



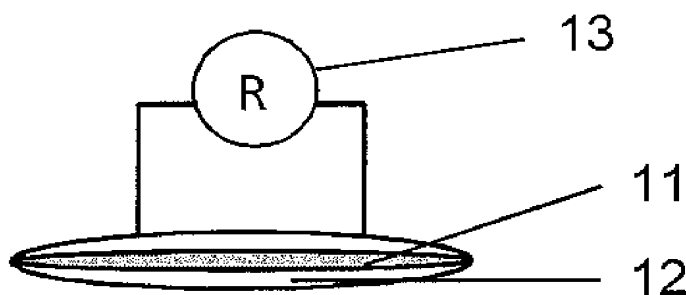
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(54) **Title:** SURFACE COATINGSFigure 1

(57) **Abstract:** A method of protecting a component from corrosion and providing electrical conductivity to one or more electrical contacts on the component, the method including the steps of placing the component in a chamber, and coating the component by plasma deposition of a polymer coating formed from any one or more of the following precursor monomers, acrylate, methacrylate or organosilane.



Surface Coatings

The present invention relates to surface coatings and is especially, although not exclusively, related to corrosion resistant and/or liquid repellent surface coatings which also afford electrical conductivity to an article to which the coating has been applied. The invention also relates to methods of applying surface coatings to articles. Articles are for example the individual components of an electronic (hand held) device.

Electrical circuits are commonly used in components such as printed circuit boards (PCBs), batteries, SIM-cards and so on. These components are put together during a final assembly to form a working device - such as a mobile phone or smartphone - that is ready for use by a customer.

It is known to provide an assembled working device with a surface coating in order to protect the device *per se* against corrosion. For instance, it is known to provide an assembled working mobile phone with a surface coating so that the surface of the mobile phone has water resistant properties.

However, coating assembled devices has significant drawbacks. For instance, protective coatings applied in such a manner do not necessarily protect the surfaces of internal components of the device, particularly the electrical contacts of the internal components. This is because the coating is applied to a device that has already been assembled and therefore not all of the inside surfaces of a device are exposed to the protective coating. Thus, if such a device subsequently comes into contact with water it may be rendered unusable due to moisture penetrating the device and damaging the circuitry.

Several methods have been proposed to address this problem, which methods include the provision of a protective coating over the electrical contacts of a component.

In one method an electrically insulating bonding layer which functions to provide a protective coating is laminated to a component. The electrically insulating bonding layer is laminated to a flat surface of the component at elevated temperature by providing pressure thereon. In a subsequent step vias or holes are drilled through the electrically insulating bonding layer at the positions where an electrical interconnection is required. It is to be appreciated that this is a complex and time consuming multi-step process which requires great accuracy when drilling to ensure that good electrical contact is achieved once the components are assembled.

In another method a thermoplastic insulating matrix which functions to provide a protective coating is applied to a component. The insulating matrix comprises a plurality of conductive nickel fibres. Ideally, the longitudinal axis of each fibre is oriented in a direction perpendicular to the major plane of the component so that once the components are assembled to form a device an electrical contact is made between the components. However, this method is problematic in that each nickel fibre requires an insulating coating to prevent the component itself from shorting. Moreover, the efficacy of such a coating is limited by the degree of accuracy of the fibre orientation. It has been found that it is not always possible to orient all of the fibres in a direction perpendicular to the major plane of the component. Therefore, components having such a coating are often vulnerable to electrical shorting.

In another method an adhesive connecting layer which functions to provide a protective coating is laminated to a component. The adhesive layer enables a second component to be connected thereto. The adhesive layer consists of an insulating, often thermoplastic, resin containing electrically conductive particles arranged such that an electrical contact is made once the components are assembled without the components themselves being vulnerable

to electrical shorting. However, due to limitations on the smallest size of the electrically conductive particles available adhesive connecting layers of this type are not suitable for components which are to be included in small devices such as mobile phones.

5 It is also known to mask the electrical contact points of a component before applying a protective conformal coating to the component. The masking is preferably by means of an adhesive strip. Once the protective coating has been applied to the component the masking is removed so that an electrical contact is made once the components are assembled. It is to be appreciated that the step of masking the electrical contacts requires great accuracy in
10 order to ensure that only the points of contact are rendered free from coating - this is time consuming. Moreover, the step of masking the contact points does not solve the problem of the circuitry becoming damaged when the device is exposed to the elements, *e.g.* water, because there remains a gap (*i.e.* after the masking has been removed) for moisture to penetrate.

15

As it will be appreciated the prior art coatings and methods of coating require a flat surface so that the coating may be laminated or adhered thereto. Moreover, the surface must be capable of withstanding pressure during the step of lamination or adhesion.

20 However, the components used by the applicant may be flexible and/or the surfaces thereof may be tightly curved. Further, the components may be delicate and therefore not able to withstand the application of physical pressure.

It is a first non-exclusive object of the invention to provide a surface coating which
25 overcomes, or at least substantially reduces, the disadvantages associated with the known coatings described above.

It is a second non-exclusive object of the invention to provide a surface coating having a substantially uniform thickness across at least one surface of an article and/or a surface coating which has better adhesion to an article than that known in the prior art.

- 5 It is a further non-exclusive object of the invention to provide an improved method of coating an article with a protective surface coating. Articles are for example the individual components of an electronic (hand held) device.

10 An even further non-exclusive object of the invention includes a method of treating delicate and/or flexible components.

An even further non-exclusive object of the invention provides a waterproof device of which one or all of the internal components are coated with a protective surface coating.

- 15 It is to be understood that by using the term “device”, the Inventors mean a completely assembled unit that is ready to use. A device has a (outer) surface that is presented to the user. The outer surface has a decorative value to attract users. A device is built up of one or more “components”. In this invention, the Inventors use the term “component” to indicate all electrical parts that are located in the inside of the device. The surfaces of these
20 components are not visible at the outside of the device once the device is fully assembled.

In a first aspect the invention provides a method of coating a component and/or a device to protect the component and/or the device from corrosion and liquid damage whilst affording electrical conductivity to the coated component and/or the coated device, the method
25 comprising providing on the component and/or the device a layer of a protective polymer species formed from any one or more of the following precursor monomers:

- acrylate;

- methacrylate; or
- organosilane.

Preferably, the method comprises the step of applying the polymer coating across one or
5 more electrical contacts of the component or the components.

Preferably, the method comprises the step of applying the polymer coating to the component
or the components such that no area of the component or the components surface is
uncoated.

10

Preferably, the coating is electrically conductive through the thickness of the coating.

Preferably, the coating is electrically insulating across the plane of the coating.

15 This is advantageous because when components are subsequently assembled, an electrical
contact is possible between the contacts of one (*e.g.* coated) component and the contacts of
an abutting or adjacent component. There is also little or no risk of the device shorting, *e.g.*
from an electrical signal passing from one conductive track on a component to another
conductive track on the same component, because the coating is not electrically conductive
20 in the transverse plane.

Preferably, the method comprises the step of protecting at least part of the outer surface of
the device from the coating. For instance, the method may comprise the initial step of
applying a barrier material, *e.g.* an adhesive tape or film, to at least part of the outer surface
25 of the device to protect the at least part of the outer surface from the coating.

The at least part of the outer surface of the device may be the screen of a mobile phone device, or a tablet computer, or the outer buttons of a music player, e.g. the volume buttons of a MP3 player, or the back cover of a mobile phone, or the camera lens of the mobile phone, or any other outer surface of the device that is visible in normal use. In some
5 embodiments substantially the entire outer surface of the device is protected from the coating so that only inner surfaces of the device, which are essentially the (outer) surfaces of the (internal) components, have a coating applied thereto. The advantage being that no unwanted visible or textured traces of the polymer coating are presented to the user.

- 10 Preferably, the method comprises the step of depositing the precursor monomer by means of low power and/or low pressure plasma polymerisation.

In some embodiments, the method comprises first the step of a pre-treatment for cleaning and/or etching and/or activating the electronic component or components prior to coating. A
15 pre-treatment in the form of an activation and/or cleaning and/or etching step might be advantageous in improving the adhesion and cross-linking of the polymer coating.

Adhesion of the polymer coating to the electronic component or components is essential for the corrosion resistance of the coated surface. After production of the electronic component,
20 it is often found that some residues from soldering, gluing, handling remain. These residues are mostly organic contamination or contamination in the form of oxides. When the component is coated without a pre-treatment, a substantial part of the polymer coating binds with these residues, which may cause pinholes later on. The pre-treatment in the form of an activation and/or a cleaning and/or an etching removes the contamination and allows
25 improved adhesion of the coating with the surface of the electronic component or components.

Preferably, this pre-treatment is carried out using reactive gases, such as H_2 , or O_2 , additionally or alternatively with etching reagents such as CF_4 . It can also be carried out with inert gases, such as Ar, N_2 or He. Mixtures of the foregoing gases can also be used.

- 5 More preferably the pre-treatment is done with O_2 , Ar, or a mixture of O_2 and Ar.

Preferably, the pre-treatment is performed from 30 seconds to 30 minutes, for example from 45 seconds to 15 minutes, preferably 1 minute to 10 minutes, e.g. 9, 8, 7, 6, 5, 4, 3, 2, or 1 minutes. The duration of the pre-treatment depends on the precursor used and on the
10 degree of contamination on the part to be treated.

The power used in the pre-treatment can be applied in continuous wave mode or in pulsed wave mode.

- 15 Preferably, when applied in continuous wave mode in a 490 litre plasma chamber, the pre-treatment takes place at powers of 5 to 5000 W, more preferably 25 to 4000 W, even more preferably at 50 to 3000 W, say 75 to 2500 W, such as 100 to 2000 W, e.g. 2000, 1900, 1800, 1750, 1700, 1600, 1500, 1400, 1300, 1250, 1200, 1100, 1000, 950, 900, 850, 800, 750, 700, 650, 600, 550, 500, 450, 400, 350, 300, 250, 200, 175, 150, 125, or 100 W.

20

- Preferably, when applied in pulsed wave mode in a 490 litre plasma chamber, the pre-treatment takes place at a power of 5 to 5000 W, more preferably 25 to 4000 W, even more preferably at 50 to 3000 W, say 75 to 2500 W, such as 100 to 2000 W, e.g. 2000, 1900, 1800, 1750, 1700, 1600, 1500, 1400, 1300, 1250, 1200, 1100, 1000, 950, 900, 850, 800,
25 750, 700, 650, 600, 550, 500, 450, 400, 350, 300, 250, 200, 175, 150, 125, or 100 W.

When applied in pulsed power mode, the pulse frequency may be from 100 Hz to 10 kHz having a duty cycle from approximately 0.05 to 50 %, with the optimum parameters being dependent on the gas or gas mixture used.

- 5 Preferably, in a 490 litre plasma chamber, the operating pressure for the pre-treatment is 10 to 500 mTorr, more preferably 15 to 250 mTorr, even more preferably 20 to 200 mTorr, say 25 to 175 mTorr, such as 30 to 150 mTorr, e.g. 150, 140, 130, 125, 120, 110, 100, 95, 90, 85, 80, 75, 70, 65, 60, 55, 50, 45, 40, 35, or 30 mTorr.
- 10 For systems of other dimensions, with another volume and/or electrode set-up, the power value, the operating pressure and the pre-treatment time are varied in a way that the best process parameters for the pre-treatment are used.

- A 490 litre plasma chamber can accommodate a number of components, for example, 200 smartphones, or 200 mobile phones, or 100 tablet computers, or 70 keyboards in one single batch. Such a chamber can be used for both pre-treatment and polymer coating treatment of components or devices.
- 15

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In the embodiments where no pre-treatment is performed, the coating step is the first and only step of the whole process. When a pre-treatment is used, the protective polymer coating is applied as a next step, which can be carried out in the same chamber. .

- 25 Clearly it is advantageous for a number of reasons to perform the pre-treatment and the coating treatment in the same chamber: this is more efficient from a handling point of view, and will be quicker and cheaper than using multiple chambers.

Preferably, the pre-treatment and the coating step are carried out in the same chamber without opening the chamber in between the steps, to avoid or at least minimise the risk of deposition of contaminants or additional contamination from the atmosphere on the electronic component or components in between pre-treatment step and coating step.

lin a 490 litre plasma chamber, , the operating pressure for the coating step is approximately 10 to 500 mTorr, preferably approximately 15 to 200 mTorr, more preferably approximately 20 to 150 mTorr, say 30 to 100 mTorr, say less than 100, 90, 80, 70, 60, 50, 40, 30 mTorr, such as 50 mTorr.

The method may apply the low power and/or low pressure plasma polymerisation in continuous wave (CW) or in pulsed power mode.

Preferably, the method involves a polymerisation time of approximately 30 seconds to approximately 30 minutes. The longer the polymerisation time the thicker the resultant polymer coating. Therefore, the choice of polymerisation time and hence coating thickness depends to a certain degree on the use or application of the component being coated.

Preferably, the method involves a polymerisation time of approximately 1 minute to approximately 25 minutes, e.g. approximately 3 minutes to approximately 25 minutes, e.g. approximately 3 minutes to approximately 20 minutes, e.g. approximately 5 minutes to approximately 20 minutes, e.g. approximately 7 minutes to approximately 20 minutes, e.g. approximately 10 minutes to approximately 20 minutes, e.g. approximately 10 minutes to approximately 18 minutes, e.g. approximately 10 minutes to approximately 16 minutes, e.g. approximately 12 minutes to approximately 16 minutes, such as approximately 13, 14 or 15 minutes.

Preferably, the method comprises the steps of:

- providing the protective polymer species to at least one component (*e.g.* SIM-card, battery, microphone, connectors or mobile phone handset); and
- 5 • assembling the component with one or more further components to form the working device.

The method may also comprise the step of initially disassembling the working device.

- 10 The method may also comprise the step of conducting a pre-treatment to clean and/or activate and/or etch one or more surfaces of the component or components prior to coating deposition.

In a second aspect the invention provides a component and/or a device having a polymer
15 coating thereon for protecting the component and/or the device from corrosion whilst affording electrical conductivity to the coated component and/or the coated device, the coating being formed from any one or more of the following precursor monomers:

- acrylate;
- methacrylate; or
- 20 • organosilane.

The device may be an electronic (hand held) device such as a mobile phone; a smart phone; a personal digital assistant (PDA); a tablet computer; a loudspeaker; a music player such as an MP3 player; an e-reader; a keyboard; a GPS system; a device used for sport such as a
25 pedometer, heart rate monitor, cadence sensor and the like; a video camera; or a photo camera.

The device is built up from one or more components, such as a printed circuit board (PCB), a battery, a SIM-card, a connector, and so on.

Preferably, the component or the components comprises polymer coating across one or
5 more electrical contacts thereof.

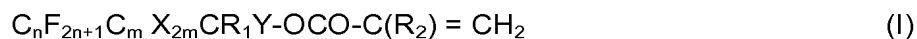
Preferably, the component or the components comprises no uncoated surface .

Alternatively, at least a part of the outer surface of the device may be uncoated, *e.g.*
10 substantially the entire outer surface of the device may be uncoated. By substantially the entire outer surface we mean the surfaces of the device visible to a user, *e.g.* the camera lens, the back cover, the (touch)screen, the outside buttons.

Preferably, the coating is a result of the or each precursor monomer being polymerised and
15 deposited by means of low power and/or low pressure plasma polymerisation.

Preferably, the acrylate and/or methacrylate precursor monomers comprise a perfluorocarbon chain.

20 Preferably, the acrylate and/or methacrylate precursor monomers have a generic formula (I):



wherein *n* is 2 to 9, *m* is 1 to 9, *X* and *Y* is H, F, Cl, Br or I and *R*₁ is –H or an alkyl, *e.g.* –CH₃, or a substituted alkyl, *e.g.* an at least partially halo-substituted alkyl, *R*₂ is H or an alkyl, *e.g.* –CH₃, or a substituted alkyl, *e.g.* an at least partially halo substituted alkyl.

25

In some embodiments *R*₁ may be H, *R*₂ may be H and *Y* may be H.

In some embodiments n is 2 to 6, m is 0 to 9, X and Y is H, F, Cl, Br or I and R₁ is H or an alkyl, e.g. -CH₃, or a substituted alkyl, e.g. an at least partially halo-substituted alkyl, R₂ is H or an alkyl, e.g. -CH₃, or a substituted alkyl, e.g. an at least partially halo substituted alkyl. In such embodiments the inventors have discovered that the polymer coating has a superhydrophobic surface with contact angles for water of more than 100 degrees. The same coatings are superoleophobic with oil repellency levels above 4, for example up to 6 according to ISO14419. Such superhydrophobic and/or superoleophobic surfaces formed from this particular class of monomer are found to be free of perfluorooctanoic acid (PFOA) or perfluorooctane sulfonate (PFOS), in contrast to the superhydrophobic and/or superoleophobic surfaces formed from embodiments with n from 7 to 9, e.g. 8, n being the number of carbon atoms of the perfluorocarbon chain of the molecule. By free we mean that the degree of PFOA and PFOS is below the detectable limit.

Surprisingly, the Inventors have found that having one or all components and the inside of the device coated with superhydrophobic and/or superoleophobic surfaces formed from monomers having the general formula (I) may make electronic devices such as electronic hand held devices splash-proof and/or waterproof by blocking the water ingress into the (re)assembled device upon accidental exposure to water, even without coating the outside of the device.

And even in those cases where water is forced to enter the electronic (hand held) device, any damage to the latter will be minimised if not obviated entirely because of the separately coated key electronic component or components. The protective coating on the inside of the electronic (hand held) device protects the device against short circuiting due to water ingress.

Superhydrophobic and/or superoleophobic surfaces formed from monomers having the general formula (I) may make electronic (hand held) devices splash-proof and/or waterproof. The coated devices reach IPX 6 to IPX 7, depending on the composition of the (re)assembled electronic (hand held) device itself and on the precursor monomer used.

5

In some industries, particularly the production of wire and cables, there has been a shift away from use of perfluorocarbons because in some but not all circumstances toxic by-products may be formed. The Inventors have surprisingly found that by use of organosilane precursor monomers no toxic by-products are formed.

10

Preferably, the organosilane precursor monomers comprise siloxanes, silanes or mixtures thereof.

Preferably, the organosilane precursor monomers have a generic formula (II), or are cyclic monomers comprising the repeating unit (III).

15

Monomers comprising formula (II) are of the structure



wherein X is O or NH, Y_1 is $\begin{array}{c} Y_3 \\ | \\ -Si-Y_4 \\ | \\ Y_5 \end{array}$, Y_2 is $\begin{array}{c} Z_3 \\ | \\ -Si-Z_4 \\ | \\ Z_5 \end{array}$ and wherein Y_3 , Y_4 , Y_5 , Z_3 , Z_4 , and Z_5 are each independently H or an alkyl group. The alkyl groups may be linear or branched. The alkyl groups are a C_1 to C_{10} -alkyl, preferably C_1 to C_5 -alkyl, more preferably C_1 to C_2 -alkyl, for example $-CH_3$.

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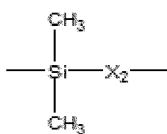
In some embodiments Y_1 and Y_2 are the same, and so Y_3 will be the same as Z_3 , Y_4 the same as Z_4 and Y_5 the same as Z_5 .

25

Preferably neither silicon atom in Y_1 and/or Y_2 is bound to three H-atoms, so that preferably at least one of Y_3 , Y_4 , or Y_5 , and at least one of Z_3 , Z_4 and Z_5 are each independently H or an alkyl group. In some embodiments, any or each of Y_3 and Z_3 , Y_4 and Z_4 , Y_5 and Z_5 may be identical.

Preferably, the organosilane precursor monomer is hexamethyldisiloxane (HMDSO) or hexamethyldisilazane (HMDS).

10 Possible cyclic monomers are monomers comprising n times the repeating unit (III)



(III)

wherein X_2 is O or NH, and wherein n is 2 to 10, preferably 3 to 6, for example 6, 5, 4, or 3.

Preferably, the method comprises the step of introducing the or each organosilane precursor monomer to a chamber, e.g. a plasma chamber, by means of a carrier gas such as H_2 , N_2 , O_2 , N_2O , CH_4 , He or Ar, most preferably O_2 .

The composition of gas introduced to the chamber preferably comprises about 1 % to about 50 % carrier gas. Preferably, the composition of gas introduced to the chamber comprises about 5 % to about 30 % carrier gas, and more preferably about 10 % carrier gas.

Preferably, the coating has a thickness in the range of about 10 nm to about 1 μm , preferably about 10 nm to about 500 nm, or more preferably about 20 nm to about 250 nm, or yet more preferably about 30 nm to about 150 nm, or most preferably about 40 nm to about 100 nm, such as about 70 nm. It is to be understood that the thickness of the coating will vary

depending on the substrate, the choice of precursor monomer, the deposition conditions (e.g. temperature, pressure, flow rate) and process time etc.

The Inventors have also found that, contrary to prior art teachings, those coatings using acrylates or methacrylate precursor monomers do not require a carrier gas because these types of monomer are able to strike the plasma themselves in order to initiate polymerisation.

Preferably, the coating is applied in a single step – in other words deposited in an uninterrupted single process. The thickness of the deposited single polymer layer is in the range from approximately 10 nm to 500 nm, usually approximately 100 nm, although this depends on the monomer precursors used and also the treatment time.

As used herein the terms “x-axis” and “y-axis” shall refer to axes extending in a plane forming or comprising a surface of the component.

As used herein the term “z-axis” shall refer to an axis perpendicular to the major surface of the component. Thus, an electrical contact through the coating between one component and an adjacent component may be termed z-axis conductivity.

In order that the invention may be more readily understood, it will now be described by way of example only and with reference to the accompanying drawings, in which:

Figure 1 shows a schematic illustration of a needle having a coating in accordance with the invention;

Figure 2 shows a schematic illustration of an assembled device (a) and a disassembled device (b);

Figure 3 shows a schematic illustration of an electronic component coated with a coating according to the invention; and

Figure 4 shows a schematic illustration of a plasma system suitable to perform the method of the present invention.

5

The Inventors have discovered that any one or more of the following precursor monomers may be utilised to form a corrosion resistant and/or liquid repellent surface coating which also affords electrical conductivity to a component to which the coating has been applied.

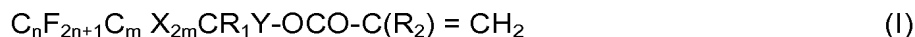
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The precursor monomers may be selected from the following families:

- acrylates;
- methacrylates;
- organosilanes; or mixtures thereof.

15

More specifically, the inventors have found that precursor monomers having the formula (I)



form coatings having particularly good corrosion resistance whilst affording electrical conductivity to the component to which they are applied.

20

In formula (I) n is 2 to 9, m is 1 to 9, X and Y is H, F, Cl, Br or I and R₁ is H or an alkyl, e.g. –CH₃, or a substituted alkyl, e.g. an at least partially halo-substituted alkyl, R₂ is H or an alkyl, e.g. –CH₃, or a substituted alkyl, e.g. an at least partially halo substituted alkyl.

25

In one embodiment n is 8, m is 1, X is H, R₁ is H, Y is H and R₂ is H, i.e. 1H,1H,2H,2H-perfluorodecyl acrylate.

In a second embodiment n is 8, m is 1, X is H, R₁ is H, Y is H, and R₂ is –CH₃, i.e. 1H,1H,2H,2H-perfluorodecyl methacrylate.

In a third embodiment n is 6, m is 1, X is H, R₁ is H, Y is H, and R₂ is H, *i.e.* 1H,1H,2H,2H-perfluorooctyl acrylate.

In a fourth embodiment n is 6, m is 1, X is H, R₁ is H, Y is H, and R₂ is –CH₃, *i.e.* 1H,1H,2H,2H-perfluorooctyl methacrylate.

5

The Inventors have found that organosilane precursor monomers, such as one or more of siloxanes or silanes also form coatings having particularly good corrosion resistance whilst affording electrical conductivity to the component to which they are applied. Organosilanes have been found to produce no toxic by-products when deposited by low power plasma deposition.

10

The organosilane precursor monomers may be represented by general formula (II), or are cyclic monomers comprising the repeating unit (III).:



wherein X is O or NH, Y₁ is $\begin{array}{c} Y_3 \\ | \\ -Si-Y_4 \\ | \\ Y_5 \end{array}$, Y₂ is $\begin{array}{c} Z_3 \\ | \\ -Si-Z_4 \\ | \\ Z_5 \end{array}$ and wherein Y₃, Y₄ and Y₅, Z₃, Z₄, and Z₅ are each independently H or an alkyl group. The alkyl groups may be linear or branched. The alkyl groups are a C₁ to C₁₀-alkyl, preferably C₁ to C₅-alkyl, more preferably C₁ to C₂-alkyl, for example –CH₃.

20

Preferably neither silicon atom in Y₁ and/or Y₂ is bound to three H-atoms, so that preferably at least one of Y₃, Y₄, or Y₅, and at least one of Z₃, Z₄ and Z₅ are each independently H or an alkyl group. In some embodiments, any or each of Y₃ and Z₃, Y₄ and Z₄, Y₅ and Z₅ may be identical.

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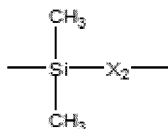
In a first embodiment, X is O, Y₁ is identical to Y₂, and Y₃, Y₄, Y₅, Z₃, Z₄ and Z₅ are –CH₃, *e.g.* hexamethyldisiloxane (HMDSO).

In a second embodiment X is NH, Y₁ is identical to Y₂, and Y₃, Y₄, Y₅, Z₃, Z₄ and Z₅ are –CH₃,
 5 indicating the monomer hexamethyldisilazane (HMDSN).

In a third embodiment X is O, Y₃, Y₄, Y₅, Z₃ and Z₄ are –CH₃ and Z₅ is H, indicating the monomer pentamethyldisiloxane.

10 In a fourth embodiment X is O, Y₁ is identical to Y₂, and Y₃, Y₄, Y₅, Z₃, Z₄ and Z₅ are –CH₃, indicating the monomer hexaethyldisiloxane.

Possible cyclic monomers are monomers comprising n times the repeating unit (III)



(III)

15 wherein X₂ is O or NH, and wherein n is 2 to 10, preferably 3 to 6, for example 6, 5, 4, or 3.

In another embodiment X₂ is O and n is 4, indicating the monomer octamethylcyclotetrasiloxane.

20 In yet another embodiment X₂ is O and n is 5, indicating the monomer decamethylcyclopentasiloxane.

In yet another embodiment X₂ is O and n is 6, indicating the monomer dodecylmethylcyclohexasiloxane.

In yet another embodiment X_2 is NH and n is 3, indicating the monomer hexamethylcyclotrisilazane.

5 In a yet further embodiment X_2 is NH and n is 4, indicating the monomer octamethylcyclotetrasilazane.

In some embodiments a pre-treatment step to clean and/or activate and/or etch one or each component of a working device is performed prior to the coating deposition step is preferred.

10 Preferably, this pre-treatment is done using reactive gases, e.g. H_2 , O_2 , etching reagents such as CF_4 , or inert gases, such as Ar, N_2 or He. Mixtures of the foregoing gases can also be used.

More preferably the pre-treatment is done with O_2 , Ar, or a mixture of O_2 and Ar.

15

In those cases where a pre-treatment is performed to clean and/or activate and/or etch the surface of the individual components, this step is done after evacuation of the chamber and before introduction of one or more different precursor monomers. Suitable reagents for performing this pre-treatment process are for example O_2 , Ar, or a mixture of O_2 and Ar.

20

During the pre-treatment, the power can be applied in continuous wave mode or in pulsed wave mode.

When applied in pulsed power mode, the pulse frequency may be from 100 Hz to 10 kHz
25 having a duty cycle from approximately 0.05 to 50 %, with the optimum parameters being dependent on the gas or gas mixture used and configuration of the chamber and the plasma used.

The Applicants have found that in a 490 litre plasma chamber, for satisfactory results the operating pressure for the pre-treatment can range from 10 to 500 mTorr, but that good results are obtained in the range 30 to 150 mTorr.

5

The pre-treatment can be performed over a period ranging from 30 seconds to 30 minutes, but more typically over periods from 1 minute to 10 minutes. Factors affecting the duration of the pre-treatment include the precursor used, the degree of contamination on the individual components to be treated, the size of the chamber, the power used and pattern or shape of the plasma.

10

The protective coating of the present invention is typically applied to the components of a working device such as a mobile phone, a smartphone or a hearing aid as follows.

15

During the manufacture of a working device, the individual components of the device are placed into a plasma chamber such that their surfaces, including the electrical contact points, will be exposed to a precursor monomer in the presence of a plasma. The chamber is evacuated to a low pressure and the monomer precursor is introduced into the chamber. The plasma is then struck. The plasma initiates polymerisation such that the components are therefore coated with a protective polymer coating (the deposition process will be discussed in further detail below). In this embodiment it is to be appreciated that the individual components are treated prior to their assembly into the final working device.

20

Alternatively, in those cases where a part or the complete outer surface of the device is already manufactured, at least part of this outer surface is covered with a barrier material, e.g. an adhesive tape or film.

25

Alternatively, if possible, the part or the complete outer surface of the device that is already manufactured, is not placed in the plasma chamber and no coating is applied.

Alternatively, a fully assembled working device, such as a mobile phone, a smartphone, a keyboard or a hearing aid, may be disassembled into its individual components so that the components can be treated at a component level. The individually coated components are subsequently reassembled to form a working device having a protective coating thereon.

Alternatively, the method comprises the step of protecting at least part of the outer surface of the device from the coating. For instance, the method may comprise the initial step of applying a barrier material, e.g. an adhesive tape or film, to at least part of the outer surface of the device to protect the at least part of the outer surface from the coating.

Once the device has been assembled or reassembled as described above, the device may have a further coating applied thereto by placing the device as a whole, into a plasma chamber and repeating the deposition process. It may be preferable that the device may be partially covered with a barrier material to prevent deposition of the polymer on parts of the device such as a screen or camera lens,

The plasma deposition process is carried out as follows. Once the individual components or the device *per se* have been introduced to the plasma chamber, the chamber is evacuated and one or more different precursor monomers are introduced. These monomers are normally introduced in gaseous form. An RF electromagnetic field is turned on and a plasma struck. During short treatment times, typically around 2 to 15 minutes, a plasma will cause a substantially uniform protective polymer coating to be deposited onto the components. The coating covers all surfaces of the component that have been exposed to the plasma,

including any electrical contact points. The RF electromagnetic field is then turned off, which will extinguish the plasma and the plasma chamber is brought back to atmospheric pressure.

The power used for the coating step can be applied in continuous wave mode or in pulsed wave mode. It is known from prior art that for complex precursors, especially acrylates and methacrylates of the present invention, the average applied power at which the plasma coating process takes place has to be low to keep the functional group of precursor molecule intact,

The average power at which the coating process will take place depends strongly on the precursor monomer used and on the size and design of the chamber and layout of the electrodes. The choice of manner in which the power is applied will depend upon the required average power for the given system and the pre-cursor monomer or monomers used. For example, in a small chamber of 50 litres volume, a low average power will normally be required. However, it may not be possible to meet the low power requirements with a continuous power mode of plasma, so a pulsed plasma mode is used instead.

Preferably, in a 490 litre plasma chamber, the applied power for the coating process, when applied in continuous wave mode, is in the range from 5 to 5000 W, more preferably approximately 10 to 2500 W, even more preferably approximately, say 15 to 2000W, for example 20 to 1500 W, say 25 to 1000 W, say 30 to 750 W, say 35 to 500 W, say 500, 475, 450, 425, 400, 375, 350, 325, 300, 275, 250, 225, 200, 190, 180, 175, 170, 160, 150, 140, 130, 125, 120, 110, 100, 95, 90, 85, 80, 75, 70, 65, 60, 55, 50, 45, 40, or 35 W.

