR 1.4(d)(4) that I am an attorney or agent registered to practice before the Patent and Trademark Office who has filed and has been granted power of attorney in this application. I also certify that this Fee(s) Transmittal form is being transmitted to the USPTO via EFS-WEB on the date indicated below.

Signature	/Diane E. Bennett/	Date	08-12-2020
Name	Diane Elizabeth Bennett	Registration Number	63240

Electronic Patent Application Fee Transmittal

Application Number:	15784258			
Filing Date:	16-Oct-2017			
Title of Invention:	RADIATION BASED PATTERNING METHODS			
First Named Inventor/Applicant Name:	Jason K. Stowers			
Filer:	Diane Elizabeth Bennett			
Attorney Docket Number:	5063.02US05			
Filed as Large Entity				
Filing Fees for Utility under 35 USC 111(a)				
Description	Fee Code	Quantity	Amount	Sub-Total in USD(\$)
Basic Filing:				
UTILITY APPL ISSUE FEE	1501	1	1000	1000
PUBL. FEE- EARLY, VOLUNTARY, OR NORMAL	1504	1	0	0
Pages:				
Claims:				
Miscellaneous-Filing:				
Petition:				
Patent-Appeals-and-Interference:				

Description	Fee Code	Quantity	Amount	Sub-Total in USD(\$)
Post-Allowance-and-Post-Issuance:				
Extension-of-Time:				
Miscellaneous:				
Total in USD (\$)				1000

Electronic Acknowledgement Receipt

EFS ID:	40262309
Application Number:	15784258
International Application Number:	
Confirmation Number:	9576
Title of Invention:	RADIATION BASED PATTERNING METHODS
First Named Inventor/Applicant Name:	Jason K. Stowers
Customer Number:	62274
Filer:	Diane Elizabeth Bennett
Filer Authorized By:	
Attorney Docket Number:	5063.02US05
Receipt Date:	12-AUG-2020
Filing Date:	16-OCT-2017
Time Stamp:	17:11:08
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	yes
Payment Type	CARD
Payment was successfully received in RAM	\$ 1000
RAM confirmation Number	E20208BH11051407
Deposit Account	
Authorized User	

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File Listing:					
Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Issue Fee Payment (PTO-85B)	Web85b.pdf	46372	no	2
			cb42af12562ad228a4fecdb8444032a7bbe65c01		
Warnings:					
Information:					
2	Fee Worksheet (SB06)	fee-info.pdf	31923	no	2
			4b3f769df81585423120c57981335f883ed85e0f		
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Doc code: IDS

PTO/SB/08a (03-15)

Doc description: Information Disclosure Statement (IDS) Filed

Approved for use through 07/31/2016. OMB 0651-0031

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INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)

Application Number	15784258
Filing Date	2017-10-16
First Named Inventor	Jason K. Stowers
Art Unit	1722
Examiner Name	Chanceity N. Robinson
Attorney Docket Number	5063.02US05

U.S.PATENTS

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Examiner Initial*	Cite No	Patent Number	Kind Code ¹	Issue Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
Change(s) applied to document, /B.P./ 8/7/2020	1	4639208	A	01/1987 1983-01-16	Inui et al. Okunaka et al.	
	2	4601917		1986-07-22	Russo et al.	Corresponds to JPS61-000586
	3	4851481		1989-01-25	Kuriyama et al.	Corresponds to JPS63-241061
	4	6566276		2003-05-20	Maloney et al.	Corresponds to CN1457504
ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /C.N.R/						

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	1	20110166268	A1	2011-07-07	Deelman et al.	
	2	20160116839	A1	2016-04-28	Meyers et al.	Corresponds to JP2018-502173.
ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /C.N.R/						

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APPLICATION NO.	ISSUE DATE	PATENT NO.	ATTORNEY DOCKET NO.	CONFIRMATION NO.
15/784,258	09/22/2020	10782610	5063.02US05	9576

62274 7590 09/02/2020

CHRISTENSEN, FONDER, DARDI & HERBERT PLLC
11322 86th Ave. N.
Maple Grove, MN 55369

ISSUE NOTIFICATION

The projected patent number and issue date are specified above.

Determination of Patent Term Adjustment under 35 U.S.C. 154 (b) (application filed on or after May 29, 2000)

The Patent Term Adjustment is 5 day(s). Any patent to issue from the above-identified application will include an indication of the adjustment on the front page.

If a Continued Prosecution Application (CPA) was filed in the above-identified application, the filing date that determines Patent Term Adjustment is the filing date of the most recent CPA.

Applicant will be able to obtain more detailed information by accessing the Patent Application Information Retrieval (PAIR) WEB site (<http://pair.uspto.gov>).

Any questions regarding the Patent Term Extension or Adjustment determination should be directed to the Office of Patent Legal Administration at (571)-272-7702. Questions relating to issue and publication fee payments should be directed to the Application Assistance Unit (AAU) of the Office of Data Management (ODM) at (571)-272-4200.

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