

SURFACE ACTIVATED CHEMICAL VAPOR DEPOSITION AND USES THEREOF

5 CROSS-REFERENCE TO RELATED APPLICATION

This application claims the benefit of and priority to U.S. Provisional Application No. 63/510,920, filed June 29, 2023, which is hereby incorporated by reference in its entirety.

10 FIELD OF THE INVENTION

This invention is in the field of polymeric coatings formed via surface activated chemical vapor deposition methods.

BACKGROUND OF THE INVENTION

15 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
20 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
25 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
30 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.

5 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, for example, microelectronics stacks, boards, electronic device components, and 3-D integrated heterogeneous packages, having high aspect ratio features, and can benefit from coatings exhibiting
10 high conformality which provide protective 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 protective benefits to coated
15 substrates and devices.

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

SUMMARY OF THE INVENTION

20 Methods for surface activated chemical vapor deposition (SACVD) and uses thereof to form highly conformal coatings are described herein. 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 be *in situ* coated with a polymer. The SACVD methods can be used to deposit one or more conformal polymeric
25 coatings on various types of substrates or devices, such as microelectronics, that have one or more high aspect ratio features thereon. Forming highly conformal coatings on such devices can be achieved using the SACVD methods described herein.

 In a first instance, surface activated chemical vapor deposition (SACVD) may be carried out under isothermal conditions. Under isothermal conditions, at least one
30 substrate or device to be coated 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 methods, heating to the initiation temperature also heats one or more

surfaces of the substrate(s) or device(s) within the reaction chamber to decompose the one or more initiators and thereby form/deposit a polymeric coating on at least a portion of the one or more surfaces of the substrate(s) or device(s).

A non-limiting first example of an isothermal SACVD method includes:

- 5 (i) placing the at least one substrate or device 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;

10 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 the one or more surfaces of the at least one substrate or
15 device;

wherein the partial pressure of the one or more gaseous monomers is sufficient to form the polymeric coating on the portion of the one or more surfaces of the at least one substrate or device at the surface temperature.

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.

In some instances, the polymeric coating formed on the one or more surfaces of the at least one substrate or device has a conformality of at least about 50%, as determined by wafer stack method; and/or wherein the polymeric coating formed on the
25 one or more surfaces of the at least one substrate or device has a microscale conformality of at least about 60%, as determined by microtrench method.

Prior to step (iv), the one or more surfaces of the at least one substrate or device have a surface temperature which is equal or substantially equal to the initiation temperature. During step (iv), the partial pressure of the one or more gaseous monomers
30 is sufficient for the one or more gaseous monomers to adsorb on the one or more surfaces of the at least one substrate or device at the surface temperature. Further, the

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

A non-limiting second example of an isothermal SACVD method includes:

- (i) sealing and purging a reactor under a vacuum;
- 5 (ii) wherein the reaction chamber is at an initiation temperature sufficient to activate one or more gaseous initiators; and
- (iii) introducing one or more gaseous monomers, one or more gaseous initiators, and optionally one or more carrier gases, into the reactor.

Prior to step (iii), one or more surfaces of the reactor have a surface temperature
10 that is equal or substantially equal to the initiation temperature. Following step (iii), a polymeric coating is formed on the one or more surfaces of the reactor that has a conformality of at least about 50%, as determined by the wafer stack method; and/or a polymeric coating is formed on the one or more surfaces of the reactor that has a microscale conformality of at least about 60%, as determined by the microtrench
15 method.

In other instances, a surface activated chemical vapor deposition (SACVD) may be carried out under non-isothermal conditions. Under non-isothermal conditions, at least one substrate or device to be coated is placed within a reaction chamber. The at least one substrate or device is placed on a temperature-controlled heating platform ("platform")
20 which can independently heat the at least one substrate or device and surface(s) in contact therewith. The platform is configured to support one or more substrates or devices within a reaction chamber during coating. The platform optionally retains and positions the one or more substrates or devices in a desired location on the platform. In such methods, the reaction chamber is independently heat controlled from the platform.
25 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 a sufficient temperature to decompose the one or more initiators and thereby form/deposit a polymeric coating on a least a portion of the one or more surfaces of the
30 substrate(s) or device(s). In such methods, the reaction chamber and/or components thereof are independently heated to a reaction chamber temperature that is lower than the

initiation temperature and is lower than the surface temperature. The reaction chamber components include the walls of the reaction chamber.