Preferably, in a 490 litre plasma chamber, the applied power for the coating process, when applied in pulsed wave mode, is approximately 5 to 5000 W, more preferably approximately 10 to 4000 W, even more preferably approximately, say 20 to 3000W, for example 30 to 2500 W, say 50 to 2000 W, say 75 to 1500 W, say 100 to 1000 W, say 1000, 975, 950, 925,

900, 875, 850, 825, 800, 775, 750, 725, 700, 675, 650, 625, 600, 575, 550, 525, 500, 475, 450, 425, 400, 375, 350, 325, 300, 275, 250, 225, 200, 190, 180, 175, 170, 160, 150, 140, 130, 125, 120, 110, or 100 W.

- 5 Preferably, when in pulsed power mode, the pulse repetition frequency may be from 100 Hz to 10 kHz having a duty cycle from approximately 0.05 to 50 %, with the optimum parameters being dependent on the monomer used.

Preferably, the radiofrequency electrode or electrodes generate a high frequency electric
10 field at frequencies of from 20 kHz to 2.45 GHz, more preferably of from 40 kHz to 13.56 MHz, with 13.56 MHz being preferred.

In some embodiments, the plasma chamber has at least two inlets for the precursor monomer or the pre-treatment reagents.

15

Preferably, during the pre-treatment step, each inlet feeds the pre-treatment gas or gas mixture into a distribution system that distributes the gas or gas mixture evenly across the chamber. For example, the inlet may feed into a manifold which feeds the chamber.

- 20 Preferably, during the coating step, each inlet feeds monomer, preferably combined with a carrier gas for organosilane precursor monomers, into a monomer distribution system that distributes the monomer, preferably combined with a carrier gas for organosilane precursor monomers, evenly across the chamber. For example, the monomer inlet may feed into a manifold which feeds the chamber.

25

In one embodiment, each inlet is spatially distinct. For instance, a first inlet may be provided in a first wall of the plasma chamber and a second inlet may be provided in a different wall to the first inlet, e.g. the opposite wall.

- 5 In some embodiments, the method may comprise introducing the pre-treatment gas or gas mixture and/or the monomer, preferably combined with a carrier gas for organosilane precursor monomers, into the plasma chamber in a first flow direction; and switching the flow after a predetermined time, for example from 10 to 200 seconds, for example from 30 to 180, 40 to 150 seconds, for example less than 150, 140, 130, 120, 110, 100, 90, 80, 70, 60, 50, 10 40, 30 or 20 seconds to a second flow direction.

Preferably, further switching of the flow direction may be executed, e.g. the flow may be switched back to the first flow direction or to one or more further flow directions.

- 15 Preferably, the monomer and/or carrier gas/gases mixture may enter the plasma chamber in the first flow direction for between 20 to 80 % of a single process time or 30 to 70 % of the time or 40 to 60 % of the time or 50 % of the time.

- 20 Preferably, the monomer and/or carrier gas/gases mixture may enter the plasma chamber in the second flow direction for between 20 to 80 % of a single process time or 30 to 70 % of the time or 40 to 60 % of the time or 50 % of the time.

- 25 Preferably, the first and second flow directions flow in substantially opposite directions. For instance, during a process, pre-treatment gas or gas mixture and/or monomer, preferably combined with a carrier gas for organosilane precursor monomers, may be introduced into the plasma chamber via walls which are substantially opposite to each another.

In another embodiment, the first and second flow directions may flow in direction oriented at a tangential angle to each other. In case of two flow directions, the flow is on one direction and then switched preferably in the reverse direction.

5 An advantage of switching the flow direction during the process is that a more uniform monomer distribution and corresponding pressure distribution is created inside the plasma chamber. In larger chambers, e.g. chambers of 200 litres and more, this allows a more uniform pre-treatment (which is a cleaning and/or activation and/or etching process), and more uniform coating thicknesses on the electronic components to be coated, throughout
10 the plasma chamber. Smaller chambers of for example 50 litres are generally small enough to allow uniform plasma distribution throughout the chamber from a single chamber inlet, although in some cases cross-flow may have a benefit in these chambers as well.

With reference to Figure 4, a plasma deposition system that may be used for the present
15 invention will now be described. The system, indicated generally at 100, includes a vacuum chamber 101 in communication with input apparatus 102 via an input line 120 and an exhaust apparatus 103 via an output line 130. The input apparatus 102 includes a liquid monomer supply system 121, a gas supply system 122 and first 125 and second 126 chamber inlet valves. In the embodiments where a pre-treatment is performed using a gas
20 mixture, additional gas supply systems may be used. The exhaust apparatus 103 includes in flow order first 131 and second 132 pump valves, a throttle valve 133, a roots and rotary pump 134 and an exhaust valve 135.

Within the vacuum chamber 101 there are electrodes 104 arranged in stacked formation.
25 Interposed between each plasma electrode set 104 is a sample tray 105. For purpose of clarity only a single sample tray 105 is shown in Figure 4, the sample tray 105 being interposed between the lower pair of electrodes 104. The space between adjacent electrode

sets 104 is a sample chamber. In use, one or more electronic components are located on or within the sample tray 105. The sample tray 105 is subsequently positioned between a pair of electrodes 104 within the vacuum chamber 101.

- 5 For the ease of the description, the process sequence that is described below only includes a coating step, using a monomer that does not require a carrier gas. In some embodiments a pre-treatment cleaning and/or activation and/or etching process is performed prior to coating deposition. In those cases where the precursor monomer is an organosilane monomer, a carrier gas is preferably used to strike the plasma.

10

Once the sample tray 105 is located within the vacuum chamber 101, the chamber 101 is evacuated and the pressure is reduced to a base level vacuum by means of the pump 134 with the first 131 and second 132 pump valves open and the first 125 and second 126 chamber inlets valves closed. A quantity of monomer is vaporized in the liquid monomer supply system 127.

15

In alternative embodiments, solid or gaseous monomer may be used. In embodiments where the monomer is a solid then it may also be vaporised, e.g. by heating in a canister. In embodiments where the monomer is a gas then there is typically no need for vaporisation.

20

Once the target lower pressure within the vacuum chamber 101 is reached, the first pump valve 131 is closed, and the first chamber inlet valve 125 and the liquid monomer supply valve 138 are opened. Controlled amounts of precursor monomer vapour flow into the chamber 101. The pressure within the chamber 101 is regulated at an operating level, which depends on the equipment and the monomer used, by either introduction of more monomer or regulation of the throttle valve 133, which is typically a butterfly valve.

25

Once the pressure within the chamber 101 is stable, the electrode sets 104 are activated to generate plasma within the chamber 101. Thus, the monomer is activated and polymerisation occurs on one or more surfaces of the electronic component or components on sample trays 105.

5

During the process, the direction of monomer flow through the chamber 101 may be switched by control of the first 125 and second 126 chamber inlet valves and first 131 and second 132 pump valves. For example, for half the time the first chamber inlet valve 125 is open and the first pump valve 131 is closed (with the second chamber inlet valve 126 closed and second pump valve 132 open). For the remainder of the time, the second chamber inlet valve 126 is open and second pump valve 132 closed (with the first chamber inlet valve 125 closed and the first pump valve 131 open). This means that for half the time monomer flows from one side of the chamber 101 to another and for the remainder of the time vice versa. For example, for half the time monomer flows from the right to the left and for the remainder of the time monomer flows from the left to the right. The direction of monomer flow may be alternated one or more times during a single process run.

10

15

The inlet 120 and outlet 130 lines are separate from each other. The inlet line 120 may be coupled to a distribution system arranged to distribute gas across the chamber 101. The distribution system may be integrated on or within the wall of the chamber 101 so that it can be maintained at the same temperature as the chamber 101.

20

At the end of either process it is recommended for operator safety that the chamber inlet valves 125, 126 are closed and the chamber 101 pressure is reduced to base level to remove any residual monomer present. An inert gas such as nitrogen is introduced from a third canister 122 by opening valve 124. The nitrogen is used as a purge fluid and is

25

pumped away with the residual monomer. After completion of the purge, the vacuum is removed and air is introduced into the chamber 101 until atmospheric pressure is achieved.

The precursor monomers of the present invention may be either gaseous or liquid. Liquid
5 precursors are evaporated by heating before being introduced into the plasma chamber. Gaseous precursors are introduced into the plasma chamber as such.

Where the precursor monomer or monomers are organosilanes, the or each monomer is preferably introduced into the plasma chamber in combination with a carrier gas, such as H₂,
10 N₂, O₂, N₂O, CH₄, He or Ar. The carrier gas also functions to initiate the polymerisation by striking the plasma.

In one embodiment the carrier gas was O₂ and the total gas flow contained 15 % carrier gas and 85 % monomer.

15 In another embodiment the carrier gas was O₂ and the total gas flow contained 10 % carrier gas and 90 % monomer.

Where the precursor monomer or monomers are acrylates or methacrylates there is no need
20 for a carrier gas because these types of monomer are able to strike the plasma in order to initiate polymerisation themselves.

The coating comprises a single thin polymer layer having a thickness in the range of approximately 20 nm to 200 nm, usually approximately 100 nm, although this depends on the
25 monomer precursors used and also the treatment time.

Once the components have been assembled into a device, the coatings are such that an electrical contact is made through the coating and between two components. In other words the coating is said to be z-axis conductive. Moreover, the risk of the device shorting is very low or close to zero because the coating is electrically insulating in a plane which is orthogonal to the z- axis and in a transverse plane, in other words the x-axis direction and the y-axis direction.

In order to prove the inventive concept the following examples are provided for demonstration purposes only.

Example 1

Referring first to Figure 1 a needle 11 formed from an electrically conductive material was coated by means of depositing a polymer coating 12 by low power plasma deposition. The precursor monomer utilised was 1H,1H,2H,2H-perfluorodecyl acrylate.

Conductivity through the coating was measured every 5 minutes during the polymerisation treatment by means of a resistance measurement meter 13. The data are shown in Table 1.

Treatment time	Coating thickness	Electrically conductive through coating
5 minutes	65 nm	Yes
10 minutes	125 nm	Yes
15 minutes	185 nm	Yes
20 minutes	250 nm	Yes
30 minutes	375 nm	Yes
40 minutes	500 nm	Yes

Table 1: Electrical conductivity as a function of treatment time and coating thickness

As will be appreciated, the results show that the coating remained conductive in the z-axis even after long treatments of 40 minutes where the polymer coating has a thickness of 500 nm.

Example 2

Small electrical components of a microphone for a hearing aid device were coated with protective coatings in accordance with Table 2. In process 1 the precursor monomer was 1H,1H,2H,2H-perfluorodecyl acrylate; in process 2 the precursor monomer used was 1H,1H,2H,2H-perfluorooctyl methacrylate; and in process 3 the precursor monomer used was hexamethyldisiloxane (HMDSO). The components were assembled and the hearing aid device was switched on. It was found that the hearing aid device operated which demonstrates that each coating was electrically conductive through its thickness (as will be appreciated from Table 3).

	Process 1	Process 2	Process 3
Precursor Monomer	C ₁₃ H ₇ O ₂ F ₁₇	C ₁₂ H ₉ O ₂ F ₁₃	HMDSO
Oil repellency (ISO 14419)	Level 8	Level 5-6	Level 0
Electrode	RF/Ground	RF/Ground	RF/Ground
Frequency	13,56 MHz	13,56 MHz	13,56 MHz
Frequency mode	pulsed	cw	cw
Treatment time	2 minutes	5 minutes	5 minutes

Table 2: Overview of process 1 to 3 when coating applied to electronic parts of a microphone for a hearing aid device

Process	Coating thickness	Electrically conductive through coating
Process 1	50 nm	Yes
Process 2	150 nm	Yes
Process 3	300 nm	Yes

Table 3: Shows the thickness of each coating of process 1 to 3 and demonstrates that the coatings are electrically conductive through their thickness

5

Example 3

Figure 2a shows an assembled mobile phone 20 comprising a handset 21, a battery 22 and a SIM-card 23. Each of the handset 21, battery 22 and SIM-card 23 have electrical contacts.

10

After disassembly of the phone 20, the handset 21, battery 22 and SIM-card 23 were placed in a plasma chamber 30 as shown in Figure 2b. The components were pre-treated with O₂ for 2 to 5 minutes and coated with a protective coating according to the invention by means of low power plasma deposition for approximately 10 to 20 minutes.

15

The handset 21, battery 22 and SIM-card 23 were subsequently reassembled to form the usable mobile phone 20. Power to the mobile phone 20 was turned on and the device worked.

20

The mobile phone 20 was then placed underwater for approximately 10 minutes. When the mobile phone 20 was removed from the water and turned on again it functioned.

The mobile phone 20 was also subjected to a complex salt-spray corrosion test and it was found that the functionality thereof was unaffected even after 6 consecutive test cycles. Furthermore, no corrosion was visible.

5 The complex salt-spray corrosion test cycle consisted of 3 steps:

- Spraying of a 5 % salt-water solution onto the sample for 30 minutes
- Storing the sample at high moisture for 120 minutes
- Storing the sample at room temperature for 60 minutes.

10 The same salt-spray test was performed on a mobile phone, the components of which had not been subjected to a protective coating according to the invention. Clear signs of corrosion were visible.

Example 4

15

Electronic components for loud speakers were coated according to the 3 processes in Table 4. Two different monomers were used. After coating the electronic components are tested with a corrosion test according to IEC 60068-2-52. Afterwards, no corrosion was visible for the components pre-treated with Ar and O₂, and a few small corrosion spots were visible on some but not all of the samples coated without pre-treatment. Uncoated reference samples showed heavy corrosion after the corrosion test.

	Process 1	Process 2	Process 3
Pre-treatment	/	Ar	O ₂
Pre-treatment time	/	5 minutes	5 minutes
Precursor Monomer	C ₁₃ H ₇ O ₂ F ₁₇	C ₁₃ H ₇ O ₂ F ₁₇	HMDSO
Frequency	13,56 MHz	13,56 MHz	13,56 MHz

Frequency mode	Cw	cw	cw
Coating time	20 minutes	20 minutes	15 minutes
Corrosion after test	Almost nothing	None	None

Table 4: Overview of process 1 to 3 when coating applied to electronic parts of a loud speaker

Example 5

5

Figure 3 shows an electronic component 40 of an MP3 player which has been coated according to one aspect of the invention with a protective coating 41 by means of low power plasma deposition for approximately 10 minutes. A resistance measurement through the coating 41 by means of a resistance measurement meter 13' indicated electrical conductivity through the thickness of the coating 41. Afterwards, the component 40 was assembled into a working MP3 player.

10

Example 6

15 The following experiment was carried out to demonstrate that the coating is able to withstand repeated weathering and testing.

A copper plate was coated with a protective polymer layer in accordance with the invention.

The coated copper plate was then subjected to the salt-spray corrosion test as described in Example 3, following which no corrosion was observed. Electrical conductivity through the coating was measured and it was confirmed that the coated copper plate was z-axis conductive.

20

This cycle was repeated a second and a third time. No corrosion was observed following each cycle and the coating remained electrically conductive through its thickness.

The fact that no corrosion was observed also confirms that no damage is inflicted on the coating by repeated measurements using the resistance measurement device.

Test cycle	Corrosion	Electrically conductive through coating
1 cycle	No	Yes
2 cycles	No	Yes
3 cycles	No	Yes

Table 5: Shows that no corrosion was observed and the coating remained z-axis conductive following repeated exposure to a corrosion test

Example 7: Oil and water repellence

Applicant discovered that the choice of mode in which the power is applied (either pulsed wave mode or continuous wave mode) depends on the monomer and the equipment used.

This is especially the case for the acrylates and methacrylates used in the present invention. The Applicant has found that perfluoro(meth)acrylates containing maximum 6 carbon atoms in the perfluorocarbon chain result in polymer coatings having significantly better oil repellency levels when deposited in continuous wave mode, rather than in pulsed wave mode. In continuous wave mode oil repellence level 6 according to ISO 14419 is obtained at low power, e.g. at 100 W, and in short treatment times, e.g. 2 minutes in a plasma chamber of 490 l – in which e.g. 200 smartphones or 100 tablet computers are coated in one single batch. It is disadvantageous to use high power, e.g. 350 W, 500 W, 1000 W or even more because the monomer precursor may fragment, leading to poor coatings which tend to have low levels of uniformity of quality and thickness.

Deposition mode	Treatment time (min)	Oil repellency
Continuous wave (cw)	2 minutes	L 6
Pulsed	2 minutes	L 3
Continuous wave (cw)	5 minutes	L 6
Pulsed	5 minutes	L 4

Table 6: Shows the oil repellency levels for continuous wave and pulsed wave processes

5

Example 8: Water ingress and submersion

A mobile phone, such as a smartphone, e.g. an iPhone 4, an iPhone 4S or a Samsung Galaxy II, was coated with a protective polymer coating as follows:

10

- The mobile phone was disassembled by removing the back cover;
- The microphone, camera, SIM-card and battery were removed from the mobile phone;
- The camera lens and the outer surface of the mobile phone were protected with a protective film;
- A plasma pre-treatment was performed to clean, activate and etch the exposed surfaces of the mobile phone;
- Low power continuous wave plasma polymerisation was used to deposit a polymer coating to the exposed surfaces of the mobile phone;
- The protective film was then removed from the camera lens and the outer surface of the mobile phone;

15

20

- The mobile phone was then re-assembled, resulting in a mobile phone having a polymer coating applied to the inside surfaces thereof.

Test 1

- 5 The mobile phone was sprayed with water for 5 minutes on the front, the back, the left and the right side. During spraying, the mobile phone was tilted by an angle of 45°. Afterwards, the mobile phone was tested and no functional defects were observed.

Test 2

- 10 The mobile phone was dropped from a height of 50 cm into a container of water. The mobile phone was left totally submerged for 1 minute. Afterwards, the mobile phone was tested and no functional defects were observed.

Test 3

- 15 An iPhone 4, iPhone 4S and Samsung Galaxy II were coated with a protective polymer coating as described above. Water was then projected at a flow rate of 100 l/min at a pressure of 100 kN/m² from all angles onto the phones for a period of 3 minutes. Afterwards, the moisture sensors had not changed colour and no functional defects were observed.

20 **Test 4**

The iPhone 4, iPhone 4S and Samsung Galaxy II of Test 3 were also submerged in water for 2 minutes. No water ingress was observed after the 2 minutes. The mobile phones were tested and no functional defects were observed.

25 **Test 5**

To force water ingress, coated hand held devices (iPhone 4 and iPhone 4S) according to the above method were submerged in water for 2 minutes. Water was forced to enter the device

via the opening of the charger by dropping the device vertically into the water. After 2 minutes, the hand held devices were taken out of the water and water was allowed to drip out. The devices were tested and no functional defects were observed. The back cover was removed for a control check and the moisture sensors had not changed colour.

5

Test 6

An iPhone 4, iPhone 4S and Samsung Galaxy II were coated according to the above method and then submerged in water for 30 minutes. Afterwards, the back cover was removed for a control check and the moisture sensors had not changed colour. All functions were tested
10 and no functional defects were found. No water ingress was observed.

The coating of the invention can be applied to all exposed surfaces of a component before the component has been assembled into the final device. Further, the subsequently assembled device operates even though the coating has been applied across the electrical
15 contacts of the individual components. The method of deposition requires no additional steps, such as the masking of contact points or the drilling of vias and therefore provides a quick and simple, yet cost effective, solution to providing a device with a corrosion resistant protective coating. The method also avoids the need to apply physical pressure to a component in order to laminate a coating thereto. Thus, the inventive coatings can be
20 applied on flexible and delicate components. As will be appreciated, the inventive coatings protect the circuitry from corrosion and/or liquid damage whilst at the same time enable an electrical contact to be made.

Finally, the embodiments of the invention which utilise organosilane monomers may be
25 preferred because such monomers do not produce toxic by-products when deposited by low power plasma deposition. Thus, organosilane monomers may be considered to be a non-toxic alternative.

Claims

1. A method of protecting a component from corrosion and providing electrical conductivity to one or more electrical contacts on the component, the method including the steps of placing the component in a chamber, and coating the component by plasma deposition of a polymer coating formed from any one or more of the following precursor monomers:
 - acrylate;
 - methacrylate; or
 - organosilane.
2. The method of Claim 1, further including the step of applying the polymer coating to the component such that substantially all of the component surface is coated.
3. The method of any preceding Claim, and in which the plasma is a low power and/or low pressure plasma.
4. The method of any preceding Claim having a polymerisation time of from approximately 30 seconds to approximately 20 minutes.
5. The method of any preceding Claim, further including the steps of:
 - polymer coating at least one component in accordance with any of claims 1 to 4; and
 - assembling the component with one or more further components to form a working device.
6. The method of Claim 5, further including the step of initially disassembling a working device prior to coating the or each component with a polymer coating.

7. A method according to any of the preceding Claims, further including the steps of a pre-treatment process for cleaning or etching or activating the surface to be coated, wherein a pre-treatment agent is an inert gas selected from any one or more of helium, argon or nitrogen, or an active agent including oxygen or CF_4 , or any mixtures thereof.

8. The method of Claim 7, wherein the pre-treatment is carried out for between 30 seconds to 30 minutes.

9. The method of Claim 7, wherein the pre-treatment is carried out for between 1 minute to 10 minutes.

10. The method according to any preceding Claim, wherein the power is applied in continuous wave mode.

11. The method according to any preceding Claim, wherein the power is applied in pulsed mode.

12. The method of any preceding Claim and in which either the pre-treatment agents or the precursor monomers or both may be introduced into the plasma chamber in a first flow direction; and switched to a second flow direction after a predetermined time.

13. The method according to Claim 12, wherein the flow direction may be further switched to a third or fourth flow direction.

14. The method according to either of Claims 12 or 13, wherein the flow direction is further switched back to the first flow direction.

15. The method according to any of Claims 10 to 14, wherein the flow direction is switched between the first and the second flow direction during the plasma deposition process.

5 16. The method according to any of Claims 1 to 6, or 10 to 15 where the precursor monomer is an organosilane, further comprising the step of introducing the precursor monomer to the chamber by means of a carrier gas selected from one or more of H₂, N₂, O₂, N₂O, CH₄, He or Ar, most preferably O₂.

10 17. The method of Claim 16, wherein the composition of gas introduced to the chamber comprises about 1 % to about 50 % of the carrier gas.

18. The method according to any preceding Claim, wherein the component is one or more of a printed circuit board (PCB), a battery, a SIM-card, a connector, or a camera.

15

19. A component having a polymer coating thereon protecting the component from corrosion and providing electrical conductivity to electrical contacts on the component, the coating being formed from any one or more of the following precursor monomers:

- acrylate;
- 20 • methacrylate; or
- organosilane.

20. The component of Claim 19, in which the component is coated across substantially the entire surface, including one or more electrical contacts thereof.

25

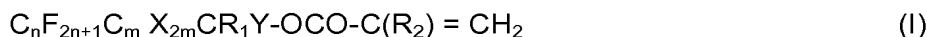
21. The component of Claim 20, wherein the polymer coating is electrically conductive in a direction extending through a thickness of the coating and is substantially electrically insulating in a direction extending parallel to the surface of the polymer coating.

5 22. The component of any one of Claims 19 to 21, wherein the component is one of a printed circuit board (PCB), a battery, a SIM-card, a connector, or a camera.

23. The component of any one of Claims 19 to 22, wherein the / or each acrylate and/or the or each methacrylate precursor monomers include a perfluorocarbon chain.

10

24. The component of any one of Claims 19 to 23, wherein the / or each acrylate and/or the or each methacrylate precursor monomers have a generic formula (I):



wherein n is 2 to 9, m is 1 to 9, X and Y is H, F, Cl, Br or I and R₁ is –H or an alkyl, e.g. –CH₃,
 15 or a substituted alkyl, e.g. an at least partially halo-substituted alkyl, R₂ is H or an alkyl, e.g. –CH₃, or a substituted alkyl, e.g. an at least partially halo substituted alkyl.

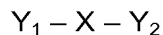
25. The component of Claim 24, wherein n is 2 to 6.

20 26. The component of any one of Claims 19 to 25, wherein the component reaches an oil repellence level from 4 to and including 7.

27. The component of any one of Claims 19 to 22 and Claim 26, wherein the organosilane precursor monomers comprise siloxanes, silanes or mixtures thereof.

25

28. The component of any one of Claims 19 to 22 and Claims 25 to 26, wherein the organosilane precursor monomers have a generic formula (II):



(II)

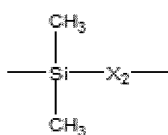
wherein X is O or NH, Y_1 is $\begin{array}{c} Y_3 \\ | \\ -Si-Y_4 \\ | \\ Y_5 \end{array}$, Y_2 is $\begin{array}{c} Z_3 \\ | \\ -Si-Z_4 \\ | \\ Z_5 \end{array}$ and wherein Y_3 , Y_4 , Y_5 , Z_3 , Z_4 , and Z_5 are each independently H or an alkyl.

5 29. The component of Claim 28, wherein the alkyl groups are C_1 to C_5 -alkyl.

30. The component of Claims 28 or 29, wherein the alkyl groups are C_1 to C_2 -alkyl.

31. The component of any one of Claims 28 to 30, wherein Y_3 , Y_4 , Y_5 , Z_3 , Z_4 , and Z_5 are –
 10 CH_3 and wherein X is O, representing the monomer hexamethyldisiloxane (HMDSO).

32. The component of any one of Claims 19 to 22 and Claims 26 to 27, wherein the organosilane precursor monomers are cyclic monomers having n times the repeating unit (III):



(III)

wherein X_2 is O or NH, and wherein n is 2 to 10.

33. The component of Claim 32, wherein n is 3 to 6.

34. The component of any one of Claims 19 to 33, wherein the polymer coating comprises a
 20 single layer.

35. The component of any one of Claims 19 to 34, wherein the coating has a thickness of about 10 nm to about 1 μm .

36. The component according to any one of Claims 17 to 35, useable in an electronic device including any one or more of a smartphone, a mobile phone, a personal digital assistant (PDA), a loudspeaker, a tablet computer, a music player such as a MP3 player, an e-reader,
5 a keyboard, a GPS system, a pedometer, a heart rate monitor, a cadence sensor, a video camera, or a photo camera.

37. An electronic device according to any one of Claims 19 to 36 which includes at least one component.

10

38. The device of Claim 37, wherein water ingress is minimised in the event of accidental exposure to water.

39. The device of Claim 37, wherein water damage is minimised in the event of forced water
15 ingress.

40. The device of Claim 37, wherein the device has an IPX level from 6 to and including 7.

41. The method according to any one of Claims 1 to 16, further comprising the step of
20 applying a protective film to at least part of an outer surface of the device, to protect the outer surface from unwanted visible or textured traces of the polymer coating.

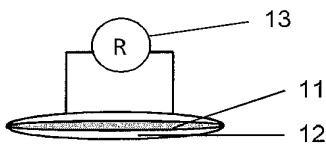


Figure 1

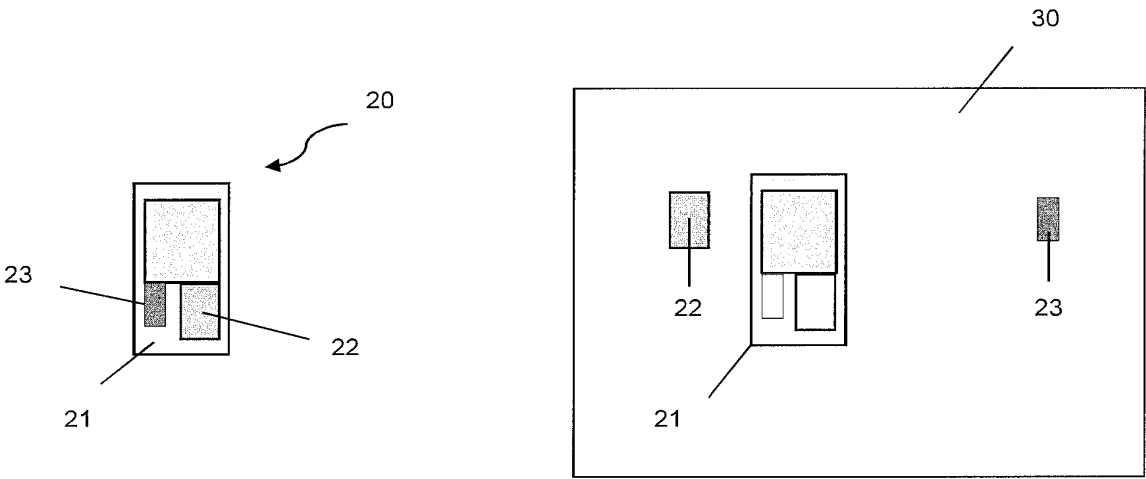


Figure 2a

Figure 2b

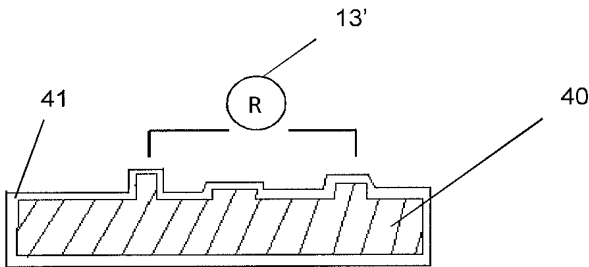
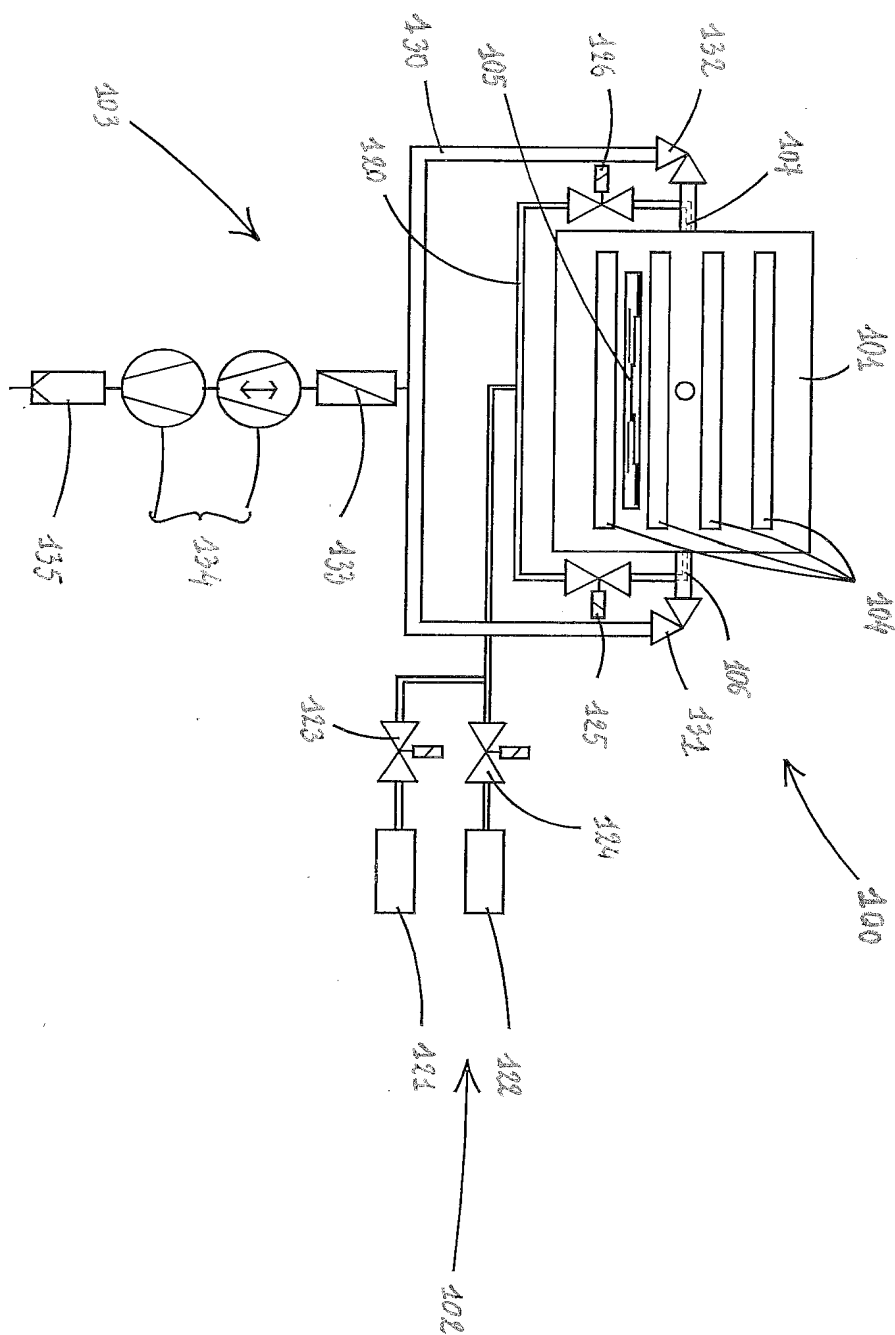


Figure 3

FIGURE 4



UNITED STATES PATENT AND TRADEMARK OFFICE

BEFORE THE PATENT TRIAL AND APPEAL BOARD

FAVORED TECH CORPORATION,

Petitioner,

v.

