

SURFACE ACTIVATED CHEMICAL VAPOR DEPOSITION AND USES THEREOF

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims the benefit of and priority to U.S. Provisional Application No. 63/567,066, filed March 19, 2024, and to U.S. Provisional Application No. 63/510,920, filed June 29, 2023, which are hereby incorporated by reference in their respective entirety.

FIELD OF THE INVENTION

This invention is in the field is surface activated chemical vapor deposition which can be used, for example, to form SiOC and SiNC coatings and films.

BACKGROUND OF THE INVENTION

Coatings play a critical role throughout many industries where they are applied to surfaces for a variety of reasons such as sealing to protect a surface from the environment, adding mechanical protection, imparting optical effects, modifying surface properties, and enhancing biological or chemical compatibility. A significant benefit of modifying a surface with a coating is that a relatively small quantity of material can be used to dictate surface properties over a large area without altering the properties of the bulk material. Typical processes for applying coatings include spraying, dipping, painting, and immersion in chemical baths. These application methods utilize liquids which add complications related to curing, surface tension, and viscous effects that can lead to pinholes, limit conformality, and increase the minimum practical thickness of the coating.

In many industries, the importance of coating conformality has become increasingly important as substrates become more intricate and surface area to volume ratios increase. Chemical vapor deposition (CVD) is a subset of coating application processes which apply coatings directly from the vapor phase. The desired coating material is directly synthesized from gaseous precursors. However, typical CVD processes rely on a spatially-located energy source to activate the chemical synthesis

process, such as filaments, plasma, ultraviolet irradiation, or lasers. These energy sources can cause conformality issues imposed by line-of-sight limitations, directionally influenced electric fields, and high energy molecules that readily react upon impact which can also cause damage to the resultant coating. These factors ultimately limit the conformality of the resultant coating.

Thus, there exists a need for alternate deposition methods which permit facile deposition of coatings without unduly limiting the conformality of coatings produced.

Further, there is a need for improved methods for coating semiconductors, for example, microelectronics stacks, boards, electronic device components, and 3-D integrated heterogeneous packages, having high aspect ratio features, which can benefit from coatings exhibiting high conformality which provide various benefits.

Therefore, it is an object of the invention to provide deposition methods which produce coatings with high conformality.

Therefore, it is also an object of the invention to provide deposition methods where the conformal coatings produced can provide particular compositions and properties on coated substrates and materials.

Therefore, it is a further object of the invention to use such methods to produce substrates or materials having highly conformal coatings for various applications.

SUMMARY OF THE INVENTION

Methods for surface activated chemical vapor deposition to form highly conformal SiOC and SiNC coatings, and uses thereof, are described herein.

In some instances, a surface activated chemical vapor deposition (SACVD) may be carried out under isothermal or non-isothermal conditions.

The SACVD methods described can be used to form or deposit polymeric coatings or films of particular compositions. In one non-limiting instance, a first example of an isothermal SACVD method for forming a polymeric coating on at least one substrate or material can include the steps of:

- (i) placing the at least one substrate or material into a reaction chamber;
- (ii) sealing and purging the reaction chamber under a vacuum;
- (iii) wherein the reaction chamber is at an initiation temperature sufficient to activate one or more gaseous initiators;

wherein one or more surfaces of the at least one substrate or material have a surface temperature which is equal to or substantially equal to the initiation temperature to which the reaction chamber is heated to; and

- (iv) flowing one or more gaseous monomers, the one or more gaseous initiators,
5 and optionally one or more carrier gases into the reaction chamber to form the polymeric coating on at least a portion of a surface of the at least one substrate or material;

wherein the partial pressure of the one or more gaseous monomers is sufficient to form the polymeric coating on the portion of the surface at the surface temperature;

- wherein the one or more gaseous monomers comprise one or more silicon-
10 containing monomers;

wherein the polymeric coating formed comprises silicon, oxygen, hydrogen, and carbon; and wherein the polymeric coating comprises an atomic carbon content in a range of about 2 to 70% of the total atomic composition of the polymeric coating.

- In some instances, the surface temperature during step (iv) is sufficient to
15 preclude the one or more gaseous monomers or the one or more gaseous initiators from exceeding their saturation pressure at the surface temperature.

In another non-limiting instance, a second example of an isothermal SACVD method for forming a polymeric coating on at least one substrate or material can include the steps of:

- 20 (i) placing the at least one substrate or material into a reaction chamber;
(ii) sealing and purging the reaction chamber under a vacuum;
(iii) wherein the reaction chamber is at an initiation temperature sufficient to activate one or more gaseous initiators;

- wherein one or more surfaces of the at least one substrate or material have
25 a surface temperature which is equal to or substantially equal to the initiation temperature to which the reaction chamber is heated to; and

- (iv) flowing one or more gaseous monomers, the one or more gaseous initiators,
and optionally one or more carrier gases into the reaction chamber to form the polymeric coating on at least a portion of a surface of the at least one substrate or material;

- 30 wherein the partial pressure of the one or more gaseous monomers is sufficient to form the polymeric coating on the portion of the surface at the surface temperature;

wherein the one or more gaseous monomers comprise one or more silicon-containing monomers;

wherein the polymeric coating formed comprises silicon, nitrogen, hydrogen, and carbon; and wherein the polymeric coating comprises an atomic carbon content in a
5 range of about 2 to 70% of the total atomic composition of the formed polymeric coating.

In some instances, the surface temperature during step (iv) is sufficient to preclude the one or more gaseous monomers or the one or more gaseous initiators from exceeding their saturation pressure at the surface temperature.

10 In certain instances of the methods, the at least one substrate or material is a plurality of substrates and/or materials and optionally each of the substrates and/or materials in the plurality is independently placed on a separate temperature-controlled platform. In one such instance, a third non-isothermal example of an SACVD method for forming a polymeric coating on at least one substrate or material can include the steps of:

15 (i) placing the at least one substrate or material onto a platform within a reaction chamber;

wherein the platform and the reaction chamber and/or components thereof are independently temperature controlled;

(ii) sealing and purging the reaction chamber under a vacuum;

20 (iii) wherein the platform is at an initiation temperature sufficient to activate one or more gaseous initiators;

wherein one or more surfaces of the at least one substrate or material have a surface temperature which is equal to or substantially equal to the initiation temperature to which the platform is heated to; and

25 (iv) flowing one or more gaseous monomers, the one or more gaseous initiators, and optionally one or more carrier gases into the reaction chamber to form the polymeric coating on at least a portion of a surface of the at least one substrate or material;

wherein the reaction chamber and/or components thereof are independently heated to a reaction chamber temperature, wherein the reaction chamber temperature is
30 lower than the initiation temperature and the surface temperature during step (iv); optionally wherein the components comprise walls of the reaction chamber;

wherein the partial pressure of the one or more gaseous monomers is sufficient to form the polymeric coating on the portion of the surface at the surface temperature;

wherein the one or more gaseous monomers comprise one or more silicon-containing monomers;

- 5 wherein the polymeric coating formed comprises silicon, oxygen, hydrogen, and carbon; and wherein the polymeric coating comprises an atomic carbon content in a range of about 2 to 70% of the total atomic composition of the polymeric coating.

- In some instances, the reaction chamber temperature during step (iv) is sufficient to preclude the one or more gaseous monomers or the one or more gaseous initiators
10 from exceeding their saturation pressure at the reaction chamber temperature.

 In another such instance, a fourth non-isothermal example of an SACVD method for forming a polymeric coating on at least one substrate or material can include the steps of:

- (i) placing the at least one substrate or material onto a platform within a reaction
15 chamber;

 wherein the platform and the reaction chamber and/or components thereof are independently temperature controlled;

 (ii) sealing and purging the reaction chamber under a vacuum;

- (iii) wherein the platform is at an initiation temperature sufficient to activate one
20 or more gaseous initiators;

 wherein one or more surfaces of the at least one substrate or material have a surface temperature which is equal to or substantially equal to the initiation temperature to which the platform is heated to; and

- (iv) flowing one or more gaseous monomers, the one or more gaseous initiators,
25 and optionally one or more carrier gases into the reaction chamber to form the polymeric coating on at least a portion of a surface of the at least one substrate or material;

 wherein the reaction chamber and/or components thereof are independently heated to a reaction chamber temperature, wherein the reaction chamber temperature is lower than the initiation temperature and the surface temperature during step (iv);

- 30 optionally wherein the components comprise walls of the reaction chamber;

 wherein the partial pressure of the one or more gaseous monomers is sufficient to form the polymeric coating on the portion of the surface at the surface temperature;

wherein the one or more gaseous monomers comprise one or more silicon-containing monomers;

wherein the polymeric coating formed comprises silicon, nitrogen, hydrogen, and carbon; and wherein the polymeric coating comprises an atomic carbon content in a
5 range of about 2 to 70% of the total atomic composition of the polymeric coating.

In some instances, the SACVD methods described above produce a polymeric coating that has a microscale conformality to the surface of at least about 60%, as determined by microtrench method.

In some instances, the reaction chamber temperature during step (iv) is sufficient
10 to preclude the one or more gaseous monomers or the one or more gaseous initiators from exceeding their saturation pressure at the reaction chamber temperature.

In some instances, the atomic carbon content of the polymeric coating is in the range of about 2 to 5%, 2 to 10%, 2 to 15%, 2 to 20%, 2 to 30%, 2 to 40%, 2 to 50%, 2 to 60%, or 2 to 70% of the total atomic composition of the polymeric coating, as well as
15 individual values and sub-ranges disclosed within the aforementioned ranges. In some other instances, the atomic carbon content of the polymeric coating is in the range of about 5 to 70%, 5 to 65%, 5 to 60%, 5 to 55%, or 5 to 50% of the total atomic composition of the polymeric coating, as well as individual values and sub-ranges disclosed within the aforementioned ranges. In still other instances, the atomic carbon
20 content of the polymeric coating is in the range of about 10 to 70%, 10 to 60%, 10 to 50%, or 10 to 40% of the total atomic composition of the polymeric coating, as well as individual values and sub-ranges disclosed within the aforementioned ranges. In yet other instances, the atomic carbon content of the polymeric coating is in the range of about 15 to 70%, 15 to 60%, 15 to 50%, or 15 to 40% of the total atomic composition of
25 the polymeric coating, as well as individual values and sub-ranges disclosed within the aforementioned ranges. In certain instances, the atomic carbon content of the polymeric coating is in the range of about 2 to 15% of the total atomic composition of the polymeric coating, as well as individual values and sub-ranges disclosed within the aforementioned ranges.

30 Achieving the atomic carbon contents described above with respect to coating composition, while maintaining the deposition of uniform, preferably defect-free,

polymeric coatings includes the selection of both reactants (i.e., gaseous monomers and gaseous initiators) and process parameters, as described in further detail herein.

In some instances of the SACVD methods described, the methods may further include a step of reducing organic content in the polymeric coating following step (iv),
5 such as by applying an annealing step. In this context, annealing is the heating of the polymeric coating or film formed by the methods, either during or subsequent to deposition, in order to modify the composition, thermal stability, electrical, and/or other material properties of the polymeric coating or film. The addition of an annealing step may be used to achieve a desired polymeric coating or film composition, or other
10 material properties, which in some instances may not be possible to achieve in the as-originally deposited film, such as due to monomer selection or other limitations. These limitations can include, but are not limited to, vapor pressure, reactivity in polymerization, thermal stability of reactants in unreacted form, and commercial availability of reactants. The annealing step can be applied during the flowing step, i.e.
15 while the polymeric coating is forming. Or, the annealing step can be occur after the flowing step (i.e., following formation of the polymeric coating). In such instances, following the annealing step, the atomic carbon content of the polymeric coating is in the range of about 2 to 5%, 2 to 10%, 2 to 15%, 2 to 20%, 2 to 25%, or 2 to 30% of the total atomic composition of the polymeric coating, as well as individual values and sub-ranges
20 disclosed within the aforementioned ranges. In some other instances, following the annealing step, the atomic carbon content of the polymeric coating is in the range of about 5 to 10%, 5 to 15%, 5 to 20%, 5 to 25%, or 5 to 30% of the total atomic composition of the polymeric coating, as well as individual values and sub-ranges disclosed within the aforementioned ranges. In still other instances, following the
25 annealing step, the atomic carbon content of the polymeric coating is in the range of between about 8 to 15%, 8 to 20%, 8 to 25%, or 8 to 30% of the total atomic composition of the polymeric coating, as well as individual values and sub-ranges disclosed within the aforementioned ranges. In yet other instances, following the annealing step, the atomic carbon content of the polymeric coating is in the range of
30 about 15 to 20%, 15 to 25%, or 15 to 30% of the total atomic composition of the polymeric coating, as well as individual values and sub-ranges disclosed within the aforementioned ranges. In certain instances, following the annealing step the atomic

carbon content of the polymeric coating is in the range of about 2 to 30% of the total atomic composition of the polymeric coating, as well as individual values and sub-ranges disclosed within the aforementioned ranges.

In some instances, the atomic hydrogen content of a polymeric coating can be in
5 a range of about 0.1% to 60% of the total atomic composition of the polymeric coating. The atomic hydrogen content of a polymeric coating can be reduced, as needed, by annealing the coating to produce a polymeric coating having a desired atomic hydrogen content. As discussed herein, the atomic hydrogen content in a polymeric coating can
10 impact the properties of the polymeric coating, such as the dielectric constant and its ability to act as a barrier to metal migration.

The SACVD methods described above can be used to deposit/form polymeric coating(s) on surface(s) of a substrate or material having a degree of conformality, which would otherwise be difficult or impossible to attain using other known deposition methods. Accordingly, in some instances, the methods described herein can be used to
15 form a polymeric coating on at least a portion of a surface of a substrate or material, where the polymeric coating and the substrate or material are included in or form at least part of a semiconductor device. In some instances, the semiconductor device is a semiconductor circuit. In certain instances, the polymeric coating is a dielectric coating or film. In certain other instances, the polymeric coating acts as an optical material, such
20 as a nonreflective coating or waveguide. In still other instances, the polymeric coating can act as a barrier coating or film against migration of metal(s).

In some instances, more than one polymeric coating is formed on a substrate or material having different properties. In one non-limiting example, first and second polymeric coatings can be formed on a substrate or material where the first and second
25 polymeric coatings are either in contact or are not in contact with each other. In other words, the first and second polymeric coatings may be separated by another layer or material. In some such instances, a substrate or material may include at least a first polymeric coating having a reduced atomic content of hydrogen and which acts as a carbon-based barrier layer to prevent or reduce migration of metals through the coating
30 and at least a second polymeric coating which has a higher atomic content of hydrogen than the first layer. In some instances, the first polymeric coating is thinner than the second polymeric coating. In some instances, the first polymeric coating is thicker than

the second polymeric coating. In yet another non-limiting example, first and second polymeric coatings can be formed on a substrate or material where the first and second polymeric coatings are either in contact with each other. In such an instance, the at least first polymeric coating, which forms a first layer, can have a reduced atomic content of hydrogen and acts as a carbon-based barrier layer to prevent or reduce migration of metals through the coating. The at least a second polymeric coating, which forms a second layer on top of the first layer, can have a higher atomic content of hydrogen and acts as a low-k dielectric coating or film. In some instances, the first polymeric coating is thinner than the second polymeric coating.

BRIEF DESCRIPTION OF THE DRAWINGS

Non-limiting embodiments are described by way of example with reference to the accompanying Figures, which are schematic and are not necessarily drawn to scale. In the Figures, each identical or nearly identical component illustrated is typically represented by a single numeral. For purposes of clarity, not every component is labeled in every figure, nor is every component shown where illustration is not necessary to allow those of ordinary skill in the art to understand the Figure(s).

Figure 1A shows a non-limiting illustration of an exemplary silicon wafer stack 100. The exemplary wafer stack includes top and bottom pieces 110 and 120 separated by two side-strips 130a, 130b, which create a tunnel feature 150, having opening 152, used for assessing conformality of a polymeric coating deposited therein, and an adhesive 140 holds the silicon wafer stack together.

Figure 1B shows a cross-sectional view of the exemplary silicon wafer stack depicted in Figure 1A.

Figure 1C shows a non-limiting depiction of a cross-sectional view of a microtrench substrate 200, containing a microtrench 210 that includes a bottom portion 220 and side-walls 230a and 230b.

Figure 2 shows a schematic of an exemplary SACVD system used for synthesizing conformal polymeric coatings. This exemplary SACVD system 200 includes a reactor chamber 210, tube furnace 220, a carrier gas vessel 230, a carrier gas mass flow controller 235, an initiator vessel 240, an initiator metering valve 245, a monomer vessel 250, a pressure transducer 260, a throttle valve 270, and a vacuum source 280.

Figure 3 shows a non-limiting schematic of an SACVD reactor 300 having the following components: initiator vessel 310, monomer vessel 320, initiator metering valve 330, monomer metering valve 340, reactor chamber 350, temperature-controlled platform 360, pressure transducer 370, throttle valve 380, and vacuum pump 390.

5 **Figure 4** shows an infra-red (IR) spectra of pV3D3 polymer synthesized using SACVD with different initiator chemistries and at different temperatures.

Figure 5 shows an infra-red (IR) spectra of pDVB polymer synthesized using SACVD with different initiators.

10 **Figure 6** shows an infra-red (IR) spectra of pTBS synthesized using SACVD with initiator TBPA.

Figure 7 shows a graph of a comparison of conformality achieved using isothermal deposition and selective deposition, where selective deposition is the highest point and isothermal deposition is the lowest point at 175, 185, and 205 °C, respectively.

15 **Figure 8** shows an infra-red (IR) spectra of pV3D3 synthesized with SACVD under using isothermal heating.

Figure 9 shows a non-limiting schematic of an iCVD reactor 400 having the following components: monomer vessel 410, initiator vessel 420, monomer metering valve 430, initiator metering valve 440, temperature-controlled platform 450, filament array 460, pressure transducer 470, throttle valve 480, and vacuum pump 490.

20 **Figure 10** shows a non-limiting schematic of iPECVD reactor 500 having the following components: monomer vessel 510, initiator vessel 520, monomer metering valve 530, initiator metering valve 540, showerhead gas diffuser 550, sample holder panels 560, electrode 570, pressure transducer 580, throttle valve 590, vacuum pump 595, and inert (argon) tank 597.

25 **Figure 11** shows a non-limiting diagram depicting the geometry of a microtrench.

Figure 12 shows a non-limiting schematic of the dielectric constant characterization setup.

30 **Figure 13** shows a graphical plot exhibiting the change in measured dielectric constant produced through changes in final atomic composition by way of a heat treatment.

DETAILED DESCRIPTION OF THE INVENTION

The present disclosure generally describes methods for surface activated chemical vapor deposition and uses thereof to form highly conformal coatings.

SACVD is distinct from traditional chemical vapor deposition (CVD) polymer coating methods in that the formation of active species is driven to surface(s) to selectively form a polymeric coating thereon. Traditional CVD methods use an energy input at a focused location (i.e., a hot filament CVD) or throughout the gas phase within the chamber (i.e., plasma-based CVD), neither of which are required in the methods described below. Instead, the substrate or device to be coated is itself heated to a temperature capable of activating a gaseous initiator species. When the initiator is activated at the heated surface(s), for example a peroxide initiator, the initiator will be cleaved to form two free radicals that can then initiate polymerization of gaseous monomer units adsorbed on the heated surface(s) to form the polymeric coating specifically thereon. This approach allows for formation of a polymeric coating without need for diffusion of the activated monomer species away from the point of activation, generating coatings with significantly higher degrees of conformality, as compared to coatings formed by traditional CVD.

I. Definitions

“Initiated”, as used herein, refers to a chemical species, such as a monomer, which when acted upon by an initiator species, which may be generated from decomposition of a suitable initiator source, renders the chemical species capable of forming a polymeric coating on a surface(s). Initiator species can include, but are not limited to, ions, and free radicals, such as di-radicals, and combinations thereof.

The term “reactive species”, as used herein, refers to one or more species which can be generated in the gas phase and which upon polymerization form a polymer. The term “reactive species” includes monomers and/or oligomers. The reactive species disclosed herein may be gaseous at room temperature and atmospheric pressure. Alternatively, the reactive species are liquids or solids at room temperature and atmospheric pressure, for example, they may be evaporated at reduced pressure or heated or both in order to perform the methods described herein.

As used herein, the term “polymer” or “polymeric coating” are used interchangeably and refer to a polymer which is generally composed of one or more

monomers or “repeat units,” which are chemically bonded together in some manner. It should be understood that the polymer formed comprising the monomers described herein or formed from the monomers described herein may comprise other components. In addition, as would be understood by a person of skill in the art, the monomer
5 generally undergoes a chemical modification during the polymerization process, and thus, one or more of the bonds present in the monomer may not be present in the polymer.

