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Xu

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(54) **METHOD FOR ADHERING MATERIALS TOGETHER**

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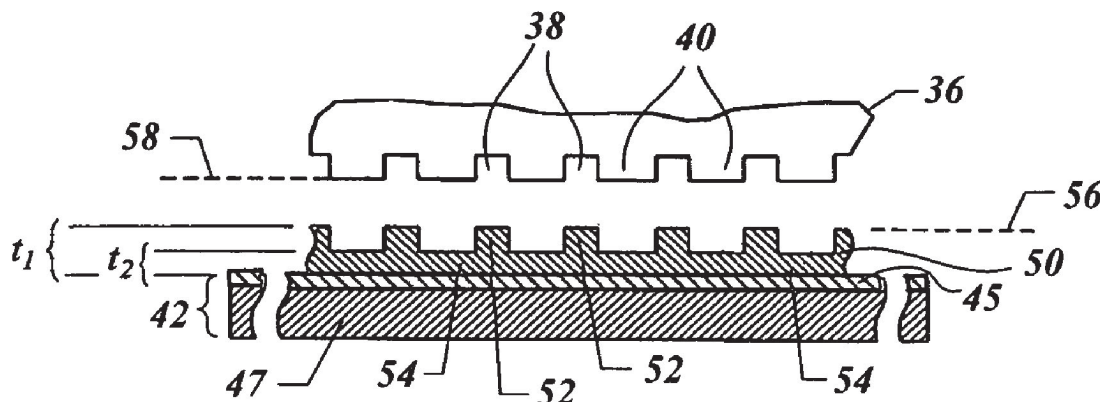
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(57) **ABSTRACT**

The present invention provides a method adhering a layer to a substrate that features defining first and second interfaces by having a composition present between the layer and the substrate that forms covalent bonds to the layer and adheres to the substrate employing one or more of covalent bonds, ionic bonds and Van der Waals forces. In this manner, the strength of the adhering force of the layer to the composition is assured to be stronger than the adhering force of the layer to the composition formed from a predetermined adhering mechanism, i.e., an adhering mechanism that does not include covalent bonding.

15 Claims, 4 Drawing Sheets



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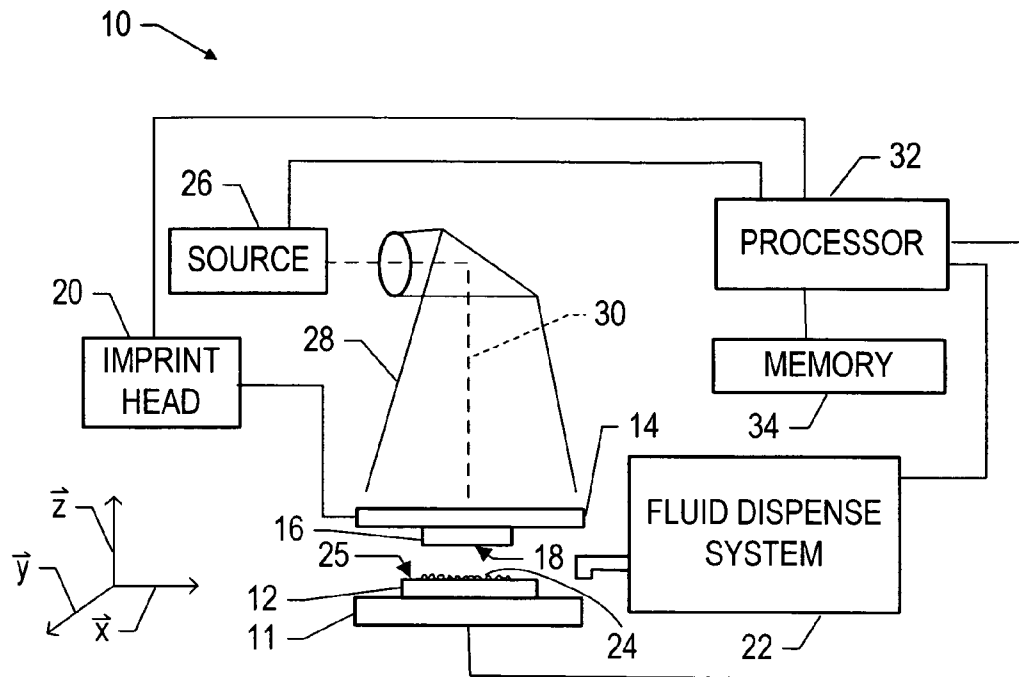


FIG. 1
(Prior Art)