P2I LTD.,

Patent Owner.

CASE: IPR2020-_____

Patent No. 10,421,876

**DECLARATION OF DR. SALVADOR BORRÓS GÓMEZ
IN SUPPORT OF PETITION FOR INTER PARTES REVIEW**

I, Salvador Borrós Gómez, hereby declare as follows:

1. My name is Salvador Borrós Gómez. I'm a professor in the Materials Engineering Group in the IQS School of Engineering, Ramon Llull University, in Barcelona, Spain.

2. In 2005, I co-authored a scientific journal article titled "Fabrication of Bioactive Surfaces by Plasma Polymerization Techniques Using a Novel Acrylate-Derived Monomer." That article became publicly available when it was published online in the journal titled *Plasma Processes and Polymers* in September 2005. Among my peers in fields relating to polymer coatings, *Plasma Processes and Polymers* was a well-known journal in September 2005, and it remains so today. The article is still publicly available at:

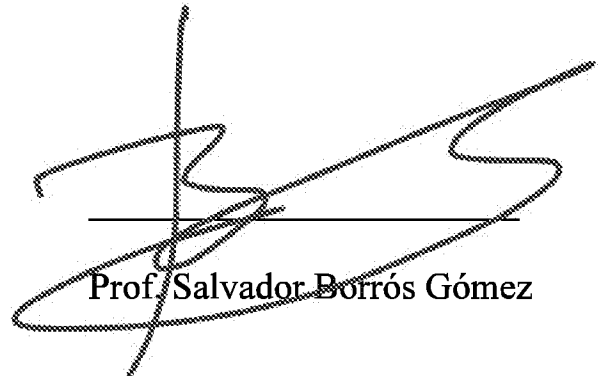
<https://onlinelibrary.wiley.com/doi/abs/10.1002/ppap.200500042>

3. I have reviewed a copy of Exhibit 1009 in this case that has been provided to me. Exhibit 1009 is a true and correct copy of the article I co-authored in 2005 titled "Fabrication of Bioactive Surfaces by Plasma Polymerization Techniques Using a Novel Acrylate-Derived Monomer," which has been publicly available in the journal *Plasma Processes and Polymers* since September 2005.

I hereby declare that all the statements made in this Declaration are of my own knowledge and true; that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like are punishable by fine or imprisonment, or both, under 18 U.S.C. § 1001.

I declare under penalty of perjury under the laws of the United States of America that all statements made in this declaration are true and correct.

Date: 06/16/20



Prof. Salvador Borrós Gómez

Ultralow Surface Energy Plasma Polymer Films

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Room-temperature pulsed plasma polymerization of long-chain perfluoroacrylates produces well-adhered liquid-repellent (hydrophobic and oleophobic) films. Critical surface tension values as low as $\gamma_c = 4.3 \text{ mN m}^{-1}$ have been measured on coated flat glass substrates. X-ray photoelectron spectroscopy, Fourier transform infrared, and atomic force microscopy characterization of these surfaces indicates that the low surface energy perfluoroalkyl chains remain intact, while polymerization occurs predominantly via the acrylate carbon–carbon double bond during the plasma duty cycle off-period.

1. Introduction

Hydrophobic and oleophobic repellency are highly desirable for numerous everyday applications, e.g. aerospace, lithography, sports and outdoor clothing, biomedical layers, integrated sensors, and protection against environmental fouling, etc.^{1–6} In the case of flat substrates, it is the chemical nature of the functional group packing which governs surface wettability.^{7,8} For instance, perfluoroalkyl chains are renowned for their liquid repellency. The tightly bound, nonbonding electron pairs surrounding each fluorine atom core shell in F–C bonds are not easily polarized, and therefore hinder hydrogen bonding and dispersion interactions with polar and nonpolar liquids, respectively.⁹ This type of nonattractive behavior increases with the degree of fluorine substitution at each carbon center (i.e. $\text{CF}_3 > \text{CF}_2 > \text{CF}$), and also depends on perfluoroalkyl chain length (greater withdrawal of electron density away from the terminal CF_3 group occurs up to a value of $n \approx 7$ for $\text{CF}_3(\text{CF}_2)_n$).^{10,11} It is on this basis that short perfluoroalkyl chains give rise to hydrophobicity, while longer perfluorinated chain lengths are necessary for additional oleophobic behavior. In the latter case, pack-

ing efficiency can become sufficient so as to effectively leave just a layer of CF_3 groups exposed at the air–solid interface.^{12,13} Conventional fluoropolymer coating methods for imparting such oil and water repellency are typically aqueous/organic solvent based.^{14,15} They usually contain combinations of resins, catalysts, homo- and or copolymers, surfactants, pH adjusters, and cross-linking agents and require heat to effect fixation, etc.^{16–18} Examples include polymers, copolymers,^{19–22} and cross-linked structures with fluorinated side chains.²³ Surface energy values well below the 18.5 mN m^{-1} for polytetrafluoroethylene (PTFE)⁸ have been reported for these systems.

An alternative solventless approach is to deposit liquid-repellent perfluoroalkyl chains onto solid surfaces by plasma polymerization.²⁴ Such “cold” plasmas contain heavy particles (gas atoms, molecules, radicals, and ions) at ambient temperature, photons, and “hot” electrons possessing sufficient kinetic energy to cause bond rupture and further ionization (thereby sustaining the discharge). The passage of pure organic vapor through

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this type of medium can lead to the deposition of polymeric films, although structural rearrangement can be a major limitation.²⁵ Pulsing the electrical discharge on the microsecond–millisecond time scale overcomes this drawback by minimizing damage to the growing polymer layer and enabling conventional polymerization reaction pathways to proceed during the duty cycle off-period.²⁶ In this study, 1*H*,1*H*,2*H*,2*H*-heptadecafluorodecyl acrylate ($\text{H}_2\text{C}=\text{CHCO}_2\text{CH}_2\text{CH}_2(\text{CF}_2)_7\text{CF}_3$) has been chosen as the feed monomer. This molecule contains the long perfluorinated alkyl chain needed for liquid repellency and a terminal acrylate group capable of undergoing conventional polymerization^{27,28} during the pulsed plasma off-period. Only continuous wave plasma polymerization of fluoroacrylates^{29–32} and pulsed plasma deposition of short chain fluoromonomers^{33,34} have been previously investigated. These were reported to exhibit limited liquid repellency (typically repelling water and high surface tension alkanes³⁰).

2. Experimental Section

Plasma polymerization experiments were carried out in an inductively coupled cylindrical glow discharge reactor (5 cm diameter, 470 cm³ volume, base pressure of 6×10^{-3} mbar, and a leak rate³⁵ of better than 6×10^{-9} mol s⁻¹). This was connected to a two stage Edwards rotary pump via a liquid nitrogen cold trap, a thermocouple pressure gauge, and a monomer tube containing the 1*H*,1*H*,2*H*,2*H*-heptadecafluorodecyl acrylate monomer (Fluorochem, 98% purity, further purified using multiple freeze–thaw cycles). All connections were grease free. An L–C matching unit was used to minimize the standing wave ratio (SWR) of the transmitted power between a 13.56 MHz radio frequency (RF) generator and the electrical discharge. For pulsed plasma deposition experiments, the RF source was triggered by a signal generator, and an oscilloscope was used to monitor the pulse width and amplitude. The average power (P) delivered to the system was calculated using the following formula:³⁶

$$\langle P \rangle = P_p [t_{\text{on}} / (t_{\text{on}} + t_{\text{off}})]$$

where $t_{\text{on}}/(t_{\text{on}} + t_{\text{off}})$ is defined as the duty cycle, and P_p is the continuous wave power. A typical experimental run comprised initially scrubbing the reactor with detergent and rinsing with isopropyl alcohol, followed by oven drying. The system was then reassembled and cleaned further with a 50 W air plasma for 30 min. Next, the chamber was vented to air, and the

substrate to be coated was placed into the center of the reactor, followed by evacuation back down to the base pressure. 1*H*,1*H*,2*H*,2*H*-heptadecafluorodecyl acrylate vapor was then introduced at a constant pressure of ~ 0.1 mbar and allowed to purge through the system for 5 min, followed by ignition of the glow discharge. Deposition was terminated after 5 min, and the monomer vapor was allowed to continue to pass over the substrate for a further 5 min; subsequently the plasma chamber was evacuated back down to the base pressure and then vented to the atmosphere. The optimum pulsing conditions were arrived at using factorial experimental design, followed by simplex optimization.

Deposition rate measurements were carried out using a gold coated quartz crystal monitor (Inficon XTM/2) located in the center of the reaction chamber.³⁷ A control experiment where the monomer vapor was allowed to pass over the substrate for 15 min in the absence of the electrical discharge indicated no deposition. Corresponding film thickness values were obtained using a Nanoptix nkd-6000 scanning spectrophotometer.

Conventional solution phase polymerization of 1*H*,1*H*,2*H*,2*H*-heptadecafluorodecyl acrylate comprised placing some uninhibited monomer into a round-bottom flask followed by deoxygenation using a stream of argon. Next, lauroyl peroxide dissolved in toluene solution was added to the monomer, followed by flushing the reaction vessel with argon gas to remove the toluene. The reaction mixture was stirred and warmed to 70 °C under a positive flow of argon for 3–4 h. The solid polymer product was then cooled, dissolved in hexafluoroxylene, and precipitated into methanol. Excess solvent was decanted off the gelatinous polymer. Further purification was achieved by agitation in hot methanol followed by decanting. Finally, the polymer was dried in a vacuum oven at 25 °C to yield a hard white solid.

A VG ESCALAB MKII electron spectrometer fitted with a nonmonochromated Mg K α X-ray source (1253.6 eV) and a hemispherical analyzer operating in the CAE mode (20 eV pass energy) was used for X-ray photoelectron spectroscopy (XPS) analysis of the deposited plasma polymer coatings. The photoemitted atomic core level electrons were collected at a takeoff angle of 30° from the substrate normal, which corresponds to a sampling depth of approximately 10–15 Å for the C(1s) envelope.³⁸ XPS peaks were fitted using a Marquardt minimization computer program assuming linear background subtraction. Elemental concentrations were calculated using instrument sensitivity factors determined from chemical standards, C(1s):O(1s):F(1s) = 1.00:0.36:0.23, respectively. During a typical XPS scan, X-ray beam damage caused less than 1% variation in the F:C ratio; this was sufficiently small that no discernible change was observable in the C(1s) envelope. Complete plasma polymer coverage of the underlying glass substrate was confirmed by the absence of any Si(2p) XPS signal showing through.

A FTIR Mattson Polaris instrument fitted with a Golden Gate single reflection diamond ATR apparatus (Graseby Specac) was used for infrared analysis. Plasma polymerization depositions were carried out onto sodium chloride plates and analyzed using 128 scans at a resolution of 4 cm⁻¹.

A Digital Instruments Nanoscope III atomic force microscope was used to examine the physical structure of the plasma polymer coatings deposited onto flat glass substrates. The microscope was operated in Tapping Mode, where changes in the oscillation amplitude of the cantilever tip provide a feedback signal for measuring variations in surface topography. All of the AFM images were acquired in air and are presented as unfiltered data. Root-mean-square (RMS) roughness values were obtained from 10 $\mu\text{m} \times 10 \mu\text{m}$ images.³⁹

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Table 1. Surface Energies of Probe Liquids

repellency	liquid	surface energy ⁴³ / (mN m ⁻¹ (at 20 °C))
hydrophobicity	water	72.8
	isopropyl alcohol	21.3
oleophobicity	dodecane	25.4
	octane	21.6
	heptane	20.1
	hexane	18.4
	pentane	16.1

Sessile drop contact angle measurements were carried out at 20 °C using a video capture apparatus (A. S. T. Products VCA2500XE). The Wilhelmy plate technique (Cahn microbalance, Model DCA322) was employed for dynamic contact angle analysis.⁴⁰ In this case, a glass slide coated on both sides was suspended from the microbalance, while a motorized stage moved a beaker containing the probe liquid upward and over the substrate at a speed of 154 $\mu\text{m s}^{-1}$. The advancing contact angle, θ , corresponds to the tangent at the three-phase solid–liquid–vapor interface formed during the initial immersion of the plate; this was calculated by applying the modified Young equation:⁴¹

$$\cos \theta = F/\gamma p$$

where F is the wetting force at the meniscus measured by the microbalance, γ is the surface tension of the probe liquid, and p is the perimeter of the meniscus formed at the three-phase interface. The obtained value of θ was used to calculate the surface energy (also referred to as surface tension with the corresponding units mJ m^{-2} and mN m^{-1} being dimensionally equivalent) using two different methods. First, the combined geometric mean Young's equation was used:⁴¹

$$(1 + \cos \theta)\gamma_i = 2[(\gamma_i^d \gamma_s^d)^{1/2} + (\gamma_i^p \gamma_s^p)^{1/2}]$$

where γ_i is the surface tension of the probe liquid, and γ_i^d and γ_i^p are the respective dispersive and polar (hydrogen bonding and dipolar–dipolar⁴²) components.⁴³ The dispersive (γ_s^d) and polar (γ_s^p) surface energy components for the coating could be calculated by substituting values for water⁴³ (representative polar liquid, $\gamma_i^d = 22.1 \text{ mN m}^{-1}$ and $\gamma_i^p = 50.7 \text{ mN m}^{-1}$) and octane⁴³ (representative nonpolar liquid, $\gamma_i^d = 21.6 \text{ mN m}^{-1}$ and $\gamma_i^p = 0.0 \text{ mN m}^{-1}$) into the equation and solving the corresponding set of simultaneous equations. Summation of γ_s^d and γ_s^p gave the total surface energy, γ . The alternative approach was to construct a Zisman plot.⁸ This comprises choosing a set of probe liquids from the same homologous series (pentane, hexane, heptane, octane, and dodecane were employed for the plasma polymer surfaces which exhibited no polar contribution^{44–47}) and measuring their advancing contact angles using the Wilhelmy plate apparatus. A plot of the cosine of the advancing contact angle versus the liquid surface tension (γ_i) approximates to a linear relationship called the Zisman plot.⁸ By extrapolating the line of best fit to $\cos \theta = 1$, the critical surface tension of spreading for the solid surface, γ_c , is obtained. Any liquid with a surface tension smaller than this value forms a zero contact angle with the coating. The Wilhelmy plate apparatus was also used to check that the

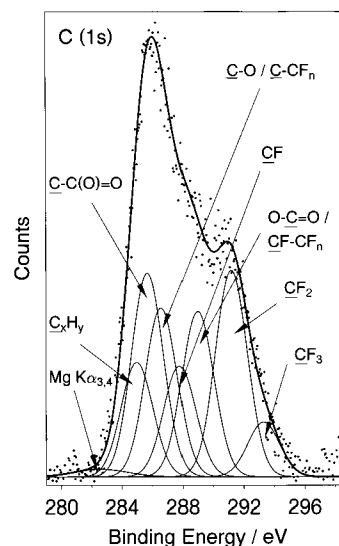


Figure 1. C(1s) XPS spectrum of 5 W continuous wave plasma polymerized 1H,1H,2H,2H-heptafluorodecyl acrylate deposited onto a flat glass substrate.

Table 2. Compilation of the Theoretical (Corresponding to the Monomer Structure, $\text{CH}_2=\text{CHCO}_2\text{CH}_2\text{CH}_2\text{C}_8\text{F}_{17}$) and Actual Chemical Environments Measured by XPS

conditions	F:C ratio	%CF ₂	%CF ₃
theoretical	1.31	53.8	7.7
conventional polymer	1.22 ± 0.02	44.8 ± 0.1	14.1 ± 0.6
optimum pulsed plasma	1.33 ± 0.06	46.7 ± 0.5	14.6 ± 1.3
5 W CW plasma	0.50 ± 0.18	17.2 ± 4.9	3.9 ± 1.4

surface tension of each probe liquid was consistent with reported literature values,⁴⁵ Table 1.

3. Results

The C(1s) XPS spectra of the plasma polymer layers deposited onto flat glass substrates could be fitted to seven Gaussian $\text{Mg K}\alpha_{1,2}$ components with equal full width at half maximum:^{48–50} C_xH_y at 285.0 eV, CC(O)=O at 285.7 eV, CO/CCF_n at 286.6 eV, CF at 287.8 eV, OC=O/CF_2 at 289.0 eV, CF_2 at 291.2 eV, and CF_3 at 293.3 eV (corresponding $\text{Mg K}\alpha_{3,4}$ satellite peaks were shifted by $\sim 9 \text{ eV}$ toward lower binding energy³⁸), Figure 1. The oxygenated/hydrogenated carbon centers originate from the acrylate group in the monomer.¹⁵ In the case of continuous wave (CW) plasma polymerization experiments, the whole range of functionalities was found to be present in significant amounts, Figure 1 and Table 2. Decreasing the duty cycle during pulsed plasma polymerization improved $>\text{CF}_2$ group incorporation, eventually becoming close to the theoretically expected value for complete structural retention of the perfluoroalkyl chain, Figures 2 and 3 and Table 2. Under these conditions, the concentration of CF_3 functionalities present in the C(1s) envelope appears to be greater than predicted by the monomer structure, Table 2; this is most likely due to the surface sensitivity of the XPS technique, yielding a more intense signal from the

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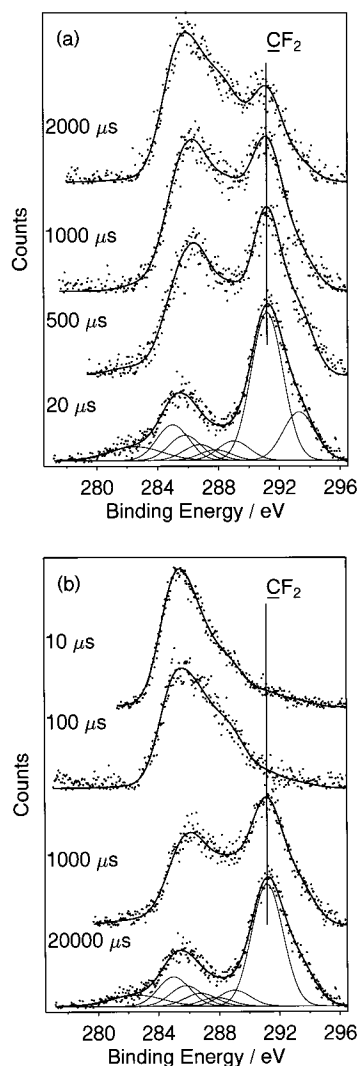


Figure 2. C(1s) XPS spectra of plasma polymerization of 1H,1H,2H,2H-heptafluorodecyl acrylate deposited onto glass with varying (a) t_{on} ($t_{\text{off}} = 20\,000\ \mu\text{s}$, $P_p = 40\ \text{W}$) and (b) t_{off} ($t_{\text{on}} = 20\ \mu\text{s}$, $P_p = 40\ \text{W}$).

terminal CF_3 group of the perfluoroalkyl chains aligned away from the coating–substrate interface.⁵¹ The C(1s) signal from ester linkages is consistent with the XPS sampling depth³⁸ (approximately 1–2 nm), being greater than the length of the perfluoroalkyl side chain.⁵² Comparable spectra were obtained for the conventional polymer prepared by solution-phase polymerization of the monomer,⁵¹ Table 2.

Corresponding differences between continuous wave and pulsed plasma deposition were also evident in the infrared spectra, Figure 4 and Table 3. The sharpness of the spectral features associated with the liquid monomer was retained for the pulsed plasma polymer coatings, whereas spectral broadening was evident for continuous wave conditions as a consequence of the higher powers leading to extensive fragmentation, rearrangement, and cross-linking reactions of the parent molecule. Disappearance of the characteristic acrylate carbon–carbon double bond absorption bands at 1640,

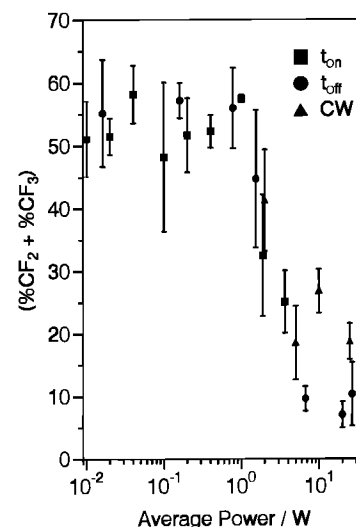


Figure 3. Variation of (% CF_2 + % CF_3) concentration versus average power for plasma polymer layers deposited onto flat glass. (t_{on} experiments have been carried out at fixed $t_{\text{off}} = 20\,000\ \mu\text{s}$ and $P_p = 40\ \text{W}$, while t_{off} data corresponds to fixed $t_{\text{on}} = 20\ \mu\text{s}$ and $P_p = 40\ \text{W}$.)

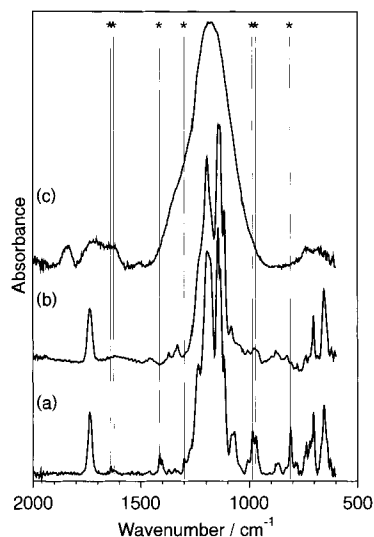


Figure 4. Comparison of infrared spectra: (a) 1H,1H,2H,2H-heptafluorodecyl acrylate monomer; (b) pulsed plasma polymerization conditions ($t_{\text{on}} = 20\ \mu\text{s}$, $t_{\text{off}} = 20\,000\ \mu\text{s}$, $P_p = 40\ \text{W}$); and (c) 5 W continuous wave plasma polymerization. NB: * denotes acrylate carbon–carbon double bond absorption bands.

1625, 1412, 1298, 986, 970, and $812\ \text{cm}^{-1}$ during pulsed plasma polymerization is consistent with reaction proceeding via the acrylate double bond while leaving the associated ester carbonyl group at $1734\text{--}1736\ \text{cm}^{-1}$ intact.

The deposition rate was found to pass through a maximum with decreasing average power during pulsed plasma polymerization, Figure 5a. Within this general trend, the observed spread of values for a specific average power indicates the dependency of the polymerization chemistry on the duty cycle parameters, i.e., off- versus on-period reactions. The optimum pulsed plasma deposition conditions ($t_{\text{on}} = 20\ \mu\text{s}$, $t_{\text{off}} = 20\,000\ \mu\text{s}$, $P_p = 40\ \text{W}$) yielded a film thickness of $47 \pm 1\ \text{nm}$.

Atomic force microscopy (AFM) studies gave a RMS roughness value of 0.7 nm for the flat glass substrate

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Table 3. Infrared Absorption Band Assignments

group	vibrational mode	wavenumber/cm ⁻¹		
		lit. ⁸⁰	monomer	pulsed plasma polymer
ester C=O	stretching	1715–1750	1734	1736
acrylate	s-trans and s-cis rotational isomers	1640 and 1625	1640 and 1625	not seen
acrylate	=CH ₂ in plane deformation	1410–1420	1412	not seen
–CF ₃	stretching	1120–1350	1117–1236	1117–1196
acrylate	CH in plane deformation	1290–1300	1298	not seen
–CF ₂ –	stretching	1120–1280	1117–1236	1117–1196
acrylate	CH out of plane deformation	985–995	986	weak
acrylate	=CH ₂ wag	965 ± 5	970	weak
acrylate	=CH ₂ twist	811 ± 3	812	not seen

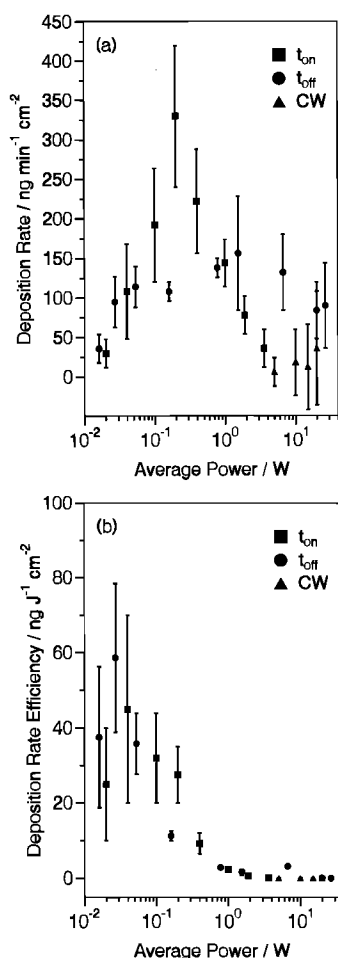


Figure 5. Influence of average power upon (a) deposition rate and (b) deposition rate efficiency. (t_{on} experiments have been carried out at fixed $t_{\text{off}} = 20\,000\ \mu\text{s}$ and $P_p = 40\ \text{W}$, while t_{off} data corresponds to fixed $t_{\text{on}} = 20\ \mu\text{s}$ and $P_p = 40\ \text{W}$.) NB: Nanograms are abbreviated to ng.

and approximately 7 nm for the continuous wave and pulsed plasma polymer films (although their respective morphologies were different), Figure 6. This compares with RMS roughness values of 0.5 nm reported for conventional solution-phase polymerized perfluoroacrylates.⁵³

Short-pulse duty cycles gave rise to a drop in surface energy, eventually reaching a limiting value of 10 mN m⁻¹ (as measured by the combined geometric mean Young's equation), Figure 7. Comparison with Figure 3

shows that the polar contribution disappears with increasing structural retention of the perfluoroalkyl chains. The absence of any polar contribution to the total surface energy under these conditions meant that it was valid to use a homologous series of alkane probe liquids to make a Zisman plot; critical surface tension values of $\gamma_c = 14.4\ \text{mN m}^{-1}$ and $\gamma_c = 4.3\ \text{mN m}^{-1}$ were obtained for continuous wave (5 W) and optimum pulsed ($t_{\text{on}} = 20\ \mu\text{s}$, $t_{\text{off}} = 20\,000\ \mu\text{s}$, $P_p = 40\ \text{W}$) plasma polymer coatings respectively, Figure 8. The extremely low critical surface tension value measured in the latter case can be correlated to the observed structural retention of long perfluoroalkyl chains at the air–solid interface. These deposited films were stored in air for over 1 year and showed no sign of aging. This is consistent with the mild nature of pulsed plasma polymerization conditions.

Finally, hydrophobicity and oleophobicity tests were undertaken using a range of pure liquids and water/isopropyl alcohol mixtures with differing surface energies,^{27,54} Table 1. This comprised placing 3 drops of each test liquid onto plasma polymer coated cotton fabric. The surface was considered to repel each liquid if, after 30 s, the drops remained spherical/hemispherical, i.e., absence of any penetration or wicking at the liquid–fabric interface. Continuous wave (5 W) plasma deposited coatings were found to be repellent only toward 40%/60% water/isopropyl alcohol mixtures and dodecane (higher concentrations of isopropyl alcohol and shorter alkane chains wetted the substrate). A significant improvement was noted for optimum pulsed plasma deposition conditions, where liquid repellency was observed toward pure isopropyl alcohol as well as water (hydrophobicity), and also alkane chains as short as heptane (oleophobicity), Figure 9. The adhesion of these plasma polymer layers was tested by boil washing in a detergent solution for 15 min followed by drying in an oven at 100 °C. No detachment of the coating from the substrate was observed.

4. Discussion

The described plasma polymerization method is quick, cheap, substrate-independent, and solventless and does not incorporate nonfluorochemical reagents (e.g. catalysts, cross-linking agent, surfactants, etc.),¹⁴ and therefore a cleaner fluoropolymer product can be expected. The greater retention of >CF₂ groups observed during electrically pulsed plasma polymerization compared to continuous wave conditions is consistent with less

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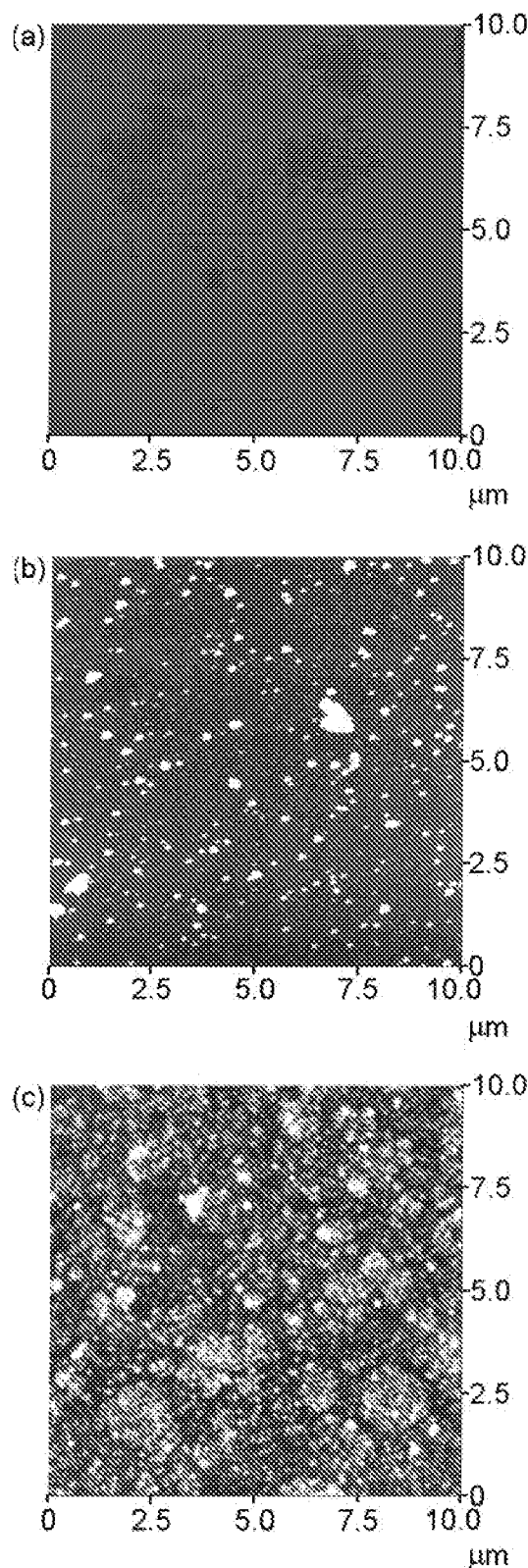


Figure 6. AFM micrographs ($z = 100$ nm): (a) flat glass substrate; (b) 5 W continuous wave plasma polymer of 1H,1H,2H,2H-heptadecafluorodecyl acrylate deposited onto glass; (c) pulsed plasma polymer of 1H,1H,2H,2H-heptadecafluorodecyl acrylate deposited onto glass ($t_{\text{on}} = 20 \mu\text{s}$, $t_{\text{off}} = 20\,000 \mu\text{s}$, $P_p = 40$ W).

fragmentation and damage of the perfluoroalkyl tail, Figure 3 and Table 2. This can be attributed to a drop in plasma sheath potential, causing less energetic ion bombardment of the growing film,⁵⁵ as well as attenu-

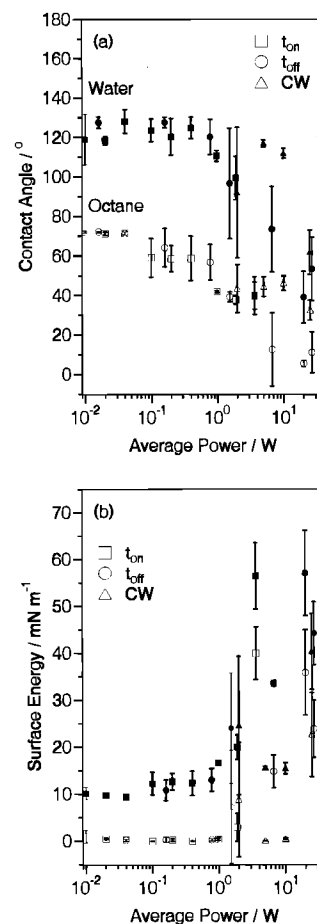


Figure 7. Influence of average power upon (a) water (shaded) and octane (unshaded) advancing contact angles and (b) surface energy values calculated using combined geometric mean Young's equation where the unshaded symbols correspond to the polar component and the shaded ones are the total surface energy.

ation of vacuum-UV irradiation.⁵⁶ Good adhesion of the plasma polymer layer occurs due to the creation of free radical sites on the substrate surface during the initial stages of plasma deposition. While the observed difference in film morphology stems from the different mechanistic modes of polymerization (pulsed versus continuous wave).