“Conformality”, as used herein, refers to the degree of uniformity in the thickness of a polymeric coating deposited on a surface based on macroscale and/or microscale
10 measurements. A conformal coating can be considered highly conformal when it has a conformality of at least about 50%, as determined by the wafer stack method.

“Microscale conformality,” as used herein, refers the degree of uniformity in the thickness of a polymeric coating deposited on a surface based on micron-scale measurements, i.e. 10 microns or less. For example, a highly conformal coating can have
15 a microscale conformality of at least about 60%, as determined by the microtrench method.

“Gaseous monomers”, as used herein, refers to reactive molecules which can be generated in the gas phase and upon polymerization form a polymer. Such polymerization includes radical polymerization. The gaseous monomers disclosed herein
20 may not necessarily be gases at room temperature and atmospheric pressure. If such species are liquids or solids, for example, they may be evaporated at reduced pressure or heated or both in order to perform the methods described herein.

“Gaseous initiators”, as used herein, refers to compounds that are able to initiate radical polymerization of monomers form a polymer. The gaseous initiators disclosed
25 herein may not necessarily be gases at room temperature and atmospheric pressure. If such species are liquids or solids, for example, they may be evaporated at reduced pressure or heated or both in order to perform the methods described herein.

“Inert Gas” or “Inert Atmosphere,” are used interchangeably herein and refer to a gas or mixture of gases which are not reactive under reaction conditions within a vacuum
30 chamber.

Numerical ranges disclosed in the present application include, but are not limited to, ranges of temperatures, ranges of pressures, ranges of molecular weights, ranges of

integers, ranges of force values, ranges of times, ranges of thicknesses, and ranges of gas flow rates. The disclosed ranges of any type, disclose individually each possible number that such a range could reasonably encompass, as well as any sub-ranges and combinations of sub-ranges encompassed therein. For example, disclosure of a
5 temperature range, is intended to disclose individually every possible temperature value that such a range could encompass, consistent with the disclosure herein. In another example, the disclosure states that conformality, expressed as a percentage, can range from about 50% to about 90%, which also refers to percentage values that can be selected independently from about 57%, 68%, and 79%, as well as any sub-range
10 between these numbers (for example, about 65% to 85%), and any possible combination of ranges between these values.

II. Surface Activated Chemical Vapor Deposition (SACVD)

In general, the SACVD process functions by thermally assisting the formation of chemically reactive species, such as initiator radicals, directly on one or more surfaces to
15 be *in situ* coated with a polymer. As result of direct formation of such species on surface(s) of substrate or material, there is a significantly reduced length of diffusion for the reactive species providing a beneficial impact on the degree of conformality attainable using SACVD methods. In contrast, an initiated chemical vapor deposition (iCVD) process uses a filament(s) to thermally decompose a chemical species, such as
20 free radical initiators, at the filaments which need to diffuse to a substrate or material, in addition to penetrating any geometric intricacies that may exist therein. Due to their reactive nature, these radical species also demonstrate relatively high sticking coefficients and demonstrate a greater likelihood of sticking to surfaces, other than those intended to be coated, they encounter rather than desorbing and continuing to diffuse
25 toward the substrate or material, as well throughout a geometrically complex substrate or material. When such species are required to diffuse from a distant filament, the result is a degree of preferential deposition within line of sight of the filaments. In contrast, SACVD is expected to produce reactive radical polymerizable species by reaction with radical based initiator(s) directly on areas of the one or more surfaces of a substrate or
30 material intended to be coated, which significantly eases issues of diffusion obstacles to producing a polymeric coating thickness having a high degree of uniformity and conformality. This is in contrast to other vapor deposition polymerization methods, such

as used to form parylene, which relies on pyrolysis (thermal decomposition) of the monomer itself to form radicals, and does not require the use of any radical initiators or other catalysts. In addition, thermal decomposition in such alternate methods does not take place on the surface of the substrate to be coated, but rather in a remote temperature controlled region away from the substrate. Various exemplary methods of SACVD are described below.

The SACVD methods described can be used to deposit one or more polymeric coatings on a substrate or material. Such substrates or materials can, for instance, be used in semiconductor applications, such as but not limited to, microelectronics stacks, boards, electronic device components, and 3-D integrated heterogeneous packages which have one or more high aspect ratio features thereon and forming highly conformal coatings can be thereon can be achieved using the SACVD methods described.

Conformality of a polymeric coating may be evaluated, for example, by depositing a given polymeric coating on a wafer stack, as shown in Figures 1A and 1B. The wafer stack can include top and bottom pieces 110 and 120 separated by two side-strips 130a, 130b, which create a tunnel feature 150 that can be used to assess conformality of a polymeric coating deposited therein. An adhesive 140, such as tape, holds the silicon wafer stack together. It is possible to analyze the thickness of the polymeric coating formed within tunnel feature 150 of the wafer stack and determine the thickness of the coating at an opening 152 of the tunnel feature to the thinnest part of the coating within the tunnel feature. The different thicknesses of the polymeric coating may be determined by reflectometry, or any other suitable method known in the art to measure coating thicknesses. In a reference wafer stack, the wafer stack has the dimensions listed in Table 1 below:

Table 1. Exemplary Wafer Stack Dimensions

Components	Length (mm)	Width (mm)	Height (mm)
110/120	25	25	0.5
130a/130b	25	4	0.5

To express conformality as a percentage, by way of the wafer stack method, the following equation can be used:

$$\frac{\text{(Thinnest thickness of polymeric coating within tunnel feature)}}{\text{(Thickness of polymeric coating at opening of tunnel feature)}} \times 100$$

where the higher the percentage value, the higher the degree of conformality.

5 Based on the exemplary wafer stack of the dimensions given in Table 1, the thinnest coating is typically measured at the center of bottom piece 120 or top piece 110, which is ~12.5 mm from the inlet of the wafer stack.

Using the wafer stack method, the conformality of the coatings formed by different methods of depositing polymeric coatings using the same conditions (i.e., composition of monomer(s), initiator(s), carrier gas(es)) can be compared. In some instances, polymeric coatings produced by SACVD have a conformality of at least about 50%, when tested using a wafer stack having the dimensions of the reference wafer stack described above, or a conformality that ranges from about 50% to about 99.9%, or higher, as determined using the wafer stack method. In some instances, the conformality is at least about 55%, 60%, 65%, 70%, 75%, 80%, 90%, 95%, 96%, 97%, 98%, 99%, or 99.9%, as determined by the wafer stack method, when tested using a wafer stack having the dimensions of the reference wafer stack described above.

Microscale conformality of a polymeric coating may be evaluated, for example, by depositing a given polymeric coating in a microtrench substrate. A non-limiting example of a microtrench substrate 200 is shown in Figure 1C. It is possible to analyze the thickness of the polymeric coating formed within the microtrench 210, where different thicknesses of the polymeric coating on the side-walls (230a/230b) and bottom (220) may be determined by electron microscopy, or any other suitable method known in the art to measure coating thicknesses. In a reference microtrench, as detailed in Table 2 below, the microtrench has the following dimensions:

Table 2. Exemplary Microtrench Dimensions

Component	Length (μm)
Each Side-wall	57
bottom	4.5

To express microscale conformality as a percentage, by way of the microtrench method, the following equation can be used:

$$\frac{(\text{Smallest thickness of polymeric coating within the microtrench})}{(\text{Thickness of polymeric coating at the inlet to the microtrench})} \times 100$$

where the higher the percentage value, the higher the degree of microscale
5 conformality.

Using the microtrench method, the microscale conformality of the polymeric coatings formed by different methods of depositing polymeric coatings using the same conditions (i.e., composition of monomer(s), initiator(s), carrier gas(es)) can be compared. In some instances, polymeric coatings produced by SACVD have a
10 microscale conformality of at least about 60%, when tested using a microtrench having the dimensions of the reference microtrench described above, or a conformality that ranges from about 60% to about 99.9%, or higher, as determined using the microtrench method, as well as individual values and sub-ranges contained within the aforementioned range. In some instances, the microscale conformality is at least about 60%, 65%, 70%,
15 75%, 80%, 90%, 95%, 96%, 97%, 98%, 99%, or 99.9%, as determined by the microtrench method when tested using a microtrench having the dimensions of the reference microtrench described above.

Following coating materials and/or surfaces containing complex and/or high aspect ratio features, such as can be found in 3-D heterogeneous integrated packages
20 (HIP), microelectronics stacks, microelectronics boards, or electronic device components, the microtrench method can be used to determine the microscale conformality of the polymeric coating.

A. Surface Activated Chemical Vapor Deposition of SiOC and SiNC Films

25 In a first instance, a surface activated chemical vapor deposition (SACVD) may be carried out under isothermal or non-isothermal conditions. Under isothermal conditions, at least one substrate or material to be coated by a polymeric coating (or polymeric film) is placed within a reaction chamber and the reaction chamber is heated to an initiation temperature sufficient to activate one or more gaseous initiators. In such
30 methods, heating to the initiation temperature also heats one or more surfaces of the substrate(s) or material(s) within the reaction chamber to allow for decomposition of the one or more initiators and formation/deposition of a polymeric coating on a least a portion of the one or more surfaces of the substrate(s) or material(s). Use of an

isothermal approach allows for SACVD formed coatings on all surfaces, having a surface temperature equal or substantially equal to the initiation temperature, within the reaction chamber without concern for thermal contact to a substrate or device stage or platform. This can be advantageous when forming polymeric coating(s) on all sides of a substrate or device is required, or when forming a polymeric coating on a large number of components of such a substrate or device, such as when closely spaced, is desired. By contrast, isothermal CVD methods do not produce as high a degree of conformality in the coatings formed, since other surfaces within the CVD reaction chamber, for example the chamber walls, are also at a high enough temperature to initiate gaseous initiator species therein. These activated initiator species can then diffuse to the substrate or device to be coated resulting in additional line-of-sight coating and reducing the overall conformality ratio of the final polymeric coating formed on the substrate or device. Such a loss of conformality can be minimized by increasing spacing between surface(s) within the deposition chamber and the substrates or devices to be coated.

The SACVD methods described can be used to form or deposit polymeric coatings or films of particular compositions. In one non-limiting instance, a first example of an isothermal SACVD method for forming a polymeric coating on at least one substrate or material can include the steps of:

- (i) placing the at least one substrate or material into a reaction chamber;
- (ii) sealing and purging the reaction chamber under a vacuum;
- (iii) wherein the reaction chamber is at an initiation temperature sufficient to activate one or more gaseous initiators;
wherein one or more surfaces of the at least one substrate or material have a surface temperature which is equal to or substantially equal to the initiation temperature to which the reaction chamber is heated to; and
- (iv) flowing one or more gaseous monomers, the one or more gaseous initiators, and optionally one or more carrier gases into the reaction chamber to form the polymeric coating on at least a portion of a surface of the at least one substrate or material;
wherein the partial pressure of the one or more gaseous monomers is sufficient to form the polymeric coating on the portion of the surface at the surface temperature;
wherein the one or more gaseous monomers comprise one or more silicon-containing monomers;

wherein the polymeric coating formed comprises silicon, oxygen, hydrogen, and carbon; and wherein the polymeric coating comprises an atomic carbon content in a range of about 2 to 70% of the total atomic composition of the polymeric coating.

In some instances of the above method, the polymeric coating has a microscale
5 conformality to the surface of at least about 60%, as determined by microtrench method.

In some instances, the surface temperature during step (iv) is sufficient to preclude the one or more gaseous monomers or the one or more gaseous initiators from exceeding their saturation pressure at the surface temperature.

In another non-limiting instance, a second example of an isothermal SACVD
10 method for forming a polymeric coating on at least one substrate or material can include the steps of:

- (i) placing the at least one substrate or material into a reaction chamber;
- (ii) sealing and purging the reaction chamber under a vacuum;
- (iii) wherein the reaction chamber is at an initiation temperature sufficient to
15 activate one or more gaseous initiators;

wherein one or more surfaces of the at least one substrate or material have a surface temperature which is equal to or substantially equal to the initiation temperature to which the reaction chamber is heated to; and

- (iv) flowing one or more gaseous monomers, the one or more gaseous initiators,
20 and optionally one or more carrier gases into the reaction chamber to form the polymeric coating on at least a portion of a surface of the at least one substrate or material;

wherein the partial pressure of the one or more gaseous monomers is sufficient to form the polymeric coating on the portion of the surface at the surface temperature;

- wherein the one or more gaseous monomers comprise one or more silicon-
25 containing monomers;

wherein the polymeric coating formed comprises silicon, nitrogen, hydrogen, and carbon; and wherein the polymeric coating comprises an atomic carbon content in a range of about 2 to 70% of the total atomic composition of the formed polymeric coating.

In some instances of the above method, the polymeric coating has a microscale
30 conformality to the surface of at least about 60%, as determined by microtrench method.

In some instances, the surface temperature during step (iv) is sufficient to preclude the one or more gaseous monomers or the one or more gaseous initiators from exceeding their saturation pressure at the surface temperature.

In certain instances of the methods, the at least one substrate or material is a plurality of substrates and/or materials and optionally each of the substrates and/or materials in the plurality is independently placed on a separate temperature-controlled platform. It is understood that when each of the substrates and/or materials in the plurality is independently placed on a separate temperature-controlled platform it means that there are a plurality of temperature-controlled platforms sufficient to hold each substrate or material. For instance, if there are four substrates there are four platforms. Nevertheless, in some other instances, there may be four substrates and there are two platforms, where two substrates are placed on one platform and two substrates are placed on the other platform. Different combinations are possible based on the size of the substrates or materials and dimensions of the platform(s). In some other instances, the at least one substrate or material is a plurality of substrates and/or materials and the plurality is placed in a suitable carrier which is placed on the single temperature-controlled platform in the reactor. In some instances, the suitable carrier is a wafer boat. In still other instances, the at least one substrate or material is a plurality of substrates and/or materials and the plurality is placed in a suitable carrier, such as a wafer boat, which is placed into the reaction chamber. Other suitable carriers are known to the skilled person.

In one such instance, a third example of a non-isothermal SACVD method for forming a polymeric coating on at least one substrate or material can include the steps of:

- (i) placing the at least one substrate or material onto a platform within a reaction chamber;
wherein the platform and the reaction chamber and/or components thereof are independently temperature controlled;
- (ii) sealing and purging the reaction chamber under a vacuum;
- (iii) wherein the platform is at an initiation temperature sufficient to activate one or more gaseous initiators;

wherein one or more surfaces of the at least one substrate or material have a surface temperature which is equal to or substantially equal to the initiation temperature to which the platform is heated to; and

- (iv) flowing one or more gaseous monomers, the one or more gaseous initiators, and optionally one or more carrier gases into the reaction chamber to form the polymeric coating on at least a portion of a surface of the at least one substrate or material;

wherein the reaction chamber and/or components thereof are independently heated to a reaction chamber temperature, wherein the reaction chamber temperature is lower than the initiation temperature and the surface temperature during step (iv); optionally wherein the components comprise walls of the reaction chamber;

wherein the partial pressure of the one or more gaseous monomers is sufficient to form the polymeric coating on the portion of the surface at the surface temperature;

wherein the one or more gaseous monomers comprise one or more silicon-containing monomers;

- wherein the polymeric coating formed comprises silicon, oxygen, hydrogen, and carbon; and wherein the polymeric coating comprises an atomic carbon content in a range of about 2 to 70% of the total atomic composition of the polymeric coating.

In some instances of the above method, the polymeric coating has a microscale conformality to the surface of at least about 60%, as determined by microtrench method.

- In some instances, the reaction chamber temperature during step (iv) is sufficient to preclude the one or more gaseous monomers or the one or more gaseous initiators from exceeding their saturation pressure at the reaction chamber temperature.

In another such instance, a fourth example of a non-isothermal SACVD method for forming a polymeric coating on at least one substrate or material can include the steps of:

- (i) placing the at least one substrate or material onto a platform within a reaction chamber;
- wherein the platform and the reaction chamber and/or components thereof are independently temperature controlled;
- (ii) sealing and purging the reaction chamber under a vacuum;
- (iii) wherein the platform is at an initiation temperature sufficient to activate one or more gaseous initiators;

wherein one or more surfaces of the at least one substrate or material have a surface temperature which is equal to or substantially equal to the initiation temperature to which the platform is heated to; and

(iv) flowing one or more gaseous monomers, the one or more gaseous initiators,
5 and optionally one or more carrier gases into the reaction chamber to form the polymeric coating on at least a portion of a surface of the at least one substrate or material;

wherein the reaction chamber and/or components thereof are independently heated to a reaction chamber temperature, wherein the reaction chamber temperature is lower than the initiation temperature and the surface temperature during step (iv);

10 optionally wherein the components comprise walls of the reaction chamber;

wherein the partial pressure of the one or more gaseous monomers is sufficient to form the polymeric coating on the portion of the surface at the surface temperature;

wherein the one or more gaseous monomers comprise one or more silicon-containing monomers;

15 wherein the polymeric coating formed comprises silicon, nitrogen, hydrogen, and carbon; and wherein the polymeric coating comprises an atomic carbon content in a range of about 2 to 70% of the total atomic composition of the polymeric coating.

In some instances of the above method, the polymeric coating has a microscale conformality to the surface of at least about 60%, as determined by microtrench method.

20 In some instances, the surface temperature during step (iv) is sufficient to preclude the one or more gaseous monomers or the one or more gaseous initiators from exceeding their saturation pressure at the surface temperature.

For the non-isothermal SACVD methods, these differ over isothermal SACVD methods described above in that they can be used to minimize the activation of reactive
25 initiator and/or monomer species at sites that are distant from the substrate or material surface(s) to be coated. Accordingly, the opportunity for such activated species undesired diffusion of reactive species away from the substrate or material surface(s) resulting in creation of non-conformal, line-of-site coatings on the s surface(s) can be minimized or eliminated using non-isothermal SACVD methods. In addition to the parameters selected
30 for control of the isothermal SACVD process (detailed above), non-isothermal SACVD includes additional parameters for selection to provide for the necessary process conditions to form a conformal coating on a substrate or material. Non-isothermal

SACVD can have a greater risk of condensation of precursors (i.e., monomers) due to the lower temperature of portions of the reaction chamber versus that of the substrate or material (which is on a heated platform), and thermal control of the substrate or material is needed to provide for uniform heating thereof, such as in the case of thermally
5 insulating substrates. Parameters can be selected to minimize or eliminate any undesired non-uniform heating which can lead to deviations in polymer coating growth rates and loss of high degrees of coating conformality.

Under non-isothermal conditions, at least one substrate or device to be coated by a polymeric coating (or polymeric film) is placed within a reaction chamber. The at least
10 one substrate or device is placed on a temperature-controlled heating platform ("platform") which can independently heat the at least one substrate or material and surface(s) present thereon. The platform is configured to support one or more substrates or materials within a reaction chamber during coating and can independently heat the one or more substrates or materials in contact therewith. The platform optionally retains and
15 positions the one or more substrates or materials. In such methods, the reaction chamber is independently heat controlled from the platform. The platform is heated to an initiation temperature sufficient to activate one or more gaseous initiators. In such non-isothermal methods, heating to the initiation temperature also heats one or more surfaces of the substrate(s) or device(s) within the reaction chamber to allow for decomposition of the
20 one or more initiators and formation/ deposition of a polymeric coating on at least a portion of the one or more surfaces of the substrate(s) or material(s). In such methods, the reaction chamber and/or components thereof are independently heated to a temperature, referred to herein as the reaction chamber temperature, which is lower than the initiation temperature. To the extent that the reaction chamber and/or components
25 thereof vary in temperature, the reaction chamber temperature refers to the lowest temperature thereof. The reaction chamber components include the walls of the reaction chamber.

In some instances, for the SACVD methods described, the polymeric coating forms via vinyl polymerization and the one or more gaseous monomers include
30 monomers having at least one vinyl moiety thereon. In some instances, the vinyl polymerization is a free-radical vinyl polymerization. Exemplary monomers containing vinyl moieties are listed below.

Regarding step (iii) of the above methods, it is understood that the reactor chamber or platform are heated to an initiation temperature where heating is applied at some point prior to step (iv) to achieve the initiation temperature. In some instances, heating may be applied prior to steps (i) or (ii), or may be applied after step (ii) and prior to step (iv). The reactor or platform are at initiation temperature and the one or more surfaces of the at least one substrate or material which is a surface temperature that is equal to or substantially equal to the initiation temperature to which the reaction chamber or platform were heated to. During step (iv), the partial pressure of the one or more gaseous monomers is sufficient to form the polymeric coating on the portion of the surface at the surface temperature. Following step (iv), the polymeric coating formed on the one or more surfaces of the at least one substrate or material has a microscale conformality of at least about 60%, as determined by microtrench method. In some instances, the microscale conformality of the polymeric coating formed on the at least one substrate or material is at least about 65%, 70%, 75%, 80%, 90%, 95%, 96%, 97%, 98%, 99%, or 99.9%, as determined by the microtrench method. In still other instances, the microscale conformality of the polymeric coating formed on the at least one substrate or material is in a range of about 60%-90%, as determined by the microtrench method, as well as individual values and subranges contained therein.