In one non-limiting example, a non-isothermal method includes

- 5 (i) placing the at least one substrate or device onto a platform within a reaction chamber;
- (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;
- 10 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 the one or more surfaces the at least one substrate or
- 15 device;

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

20 wherein the partial pressure of the one or more gaseous monomers is sufficient to form the polymeric coating on the portion of the one or more surfaces of the at least one substrate or device at the surface temperature.

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

25 from exceeding their saturation pressure at the reaction chamber temperature.

In some instances, the polymeric coating formed on the one or more surfaces of the at least one substrate or device has a conformality of at least about 50%, as determined by wafer stack method; and/or wherein the polymeric coating formed on the one or more surfaces of the at least one substrate or device has a microscale conformality

30 of at least about 60%, as determined by microtrench method.

During step (i), the platform and the reaction chamber and/or components thereof are independently temperature controlled. Prior to step (iv), one or more surfaces of the

at least one substrate or device have a surface temperature which is equal or substantially equal to the initiation temperature. During step (iv), the reaction chamber and/or components thereof are independently heated to a reaction chamber temperature that is lower than the initiation temperature, optionally the components comprise walls of the reaction chamber. During step (iv), the partial pressure of the one or more gaseous monomers is sufficient for the one or more gaseous monomers to adsorb on the at least one substrate or device at the surface temperature. Further, 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.

10 The SACVD methods described herein can be used to deposit/form polymeric coating(s) on surface(s) of a substrate or device having a degree of conformality, which are difficult to achieve using other deposition methods. In some instances, a substrate or device includes a polymeric coating on at least one surface of the substrate or device. The polymeric coating formed using the SACVD methods described herein:

15 has a conformality, as determined by the wafer stack method, and has a step coverage of at least 50%, at least 60%, at least 65%, at least 70%, at least 75%, at least 80%, at least 85%, or at least 90% or more; and/or
 has a microscale conformality, as determined by the microtrench method, of at least 60%, at least 65%, at least 70%, at least 75%, at least 80%, at least
20 85%, or at least 90%, or more.

 In some instances, the coated devices are, 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
25 references, frequency selective filters, miniaturized arrays, digital to analog converters, analog to digital converters, and/or low noise amplifiers or one or more substrates thereof. The conformal polymeric coatings on the surface(s) of such devices or substrates thereof can provide protection from the environment, mechanical protection, electrical insulation, electrical protection, and/or can impart optical effects, modify surface
30 properties, and/or enhance biological or chemical compatibility.

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. 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 non-limiting 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 exemplary 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.

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.

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.

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.

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.

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

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.

5 **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
10 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.
15 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
20 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 generally undergoes a chemical modification during the polymerization process, and
25 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 measurements. A conformal coating can be considered highly conformal when it has a
30 conformality of at least about 50%, as determined by the wafer stack method.

“Microscale conformality,” as used herein, refers to 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 a microscale conformality of at least about 60%, as determined by the microtrench method.

“Gaseous polymerizable species”, as used herein, refers to reactive species which
5 can be generated in the gas phase and upon polymerization form a polymer. The term
“gaseous polymerizable species” includes monomers, oligomers, and metal-organic
compounds. The gaseous polymerizable species disclosed 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
10 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
chamber.

Numerical ranges disclosed in the present application include, but are not limited
15 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
20 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
25 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
30 be *in situ* coated with a polymer. As result of direct formation of such species on
surface(s) of substrate or device, 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 free radical initiators, at the filaments which need to diffuse to a substrate or device, in addition to penetrating any geometric intricacies that may exist therein. Due to their
5 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 toward the substrate or device, as well throughout a geometrically complex substrate or device. When such species are required to diffuse from a distant filament, the result is a
10 degree of preferential deposition within line of sight of the filaments. In contrast, SACVD is expected to produce reactive species, such as radical species, directly on areas of the one or more surfaces of a substrate or device 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. Various methods of
15 SACVD are described below.

The SACVD methods described can be used to deposit one or more polymeric coatings on a substrate or device. Certain substrates or devices, for instance, microelectronics stacks, boards, electronic device components, and 3-D integrated heterogeneous packages can have one or more high aspect ratio features thereon and
20 forming highly conformal coatings can be thereon can be achieved using the SACVD methods described herein.