Normally the deposition rate is found to increase with rising average power for continuous wave conditions.²⁵ However a reversal in this trend occurred during pulsed plasma polymerization of 1H,1H,2H,2H-heptadecafluorodecyl acrylate, Figure 5a. Poor deposition measured at very short duty cycles can be ascribed to the lack of polymerization sites. A maximum is reached at intermediate pulse cycles, corresponding to the highest ratio of polymerizable species to nonpolymerizable/ablative species. Eventually toward continuous wave conditions, the deposition rate drops as a consequence of ablation becoming a competing process. To factor out the effect of variation in average power, the deposition rate efficiency was calculated (defined as deposition rate

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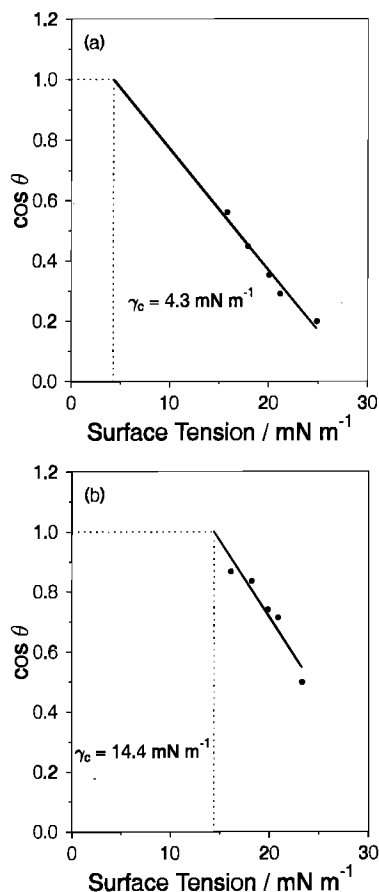


Figure 8. Zisman plot of plasma polymer coated glass slide: (a) pulsed ($t_{\text{on}} = 20 \mu\text{s}$, $t_{\text{off}} = 20\,000 \mu\text{s}$, $P_p = 40 \text{ W}$) and (b) 5 W continuous wave.

divided by average power).⁵⁷ Figure 5b. It is found that the deposition rate per joule of energy increases with decreasing average power, which can be taken as being indicative of species which are activated during the on-period (via UV irradiation, ion, or electron bombardment etc.), continuing conventional polymerization either in the gas phase or at the plasma–substrate interface during the off-period of the pulse cycle.⁴⁵

Most previous studies have utilized the Zisman method to assess low surface energy coatings. The critical surface tension values, γ_c , measured for solution phase polymerized 1*H*,1*H*,2*H*,2*H*-heptadecafluorodecyl acrylate and other long-chain perfluoromonomers and copolymers can be as low as 3 mN m^{-1} .^{11,13,14,16,51,53,58–63} It appears that the value of $\gamma_c = 4.3 \text{ mN m}^{-1}$ attained in the present case for the pulsed plasma polymer coatings is comparable. This is particularly surprising since the perfluoroalkyl groups attached to alternate carbon atoms along the polymer backbone should not pack as close together (if this is indeed what actually happens for the pulsed plasma polymer) as fluorocarbon acid monolayers¹³ or epitaxially grown perfluoroalkane

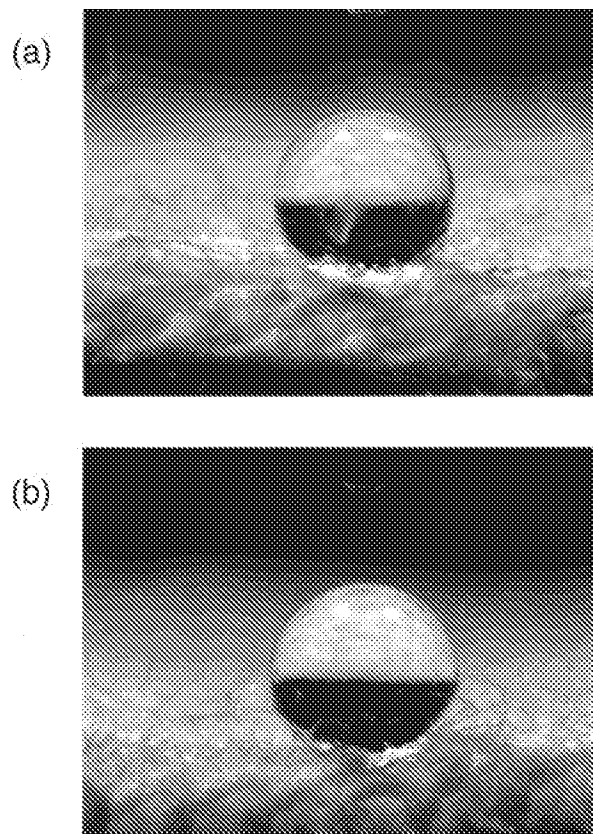


Figure 9. Optical images illustrating liquid repellency ($2 \mu\text{L}$ droplet volume) for 1*H*,1*H*,2*H*,2*H*-heptadecafluorodecyl acrylate pulsed plasma polymer layer deposited onto cotton fabric ($t_{\text{on}} = 20 \mu\text{s}$, $t_{\text{off}} = 20\,000 \mu\text{s}$, $P_p = 40 \text{ W}$): (a) pure isopropyl alcohol droplet and (b) heptane droplet.

crystallites,^{64,65} for which γ_c values of 6 mN m^{-1} have been reported.^{9,12,65,66} The microroughness discernible in the AFM micrographs could potentially distort the Zisman plot to give anomalous γ_c values. If the roughness causes air to become trapped in the voids (i.e. the liquid cannot penetrate into the troughs), then a composite interface will be formed in accordance with the Cassie–Baxter relationship⁶⁷ (in fact this is how high water repellency has been achieved in the past for powdered plasma polymer films^{30,68–71}). However such behavior appears to be unlikely, since the low contact angle hysteresis normally associated with a composite interface^{30,72,73} is absent for the pulsed plasma polymer layers (advancing and receding contact angle values, $\theta_{\text{adv}}/\theta_{\text{rec}} = 134^\circ/66^\circ$ and $73^\circ/56^\circ$ for water and octane, respectively). The observed contact angle hysteresis is more consistent with the surface roughness only being

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sufficient to produce an effective increase in surface area without pore formation. This can be described in terms of Wenzel's law,^{30,68,74} which predicts that surface roughening decreases/increases the repellency of liquids which make a contact angle of less/greater than 90° on the corresponding flat surface. On this basis, any distortion of the critical surface tension value, γ_c , to an abnormally small value as a consequence of surface roughness is also unlikely, since the chosen series of low surface tension alkane probe liquids all exhibit contact angles less than 90°, and according to Wenzel's law,^{75,76} surface roughness will actually make the measured liquid contact angle lower than the true value;^{75,77,78} hence $\cos \theta$ will be greater for each probe liquid on the Zisman plot, thereby shifting the γ_c value artificially higher. Hence, the true γ_c value would be expected to be lower than 4.3 mN m⁻¹. This may be attributed to atomic fluorine generated via minor fragmentation of some monomer during the duty cycle on-period substi-

tuting hydrogen atoms⁷⁹ belonging to the 1*H*,1*H*,2*H*,2*H*-heptadecafluorodecyl acrylate repeat unit contained in the growing plasma polymer film. For instance, it is well-known that replacement of the hydrogen atom located at the 2-position in the acrylate group with fluorine reduces the critical surface tension of the corresponding solution-phase polymerized product.^{14,61}

5. Conclusions

Pulsed plasma polymerization is an effective method for the solventless functionalization of solid surfaces. Short duty cycle on-times in conjunction with long off-times enable selective activation of reactive bonds within a monomer. Precursors containing long perfluoroalkyl chains (e.g. 1*H*,1*H*,2*H*,2*H*-heptadecafluorodecyl acrylate) have been found to yield low surface energy coatings which display no polar contribution and exhibit excellent repellency toward low surface tension liquids.

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Synthesis of Cross-Linked Ethylene Glycol Dimethacrylate and Cyclic Methacrylic Anhydride Polymer Structures by Pulsed Plasma Deposition

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ABSTRACT: New types of reaction pathways have been identified during pulsed plasma polymerization of difunctional precursor molecules. Ethylene glycol dimethacrylate is found to give rise to a highly cross-linked polymeric network, while methacrylic anhydride undergoes cyclopolymerization. The deposited films have been characterized by infrared spectroscopy and solvent swelling studies.

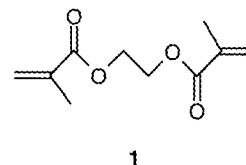
1. Introduction

The quest for retention of precursor functional groups during plasma polymerization has been actively pursued in the past. The very nature of an electrical discharge (ultraviolet photons, electrons, ions, as well as excited neutrals) tends to dissociate the precursor molecule into many fragments to give films which often bear little or no resemblance to the molecular structure of the original monomer.^{1–3} The most effective method to date for achieving high structural retention in the final plasma polymer film has been pulsing the electrical discharge on the millisecond–microsecond time scales.^{4–8} This comprises the generation of active sites (predominantly radicals) at the surface and in the plasma during the duty cycle on-period, followed by conventional polymerization reaction pathways proceeding during the extinction period. Typical time scales are of the order of microseconds and milliseconds, respectively. Plasma polymer films containing high levels of anhydride,⁵ carboxylic acid,⁹ cyano,¹⁰ epoxide,¹¹ hydroxyl,¹² perfluoroalkyl,¹³ perfluoromethylene,^{4,14} and trifluoromethyl¹⁵ groups have been successfully prepared by this technique.

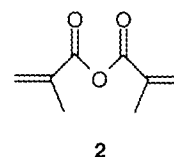
In this article, the pulsed plasma chemistry of diene monomers is explored with respect to cross-linking and cyclopolymerization reaction pathways. Monomers of this type containing two equivalent polymerizable groups are often employed in solution phase chemistry to make cross-linked polymer networks.¹⁶ One notable exception is 1,6-dienes, which are capable of undergoing cyclopolymerization to give linear polymers via an intramolecular–intermolecular chain propagation mechanism.¹⁷ This latter process is favored due to the intramolecular proximity of the vinyl groups and the strong driving force associated with five- or six-membered ring formation.¹⁸

Two different length diene monomers have been chosen in the present study to see whether analogous cross-linking and cyclopolymerization reactions can proceed in the proximity of pulsed electrical discharges. First, there is a 1,9-diene, ethylene glycol dimeth-

acrylate, structure **1**, which is often used to make highly



cross-linked films imparting good chemical and mechanical stability characteristics.¹⁶ The other monomer is methacrylic anhydride, structure **2**, which is a typical



1,6-diene, renowned for its ability to undergo conventional cyclopolymerization in solution.^{17,19} Infrared spectroscopy and swelling studies have been employed to establish whether these monomers follow equivalent cross-linking or cyclopolymerization reaction pathways during exposure to a pulsed electrical discharge.

2. Experimental Section

Plasma polymerization was carried out in a cylindrical glass reactor pumped by a mechanical rotary pump via a liquid nitrogen cold trap (base pressure = 1×10^{-3} mbar, leak rate = 1.2×10^{-9} mol s⁻¹). A copper coil wrapped around the reactor was coupled to a 13.56 MHz radio-frequency power supply in conjunction with an LC matching network. Prior to each experiment, the chamber was cleaned using a 50 W air plasma at 0.2 mbar pressure for 30 min. Monomer vapor (freeze–pump–thawed several times) was then introduced through a fine control needle valve into the chamber for 5 min, followed by plasma ignition. Upon completion of film deposition, the electrical discharge was switched off and the precursor allowed to continue to pass over the substrate for a further 5 min (capping of reactive sites). In the case of pulsed plasma polymerization, a signal generator was used to trigger the rf

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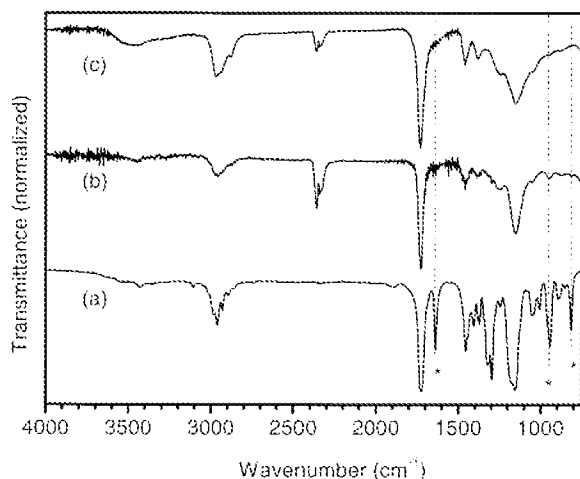


Figure 1. Infrared spectra of (a) ethylene glycol dimethacrylate monomer, (b) pulsed plasma polymer (time on = 20 μ s, time off = 20 ms, peak power = 40 W), and (c) 3 W continuous wave plasma polymer. (Asterisk denotes C=O bond features in the monomer, and the weak band in the 2360–2330 cm^{-1} region is due to residual CO_2 in the spectrometer.)

power supply, and the pulse shape was monitored with an oscilloscope.

Plasma polymerization of ethylene glycol dimethacrylate (Aldrich, 99% purity) was carried out at 0.1 mbar pressure for 30 min onto sodium chloride disks and silicon wafers for infrared analysis and thickness measurements, respectively. In the case of methacrylic anhydride (Aldrich, 99% purity), plasma polymer films were deposited onto potassium bromide disks at 0.2 mbar pressure under continuous wave and pulsed plasma conditions for 30 and 120 min, respectively. Different times were employed in order to give equivalent thicknesses, i.e., rule out solvent diffusion effects. Deposition time did not affect film structure.

Infrared spectra of the plasma deposited films were acquired in air using a Perkin-Elmer Spectrum One spectrometer operating in transmittance mode at 4 cm^{-1} resolution and averaged over 32 scans. No aging effects were observed for the plasma polymer layer over a period of 2 months. A reference spectrum of each monomer was obtained by placing a drop of liquid between pairs of either sodium chloride or potassium bromide plates.

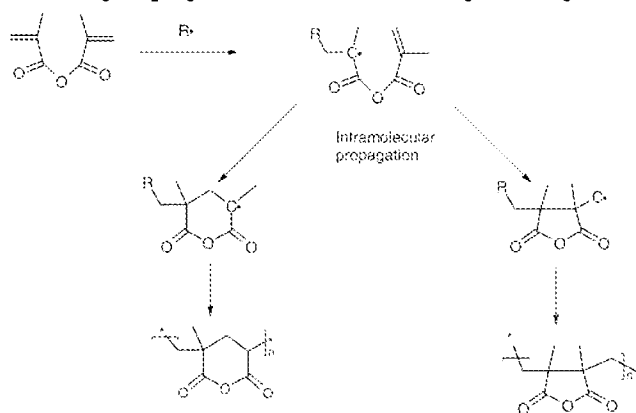
Plasma polymer film thicknesses were measured using a spectrophotometer (Nanoptix NKD 6000). Transmittance–reflectance curves spanning the 350–1000 nm range were fitted with the Cauchy model using a modified Levenburg–Marquardt procedure.

Swelling studies of the cross-linked ethylene glycol dimethacrylate plasma polymer films were carried out by immersing coated silicon substrates into tetrahydrofuran (Rectapur, 99%) for 18 h, followed by measurement of thickness.

3. Results and Discussion

3.1. Ethylene Glycol Dimethacrylate. Infrared band assignments of the monomer were made as follows:²⁰ unsaturated C–H stretching (3106 and 2981 cm^{-1}), methyl C–H stretching (2960 cm^{-1} antisymmetric, 2929 cm^{-1} symmetric), ethylene C–H stretching (2930 cm^{-1} antisymmetric, 2894 cm^{-1} symmetric), acrylate C=O stretching (1725 cm^{-1}), acrylate C=C stretching (1638 cm^{-1}), CH_3 bending (1453 cm^{-1} antisymmetric and 1368 cm^{-1} symmetric), $=\text{CH}_2$ wagging (943 cm^{-1}), and $=\text{CH}_2$ twist (814 cm^{-1}) (Figure 1). The pulsed plasma deposited films were found to display all the bands associated with the monomer apart from the carbon–carbon double-bond features (1638, 943, and 814 cm^{-1}). This signifies

Scheme 1. Mechanism of Conventional Solution Phase Cyclopolymerization of Methacrylic Anhydride



polymerization of the two methacrylate groups to form a cross-linked network.¹⁶ Furthermore, the C–O stretching band at 1150 cm^{-1} appeared to be far better resolved compared to its continuous wave counterpart (reflecting better structural retention). In fact, the general spectral broadening observed under continuous wave plasma conditions was taken as being indicative of extensive monomer fragmentation and rearrangement.

The degree of cross-linking present in the two types of ethylene glycol dimethacrylate plasma polymer film was compared using solvent swelling experiments. It was found that a 234 ± 3 nm thick pulsed plasma polymer film increased to 258 ± 5 nm upon immersion in tetrahydrofuran, whereas a 180 ± 4 nm thick continuous wave plasma polymer film swelled to 350 ± 5 nm (almost double) under similar conditions. Hence, it would appear that the former contains a far higher level of cross-linking attributable to its better structural integrity. Cross-linking will have taken place by activation and polymerization of the two methacrylate groups contained in the monomer. Further evidence to support this conclusion is provided by taking into consideration that a 220 nm thick conventional solution phase polymerized (cross-linked) poly(ethylene glycol dimethacrylate) film is reported to increase to 280 nm thickness upon soaking in tetrahydrofuran¹⁶ (which is comparable to the behavior observed for the pulsed plasma layer deposited in the present study).

3.2. Methacrylic Anhydride. Methacrylic anhydride is a 1,6-diene molecule which readily undergoes cyclopolymerization in the solution phase. By varying the experimental conditions, it is reported that the ring size can be controlled during homopolymerization. Temperature, solvent polarity, and monomer concentration are considered to be key parameters which govern whether five- or six-membered anhydride ring formation occurs^{18,19,21–25} (Scheme 1).

The following infrared band assignments can be made for the methacrylic anhydride precursor molecule:²⁰ unsaturated C–H stretching (3111 and 2986 cm^{-1}), saturated C–H stretching (2931 and 2963 cm^{-1}), anhydride C=O stretching (1800 cm^{-1} , 1785, 1749, and 1723 cm^{-1}), acrylate C=C stretching (1637 cm^{-1}), $=\text{CH}_2$ wagging (948 cm^{-1}), and $=\text{CH}_2$ twisting (808 cm^{-1}) (Figure 2).

Pulsed plasma deposited films of methacrylic anhydride were found to display the following bands: C–H stretching (2978, 2936, and 2879 cm^{-1}), anhydride C=O stretching (1858, 1804, 1762, and 1737 cm^{-1}). Some absorbed water was also detected (O–H stretching at

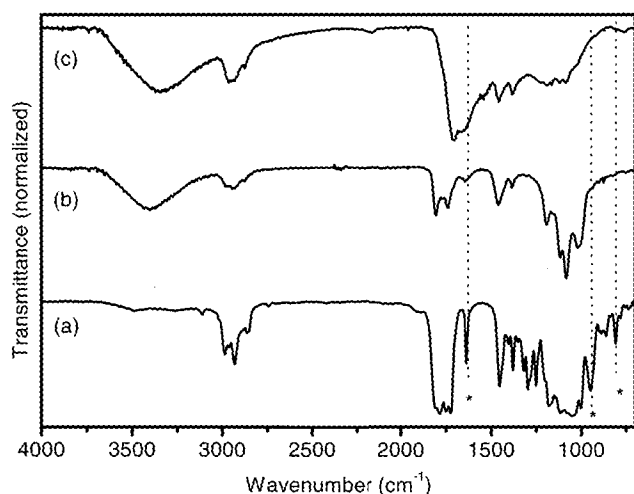


Figure 2. Infrared spectra of (a) methacrylic anhydride monomer, (b) pulsed plasma polymer (time on = 20 μ s, time off = 20 ms, peak power = 40 W), and (c) 3 W continuous wave plasma polymer. (Asterisk denotes C=C bond features in the monomer.)

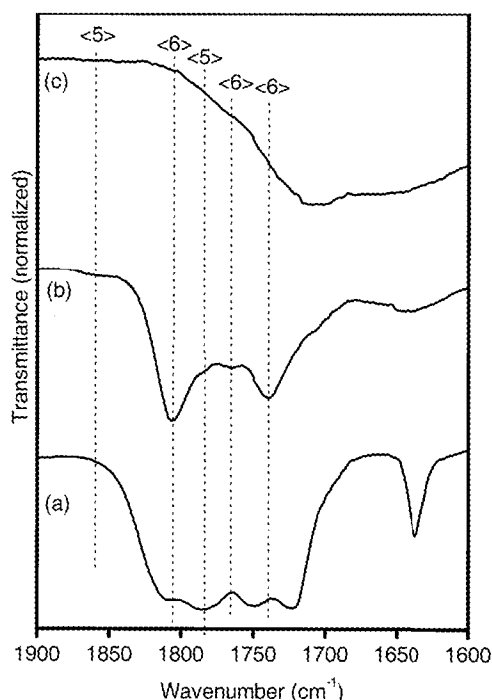


Figure 3. The 1900–1600 cm^{-1} infrared absorption region of (a) methacrylic anhydride monomer, (b) pulsed plasma polymer (time on = 20 μ s, time off = 20 ms, peak power = 40 W), and (c) 3 W continuous wave plasma polymer. (The numbers denote the assigned ring size.)

3397 cm^{-1} and O–H bending at 1641 cm^{-1}). The exact position of the C=O stretching bands associated with the anhydride group acts as a fingerprint region to help distinguish between linear and cyclic anhydrides as well as the actual ring size²⁰ (Figure 3). It is reported that linear anhydride C=O stretching absorbances should appear at 1827 and 1766 cm^{-1} .²⁰ However, these are not observed. Instead, peaks at 1805, 1765, and 1740 cm^{-1} were identified, which are indicative of C=O stretching features belonging to six-membered poly(methacrylic anhydride) rings.¹⁹ The multiple peaks stem from different stereoisomers.² Also, the very weak C=O stretching absorbances at 1860 and 1780 cm^{-1} suggest the presence of a minor constituent of five-

membered poly(methacrylic anhydride) rings present in the overall polymer structure.²⁰ The high selectivity toward six-membered ring formation in the case of pulsed plasma polymerization of methacrylate anhydride can be attributed to the greater stability of the tertiary radical intermediate formed in this case compared to the primary radical intermediate required for five-membered ring cyclopolymerization (Scheme 1).

Continuous wave plasma polymer deposition gave rise to poorly resolved peaks (e.g., 1000–1250 cm^{-1}) as well as only one broad peak at 1710 cm^{-1} in the 1800–1700 cm^{-1} region. These features implicate the destruction of the anhydride functionality contained in the precursor molecule during continuous wave conditions.

4. Conclusions

In the case of difunctional monomers, two alternative reaction pathways have been identified during pulsed plasma polymerization. Ethylene glycol dimethacrylate (a 1,9-diene) leads to the formation of a cross-linked polymer network, while methacrylic anhydride (a 1,6-diene) undergoes homocyclopolymerization. This is in marked contrast to continuous wave plasma conditions, where for both precursors the more energetic environment gives rise to poor overall reaction selectivity.

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Plasma Polymerization

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PLASMA POLYMERIZATION

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H. Yasuda

Institute for Thin Film Processing Science
Materials Research Center
University of Missouri-Rolla
Rolla, Missouri

1985



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CHAPTER 1

Introduction

Plasma polymerization refers to the formation of polymeric materials under the influence of plasma (partially ionized gas). Because the most practical means of carrying out plasma polymerization involves the use of an electric glow discharge in a vacuum, the term *glow discharge polymerization* has been used, in every practical sense, synonymously with plasma polymerization, although plasma polymerization can be carried out by means other than glow discharge.

It was known for many years that some organic compounds form solid deposits in plasma generated by some kind of electrical discharge (1-9). In most cases, however, the deposits were recognized as by-products of phenomena associated with electric discharge; consequently, little attention was paid either to the properties of these materials (undesirable by-products) or to the process as a means of forming useful materials.

At these early stages of discovery, the concept of polymers was not well developed, and obviously these processes had never been considered to be polymerization, that is, plasma polymerization or glow discharge polymerization. Only since the 1960s has the formation of materials in plasma been recognized as a means of synthesizing polymers, and the process, when used to make a special coating on metals, has been referred to as plasma polymerization or glow discharge polymerization (10-14).

Following the advancement of polymer science, the formation of organic solids or films in plasma has attracted considerable attention, and the process has been generally recognized as plasma polymerization or glow discharge polymerization. The American Chemical Society has held symposiums (1970, 1974, 1978, and 1982) on this subject.

In these developments (i.e., up to the 1970s), however, the concept of plasma polymerization has been based on the application of the concept of polymerization and/or of polymers developed in preceding decades to the formation of organic material under plasma conditions. In other words, the process has attracted the attention of scientists and engineers as an exotic method of polymerization. Although a great number of research studies have

been published and numerous potential applications and the uniqueness of the polymer formation process have been demonstrated, the subject has not drawn much academic interest as a new subject area of polymer science. This is due largely to the fact that the very unique and advantageous feature (in certain applications) of forming insoluble, infusible polymers has hampered the basic study of the process at the molecular level.

In more recent years, however, the question of whether the concepts of polymers and of polymerization can be applied to plasma-formed materials and to plasma polymerization, respectively, has been reexamined (15). The well-recognized concept of polymerization today is based on the molecular processes by which the size of molecules increases. The arrangement of the atoms that constitute the molecules of a monomer is accomplished during the organic synthesis of the monomer. During the polymerization of a monomer, rearrangement of atoms within the molecule seldom occurs.

In contrast to such molecular processes, polymer formation in plasma has been recognized as an atomic (nonmolecular) process (15). If one adopted such an atomic process to form materials in which the reaction of new covalent bonds between atoms played a predominant role, one could find numerous new processes and resulting materials that would play vitally important roles in modern technologies. The processes recognized as chemical vapor deposition, plasma chemical vapor deposition, ion-assisted vapor deposition, and sputter coating of polymers all fall into this category.

Plasma polymerization was dealt with in the 1960s and 1970s as a method of polymerization. Although some important differences in polymer formation mechanisms and the properties of resultant polymers were recognized, the underlying concept was an extension of the concepts of polymerization and polymers developed with conventional polymers. Consequently, the underlying concept was represented, for example, by the preparation of a thin layer of polystyrene by the plasma polymerization of styrene or the preparation of a thin layer of polytetrafluoroethylene by the plasma polymerization of tetrafluoroethylene. In other words, plasma polymerization was conceived as a new and exotic method of polymerization.

Plasma polymerization today is gaining recognition as an important process for the formation of entirely new kinds of materials. The materials obtained by plasma polymerization are significantly different from conventional polymers and are also different from most inorganic materials. Thus, plasma polymers lie somewhere between organic polymers and inorganic materials. Plasma polymerization should be considered a method of forming such new types of materials rather than a method of preparing conventional polymers. Consequently, the term *plasma polymerization* should not be limited to the formation of organic materials but should cover a wider area that includes metallic or inorganic elements, although the major portion of studies

covered in this volume involve the formation of polymeric materials from organic compounds.

To take full advantage of the new kinds of materials recognized as plasma polymers and of the process by which they are made, it is important to recognize that we are not dealing with conventional polymers and polymerization in the strict sense, although these terms are used. Therefore, considerable effort is spent comparing plasma polymerization with conventional polymerization.

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CHAPTER 4

Fundamental Aspects of Ionized Gas

4.1 Plasma for Plasma Polymerization

The term *plasma* describes the state of ionized gas (e.g., glow discharge) (*I*). An ionized gas consists mainly of positively charged (ionized) molecules or atoms (ions) and negatively charged electrons. The state of plasma can be created by a variety of means. In general, when a molecule is subjected to a severe condition, such as intense heat, ionization of the molecule occurs. At temperatures greater than 10,000 K, all molecules and atoms tend to become ionized. The sun and other stars of the universe have temperatures ranging from 5000 to 70,000 K or more, and they consist entirely of plasma. The space between the galaxies is also filled with plasma, although its density is much lower.

The classical definition of plasma limits the term to an appreciably ionized gas or vapor that conducts electricity and is, at the same time, electrically neutral, fluid, "hot," and viscous. The modern definition of plasma is less restrictive; the term simply denotes a more or less ionized gas. A gaseous complex that may be composed of electrons, ions of either polarity, gas atoms, and molecules in the ground or any higher state of any form of excitation, as well as of light quanta, is referred to as *plasma*. Plasma in this sense may be *cold*. Plasma created by an electric glow discharge is often called *low-temperature* plasma to distinguish it from *hot* plasma.

In the laboratory, plasma is generated by combustion, flames, electric discharge, controlled nuclear reactions, shocks, and other means. Because plasma loses energy to its environment mainly by radiation and conduction to the walls, in order to maintain the plasma state continuously in a laboratory apparatus, energy must be supplied as fast as it is lost. Of the various means of maintaining the plasma state continuously for a relatively long period of time, the most obvious and most common method is the use of an electric discharge. For this reason, most experimental work, particularly in the study of polymerization, is carried out using some kind of electric discharge.

There are many types of electric discharges, all characterized by the presence of free electrons and/or an electric field. Among the many types of electric discharge, glow discharge is by far the most frequently used in plasma polymerization. Consequently, the term *glow discharge polymerization* can be used nearly synonymously with *plasma polymerization*, although the latter covers polymerization obtained by a variety of technical processes.

4.2 Macroscopic Treatment of Glow Discharge

In its simplest form, a glow discharge can be established by passing a dc electric current through a gas under low pressure between two electrodes. Electric multiplication is due to an increase in the energy of the primary electrons as they move through the applied electric field until they gain sufficient energy to ionize the gas molecules, which collide with electrons. When a glow discharge is established, the space between the electrodes becomes visible by a characteristic glow. The actual distribution of light in the glow discharge is significant and is dependent on the voltage-current characteristics of the discharge. The general shape of the current-voltage characteristics of gaseous discharges for pressure in the range 0.1–10 torr is shown in Fig. 4.1, which delineates the conditions under which various discharges are stable. (1).