For the methods described, during step (iv) the surface temperature, which is typically equal or substantially equal to the initiation temperature, precludes the one or more gaseous monomers or the one or more gaseous initiators from exceeding their respective saturation pressures at the surface temperature of the substrate or material during step (iv). In some instances, the temperature is sufficient to preclude the one or more gaseous monomers or the one or more gaseous initiators from reaching their respective saturation pressures at the surface temperature of the substrate or material during step (iv). In such instances, the reactor chamber, and components thereof (i.e., walls, etc.), can also have a surface temperature that precludes the one or more gaseous monomers or the one or more gaseous initiators from exceeding (or reaching) their respective saturation pressures at the surface temperature of the substrate or material during step (iv). By preventing the one or more gaseous monomers or the one or more gaseous initiators from exceeding (or reaching) their respective saturation pressures the

methods prevent or limit any condensation formation of the reactant gases during the polymerization.

In some instances of the methods, the initiation temperature is in a range from about 50 °C to about 400 °C, about 50 °C to about 300 °C, about 50 °C to about 200 °C, or about 50 °C to about 100 °C. In some instances, use of lower temperatures to produce initiation and formation of the polymeric coating/film is beneficial in reducing the thermal budget for semiconductor processing applications and allows for the SACVD methods to be used/integrated with materials and processes which are less tolerant or intolerant to high temperatures (such as above about 100 °C, 150 °C, 200 °C, or 250 °C or higher).

For the SACVD methods described the polymeric coatings formed have a specified atomic carbon content, expressed as a percentage. The atomic carbon content percentage represents the amount of carbon atoms in the polymeric coating or film, relative to all other atoms in the coating or film. The skilled person is familiar with various techniques which can be used to quantify the elemental composition of polymeric coatings or films, such as x-ray photoelectron spectroscopy (XPS), energy dispersive spectroscopy (EDS), mass spectrometry, and/or other suitable methods.

In some instances, the atomic carbon content in the polymeric coating or film is dependent on the atomic carbon content of the one or more gaseous monomers and/or one or more gaseous initiators. The atomic carbon content of a monomer or initiator can be determined by the following equation:

$$\text{Atomic Carbon Content (\%)} = \frac{N_{\text{carbon}}}{N_{\text{total}}} \times 100$$

where N_{carbon} is the total number of carbon atoms in a monomer or initiator molecule and N_{total} is the total number of atoms in the monomer or initiator molecule excluding all hydrogen atoms.

In some instances, the one or more gaseous monomers include carbon-containing monomers each independently have an atomic carbon content of at least about 25%, 30%, 35%, 40%, 45%, 50%, 55%, 60%, 65%, 70%, 75%, 80%, 85%, 90%, 95%, or 100% of the total atomic composition of the carbon-containing monomer; or in a range from about 25% to 100% of the total atomic composition of the carbon-containing

monomer. In some instances, the one or more gaseous initiators include carbon-containing initiators each independently have an atomic carbon content of at least about 20%, 25%, 30%, 35%, 40%, 45%, 50%, 55%, 60%, 65%, 70%, 75%, 80% of the total atomic composition of the carbon-containing initiator; or in a range from about 20% to 100% of the total atomic composition of the carbon-containing initiator. Accordingly, by selecting the monomers and/or initiators based on their atomic carbon content, a polymeric coating or film can be produced having an atomic carbon content within the specified range of about 2 to 80% of the total atomic composition of the polymeric coating/film. For instance, if a polymeric coating having a higher atomic carbon content is desired, monomers and/or initiators with higher atomic carbon contents, such as in the range of about 30% to 50%, can be selected to flow into the reaction chamber. By contrast, if a polymeric coating having a lower atomic carbon content is desired, monomers and/or initiators with lower atomic carbon contents, such as in the range of about 20% to 25%, can be selected to flow into the reaction chamber.

In some instances, the atomic carbon content of the polymeric coating is in the range of about 2 to 5%, 2 to 10%, 2 to 15%, 2 to 20%, 2 to 30%, 2 to 40%, 2 to 50%, 2 to 60%, or 2 to 70% of the total atomic composition of the polymeric coating, as well as individual values and sub-ranges disclosed within the aforementioned ranges. In some other instances, the atomic carbon content of the polymeric coating is in the range of about 5 to 70%, 5 to 65%, 5 to 60%, 5 to 55%, or 5 to 50% of the total atomic composition of the polymeric coating, as well as individual values and sub-ranges disclosed within the aforementioned ranges. In still other instances, the atomic carbon content of the polymeric coating is in the range of about 10 to 70%, 10 to 60%, 10 to 50%, or 10 to 40% of the total atomic composition of the polymeric coating, as well as individual values and sub-ranges disclosed within the aforementioned ranges. In yet other instances, the atomic carbon content of the polymeric coating is in the range of about 15 to 70%, 15 to 60%, 15 to 50%, or 15 to 40% of the total atomic composition of the polymeric coating, as well as individual values and sub-ranges disclosed within the aforementioned ranges. In certain instances, the atomic carbon content of the polymeric coating is in the range of about 2 to 15% of the total atomic composition of the polymeric coating, as well as individual values and sub-ranges disclosed within the aforementioned ranges.

For the isothermal methods described herein, there may be a time period between steps (i) and (iii), and up to step (iv), which is dwell time during which the temperature of the surface of the substrate increases to the surface temperature, and wherein the dwell time is at least about 1, 2, 3, 4, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, or 60 minutes.

- 5 Heating may be carried out for any suitable period of time during the dwell time which is sufficient to cause the one or more surfaces of the substrate(s) or device(s), in the first method, or of the reactor, in the second method, to be equal or substantially equal to the selected initiation temperature. “Substantially equal” as used herein with respect to the initiation temperature, refers to a surface temperature that is about $\pm 10\%$, $\pm 9\%$, $\pm 8\%$,
10 $\pm 7\%$, $\pm 6\%$, $\pm 5\%$, $\pm 4\%$, $\pm 3\%$, $\pm 2\%$, or $\pm 1\%$ of the selected initiation temperature. In some instances, the heating may be applied for at least about 1 to 90 minutes, or any sub-ranges or individual value of minutes disclosed within to cause the one or more surfaces of the substrate(s) or device(s) to reach the desired initiation temperature.

- The flowing step may be carried out for any suitable period of time sufficient to
15 form/deposit a polymeric film having one or more desired properties, such as thickness. In some instances, the flowing step may be carried out for at least about 1 to 800 minutes or 30 to 800 minutes, as well as any sub-ranges or individual value of minutes disclosed within these ranges.

- In some instances, following formation/deposition of the polymeric coating
20 during the flowing step, the reaction chamber or reactor of the above methods is purged and allowed to cool to room temperature (about 25 °C) followed by venting of the reaction chamber or reactor.

- Each of the gaseous monomers, gaseous initiators, and optional carrier gases may flow continuously or non-continuously during the flowing step of the methods described.
25 In certain instances, the polymeric coating is formed either continuously or semi-continuously during the flowing step, depending on the selected parameters controlling the flow of monomer(s) and initiator(s) during that step. “Semi-continuously,” as used herein, refers to a method where formation of the polymeric coating occurs continuously for only some portion of step (iv), which includes portion(s) where there is no deposition
30 of the polymeric coating. In instances, where flow of any of the gaseous monomers, gaseous initiators, and optional carrier gases is non-continuous during the flowing step, these may be independently controlled by flow controllers and metering valves, where

the flow times, stop times, number of on/off cycles, and other parameters (such as pressure) during the flowing step of each gaseous component may be independently selected, as needed, to produce a desired polymeric coating.

For the methods described, the flowing step (iv) may be repeated more than once
5 with the same or different compositions of gaseous monomers, gaseous initiators, and optional carrier gases. When different monomers are used in repetitions of the flowing step, the polymeric coating includes a plurality of polymeric layers. Accordingly, in some cases, where the polymeric coating is formed of more than one layer, the polymeric coating includes at least one layer formed of a polymer which differs from the polymer
10 forming another/different layer.

In some instances, the polymeric coating formed contains one or more polymers, copolymers, and/or two or more cross-linked polymers by flowing at least two different types of gaseous monomers during the flowing step, and one or more gaseous crosslinkers are also optionally flowed during the same step, when forming cross-linked
15 polymers.

In some instances of the methods, step (iv) is repeated one or more times with the same or different types of the one or more gaseous monomers and/or the one or more gaseous initiators to form a polymeric coating including a plurality of layers, where the method further includes changing the initiation temperature when a different type of
20 gaseous initiator is used. For example, after forming a polymeric coating with a first monomer and a first initiator, a second polymeric coating may be formed using a second monomer and a second initiator where the initiation temperature is changed when the first and second initiator are different and have different initiation temperatures to cause their activation.

25 It is understood that the methods described herein can be used to deposit more than one polymeric coating onto a substrate or material. For example, first and second polymeric coatings can be formed on a substrate or material where the first and second polymeric coatings are in contact or are not in contact. In other words, the first and second polymeric coatings may be separated by another layer or material. The
30 compositions and thicknesses of the first and second polymeric coatings are independent of each other and are based on the conditions used for their formation. It is further understood that more than two polymeric coatings are possible. Accordingly, the

plurality of polymeric coatings, as may be present, can have the same or different thicknesses.

In some instances, the initiation temperature is selected to provide a deposition rate of the polymer(s) to form the polymeric coating at least 0.5 nm/min.

- 5 In certain instances, conditions within the reaction chamber/reactor are selected to provide a defect free or substantially defect free polymeric coating. To provide a defect free or substantially defect free polymeric coating, conditions in the reaction chamber/reactor are selected to prevent formation of defects in the polymeric coating at least during formation, where defects can include bubbling, blistering, pin holes, cracks, 10 or particles. "Substantially defect free," as used herein refers to the presence of a low number of defects in a polymeric coating, where at least 95%, 96%, 97%, 98%, 99%, or greater of the polymeric coating is free of defects, as determined by a suitable means of visualization, such as scanning electron microscopy (SEM). In some instances, defects can be avoided when the partial pressure of any single gaseous component does not 15 exceed its saturation pressure on the substrate or material to be coated. If the saturation pressure is exceeded for any gaseous component, then a liquid film of that respective component may form over a given surface which can produce blisters, if initiation occurs at the surface. Additionally, the presence of a liquid film anywhere in the CVD chamber can give rise to the formation of particles that can spread throughout the chamber can 20 create coating defects. Accordingly, SACVD deposition methods should avoid conditions where deposition may be performed on a liquid surface, such that the thermodynamics of the SACVD process should be controlled to prevent any conditions that lead to undesirable liquid formation during the deposition process. As a non-limiting example, discussed below is an example of a process using a single monomer, 25 initiator, and carrier gas.

In some instances, the SACVD deposition of the methods described are operated such that the following conditions are satisfied simultaneously:

$$P_{monomer} < P_{monomersat}$$

$$P_{initiator} < P_{initiatorsat}$$

$$P_{carriergas} < P_{carriergassat}$$

where the partial pressures are related to the total pressures and flowrates through the following relationships:

$$P_{total} = P_{monomer} + P_{initiator} + P_{carriergas}$$

$$P_{monomer} = P_{total} \times \frac{Flowrate_{monomer}}{Flowrate_{monomer} + Flowrate_{initiator} + Flowrate_{carriergas}}$$

$$P_{initiator} = P_{total} \times \frac{Flowrate_{initiator}}{Flowrate_{monomer} + Flowrate_{initiator} + Flowrate_{carriergas}}$$

$$P_{carriergas} = P_{total} \times \frac{Flowrate_{carriergas}}{Flowrate_{monomer} + Flowrate_{initiator} + Flowrate_{carriergas}}$$

- 5 Thus, the saturation pressures of each gaseous component can be approximated using several art known methods. Process conditions can be selected that allow for coating deposition while avoiding saturation. For instance, parameters which can be controlled include: reaction chamber temperature, total pressure, individual gaseous species partial pressure(s), gas residence time, temperature of precursors (such as if liquids), heat
- 10 tolerance of the substrate or device to the required initiation temperature, and/or spacing of components of the substrate or device within the chamber. Selection of each criteria can be made in order to avoid polymeric coating outcomes with reduced degree of conformality resulting from diffusion of reactive monomer species away from heated surface(s) of the substrate or device to be coated, condensation of reactants (i.e., gaseous
- 15 monomers and/or initiators), an inability to achieve desired reactant ratios due to high chamber pressure, deposition rates which are not sufficient for effective formation of a conformal polymeric coating due to, for instance, low chamber pressure or high surface

temperature, and/or a lack of polymeric coating uniformity due to consumption of the reactants before encountering at least a portion of the substrate's surface to be coated.

In certain instances, the one or more surfaces of the substrate(s) or material(s) in the first method, or of the reactor, in the second method, can be treated prior to the first step, where the treatment is silane deposition, electron beam, IR radiation, gamma radiation, plasma exposure, thermal treatment, laser exposure, or a combination thereof. In certain instances, following formation/deposition of the polymeric coating a treatment, such as electron beam, IR radiation, gamma radiation, plasma exposure, thermal treatment, laser exposure, or a combination thereof, is applied.

1. Optional Annealing Step

In some instances, where an annealing step is performed, a treatment, such as electron beam, IR radiation, gamma radiation, ultraviolet exposure, ozone exposure, gamma exposure, plasma exposure, thermal treatment, laser exposure, or a combination thereof, is applied to the polymeric coating before starting the annealing.

In some instances of the SACVD methods described, the methods may further include an annealing step. The annealing step can be applied during the flowing step, i.e. while the polymeric coating is forming. Or, the annealing step can occur after the flowing step (i.e., following formation of the polymeric coating). In some instances, where the annealing step occurs after the flowing step, the method may include the step of transferring the substrate or material that contains the polymeric coating into another chamber to perform the annealing process, which can be achieved, for example, using cluster tool technology or with a load-locked system. This second chamber may be temperature controlled to maintain the second chamber at the annealing temperature.

In some instances, the annealing step occurs at a temperature ranging from about 200 °C to 800 °C, 200 °C to 750 °C, 200 °C to 700 °C, 200 °C to 650 °C, 200 °C to 600 °C, 200 °C to 550 °C, 200 °C to 500 °C, 200 °C to 450 °C, 200 °C to 400 °C, 200 °C to 350 °C, or 200 °C to 250 °C, as well as individual values or sub-ranges contained within the aforementioned ranges.

When the annealing step occurs during the flowing step (step (iv)). In these instances, the polymeric coating is forming during the annealing step, thus the annealing temperature is also the initiation temperature. The initiation temperature is optionally a

high temperature, and is in the range of about 250 °C to 400 °C, as well as individual values or sub-ranges contained within the aforementioned range.

In some instances, the annealing step is carried out under a suitable process gas, such as nitrogen, argon, ammonia, hydrogen, a syn gas, or a combination thereof. In

5 some instances, the process gas is free or substantially free of oxygen (O₂) gas. “Substantially free of oxygen gas,” as used herein, refers to a process gas having less than 3%, 2%, 1%, 0.5%, or 0.1% of oxygen gas (v/v%) based on the total volume of the process gas. In some other instances, the process gas includes oxygen gas or air.

10 In some instances, the annealing step occurs for about 5 minutes to about 3 hours, or individual time values or sub-ranges of times contained within the aforementioned time range.

In some instances, following the annealing step, the polymeric coating or film is denser compared to prior to the annealing step. In such instances, the mass of the polymeric coating will not decrease substantially, but the volume of the polymeric
15 coating will, usually presenting as a decrease in coating thickness with substantially no mass loss. Standard methodologies for measuring thin film thickness and mass can be utilized to confirm the densification.

In some instances, the annealing step produces a loss in mass of the polymeric coating, such that the mass of the polymeric coating is about 80%, 75%, 70%, 65%,
20 60%, 55%, 50%, 45%, 40%, 35%, 30%, 25%, 20%, 15%, 10%, 5%, 1%, or less of the mass of the polymeric coating formed in step (iv). Mass loss versus temperature can be examined by various methods, such as differential scanning calorimetry (DSC) or thermogravimetric analysis (TGA).

In some instances, mass loss is primarily of the organic (carbon) content of the
25 film. In such instances, following the annealing step, the atomic carbon content of the polymeric coating is in the range of about 2 to 5%, 2 to 10%, 2 to 15%, 2 to 20%, 2 to 30%, 2 to 40%, 2 to 50%, 2 to 60%, or 2 to 70% of the total atomic composition of the polymeric coating, as well as individual values and sub-ranges disclosed within the aforementioned ranges. In some other instances, following the annealing step, the atomic
30 carbon content of the polymeric coating is in the range of about 5 to 70%, 5 to 65%, 5 to 60%, 5 to 55%, or 5 to 50% of the total atomic composition of the polymeric coating, as well as individual values and sub-ranges disclosed within the aforementioned ranges. In

still other instances, following the annealing step, the atomic carbon content of the polymeric coating is in the range of between about 10 to 70%, 10 to 60%, 10 to 50%, or 10 to 40% of the total atomic composition of the polymeric coating, as well as individual values and sub-ranges disclosed within the aforementioned ranges. In yet other instances, following the annealing step, the atomic carbon content of the polymeric coating is in the range of about 15 to 70%, 15 to 60%, or 15 to 40% of the total atomic composition of the polymeric coating, as well as individual values and sub-ranges disclosed within the aforementioned ranges. In certain instances, following the annealing step the atomic carbon content of the polymeric coating is in the range of about 2 to 15% of the total atomic composition of the polymeric coating, as well as individual values and sub-ranges disclosed within the aforementioned ranges.

In some instances, the atomic hydrogen content of a polymeric coating can be in a range of about 0.1% to 60% of the total atomic composition of the polymeric coating. The atomic hydrogen content of a polymeric coating can be reduced, as needed, by annealing the coating to produce a polymeric coating having a desired atomic hydrogen content. As discussed below, the atomic hydrogen content in a polymeric coating can impact the properties of the polymeric coating, such as the dielectric constant and its ability to act as a barrier to metal migration.

B. General SACVD Parameters

For the SACVD methods described above, the following parameters are generally applicable to the methods described.

The SACVD methods described herein may include the use of heating with hot filaments, resistance heating, induction heating, radiant heating, electron beam, laser exposure, radiofrequency (RF), microwave excitation, ultraviolet (UV), infrared (IR) radiation, and/or gamma radiation to initiate or cause decomposition of the one or more gaseous initiators or gaseous monomers.

a. Gaseous Monomers

The polymeric coatings can be formed using a variety of different gaseous monomer(s) which form gaseous polymerizable species, when initiated by a suitable radical or ionic species, and deposit to form a polymeric coating on a surface(s). As explained above, the monomers can be selected based on their carbon content.

Without particular limitation, the one or more gaseous monomers can be a(n) acrylate monomer, methacrylate monomer, vinyl-containing monomer, paracyclophane monomer, oxirane-based monomer, or a combination thereof.

In certain instances, the acrylate monomers are hydroxyethyl acrylate, ethylene glycol diacrylate, 1H,1H,2H,2H-perfluorodecyl acrylate, or a combination thereof. In certain instances, the methacrylate monomers are hydroxyethyl methacrylate, ethylene glycol dimethacrylate, 1H,1H,2H,2H-perfluorodecyl methacrylate, or a combination thereof.

In certain instances, the vinyl containing monomers are 1,3,5-trivinyl-1,3,5-trimethylcyclotrisiloxane, divinylbenzene, 4-vinylpyridine, styrene, 1H,1H,2H-perfluoro-1-dodecene, di(ethylene glycol) divinyl ether, or a combination thereof.

In certain instances, the paracyclophane monomers are [2,2]paracyclophane, dichloro-[2,2]-paracyclophane, 1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane, or 4,5,7,8,12,13,15,16-octafluoro[2.2]paracyclophane.

In certain instances, the oxirane-based monomer is hexafluoropropylene oxide.

b. Gaseous Initiators

The polymeric coatings can be formed using a variety of different gaseous initiator(s) which can be thermally decomposed to produce reactive species that initiates polymerization of the gaseous monomer(s). As explained above, the initiators can be selected based on their carbon content.

In some instances, gaseous initiator(s) may include one or more groups which are capable of generating free radicals under the reaction conditions. Such free radicals may be capable of reacting with monomers to form growing polymer chains. Initiators are capable of thermally decomposing to form one or more molecules having free radicals. In certain cases, initiators may include functional groups which are capable of forming radicals under the experimental conditions (e.g., by decomposing). Non-limiting examples of suitable functional groups include peroxide groups, persulfate groups, and azo groups. In still other instances, initiator(s) may include one or more groups which are capable of generating ions under the experimental conditions.