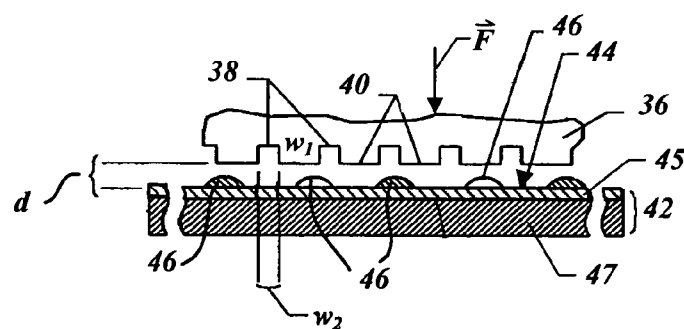


FIG. 2

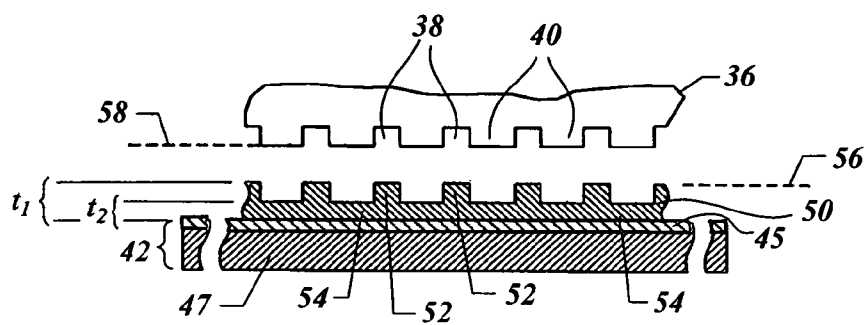


FIG. 3

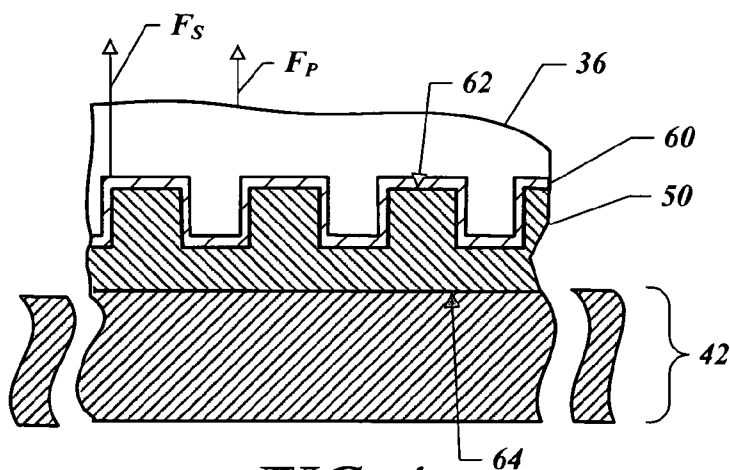


FIG. 4

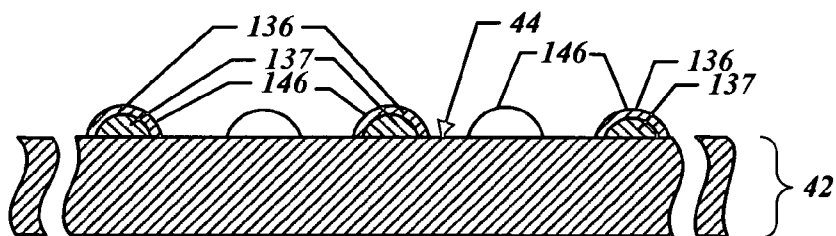


FIG. 5

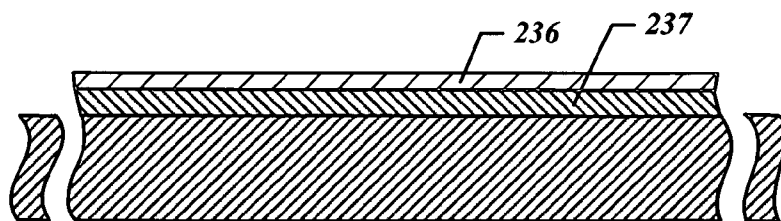
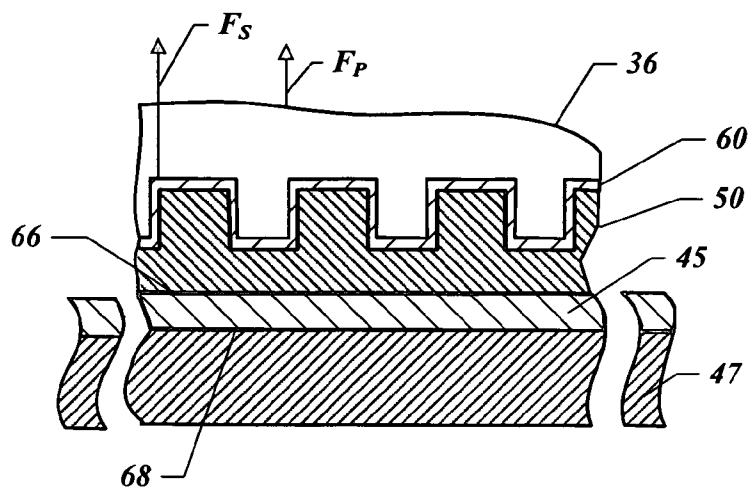
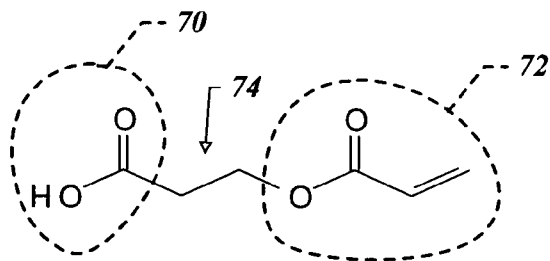
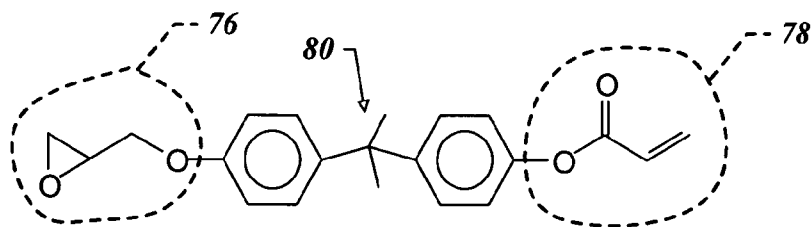
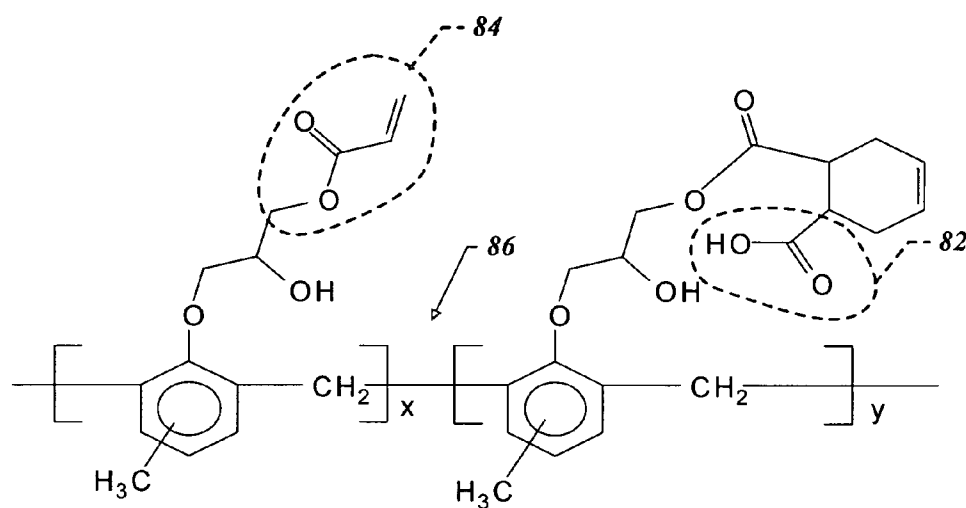
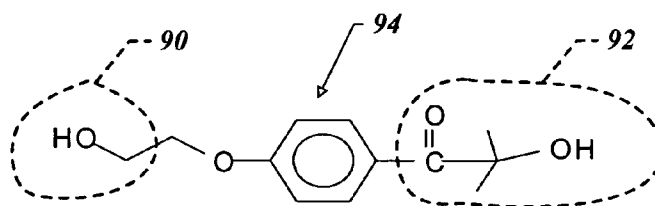


FIG. 6

*FIG. 7**FIG. 8**FIG. 9*

**FIG. 10****FIG. 11**

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METHOD FOR ADHERING MATERIALS TOGETHER

CROSS-REFERENCE TO RELATED APPLICATION

The present application is a divisional of U.S. patent application Ser. No. 11/187,406 (now U.S. Pat. No. 7,759,407), filed Jul. 22, 2005, entitled "Composition for Adhering Materials Together," listing Frank Y. Xu as inventor, which is incorporated by reference herein.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

The United States government has a paid-up license in this invention and the right in limited circumstance to require the patent owner to license others on reasonable terms as provided by the terms of 70NANB4H3012 awarded by National Institute of Standards (NIST) ATP Award.