Glow discharge is characterized by the appearance of several luminous zones and by a constant potential difference between the electrodes independent of current. The relative size of these zones varies with pressure and the distance between the electrodes. A typical distribution is shown in Fig. 4.2a; the distribution of potential among different zones is shown in Fig. 4.2b.

As the pressure decreases, the negative glow and the Faraday dark space expand at the expense of the positive glow, which may disappear altogether. If the distance between the electrodes decreases, the positive glow diminishes while the size of the other zones remains intact. This indicates that the positive glow is not an essential feature of the discharge, as are the zones in the neighborhood of the cathode (1).

Apart from the cathode region, the resultant space charge is practically zero over the whole length of the tube, and the gas in the tube is in the form of a plasma. An important factor is that the density of the plasma in the negative glow is 10–100 times greater than that of the positive column (1).

The electric field is much higher in the cathode region. Right at the cathode, most of the current is carried by ions flowing to the cathode; in the rest of the discharge, including the negative glow and the Faraday dark space, nearly all of the current is carried by electrons. The Faraday dark space is dark because there is little or no accelerating electric field in this region.

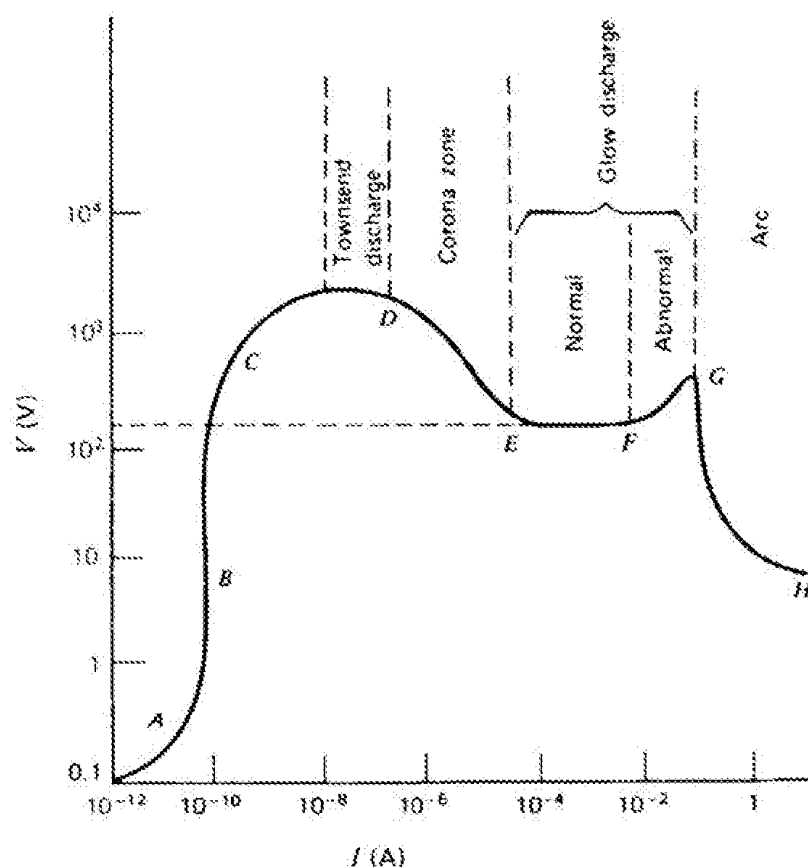


Fig. 4.1 Voltage-current characteristics of a dc discharge. From Shakin (*I*, Fig. 10). Copyright 1971 John Wiley & Sons, Inc.

Of the three main parts of the glow discharge, the cathode fall region is probably the least understood from a theoretical viewpoint. Although some theoretical treatments exist, Ingold considers the cathode fall, negative glow, and Faraday dark space together by assuming that they form a diode (2). This is because these regions are related to cathode properties, whereas the positive column is independent of the cathode.

It is important to note that the operation of the glow discharge depends critically on the role of the cathode dark space. In order to have a steady state, each electron emitted by the cathode must produce sufficient ionization and excitation to effect the release of a sufficient number of secondary electrons from the cathode upon impact of the ions.

In the positive column, the axial component of the electric field is constant, and hence all of the measurable quantities—particle densities, current densities, and particle temperature—vary with radial position only. The low

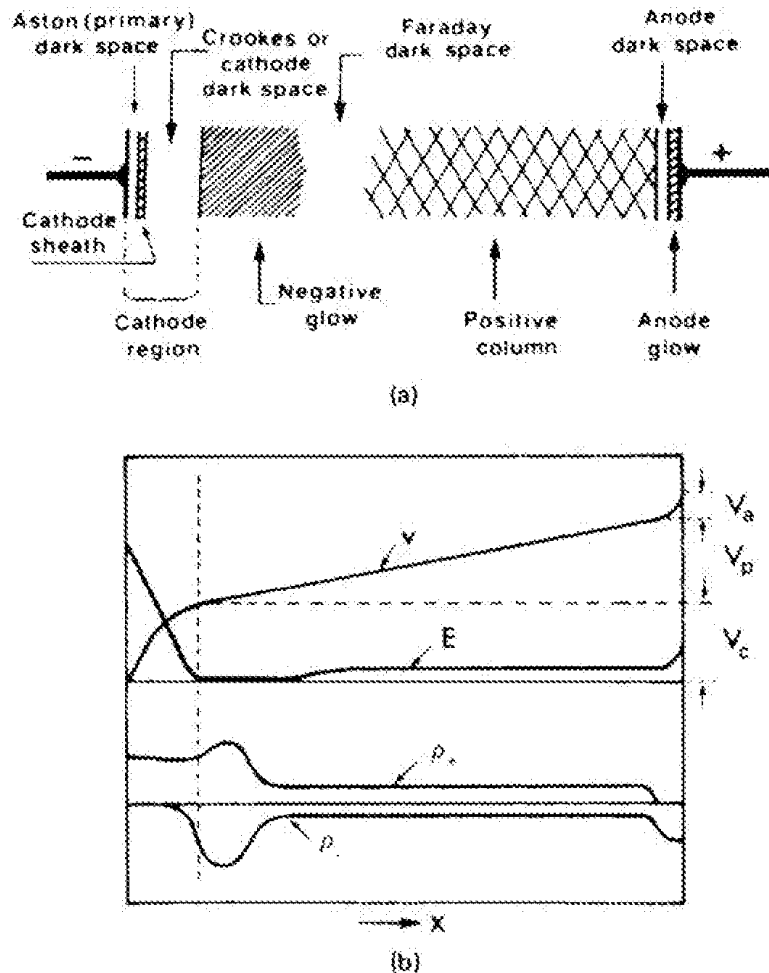


Fig. 4.2 (a) Normal glow discharge; the shaded areas are luminous. (b) Distribution of potential among luminous zones (4). From Shakin (*l*, p. 299, Fig. 11). Copyright 1971 John Wiley & Sons, Inc.

field as well as the uniform appearance of the positive column indicates that ionization is not obtained from the drift velocity of electrons in the field direction, but rather from their large random velocity acquired by numerous elastic collisions in the electric field (*l*).

The role of the anode is to transform current from the glow discharge to the external circuit. When there is no positive column, the anode is usually in the Faraday dark space. In this case, the anode fall of potential can be very small, or even negative, because ions and electrons diffuse together to the anode from

the negative glow in such a way that charge neutrality is maintained (2). In the presence of a positive column, however, a negative space charge is generally present in the neighborhood of the anode. The anode fall potential is of the order of the ionization potential of the gas, because it is in this region of the discharge that most of the ions that traverse the positive column are generated (1, 2).

In the region of normal glow discharge (E-F, Fig. 4.1) the effect of a rise in current is to increase the diameter of the discharge so that the current density will remain constant. For an abnormal glow discharge (F-G, Fig. 4.1) the current density rises with an increase in total current, causing both the cathode and the gas to become more heated.

4.3 Microscopic Treatment of Glow Discharge

4.3.1 IONIZATION OF MOLECULES BY AN ELECTRON BEAM

If a free electron is somehow produced in a gas and a dc electric field is imposed, the electron will respond according to Newton's law,

$$a = \frac{q}{m_e} E, \quad (4-1)$$

where a is the acceleration of the electron, q its electric charge, m_e its mass, and E an electric field, and will begin to accelerate in free fall. Three types of collisions can occur between the electron and a gas molecule. At low energies, elastic collisions will take place. At high energies, a large amount of energy can be lost by the electron in exciting the molecules to a higher energy level. At still higher energy levels, ionization of the molecule can occur. The last process is essential for maintaining an electric discharge.

Although we do not intend to review the fundamentals of ionization or electric discharge in this book, some important aspects that are relevant to plasma polymerization are presented in a simplified way in this chapter. A more detailed treatment of ionization and discharge can be found elsewhere (3-5). In the following sections, the excellent illustrations of Hatta (6) are adapted to explain the basic concept.

4.3.2 CROSS SECTION OF ELECTRON-ATOM COLLISIONS

To express the frequency of collision, the term *cross section of collision* or simply *cross section* is generally used. The collisions of electrons with gas atoms can be determined by the experiment described in Fig. 4.3, where K is a

CHAPTER 6

Kinetic and Mechanistic Aspects of Plasma Polymerization

As pointed out in Chapter 5, the level of vacuum generally used in plasma polymerization (10^{-3} – 10^1 torr) is too low to form polymers in a practical manner by ordinary polymerization such as the addition polymerization of olefinic monomers. At this point, the most important thing to recognize is that plasma polymerization is an entirely different type or category of polymerization than the polymerizations discussed in Section 5.2. In this chapter, the kinetic and mechanistic aspects of plasma polymerization are discussed as an extension of the comparisons presented in Section 5.4.

Most studies dealing with the kinetic and mechanistic aspects of plasma polymerization have been based on an *a priori* concept of polymerization, such as (addition type) chain-growth polymerization, which is, according to the considerations discussed in Section 5.4, very unlikely to play a significant role in plasma polymerization or any polymerization that occurs in a vacuum.

Another prevailing trend in studies of the kinetics or mechanisms of plasma polymerization has been the direct application of theories of, or data on, the ionization of gases (the majority of data having been obtained with nonreactive gases such as monoatomic inert gases and relatively simple diatomic gases including N_2 , O_2 , etc.) to polymerizable monomers such as vinyl monomers. In this sense, perhaps too much emphasis has been placed on the ionization aspects of plasma, and too little attention has been paid to the elementary steps of polymer formation (the growth mechanism of polymerization).

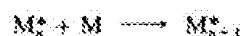
Among the polymerizations described in Chapter 5, the closest to plasma polymerization are radiation polymerization and Parylene polymerization. The former involves the ionization of monomers as the primary step of the

because the degree of polymerization obtainable by radiation polymerization is usually smaller than 1000. Thus, even if chain-growth radiation polymerization were possible, the polymer could not be formed at such a high dose rate, the recombination of primary free radicals would predominate.

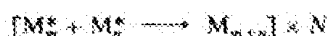
In reality, at such a high dose rate, polymer would be formed by different mechanisms, as evidenced by plasma polymerization. In this sense, the study of plasma polymerization would lead to a prediction of what one could expect if the dose rate in radiation polymerization were increased by a few orders of magnitude. Namely, in such a case, the square root dependence on the dose rate would not be obeyed, and polymers would be formed by the rapid step-growth mechanism.

6.2 Growth Mechanism of Plasma Polymerization

The discussions presented so far suggest that chain-growth polymerization, represented by

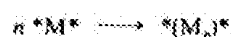


where M^* is the reactive chain-carrying species and M the monomer molecule, would not play a significant role in plasma polymerization and also that the growth mechanism of plasma polymerization would very likely be the rapid step-growth reaction,



where N represents the number of repetitions of similar reactions. This reaction mechanism differs from conventional step-growth polymerization, in which the reaction occurs between molecules.

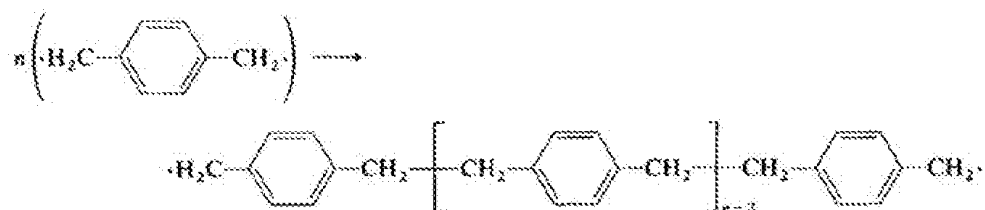
In case of Parylene polymerization, $^*M^*$ is a difunctional reactive species and the overall polymerization can be represented by



that is, if we take the diradical form of *p*-xylylene,



the reaction can be written as



(The exact mechanism of the propagation of *p*-xylylene is not well elucidated, and this mechanism is a model representing the rapid step-growth mechanism based on the difunctional reactive species.) Thus, the polymer formed should contain a considerable quantity of unreacted free radicals. It was found that as-polymerized polymers of Parylene indeed contain a measurable quantity of free radicals.

If the reactive species represented by M^* is monofunctional, such as a free radical R^* , the reaction given by $M_m^* + M_n^* \rightarrow M_{m+n}$ is essentially a termination process that occurs in free radical polymerization and does not contribute to growth without additional elementary steps.

In the case of monofunctional reactive species, a single elementary step is indeed a termination process; in plasma polymerization, however, the product of the reaction is not immune to the activation process that produced the active species considered in the reaction. In other words, the reactivation of the product of an elementary reaction is bound to occur in plasma, as pointed out by Yasuda and Lamaze in 1973 (2).

The overall polymerization mechanism based on the rapid step-growth principle is shown in Fig. 6.1. There M_x refers to a neutral species that can be the original monomer molecule or any of the dissociation products including some atoms such as hydrogen, chlorine, fluorine, and others. The activated species that are capable of participating in the chemical reaction to create a covalent bond are given by M^* . Difunctional activated species are shown by $\cdot M^*$. The subscripts i , j , and k merely indicate the difference in the size of

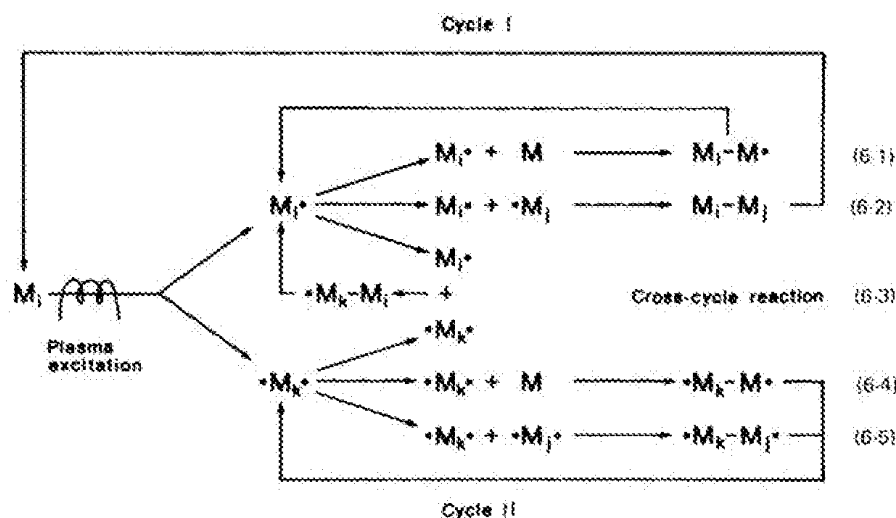
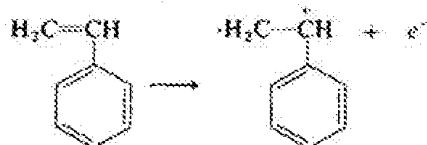


Fig. 6.1 Schematic representation of bicyclic step-growth mechanism of plasma polymerization.

species involved ($i = j$ is possible); thus, $i = j = 1$ corresponds to the original monomer.

Although the activated species are represented by the symbol for a free radical, for simplicity and reasons to be explained later, any activated species can be considered in the reactions shown in Fig. 6.1. For instance, the opening of a double bond by ionization produces an ion-radical, as shown in Sec-



tion 5.3. The ionization of styrene yields a cation-radical, represented by the symbol $\cdot\text{M}\cdot$, indicating that the species has two reactive sites. Thus, the opening of a double bond and of a cyclic structure in plasma (not by the addition of a reactive species) produces the difunctional reactive intermediate $\cdot\text{M}\cdot$.

As shown in Fig. 6.1, the overall reaction contains two major routes of rapid step growth. Cycle I is via the repeated activation of the reaction products from monofunctional activated species, and cycle II is via difunctional or multifunctional activated species similar to what is found in Parylene polymerization. As shown in later sections, plasma diagnostic analysis indicates that ample difunctional species such as $\cdot\text{CH}_2\cdot$ and $\cdot\text{CF}_2\cdot$ are found in plasmas of organic compounds. Therefore, it seems likely that cycle I and cycle II may play equally significant roles. In both cases, however, the growth mechanism of polymerization is rapid step-growth polymerization (RSGP).

Chain-growth polymerization carried by the activated species, particularly free radicals, of certain monomers is possible under certain conditions. For instance, if the plasma polymerization of a vinyl monomer such as styrene were carried out at high vapor pressure and low substrate temperature (low enough to condense the liquid monomer), addition polymerization by the activated species created in plasma would occur. The infrared (IR) spectrum of the plasma polymer of styrene carried out under such conditions indicates that the polymer is almost identical to conventional polystyrene.

Reactions (6-1) and (6-4) in Fig. 6.1 are essentially the same as the first step of propagation by the addition mechanism. Therefore, those reactions require a chemical structure that allows for the addition of $\text{M}\cdot$. For the reasons mentioned in Chapter 5, consecutive addition to a sizable kinetic chain length does not occur in a vacuum. Reaction (6-2) is essentially a termination by the recombination mechanism. Reaction (6-3) is similar to reaction (6-2), but one reactant is bifunctional. The loss of a reactive site due to disproportionation in free radical polymerization can be included in reactions (6-2) and (6-3). Reaction (6-4) is the same as reaction (6-1), except that a reactant is

bifunctional. Reaction (6-5) is a combination of bifunctional intermediates, which may play a major role in certain monomers under certain conditions. This reaction represents the principal growth mechanism in the Parylene polymerization discussed in Section 5.4.2. Some of the reactions involved may be identical to those in free radical addition polymerization; a major distinction, however, is the absence of the chain-growth mechanism.

If we examine these mechanisms further, the types of activated species, $M^\bullet$, that can contribute to this kind of RSGP become clear. Namely, ionic species can contribute in this scheme via the reaction between a cation and an anion, that is, $M_i^+ + M_k^- \rightarrow M_{i+k}$, because M^+ cannot react with M^+ , and M^- cannot react with M^- , due to the similar charge they carry.

As discussed in Chapter 4, in most plasma, the number of positive ions, n_+ , is equal to the number of electrons, n_e . Therefore, such a contribution of ionic species would be possible only in plasma that contained a considerable quantity of negative ions (i.e., plasma containing negative ions of halogens and/or oxygen). Thus, it seems quite probable that plasma polymerization proceeds mainly via reactions of neutral species ($\neq$), although ions do indeed exist in plasma.

6.3 Reactive Species in Plasma Polymerization

Although plasma cannot be created without ionizing monomer molecules used for plasma polymerization, it is more appropriate to consider plasma polymerization as a side reaction of the ionization process. Without recognition of this situation, some plasma diagnostic data cannot be appropriately interpreted. Namely, one falls into the situation in which everything found in a plasma must be correlated with the plasma polymerization. It may be, however, that many species in the plasma do not contribute to the plasma polymerization but rather contribute to the ablation. Therefore, it is important to recognize the regime of the plasma polymerization within the overall plasma that exists in the reactor.

Among the possible neutral activated species that can participate in the RSGP mechanism given by Fig. 6.1, the free radical is the most probable and important species. Direct support for this assumption is the fact that most polymers formed in plasma contain a high concentration of free radicals (i.e., 10^{17} – 10^{20} spins per cubic centimeter). Although a number of possible alternative mechanisms can be written for the presence of free radicals in plasma polymers, the most probable one is based on this polymer formation mechanism.

Direct proof that the residual free radicals involved in the RSGP mechanism remain in the polymer as trapped free radicals can be seen in Parylene polymerization, in which an alternative mechanism such as the

Table 6.31

RELATIVE AREAS IN THE ^{13}C -NMR SPECTRA OF PLASMA-POLYMERIZED C_2 HYDROCARBONS*

	Peak				
	I	II	III	IV	V
Injected gas	---C<	---CH + =CH_2	>C<	>CH + >CH_2	---CH_2
Ethane	9	10	17	47	17
Ethylene	12	12	12	43	21
Acetylene	17	21	16	40	6

* Data reproducibility, $\pm 15\%$. From Dilks *et al.* (24).

6.7.4 ELECTRON SPECTROSCOPY FOR CHEMICAL ANALYSIS

ESCA offers a distinct advantage in the study of the structure of plasma polymers, because the method provides information pertinent to the top surface of a material (e.g., 20–50 Å) and hence is free of the overwhelming signals from the substrate material, which greatly hamper many other physical analytical methods applied to an ultrathin film. ESCA is used primarily for the analysis of elements, however, and its application to the determination of structural features of an organic material is limited.

Considerable effort has been expended to obtain structural information on plasma-polymerized materials by means of ESCA. In this respect, the outstanding contributions of Clark and co-workers in this field are noteworthy. Clark extended the use of ESCA to obtain structural information on polymers of fluorine-containing compounds and polymers with aromatic structure.

Because fluorine is the most electronegative element in the periodic table, it causes a sufficiently large shift in the binding energy of carbons bonded to a fluorine atom or atoms. ESCA has been used to study the structure of plasma polymers in the following manner (25–30):

1. The relative overall intensity ratios of F_{1s} to C_{1s} levels in a fluoropolymer film can be used to derive the stoichiometry after sensitivity factors for a particular instrumental configuration have been established.
2. An analysis of the overall C_{1s} line profiles with component peaks that correspond to distinctive structural features (e.g., CF_3 groups) also allows an independent determination of stoichiometry and provides information on the structural features present.

Table 6.32
STOICHIOMETRIES DETERMINED BY ESCA FOR POLYMER FILMS PRODUCED FROM INDUCTIVELY COUPLED RADIO
FREQUENCY PLASMAS EXCITED IN PERFLUOROBENZENE^a

Stoichiometries	0.05 torr						0.10 torr						0.2 torr					
	Incl. H/C		Excl. H/C		F _{1s} ^b		Incl. H/C		Excl. H/C		F _{1s} ^b		Incl. H/C		Excl. H/C		F _{1s} ^b	
	C/F 1 ^c	C/F 2 ^c	C/F 1 ^c	C/F 2 ^c	C/F 1 ^c	C/F 2 ^c	C/F 1 ^c	C/F 2 ^c	C/F 1 ^c	C/F 2 ^c	C/F 1 ^c	C/F 2 ^c	C/F 1 ^c	C/F 2 ^c	C/F 1 ^c	C/F 2 ^c	C/F 1 ^c	C/F 2 ^c
5.0 W																		
Glow 30°	1.0	0.86	1.06	0.92	8.92	0.96	0.96	0.90	1.01	0.94	8.29	0.78	0.72	0.92	0.85	8.4		
Glow 70°	0.80	0.70	1.05	0.83	7.57	0.92	0.71	0.71	1.04	0.79	6.94	0.75	0.61	0.86	0.70	8.71		
Nonglow 30°	0.98	1.02	1.07	1.11	11.55	1.33	1.60	1.63	1.63	1.83	17.27	0.94	0.81	1.10	0.95	11.8		
Nonglow 70°	0.98	0.85	1.14	0.98	8.38	—	—	—	—	—	—	0.8	0.79	0.99	0.98	12.6		
10.0 W																		
Glow 30°	1.12	0.95	1.18	0.98	8.7	1.04	0.79	0.92	0.92	0.90	7.72	0.87	0.67	0.96	0.74	7.64		
Glow 70°	—	—	—	—	—	0.79	0.62	1.0	1.0	0.79	7.33	0.82	0.65	1.01	0.79	7.93		
Nonglow 30°	1.37	1.24	1.59	1.44	13.13	1.13	0.9	1.25	1.25	0.99	7.96	1.10	0.95	1.21	1.04	12.09		
Nonglow 70°	—	—	—	—	—	0.92	0.77	1.15	1.15	0.97	7.93	1.0	0.79	1.17	0.91	8.76		

^a From Clark and Shurtleworth (37).

^b C/F is the stoichiometry obtained from the C_{1s} profile.

^c C/F 2 is the stoichiometry obtained from the C_{1s}/F ratios.

3. Angular dependence studies in which data are recorded as a function of electron takeoff angle with respect to the normal to the sample surface, coupled with investigation of intensity ratios for photoemission from different levels of the same element (e.g., F_{1s} and F_{2s}), provide direct information on the vertical homogeneity of the polymer films. With an $Mg_{K\alpha 1,2}$ photon source ($h\nu = 1253.7$ eV), typical sampling depths for levels of interest (three times the typical mean free paths) are F_{1s} , ~ 25 Å; C_{1s} , ~ 45 Å; and F_{2s} , ~ 90 Å.

4. Monitoring of O_{1s} and C_{1s} core levels at 285 eV (CH) provides direct information on the low level of extraneous surface contamination or oxidation of the surface. Combined with an angular dependence study, the depth profile of oxidation can be studied. In many studies, it has been shown that the oxygen incorporation occurs at the surface.

The large chemical shift caused by the attached fluorine atom(s) can be used to determine some structural features of plasma polymers formed from fluorine-containing organic compounds. Chemical shifts observed with fluorine-containing structures (31) are shown in Table 6.32.

Typical examples of C_{1s} spectra obtained with the plasma polymer of perfluorocyclohexane (31) are shown in Fig. 6.37 for polymers formed in the glow region and in Figure 6.38 for polymers formed in the nonglow region. The stoichiometries of the plasma polymers based on these ESCA data are summarized in Table 6.33.

When the conditions of plasma polymerization are varied widely or the polymer samples are collected in various sections of a plasma polymerization reactor, ESCA C_{1s} spectra reveal the system-dependent nature of the RSGP mechanism. For example, O'Kane and Rice (32) used the plasma polymerization reactor shown in Fig. 6.39 in which an inductively coupled rf (13.56 MHz) power source was used to create plasma. Substrates were placed immediately before the rf coil (A), inside the rf coil (B), immediately after the rf coil (C), in the deposition chamber (0.41 m diameter $\times$ 0.21 m) (D), and at the exit of the deposition chamber (E). Figure 6.40 shows the ESCA C_{1s} spectra for the corresponding films deposited in the plasma regions as compared with conventional polytetrafluoroethylene. This figure clearly indicates that a certain structural feature (e.g., $-\text{CF}_3$) is incorporated into the polymer in the preferred region. In other words, considerable fragmentation of the monomer or rearrangement of atoms occurs in plasma, and the resultant fragments behave according to their gas-phase kinetic characteristics. Because of this aspect, the kind of polymer that is deposited and the portion within a reactor on which it is deposited are dependent on the size (cross-sectional area) of a tube or a reactor.

A similar experiment using a relatively small glass tube (33) (~ 14 mm) shows a completely different pattern of deposition of structural features.

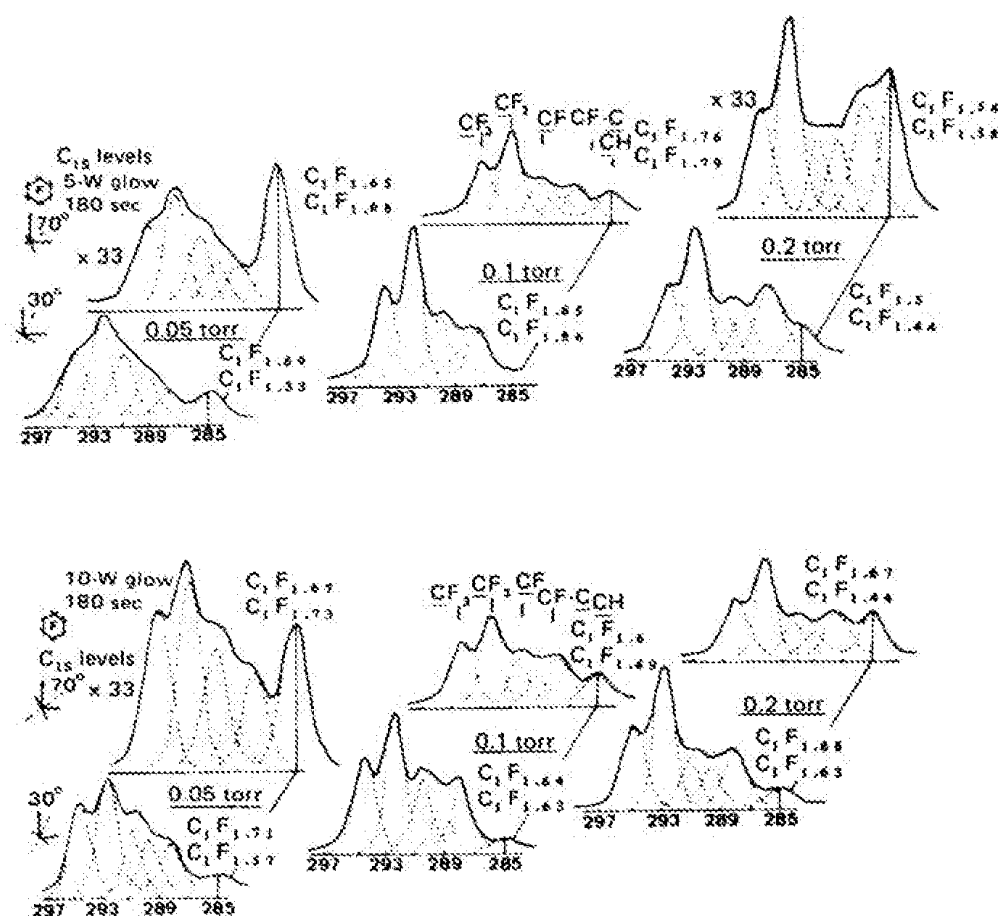


Fig. 6.37 The C_{1s} levels of plasma-polymerized C_6F_{12} prepared in the glow region. Adapted from Clark and Shuttleworth (31).

Characteristic shapes of ESCA C_{1s} peaks are shown in Figs. 6.41 and 6.42. At the lower energy input level, the more fluorinated polymer is deposited before the rf coil and very few fluorine atoms are found in the polymer that is deposited on the downstream side of the rf coil in the nonglow region. At the higher level of energy input, the polymers found at both locations contain very few fluorine atoms, indicating that the preferred location of deposition for $-\text{CF}_3$, $>\text{CF}_2$, and others shifted beyond the region of the reactor where samples were collected.