For the gaseous initiators, the SACVD methods involve selecting an appropriate initiation temperature based on the particular initiator(s) used in a given deposition. The initiation temperature is a temperature at which a sufficient amount of the gaseous

initiator(s) decompose and are able to initiate, for example, a free radical or ionic polymerization of the gaseous monomer(s) present during the flowing step of the SACVD methods described. In some instances, the initiation temperature can range from about 50 °C to about 400 °C, as well as sub-ranges or individual temperature values disclosed within. In some other instances, the initiation temperature ranges from about 100 °C to about 250 °C, as well as sub-ranges or individual temperature values disclosed within. In still other instances, the initiation temperature ranges from about 50 °C to about 150 °C, as well as sub-ranges or individual temperature values disclosed within.

In some instances of the SACVD methods, the one or more gaseous initiators can be selected from peroxide-based initiators, persulfate-based initiators, sulfate-based initiators, azonitrile-based initiators, and/or ionic (i.e. cationic or anionic) thermal-based initiators.

In some instances, the peroxide-based initiators are selected from tert-butyl hydroperoxide, cumene hydroperoxide, tert-amyl hydroperoxide, p-menthane hydroperoxide, di-tert-butyl peroxide, tert-butylperoxybenzoate, dicumyl peroxide, benzoyl peroxide, 1,1-bis(tert-butylperoxy)cyclohexane, 1,1-di(tert-amylperoxy)cyclohexane, 1,1-di(tert-butylperoxy)-3,3,5-trimethylcyclohexane, tert-butyl peracetate, tert-butyl peroxy-pivalate, tert-amylperoxy-pivalate, hydrogen peroxide, di(4-tert-butylcyclohexyl)peroxydicarbonate, 2,2-di(tert-butylperoxy)butane, dicetylperoxydicarbonate, di(2-ethylhexyl)peroxydicarbonate, acetylacetone peroxide, methyl ethyl ketone peroxide, methyl isobutyl ketone peroxide, tert-amylperoxy-2-ethylhexylcarbonate, tert-butylperoxy-2-ethylhexylcarbonate, 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane, 2,5-dimethyl-2,5-di(tert-butylperoxy)hexyne-3, di(2,4-dichlorobenzoyl)peroxide, di(3,5,5-trimethylhexanoyl)peroxide, tert-butylperoxy-3,5,5-trimethylhexanoate, dilauroyl peroxide, dimyristylperoxydicarbonate, tert-butylperoxy-2-ethylhexanoate, tert-butylperoxy-2-ethylhexylcarbonate, tert-butylperoxyneodecanoate, disuccinoylperoxide, tert-butyl-peroxy-isobutyrate, 1,1,3,3-Tetramethylbutylperoxy neodecanoate and combinations thereof.

In some instances, the persulfate-based initiators are selected from ammonium persulfate, potassium persulfate, sodium persulfate, and combinations thereof. In some instances, the sulfate-based initiator is potassium peroxymonosulfate.

In some instances, the azonitrile-based initiators are selected from 2,2'-azobis(isobutyronitrile), 2,2'-azobis(2-methylbutyronitrile), 2,2'-azobis(2,4-dimethylvaleronitrile), 2,2'-azobis[2-(2-imidazolin-2-yl)propane], 2,2'-azobis[2-(2-imidazolin-2-yl)-propane] dihydrochloride, 2,2'-azobis(2-methylpropionamidine) dihydrochloride, 2,2'-azobis(N-(2-hydroxyethyl)-2-methylpropionamide), 4,4'-azobis(4-cyanovaleric acid), 2,2'-azobis[N-(2-carboxyethyl)-2-methylpropionamidine]tetrahydrate, dimethyl 2,2'-azobis(2-methylpropionate), 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile), 1,1'-azobis(cyclohexane-1-carbonitrile), 2,2'-azobis(N-butyl-2-methylpropionamide), 2,2'-azobis(2,4,4-trimethylpentane), and combinations thereof.

In some instances, the ionic thermal-based initiators are selected from dicyandiamide, cyclohexyl tosylate, (4-hydroxyphenyl)-dimethylsulfonium hexafluorophosphate, diphenyl(methyl)sulfonium tetrafluoroborate, benzyl(4-hydroxyphenyl)-methylsulfonium hexafluoroantimonate, (4-hydroxyphenyl)methyl-(2-methylbenzyl)sulfonium hexafluoroantimonate, triphenylsulphonium nonaflate, and combinations thereof.

In still other instances, a gaseous initiator can be selected from compounds of Formula I:

A—X—B (Formula I)

wherein, independently for each occurrence, A is hydrogen, alkyl, cycloalkyl, aryl, heteroaryl, aralkyl or heteroaralkyl; X is —O—O— or —N=N—; and B is hydrogen, alkyl, cycloalkyl, aryl, heteroaryl, aralkyl or heteroaralkyl.

In certain instances, the initiator is a compound of formula I, wherein A is alkyl.

In certain instances, the initiator is a compound of formula I, wherein A is hydrogen.

In certain instances, the initiator is a compound of formula I, wherein B is alkyl.

In certain instances, the initiator is a compound of formula I, wherein X is —O—O—

In certain instances, the initiator is a compound of formula I, wherein X is —N=N—

In certain instances, the initiator is a compound of formula I, wherein A is $-\text{C}(\text{CH}_3)_3$; and B is $-\text{C}(\text{CH}_3)_3$. In certain instances, the gaseous initiator of the invention is a compound of formula I, wherein A is $-\text{C}(\text{CH}_3)_3$; X is $-\text{O}-\text{O}-$; and B is $-\text{C}(\text{CH}_3)_3$.

The initiators described above are capable of being in a gas state. Note that a
5 "gaseous" initiator encompasses initiators which may be liquids or solids at standard temperature and pressure (STP), but upon heating may be vaporized and flowed into a reaction chamber.

c. Silicon-containing Monomers

In some instances, the atomic carbon content in the polymeric coating or film is
10 also dependent on the atomic carbon content of the one or more silicon-containing monomers. The atomic carbon content of a silicon-containing monomer can be determined by the following equation:

$$\text{Atomic Carbon Content (\%)} = \frac{N_{\text{carbon}}}{N_{\text{total}}} \times 100$$

15

where N_{carbon} is the total number of carbon atoms in a silicon-containing monomer and N_{total} is the total number of atoms in the silicon-containing monomer molecule excluding all hydrogen atoms.

In some instances, the silicon-containing monomers each independently have an
20 atomic carbon content of at least about 25%, 30%, 35%, 40%, 45%, 50%, 55%, 60%, 65%, 70%, 75%, 80%, 85% or 90% of the total atomic composition of the silicon-containing monomer; or in a range from about 25% to 90% of the total atomic composition of the silicon-containing monomer, as well as individual values or sub-ranges contained within the aforementioned range. Accordingly, silicon-containing
25 monomers (which may be in combination with other monomers/initiators, as discussed above) can be selected based on their carbon content to form a polymeric coating having an atomic carbon content in the specified range of about 2 to 70% of the total atomic composition of the polymeric coating/film.

In some instances, the concentration of the one or more silicon-containing
30 monomers in the one or more gaseous monomers is at least about 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90, or 95 v/v% of the total composition of the one or more gaseous monomers used in the method. In some instances, the concentration of the one

or more silicon-containing monomers in the one or more gaseous monomers is in a range from about 10 to 95 v/v% of the total composition of the one or more gaseous monomers used in the method, as well as individual values or sub-ranges contained within the aforementioned range.

5 In some instances, where the polymeric coating includes silicon, oxygen, hydrogen, and carbon, suitable silicon-containing monomers include, but are not limited to, 1,3,5-trivinyl-1,3,5-trimethylcyclotrisiloxane, 1,3,5,7-tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane, pentavinylpentamethylcyclopentasiloxane, 1,3-divinyltetramethyldisiloxane, divinyl dimethylsilane, 1,4-divinyltetramethyldisilylethane, 1,5-divinyl-3,3-diphenyl-1,1,5,5-tetramethyltrisiloxane, 1,3-divinyl-1,3-diphenyl-1,3-dimethyldisiloxane, 1,5-divinyl-3-phenylpentamethyltrisiloxane, 1,5-divinylhexamethyltrisiloxane, 1,2-divinyltetramethyldisilane, 1,3,5-trivinyl-1,1,3,5,5-pentamethyltrisiloxane, trivinylsilane, trivinylmethylsilane, tetravinylsilane, and combinations thereof.

15 In some instances, where the polymeric coating includes silicon, nitrogen, hydrogen, and carbon, suitable silicon-containing monomers include, but are not limited to, bis(dimethylamino)vinylmethysilane, 1,3-divinyl-1,1,3,3-tetramethyldisilazane, 1,3,5-trivinyl-1,3,5-trimethylcyclotrisilazane, 1,3,5,7-tetravinyl-1,3,5,7-tetramethylcyclotetrasilazane, 3-(n-styrylmethyl-2-
20 aminoethylamino)propyltrimethoxysilane, styrylmethoxy(polyethyleneoxide), and combinations thereof.

In some instances, the one or more silicon-containing monomers are selected from the group consisting of 1,3,5-trivinyl-1,3,5-trimethylcyclotrisiloxane, 1,3,5,7-tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane, pentavinylpentamethylcyclopentasiloxane, 1,3-divinyltetramethyldisiloxane, divinyl dimethylsilane, 1,4-divinyltetramethyl-diisylethane, 1,5-divinyl-3,3-diphenyl-1,1,5,5-tetramethyltrisiloxane, 1,3-divinyl-1,3-diphenyl-1,3-dimethyldisiloxane, 1,5-divinyl-3-phenylpentamethyltrisiloxane, 1,5-divinylhexamethyltrisiloxane, 1,2-divinyltetramethyldisilane, 1,3,5-trivinyl-1,1,3,5,5-pentamethyltrisiloxane, trivinylsilane, trivinylmethylsilane, tetravinylsilane, vinylpentamethylcyclotrisiloxane, 1,4-bis(vinyl dimethylsilyl)benzene, vinylphenyldimethylsilane, vinylsilatrane,

vinylpentamethyldisiloxane, vinyl-1,1,3,3-tetramethyldisiloxane, hexavinylsiloxane, p-(t-butyltrimethylsiloxy)styrene, and combinations thereof.

In some instances, the one or more silicon-containing monomers are selected from the group consisting of bis(dimethylamino)vinylmethylsilane, 1,3-divinyl-1,1,3,3-tetramethyldisilazane, 1,3,5-trivinyl-1,3,5-trimethylcyclotrisilazane, 1,3,5,7-tetravinyl-1,3,5,7-tetramethylcyclotetrasilazane, 3-(n-styrylmethyl-2-aminoethylamino)propyltrimethoxysilane, styrylmethoxy(polyethyleneoxide), and combinations thereof.

In some instances, for some of the aforementioned silicon-containing monomers, condensation reactions between repeat units in adjacent polymeric chains may be possible subsequent to deposition of the coating. These reactions, driven by thermal or other means, can serve to form new Si-O-Si or Si-N-Si moieties within the deposited polymeric coating/film and decrease overall carbon and hydrogen content.

d. SACVD Reactant Pressures and Optional Carrier Gases

For the SACVD methods described herein, the polymeric coating may be formed under any suitable total pressure in the reaction chamber or reactor. The SACVD systems described herein include systems and components for controlling and regulating the desired partial and total pressures of each of the monomers, initiators, and optional carrier gases used in the methods. In some instances, the total pressure of all gaseous components during the flowing step ranges from about 1 to 200,000 mTorr, as well as individual values or sub-ranges contained within the aforementioned range. In some instances, the total pressure of all gaseous components during the flowing step ranges from about 1 to 760,000 mTorr, as well as individual values or sub-ranges contained within the aforementioned range. Selection of partial pressures can be made to prevent condensation of any reactant species at all surface temperatures present within the reaction chamber while maximizing the adsorption of such species to allow for polymerization reactions and polymeric coating growth to proceed.

In some other instances, the total pressure of all gaseous components during the flowing step ranges from about 100 mTorr to 10 Torr. In still other instances, the total pressure of all of the gaseous components (e.g., monomer(s), initiator(s), inert gas(es)) present during polymerization in the flowing step of the methods may fall within a specified range. In some instances, the total pressure of all gaseous components present during polymerization is greater than or equal to 10 mTorr, greater than or equal to 25

mTorr, greater than or equal to 50 mTorr, greater than or equal to 75 mTorr, greater than or equal to 100 mTorr, greater than or equal to 200 mTorr, greater than or equal to 300 mTorr, greater than or equal to 400 mTorr, greater than or equal to 500 mTorr, greater than or equal to 750 mTorr, greater than or equal to 1000 mTorr, or greater than or equal to 2500 mTorr. In certain embodiments, the total pressure of all gaseous components present during polymerization is less than or equal to 5000 mTorr, less than or equal to 2500 mTorr, less than or equal to 1000 mTorr, less than or equal to 750 mTorr, less than or equal to 500 mTorr, less than or equal to 400 mTorr, less than or equal to 300 mTorr, less than or equal to 200 mTorr, less than or equal to 100 mTorr, less than or equal to 75 mTorr, less than or equal to 50 mTorr, or less than or equal to 25 mTorr. Combinations of the above-referenced ranges are also possible (e.g., greater than or equal to 50 mTorr and less than or equal to 5000 mTorr, greater than or equal to 50 mTorr and less than or equal to 300 mTorr, greater than or equal to 50 mTorr and less than or equal to 200 mTorr, greater than or equal to 75 mTorr and less than or equal to 200 mTorr, or greater than or equal to 75 mTorr and less than or equal to 100 mTorr). In some embodiments, the total pressure of all gaseous components present during polymerization may be atmospheric pressure, or higher.

Polymerization occurs under conditions including the presence of one or more gaseous monomers, which may be present at any suitable partial pressure. In some instances, any of the one or more monomers may be at a partial pressure of less than or equal to 300 mTorr, 200 mTorr, 100 mTorr, 75 mTorr, less than or equal to 50 mTorr, less than or equal to 30 mTorr, less than or equal to 20 mTorr, less than or equal to 15 mTorr, less than or equal to 10 mTorr, less than or equal to 5 mTorr, or less than or equal to 3 mTorr. In some instances, the partial pressure is less than 50 mTorr. In some instances, the partial pressure is about 5 mTorr. In certain instances, any of the one or more monomers may be at a partial pressure of greater than or equal to 1 mTorr, greater than or equal to 5 mTorr, greater than or equal to 10 mTorr, or greater than or equal to 20 mTorr. Combinations of the above-referenced ranges are also possible (e.g., greater than or equal to 3 mTorr and less than or equal to 50 mTorr, greater than or equal to 1 mTorr and less than or equal to 50 mTorr, greater than or equal to 1 mTorr and less than or equal to 20 mTorr, greater than or equal to 3 mTorr and less than or equal to 10 mTorr).

The polymerization of the one or more monomers occurs in the presence of one or more gaseous initiators. Gaseous initiators which contain free radical generating groups or which are capable of undergoing a reaction to form free radical species are preferred. The gaseous initiator(s) may be present at any suitable partial pressure. In some embodiments, the initiator(s) may be at a partial pressure of less than or equal to 300mTorr, 200mTorr, 100mTorr, 75 mTorr, less than or equal to 50 mTorr, less than or equal to 30 mTorr, less than or equal to 20 mTorr, less than or equal to 15 mTorr, less than or equal to 10 mTorr, less than or equal to 5 mTorr, or less than or equal to 3 mTorr. In certain instances, the gaseous initiator(s) may be at a partial pressure of greater than or equal to 1 mTorr, greater than or equal to 5 mTorr, greater than or equal to 10 mTorr, or greater than or equal to 20 mTorr. In some embodiments, the partial pressure of the monomer is less than about 75 mTorr. In some embodiments, the partial pressure of the initiator is about 7.5 mTorr. Combinations of the above-referenced ranges are also possible (e.g., greater than or equal to 1 mTorr and less than or equal to 75 mTorr, or greater than or equal to 1 mTorr and less than or equal to 50 mTorr, greater than or equal to 1 mTorr and less than or equal to 20 mTorr, greater than or equal to 1 mTorr and less than or equal to 10 mTorr, greater than or equal to 5 mTorr and less than or equal to 10 mTorr). In instances where the SACVD method is carried out at lower temperatures (i.e., less than about 300 °C, 200 °C, or 100 °C), more labile initiators may be selected, such as peroxide-based initiators. Further, under such low temperature conditions, the partial pressure of the one or more initiators can be increased to offset low conversion rates.

The one or more gaseous monomers and one or more gaseous initiator may be provided in any suitable ratio. In some instances, the ratio may be based on the partial pressures of the one or more gaseous monomer(s) to the one or more gaseous initiator(s) present during the flowing step of the SACVD methods described. The ratio of the partial pressure of the one or more gaseous initiator(s) to the partial pressure of the one or more gaseous monomer(s), defined as the partial pressure of the one or more gaseous initiator(s) divided by the partial pressure of the one or more gaseous monomer(s) present, may be any suitable value. In certain instances, the ratio of the partial pressure of the initiators to the partial pressure of the monomers may be greater than or equal to 0.1, greater than or equal to 0.2, greater than or equal to 0.5, greater than or equal to 0.8, greater than or equal to 1, greater than or equal to 2, greater than or equal to 5, or greater

than or equal to 8. In some instances, the ratio of the partial pressure of the one or more gaseous initiator(s) to the partial pressure of the one or more gaseous monomer(s) may be less than or equal to 10, less than or equal to 8, less than or equal to 5, less than or equal to 2, less than or equal to 1, less than or equal to 0.8, less than or equal to 0.5, or
5 less than or equal to 0.2. Combinations of the above-referenced ranges are also possible (e.g., greater than or equal to 0.1 and less than or equal to 10).

In some instances (e.g., during the deposition of a polymeric coating), a reaction chamber or reactor may include a relatively high amount of monomers and/or of precursors to monomers. In some instances, monomers and/or precursors to monomers
10 make up greater than or equal to 1 mol%, greater than or equal to 2 mol%, greater than or equal to 5 mol%, greater than or equal to 7.5 mol%, greater than or equal to 10 mol%, greater than or equal to 15 mol%, greater than or equal to 20 mol%, greater than or equal to 30 mol%, greater than or equal to 40 mol%, greater than or equal to 50 mol%, or greater than or equal to 75 mol% of the gases in the reaction volume. In some instances,
15 monomers and/or precursors to monomers make up less than or equal to 100 mol%, less than or equal to 75 mol%, less than or equal to 50 mol%, less than or equal to 40 mol%, less than or equal to 30 mol%, less than or equal to 20 mol%, less than or equal to 15 mol%, less than or equal to 10 mol%, less than or equal to 7.5 mol%, less than or equal to 5 mol%, or less than or equal to 2 mol% of the gases in the reaction volume.
20 Combinations of the above-referenced ranges are also possible (e.g., greater than or equal to 1 mol% and less than or equal to 100 mol%).

Polymerization may optionally occur in the presence of one or more inert gases which do not participate in the polymerization process. In some cases, such gases may be called carrier gases. Carrier gases are typically inert gases. In some instances, one type of
25 inert gas, two types of inert gases, three types of inert gases, or more, may be present during polymerization in the flowing step of the SACVD methods. Non-limiting examples of inert gases include nitrogen, helium, and argon. The inert gases may contribute any suitable percentage of the total pressure during polymerization. Total pressure during polymerization may be defined as the sum of the partial pressures of the
30 gaseous monomer(s), gaseous initiator(s), and inert gas(es) present during polymerization. In some instances, the inert gas(es) comprise greater than or equal to 50% of the total pressure, greater than or equal to 60% of the total pressure, greater than

or equal to 70% of the total pressure, greater than or equal to 80% of the total pressure, greater than or equal to 90% of the total pressure, or greater than or equal to 95% of the total pressure. In certain embodiments, the inert gas(es) comprise less than or equal to 98% of the total pressure, less than or equal to 95% of the total pressure, less than or equal to 90% of the total pressure, less than or equal to 80% of the total pressure, less than or equal to 70% of the total pressure, or less than or equal to 60% of the total pressure. Combinations of the above-referenced ranges are also possible (e.g., greater than or equal to 50% of the total pressure and less than or equal to 90% of the total pressure, greater than or equal to 70% of the total pressure and less than or equal to 90% of the total pressure, or greater than or equal to 80% of the total pressure and less than or equal to 90% of the total pressure).