BACKGROUND OF THE INVENTION

The field of invention relates generally to nano-fabrication of structures. More particularly, the present invention is directed to a method for adhering differing materials together suitable for use in imprint lithographic processes.

Nano-scale fabrication involves the fabrication of very small structures, e.g., having features on the order of one nanometer or more. A promising process for use in nano-scale fabrication is known as imprint lithography. Exemplary imprint lithography processes are described in detail in numerous publications, such as United States published patent application 2004-0065976 filed as U.S. patent application Ser. No. 10/264,960, (now U.S. Pat. No. 8,349,241) entitled "Method and a Mold to Arrange Features on a Substrate to Replicate Features having Minimal Dimensional Variability"; United States published patent application 2004-0065252 filed as U.S. patent application Ser. No. 10/264,926 (now abandoned) entitled "Method of Forming a Layer on a Substrate to Facilitate Fabrication of Metrology Standards"; and United States published patent application 2004-0046271 filed as U.S. patent application 10/235,314 (now U.S. Pat. No. 6,936,194) application Ser. No. 10/235,314 (U.S. Pat. No. 6,936,194), entitled "Method and a Mold to Arrange Features on a Substrate to Replicate Features having Minimal Dimensions Variability"; all of which are assigned to the assignee of the present invention.

Referring to FIG. 1, the basic concept behind imprint lithography is forming a relief pattern on a substrate that may function as, inter alia, an etching mask so that a pattern may be formed into the substrate that corresponds to the relief pattern. A system 10 employed to form the relief pattern includes a stage 11 upon which a substrate 12 is supported, and a template 14 having a mold 16 with a patterning surface 18 thereon. Patterning surface 18 may be substantially smooth and/or planar, or may be patterned so that one or more recesses are formed therein. Template 14 is coupled to an imprint head 20 to facilitate movement of template 14. A fluid dispense system 22 is coupled to be selectively placed in fluid communication with substrate 12 so as to deposit polymerizable material 24 thereon. A source 26 of energy 28 is coupled to direct energy 28 along a path 30. Imprint head 20 and stage 11 are configured to arrange mold 16 and substrate 12, respectively, to be in superimposition, and disposed in path 30. Either imprint head 20, stage 11, or both vary a distance

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between mold 16 and substrate 12 to define a desired volume therebetween that is filled by polymerizable material 24.

Typically, polymerizable material 24 is disposed upon substrate 12 before the desired volume is defined between mold 16 and substrate 12. However, polymerizable material 24 may fill the volume after the desired volume has been obtained. After the desired volume is filled with polymerizable material 24, source 26 produces energy 28, which causes polymerizable material 24 to solidify and/or cross-link, forming polymeric material conforming to the shape of the substrate surface 25 and mold surface 18. Control of this process is regulated by processor 32 that is in data communication with stage 11, imprint head 20, fluid dispense system 22, and source 26, operating on a computer-readable program stored in memory 34.

An important characteristic with accurately forming the pattern in the polymerizable material is to reduce, if not prevent, adhesion to the mold of the polymeric material, while ensuring suitable adhesion to the substrate. This is referred to as preferential release and adhesion properties. In this manner, the pattern recorded in the polymeric material is not distorted during separation of the mold. Prior art attempts to improve the release characteristics employ a release layer on the surface of the mold. The release layer is typically hydrophobic and/or has low surface energy. The release layer adheres to the mold. Providing the release layer improves release characteristics. This is seen by minimization of distortions in the pattern recorded into the polymeric material that are attributable to mold separation. This type of release layer is referred to, for purposes of the present discussion, as an a priori release layer, i.e., a release layer that is solidified to the mold.

Another prior art attempt to improve release properties is described by Bender et al. in "Multiple Imprinting in UV-based Nanoimprint Lithography: Related Material Issues," *Microelectronic Engineering* 61-62 (2002), pp. 407-413. Specifically, Bender et al. employ a mold having an a priori release layer in conjunction with a fluorine-treated UV curable material. To that end, a UV curable layer is applied to a substrate by spin-coating a 200 cPs UV curable fluid to form a UV curable layer. The UV curable layer is enriched with fluorine groups to improve the release properties.

A need exists, therefore, to improve the preferential release and adhesion properties of a mold employed in imprint lithography processes.

SUMMARY OF THE INVENTION

The present invention provides a method of adhering a layer to a substrate that features defining first and second interfaces by having a composition present between the layer and the substrate that forms covalent bonds to the layer and adheres to the substrate employing one or more of covalent bonds, ionic bonds and Van der Waals forces. In this manner, the strength of the adhering force of the layer to the composition is assured to be stronger than the adhering force of the layer to the composition having a predetermined adhering mechanism, i.e., an adhering mechanism that does not include covalent bonding. These and other embodiments are described herein.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a simplified plan view of a lithographic system in accordance with the prior art;

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FIG. 2 is a simplified elevation view of a template and imprinting material disposed on a substrate in accordance with the present invention;

FIG. 3 is a simplified elevation view of the template and substrate, shown in FIG. 2, with the imprinting material being shown as patterned and solidified upon the layer;

FIG. 4 is a cross-sectional view of the template contacting imprinting material demonstrating the formation of the weak boundary lamella between solidified imprinting material and a template;

FIG. 5 is a detailed view of the droplets of imprint material, shown in FIG. 2, showing the bifurcation of the droplets into surfactant-rich regions and surfactant-depleted regions;

FIG. 6 is a detailed view of a layer of imprinting material, deposited employing spin-on techniques, showing the bifurcation of the layer into surfactant-rich regions and surfactant-depleted regions;

FIG. 7 is a cross-sectional view of the template contacting solidified imprinting material, deposited as shown in either FIG. 5 or 6, formed on a substrate including a primer layer;

FIG. 8 is a plan view showing the chemical structure of a component of a composition that may be employed to form the primer layer shown in FIGS. 2, 3, and 7, in accordance with one embodiment of the present invention;

FIG. 9 is a plan view showing the chemical structure of a component of a composition that may be employed to form the primer layer shown in FIGS. 2, 3, and 7, in accordance with a second embodiment of the present invention;

FIG. 10 is a plan view showing the chemical structure of a component of a composition that may be employed to form the primer layer shown in FIGS. 2, 3, and 7, in accordance with a third embodiment of the present invention; and

FIG. 11 is a plan view showing the chemical structure of a component of a composition that may be employed to form the primer layer shown in FIGS. 2, 3, and 7, in accordance with a fourth embodiment of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

Referring to FIGS. 1 and 2, a mold 36, in accordance with the present invention, may be employed in system 10, and may define a surface having a substantially smooth or planar profile (not shown). Alternatively, mold 36 may include features defined by a plurality of spaced-apart recessions 38 and protrusions 40. The plurality of features defines an original pattern that forms the basis of a pattern to be formed on a substrate 42. Substrate 42 may comprise a bare wafer or a wafer with one or more layers disposed thereon, one of which is shown as primer layer 45. To that end, reduced is a distance “d” between mold 36 and substrate 42. In this manner, the features on mold 36 may be imprinted into a conformable region of substrate 42, such as an imprinting material disposed on a portion of surface 44 that presents a substantially planar profile. It should be understood that the imprinting material may be deposited using any known technique, e.g., spin-coating, dip coating and the like. In the present example, however, the imprinting material is deposited as a plurality of spaced-apart discrete droplets 46 on substrate 42. Imprinting material is formed from a composition that may be selectively polymerized and cross-linked to record the original pattern therein, defining a recorded pattern.