In a system in which the flow does not pass through the energy input zone (rf coil) and plasma polymerization is carried out in the tail-flame portion of the glow discharge with a very low W/FM level (in a relatively larger tube, e.g., 5 cm i.d.), the polymer formed in the downstream nonglow region (33) is

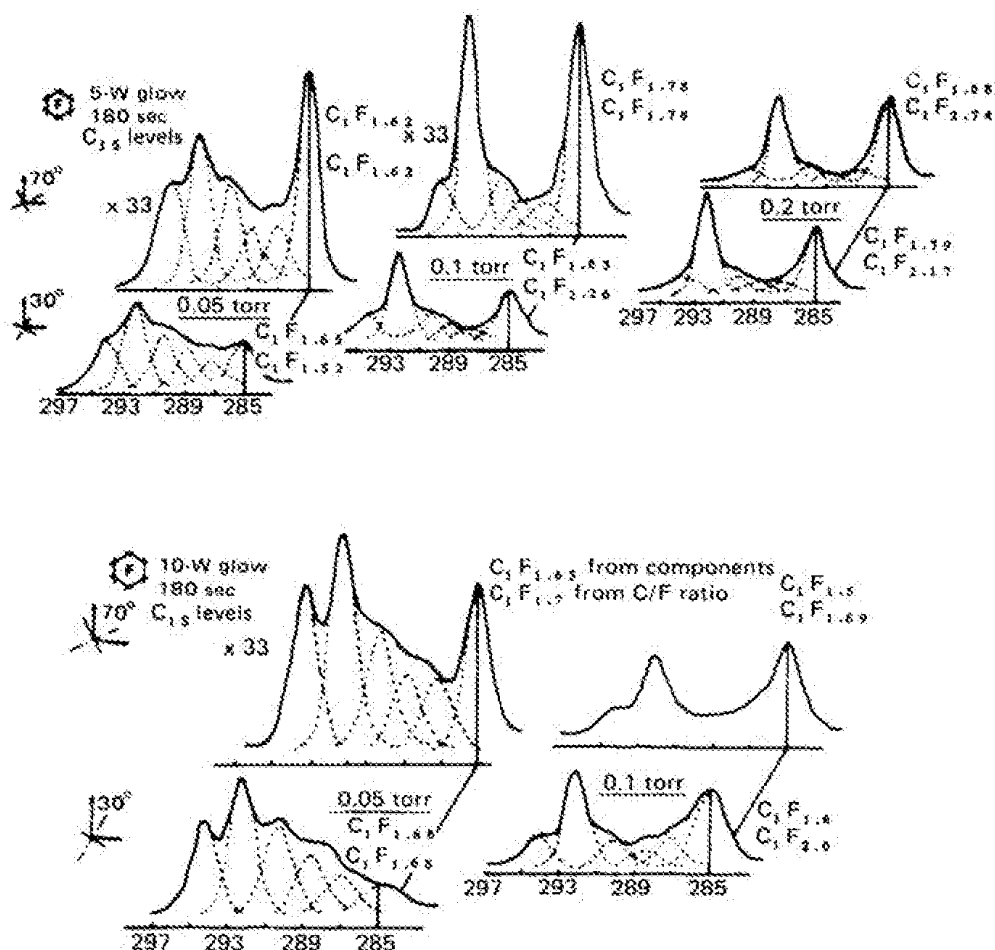


Fig. 6.38 The C_{1s} levels of plasma-polymerized C_6F_{12} prepared in the nonglow region. Adapted from Clark and Shuttleworth (37).

completely different from that formed in the downstream nonglow region of a small-tube reactor (Fig. 6.43). In this case, the polymer formed in the nonglow region is nearly identical to conventional polytetrafluoroethylene.

Thus, ESCA reveals that plasma polymers formed from the same monomer but in different sections of a reactor, by different reactors, or under different conditions are significantly different. Clark and Abraham (34) used ESCA to measure the initial deposition rate, together with ESCA spectrum analysis, for the plasma polymerization of perfluoro-2-butyltetrahydrofuran, and the result is a good illustration of this aspect of plasma polymerization. Because of the presence of another electronegative element, oxygen, and because of the

Table 6.33
STOICHIOMETRIES DETERMINED BY ESCA FOR POLYMER FILMS PRODUCED FROM INDUCTIVELY COUPLED RADIO
FREQUENCY PLASMAS EXCITED IN PERFLUOROCYCLOHEXANE^a

Stoichiometries	0.05 torr						0.1 torr						0.2 torr					
	Incl. H/C			Excl. H/C			Incl. H/C			Excl. H/C			Incl. H/C			Excl. H/C		
	C/F 1 ^b	C/F 2 ^c	C/F 1 ^b	C/F 1 ^b	C/F 2 ^c	F _{1s} / F _{2s}	C/F 1 ^b	C/F 2 ^c	C/F 1 ^b	C/F 2 ^c	F _{1s} / F _{2s}	C/F 1 ^b	C/F 2 ^c	C/F 1 ^b	C/F 2 ^c	F _{1s} / F _{2s}	C/F 1 ^b	C/F 2 ^c
5.0 W																		
Glow 30°	1.23	1.30	1.28	1.28	1.58	8.4	—	—	—	—	8.7	1.21	1.13	1.26	1.24	8.4	—	—
Glow 70°	1.12	1.11	1.29	1.29	1.27	8.22	1.13	1.18	1.22	1.27	8.5	1.19	1.16	1.26	1.24	8.57	—	—
Nonglow 30°	1.4	1.37	1.52	1.52	1.49	10.24	0.83	1.06	1.31	1.68	—	0.9	1.3	1.26	1.73	19.17	—	—
Nonglow 70°	1.12	1.04	1.38	1.38	1.27	8.8	0.68	0.95	1.37	1.86	—	—	—	—	—	—	—	—
10.0 W																		
Glow 30°	1.29	1.24	1.37	1.37	1.33	8.2	1.19	1.24	1.21	1.27	8.7	1.08	1.08	1.26	1.27	9.57	—	—
Glow 70°	1.14	1.04	1.36	1.36	1.24	8.94	1.05	1.08	1.19	1.21	7.89	0.78	0.83	1.18	1.24	8.75	—	—
Nonglow 30°	1.46	1.63	1.59	1.59	1.79	10.2	0.86	1.08	1.47	1.86	—	0.32	0.39	0.91	1.13	—	—	—
Nonglow 70°	1.31	1.37	1.57	1.57	1.68	10.7	0.86	1.27	1.46	2.17	11.54	—	0.27	—	—	—	—	—

^a From Clark and Shuttleworth (31).

^b C/F 1 is the stoichiometry obtained from the C_{1s} profile.

^c C/F 2 is the stoichiometry obtained from the C/F area ratios.

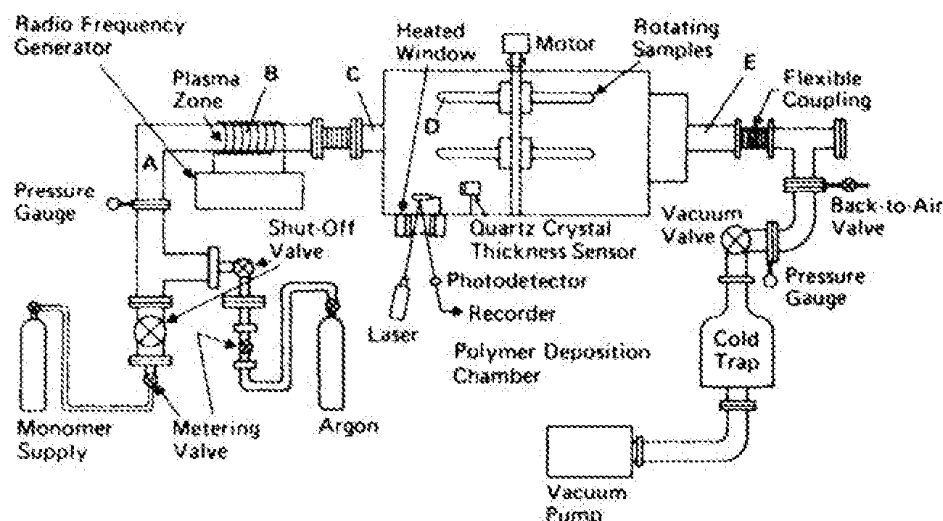


Fig. 6.39 Glow discharge thin polymer film deposition system. Adapted from O'Kane and Rice (32).

relatively large molecular weight of the monomer, the plasma polymerization of this monomer is very sensitive to variations of plasma polymerization conditions. An important aspect found in a comparative study of perfluoro-2-butyltetrahydrofuran and perfluorocyclohexane is that the ether oxygen atom in the furan ring is much more sensitive to ionization than the fluorine atoms in the rest of the perfluorocarbon structure. The ionization potential for the oxygen lone pair is significantly lower ($\Delta E \approx 3$ eV) than that for perfluorocyclohexane, and consequently the oxygen atom becomes the unbuttoning site, which evidently occurs at a relatively low level of W/FM (e.g., 10^{-7} J/kg). ESCA results show a dramatic decrease of oxygen in the polymer as the power input level (W/FM) increases (Fig. 6.44).

The ring opening, or breaking up, of the cyclic structure occurs in the plasma polymerization of both perfluorocyclohexane and perfluoro-2-butyltetrahydrofuran, but because of the preferential unbuttoning site (ether oxygen), the loss of fluorine in the plasma polymer of perfluoro-2-butyltetrahydrofuran is significantly less than that in the plasma polymer of perfluorocyclohexane. Even in this case, however, the F/C ratio is significantly lower than that for the monomer, and conversion of CF_2 sites to both CF_3 and CF sites take place. The relative percent contribution of $CF_3/CF_2/CF$ structural features in the polymer film of 33/42/21 may be compared with corresponding figures of 12.2/75/12.5 for the monomer perfluoro-2-butyltetrahydrofuran.

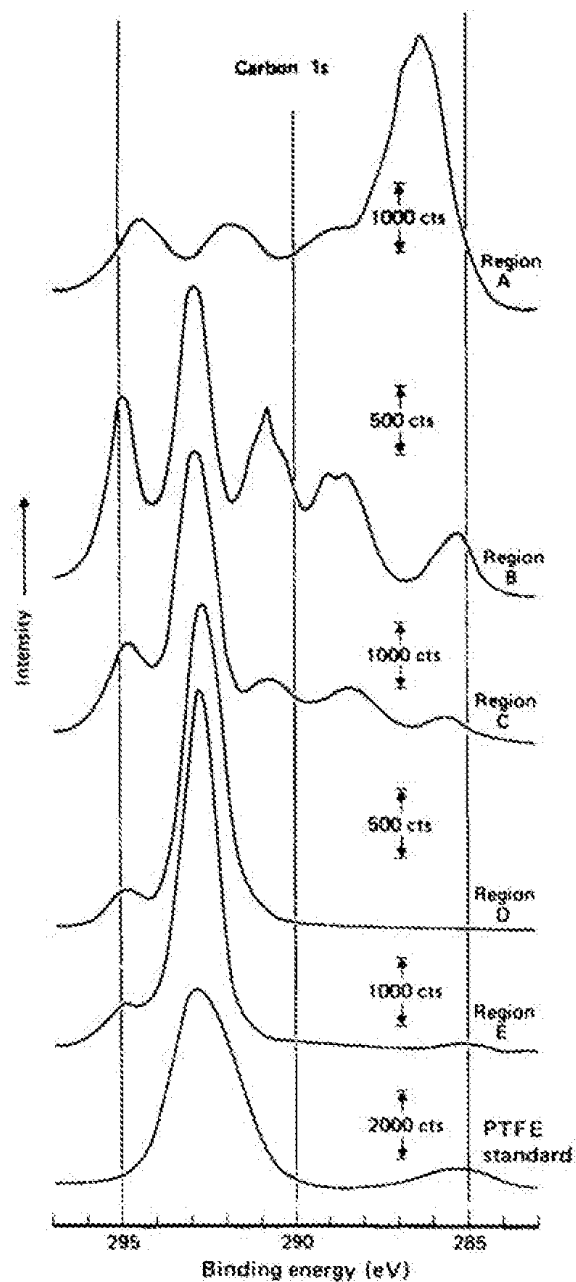


Fig. 6.40 The C_{1s} X-ray photoelectron spectra of plasma-deposited fluorocarbon polymer films from different regions of the plasma system (PTFE, polytetrafluoroethylene; cts, counts). Adapted from O'Kane and Rice (32).

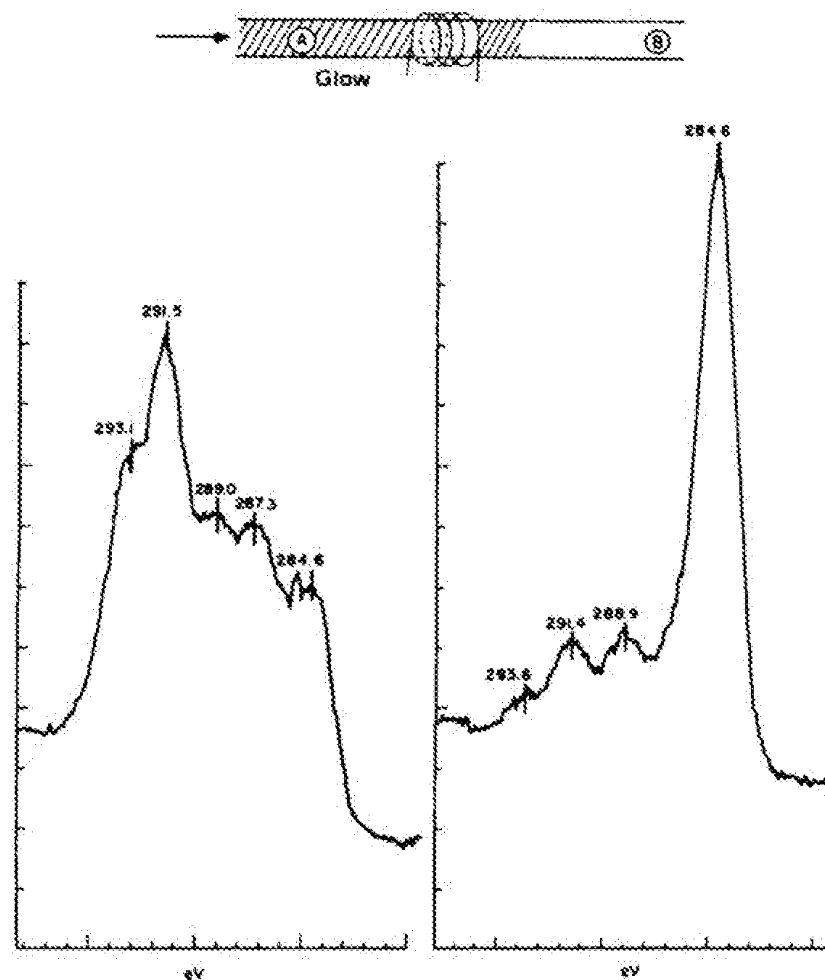


Fig. 6.41 Dependence of the ESCA C_{1s} peaks of glow discharge polymers of tetrafluoroethylene on discharge conditions and location of polymer deposition. Polymer deposition occurred at two locations in the reactor shown in the inset: (A) before the radio frequency coil and (B) after the radio frequency coil. Discharge power level, 1.9×10^7 J/kg. Adapted from Yasuda (33).

Thus, in plasma polymerization, no single dominant mechanism can be found, and many simultaneous and competitive reactions occur. The competitive nature of reactions is highly dependent on the conditions of plasma polymerization, in particular the energy input level. These characteristic aspects of plasma polymerization have been clearly demonstrated by ESCA studies.

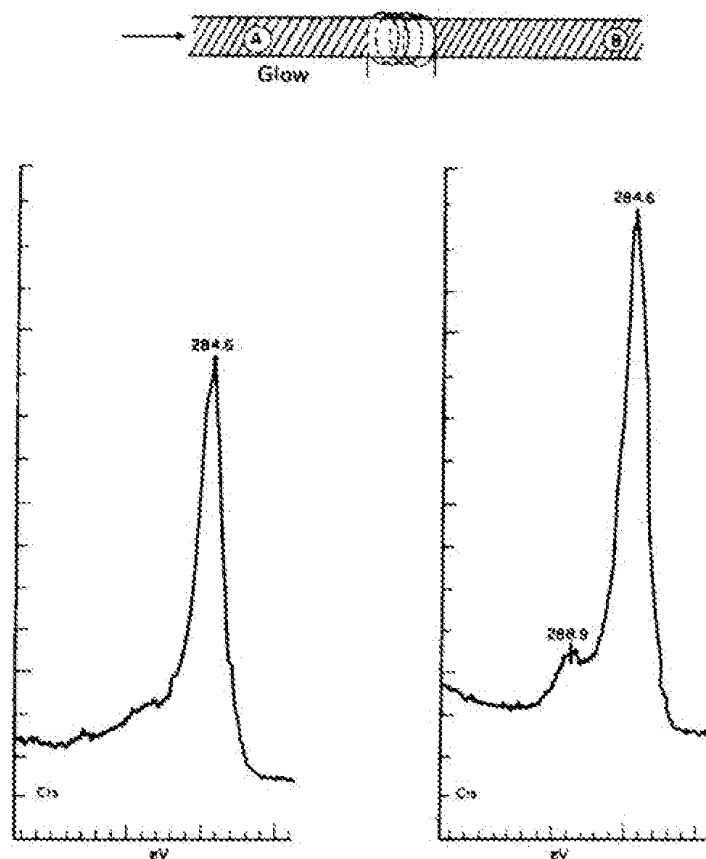


Fig. 6.42 ESCA C_{1s} peaks of glow discharge polymers of tetrafluoroethylene in the same reactor shown in Fig. 6.41, but at the higher discharge power level of 7.7×10^8 J/kg. Adapted from Yasuda (33).

6.8 Atomic (Nonmolecular) Nature of Plasma Polymerization

The plasma polymerization so far discussed is characterized by (1) the extensive fragmentation and/or rearrangement of a structural moiety or atoms in the starting material and (2) simultaneously occurring reactions involving many kinds of chemical species.

These phenomena are seldom found in conventional polymerizations, which can be recognized as molecular reactions. In other words, in conventional polymerizations, molecules of monomers are linked together with a minimum alteration of chemical structure of the monomer, and the structure of a polymer can be well predicted from the structure of the monomer. In

CHAPTER 7

Competitive Ablation and Polymer Formation in Plasma

7.1 Overall Reactions in a Plasma Polymerization System

As mentioned in Chapter 6, many reactions occur simultaneously in a plasma polymerization system. In order to understand polymer formation in plasma, one should recognize the nature of other processes as well, because it is nearly impossible to single out one particular process by eliminating others completely.

From the viewpoint of plasma polymerization as a material production process, there are two opposing processes: polymer formation, which leads to the deposition of material, and ablation, which leads to the removal of material. For instance, saturated fluorine-containing compounds are widely used in the etching process of silicon and silicon-containing materials for the production of microelectronic circuitry. On the other hand, perfluorocarbons are used as monomers of plasma polymerization to deposit materials in the form of coatings. In the early stage of the development of plasma polymerization, those two processes were considered to be independent, and for many years it was thought that certain perfluorohydrocarbons used for plasma etching could not be polymerized by plasma.

The interaction of these two opposing processes and their coexistence in plasma were recognized in the early 1970s. Kay (1) demonstrated that the main effect of CF_4 plasma can be shifted from etching to polymer deposition by the addition of H_2 into the plasma and that, depending on the amount of H_2 added to the CF_4 , the balance between polymerization and ablation can be controlled. A similar phenomenon attributable to ablation in the plasma polymerization of tetrafluoroethylene was reported by Yasuda and Hsu (2). When the dependence of polymer deposition rate on discharge wattage was

investigated, it was found that, at a very low flow rate, there was very little polymer deposition and the deposition rate decreased with increasing discharge wattage. At higher flow rates, the deposition rate increased nearly linearly but reached a maximum and started to decrease with increasing discharge power (Fig. 7.1).

These two early findings are illustrative of two major factors that influence the balance between polymer formation and ablation. The first demonstrates the control of ablation due to extremely reactive fluorine-related species (atomic fluorine, $F^\cdot$, etc.) by chemical reactions, and the second demonstrates the role of discharge conditions that control the production of highly ablative species.

Although tetrafluoroethylene normally undergoes olefinic double bond polymerization in plasma, at a high level of energy input (W/FM), splitting of the $C-F$ bond becomes the dominating factor and ablation prevails. The CF_4

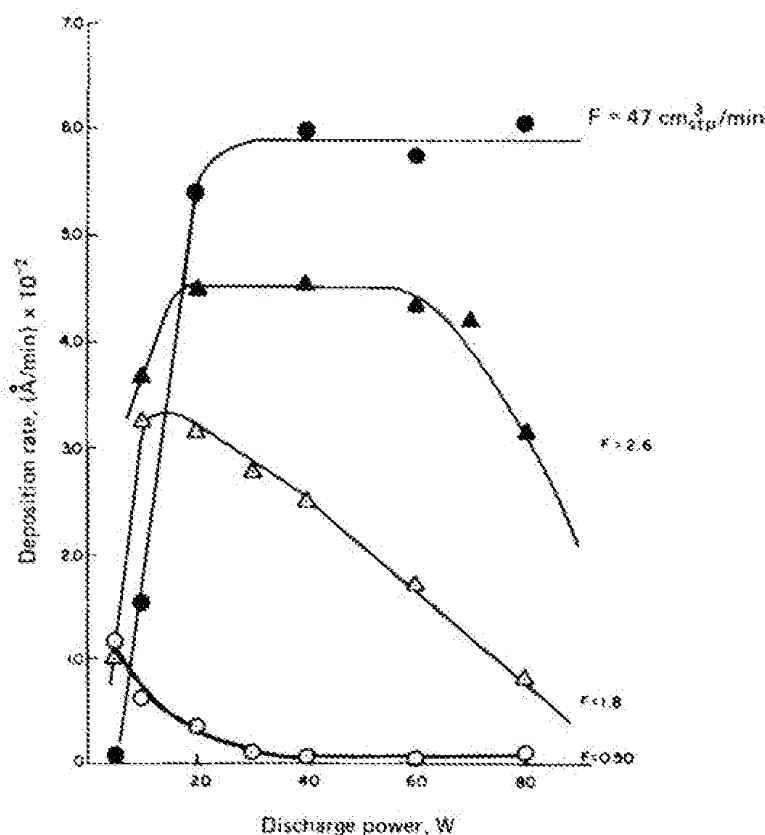


Fig. 7.1 Dependence of polymer deposition rate on discharge power at various flow rates for tetrafluoroethylene. Adapted from Yasuda and Hsu (2).

cannot polymerize without breaking of the C—F bond; once fluorine is split off, however, its ablative effect becomes predominant. The addition of H_2 to such a system has a stabilizing effect. This situation can be easily visualized by comparing bond energies. The high reactivities of fluorine-based species can be seen from the fact that the F—F bond energy is only 37 kcal/mol. The bond energy for H—F is 135 kcal/mol, indicating that nearly 100 kcal/mol of stabilization is gained by the reaction of H_2 . Thus, the role of H_2 is that of a scavenger of ablative species.

Perfluorocarbons represent, perhaps, the most extreme case of ablation competing with polymer formation. The principle found with perfluorocarbons, however, should be applicable to nearly all cases. The overall scheme of plasma polymerization (Fig. 7.2) encompasses the principle of the competitive ablation and polymerization (CAP) mechanism (3).

As soon as plasma is created, the gas phase is no longer the vapor of the original monomer but becomes a complex mixture of the original monomer, ionized species, excited species of the original monomer, excited species of fragments from the monomer, and gas products that do not participate in polymer formation such as H_2 and F_2 . Because the vacuum must be

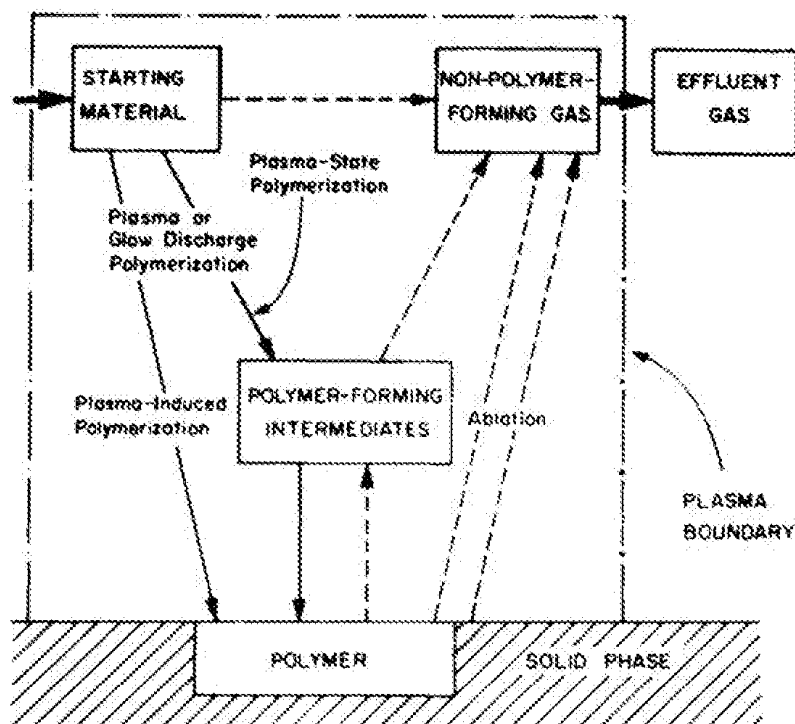


Fig. 7.2 Overall mechanism of glow discharge polymerization.

maintained by solid surfaces, the plasma also interacts with wall materials as well as any other materials that exist in the plasma, such as substrate and support. Therefore, polymer-forming intermediates and gas by-products may also originate from solid materials with which plasma interacts. In this sense, any material that interacts with plasma becomes a source of monomer for plasma polymerization.

The term *ablation* in the CAP mechanism represents two types of reactions. One is the splitting of a portion of solid materials, and the other is the splitting of a portion of the monomer molecule. The first process might be closely related to the etching of material; the ablation process in a plasma polymerization system, however, does not necessarily result in the removal of material. The ablated material may be redeposited as plasma polymer at different locations or leave the system as gas products (effluent gas) depending on the nature of the species.

The ablation process associated with monomer can be visualized as the splitting of a molecule or the fragmentation of the monomer. This aspect is very important in plasma polymerization, and it is not an exaggeration to state that no monomer polymerizes without fragmentation in plasma.

As discussed in Chapter 6, it seems that the main route of polymer formation occurring under the influence of plasma is via plasma-state polymerization; the possibility of plasma-induced polymerization always exists, however. This possibility is high and becomes important when a cold substrate is used with a condensable vinyl-type monomer. Plasma-induced polymerization in the gas phase can be ruled out in most practical senses, and plasma-induced polymerization represents the polymerization of condensed monomer on the surface by the interaction of plasma.

From Fig. 7.2, it is clear that the effect of the addition of H_2 to CF_4 can also be seen by the addition of hydrocarbons such as CH_4 or the presence of hydrocarbon polymers in the plasma. Polymer formation from CF_4 by the addition of CH_4 was also found by N. Inagaki and H. Yasuda (unpublished data) in 1978. Perhaps the most important factor to keep in mind is that everything that comes in contact with plasma becomes an important participating segment of plasma polymerization. In other words, one cannot completely control plasma polymerization by the selection of a monomer and discharge conditions without considering this factor. Even the substrate for polymer deposition becomes a part of the plasma polymerization system. In certain cases, the wall of the reactor becomes a source of a comonomer of plasma polymerization. These situations are illustrated by the following example.

When plasma polymerization of tetrafluoroethylene is carried out in a glass tube and an NaCl powder spread on a glass plate is used as the substrate in order to measure the IR spectrum by the formation of pellets of NaCl coated with plasma polymer, conspicuous IR peaks appear at 1130, 1080, and 1035 cm^{-1} (Fig. 7.3) (4). When the same polymerization is carried out with a

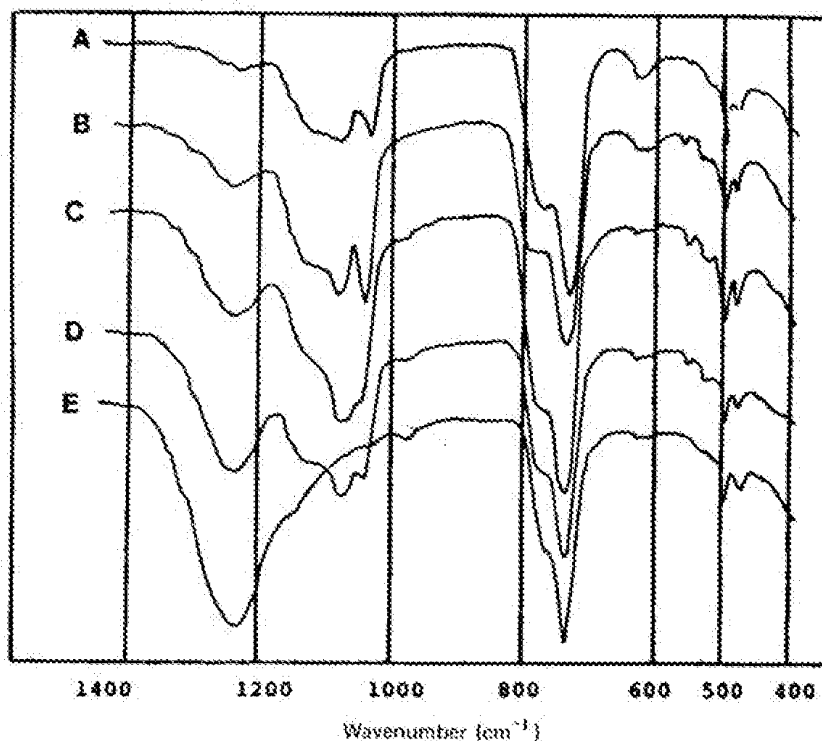


Fig. 7.3 Infrared spectra of plasma-treated NaCl powder under various monomer flow rate conditions (70 W). $F(\text{C}_2\text{F}_4)$ (cm^3/min) for each spectrum is as follows: A, 0.1; B, 0.15; C, 0.27; D, 0.51; E, 0.86. Adapted from Masuoka and Yasuda (4).

KRS-5 internal reflection prism as the substrate instead of NaCl powder, the IR spectrum shows no peak at this region (5). The peaks are attributed to Na_2SiF_6 formed by the reaction of NaCl and a fluorosilicone compound, which is an ablation product of the glass wall formed by the reaction between glass and reactive species of fluorine in the plasma (atomic fluorine, $\text{F}^\cdot$, etc.). The intensity of these peaks increases as the flow rate of tetrafluoroethylene is lowered (at a fixed wattage of 70 W). At the highest flow rate used (i.e., $0.86 \text{ cm}^3_{\text{STP}}/\text{min}$), no peak attributable to Na_2SiF_6 is observed. Similar results obtained under conditions of fixed flow rate and varying discharge power are shown in Fig. 6.48. Under such conditions, no peak for Na_2SiF_6 appears at low wattage, and the intensity of peaks increases with increasing wattage. From Figs. 7.3 and 6.48 we can conclude that when the discharge energy input per unit mass of monomer (i.e., the W/FM parameter, which is discussed in detail in Chapter 9) reaches a certain level the ablation of glass by plasma of tetrafluoroethylene becomes evident and increases with the increasing parameter W/FM .

Thus, it is clear that every material that makes contact with plasma should be considered a part of the plasma polymerization system. It is also evident that the balance between polymer formation and ablation is dependent not only on the chemical nature of the monomer, of the wall material, of the substrate, and so on, that come into contact with the plasma, but also on the discharge conditions, particularly the plasma energy density.

7.2 Classification of Gases for Plasma

As far as plasma polymerization and plasma treatment of materials, particularly organic polymers, are concerned, plasma can be divided into three major groups based on the mode of consumption of the gas used to create the plasma: (1) chemically nonreactive plasma, (2) chemically reactive plasma, and (3) polymer-forming plasma. The terms *chemically reactive* and *nonreactive* are based strictly on whether the gas used in a plasma is consumed in chemical processes in the plasma, yielding products in the gas phase or being incorporated into the solid phase by chemical bonds.

Chemically nonreactive types of plasma are mainly those of monoatomic inert gases. Argon plasma can ionize other molecules or sputter materials but is not consumed in chemical reactions. Chemically reactive types of plasma are those of inorganic and organic molecular gases such as O_2 , N_2 , and CF_4 , which are chemically reactive but do not form polymeric deposits in their pure gas plasma. Polymer-forming types of plasma are obviously chemically reactive but form a polymeric solid deposit by themselves. Many organic and inorganic vapors are in the polymer-forming group.