The one or more monomer(s), initiator(s), and optional carrier or inert gas(es) are typically flowed into the reaction chamber or reactor to produce polymerization of the monomers and cause the deposition of a polymeric coating on one or more surface(s) which are at an appropriate initiation temperature. In some instances, the residence time of a given gaseous species may be defined as the total amount of time that that species spends in the reaction chamber prior to either flowing out or undergoing polymerization. The residence times for the monomer(s), initiator(s), and inert gas(es) may be each be independently of any suitable value. In some cases, each of the one or more monomer(s), initiator(s) and inert gas(es) may independently have a residence time of greater than or equal to 5 seconds, greater than or equal to 10 seconds, greater than or equal to 15 seconds, greater than or equal to 30 seconds, greater than or equal to 45 seconds, greater than or equal to 60 seconds, greater than or equal to 90 seconds, greater than or equal to 120 seconds, or greater than or equal to 180 seconds. In certain instances, each of the one or more monomer(s), initiator(s) and inert gas(es) can have a residence time of less than or equal to 300 seconds, less than or equal to 180 seconds, less than or equal to 120 seconds, less than or equal to 90 seconds, less than or equal to 60 seconds, less than or equal to 45 seconds, less than or equal to 30 seconds, less than or equal to 15 seconds, or less than or equal to 10 seconds. Combinations of the above-referenced ranges are also possible (e.g., greater than or equal to 15 seconds and less than or equal to 90 seconds). In some embodiments, the residence time of all of the species is substantially similar. In

some instances, an SACVD method for forming/depositing a polymeric coating may include one or more deposition cycles.

e. Polymeric Coatings or Films

- In certain instances of the SACVD methods, polymeric coating deposition
- 5 includes forming a polymer on one or more surfaces of, for example, a substrate or material, at any suitable deposition rate. In some instances, the deposition rate may be greater than or equal to 0.01 nm/min, greater than or equal to 0.025 nm/min, greater than or equal to 0.05 nm/min, greater than or equal to 0.1 nm/min, greater than or equal to 0.25 nm/min, greater than or equal to 0.5 nm/min, greater than or equal to 1 nm/min,
- 10 greater than or equal to 2.5 nm/min, greater than or equal to 5 nm/min, greater than or equal to 10 nm/min, greater than or equal to 25 nm/min, greater than or equal to 50 nm/min, greater than or equal to 75 nm/min, or greater than or equal to 100 nm/min. In certain instances, the deposition rate may be less than or equal to 100 nm/min, less than or equal to 75 nm/min, less than or equal to 50 nm/min, less than or equal to 25 nm/min,
- 15 less than or equal to 10 nm/min, less than or equal to 5 nm/min, less than or equal to 2.5 nm/min, less than or equal to 1 nm/min, less than or equal to 0.5 nm/min, less than or equal to 0.25 nm/min, less than or equal to 0.1 nm/min, less than or equal to 0.05 nm/min, or less than or equal to 0.025 nm/min. Combinations of the above-referenced ranges are also possible (e.g., greater than or equal to 0.025 nm/min and less than or
- 20 equal to 1 nm/min). In some instances, the initiation temperature, as discussed above, is selected to provide a deposition rate of the polymeric coating of at least 0.5 nm/min. In some other instances, the initiation temperature is selected to provide a deposition rate of the polymeric coating of in a range from at least about 0.1 nm/min to about 100 nm/min, as well as individual values or sub-ranges contained within the aforementioned range.
- 25 According to some embodiments, the polymeric coating may be formed on at least a portion of one or more surfaces of, for example, a substrate or material, all of the surface(s), or on substantially all of the surfaces. Any suitable substrate or material may be used in suitable SACVD methods, as described below. As noted, in certain SACVD methods the surface(s) to be coated by polymer(s) are those of a reactor itself, in which
- 30 the SACVD process is performed.

In instances where the polymeric coating is formed on substantially all of or all of the surface(s), the polymeric coating substantially encompasses or covers substantially

all of the surface(s) intended to be coated (e.g., greater than about 99%, about 99.5%, about 99.8%, about 99.9%, about 99.99%, or 100% of the surface(s) to be coated by the polymer(s)). In such instances, as described herein, the polymeric coating may be capable of protecting the substrate or material (e.g., from deleterious environmental conditions, such as high temperature and/or humidity; and deleterious electrical effects/conditions by providing electrical insulation). In other instances, only a portion of the substrate is covered by the polymeric coating.

In certain instances, polymeric coatings formed by the SACVD methods described herein are formed as polymeric coatings on one or more surface(s) of, for example, a substrate or material. These polymeric coatings may have any average suitable thickness. In some instances, the polymeric coatings may have an average thickness of greater than or equal to 1 nm, greater than or equal to 5 nm, greater than or equal to 10 nm, greater than or equal to 15 nm, greater than or equal to 20 nm, greater than or equal to 25 nm, greater than or equal to 50 nm, greater than or equal to 75 nm, greater than or equal to 100 nm, greater than or equal to 250 nm, greater than or equal to 500 nm, greater than or equal to 750 nm, greater than or equal to 1 μ m, greater than or equal to 2.5 μ m, greater than or equal to 5 μ m, greater than or equal to 7.5 μ m, greater than or equal to 10 μ m, greater than or equal to 25 μ m, or greater than or equal to 50 μ m. In certain instances, polymeric coatings may have an average thickness of less than or equal to 100 μ m, less than or equal to 50 μ m, less than or equal to 25 μ m, less than or equal to 10 μ m, less than or equal to 7.5 μ m, less than or equal to 5 μ m, less than or equal to 2.5 μ m, less than or equal to 1 μ m, less than or equal to 750 nm, less than or equal to 500 nm, less than or equal to 250 nm, less than or equal to 100 nm, less than or equal to 75 nm, or less than or equal to 50 nm. Combinations of the above-referenced ranges are also possible (e.g., greater than or equal to 50 nm and less than or equal to 10 μ m, greater than or equal to 100 nm and less than or equal to 10 μ m, or greater than or equal to 100 nm and less than or equal to 1 μ m).

As explained above, the polymeric coatings formed by SACVD typically demonstrate a high degree of uniformity. In some cases, the thickness of polymeric coatings may be of substantially the same throughout coating. The thickness of the polymeric coatings may be determined by determining the thickness of the polymeric

coating at a plurality of areas (e.g., at least 2, at least 4, at least 6, at least 10, at least 20, at least 40, at least 50, at least 100, or more areas) and calculating the average thickness.

One of ordinary skill in the art would be aware of methods for determining the thickness of polymeric coatings. In one approach, a witness coupon (i.e., a substrate
5 having a smooth surface such as a silicon wafer or a glass wafer) is placed in the deposition chamber during polymeric coating. Subsequent to deposition, a scratch is made on the witness coupon down to the bare substrate and the thickness of the coating measured using a contact profilometer.

f. Substrates and Materials

10 Substrates or materials may be of any size or shape. Non-limiting examples of shapes include sheets, cubes, cylinders, hollow tubes, spheres, and the like. The substrate or material may be of any suitable size. In some stances, the substrate or material includes a metal and/or a polymeric material (e.g., a plastic, an elastomer).

The substrates or materials may be or include a variety of suitable articles, non-
15 limiting examples of which include seals, gaskets, o-rings, and molds. In some instances, the substrates or materials may include, without limitation, microelectronics, micro-electromechanical systems (MEMS), microfluidics, 3-D integrated heterogeneous packages (IHP), CMOS chips, radiofrequency (RF) devices, microchips, boards, transistors, ultra-high-speed mixed-signal circuits, power devices, switches, clock
20 references, frequency selective filters, miniaturized arrays, digital to analog converters, analog to digital converters, and/or low noise amplifiers.

In some instances, the substrate or material may include indium phosphide and silicon, such as in an indium phosphide bipolar CMOS integrated circuit. The indium phosphide bipolar CMOS circuit may include both indium phosphide heterojunction
25 bipolar transistors and silicon CMOS. According to some cases, the substrate or material may include gallium nitride, gallium arsenide, and silicon. For instance, the substrate or material may comprise gallium nitride or gallium arsenide high-electron-mobility transistors and silicon CMOS. In some instances, the substrate or material may include indium phosphide, gallium nitride, gallium arsenide, and silicon. In certain instances, the
30 substrate or material may include indium phosphide heterojunction bipolar transistors, gallium nitride high-electron-mobility transistors, gallium arsenide high-electron-mobility transistors, and silicon CMOS. Other combinations of semiconductors and

compound semiconductors are also possible for the substrate(s) or material(s) to be coated.

In some instances, the polymeric coatings can be deposited by SACVD methods on silicon wafers during the formation of microchips, such as polymeric coatings on
5 through-silicon vias (TSVs).

The substrates or materials may include one or more depressions in their surface. These depressions may have any suitable depth.

The SACVD methods described herein are particularly amenable to forming a polymer on any shape and/or size of a substrate or material. In some cases, the maximum
10 dimension of a substrate in any one dimension may be at least about 1 mm, at least about 1 cm, at least about 5 cm, at least about 10 cm, at least about 1 m, at least about 2 m, or greater. In some cases, the minimum dimension of the substrate in one dimension may be less than about 50 cm, less than about 10 cm, less than about 5 cm, less than about 1 cm, less than about 10 mm, less than about 1 mm, less than about 1 μ m, less than about 100
15 nm, less than about 10 nm, less than about 1 nm, or less. The substrate or material may or may not be substantially planar. For example, the substrate or material may comprise ripples, waves, dendrimers, spheres (e.g., nanospheres), rods (e.g., nanorods), a powder, a precipitate, a plurality of particles, and the like.

In certain instances, the substrate or material may undergo one or more
20 preparation steps prior to serving deposition of the polymeric coating thereon. Several possible preparation steps are described below. For example, in some instances, the substrate, device, or reactor may be cleaned by exposing the substrate, device, or reactor to a fluid and then soaking the substrate, device, or reactor in the fluid, rinsing the substrate, device, or reactor with the fluid, and/or sonicating the substrate, device, or
25 reactor in the presence of the fluid prior to the reaction. Non-limiting examples of suitable fluids for such processes include organic solvents, water, and/or solutions comprising an organic or aqueous solvent and a surfactant.

In some instances, the substrate or material may be exposed to an elevated temperature and/or a reduced pressure in order to remove volatile contaminants. Suitable
30 temperatures include temperatures between 20 °C and 300 °C. Suitable pressures include pressures between 0.1 mTorr and 1 atm.

According to certain instances, the substrate or material may undergo a plasma cleaning step prior to the reaction. Other preparation steps are also possible.

In some embodiments, one or more adhesion-promoting linkers may be applied to the substrate, device, or reactor prior to deposition of the polymeric coating. Non-
5 limiting examples of such linkers include silane-containing compounds, organophosphate-containing compounds, and thiol-containing compounds.

g. Physical Properties of Conformal Polymeric Coating(s)

In some instances, the polymeric coatings exhibit thermal stability when heated up to a temperature of at least about 400 °C. Thermal stability refers to a mass loss of
10 less than about 5%, 4%, 3%, 2%, 1% or less when the polymeric coating is heated to about 400 °C, 500 °C, 600 °C, 700 °C, or 800 °C for at least about 5 minutes to up to about 24 hours under a process gas, such as ammonia, syn gas, or hydrogen gas. The polymeric coating(s) may maintain one or more of these benefits, effects, or properties for a time period of at least one day, at least one week, at least one month, at least one
15 year or at least 10 years.

In certain instances, polymeric coatings synthesized by the SACVD methods described herein may include certain dielectric properties. It is believed that the dielectric constant of a polymeric coating or film may be influenced by the composition of the coating. According to some instances, polymeric coatings including higher degrees of
20 organic content may demonstrate lower dielectric constants. In some instances, polymeric coatings may exhibit dielectric constants of greater than or equal to 2.0, greater than or equal to 2.1, greater than or equal to 2.2, greater than or equal to 2.3, greater than or equal to 2.4, greater than or equal to 2.5, greater than or equal to 2.6, greater than or equal to 2.65, greater than or equal to 2.7, greater than or equal to 2.75,
25 greater than or equal greater than or equal to 2.8, greater than or equal to 2.85, greater than or equal to 2.9, greater than or equal to 2.95, greater than or equal to 3.0, greater than or equal to 3.05, greater than or equal to 3.1, or greater than or equal to 3.15. According to certain instances, polymeric coatings may exhibit dielectric constants of less than or equal to 3.2, less than or equal to 3.15, less than or equal to 3.1, less than or
30 equal to 3.05, less than or equal to 3.0, less than or equal to 2.95, less than or equal to 2.9, less than or equal to 2.85, less than or equal to 2.8, less than or equal to 2.75, less than or equal to 2.7, less than or equal to 2.65, less than or equal to 2.6, less than or equal

to 2.5, less than or equal to 2.4, less than or equal to 2.3, less than or equal to 2.2, less than or equal to 2.1, or less than or equal to 2.0. Combinations of the above-referenced ranges are also possible (e.g., greater than or equal to 2.0 and less than or equal to 3.0, greater than or equal to 2.0 and less than or equal to 2.75, or greater than or equal to 2.0 and less than or equal to 2.7). In some instances, the polymeric coating formed by the method described herein is a dielectric coating or film that has a dielectric constant of less than about 4, less than about 3.5, or less than about 3. In some instances, the dielectric coating or film has a dielectric constant of less than about 3.

According to some instances, polymeric coatings may exhibit a dielectric breakdown voltage. In certain instances, polymeric coatings may exhibit a dielectric breakdown voltage measured in the units of V/mil, where a mil is a unit of measurement equivalent to 0.001 inches. In some instances, polymeric coatings exhibit a dielectric breakdown voltage of greater than or equal to 1000 V/mil, greater than or equal to 1500 V/mil, greater than or equal to 2000 V/mil, greater than or equal to 2500 V/mil, greater than or equal to 3000 V/mil, greater than or equal to 3500 V/mil, greater than or equal to 4000 V/mil, greater than or equal to 4500 V/mil, greater than or equal to 5000 V/mil, greater than or equal to 5500 V/mil, greater than or equal to 6000 V/mil, greater than or equal to 7500 V/mil, greater than or equal to 8000 V/mil, greater than or equal to 8500 V/mil, greater than or equal to 9000 V/mil, or greater than or equal to 9500 V/mil.

According to certain instances, the polymeric coatings exhibit a dielectric breakdown voltage of less than or equal to 25000 V/mil, less than or equal to 20000 V/mil, less than or equal to 15000 V/mil, less than or equal to 10000 V/mil, less than or equal to 9500 V/mil, less than or equal to 9000 V/mil, less than or equal to 8500 V/mil, less than or equal to 8000 V/mil, less than or equal to 7500 V/mil, less than or equal to 7000 V/mil, less than or equal to 6500 V/mil, less than or equal to 6000 V/mil, less than or equal to 5500 V/mil, less than or equal to 5000 V/mil, less than or equal to 4500 V/mil, less than or equal to 4000 V/mil, less than or equal to 3500 V/mil, less than or equal to 3000 V/mil, less than or equal to 2500 V/mil, less than or equal to 2000 V/mil, or less than or equal to 1500 V/mil. Combinations of the above-referenced ranges are also possible (e.g., greater than or equal to 2500 V/mil and less than or equal to 8500 V/mil, greater than or equal to 4000 V/mil and less than or equal to 7000 V/mil, or greater than or equal to 6000 V/mil and less than or equal to 20000 V/mil). In some instances, the polymeric coating is a

dielectric coating that exhibits a dielectric breakdown voltage of between greater than or equal to 1000 V/mil and less than or equal to 25000 V/mil, as well as individual values or sub-ranges contained within the aforementioned range. The dielectric breakdown voltage of the polymeric coatings may be measured by ASTM D149 using the step by step method, which includes exposing the coating to a voltage that is raised uniformly from zero until the dielectric breakdown voltage is reached. Then, a fresh coating is exposed to a voltage at 50% of the measured breakdown voltage and the voltage is increased in a stepwise manner until breakdown is reached. The dielectric breakdown voltage for the coating is considered to be that measured using the stepwise test.

In some instances, polymeric coatings exhibit a leakage current of less than or equal to 10^{-15} A, less than or equal to 10^{-14} A, less than or equal to 10^{-13} A, less than or equal to 10^{-12} A, less than or equal to 10^{-10} A, or less than or equal to 10^{-8} A. In some instances, polymeric coatings act as dielectric coatings that exhibit a leakage current of less than about 1×10^{-12} A/m², 1×10^{-11} A/m², 1×10^{-10} A/m², 1×10^{-9} A/m², 1×10^{-8} A/m², 1×10^{-7} A/m², 1×10^{-6} A/m², 1×10^{-5} A/m², or 1×10^{-4} A/m².

In some instances, the polymeric coating formed by the SACVD methods described are free or substantially free of pin-holes and/or defects. "Substantially free of pin-holes and/or defects" refers to less than about 5%, 4%, 3%, 2%, or 1% of the polymeric coating surface showing such pin-holes or defects, based on evaluation of the coating using art known methods.

III. Surface Activated Chemical Vapor Deposition (SACVD) System

In certain instances of the SACVD methods described, the SACVD methods described may be carried out in an SACVD system including:

- a reaction chamber comprising
- a platform able to support the at least one substate or material in the reaction chamber; the platform including one or more heating elements for independently heating the platform to and/or maintaining that platform at a first temperature;
- a temperature sensor for measuring and providing feedback on the first temperature of the platform;

- wherein the reaction chamber and/or components thereof can be maintained at a second temperature that is lower than the first temperature;
- at least one gas inlet port to introduce one or more gaseous reactants and optional gas carriers into the reaction chamber;
- 5 at least one gas outlet port;
- a first temperature controller for maintaining the first temperature of the platform;
- a second temperature controller for maintaining the second temperature of the reaction chamber;
- 10 optionally one or more gas metering valves and/or mass flow controllers; optionally a pressure transducer; optionally a throttle valve; and optionally a vacuum source.

In one non-limiting example, a system for SACVD is shown in Figure 2, where

15 SACVD system 200 includes reactor chamber 210, tube furnace 220, a carrier gas vessel 230, a carrier gas mass flow controller 235, an initiator vessel 240, an initiator metering valve 245, a monomer vessel 250, a pressure transducer 260, a throttle valve 270, and a vacuum source 280.

In certain instances, the platform holding the substrate or material is selected to

20 possess a high degree of thermal uniformity and good thermal contact with the substrate or material in order to ensure that the substrate or material itself is heated to a uniform temperature.

In certain instances, the reaction chamber of an SACVD system, as described above, further includes a gas distributor to distribute the one or more gaseous reactants

25 and/or optional carrier gases introduced through the at least one gas inlet port into the reaction chamber.

In some instances, the gaseous reactants (i.e., monomer and initiator) and carrier gas(es) originate from a source which takes the form of a reservoir (such as a vessel) of a material that may be placed in and/or removed from fluidic communication with the

30 reaction chamber by a (inlet/outlet) port. As one example, a source of gas or reactants may take the form of and/or include a gas cylinder (e.g., having pressurized gas therein). The port may separate the reaction volume from the source, and may be opened and/or

closed to place the source in and/or out of fluidic communication with the reaction chamber. The port may be in direct or indirect fluidic communication with the source. For instance, the port may be in fluidic communication with the source via tubing.

In some instances, the interface between a port and the reaction chamber may have a variety of suitable designs. In some instances, the port has a single opening through which, when the port is open, the source is placed in fluidic communication with the reaction chamber. The single opening may have a variety of suitable shapes and sizes. For instance, it may be round, rectangular, square, etc. Some suitable ports have multiple openings. As one specific example, a port may comprise a plurality of openings. The plurality of openings may be positioned along a wall of the reaction chamber and/or along a tube present in the reaction chamber. In some instances, the system may include two sources and includes ports in fluidic communication with the sources and the reaction chamber.

In some instances, in addition to or instead of a port(s), a flow controller may be positioned between a source and a reaction chamber. As one example, in some cases, a mass flow controller is placed between a source of gas and the reaction chamber. As another example, a throttling valve may be placed between a source of vacuum and the reaction chamber.

As noted above, it is also possible for the system to include a source of vacuum. The source of vacuum may be configured to evacuate the reaction chamber when in fluidic communication therewith. A variety of suitable types of sources of vacuum may be employed. As an example, in some instances, a source of vacuum comprises a vacuum pump. The vacuum pump, when turned on and in fluidic communication with the reaction volume, may evacuate the reaction volume by pumping out its contents.

In some instances, a source of vacuum has one or more properties that render it advantageous for removing air and/or other gases from a reaction chamber. As one example, in some instances, a source of vacuum is configured such that the removal of gas from the reaction volume occurs over a period of time that is relatively slow. The slow and/or controlled removal of gas from a reaction volume may be accomplished by the use of a throttling valve positioned between the source of vacuum and the reaction chamber. The throttling valve may restrict the exposure of the reaction chamber to the source of vacuum and/or may slowly open to allow increasing exposure of the reaction

volume to the source of vacuum over time. These processes may cause the source of vacuum to remove the gases therein at a slower rate than the source of vacuum would absent such a throttling valve.