Specifically, the pattern recorded in the imprinting material is produced, in part, by interaction with mold 36, e.g., electrical interaction, magnetic interaction, thermal interaction, mechanical interaction or the like. In the present example, mold 36 comes into mechanical contact with the imprinting material, spreading droplets 36, so as to generate a contiguous

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formation 50 of the imprinting material over surface 44. In one embodiment, distance “d” is reduced to allow sub-portions 52 of imprinting material to ingress into and fill recessions 38. To facilitate filling of recessions 38, before contact between mold 36 and droplets 46, the atmosphere between mold 36 and droplets 46 is saturated with helium or is completely evacuated or is a partially evacuated atmosphere of helium.

The imprinting material is provided with the requisite properties to completely fill recessions 38 while covering surface 44 with a contiguous formation of the imprinting material. In the present embodiment, sub-portions 54 of imprinting material in superimposition with protrusions 40 remain after the desired, usually minimum, distance “d” has been reached. This action provides formation 50 with sub-portions 52 having a thickness t_1 , and sub-portions 54, having a thickness t_2 . Thicknesses “ t_1 ” and “ t_2 ” may be any thickness desired, dependent upon the application. Thereafter, formation 50 is solidified by exposing the same to the appropriate curing agent, e.g., actinic energy, such as broadband ultraviolet energy, thermal energy or the like, depending upon the imprinting material. This causes the imprinting material to polymerize and cross-link. The entire process may occur at ambient temperatures and pressures, or in an environmentally-controlled chamber with desired temperatures and pressures. In this manner, formation 50 is solidified to provide side 56 thereof with a shape conforming to a shape of a surface 58 of mold 36.

Referring to FIGS. 1, 2 and 3, the characteristics of the imprinting material are important to efficiently pattern substrate 42 in light of the unique patterning process employed. For example, it is desired that the imprinting material have certain characteristics to facilitate rapid and even filling of the features of mold 36 so that all thicknesses t_1 are substantially uniform and all thicknesses t_2 are substantially uniform. To that end, it is desirable that the viscosity of the imprinting material be established, based upon the deposition process employed, to achieve the aforementioned characteristics. As mentioned above, the imprinting material may be deposited on substrate 42 employing various techniques. Were the imprinting material deposited as a plurality of discrete and spaced-apart droplets 46, it would be desirable that a composition from which the imprinting material is formed have relatively low viscosity, e.g., in a range of 0.5 to 20 centipoises (cPs). Considering that the imprinting material is spread and patterned concurrently, with the pattern being subsequently solidified into formation 50 by exposure to radiation, it would be desired to have the composition wet surface of substrate 42 and/or mold 36 and to avoid subsequent pit or hole formation after polymerization. Were the imprinting material deposited employing spin-coating techniques, it would be desired to use higher viscosity materials, e.g., having a viscosity greater than 10 cPs and typically, several hundred to several thousand cPs, with the viscosity measurement being determined in the absence of a solvent.

In addition to the aforementioned characteristics, referred to as liquid phase characteristics, it is desirable that the composition provide the imprinting material with certain solidified phase characteristics. For example, after solidification of formation 50, it is desirable that preferential adhesion and release characteristics be demonstrated by the imprinting material. Specifically, it is beneficial for the composition from which the imprinting material is to be fabricated to provide formation 50 with preferential adhesion to substrate 42 and preferential release of mold 36. In this fashion, reduced is the probability of distortions in the recorded pat-

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tern resulting from the separation of mold **36** therefrom due to, inter alia, tearing, stretching or other structural degradation of formation **50**.

The constituent components of the composition that form the imprinting material to provide the aforementioned characteristics may differ. This results from substrate **42** being formed from a number of different materials. As a result, the chemical composition of surface **44** varies dependent upon the material from which substrate **42** is formed. For example, substrate **42** may be formed from silicon, plastics, gallium arsenide, mercury telluride, and composites thereof. As mentioned above, substrate **42** may include one or more layers shown as primer layer **45**, e.g., dielectric layer, metal layer, semiconductor layer, planarization layer and the like, upon which formation **50** is generated. To that end, primer layer **45** would be deposited upon a wafer **47** employing any suitable technique, such as chemical vapor deposition, spin-coating and the like. Additionally, primer layer **45** may be formed from any suitable material, such as silicon, germanium and the like. Additionally, mold **36** may be formed from several materials, e.g., fused-silica, quartz, indium tin oxide, diamond-like carbon, MoSi, sol-gels and the like.

It has been found that the composition from which formation **50** is generated may be fabricated from several different families of bulk materials. For example, the composition may be fabricated from vinyl ethers, methacrylates, epoxies, thiolenes and acrylates, just to name a few.

An exemplary bulk material from which to form formation **50** is as follows:

Bulk Imprinting Material

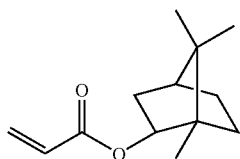
isobornyl acrylate

n-hexyl acrylate

ethylene glycol diacrylate

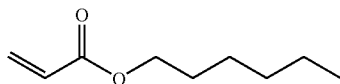
2-hydroxy-2-methyl-1-phenyl-propan-1-one

The acrylate component, isobornyl acrylate (IBOA), has the following structure:



and comprises approximately 47% of bulk material by weight, but may be present in a range of 20% to 80%, inclusive. As a result, the mechanical properties of formation **50** are primarily attributable to IBOA. An exemplary source for IBOA is Sartomer Company, Inc. of Exton, Pa. available under the product name SR 506.

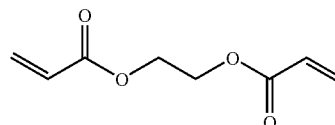
The component n-hexyl acrylate (n-HA) has the following structure:



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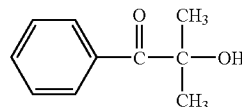
and comprises approximately 25% of bulk material by weight, but may be present in a range of 0% to 50%, inclusive. Also providing flexibility to formation **50**, n-HA is employed to reduce the viscosity of the prior art bulk material so that bulk material, in the liquid phase, has a viscosity in a range 2-9 Centipoises, inclusive. An exemplary source for the n-HA component is the Aldrich Chemical Company of Milwaukee, Wis.