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-1B. The wafer stack can include top and bottom pieces 110 and 120 separated by two side-strips
25 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
30 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

- 5 To express conformality as a percentage, by way of the wafer stack method, the following equation can be used:
- $$\frac{(\text{Thinnest thickness of polymeric coating within tunnel feature})}{(\text{Thickness of polymeric coating at opening of tunnel feature})} \times 100$$
- 10 where the higher the percentage value, the higher the degree of conformality. 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.
- 15 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 40%, when tested using a wafer stack having the dimensions of the reference wafer stack described above, or a conformality that ranges from about 40% to about 90%, or higher,
- 20 as determined using the wafer stack method. In some instances, the conformality is at least about 40%, 45%, 50%, 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.
- 25 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

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

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

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

Using the microtrench method, the microscale 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 microscale conformality of at least about 50%, when tested using a microtrench having the dimensions of the reference microtrench described above, or a conformality that ranges from about 50% to about 90%, or higher, as determined using the microtrench method. In some instances, the microscale conformality is at least about 50%, 55%, 60%, 65%, 70%, 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 devices and/or surfaces containing complex and/or high aspect ratio features, such as can be found in 3-D heterogeneous integrated packages (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. Isothermal Surface Activated Chemical Vapor Deposition

In a first instance, a surface activated chemical vapor deposition (SACVD) may be carried out under isothermal conditions. Under isothermal conditions, at least one substrate or device to be coated by a polymeric coating (or polymeric film) is placed
5 within a reaction chamber and the reaction chamber is heated to an initiation temperature sufficient to activate one or more gaseous initiators. In such 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 one or more initiators and formation/deposition of a polymeric coating on at least a portion of the one or more
10 surfaces of the substrate(s) or device(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
15 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
20 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.

25 A non-limiting first example of an isothermal SACVD method can include the steps of:

- (i) placing the at least one substrate or device 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
30 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 the one or more surfaces of the at least one substrate or device;

wherein the partial pressure of the one or more gaseous monomers is sufficient to form the polymeric coating on the portion of the one or more surfaces of the at least one
10 substrate or device at the surface temperature.

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 some instances, the polymeric coating formed on the one or more surfaces of
15 the at least one substrate or device has a conformality of at least about 40%, as determined by wafer stack method; and/or wherein the polymeric coating formed on the one or more surfaces of the at least one substrate or device has a microscale conformality of at least about 50%, as determined by microtrench method.

Prior to step (iv), one or more surfaces of the at least one substrate or device have
20 a temperature which is equal or substantially equal to the initiation temperature. During step (iv), the partial pressure of the one or more gaseous monomers is sufficient for the one or more gaseous monomers to adsorb on the one or more surfaces of the at least one substrate or device at the surface temperature. In addition, the partial pressure of the one or more gaseous monomers is sufficient to form the polymeric coating on the portion of
25 the surface at the surface temperature.

In certain instances of the above method, the at least one substrate or device is a plurality of substrates and/or devices and optionally each of the substrates and/or devices in the plurality is independently placed on a separate temperature-controlled platform.

In an alternative to the above isothermal method, the substrate to be coated may
30 act as a reaction chamber or reactor itself. In such instances, the reactor and one or more surfaces of the reactor, intended to be coated by a polymeric coating (or polymeric film), are heated to an initiation temperature sufficient to activate one or more gaseous

initiators. Heating the reactor to an initiation temperature allows for decomposition of the one or more initiators and formation/deposition of a polymeric coating on at least a portion of the one or more surfaces of the reactor.

5 A non-limiting second example of an isothermal SACVD method can include the steps of:

- (i) sealing and purging a reactor under a vacuum;
- (ii) wherein the reaction chamber is at an initiation temperature sufficient to activate one or more gaseous initiators;; and
- (iii) introducing one or more gaseous monomers, one or more gaseous initiators,
10 and optionally one or more carrier gases, into the reactor to form a polymeric coating on at least a portion of one or more surfaces of the reactor.

Prior to step (iii), one or more surfaces of the reactor have a surface temperature that is equal or substantially equal to the initiation temperature. Following step (iii), the polymeric coating formed on the one or more surfaces of the reactor has a conformality
15 of at least about 50%, as determined by the wafer stack method; and/or the polymeric coating formed on the one or more surfaces of the reactor has a microscale conformality of at least about 60%, as determined by microtrench method.