An important point is that the ablation of material can occur in all types of plasma, although the extent of the process and the dominating mechanisms vary with the type of gas and the discharge conditions. Ablation by chemically nonreactive plasma occurs by the momentum-exchange process (physical sputtering). Ablation by chemically reactive plasma can occur by both physical and chemical etching processes depending on the stability and volatility of the products of the chemical reaction between the etching gas and the material. For instance, CF_4 plasma (chemically reactive plasma) can etch metals by either mechanism depending on the volatility of metal fluorides. Silicon, germanium, molybdenum, and tungsten form volatile fluoride and are consequently etched primarily by chemical etching. In contrast, copper forms nonvolatile fluoride but is etched by CF_4 plasma by physical sputtering (6).

Because polymer formation and ablation are competitive and opposing processes, polymer-forming plasma has the least ablative effect; ablation in such a plasma, however, cannot be completely ruled out. Sputtering of metals used as the internal electrodes for plasma polymerization has been recognized

as a contamination of plasma polymers. Under certain conditions, the sputtering of the electrode materials becomes significant and plays an important role in certain aspects of plasma polymerization (Section 7.5).

7.3 Ablation by Plasma

Ablation of materials by plasma can occur by two principal processes. One is physical sputtering, and the other is chemical etching. The sputtering of materials by an inert gas plasma (e.g., of argon) is a typical example of physical sputtering, which is essentially a momentum-exchange process. The energy of the impinging Ar^+ is transferred to the colliding atom and dislodges the atom from the crystalline structure, transferring its energy to a neighboring atom. This energy transfer process continues until one of the atoms is knocked out into the vapor phase.

Chemical etching involves the chemical reaction of the impinging species with the dislodging elements, such as oxidation by O_2 plasma and fluoride formation by CF_4 plasma.

Ablation under the influence of plasma has been used in the removal of materials and the cleaning of surfaces, but it has also been utilized in the vacuum deposition of sputtered materials. Vacuum deposition by sputtering of a target material is often called *sputter coating*. Metal deposition by sputtering is a widely used method of vacuum deposition of metal coating and is a typical example of sputter coating. A similar process has been applied to sputter coating of polymeric materials; the mechanism involved, however, is considerably different from sputtering of metals, and the term *sputter coating* applied to polymer materials is not descriptive of the actual processes that take place under the technically identical setup.

First of all, small Ar^+ , regardless of how energetic it might be, cannot sputter a polymer molecule with mass greater than the mass of the impinging ion by the order of 10^3 to 10^6 . A fraction of a polymer molecule can be split off by an impinging ion, but such a fragment cannot be deposited in the same way that a sputtered metal is deposited on the substrate. What actually takes place is the fragmentation of polymer molecules by plasma and the subsequent plasma polymerization of the ablation products in the gas plasma. Tibbitt *et al.* showed that all analytical data for the plasma polymer of tetrafluoroethylene and sputter-coated polytetrafluoroethylene are virtually identical (7). Furthermore, both of them are significantly different from polytetrafluoroethylene. The IR spectra and dynamic electrical properties of these polymers are shown in Figs. 7.4 and 7.5.

The sputter coating of polymers is another important demonstration of how important the CAP mechanism is not only in plasma polymerization

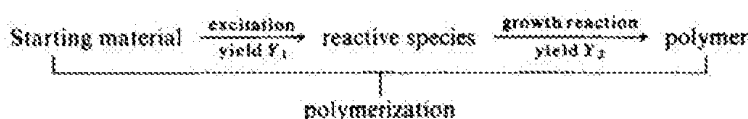
CHAPTER 8

Kinetic and Mechanistic Aspects of Polymer Deposition in Plasma Polymerization

8.1 Polymerization and Deposition Mechanisms

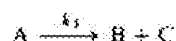
In Chapter 6, the essential mechanisms of forming polymeric materials in plasma are discussed. The kinetic aspects of polymer deposition observed in a plasma polymerization system are not a direct measure of the polymerization mechanisms. This situation can be explained by a reexamination of polymerization mechanisms with respect to the deposition of polymers.

In general, the polymerization process is expressed by the following scheme:



The entire process of polymer formation is generally termed *polymerization*, and the starting material for the polymerization is called the *monomer*. As discussed in Chapter 6, however, the starting material for plasma polymerization is not the same as a monomer in conventional polymerization because of the great extent of fragmentation of the starting molecule. Furthermore, the extent of fragmentation is not determined solely by the chemical structure of the monomer, but also depends on the discharge conditions, particularly the energy input level.

A chemical reaction is generally associated with a positive activation energy; that is, a reactant must be activated to overcome an energy barrier. Let us first consider a simple chemical reaction:



The rate constant k_1 of the reaction can be given in terms of the activation

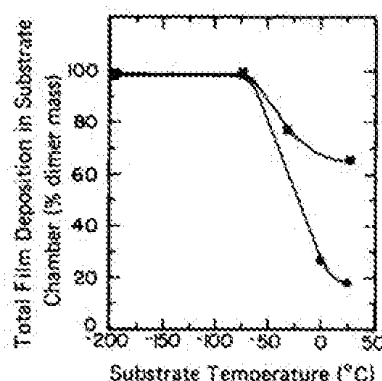


Fig. 8.5 Effect of variation of sublimation temperature on Parylene N film growth rate in the center of the substrate chamber at different argon pressures. Key: ●, no inert gas; ■, argon (42 mtorr). From Kramer *et al.* (2).

An important point to keep in mind is that the increase in polymer deposition or deposition rate at a fixed position can be achieved only by a corresponding loss of polymer deposition elsewhere, because the total mass of polymer in a closed-ended flow system is constant. This is an obvious condition in Parylene polymerization, where $Y_1 = Y_2 = 1.0$; however, a similar situation also applies to plasma polymerization (i.e., the mass balance should be maintained). Therefore, a claim such as “a catalytic amount of the second gas increases the polymerization rate in orders of magnitude” can be made only in the context of the local polymer deposition rate, not in the context of the polymerization rate. Such a significant increase in the deposition rate is attainable only in (1) a very poorly polymerizable system where Y_1, Y_2 is very low or (2) a system in which the location of polymer deposition shifts to a very narrow region where the deposition of polymer is measured. This important aspect has often been overlooked in the study of plasma polymerization, because in an open-ended flow system it is not easy to establish the mass balance in the reaction system.

8.3 Distribution of Polymer Deposition

8.3.1 FACTORS THAT INFLUENCE THE DISTRIBUTION

The deposition of polymer in a plasma polymerization system occurs on surfaces that are either in contact with plasma (glow discharge) or in the vicinity of plasma. The amount of polymer deposition is influenced by three

important geometric factors of plasma polymerization (3). These are the relative position of polymer deposition with respect to (1) the location of electric energy input, (2) the monomer flow, and (3) the position within the reactor.

The system pressure, which determines the mean free path of gaseous species, has, of course, a great influence on the distribution of polymer deposition. In general, the lower the system pressure, the wider or more even is the distribution (4).

Another factor that determines the pattern of polymer deposition is the reactivity of the active species involved. Some monomers produce more reactive species or a greater number of reactive species than others and appear to be more reactive in the overall polymer deposition process. These "reactive monomers" tend to deposit near the site of the electric energy input, where the plasma energy density is the highest, or at the inlet where monomer passes into the plasma zone and cause uneven distributions of polymer deposition within a reactor.

The overall combined effects of these factors (geometry, pressure, and reactivity) can be visualized by the following examples.

8.3.2 DISTRIBUTION OBSERVED IN A TUBULAR REACTOR

A tubular reactor with an external rf power coupling is ideally suited to the study of the distribution of polymer deposition. In such a reactor, 100% of the monomer passes through the reactor, and the situation is very similar to the closed-ended flow system described for Parylene polymerization. In contrast to Parylene polymerization, $Y_1 Y_2$ for plasma polymerization is not well defined but is thought to be considerably lower than 1.0. The experimental setup used for the following study of the distribution of polymer deposition is shown in Fig. 8.6.

The distribution of polymer deposition observed in the plasma polymerization of acetylene at different flow rates (and different system pressures under plasma conditions) is shown in Fig. 8.7. The results indicate that a rather uniform distribution of polymer is obtained at a low flow rate (and low system pressure). Slightly higher deposition rates are found at the downstream side of the monomer inlet. At higher flow rates (and higher system pressures), the entire distribution curve is lifted up and a conspicuous maximum develops. The location of maximum deposition tends to shift slightly more to the downstream side of the monomer inlet as the flow rate increases.

The addition of a carrier gas (mixed into a constant flow of acetylene before the monomer inlet) changes the pattern of polymer deposition more

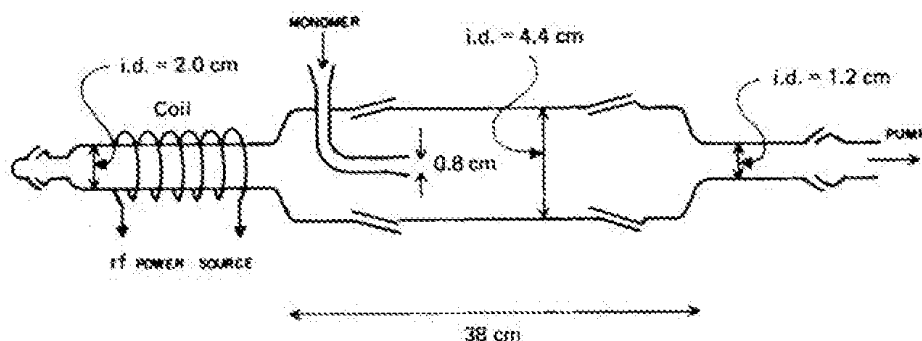


Fig. 8.6 Schematic representation of the standard reactor used in the study of the distribution of polymer deposition under discussion. From Yasuda and Hirotsu (3).

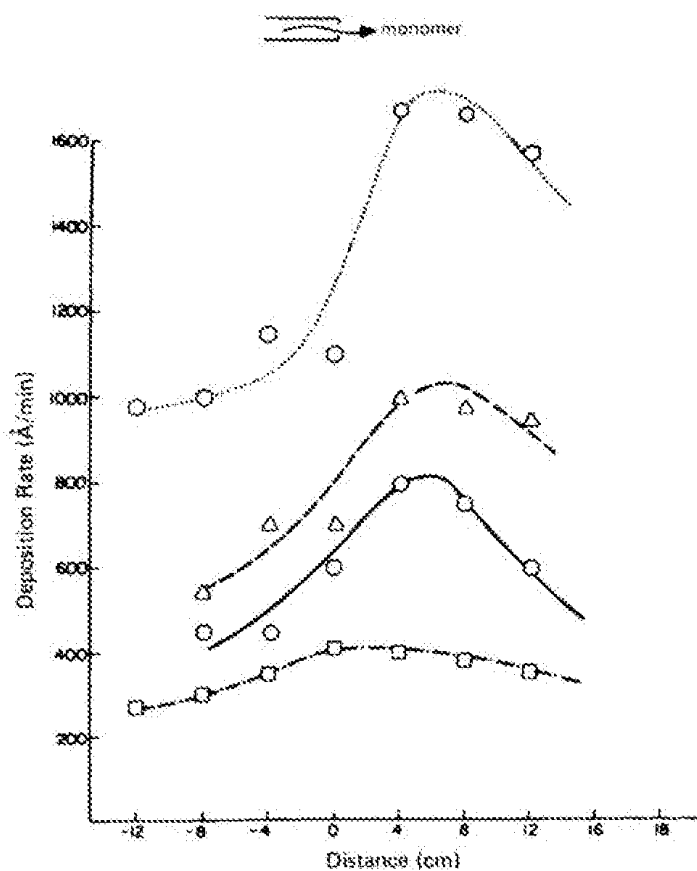


Fig. 8.7 Distribution of polymer deposition in the plasma polymerization of acetylene at various flow rates. Key: (○) $F = 9.0$, $p_g = 35$; (△) $F = 7.7$, $p_g = 28$; (○) $F = 5.2$, $p_g = 20$; (□) $F = 2.4$, $p_g = 10$; F denotes flow rate (cm^3/min), and p_g is the system pressure in the glow discharge (micrometers mercury). From Yasuda and Hirotsu (4).

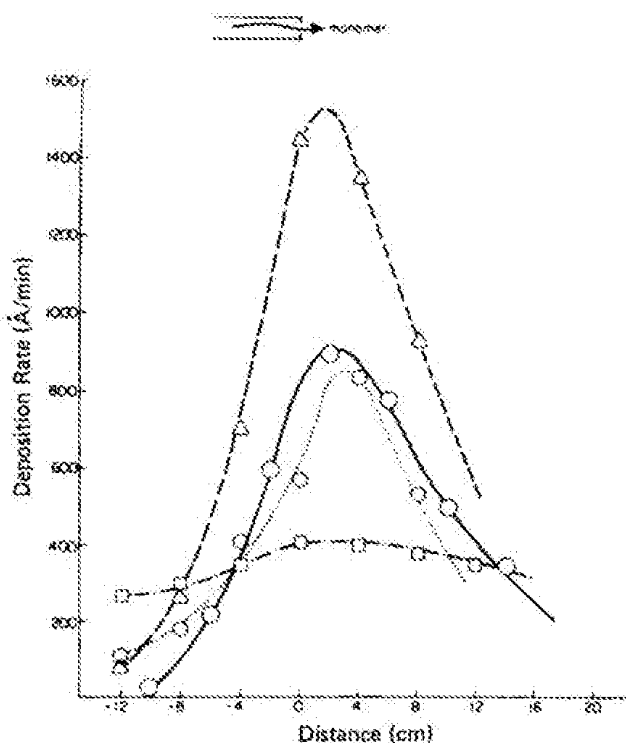


Fig. 8.8 Distribution of polymer deposition in the plasma polymerization of acetylene with the addition of gas. Key: (□) acetylene ($P = 2.5 \text{ cm}^3_{\text{TP}}/\text{min}$), $p_g = 8$; (○) $\text{H}_2/\text{Ac} = 1.3$, $p_g = 70$; (●) $\text{Ar}/\text{Ac} = 0.8$, $p_g = 8.8$; (△) $\text{N}_2/\text{Ac} = 1.0$, $p_g = 45$; N_2/Ac , H_2/Ac , and Ar/Ac denote the mole ratios of gas to acetylene. The system pressure p_g in the glow discharge is given in micrometers mercury. From Yasuda and Hirotsu (4).

drastically (Fig. 8.8). It is important to note that the addition of H_2 or argon increases the peak height of the maximum without changing the average deposition rate; that is, the distribution becomes narrower on the addition of these gases. Therefore, a considerable decrease in polymer deposition was observed at the locations on the upstream side of the monomer inlet. The effect of argon, which does not participate chemically in the polymer formation, can be seen as a sharpening of the distribution curve. The possible reason for this is discussed later in the section.

The effect of N_2 may be due to two factors. The first is the same as that in the case of argon. The second factor is the chemical participation of N_2 . Nitrogen in the plasma state is chemically reactive and should be considered a comonomer of the plasma polymerization, although it does not polymerize alone in plasma. This effect is seen in the obvious increase in total polymer deposition. Perhaps the same is true with H_2 , but because of the small

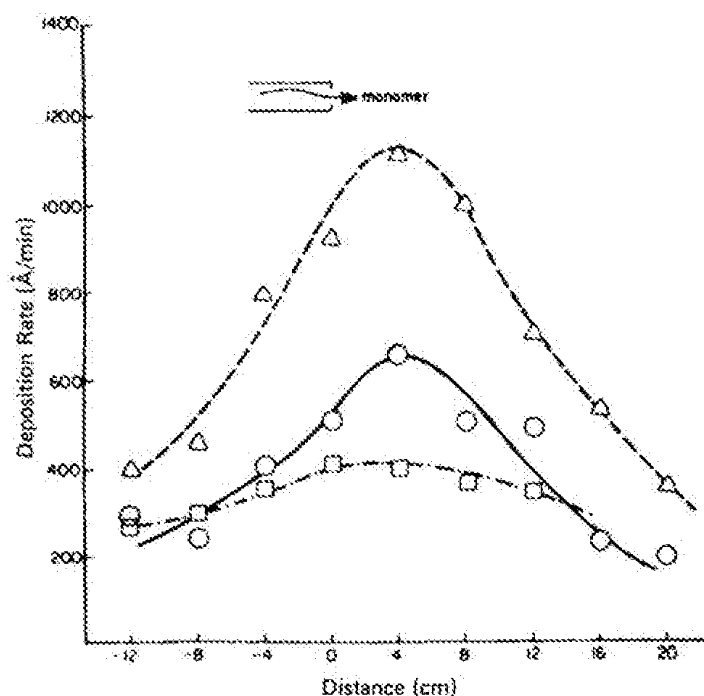


Fig. 8.9 Effect of adding Freon 12 (CCl_2F_2) to acetylene at flow rate $F = 2.5 \text{ cm}^3_{\text{STP}}/\text{min}$ on the distribution of polymer deposition. Key: ($\square$) acetylene, $p_g = 8$; ($\circ$) Freon 12/Ac = 0.13, $p_g = 11$; ($\triangle$) Freon 12/Ac = 0.75, $p_g = 24$. Freon 12/Ac denotes the mole ratio of CCl_2F_2 to acetylene. The system pressure p_g in the glow discharge is given in micrometers mercury. From Yasuda and Hirotsu (4).

contribution of the mass of H_2 , this factor is not reflected in the deposition, which is measured by the mass of deposition.

Thus, the increase in polymer deposition near the monomer inlet is due to both a physical factor and a chemical factor (copolymerization of gas). Copolymerization obviously increases the total mass due to the incorporation of the second gas. This increase is clearly seen in the plasma polymerization of acetylene on the addition of Freon 12 (CCl_2F_2 ; Fig. 8.9).

With monomers that are less reactive than acetylene, such as ethylene, the distribution of polymer deposition is much flatter (Fig. 8.10). It is interesting that (1) the distribution of polymer deposition is much more uniform than that of acetylene (Fig. 8.7) and no obvious maximum is observed at low flow rates, and (2) the minimum (rather than the maximum) deposition is observed in the vicinity of the monomer inlet at high flow rates (and high system pressures under plasma conditions). Moreover, the glow in the vicinity of the monomer inlet is noticeably weaker than that in the rest of the reactor at the high flow rate that showed the minimum deposition in the region.

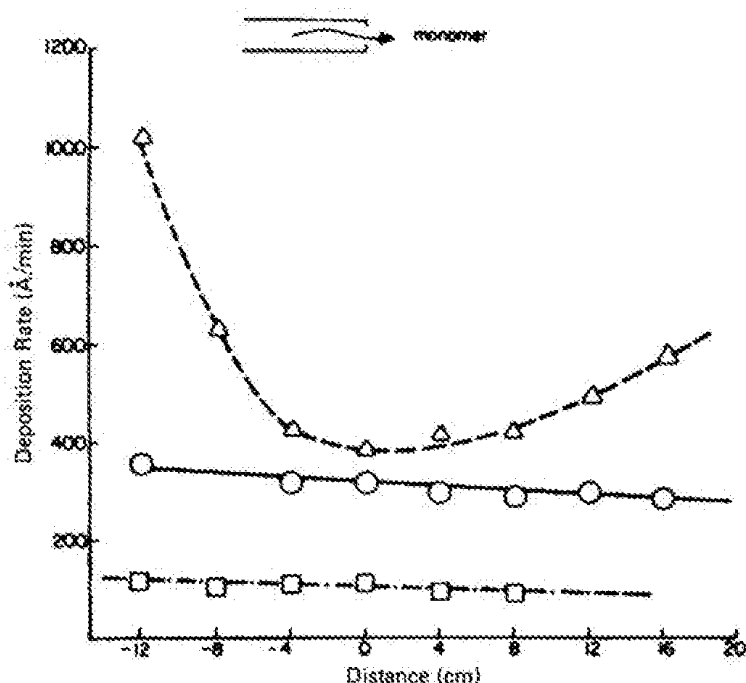


Fig. 8.10 Distribution of polymer deposition in the plasma polymerization of ethylene. Key: (Δ) $F = 9.6$, $p_g = 117$; ($\circ$) $F = 2.5$, $p_g = 44$; ($\square$) $F = 1.1$, $p_g = 24$; F denotes flow rate ($\text{cm}^3_{\text{STP}}/\text{min}$), and p_g is the system pressure in the glow discharge (micrometers mercury). From Yasuda and Hirotsu (4).

The effects of carrier gases added to ethylene are shown in Fig. 8.11. The addition of N_2 or argon causes a narrowing of the distribution, but the effects are much smaller than those found for the plasma polymerization of acetylene. A maximum with broad shoulders appears farther downstream (8 cm) than the maximum observed with acetylene, which appears near the inlet (0 cm). Thus, the enhancement of polymer deposition by the addition of an inert gas into the monomer feed flow is highly dependent on the nature of the monomer.

The effect of the addition of Freon 12 (CCl_2F_2) to ethylene at a flow rate of $2.5 \text{ cm}^3_{\text{STP}}/\text{min}$ is shown in Fig. 8.12. The appearance of a maximum and the increase in its peak height with the partial pressure of the Freon is similar to the case of acetylene, but the half-widths of the peaks are much wider with ethylene. At higher flow rates of ethylene, however, the distribution pattern is quite different (Fig. 8.13). The minimum observed with ethylene at a flow rate of $9.6 \text{ cm}^3_{\text{STP}}/\text{min}$ shown in Fig. 8.10 is an indication of at least two peaks: one at the upstream side toward the rf coil and another at the downstream side with respect to the monomer inlet. The addition of Freon tends to shift these two peaks closer to the monomer inlet as the peak heights increase with the partial pressure of Freon.

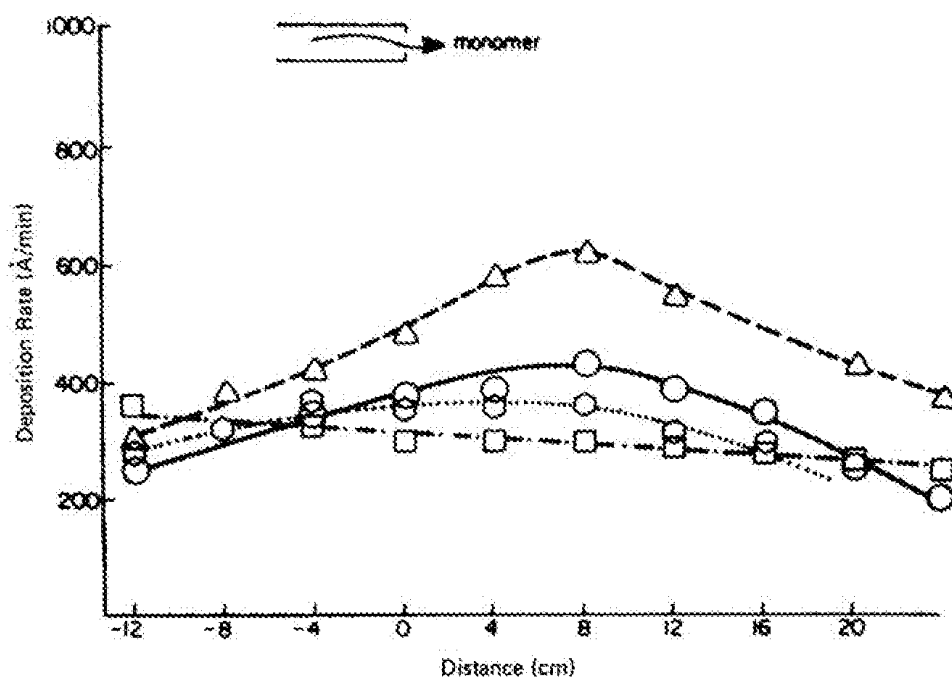


Fig. 8.11 Distribution of polymer deposition in plasma polymerization of ethylene with the addition of gas. Key: (Δ) $N_2/Et = 0.9$, $p_g = 96$; ($\circ$) $Ar/Et = 0.8$, $p_g = 110$; ($\circ$) $H_2/Et = 1.1$, $p_g = 87$; ($\square$) $Et (F = 2.5)$, $p_g = 44$; N_2/Et , H_2/Et , and Ar/Et denote the mole ratios of gas to ethylene. The system pressure p_g in the glow discharge is given in micrometers mercury. From Yasuda and Hirotsu (4).

EFFECT OF MONOMER FLOW PATTERN IN A REACTOR

By the use of a tubular reactor similar to that used in the study of the distribution of polymer, the effect of flow pattern in a reactor was investigated with ethylene as the monomer. A relatively high flow rate of $\sim 9.8 \text{ cm}^3_{STP}/\text{min}$, which showed a conspicuous minimum at the location near the monomer inlet, was used throughout this series of experiments.

Various patterns of the flow in relation to the rf coil and to the outlet (the pump) of the reactor are shown in Fig. 8.14. In case I, the position of the monomer inlet is changed by the insertion of a tube of different length to the standard inlet by means of standard tapered glass joints. In case II, the position of the monomer inlet is changed by means of a special A tube (without an inner sealed tube) or a special B tube (with three side-arm joints). In case III, a special A tube is used, and the connections to the monomer feed-in system and to the pump system are reversed. In cases IV and V, a special A tube is used, and the monomer inlet and outlet are reversed. In the distribution curves of Figs. 8.15 to 8.21, the origin (0) of the abscissas was chosen as the same point used in Figs. 8.7 to 8.13.

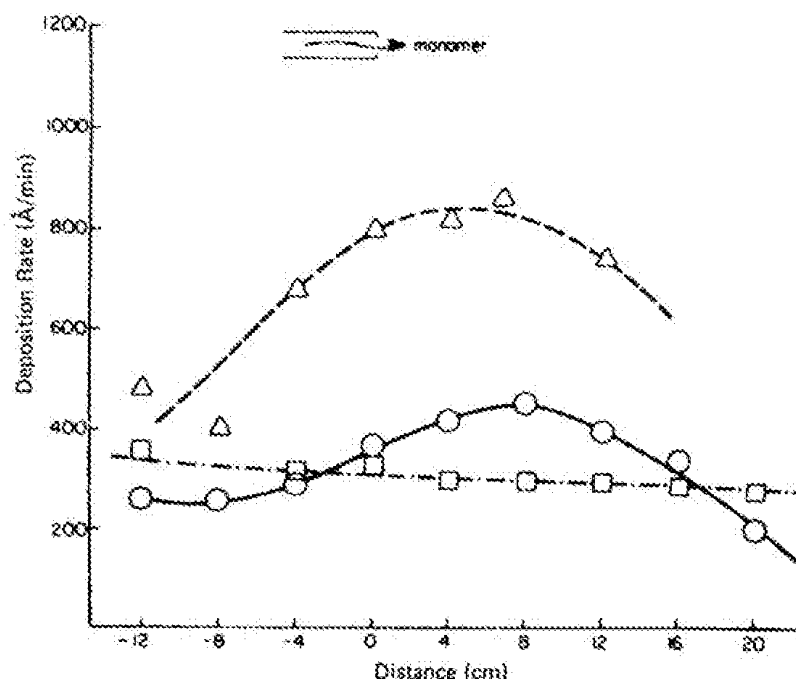


Fig. 8.12 Distribution of polymer deposition in the plasma polymerization of ethylene with the addition of Freon 12 (CCl_2F_2). Key: ($\square$) ethylene ($F = 2.5 \text{ cm}^3_{\text{TF}}/\text{min}$), $p_g = 44$; ($\circ$) Freon 12/Et = 0.10, $p_g = 43$; (Δ) Freon 12/Et = 0.76, $p_g = 45$. Freon 12/Et denotes the mole ratio of CCl_2F_2 to ethylene. The system pressure p_g in the glow discharge is given in micrometers mercury. From Yasuda and Hirotsu (4).

The changes in polymer distribution due to flow patterns are compared in Figs. 8.15 to 8.21. Figure 8.15 indicates that the direction of monomer flow (i.e., whether parallel or perpendicular to the pumping direction) does not cause a significant difference if the inlet location is the same. This means that the location of the inlet in a reactor is a more important factor than the way in which the inlet is inserted into the reactor, which is indeed found to be the case in Fig. 8.16. The minimum in the distribution curve shifts with the location of the inlet. This trend was also found in an experiment employing a long extended inner tube (Fig. 8.17).

Whether or not the monomer is fed through the rf coil also has an important influence on the distribution of polymer deposition. When the monomer flows through the rf coil, a large amount of polymer is deposited in the rf coil zone, which is beyond the range of the measurements, and there is a considerable decrease in the polymer deposition in the tail-flame portion of the reactor (Fig. 8.18).

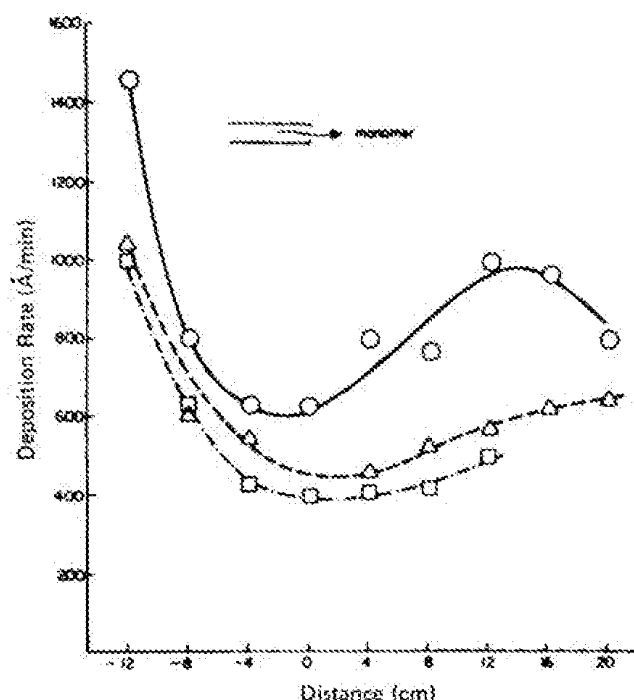


Fig. 8.13 Effect of adding Freon 12 (CCl_2F_2) to ethylene at a high flow rate ($9.6 \text{ cm}^3_{\text{STP}}/\text{min}$) on the distribution of polymer deposition. Key: (□) ethylene, $p_g = 117$; (△) Ar/Et = 0.14, $p_g = 143$; (○) Freon 12/Et = 0.15, $p_g = 126$. Freon 12/Et denotes the mole ratio of CCl_2F_2 to ethylene. The system pressure p_g in the glow discharge is given in micrometers mercury. From Yasuda and Hirotsu (4).

A reversal of the flow pattern causes a change in the polymer deposition pattern, which can be predicted by the location of the monomer inlet and the effect of flow direction (Fig. 8.19). When the monomer flow direction is reversed (i.e., the major reactor is on the upstream side of the rf coil, or the rf coil is located in the downstream end of a reactor), whether or not the monomer flows through the rf coil has very little effect on the polymer deposition pattern (Fig. 8.20). Regardless of whether the rf coil is located at the upstream end or the downstream end of a reactor, a reactor design that employs a flow pattern in which the monomer flows through the rf coil zone yields the most uneven and least efficient polymer deposition in the main reactor portion used in this type of tube reactor (Fig. 8.21).