A cross-linking component, ethylene glycol diacrylate, has the following structure:



and comprises approximately 25% of bulk material by weight, and may be present in a range of 10% to 50%, inclusive. EGDA also contributes to the modulus and stiffness buildup, as well as facilitates cross-linking of n-HA and IBOA during polymerization of the bulk material.

An initiator component, 2-hydroxy-2-methyl-1-phenyl-propan-1-one is available from Ciba specialty Chemicals of Tarrytown, N.Y. under the trade name DAROCUR® 1173, and has the following structure:



and comprises approximately 3% of the bulk material by weight, and may be present in a range of 1% to 5%, inclusive. The actinic energy to which the initiator is responsive is broadband ultraviolet energy generated by a medium-pressure mercury lamp. In this manner, the initiator facilitates cross-linking and polymerization of the components of the bulk material.

It has been disclosed, however, in co-pending U.S. patent application Ser. No. 11/068,171, (now U.S. Pat. No. 7,307,118), filed Feb. 28, 2005, entitled "Composition to Reduce Adhesion Between a Conformable Region and a Mold," having Frank Xu and Michael N. Miller listed as inventors, that desirable preferential adhesion and release properties, as discussed above, may be achieved by producing a weak boundary layer, lamella **60**, between mold **36**, surface **58** and formation **50**, shown in FIGS. **3** and **4**. Lamella **60** remains after solidification of the imprinting material. As a result, the adhesion forced between mold **36** and formation **50** are minimal. To that end, found beneficial was employing a composition for the imprinting material that includes one of several compositions, such as the BULK IMPRINTING MATERIAL discussed above, along with a component that contains low surface energy groups, referred to as a surfactant component and fully described in U.S. patent application Ser. No. 11/068,171, filed Feb. 28, 2005, entitled "Composition to Reduce Adhesion Between a Conformable Region and a Mold," having Frank Xu and Michael N. Miller listed as inventors, which is incorporated by reference herein.

Referring to FIG. **5**, after deposition of the imprinting material, the surfactant component rises, after a period of time, to the air liquid interface, providing droplets **146** of imprinting material with a bifurcated concentration of mate-

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rials. In a first portion, droplets **146** include a higher concentration of the surfactant component, referred to as a surfactant-component-rich (SCR) sub-portion **136**, than the second portion, referred to as a surfactant-component-depleted (SCD) sub-portion **137**. SCD sub-portion **137** is positioned between surface **44** and SCR sub-portion **136**. SCR sub-portion **136** attenuates the adhesion forces between mold **36** and the imprinting material, once the imprinting material is solidified. Specifically, the surfactant component has opposed ends. When the imprinting material is in the liquid phase, i.e., polymerizable, one of the opposed ends has an affinity for the bulk material included in the imprinting material. The remaining end has a fluorine component.

Referring to FIGS. **4** and **5**, as a result of the affinity for the bulk material, the surfactant component is orientated so that the fluorine component extends from an air-liquid interface defined by the imprinting material and the surrounding ambient.

Upon solidification of the imprinting material, a first portion of the imprinting material generates a lamella **60** and a second portion of the imprinting material is solidified, i.e., polymeric material shown as formation **50**. Lamella **60** is positioned between formation **50** and mold **36**. Lamella **60** results from the presence and location of the fluorine components in the SCR sub-portion **136**. Lamella **60** prevents strong adhesion forces from being developed between mold **36** and formation **50**. Specifically, formation **50** has first and second opposed sides **62** and **64**. Side **62** adheres to mold **36** with a first adhesion force. Side **64** adheres to substrate **42** with a second adhesion force. Lamella **60** results in the first adhesion force being less than the second adhesion force. As a result, mold **36** may be easily removed from formation **50** while minimizing distortions and/or the force required to separate mold **36** therefrom. Although formation **50** is shown with side **62** being patterned, it should be understood that side **62** may be smooth, if not planar.

Furthermore, if desired, it is possible to generate lamella **60** so as to be disposed between formation **50** and substrate **42**. This may be achieved, for example, by applying imprinting material to mold **36** and subsequently contacting substrate **42** with the imprinting material on mold **36**. In this manner, it can be said that formation **50** will be disposed between lamella **60** and the body, e.g., mold **36** or substrate **42**, upon which the polymerizable material is deposited. It should be understood that were the imprinting material deposited employing spin-coating techniques, similar bifurcated concentration of materials would occur, as shown in FIG. **6** with respect to SCR sub-portion **236** and second and SCD sub-portion **237**. The time required for the bifurcation is dependent upon several factors, including the size of molecules in the composition and the viscosity of the composition. Only a few seconds is needed to achieve the aforementioned bifurcation of composition with viscosity below twenty cPs. Material with viscosity in the hundreds of cPs, however, may require a few seconds to several minutes.

It has been discovered, however, that lamella **60** may not be uniform. Some regions of lamella **60** are thinner than others, and in some extreme cases, lamella **60** may be absent in an extremely small percentage of the template surface so that template **36** is in contact with formation **50**. As a result of the thinner regions of lamella **60** and in the absence of lamella **60**, distortion and/or delamination of formation **50** from substrate **42** may occur. Specifically, upon separation of mold **36**, formation **50** is subjected to a separation force F_S . Separation force F_S is attributable to a pulling force F_P on mold **36** and adhering forces, e.g., Van der Waals forces, between formation **50** and mold **36** as reduced by lamella **60**. Due to the

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presence of lamella **60** separation force F_S typically has a magnitude that is less than the magnitude of an adhering force F_A between formation **50** and substrate **42**. However, with the reduction, or absence, of lamella **60**, local separation force F_S may approach the magnitude of local adhering force F_A . By local forces what is meant are the forces present in a given region of lamella layer **60**, which in this example are the local forces proximate to a thin region of lamella layer **60** or where lamella layer **60** is substantially absent. This leads to distortion and/or delamination of formation **50** from substrate **42**.

Referring to FIG. **7**, in the presence of primer layer **45**, a more complex situation exists due to the presence of two interfaces **66** and **68**. At a first interface **66** a first adhering force F_1 is present between primer layer **45** and formation **50**. At a second interface **68** a second adhering force, F_2 , is present between primer layer **45** and wafer **47**. It is desired that the separation force F_S have a magnitude that is less than either adhering forces F_1 and F_2 . However, due to variations in the thickness, or absence, of lamella **60**, as discussed above, separation force F_S may be similar or approach the magnitude of one or both of adhering forces F_1 and F_2 . This may cause delamination of formation **50** from primer layer **45**, primer layer **45** from wafer **47** or both.