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
20 of the surface of the substrate increases to become 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. 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
25 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 $\pm 10\%$, $\pm 9\%$, $\pm 8\%$, $\pm 7\%$, $\pm 6\%$, $\pm 5\%$, $\pm 4\%$, $\pm 3\%$, $\pm 2\%$, or $\pm 1\%$ of the selected initiation temperature. In some instances, the heating may be applied for at least about 1 to 90
30 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 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
5 within these ranges.

In some instances, following formation/deposition of the polymeric coating 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.

10 Each of the gaseous monomers, gaseous initiators, and optional carrier gases may flow continuously or non-continuously during the flowing step of the isothermal methods. 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. In instances, where
15 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
20 coating.

For the isothermal methods described, the flowing step may be repeated more than once 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.
25 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 forming another/different layer.

In some instances of the methods, the flowing step is repeated one or more times with the same or different types of the one or more gaseous monomers and/or the one or
30 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 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.

5 In some instances, the polymeric coating formed contains one or more polymers, copolymers, and/or one 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 polymers.

10 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.

 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
15 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, 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
20 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 exceed its saturation pressure on the substrate or device 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
25 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 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
30 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, initiator, and carrier gas. In order to avoid defects, such as blisters, the SACVD

deposition of the methods described would be operated such that the following conditions are satisfied simultaneously:

$$P_{\text{monomer}} < P_{\text{monomersat}}$$

$$P_{\text{initiator}} < P_{\text{initiatorsat}}$$

$$P_{\text{carriergas}} < P_{\text{carriergassat}}$$

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

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

$$P_{\text{monomer}} = P_{\text{total}} \times \frac{\text{Flowrate}_{\text{monomer}}}{\text{Flowrate}_{\text{monomer}} + \text{Flowrate}_{\text{initiator}} + \text{Flowrate}_{\text{carriergas}}}$$

$$P_{\text{initiator}} = P_{\text{total}} \times \frac{\text{Flowrate}_{\text{initiator}}}{\text{Flowrate}_{\text{monomer}} + \text{Flowrate}_{\text{initiator}} + \text{Flowrate}_{\text{carriergas}}}$$

$$P_{\text{carriergas}} = P_{\text{total}} \times \frac{\text{Flowrate}_{\text{carriergas}}}{\text{Flowrate}_{\text{monomer}} + \text{Flowrate}_{\text{initiator}} + \text{Flowrate}_{\text{carriergas}}}$$

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 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 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 device(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.

B. Non-Isothermal Surface Activated Chemical Vapor Deposition

In a second instance, a surface activated chemical vapor deposition (SACVD) may be carried out under non-isothermal conditions. 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 one substrate or device is placed on a temperature-controlled heating platform ("platform") which can independently heat the at least one substrate or device and surface(s) present thereon. The platform is configured to support one or more substrates or devices within a reaction chamber during coating and can independently heat the one or more substrates or devices in contact therewith. The platform optionally retains and positions the one or more substrates or devices. 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 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 device(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 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.

Non-isothermal SACVD differs over isothermal SACVD, as described above, in that it can be used to minimize the activation of reactive initiator and/or monomer species at sites that are distant from the substrate or device surface(s) to be coated. Accordingly, the opportunity for such activated species undesired diffusion of reactive species away from the substrate or device 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 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 device. 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 device (which is on a heated platform), and thermal control of the substrate or device is needed to provide for uniform heating thereof, such as in the case of thermally 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.

A non-limiting example of a non-isothermal method includes the steps of:

- (i) placing the at least one substrate or device onto a platform within a reaction chamber;
- (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 that 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 the one or more surfaces the at least one substrate or device;

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

during step (iv) and is lower than the surface temperature; 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 one or more surfaces of the at least one substrate or device at the surface temperature. 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 some instances, the polymeric coating formed on the one or more surfaces of the at least one substrate or device has a conformality of at least about 40%, as determined by wafer stack method; and/or wherein the polymeric coating formed on the one or more surfaces of the at least one substrate or device has a microscale conformality of at least about 50%, as determined by microtrench method.

During step (i), the platform and the reaction chamber and/or components thereof are independently temperature controlled. Prior to step (iv), one or more surfaces of the at least one substrate or device have a surface temperature which is equal or substantially equal to the initiation temperature. During step (iv), the reaction chamber and/or components thereof are independently heated to a reaction chamber temperature which is lower than the initiation temperature optionally wherein the components comprise walls of the reaction chamber. During step (iv), the partial pressure of the one or more gaseous monomers is sufficient for the one or more gaseous monomers to adsorb on the at least one substrate or device at the surface temperature. In addition, 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.