Use of a vacuum may be advantageous when, for instance, the reaction chamber
5 initially comprises a combination of gases that it would be undesirable for the reaction chamber to include during the deposition of a polymeric coating. For instance, and without wishing to be bound by any particular theory, it is believed that some gases may inhibit polymerization reactions. Such gases may react with the growing polymeric chains before they reach an appreciable length in a manner that terminates further growth
10 and/or may react with monomers prior to being incorporated into growing polymeric chains in a manner that renders them non-reactive. Non-limiting examples of such gases include air, water vapor, acetone, and isopropanol. An example of a situation in which it may be desirable to remove one or more gases from a reaction chamber is at the conclusion of a step performed during the deposition of a polymeric coating. During
15 deposition of the polymeric coating, the reaction volume may include a variety of reactive and/or toxic gases. It may be desirable for the reaction volume to be purged of such gases before one or more further processes are performed. For instance, if the system is employed to perform a method including sequentially depositing two layers with two distinct chemical compositions, it may be desirable to remove the gases that
20 reacted to form the first layer prior to beginning deposition of the second layer. Removal of these species may facilitate the deposition of a second layer that has the desired chemical composition, as it may prevent the incorporation of reaction products of these gases into the second layer and/or deleterious reactions between these gases and the gases configured to react to form the second layer. Another example of a situation in
25 which it may be desirable to remove one or more gases from a reaction volume is at the conclusion of a process for depositing a polymeric coating. As described above, the reaction volume may comprise reactive and/or toxic gases during coating deposition. It may be undesirable for an operator to be exposed to such gases and/or for such gases to be released in an uncontrolled manner to an environment external to the reaction volume.
30 Accordingly, in such cases, it may be desirable for the gases present in the reaction volume to be removed therefrom prior to exposure of the reaction volume to an

environment external thereto to retrieve a coated substrate or material at the conclusion of a coating process.

In some other instances, a system can be configured such that one or more gases may be removed from a reaction volume in a manner other than placing a source of vacuum in fluidic communication with the reaction chamber. As one example, in some cases, a system may be configured such that one or more gases may be introduced into the reaction volume that displace other gases present in the reaction volume therefrom. For instance, a system may be configured such that an inert gas (and/or a plurality of inert gases) may be introduced into a reaction volume to displace a reactive and/or toxic gas (and/or a plurality of reactive and/or toxic gases). The inert gas(es) may be introduced from one or more sources in fluidic communication with the reaction volume, such as one or more sources other than the source(s) supplying (and/or previously supplying) the reactive and/or toxic gas(es). Introducing one or more inert gases into a reaction chamber may be performed instead of removing gas(es) from the reaction volume by placing a source of vacuum in fluidic communication therewith, or in conjunction with such a process. In the latter case, the source of vacuum, when in fluidic communication with the reaction volume, may evacuate both the inert gas(es) and the reactive and/or toxic gas(es) from the reaction volume. In one specific example, the source of vacuum may be placed in fluidic communication with a reaction volume that includes the reactive and/or toxic gases and that is in fluidic communication with one or more sources of inert gases. The source of vacuum may initially evacuate both types of gases. Then, the source(s) of inert gases may be removed from fluidic communication with the reaction volume while maintaining fluidic communication between the source of vacuum and the reaction volume. The source of vacuum may then further evacuate the reaction volume of any remaining gases therein.

In some instances, a system includes an outlet that may be placed in fluidic communication with the reaction chamber. The outlet may be configured to allow one or more gases present in the reaction chamber to flow out of the reaction volume when in fluidic communication with the reaction chamber. The outlet may be in fluidic communication with a location to which the gases present in the reaction volume may be safely exhausted, such as a fume hood. In some instances, the outlet may be in reversible fluidic communication with the reaction chamber. For instance, the outlet may be

removed from fluidic communication with the reaction chamber during time periods in which the reaction volume is in fluidic communication with a source vacuum. It is also possible for the outlet to be configured such that gases may flow out of the reaction volume through the outlet but that gases are not able to flow into the reaction volume through the outlet. For instance, in some embodiments, the outlet may comprise a check valve, a gas bubbler, and/or another component that provides this functionality. In some instances, the outlet is configured to allow for gases to both flow into and flow out of the reaction chamber, but the gases flowing into the reaction chamber (e.g., from one or more sources) may be flowing into the reaction chamber in sufficient amounts and/or at sufficient rates such that there is no appreciable flow into the reaction chamber from the outlet.

In some instances, the SACVD system the reactor chamber is a load-locked reactor chamber which can maintain a controlled environment inside the reaction chamber while allowing for the introduction and removal of substrates or materials without exposing the reaction chamber to external conditions. For example, the system can further include a separate loading chamber or vestibule that is connected to the main reaction chamber through a vacuum-sealed door or gate valve. This loading chamber can serve as a transition area where substrates or materials can be loaded into or removed from the main reactor chamber without disturbing the internal environment of the main reactor chamber, where the polymeric coatings/films are formed. Use of a load-locked reactor can minimize contamination risks, improve process reproducibility, and enhance overall SACVD system throughput by allowing for faster turnaround times between batches and reduced downtime associated with venting and purging the main reaction chamber between each transfer.

In one non-limiting instance, a sequence of operation in a load-locked system involves the steps of: (1) loading, (2) pumping, (3) transferring, (4) processing, and (5) unloading. During the loading step, substrates or materials are placed inside the loading chamber, which is then sealed off from the external environment. In the pumping step, the loading chamber is evacuated to create a vacuum environment, ensuring that the substrates or materials are not exposed to contaminants or atmospheric gases before they are transferred into the main reaction chamber. The transferring step occurs after the loading chamber reaches the desired vacuum level. During the transfer step, a vacuum-

sealed door or gate valve separating the loading chamber and the main reaction chamber is opened, allowing the substrates or materials to be transferred into the reaction chamber. In the processing step the substrates or materials undergo the desired deposition or reaction processes inside the main reaction chamber according to the methods described herein. The unloading step occurs after the processing is complete. In the unloading step, the vacuum-sealed door or gate valve is closed, isolating the main reaction chamber from the loading chamber and the loading chamber is then pumped down to a vacuum again, and the substrates or materials are removed.

Gases may be flowing through the reaction chamber in a one-dimensional manner. One-dimensional flow may be a flow in which the relevant gases flow primarily or entirely in one direction. It is also possible for one-dimensional flow to be laminar. As one example of one-dimensional flow, the one-dimensional flow of a gas may be flow in which the gas flows entirely in one direction and does not flow in any direction other than that direction. As another example, in some instances, one-dimensional flow of a gas comprises flow that is primarily, but not entirely in one direction. For instance, the one-dimensional flow may comprise small amounts of flow in directions other than the primary direction. These small amounts of flow may make up less than or equal to 50%, less than or equal to 20%, less than or equal to 10%, and/or less than or equal to 5% of the one-dimensional flow.

When two or more different types of gases are flowing through a reaction volume (e.g., two or more types of gases provided from a common source, two or more types of gases provided from different sources, provided from the same source), the different types of gases may together exhibit one-dimensional flow in a single direction. In other words, all of the gases together may flow entirely in the same direction and/or may together comprise amounts of flow in a direction other than the primary direction in one or more of the ranges described in the preceding paragraph. It is also possible for two or more different types of gases (e.g., provided from different sources, provided from the same source) to have flows that differ from each other. For instance, two or more different types of gases may each flow through the reaction volume in a one-dimensional manner, but the directions in which the different types of gases flow may differ from each other. As another example, in some instances, one or more types of gases may exhibit one-dimensional flow and one or more types of gases may not exhibit one-

dimensional flow (e.g., one or more types of gases may exhibit convective and/or turbulent flow).

In some instances, the reaction chamber includes a relatively low level of air at one or more points in time. This relatively low level of air may be present at times when, for instance, a reaction (e.g., a reaction to deposit a polymeric coating) is performed in the reaction chamber. It is also possible for a reaction chamber to include a relatively low level of water. This relatively low level of water may be present at times when, for instance, a reaction (e.g., a reaction to deposit a polymeric coating) is performed in the reaction chamber. In some instances, the relative humidity of the reaction chamber may be less than or equal to 0.5%, less than or equal to 0.4%, less than or equal to 0.3%, less than or equal to 0.2%, or less than or equal to 0.1%. The relative humidity of the reaction chamber may be greater than or equal to 0%, greater than or equal to 0.1%, greater than or equal to 0.2%, greater than or equal to 0.3%, or greater than or equal to 0.4%. Combinations of the above-referenced ranges are also possible (e.g., less than or equal to 0.5% and greater than or equal to 0%).

In some instances, the processes that are performed in a reaction chamber (e.g., polymerization, etc.) of a system may be automated. Such automation may include providing software that reads instructions for the various processes being performed (e.g., the flow rates and/or types of gases introduced into the reaction system, the filament temperature, the temperature of the substrate, etc.) and then executes these instructions by directing further system components to carry them out. In some instances, the systems described herein are maintained at or close to their optimal performance. It is also possible for this performance to be maintained while simultaneously reducing the effort of the operators of the systems to do so. This may be accomplished by use of automated software that records one or more conditions of the system and then alerts the operator when one or more such conditions indicates that carrying out one or more maintenance steps would improve system performance. Such system conditions may include the amount of time required for exposure to a source of vacuum to cause the reaction volume to reach a desired pressure, the state of any valves positioned between any sources and the reaction volume (e.g., a valve, such as a throttle valve, positioned between a source of vacuum and the reaction volume), the amount of time since a prior maintenance step, the amount of time the system has been employed to deposit

polymeric coatings, the amount of gases that have passed through the system, the amount of time that one or more filament(s) have been resistively heated, etc.

IV. Uses of Surface Activated Chemical Vapor Deposition (SACVD)

5 The SACVD methods described above can be used to deposit/form polymeric coating(s) on surface(s) of a substrate or material having a degree of conformality, which would otherwise be difficult or impossible to attain using other known deposition methods. Accordingly, in some instances, the methods described herein can be used to form a polymeric coating on at least a portion of a surface of a substrate or material,
10 where the polymeric coating and the substrate or material are included in or form at least part of a semiconductor device. In some instances, the semiconductor device is a semiconductor circuit. In certain instances, the polymeric coating is a dielectric coating or film. In certain other instances, the polymeric coating acts as an optical material, such as a nonreflective coating or waveguide.

15 In some instances, such substrates or materials having such conformal polymeric coatings thereon can benefit from the one or more coated surface(s) having: protection from the environment, by adding mechanical protection, by adding electrical insulation, by adding electrical protection, by imparting optical effects, by modifying surface properties, and/or by enhancing biological or chemical compatibility.

20 Other non-limiting uses for the polymeric coatings formed according to the methods described are described below.

A. Conformal Dielectric Polymeric Coatings or Films for Forming Semiconductor Circuits

 In some instances, the polymeric coatings or films formed according to the
25 methods described function as dielectric coatings or films. Such dielectric coatings/films are useful in semiconductor fabrication.

 In some instances, the dielectric properties of polymeric coatings are dependent on the atomic content of hydrogen present in the polymeric coating. In some instances, the atomic content of hydrogen in a coating can be increased to afford a lower dielectric
30 constant. In some instances, the monomers and/or initiators used in the method, can be selected based on their atomic hydrogen content (i.e., number of hydrogen atoms divided by total number of atoms in monomer or initiator molecule) to form a polymeric coating

having a desired atomic hydrogen content. For example, if a polymeric coating having a higher atomic hydrogen content is desired, such as when a coating having a low dielectric constant is desired, monomers and/or initiators with higher atomic hydrogen contents, such as in the range of about greater than 25% to 60%, can be selected to flow
5 into the reaction chamber. Alternatively, if a polymeric coating having a lower atomic hydrogen content is desired, monomers and/or initiators with lower atomic hydrogen contents, such as in the range of about 0.1% up to 25%, can be selected to flow into the reaction chamber.

In some instances, the annealing step is carried in a process gas which promotes
10 retention or preservation of the atomic hydrogen content of the polymeric coating during the annealing step. In other words, the process gas should prevent or limit a reduction of the atomic content of hydrogen in the polymeric coating subjected to the annealing step. In some instances, the annealing step is carried out and the atomic content of hydrogen in the polymeric coating following the annealing step is reduced by less than about 25%,
15 20%, 15%, 10%, 5%, 1%, 0.5%, or 0.1%, as compared to the atomic hydrogen content prior to annealing. In some other instances, the annealing step is carried out and the atomic content of hydrogen in the polymeric coating following the annealing step is reduced by an amount in a range from about 0.1% to 25%, as compared to the atomic hydrogen content prior to annealing, as well as individual values or sub-ranges contained
20 within the aforementioned range.

For example, the SACVD methods can form polymeric coatings or films for gate all around transistors. In some instances, the polymeric coatings or films can be used in new generation nodes (2nm or less) which use gate all around transistor structures. In such structures, the gate dielectric well has to be conformal to the channel, as opposed to
25 on a high step height, but also under/between channels. Accordingly, the microscale conformality of the polymeric coatings or films formed according to the methods described herein can be particularly useful for such applications and fabrication methods.

In some instances, the polymeric coatings or films formed according to the methods described herein are also useful for providing, for example, deep vias for
30 backside power and other similar applications. Currently, most fabrication in production is conducted on one face of a silicon wafer. In 2 nm and beyond nodes, moving power wires to the back side of the wafer is possible, which necessitates etches for providing

interconnects. Thus, because of the need for deep power vias, a conformal dielectric may be useful for line isolation between multiple layers or lines. Additionally, conformal dielectrics materials may be useful as an etch stop for etching deep vias from the backside, to avoid damaging Si devices that were fabricated on the top side. The SACVD methods described herein can be used to provide dielectric polymeric coatings or films which are conformal and can be used for the aforementioned purposes.

B. Polymeric Coatings or Films for use in Semiconductor Manufacturing

In some instances, the polymeric coatings or films formed according to the methods described herein are used in semiconductor manufacturing. In certain instances, where the polymeric coating comprises SiNC the coating is expected to be an amorphous material with properties between those of SiO₂ (silicon oxide) and Si₃N₄ (silicon nitride). Such a polymeric coating can be used as an optical material, such as a nonreflective coating or waveguide, due to the refractive index being tunable to be between that of glass (1.45) and silicon nitride (~2) by changing the atomic proportions of the coating, such as the carbon content. Such SiNC polymeric coatings can also possess a high density of charge traps and can be used as a memory device. Moreover, SiNC polymeric coatings or films are expected to provide better fracture resistance than silicon nitride, while maintaining similar thermal stability to Si₃N₄ (Lin, S.; *et al.*, Mechanical, Dielectric Properties and Thermal Shock Resistance of Porous Silicon Oxynitride Ceramics by Gas Pressure Sintering. Mater. Sci. Eng. A **2015**, 635, 1–5).

C. Polymeric Coatings or Films with High Temperature Stability for use in Semiconductor Manufacturing

In some instances, the polymeric coatings or films formed according to the methods described herein demonstrate high temperature stability. As noted above, the polymeric coatings can exhibit thermal stability when heated up to a temperature of at least about 400 °C, 500 °C, 600 °C, 700 °C, or 800 °C.

In instances, polymeric films, such as formed of SiOC or SiNC, are used for dielectric purposes they are compatible with several annealing processes, particularly those used in art known back-end-of-line (BEOL) processes related to copper or other metallization. Currently, the semiconductor industry uses the so-called “damascene” process where each interconnect layer also needs isolation using low-k dielectrics. In some cases, annealing following electroplating (~<400 °C) is associated to an increased

Cu grain size and reduced resistance. Accordingly, suitable low-k materials need to be able to survive such conditions. Such low-k dielectrics can be the SiOC or SiNC based polymeric coatings and films formed according to the SACVD methods described.

D. Polymeric Coatings or Films with High Environmental/Chemical

5 **Stability for use in Semiconductor Manufacturing**

In some instances, the polymeric coatings or films formed according to the methods described herein exhibit high environmental and chemical stability.

In instances, polymeric films, such as formed of SiOC or SiNC, are used for dielectric purposes and are compatible with and able to maintain chemical stability when
10 exposed to front end of the line (FEOL) CVD and ALD processes and the gases used in such processes. For example, deposition of TaN or TiN using ALD/PECVD commonly used semiconductor materials requires the introduction of ammonia in the gas phase. Additionally, gases such as H₂, SiH₄, GeH₄ and SiCl₄ are used for epitaxial growth of layers for FinFET or GAAFET structures via PECVD, or LPCVD. The polymeric films,
15 such as formed of SiOC or SiNC by the methods described, demonstrate environmental and chemical stability to such gases and conditions.

E. Polymeric Coatings or Films with Barrier Properties for use in Semiconductor Manufacturing

In some instances, the polymeric coatings or films formed according to the
20 methods described herein can act as a barrier layer to prevent or reduce migration of metals through the coating or film. Such metals may be present in layers, materials, or components which are in contact with the coating or film.

In some instances, the barrier properties of polymeric coatings against migration of metals are increased by reducing the atomic content of hydrogen to be in a range of
25 about 5% to 25% or about 0.1% to 5% of the total atomic composition of the formed polymeric coating. In some instances, a polymeric coating or film formed during step (iv) can have its initial atomic content of hydrogen reduced further by applying an annealing step (*see* details of annealing step above). In some such instances, the annealing step is carried in a process gas that promotes the annealing step reducing the
30 atomic content of hydrogen in the annealed coating. In some instances, the annealing step is carried out and the atomic content of hydrogen in the polymeric coating following the annealing step is less than about 25%, 20%, 15%, 10%, 5%, 1%, 0.5%, or 0.1%. In

some other instances, the annealing step is carried out and the atomic content of hydrogen in the polymeric coating following the annealing step is in a range from about 0.1% to 25%, as well as individual values or sub-ranges contained within the aforementioned range. In yet other instances, the annealing step is carried out and the atomic content of hydrogen in the polymeric coating following the annealing step is free or essentially free of any atomic hydrogen content, where “essentially free,” refers to an atomic content of hydrogen of less than about 5%, 4%, 3%, 2%, 1%, 0.5%, or 0.1% of total atomic composition of the annealed coating.

For example, a polymeric coating or film may be formed atop a layer which contains copper metal and another layer may be present atop the polymeric coating or film, whereby the polymeric coating or film acts as a barrier that stops copper atoms from migrating through the polymeric coating or film into the layer atop the polymeric coating or film. In some instances, the polymeric coating or film completely prevents metal migration through the coating or film. In some other instances, the polymeric coating or film reduces the metal migration by at least about 50%, 60%, 70%, 80%, 90%, 95%, or 99%, as compared to metal migration in the absence of the polymeric coating. In some instances, the metal is selected from the group consisting of copper, gold, silver, tin, nickel, and combinations thereof. In certain instances, the metal is copper.

F. Combinations of Polymeric Coatings with Different Properties

In some instances, more than one polymeric coating is formed on a substrate or material having different properties, such as those described immediately above.

In one non-limiting example, first and second polymeric coatings can be formed on a substrate or material where the first and second polymeric coatings are either in contact or are not in contact with each other. In other words, the first and second polymeric coatings may be separated by another layer or material. In some such instances, a substrate or material may include at least a first polymeric coating having a reduced atomic content of hydrogen and which acts as a carbon-based barrier layer to prevent or reduce migration of metals through the coating and at least a second polymeric coating which has a higher atomic content of hydrogen than the first layer. In some instances, the first polymeric coating is thinner than the second polymeric coating. In some instances, the first polymeric coating is thicker than the second polymeric coating.

In another non-limiting example, first and second polymeric coatings can be formed on a substrate or material where the first and second polymeric coatings are either in contact with each other. In such an instance, the at least first polymeric coating, which forms a first layer, can have a reduced atomic content of hydrogen and acts as a carbon-based barrier layer to prevent or reduce migration of metals through the coating. The at least a second polymeric coating, which forms a second layer on top of the first layer, can have a higher atomic content of hydrogen and acts as a low-k dielectric coating or film. In some instances, the first polymeric coating is thinner than the second polymeric coating. In some cases, the thickness of the first polymeric coating is about 25%, 20%, 15%, 10%, 5%, or 1% of the thickness of the second polymeric coating. In some other cases, the thickness of the first polymeric coating is about 1% to 25% of the thickness of the second polymeric coating, as well as individual values or sub-ranges contained within the aforementioned range.

Other combinations of polymeric coatings having different properties and relative thicknesses can be formed according to the methods described.