The present invention reduces, if not avoids, the delamination problem mentioned above by forming primer layer **45** from a material that increases the probability that first F_1 and second F_2 adhering forces of the first and second interface, respectively, are greater than the separation force F_S in view of lamella layer fluctuations. To that end, primer layer **45** is formed from a composition that forms strong bonds at interface **66**, i.e., between primer layer **45** and formation **50**, as well as, i.e., between interface **66**, primer layer **45** and wafer **47**. In the present example, adhesion between primer layer **45** and formation **50** at first interface **66** is the result of covalent bonding, i.e., covalent bonds between the composition from which primer layer **45** is formed and the composition from which formation **50** is formed are present. Adhesion between primer layer **45** and wafer **47** may be achieved through any one of various mechanisms. These mechanisms may include covalent bonds formed between the composition from which primer layer **45** is formed and the material from which wafer **47** is formed. Alternatively, or in addition to, the covalent bonds, ionic bonds may be formed between the composition from which primer layer **45** is formed and the material from which wafer **47** is formed. Alternatively, or in addition to, the covalent bonds, and/or the ionic bonds or both, adhesion between the composition from which primer layer **45** is formed and the material from which wafer **47** is formed may be achieved vis-à-vis Van der Waals forces.

This is achieved by forming primer layer **45** from a composition that includes a multi-functional reactive compound, i.e., a compound that contained two or more functional groups generally represented as follows:



In which R, R', R'' and R''' are linking groups and x, y, z are averaged repeating numbers of the groups associated therewith. These repeating units could be randomly distributed. The groups X and X' denote the functional groups, with the understanding that typically, the functional group X differs

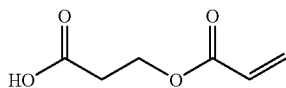
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from functional group X'. One of the functional groups X and X', for example X', is selected to achieve cross-reaction with the material from which substrate **42** is formed to adhere thereto by forming a covalent bond therewith, ionic bond therewith and/or Van der Waals forces.

One of the remaining functional groups X and X', for example X, is selected to achieve cross-reaction with the material from which formation **50** is formed to form a covalent bond therebetween. The functionality of the X group is established so the cross-reaction occurs during polymerization of formation **50**. As a result, the selection of functional group X depends upon the characteristics of the material from which formation **50** is formed. It is desired that functional group X react with the functional groups of the composition from which formation **50** is formed. For example, were formation **50** formed from acrylate monomers, X might be comprised of acrylic, vinyl ether, and or alkoxyl functional groups, and/or functional groups that could copolymerize with acrylic groups in formation **50**. As a result, X functional groups cross-react in response to ultraviolet actinic energy.

Functional groups X' may also participate in the cross-linking and polymerization reactions of primer layer **45**. Typically, X' functional groups facilitate polymerization and cross-linking in response to an actinic energy that differs from the actinic energy in response to which X functional groups cross-react. The X' functional groups in the present example facilitate cross-linking of molecules in primer layer **45** in response to exposure to thermal energy. Typically, functional groups X' are selected to facilitate cross-reaction with substrate **42** through three mechanisms: 1) direct reaction with material from which substrate **42** is formed; 2) reaction with cross-linker molecules with a linking functional group of the cross-linker reacting with substrate **42**; and 3) polymerization of and cross-linking of primer layer **45** so that chains of molecules of sufficient length may be developed to connect between formation **50** and substrate **42**.

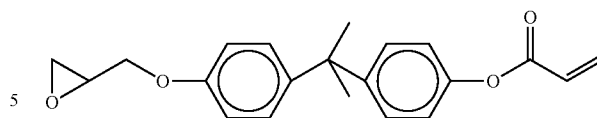
Referring to FIGS. 7 and 8, an exemplary multi-functional reactive compound that may be employed to form primer layer **45** in the presence of formation **50** being formed from BULK MATERIAL includes a β -carboxyethyl acrylate, available from UCB Chemicals in Smyrna, Ga. under the product name β -CEA. β -CEA is an aliphatic compound having the following structure:



The X' functional group **70** provides carboxylic functionality. The X functional group **72** provides acrylate functionality. Functional groups **70** and **72** are coupled to opposing ends of a backbone component **74**.

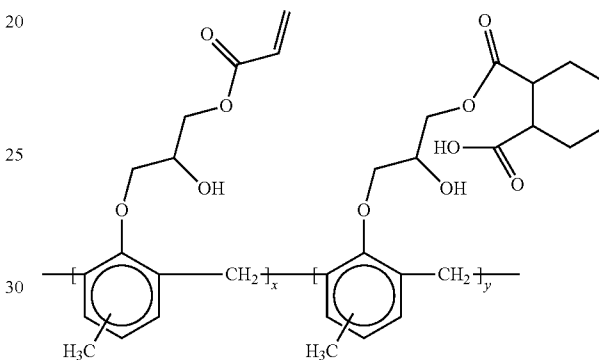
Referring to FIGS. 7 and 9, another multi-functional reactive compound that may be employed to form primer layer **45** in the presence of formation **50** being formed from BULK MATERIAL includes an aromatic bis-phenyl compound available from UCB Chemicals in Smyrna, Ga. under the product name Ebecryl 3605 that has the following structure:

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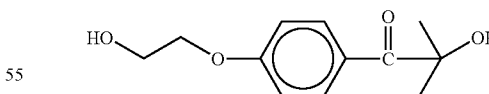
The X' functional group **76** provides epoxy functionality. The X functional group **78** provides acrylate functionality. Functional groups **76** and **78** are coupled to opposing ends of a backbone component **80**.

Referring to FIGS. 7 and 10, another multi-functional reactive compound that may be employed to form primer layer **45** in the presence of formation **50** being formed from BULK MATERIAL includes an aromatic compound available from Schenectady International, Inc. in Schenectady, N.Y. under the product name Isorad 501 that has the following structure:



where x and y are integers indicating repeating units that are randomly distributed. The X' functional group **82** provides carboxylic functionality. The X functional group **84** provides acrylate functionality. Functional groups **82** and **84** are coupled to opposing ends of a backbone component **86**.

Referring to FIGS. 7 and 11, in addition to cross-reaction with formation **50**, functional group X may generate radicals that function to facilitate polymerization of the composition from which formation **50** is formed during solidification of the same. As a result, the functional group X would facilitate polymerization of formation **50** upon exposure to actinic energy, e.g., broadband ultraviolet energy. An exemplary multi-functional reactive compound that includes these properties is a photoinitiator available from Ciba Specialty Chemicals in Tarrytown, N.Y. under the tradename Irgacure 2959 and has the following structure:



The X' functional group **90** provides hydroxyl functionality. The X functional group **92** provides initiator-type functionality. Specifically, in response to exposure to broadband ultraviolet energy, the functional group X undergoes alpha-cleavage to generate benzoyl type of radicals. The radicals facilitate radical polymerization of the composition from which formation **50** is formed. Functional groups **90** and **92** are coupled to opposing ends of a backbone component **94**.