These experimental data indicate that three major factors influence the polymer deposition in a plasma reactor: the locations of (1) the energy input (rf coil in these cases), (2) the monomer inlet, and (3) the outlet of monomer flow. In Eq. (8-8), the deposition rate d_i observed at a location is expressed as a

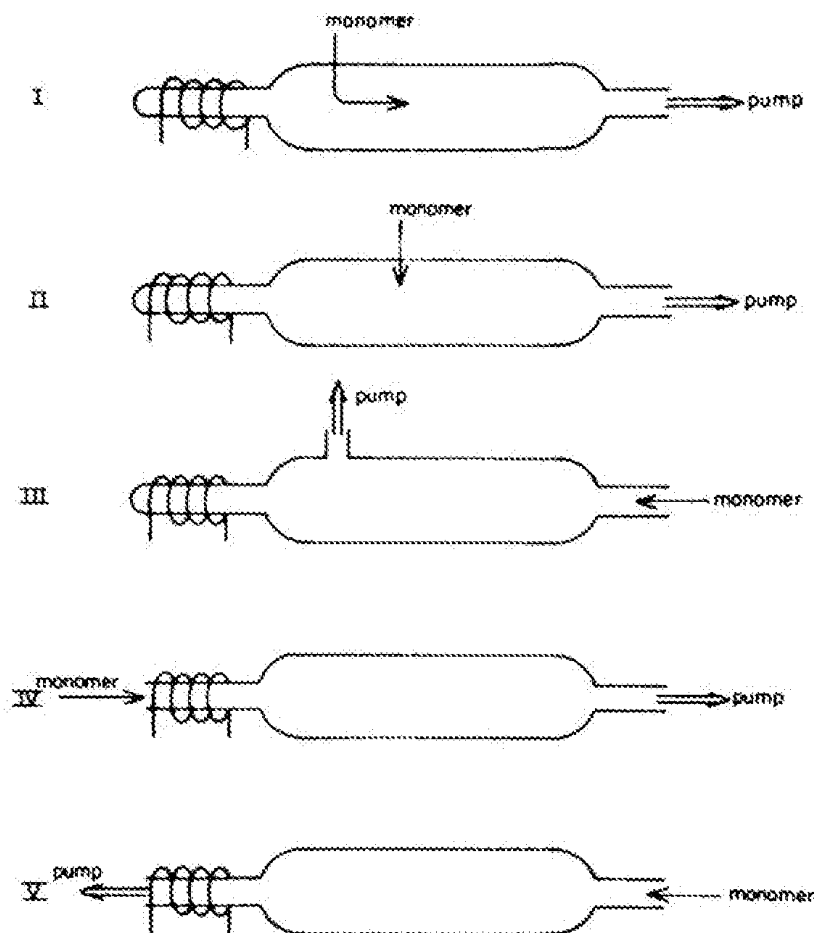


Fig. 8.14 Schematic representation of flow patterns. From Yasuda and Hirotsu (3).

function of the location of polymer deposition. These experimental data indicate that the major parameter determining d_i is the distance from the energy input. Other factors (i.e., the monomer inlet and outlet) determine the direction of flow, which can be either along or against the direction of the energy input to the point of polymer deposition. The direction of monomer flow has less influence on the polymer deposition than the distance from the energy input.

A plasma polymerization system is somewhat similar to a gas flame in which the combustion rate and the gas flow rate establish a steady-state flame. In a plasma polymerization system, the monomer flow rate and the polymer formation rate establish a steady-state polymer-forming plasma. This situation is schematically expressed in Fig. 8.22, where (a) indicates the diffusional

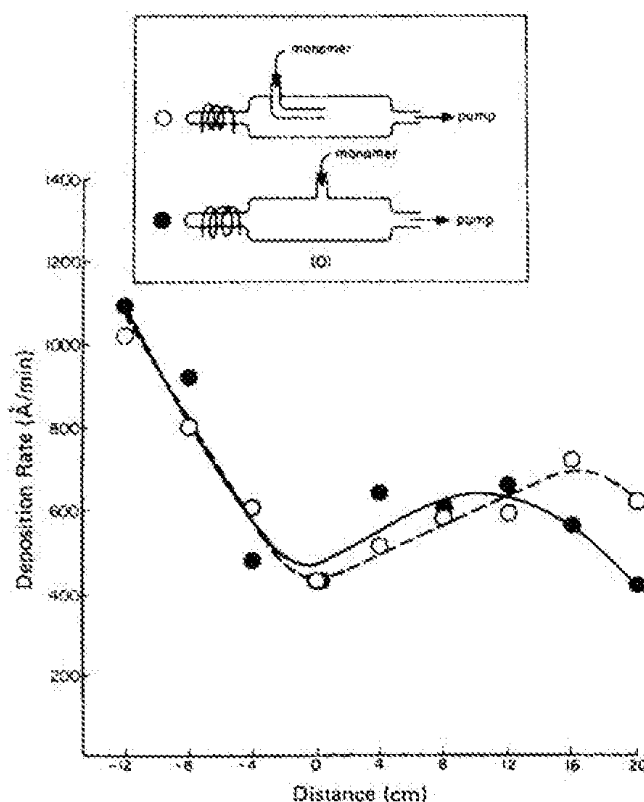


Fig. 8.15 Effect of the direction of monomer injection on the distribution of polymer deposition. From Yasuda and Hirotsu (3).

transport of the energy-carrying species of plasma (shown in Fig. 6.1) (b) indicates the flow of monomer and product gases, and (c) indicates the diffusional transport of polymer-forming species.

It is important to recall the principle dealing with the probability of photon emission versus chemical reaction (polymerization) discussed in Chapter 6. When excited species is created by the collision of an ion or an electron, it either loses the excess energy by emitting a photon or dissipates the excess energy by initiating a chemical reaction (formation of reactive species). Metastable species do not emit photons and lose their energy only by collision. Polymer-forming species take the second route.

Polymer-forming species are therefore energy-consuming species as far as the energy transfer associated with the ionization process is concerned. In contrast, metastable species are clearly energy-carrying species. Other excited species may act as energy-carrying species within the lifetime of the excitation. The effect of the addition of argon discussed earlier can be explained by the

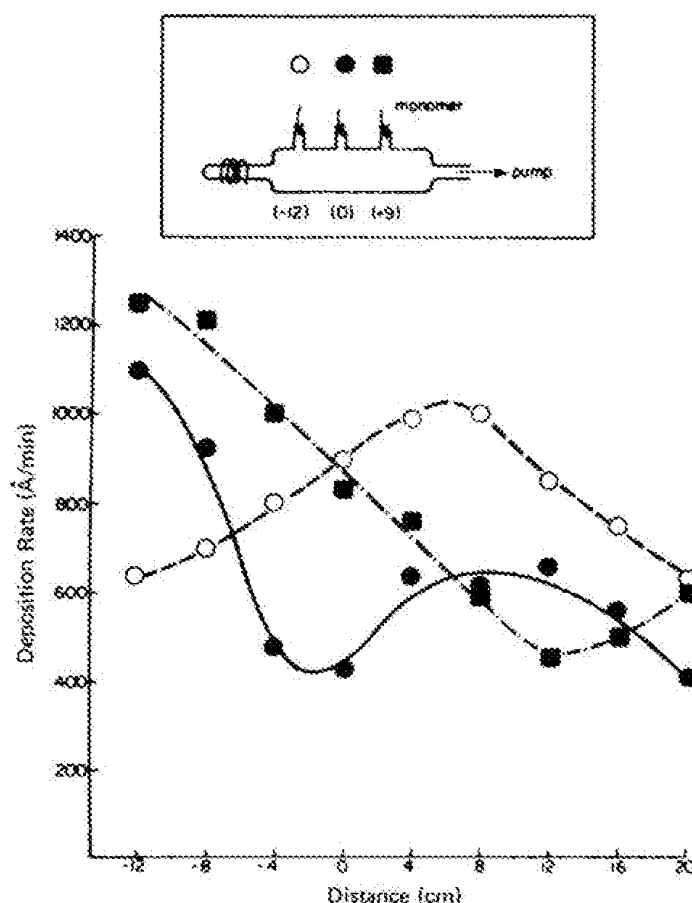


Fig. 8.16 Effect of the location of the monomer inlet on the distribution of polymer deposition. From Yasuda and Hirotsu (3).

effect of adding energy-carrying species, which increases the effective plasma energy density (to initiate a chemical reaction) at the location of the monomer inlet.

The density of the energy-carrying species decreases with the distance from the energy input zone. Therefore, where the monomer is introduced with respect to the energy input is a very important factor. Upon the inception of plasma, polymer-forming species (see Fig. 6.1) are created and diffuse in both directions. During this diffusional transport, polymer formation reactions proceed. The flow of monomer or the pumping direction may be in the direction of diffusional transport or against it. If the flow is against the diffusional transport, the quenching of plasma can occur and very little

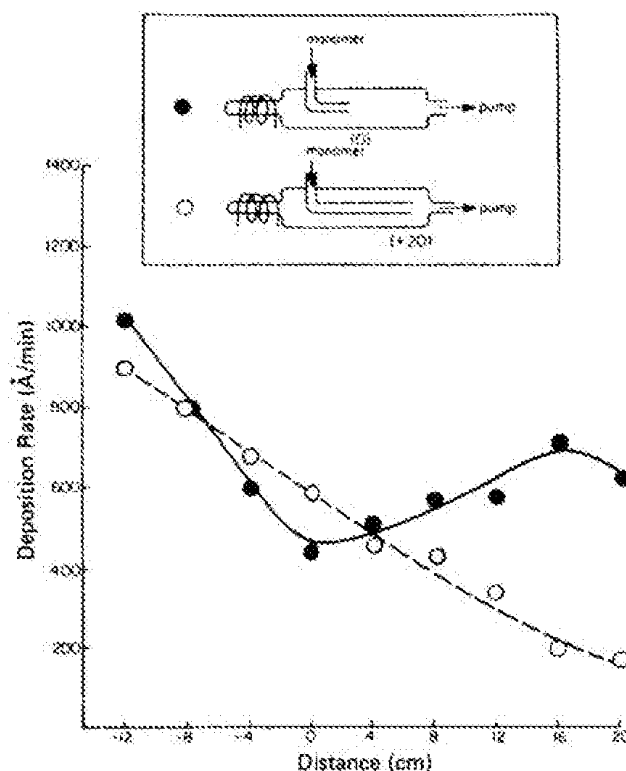


Fig. 8.17 Effect of the length of the monomer inlet on the distribution of polymer deposition. From Yasuda and Hirotsu (3).

polymer deposition is observed in the nonglow (quenched) zone (Figs. 8.20 and 8.21).

The importance of the glow zone for polymer formation can be seen in the polymer distribution pattern obtained by a small straight-tube reactor (o.d. 11 mm) with an rf coil placed in the middle of the tube (5). In Fig. 8.23, deposition rates of plasma polymers of tetrafluoroethylene, given by values of deposition rate divided by monomer flow rate, are plotted against the location. The location is measured from the center of the rf coil in the direction of gas flow. The extent of glow is shown by the shaded band. The solid line represents the polymer distribution curve for $F = 5.6 \text{ cm}^3_{\text{STP}}/\text{min}$, $W = 8 \text{ W}$, and $W/FM = 1.9 \times 10^7 \text{ J/kg}$, and the dashed line represents that for $F = 0.56 \text{ cm}^3_{\text{STP}}/\text{min}$, $W = 32 \text{ W}$, and $W/FM = 7.7 \times 10^8 \text{ J/kg}$. Thus, the plasma polymer is deposited in and near the glow zone, and any factor that diminishes the glow zone would cause a sharp decrease in the polymer deposition rate.

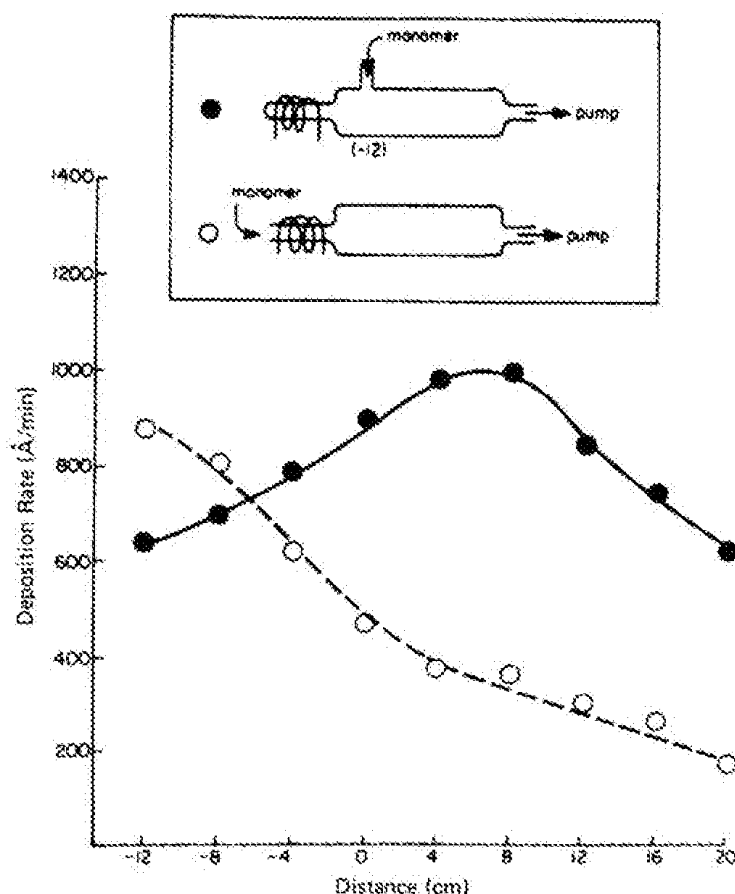


Fig. 8.18 Effect of flow passing through the radio frequency coil on the distribution of polymer deposition. From Yasuda and Hirotsu (3).

8.3.3 DISTRIBUTION OBSERVED IN A BELL-JAR TYPE OF REACTOR

A bell-jar type of reactor used for plasma polymerization usually employs a set of parallel electrodes, and the glow is more or less confined to the space between the electrodes. In such a system, the total volume of the reactor is considerably larger (e.g., more than a factor of 10) than the plasma volume. A reactor that consists of a large tube and a pair of electrodes located inside can also be considered a bell-jar type of reactor. In other words, whether a bell jar or a vessel of another shape is used is not a major factor.

In such a reactor, which has a large reservoir of monomer surrounding the plasma zone, the direct effect of the monomer flow is much less pronounced than in other reactors, and the diffusional transport seems to predominate.

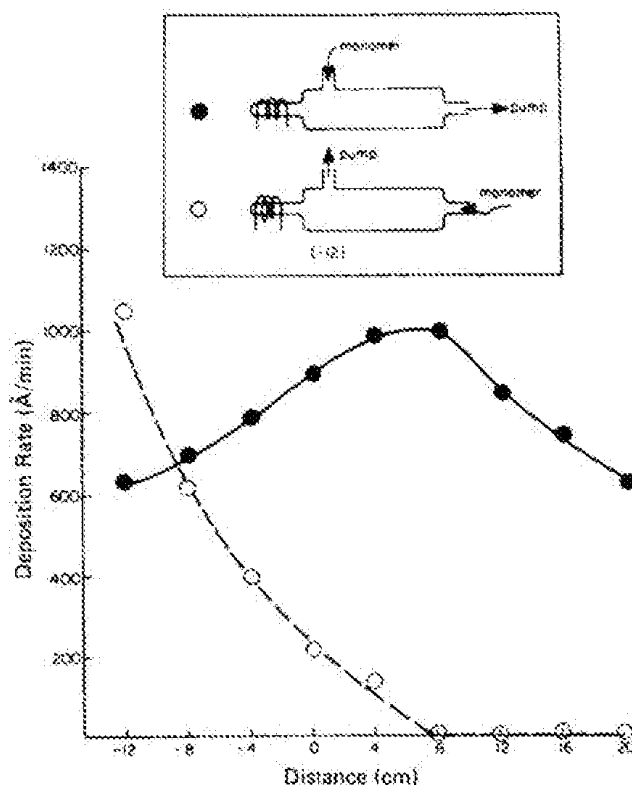


Fig. 8.19 Effect of the direction of flow on the distribution of polymer deposition for cases in which there is no flow through the radio frequency coil. From Yasuda and Hirotsu (3).

Plasma polymer is collected either on the surface of the electrode (a substrate placed on the electrode) or on the surface of the substrate, which is placed in between the electrodes. Obviously, the polymer deposition pattern is quite different depending on the mode of polymer collection.

8.3.3.1 POLYMER DEPOSITION ONTO AN ELECTRODE SURFACE

The electrode surface is considered the energy input plane according to the concept discussed in Section 8.3.2. Therefore, in this case, the major factor that determines the distribution of polymer deposition is the diffusional transport of polymer-forming species and reactive plasma species, because the plane of polymer deposition is very close to the plane of energy input.

Even in this case, a variation in the polymer deposition is observed due to the diffusional mass transport of the polymer-forming species. During the process of diffusional mass transport, the growth reactions described in

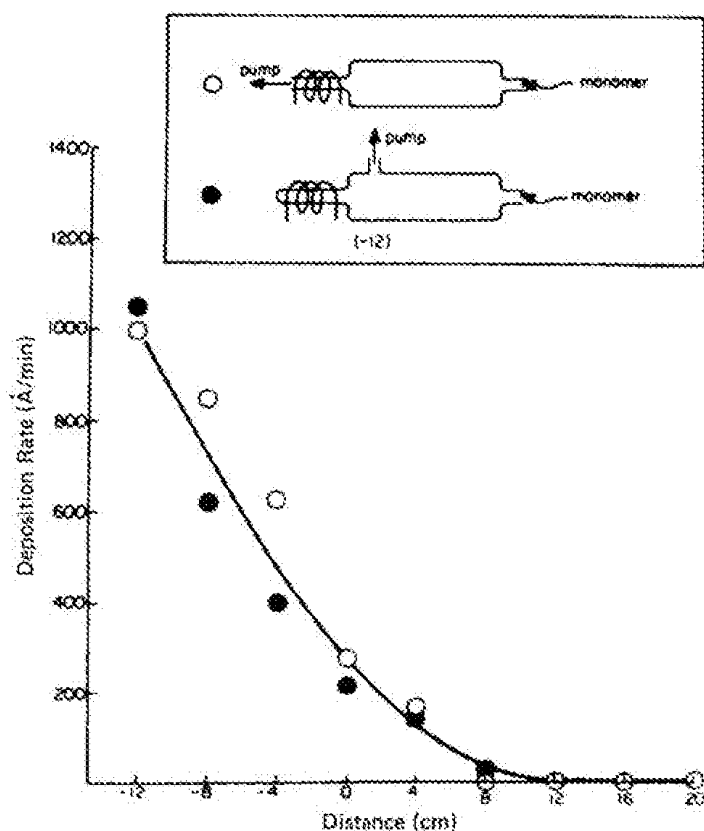


Fig. 8.20 Effect of flow passing through the radio frequency coil in the reverse direction on the distribution of polymer deposition. From Yasuda and Hirotsu (3).

Chapter 6 (see Fig. 6.1) occur. According to the concept analogous to the gas flame concept described in Section 8.3.2, the inception of monomer plasma occurs at the plane at the periphery of the electrode and perpendicular to the electrode surface and starts the consecutive processes described in Fig. 6.1 while it diffuses into the inner sphere.

Therefore, the gaseous species that strike the polymer-depositing surface and form polymer (solid) differ depending on the distance from the periphery of the electrode. The mass of striking gaseous species in plasma increases with the distance from the periphery, which means that the deposition rate determined by the weight of polymer is highest at the center of the electrode. If the monomer is injected at the center of the electrode, then this trend should be reversed and the minimum deposition rate should be observed at the center of the electrode.

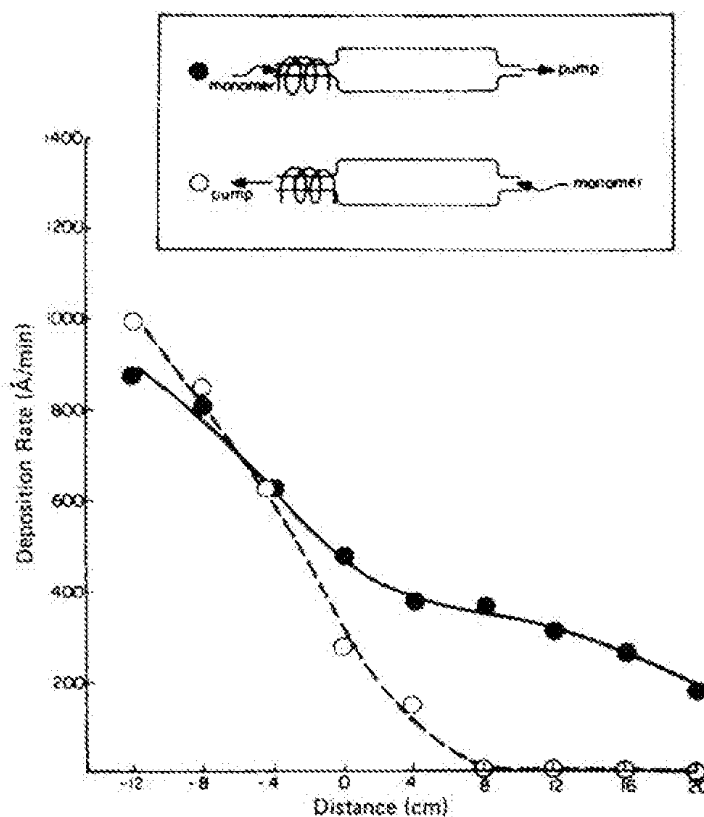


Fig. 8.21 Effect of the direction of flow on the distribution of polymer deposition for cases in which flow passes through the radio frequency coil. From Yasuda and Hirotsu (3).

This situation can be seen clearly in the distribution pattern observed by Kobayashi *et al.* (6) shown in Fig. 8.24 (the arrangement of monomer inlet) and Fig. 8.25 (the distribution of polymer deposition for corresponding cases). The slight asymmetry of the polymer deposition pattern can be attributed to the overall flow pattern existing in the entire reactor system. The principle of the polymer deposition is identical to that for the tubular reactor shown in Fig. 8.22.

An important implication of the data obtained with both a tubular reactor and a bell-jar type of reactor is that the polymer deposition onto a stationary substrate cannot be uniform due to the diffusional transport of polymer-forming species and the path-dependent growth mechanism. The variation of polymer deposition rates at various locations becomes smaller as the system pressure decreases, because the diffusional displacement distance of gaseous

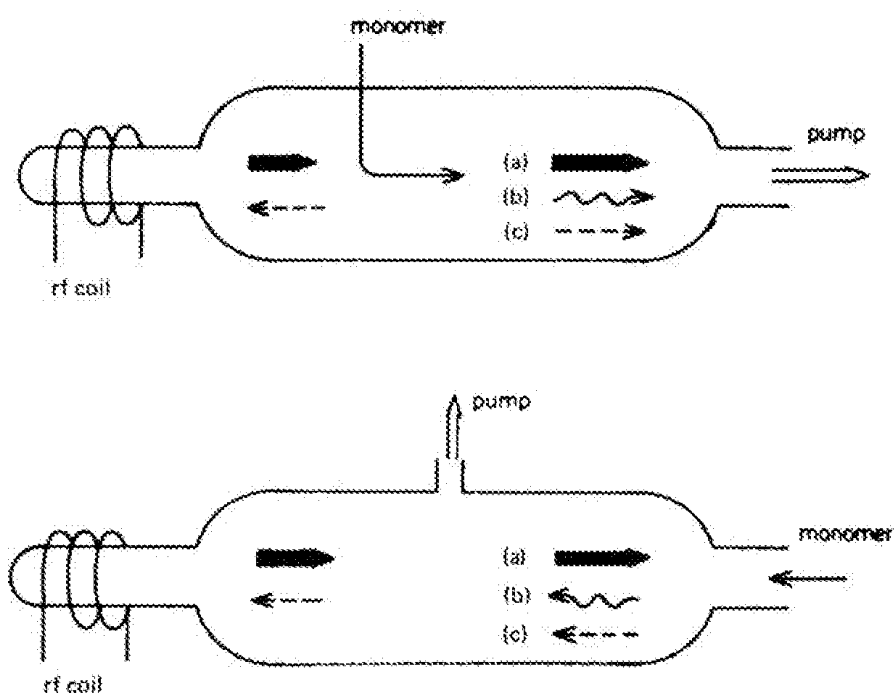


Fig. 8.22 Schematic representation of the contribution of (a) diffusion transport of active species created by the radio frequency coil, (b) flow of monomer and/or product gas, and (c) diffusional transport of polymer-forming species. From Yasuda and Hirotsu (3).

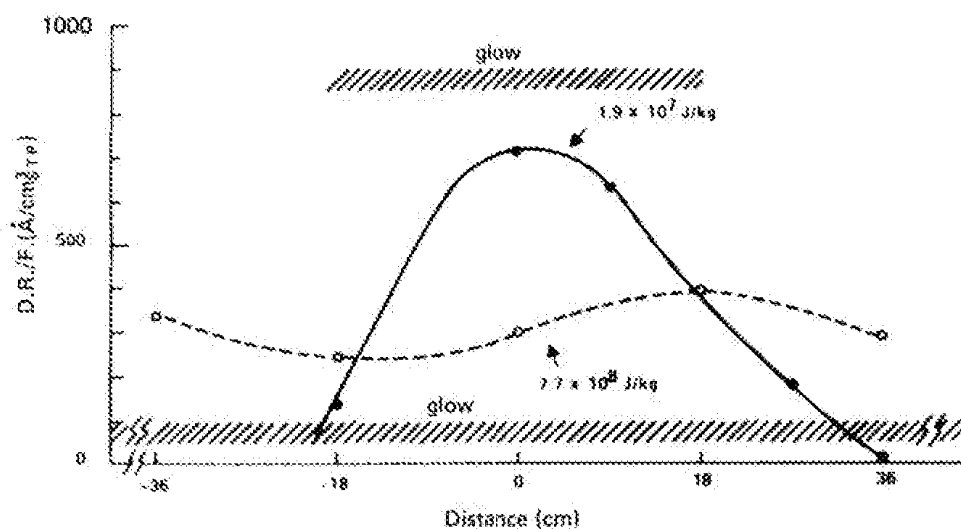


Fig. 8.23 Distribution of polymer deposition observed with high and low energy input. (D.R., deposition rate). From Yasuda and Morosoff (5).

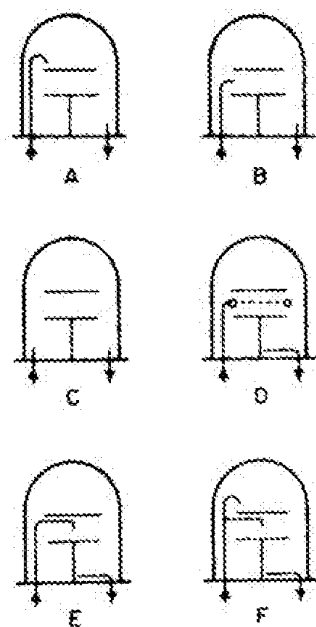


Fig. 8.24 Schematic of inlet-outlet configuration of the bell-jar type of reactor. From Kobayashi *et al.* (6).

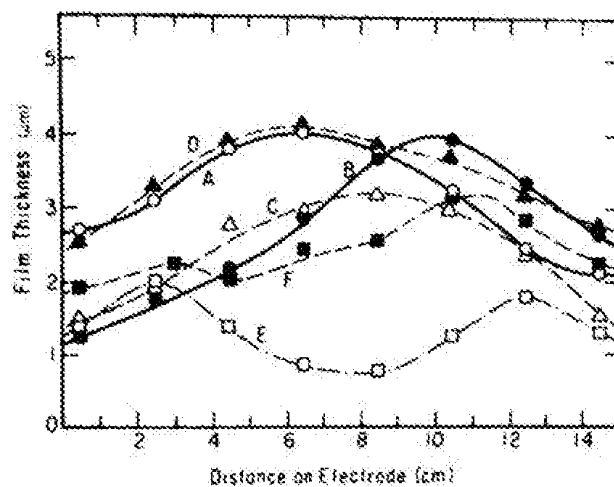


Fig. 8.25 Effect of reactor configurations (refer to Fig. 8.24 for configurations) on the distribution of film thickness on the electrode. Bell-jar type of reactor; in the flow direction; pressure, 2 torr; power, 100 W; ethylene flow rate, $80 \text{ cm}^3_{\text{STP}}/\text{min}$; discharge time, 60 min. From Kobayashi *et al.* (6).

species increases at lower pressure [see Eqs. (3-17) and (3-18)]. Nevertheless, it is important to recognize that a certain degree of thickness variation always exists when the plasma polymer is deposited onto a stationary substrate regardless of the type of reactor and the location of the substrate in the reactor. This effect is further discussed in Section 9.14 dealing with moving substrates.

8.3.3.2 POLYMER DEPOSITION ONTO SURFACES OTHER THAN ELECTRODES

Although the plasma that develops in the interelectrode space is treated as a uniform plasma in comparison with the tail-flame portion of the inductively coupled rf discharge in the preceding section, the actual plasma density or the visual intensity of glow within the space is not always uniform. Particularly at relatively high system pressure under discharge, this is not at all true. The glow is more intense near the electrode surface. Consequently, the polymer deposition rates observed at a substrate surface located away from the electrode surface could be considerably smaller than the corresponding values at the electrode surface.

The patterns of polymer distribution observed in the plasma polymerization of ethylene at a relatively high pressure on substrates placed on the electrode surface (designated the electrode) and on substrates placed midway between the electrodes (designated the substrate) are shown in Fig. 8.26 (7). At high pressure, the difference between the polymer depositions at the electrode and at the substrate is large, and this difference is greater with a lower-frequency discharge. Similar patterns of distribution shown in Fig. 8.25 (onto the electrode surface by the rf discharge of ethylene) are also seen for the substrate (midway between the electrodes). In Fig. 8.26, a half distribution curve is shown. A considerably sharper distribution found on the substrate with an alternating current (ac) discharge is in accordance with the mechanism of polymer deposition based on the (kinetic) diffusional path length. Namely, at a high pressure the active zones of glow discharge [negative glow of direct current (dc) discharge] are pulled closer to the electrodes, which results in a very high polymer deposition at the electrode surface, and this trend is stronger with a lower-frequency discharge. At the same time, the remaining interelectrode space becomes a relatively inactive zone where the effect of the diffusional transport of the reactive species, as discussed in terms of the rf inductive discharge in Section 8.3.2, becomes more pronounced.

The integrated deposition rates and the ratio of conversion of monomer to polymer at the electrode surface and at the substrate (placed midway between the electrodes) are shown in Table 8.1 (p. 226).

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Title of Invention:	COATINGS			
First Named Inventor/Applicant Name:	Stephen Richard COULSON			
Filer:	Paul John Parins/Bethany Lichtscheidl			
Attorney Docket Number:	GBL0007/US/2			
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:				
SUBMISSION- INFORMATION DISCLOSURE STMT	1806	1	260	260
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First Named Inventor/Applicant Name:	Stephen Richard COULSON
Customer Number:	33072
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Warnings:					
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2	Information Disclosure Statement (IDS) Form (SB08)	GBL0007US2_SIDS.pdf	1062051	no	7
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Warnings:					
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Warnings:					
Information:					
4	Non Patent Literature	NPL2_Yao_et_al.pdf	2099619	no	15
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Information:					
5	Non Patent Literature	NPL3_Sartomer_Comp_Material_Safety_Data_Sheet.pdf	73591	no	7
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6	Non Patent Literature	NPL4_Declaration_for_Gleason.pdf	771231	no	117
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7	Non Patent Literature	NPL5_Curriculum_for_Gleason.pdf	353950	no	34
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21	Non Patent Literature	NPL11_Yasuda_.pdf	9229297	no	58
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Warnings:

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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

Inventor(s): COULSON et al.	Examiner: NICOLE M. BUIE-HATCHER
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Filing Date: August 22, 2019	Confirmation No.: 6664
For: COATINGS	Docket No.: GBL0007/US/2

Mail Stop Amendment
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

I CERTIFY THAT ON **OCTOBER 8, 2020**, THIS CORRESPONDENCE IS
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BETHANY L. LICHTSCHEIDL

INFORMATION DISCLOSURE STATEMENT

The document listed on the enclosed Form PTO-1449 are presented pursuant to
Applicants' duty of disclosure under 37 C.F.R. 1.56.

Applicant notes that the present application is a Continuation of application Serial
No. 15/735,130 filed December 8, 2017, which issued into U.S. Pat. No. 10,421,876 and
is now involved in an Inter Partes Review having trial numbers IPR2020-01198 and filing
date of July 17, 2020. The petition and exhibits of which are cited on the enclosed Form PTO-
1449. The Form PTO-1449 includes references listed in the Exhibit List of the petition that are
not already of record.

Respectfully Submitted,

Dated: _October 8, 2020

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