EXAMPLES

Example 1 – Selective Heating Deposition of SACVD Coatings

Materials and Methods:

Poly(1,3,5-trivinyl-1,3,5-trimethylcyclotrisiloxane) (pV3D3), poly(divinylbenzene) (pDVB), and tert-butyl styrene (pTBS) by Selective Heating SACVD using di-tert butyl peroxide (TBPO) and tert-butyl peracetate (TBPA) as initiators. Polymer materials were synthesized using SACVD within a 0.025 m³ reactor, as shown in Figure 3.

Silicon wafer samples were placed on a temperature-controlled stage fixtured within the reactor and evacuated to a base pressure of 10 mTorr. The stage temperature was then heated to a target temperature prior to heating the reactor body. A gas stream comprised of a monomer and an initiator was then introduced into the chamber a target pressure was achieved. Monomers and initiators were used as purchased without additional purification. Depositions were maintained at the target pressure using a throttle valve until the desired thickness on the stage was achieved, which was confirmed using reflectometry.

For each deposition, stage temperature was controlled between 95-215°C, while reactor temperature was maintained between 85-100°C. Monomer flow rates of 3-9sccm were utilized with associated initiator flow rates of 1.5-9sccm. Total chamber pressure was between 2.5-6.0 Torr. Using these conditions, deposition rates of between 0.1-3.0
5 Nm/min were achieved for the growth of the varying film composition. Final sample thickness of 90-600nm were achieved and analyzed for confirmation of desired polymer structure.

Results:

Each polymer coating formed by SACVD was analyzed using Fourier transform
10 infrared spectroscopy using a Perkin-Elmer System 2000 FT-IR system to confirm the synthesis of the target material. A measurement of the native silicon wafer was also collected and subtracted from the spectra of the coated wafer. Each spectrum covered a range of wavenumbers from 500 cm^{-1} to 4000 cm^{-1} . Spectra were baselined after measurements and normalized to correct for thickness for comparative analysis.

15 Figure 4 shows the IR absorbance values as a function of wavenumber for the pV3D3 coatings of Example 1 formed with TBPO or TBPA. The absorbance peak at 1000-1050 cm^{-1} is characteristic of Si-O cyclic trimers in pV3D3. The shoulder on the left side of this peak is resultant of a vinyl C-H absorbance peak around 960 cm^{-1} , the presence of which depends on the vinyl conversion from initiator radicals due to
20 deposition conditions. Absorbance peaks at 800 cm^{-1} and 1260 cm^{-1} are characteristic Si-CH₃ bonds in pV3D3. Absorbance peaks from 2870-2960 cm^{-1} are indicative of C-H stretching in the methylene carbon backbone and methyl groups of pV3D3. Positive or negative absorbance peaks at 1100-1115 commonly result from differences in native SiO₂ on the backgrounding silicon wafer and the measurement sample wafer in this FTIR
25 set-up.

The spectra shown in Figure 5 display IR absorbance values as a function of wavenumber for the pDVB coatings of Example 1 formed with TBPO or TBPA. Absorbance peaks from 690-850 cm^{-1} are characteristic of para-substituted and meta-substituted benzene vibrations (DVB monomer is a mixture of para- and meta-substituted
30 isomers). Characteristic C=C aromatic stretching is seen from absorbance peaks between 1450-1600 cm^{-1} . Absorbance peaks from 2870-2960 cm^{-1} are indicative of C-H

stretching in the methylene carbon backbone of pDVB and methyl groups from TBPO initiator incorporation.

The spectrum in Figure 6 displays IR absorbance values as a function of wavenumber for the pTBS coating of Example 1. A characteristic absorbance peak at 830 cm^{-1} is indicative of para-substituted benzene vibrations (TBS monomer is purely para-substituted). Characteristic C=C aromatic stretching is seen from absorbance peaks between 1450-1600 cm^{-1} . Absorbance peaks from 2870-2960 cm^{-1} are indicative of C-H stretching in the methylene carbon backbone and methyl groups of pTBS, with the methyl peak at 2960 cm^{-1} significantly stronger relative to the methylene peaks when compared to the same peaks seen in the pDVB spectra of Figure 5.

Example 2 – Isothermal versus Selective Heating Deposition of SACVD Coatings

This example describes the synthesis of pV3D3 using an isothermal SACVD method.

pV3D3 polymer films were synthesized using SACVD within a 0.0012 m^3 reactor as shown in Figure 3. A silicon wafer sample and a silicon wafer stack were placed on a temperature-controlled stage fixtured within the reactor and pumped down to a base pressure of 10 mTorr. The configuration of the wafer stack is shown in Figures 1A and 1B.

Methods:

For isothermal SACVD depositions, the heating platform (or stage) and reactor body were heated to a range of target temperatures between 175 °C - 205 °C before introducing a gas stream comprised of 1,3,5-trivinyl-1,3,5-trimethylcyclotrisiloxane monomer and di-tert butyl peroxide initiator. A second set of samples were generated in an identical manner by selective heating SACVD where only the stage was heated to the target temperature while the reactor body was maintained at 100 °C. These deposition conditions are Pressure was maintained within the chamber using an automated throttle valve until a target thickness was achieved. Polymer thickness was confirmed using reflectometry.

Results:

Thickness outside of the wafer stack versus at the center, as described in the specification, was measured for each set of conditions and the conformality achieved using isothermal and selective deposition is shown in Figure 7.

5 The coated silicon wafers were also analyzed using Fourier transform infrared spectroscopy (FTIR) to confirm the synthesis of pV3D3. The IR spectra in Figure 8 display IR absorbance values as a function of wavenumber for a pV3D3 isothermal coating synthesized by the conditions described in Example 2. The absorbance peak at 1000-1050 cm^{-1} is characteristic of Si-O cyclic trimers in pV3D3. The shoulder on the
10 left side of this peak is resultant of a vinyl C-H absorbance peak around 960 cm^{-1} , the presence of which depends on the vinyl conversion from initiator radicals due to deposition conditions. Absorbance peaks at 800 cm^{-1} and 1260 cm^{-1} are characteristic Si-CH₃ bonds in pV3D3. Absorbance peaks from 2870-2960 cm^{-1} are indicative of C-H stretching in the methylene carbon backbone and methyl groups of pV3D3.

15

Example 3 – Conformality

This example describes the conformality of pV3D3 and pDVB coatings achieved using SACVD, iCVD, and iPECVD methods.

Methods:

20 The conformality of coatings produced by SACVD was compared to iCVD and iPECVD using pV3D3 and pDVB as test materials.

For this example, SACVD coatings were deposited on test substrates using conditions as described in Example 1 above. iCVD coatings were synthesized using a 0.0026 m^3 reactor as shown in Figure 9 while iPECVD coatings were synthesized in a
25 0.210 m^3 reactor as shown in Figure 10.

For iCVD, silicon wafer samples were placed on a temperature-controlled stage at the base of the reactor. A heated filament array was placed over the samples and then connected to a power supply through vacuum electrical feedthroughs. The reactor chamber was evacuated to a base pressure of 40 mTorr. The stage temperature was
30 controlled to a temperature between 25-50°C. The reactor chamber walls were heated to 70°C. Monomer and initiator feed lines were heated to 100°C. A gas stream comprised of a monomer and an initiator was then introduced into the chamber and pressurized to a

target pressure using a throttle valve. Monomers and initiators were used as purchased without additional purification. Filament temperature was controlled by setting the voltage on the Variac power supply, which was pre-calibrated to determine filament temperature setpoints. The filament was turned on, and depositions were maintained at the target pressure until the desired thickness was achieved, which was confirmed using profilometry.

For iPECVD, silicon wafer samples were vertically suspended on aluminum boards within the reactor chamber below the showerhead gas diffuser and above the electrode. The reactor chamber was evacuated to a base pressure of 4 mTorr. The monomer, initiator, and diluent gases were introduced uniformly across the width of the chamber using a showerhead that spanned the entire electrode area. Monomers and initiators were used as purchased without additional purification. The chamber was pressurized to a target pressure using a throttle valve. Then, an RF plasma was utilized for initiator activations, while target pressure was maintained until the desired thickness was achieved, which was confirmed using interferometry.

The conformality of the coatings were also measured on microtrenches to assess conformality on features on the order of single microns. The geometry of the microtrenches is shown in Figure 11. In this case, conformality was determined by comparing the coating thickness at the top of the microtrench to the thickness of coating at the bottom of the microtrench.

After deposition, microtrench samples were fractured after coating using a diamond tip scribe to obtain a clean edge for imaging via scanning electron microscopy. Samples were then fixed to stubs at 90° with carbon tape with the exposed edges of the microtrenches facing upwards, and colloidal silver was painted on the edges of the samples to the sample fixture to minimize charge accumulation from the electron beam on the polymer film surface. Accelerating voltages for the electron beam were set at 1 kV for imaging and did not exceed 3 kV during the imaging process to prevent damage to the polymers.

Results:

To assess conformality on substrates with features on the order of hundreds of microns, wafer stacks as described in Example 3 were coated and evaluated by comparing the coating thickness at the center of the wafer stack to the thickness of a

coating on a silicon wafer positioned next to the wafer stack. A comparison of the conformalities achieved by the various processes on wafer stacks is summarized in Table 3 below.

Table 3. Summary of Conformality achieved using SACVD, iCVD, and iPECVD on Wafer Stacks.

	Conformality on wafer stack		
Chemistry	SACVD selective deposition	iCVD	iPECVD
pV3D3 with TBPO	54 %	2 %	1 %
pV3D3 with TBPA	55 %	2 %	--
pDVB with TBPO	68 %	2%	--

An example demonstrating the thickness analysis using SEM micrographs on microtrenches coated with pV3D3 synthesized using TBPO was performed (images not shown) and a summary of the conformalities achieved by the various processes on microtrenches is shown in Table 4 below.

Table 4. Summary of Conformality achieved using SACVD, iCVD, and iPECVD on Microtrenches.

	Conformality on microtrench		
Chemistry	Selective Heating SACVD	iCVD	iPECVD
pV3D3 with TBPO	73.4 %	23.2 %	5 %
pDVB with TBPO	80.2 %	6.2 %	--

Example 4 – Process Condition Selections for Formation of Defect-free Polymeric Coatings/Films

This example describes various film defect(s) that can be produced depending on process conditions which may fall outside of the desired ranges selected for SACVD deposition.

Methods:

Using a 0.0012 m³ reactor, as shown Figure 3, pV3D3 coatings were synthesized with two sets of conditions. The resultant coatings were then imaged using SEM microscopy to evaluate their morphology. A summary of the conditions used are listed in Table 5. Condition 4A is an example of a deposition where the ratio of the partial

pressure to the saturation pressure of the coldest portion of the reactor never exceeds 1, avoiding reactant condensation. In contrast, condition 4B included a gradually decrease of initiator flow rate from 3 sccm to 0 sccm, resulting in a ratio of the partial pressure to the saturation pressure of the coldest portion of the reactor to exceed 1, allowing for
5 reactant condensation.

Table 5. Summary of Deposition Conditions used to generate Various Coating Morphologies.

Condition	4A	4B
Stage Temperature (°C)	205	160
Reactor Temperature (°C)	100	85
Monomer	V3D3	V3D3
Monomer flow rate (sccm)	3	10
Initiator flow rate (sccm)	1	3-0
Initiator	TBPO	TBPO
Pressure (Torr)	4.0	10
Coating morphology	Smooth dense coating	Blister formation

Results:

10 SEM micrographs of the resultant coating morphologies (not shown) demonstrated smooth dense coatings are produced under the 4A conditions and blisters are formed under the 4B conditions. Accordingly, depending on selections of process conditions film morphology can exhibit a large number of nodular defects in the film deposited under 4B conditions.

15

Example 5 – Process Setup and Reactor Geometry Impacts on Coating Morphology

This example describes the impact of proximity of heated surface areas using SACVD.

Methods:

20 Using a custom sample stage, depositions were performed with two separate stages controlled to a surface temperature of 215 °C. Custom sample stage not shown.

A gas profile comprised of 4.5 Torr of V3D3 partial pressure and 1.5 Torr of TBPO partial pressure was maintained across four discrete depositions where the separation between the shelves was varied from 1 to 4 inches. The deposition rates were recorded on the top and bottom shelves and confirmed using reflectometry.

5 **Results:**

A summary of the deposition rates is shown in Table 6. Across the range of shelf separation, no significant variation between deposition rates was detectable between the top and bottom shelves until the spacing was reduced to 1". At a 1" separation the bottom shelf exhibited a significantly higher deposition rate compared to the top shelf.

10 Also included within two of the depositions were wafer stacks, as described in Example 3 above. The measurements from on these wafer stacks indicated that the conformality decreased from 51 % to 38 % when decreasing the stage separation distance from 4" to 1". Morphology changes were also observed as stage spacing was decreased, where the formation of particles and coating blisters increased as stage separation decreased.

15 **Table 6. Deposition Rates measured on Top and Bottom Shelves
at Various Separation Distances.**

Stage spacing (inches)	Top shelf deposition rate (nm/min)	Bottom shelf deposition rate (nm/min)	Bottom shelf wafer stack conformality	Coating morphology
4	2.9	2.8	51 %	Smooth and dense coating
3	2.9	2.9	--	Smooth and dense coating
2	2.7	2.7	--	Slight particle/blister formation
1	2.8	3.8	38 %	Particle/blister formation

Example 6 – Dielectric Constant of SACVD Coatings

20 This example describes methods of altering the electrical properties of materials produced by SACVD using heat treatments.

Methods:

Dielectric constant measurements were carried out by measurement of a parallel plate capacitor structure fabricated in the following manner. First, commercially purchased indium tin oxide (ITO) coated glass slides were used as the bottom conductive plate. Onto this substrate, pV3D3 depositions with resulting coating thicknesses ranging from 0.5 μm – 4 μm were produced using iPECVD, iCVD, SACVD as described in the above examples. Post deposition heat treatment was conducted on a subset of the samples by heating the coatings in dry air to 300 °C for 15 hours or 400 °C for 3 hours. Electron beam physical vapor deposition was used to deposit 10 nm of chromium followed by 200 nm of Au with a shadow mask containing 0.0625'' diameter circles to generate the top plate of the capacitor. The indium tin oxide (ITO) coated glass was exposed via physical abrasion near the edge of the sample and contact to the bottom and top plates were made using a wafer probe station. A schematic and picture of the measurement setup is shown in Figure 12.

Capacitance measurements were carried out using a capacitance measurement unit around the frequency of 1-10 kHz at 2 V with the model of a capacitor and resistance in series modeling the contact resistance to the electrodes and capacitance of the dielectric layer. The average capacitance value (C) in this frequency range along with the thickness of the coating (t), the permittivity of free space (ϵ_0) and the surface area of the top plate (A) was used to calculate the dielectric constant (k), with the assumption of an ideal parallel plate capacitor based on using the following equation:

$$k = \frac{Cd}{\epsilon_0 A}$$

Results:

The measurements taken showed a statistically significant increase in the dielectric constant prior to and following thermal treatment, as detailed in Figure 13, indicating that heat treatment can increase dielectric constant.

After measuring the dielectric constant, X-ray photoelectron spectroscopy was used to compare the composition of the native coating to the thermally treated coating with the results summarized below in Table 7. Changes in the composition and dielectric constant are also known to alter related materials properties including dielectric strength or breakdown voltage. (McPherson, J.W.; Jinyoung Kim; Shanware, A.; Mogul, H.;

Rodriguez, J.. (2003). Trends in the ultimate breakdown strength of high dielectric-constant materials. , 50(8), 1771–1778. doi:10.1109/ted.2003.815141).

**Table 7. Elemental composition of pV3D3 coatings
before and after thermal treatment.**

	Elemental Composition % 5		
Sample	C	O	Si
pV3D3 no heat treatment	58	23	19
pV3D3 400 °C dry air	28	46	26

Unless defined otherwise, all technical and scientific terms used herein have the same meanings as commonly understood by one of skill in the art to which the disclosed
10 invention belongs. Publications cited herein and the materials for which they are cited are specifically incorporated by reference.

Those skilled in the art will recognize, or be able to ascertain using no more than routine experimentation, many equivalents to the specific instances of the invention described herein. Such equivalents are intended to be encompassed by the following
15 claims.

We claim:

1. A method for forming a polymeric coating on at least one substrate or material, the method comprising the steps of:
 - (i) placing the at least one substrate or material into a reaction chamber;
 - (ii) sealing and purging the reaction chamber under a vacuum;
 - (iii) wherein the reaction chamber is at an initiation temperature sufficient to activate one or more gaseous initiators;
wherein one or more surfaces of the at least one substrate or material have a surface temperature equal to or substantially equal to the initiation temperature; and
 - (iv) flowing one or more gaseous monomers, the one or more gaseous initiators, and optionally one or more carrier gases into the reaction chamber to form the polymeric coating on at least a portion of a surface of the at least one substrate or material;
wherein the partial pressure of the one or more gaseous monomers is sufficient to form the polymeric coating on the portion of the surface at the initiation temperature;
optionally wherein the surface temperature during step (iv) is sufficient to preclude the one or more gaseous monomers or the one or more gaseous initiators from exceeding their saturation pressure at the surface temperature;
wherein the one or more gaseous monomers comprise one or more silicon-containing monomers;
wherein the polymeric coating comprises silicon, oxygen, hydrogen, and carbon;
wherein the polymeric coating has an atomic carbon content in a range of about 2 to 70% of the total atomic composition of the polymeric coating.
2. A method for forming a polymeric coating on at least one substrate or material, the method comprising the steps of:
 - (i) placing the at least one substrate or material onto a platform within a reaction chamber;
wherein the reaction chamber and/or components thereof and the platform are independently temperature controlled;
 - (ii) sealing and purging the reaction chamber under a vacuum;

(iii) wherein the platform is at an initiation temperature sufficient to activate one or more gaseous initiators;

wherein one or more surfaces of the at least one substrate or material have a surface temperature equal to or substantially equal to the initiation temperature; and

(iv) flowing one or more gaseous monomers, the one or more gaseous initiators, and optionally one or more carrier gases into the reaction chamber to form the polymeric coating on at least a portion of a surface of the at least one substrate or material;

wherein the reaction chamber and/or components thereof are independently heated to a reaction chamber temperature, wherein the reaction chamber temperature is lower than the initiation temperature and the surface temperature during step (iv); optionally wherein the components comprise walls of the reaction chamber;

wherein the partial pressure of the one or more gaseous monomers is sufficient to form the polymeric coating on the portion of the surface at the surface temperature;

optionally wherein the reaction chamber temperature during step (iv) is sufficient to preclude the one or more gaseous monomers or the one or more gaseous initiators from exceeding their saturation pressure at the reaction chamber temperature;

wherein the one or more gaseous monomers comprise one or more silicon-containing monomers;

wherein the polymeric coating comprises silicon, oxygen, hydrogen, and carbon; wherein the polymeric coating has an atomic carbon content in a range of about 2 to 70% of the total atomic composition of the polymeric coating.

3. A method for forming a polymeric coating on at least one substrate or material, the method comprising the steps of:

(i) placing the at least one substrate or material into a reaction chamber;

(ii) sealing and purging the reaction chamber under a vacuum;

(iii) wherein the reaction chamber is at an initiation temperature sufficient to activate one or more gaseous initiators;

wherein one or more surfaces of the at least one substrate or material have a surface temperature equal to or substantially equal to the initiation temperature; and

(iv) flowing one or more gaseous monomers, the one or more gaseous initiators, and optionally one or more carrier gases into the reaction chamber to form the polymeric coating on at least a portion of a surface of the at least one substrate or material;

wherein the partial pressure of the one or more gaseous monomers is sufficient to form the polymeric coating on the portion of the surface at the initiation temperature;

optionally wherein the surface temperature during step (iv) is sufficient to preclude the one or more gaseous monomers or the one or more gaseous initiators from exceeding their saturation pressure at the surface temperature;

wherein the one or more gaseous monomers comprise one or more silicon-containing monomers;

wherein the polymeric coating comprises silicon, nitrogen, hydrogen, and carbon; wherein the polymeric coating has an atomic carbon content in a range of about 2 to 70% of the total atomic composition of the polymeric coating.