Several compositions were formed, including some of the aforementioned multi-functional reactive compounds, to

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determine the adhering strength of interfaces **66** and **68**. An exemplary composition including a multi-functional reactive compound is as follows:

Composition 1

β -CEA

DUV30J-16

where DUV30J-16 comprises approximately 100 grams of composition 1 and β -CEA comprises approximately 0.219 grams. DUV30J-16 is a bottom anti-reflective coating, BARC, available from Brewer Science in Rolla, Mo. containing 93% solvent, and 7% non-solvent reactive components. DUV30J-16 contains phenolic resins, and its crosslinker can react with the carboxylic functional group. It is believed that DUV30J-16 will not form covalent bonds with formation **50**. In another composition, β -CEA was replaced by a cross-linking agent, a catalyst and IsoRad 501. Both the cross-linking agent and catalyst is sold by Cytec Industries, Inc. of West Patterson, N.J. The cross-linking agent is sold under the product name Cymel 303ULF. One of the main components of Cymel 303ULF is hexamethoxymethyl-melamine (HMMM). The methoxyl functional groups of HMMM can participate in many condensation reactions. The catalyst is sold under the product name Cycat 4040 providing the following composition:

Composition 2

DUV30J-16

IsoRad 501

Cymel 303ULF

Cycat 4040

Approximately 100 grams of COMPOSITION 2 comprises DUV30J-16, 0.611 gram of COMPOSITION 2 comprises IsoRad 501, 0.175 gram of COMPOSITION 2 comprises Cymel 303ULF and 0.008 gram of COMPOSITION 2 comprises Cycat 4040.

Another composition that may be employed as the multi-functional reactive compound omits DUV30J-16. The composition is as follows:

Composition 3

IsoRad 501

Cymel 303ULF

Cycat

PM Acetate

Composition 3 includes approximately 77 grams of IsoRad 501, 22 grams of Cymel 303ULF and one gram of Cycat 4040. IsoRad 501, Cymel 303ULF and Cycat are combined. The combination of IsoRad 501, Cymel 303ULF and Cycat are then introduced into approximately 1900 grams of PM Acetate. PM Acetate is a product name of a solvent consisting of 2-(1-Methoxy)propyl acetate sold by Eastman Chemical Company of Kingsport, Tenn.

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A fourth composition is identical to COMPOSITION 3, excepting for the amount of the constituent components included. For example, COMPOSITION 4 includes approximately 85.2 grams of IsoRad 501, 13.8 grams of Cymel 303ULF and one gram of Cycat 4040. IsoRad 501, Cymel 303ULF and Cycat are combined. The combination of IsoRad 501, Cymel 303ULF and Cycat are then introduced into approximately 1900 grams of PM Acetate.

A fifth composition is identical to COMPOSITION 3, excepting for the amount of the constituent components included. For example, COMPOSITION 5 includes approximately 81 grams of IsoRad 501, 18 grams of Cymel 303ULF and one gram of Cycat 4040. IsoRad 501, Cymel 303ULF and Cycat are combined. The combination of IsoRad 501, Cymel 303ULF and Cycat are then introduced into approximately 1900 grams of PM Acetate.

Each of the five compositions discussed above with respect to primer layer **45**, COMPOSITIONS 1-5, are deposited upon substrate **42** employing spin-coating techniques wherein the substrate is rotated at a velocity between 500 and 4,000 revolutions per minute so as to provide a substantially smooth, if not planar layer with uniform thickness. This is followed by exposing the compositions to thermal actinic energy of 180° C. (Celsius) for approximately two minutes.

The five compositions described above, COMPOSITIONS 1-5, were employed, along with IMPRINTING MATERIAL, to generate comparative data of the strength of the adhesion forces of interfaces **66** and **68** which was compared against baseline measuring of a primer layer **45** formed entirely from DUV30J-16, which is not known to form covalent bonds with formation **50** formed from IMPRINTING MATERIAL. To that end, formation **50**, formed from BULK IMPRINTING MATERIAL, and primer layer **45**, formed from COMPOSITIONS 1-5 and the base line COMPOSITION, were deposited and then solidified between two glass slides (not shown). Each glass slide (not shown) is approximately 1 mm thick, 75×25 mm in the lateral dimension.

Before deposition of primer layer **45** and formation **50** the glass slides (not shown) are cleaned. Specifically each glass slide (not shown) is exposed to Piranha solution (H₂SO₄: H₂O₂=2.5:1 by volume). The glass slides (not shown) are subsequently rinsed with de-ionized water, sprayed with isopropyl alcohol, and exposed to a stream of fluid for drying, e.g., a stream of nitrogen gas. Thereafter, the glass slides (not shown) are baked at 120° C. (Celsius) for 2 hours.

Primer layer **45** is deposited onto each of the two glass slides (not shown) employing spin-on techniques with a spin speed up to 3000 rpm. Primer layer **45** is laid on the glass slides (not shown) on hot plates at 180C for 2 minutes. In other words, each of COMPOSITIONS 1-5, as well as the baseline composition, are solidified, i.e., polymerized and cross-linked, by exposure to thermal energy. Formation is formed employing drop dispense techniques mentioned above. Specifically, BULK IMPRINTING MATERIAL is disposed as a plurality of droplets onto primer layer **45** on one of the two glass slides. The BULK IMPRINTING MATERIAL is then sandwiched between two primer layers **45** by having the primer layer on the two glass slides (not shown) facing one another and contacting BULK IMPRINTING MATERIAL. Typically, a longitudinal axis of one of the two glass slides (not shown) extends orthogonally to the longitudinal axis of the remaining glass slide (not shown). The BULK IMPRINTING MATERIAL is solidified, i.e., polymerized, and cross-linked by exposing the two glass slides (not shown) to actinic energy, such as broadband ultraviolet wavelengths, using a medium pressure mercury UV lamp for 40 seconds at 20 mW/cm² intensity.

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To measure the strength of the adhesion, a four-point bending fixture (not shown) was adopted for the adhesion test and technique, similar to that described in "Measurement of Adhesive Force Between Mold and Photocurable Resin in Imprint Technology" Japanese Journal of Applied Physics, Vol. 41 (2002) pp. 4194-4197. The maximum force/load was taken as the adhesion value. The beam distance of the top and bottom two points is 60 mm. The load was applied at the speed of 0.5 mm per minute. Employing this test, it was determined that delamination occurred at 6.1 pounds of force when primer layer 45 was formed with the baseline composition. A separation force of approximately 6.5 pounds was reached before delamination occurred with primer layer 45 being formed from COMPOSITION 1. A separation force of approximately 9.1 pounds was reached before delamination occurred with primer layer 45 being formed from COMPOSITION 2. When primer layer 45 was formed from each of COMPOSITIONS 3, 4 or 5, one or both of the two glass slides (not shown) failed (broke) before delamination occurred. As a result, forces of up to 11 pounds were measured without delamination being observed. As a result, it is observed that COMPOSITIONS 3, 4 and 5 provide primer layer 45 with superior operational characteristics in that it effectively prevents delamination were lamella layer 60 to have undesirably thin regions or be altogether absent.