4. A method for forming a polymeric coating on at least one substrate or material, the method comprising the steps of:

(i) placing the at least one substrate or material onto a platform within a reaction chamber;

wherein the reaction chamber and/or components thereof and the platform are independently temperature controlled;

(ii) sealing and purging the reaction chamber under a vacuum;

(iii) wherein the platform is at an initiation temperature sufficient to activate one or more gaseous initiators;

wherein one or more surfaces of the at least one substrate or material have a surface temperature which is equal to or substantially equal to the initiation temperature; and

(iv) flowing one or more gaseous monomers, the one or more gaseous initiators, and optionally one or more carrier gases into the reaction chamber to form the polymeric coating on at least a portion of a surface of the at least one substrate or material;

wherein the reaction chamber and/or components thereof are independently heated to a reaction chamber temperature, wherein the reaction chamber temperature is lower than the

initiation temperature and the surface temperature during step (iv); optionally wherein the components comprise walls of the reaction chamber;

wherein the partial pressure of the one or more gaseous monomers is sufficient to form the polymeric coating on the one or more surfaces of the portion of the surface at the initiation temperature;

optionally wherein the reaction chamber temperature during step (iv) is sufficient to preclude the one or more gaseous monomers or the one or more gaseous initiators from exceeding their saturation pressure at the reaction chamber temperature;

wherein the one or more gaseous monomers comprise one or more silicon-containing monomers;

wherein the polymeric coating comprises silicon, nitrogen, hydrogen, and carbon; wherein the polymeric coating has an atomic carbon content in a range of about 2 to 70% of the total atomic composition of the polymeric coating.

5. The method of any one of claims 1-4, wherein the polymeric coating forms via vinyl polymerization, wherein the one or more gaseous monomers comprise monomers having at least one vinyl moiety thereon.

6. The method of claim 5, wherein the vinyl polymerization is a free-radical vinyl polymerization.

7. The method of any one of claims 1-6, wherein the polymeric coating has a microscale conformality to the surface of at least about 50%, as determined by microtrench method.

8. The method of claim 7, wherein the microscale conformality is at least about 60%, 65%, 70%, 75%, 80%, 90%, 95%, 96%, 97%, 98%, 99%, or 99.9%, as determined by the microtrench method.

9. The method of any one of claims 1-8, wherein the initiation temperature ranges from about 50 °C to about 400 °C, about 50 °C to about 300 °C, about 50 °C to about 200 °C, or about 50 °C to about 100 °C.

10. The method of any one of claims 1-9, wherein the one or more gaseous monomers comprise carbon-containing monomers each independently having an atomic carbon content of at least about 25%, 30%, 35%, 40%, 45%, 50%, 55%, 60%, 65%, 70%, 75%, 80%, 85%, 90%, 95%, or 100% of the total atomic composition of the carbon-containing monomer; or in a range from about 25% to 100% of the total atomic composition of the carbon-containing monomer.

11. The method of any one of claims 1-10, wherein the one or more gaseous initiators comprise carbon-containing initiators each independently having an atomic carbon content of at least about 20%, 25%, 30%, 35%, 40%, 45%, 50%, 55%, 60%, 65%, 70%, 75%, or 80% of the total atomic composition of the carbon-containing initiator; or in a range from about 20% to 80% of the total atomic composition of the carbon-containing initiator.

12. The method of any one of claims 1-11, wherein the polymeric coating has an atomic carbon content in the range of about 2 to 5%, 2 to 10%, 2 to 15%, 2 to 20%, 2 to 30%, 2 to 40%, 2 to 50%, 2 to 60%, or 2 to 70%, of the total atomic composition of the polymeric coating.

13. The method of any one of claims 1-11, wherein the polymeric coating has an atomic carbon content in the range of about 5 to 70%, 5 to 65%, 5 to 60%, 5 to 55%, or 5 to 50% of the total atomic composition of the polymeric coating.

14. The method of any one of claims 1-11, wherein the polymeric coating has an atomic carbon content in the range of about 10 to 70%, 10 to 60%, 10 to 50%, or 10% to 40%, of the total atomic composition of the polymeric coating.

15. The method of any one of claims 1-11, wherein the polymeric coating has an atomic carbon content in the range of about 15 to 70%, 15 to 60%, 15 to 50%, or 15 to 40% of the total atomic composition of the polymeric coating.

16. The method of any one of claims 1-11, wherein the polymeric coating has an atomic carbon content in the range of about 2 to 50% of the total atomic composition of the polymeric coating.
17. The method of any one of claims 1-16, wherein the method further comprises a step of reducing organic content in the polymeric coating following step (iv), such as by applying an annealing step.
18. The method of claim 17, wherein the annealing step occurs during the flowing step (iv).
19. The method of claim 17, wherein the annealing step occurs after the flowing step (iv).
20. The method of claim 19, further comprising prior to the annealing step, transferring the substrate or material having the polymeric coating thereon into another chamber where the annealing step is carried out.
21. The method of any one of claims 17-20, wherein the annealing step occurs at a temperature ranging from about 200 °C to 800 °C, 200 °C to 750 °C, 200 °C to 700 °C, 200 °C to 650 °C, 200 °C to 600 °C, 200 °C to 550 °C, 200 °C to 500 °C, 200 °C to 450 °C, 200 °C to 400 °C, 200 °C to 350 °C, or 200 °C to 250 °C.
22. The method of any one of claims 17-21, wherein the annealing step is carried out under a process gas selected from the group consisting of nitrogen, argon, ammonia, hydrogen, syn gas, and combinations thereof; and
wherein the process gas is free or substantially free of oxygen (O₂) gas; or
wherein the process gas comprises oxygen (O₂) gas or air.
23. The method of any one of claims 17-22, wherein the annealing step occurs for a time period ranging from about 5 minutes to about 3 hours.

24. The method of any one of claims 17 and 19-23, wherein the annealing step occurs after step (iv) and wherein following the annealing step, the polymeric coating is denser, as compared to the polymeric coating formed in step (iv).
25. The method of any one of claims 17 and 18 -22, wherein the annealing step occurs after step (iv) and wherein following the annealing step, the mass of the polymeric coating is about 80%, 75%, 70%, 65%, 60%, 55%, 50%, 45%, 40%, 35%, 30%, 25%, 20%, 15%, 10%, 5%, 1%, or less of the mass of the polymeric coating formed in step (iv).
26. The method of any one of claims 17-25, wherein following the annealing step, the atomic carbon content of the polymeric coating is in the range of about 2 to 5%, 2 to 10%, 2 to 15%, 2 to 20%, 2 to 25%, or 2 to 30% of the total atomic composition of the polymeric coating.
27. The method of any one of claims 17-25, wherein following the annealing step, the atomic carbon content of the polymeric coating is in the range of about 5 to 10%, 5 to 15%, 5 to 20%, 5 to 25%, or 5 to 30% of the total atomic composition of the polymeric coating.
28. The method of any one of claims 17-25, wherein following the annealing step, the atomic carbon content of the polymeric coating is in the range of about 8 to 15%, 8 to 20%, 8 to 25%, or 8 to 30% of the total atomic composition of the polymeric coating.
29. The method of any one of claims 17-25, wherein following the annealing step, the atomic carbon content of the polymeric coating is in the range of about 15 to 20%, 15 to 25%, or 15 to 30% of the total atomic composition of the polymeric coating.
30. The method of any one of claims 17-25, wherein following the annealing step, the atomic carbon content of the polymeric coating is in the range of about 2 to 30% of the total atomic composition of the polymeric coating.
31. The method of any one of claims 17-30, wherein the polymeric coating is free or substantially free of pin-holes and/or defects.

32. The method of any one of claims 1-31, wherein the one or more gaseous monomers is selected from the group consisting of acrylate monomers, methacrylate monomers, vinyl-containing monomers, paracyclophane monomers, oxirane-based monomers, and combinations thereof.

33. The method of claim 32, wherein:

the acrylate monomers are selected from the group consisting of hydroxyethyl acrylate, ethylene glycol diacrylate, 1H,1H,2H,2H-perfluorodecyl acrylate, and combinations thereof;

the methacrylate monomers are selected from the group consisting of hydroxyethyl methacrylate, ethylene glycol dimethacrylate, 1H,1H,2H,2H-perfluorodecyl methacrylate, and combinations thereof; and/or

the vinyl containing monomers are selected from the group consisting of 1,3,5-trivinyl-1,3,5-trimethylcyclotrisiloxane, divinylbenzene, 4-vinylpyridine, styrene, 1H,1H,2H-perfluoro-1-dodecene, di(ethylene glycol) divinyl ether, and combinations thereof.

34. The method of claim 32, wherein the paracyclophane monomers are selected from the group consisting of [2,2]paracyclophane, dichloro-[2,2]-paracyclophane, 1,1,2,2,9,9,10,10-octafluoro[2,2]paracyclophane, and 4,5,7,8,12,13,15,16-octafluoro[2,2]paracyclophane, and combinations thereof.

35. The method of claim 32, wherein the oxirane-based monomer is hexafluoropropylene oxide.

36. The method of any one of claims 1-35, wherein the one or more gaseous initiators comprise peroxide-based initiators, persulfate-based initiators, sulfate-based initiators, azonitrile-based initiators, and/or ionic (i.e. cationic or anionic) thermal-based initiators, and combinations thereof.

37. The method of claim 36, wherein the peroxide-based initiators are selected from the group consisting of tert-butyl hydroperoxide, cumene hydroperoxide, tert-amyl

hydroperoxide, p-menthane hydroperoxide, di-tert-butyl peroxide, tert-butylperoxybenzoate, dicumyl peroxide, benzoyl peroxide, 1,1-bis(tert-butylperoxy)cyclohexane, 1,1-di(tert-amyloxy)cyclohexane, 1,1-di(tert-butylperoxy)-3,3,5-trimethylcyclohexane, tert-butyl peracetate, tert-butyl peroxy-pivalate, tert-amyloxy-pivalate, hydrogen peroxide, di(4-tert-butylcyclohexyl)peroxydicarbonate, 2,2-di(tert-butylperoxy)butane, dicetylperoxydicarbonate, di(2-ethylhexyl)peroxydicarbonate, acetylacetone peroxide, methyl ethyl ketone peroxide, methyl isobutyl ketone peroxide, tert-amyloxy-2-ethylhexylcarbonate, tert-butylperoxy-2-ethylhexylcarbonate, 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane, 2,5-dimethyl-2,5-di(tert-butylperoxy)hexyne-3, di(2,4-dichlorobenzoyl)peroxide, di(3,5,5-trimethylhexanoyl)peroxide, tert-butylperoxy-3,5,5-trimethylhexanoate, dilauroyl peroxide, dimyristylperoxydicarbonate, tert-butylperoxy-2-ethylhexanoate, tert-butylperoxy-2-ethylhexylcarbonate, tert-butylperoxyneodecanoate, disuccinoylperoxide, tert-butylperoxy-isobutyrate, 1,1,3,3-Tetramethylbutylperoxyneodecanoate, and combinations thereof.

38. The method of claim 36, wherein the persulfate-based initiators are selected from the group consisting of ammonium persulfate, potassium persulfate, sodium persulfate, and combinations thereof.

39. The method of claim 36, wherein the sulfate-based initiator is potassium peroxymonosulfate.

40. The method of claim 36, wherein the azonitrile-based initiators are selected from the group consisting of 2,2'-azobis(isobutyronitrile), 2,2'-azobis(2-methylbutyronitrile), 2,2'-azobis(2,4-dimethylvaleronitrile), 2,2'-azobis[2-(2-imidazolin-2-yl)propane], 2,2'-azobis[2-(2-imidazolin-2-yl)-propane] dihydrochloride, 2,2'-azobis(2-methylpropionamidine) dihydrochloride, 2,2'-azobis(N-(2-hydroxyethyl)-2-methylpropionamide), 4,4'-azobis(4-cyanovaleric acid), 2,2'-azobis[N-(2-carboxyethyl)-2-methylpropionamidine]tetrahydrate, dimethyl 2,2'-azobis(2-methylpropionate), 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile), 1,1'-azobis(cyclohexane-1-carbonitrile), 2,2'-azobis(N-butyl-2-methylpropionamide), 2,2'-azobis(2,4,4-trimethylpentane), and combinations thereof.

41. The method of claim 36, wherein the ionic thermal-based initiators are selected from the group consisting of dicyandiamide, cyclohexyl tosylate, (4-hydroxyphenyl)-dimethylsulfonium hexafluorophosphate, diphenyl(methyl)sulfonium tetrafluoroborate, benzyl(4-hydroxyphenyl)-methylsulfonium hexafluoroantimonate, (4-hydroxyphenyl)methyl-(2-methylbenzyl)sulfonium hexafluoroantimonate, triphenylsulphonium nonaflate, and combinations thereof.
42. The method of any one of claims 1-41, wherein the time period between steps (i) and (iii) is a dwell time during which the temperature of the surface of the substrate increases to the surface temperature, and wherein the dwell time is at least about 1, 2, 3, 4, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, or 60 minutes.
43. The method of any one of claims 1-42, wherein step (iv) is performed for a period of time ranging from about 1 to 800 minutes.
44. The method of any one of claims 1-43, wherein the polymeric coating is formed under a pressure ranging from about 1 to 760,000 mTorr.
45. The method of any one of claims 1-43, wherein the polymeric coating is formed under a pressure ranging from about 100 mTorr to 10 Torr.
46. The method of any one of claims 1-45, wherein during step (iv), the one or more gaseous monomers, the one or more gaseous initiators, and/or the one or more carrier gases flow continuously through the reaction chamber.
47. The method of any one of claims 1-45, wherein during step (iv), the one or more gaseous monomers, the one or more gaseous initiators, and/or the one or more carrier gases do not flow continuously through the reaction chamber.
48. The method of any one of claims 2 or 4, wherein the at least one substrate or material comprises a plurality of substrates and/or materials and wherein optionally each of the

substrates and/or materials in the plurality is independently placed on a separate temperature-controlled platform;

or

wherein the at least one substrate or material comprises a plurality of substrates and/or materials and wherein the plurality is placed in a carrier which is placed on the temperature-controlled platform.

49. The method of any one of claims 1-48, wherein step (iv) is repeated one or more times with the same or different types of the one or more gaseous monomers and/or the one or more gaseous initiators to form a polymeric coating comprising a plurality of layers;

wherein the method further comprises changing the initiation temperature when a different type of the one or more gaseous initiators is used.

50. The method of claim 49, wherein at least one of the plurality of layers is formed of a second polymer that is different from a first polymer forming at least one other layer of the plurality of layers.

51. The method of any one of claims 1-48, wherein the at least one polymeric coating is formed of two or more polymers, copolymers, and/or one or more cross-linked polymers by flowing at least two different types of the one or more gaseous monomers during step (iv); and wherein one or more gaseous crosslinkers are further optionally flowed during step (iv), when forming the cross-linked polymers.

52. The method of any one of claims 1-51, wherein the initiation temperature is selected to provide a deposition rate of the polymeric coating of at least about 0.1 nm/min to 100 nm/min.

53. The method of any one of claims 1-52, wherein the at least one substrate or material is treated prior to step (i),

wherein the treatment is selected from the group consisting of silane deposition, electron beam, IR radiation, gamma radiation, plasma exposure, thermal treatment, laser exposure, and combinations thereof.

54. The method of any one of claims 1-53, further comprising treating the polymeric coating on the at least one substrate or material following step (iv), with a treatment selected from the group consisting of electron beam, IR radiation, gamma radiation, plasma exposure, thermal treatment, laser exposure, and combinations thereof.
55. The method of any one of claims 1-54, wherein the polymeric coating formed is a dielectric coating or film.
56. The method of claim 55, wherein the dielectric coating has a dielectric constant of less than about 4, less than about 3.5, or less than about 3.
57. The method of claim 55, wherein the dielectric coating exhibits a dielectric breakdown voltage of between greater than or equal to 1000 V/mil and less than or equal to 25000 V/mil.
58. The method of claim 55, wherein the dielectric coating exhibits a leakage current of less than about 1×10^{-12} A/m², 1×10^{-11} A/m², 1×10^{-10} A/m², 1×10^{-9} A/m², 1×10^{-8} A/m², 1×10^{-7} A/m², 1×10^{-6} A/m², 1×10^{-5} A/m², or 1×10^{-4} A/m².
59. The method of any one of claims 1-2, wherein the one or more silicon-containing monomers are selected from the group consisting of 1,3,5-trivinyl-1,3,5-trimethylcyclotrisiloxane, 1,3,5,7-tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane, 1,3-divinyltetramethyldi siloxane, divinyl dimethylsilane, 1,4-divinyltetramethyl-disiylethane, 1,5-divinyl-3,3-diphenyl-1,1,5,5-tetramethyltrisiloxane, 1,3-divinyl-1,3-diphenyl-1,3-dimethyldisiloxane, 1,5-divinyl-3-phenylpentamethyltrisiloxane, 1,5-divinylhexamethyltrisiloxane, 1,2-divinyltetramethyldisilane, 1,3,5-trivinyl-1,1,3,5,5-pentamethyltrisiloxane, trivinylsilane, trivinylmethylsilane, tetravinylsilane, and combinations thereof.
60. The method of any one of claims 1-2, wherein the one or more silicon-containing monomers are selected from the group consisting of 1,3,5-trivinyl-1,3,5-

trimethylcyclotrisiloxane, 1,3,5,7-tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane, pentavinylpentamethylcyclopentasiloxane, 1,3-divinyltetramethyldisiloxane, divinyl dimethylsilane, 1,4-divinyltetramethyl-disiylethane, 1,5-divinyl-3,3-diphenyl-1,1,5,5-tetramethyltrisiloxane, 1,3-divinyl-1,3-diphenyl-1,3-dimethyldisiloxane, 1,5-divinyl-3-phenylpentamethyltrisiloxane, 1,5-divinylhexamethyltrisiloxane, 1,2-divinyltetramethyldisilane, 1,3,5-trivinyl-1,1,3,5,5-pentamethyltrisiloxane, trivinylsilane, trivinylmethylsilane, tetravinylsilane, vinylpentamethylcyclotrisiloxane, 1,4-bis(vinyl dimethylsilyl)benzene, vinylphenyldimethylsilane, vinylsilatrane, vinylpentamethyldisiloxane, vinyl-1,1,3,3-tetramethyldisiloxane, hexavinyl disiloxane, p-(t-butyl dimethylsiloxy)styrene, and combinations thereof.

61. The method of any one of claims 3-4, wherein the one or more silicon-containing monomers are selected from the group consisting of bis(dimethylamino)vinylmethylsilane, 1,3-divinyl-1,1,3,3-tetramethyldisilazane, 1,3,5-trivinyl-1,3,5-trimethylcyclotrisilazane, 1,3,5,7-tetravinyl-1,3,5,7-tetramethylcyclotetrasilazane, and combinations thereof.

62. The method of any one of claims 3-4, wherein the one or more silicon-containing monomers are selected from the group consisting of bis(dimethylamino)vinylmethylsilane, 1,3-divinyl-1,1,3,3-tetramethyldisilazane, 1,3,5-trivinyl-1,3,5-trimethylcyclotrisilazane, 1,3,5,7-tetravinyl-1,3,5,7-tetramethylcyclotetrasilazane, 3-(n-styrylmethyl-2-aminoethylamino) propyltrimethoxysilane, styrylmethoxy(polyethyleneoxide), and combinations thereof.

63. The method of any one of claims 1-62, wherein the method is performed without the use of heating with hot filaments, resistance heating, induction heating, radiant heating, electron beam, laser exposure, radiofrequency (RF), microwave excitation, ultraviolet (UV), infrared (IR) radiation, and/or gamma radiation to initiate or cause decomposition of the one or more gaseous initiators or gaseous monomers.

64. A polymeric coating on at least a portion of a surface of the substrate or material, formed according to the method of any one of claims 1-63.

65. The polymeric coating of claim 64, wherein the polymeric coating and the substrate or material are included in or form at least part of a semiconductor device.
66. The polymeric coating of claim 64, wherein the semiconductor device is a semiconductor circuit.
67. The polymeric coating of any one of claims 64-66, wherein the polymeric coating is a dielectric coating or film.
68. The polymeric coating of any one of claims 64-66, wherein the polymeric coating acts as an optical material, such as a nonreflective coating or waveguide.
69. The polymeric coating of any one of claims 64-66, wherein the polymeric coating acts as a barrier layer that reduces or prevents migration of a metal through the polymeric coating.
70. The polymeric coating of claim 69, wherein the metal is selected from the group consisting of copper, gold, silver, tin, nickel, and combinations thereof.
71. The polymeric coating of claim 69, wherein the metal is copper.
72. The polymeric coating of any one of claims 64-71, wherein the polymeric coating is thermally stable when heated to a temperature of at least about 400 °C, 500 °C, 600 °C, 700 °C, or 800 °C.
73. A device comprising:
a substrate;
a first polymeric coating which acts as a barrier layer that reduces or prevents migration of a metal through the first polymeric coating; and
a second polymeric coating which is a dielectric coating on top of the first polymeric coating;
wherein the first and the second polymeric coatings are formed according to the method of any one of claims 1-63.

74. The device of claim 72, wherein the first polymeric coating has a thickness which is less than the second polymeric coating's thickness.

75. The device of claim 72, wherein the first polymeric coating has a thickness which is about 25%, 20%, 15%, 10%, 5%, or 1% of the thickness of the second polymeric coating.