The embodiments of the present invention described above are exemplary. Many changes and modifications may be made to the disclosure recited above while remaining within the scope of the invention. For example, the solvent PM Acetate is employed primarily to dissolve the other constituent components of COMPOSITIONS 3, 4 and 5. As a result, many common photo-resist solvents may be employed in lieu of PM Acetate, such as Diethylene Glycol Monoethyl Ether Acetate, Methyl Amyl Ketone or the like. Further, the solid contents of COMPOSITIONS 3, 4 and 5, i.e., IsoRad 501, Cymel 303ULF and Cycat may comprise between 0.1% to 70% of the composition, weight, and more preferably in a range of 0.5% to 10% by weight, with the remaining quantity consisting of the solvent. The solid component of each of COMPOSITIONS 3, 4, and 5 may comprise 50% to 99%, by weight of IsoRad 501, 1% to 50%, by weight of Cymel 303ULF and 0% to 10% by weight of Cycat 4040. The scope of the invention should not, therefore, be limited by the above description, but instead should be determined with reference to the appended claims along with their full scope of equivalents.

What is claimed is:

1. A method of adhering a layer to an imprint lithography substrate, said method comprising:

- (i) depositing a composition comprising a cross-linker and a multi-functional reactive compound upon said imprint lithography substrate, wherein the multi-functional reactive compound comprises:
 - (a) an organic backbone group; and
 - (b) a first functional group and a second functional group coupled to opposing ends of the organic backbone group, wherein the functional groups are different, and wherein the first functional group is acrylate and the second functional group is selected from the group consisting of a carboxylic group and an epoxy group;
- (ii) thermally curing said composition, wherein thermally curing comprises:
 - (a) forming interactions between the imprint lithography substrate and the multi-functional reactive compound through the second functional group;

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- (b) forming interactions between the substrate and the second functional group of the multi-functional reactive compound through the cross-linker; and
 - (c) forming covalent or ionic bonds between the cross-linker and the multi-functional reactive compound through the second functional group;
 - (iii) depositing a polymerizable material on said thermally cured composition to form said layer; and
 - (iv) exposing the polymerizable material to actinic energy to polymerize the polymerizable material, wherein polymerizing the polymerizable material comprises forming covalent bonds between the polymerizable material and the multi-functional reactive compound in the thermally cured composition through the first functional group.
2. The method as recited in claim 1, wherein said interactions are selected from a set of mechanisms consisting of covalent bonds, ionic bonds and van der Waals forces.
3. The method as recited in claim 1, wherein depositing the polymerizable material comprises depositing discrete drops of the polymerizable material on the thermally cured composition.
4. The method of claim 1, wherein the cross-linker and the multi-functional reactive compound are different.
5. The method of claim 1, further comprising forming interactions between the cross-linker and the multi-functional reactive compound through the second functional group, wherein forming interactions between the cross-linker and the multi-functional reactive compound through the second functional group comprises cross-linking the composition.
6. A method of adhering a layer to an imprint lithography substrate, said method comprising:
- (i) depositing a composition comprising a cross-linker and a multi-functional reactive compound upon said imprint lithography substrate, wherein the multi-functional reactive compound comprises:
 - (a) an organic backbone group; and
 - (b) a first functional group and a second functional group coupled to opposing ends of the organic backbone group, wherein the first functional group is an acrylate group and the second functional group is selected from the group consisting of a carboxylic group and an epoxy group;
 - (ii) solidifying said composition to form a solidified composition adhered to the imprint lithography substrate, wherein solidifying comprises:
 - (a) forming an interaction between the second functional group and the imprint lithography substrate, and wherein the interaction is selected from the group consisting of covalent bonds, ionic bonds, and van der Waals forces; and
 - (b) forming interactions between the substrate and the second functional group of the multi-functional reactive compound through the cross-linker; and
 - (c) forming covalent or ionic bonds between the cross-linker and the multi-functional reactive compound through the second functional group;
 - (iii) depositing discrete drops of a polymerizable material upon said solidified composition;
 - (iv) contacting the polymerizable material with an imprint lithography mold;
 - (v) polymerizing the polymerizable material, wherein polymerizing comprises forming covalent bonds between the polymerizable material and the first functional groups in the solidified composition during polymerization of the polymerizable material; and
 - (vi) separating the imprint lithography mold from the polymerized material.

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7. The method as recited in claim 6, wherein solidifying said composition comprises thermally curing said composition and wherein polymerizing the polymerizable material comprises exposing the polymerizable material to actinic energy.

8. The method of claim 6, wherein the cross-linker and the multi-functional reactive compound are different.

9. The method of claim 6, further comprising forming interactions between the cross-linker and the multi-functional reactive compound through the second functional group, wherein forming interactions between the cross-linker and the multi-functional reactive compound through the second functional group comprises cross-linking the composition.

10. A method of adhering a layer to an imprint lithography substrate, said method comprising:

(i) depositing a composition comprising an organic multi-functional reactive compound upon said imprint lithography substrate, wherein the multi-functional reactive compound comprises:

(a) an organic backbone group; and

(b) a first functional group and a second functional group coupled to opposing ends of the organic backbone group, wherein the functional groups are different, and wherein the first functional group is an acrylate group and the second functional group is selected from the group consisting of a carboxylic group and an epoxy group;

(ii) thermally curing said composition, wherein thermally curing comprises forming interactions between the imprint lithography substrate and the multi-functional reactive compound through the second functional group;

(iii) depositing a polymerizable material on said thermally cured composition to form said layer; and

(iv) exposing the polymerizable material to actinic energy to polymerize the polymerizable material, wherein polymerizing the polymerizable material comprises forming covalent bonds between the polymerizable material and the multi-functional reactive compound in the thermally cured composition through the first functional group.

11. The method of claim 10, wherein the second functional group is a carboxylic group.

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12. The method of claim 10, wherein the second functional group is an epoxy group.

13. The method of claim 10, wherein thermally curing further comprises forming interactions between the cross-linker and the imprint lithography substrate.

14. A method of adhering a layer to an imprint lithography substrate, said method comprising:

(i) depositing a composition comprising an organic multi-functional reactive compound upon said imprint lithography substrate, wherein the multi-functional reactive compound comprises:

(a) an organic backbone group; and

(b) a first functional group and a second functional group coupled to opposing ends of the organic backbone group, and wherein the first functional group is an acrylate group and the second functional group is selected from the group consisting of a carboxylic group and an epoxy group;

(ii) solidifying said composition to form a solidified composition adhered to the imprint lithography substrate, wherein solidifying comprises forming an interaction between the second functional group and the imprint lithography substrate, and wherein the interaction is selected from the group consisting of covalent bonds, ionic bonds, and van der Waals forces;

(iii) depositing discrete drops of a polymerizable material upon said solidified composition;

(iv) contacting the polymerizable material with an imprint lithography mold;

(v) polymerizing the polymerizable material, wherein polymerizing comprises forming covalent bonds between the polymerizable material and the first functional groups in the solidified composition during polymerization of the polymerizable material; and

(vi) separating the imprint lithography mold from the polymerized material.

15. The method of claim 14, wherein the solidifying further comprises forming interactions between the cross-linker and imprint lithography substrate.

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