In certain instances of the above method, the at least one substrate or device is a plurality of substrates and/or devices and optionally each of the substrates and/or devices in the plurality can be independently placed on a separate temperature-controlled platform.

For the non-isothermal methods described herein, the temperature(s) to which the reaction chamber (and/or reaction chamber temperature) and/or components thereof is independently heated to can be selected to preclude the one or more gaseous monomers

and the one or more gaseous initiators partial pressures from exceeding their respective saturation pressures at the selected temperature.

In some instances, 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 become 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. Heating which 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) to be equal or substantially equal to the selected initiation temperature. In some instances, the heating is carried out for at least about 1 to 60 minutes, or any sub-ranges or individual value of minutes disclosed within.

The flowing step may be carried out for any suitable period of time sufficient to form/deposit a polymeric film having one or more desired properties, such as thickness. In some instances, the flowing step is 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 during the flowing step, the reaction chamber is purged and allowed to cool to room temperature (about 25 °C) followed by venting of the reaction chamber.

Each of the gaseous monomers, gaseous initiators, and optional carrier gases may be flowed continuously or non-continuously during the flowing step of the non-isothermal methods. 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. 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 non-isothermal methods described, the flowing step may be repeated more than once 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
5 differs from the polymer forming another/different layer.

In some instances, the polymeric coating formed contains one or more polymers, copolymers, and/or one 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
10 polymers.

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. Optionally, the initiation temperature can also be selected to be sufficiently low to prevent formation of defects in the polymeric coating at least during formation, where defects can include
15 bubbling, blistering, pin holes, cracks. In some instances, the polymeric coatings formed are defect free or substantially defect free.

In certain instances, the one or more surfaces of the substrate(s) or device(s) 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
20 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 may be applied.

C. General SACVD Parameters

25 For the SACVD methods described above in Sections II.A and II.B, the following parameters are generally applicable to the methods described herein.

The SACVD methods described may exclude 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)
30 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).

5 In some instances, for the SACVD methods described above the polymeric coating forms via vinyl polymerization, where the one or more gaseous monomers include monomers having at least one vinyl moiety thereon.

In some instances, the vinyl polymerization is a free-radical vinyl polymerization.

Without particular limitation, the one or more gaseous monomers can be a(n)
10 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
15 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.

20 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

25 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).

In some instances, gaseous initiator(s) may include one or more groups which are capable of generating free radicals under the experimental conditions. Such free radicals
30 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.

5 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
10 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.

15 In some instances of the SACVD methods, the one or more gaseous initiators include at least one free-radical thermal initiator and/or at least one ionic (i.e. cationic or anionic) thermal initiator, more preferably at least one free-radical thermal initiator.

 In certain instances, the free-radical thermal initiator can be a peroxide-based initiator, a paracyclophane-based initiator, an oxirane-based initiator, or combination
20 thereof.

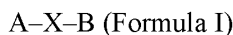
 In certain instances, a peroxide-based gaseous initiator is hydrogen peroxide, an alkyl or aryl peroxide (e.g., tert-butyl peroxide), a hydroperoxide, or a combination thereof. In still other instances, a peroxide-based gaseous initiator can be tert-butyl hydroperoxide, cumene hydroperoxide, di-tert-butyl peroxide, dicumyl peroxide, benzoyl
25 peroxide, ammonium persulfate, or a combination thereof. In still other cases, the at least one free-radical thermal initiator may be an azo nitrile-based initiator, where the azo nitrile-based initiator can be azobisisobutyronitrile, 2,2'-azobis[2-(2-imidazolin-2-yl)-propane] dihydrochloride, or a combination thereof.

 In some instances, the gaseous ionic thermal initiator is dicyandiamide, cyclohexyl tosylate, (4-hydroxyphenyl)-dimethylsulfonium hexafluorophosphate,
30 diphenyl(methyl)sulfonium tetrafluoroborate, benzyl(4-hydroxyphenyl)-methylsulfonium hexafluoroantimonate, (4-hydroxyphenyl)methyl-(2-

methylbenzyl)sulfonium hexafluoroantimonate, truphenylsulphonium nonaflate, or a combination thereof.

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

5



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.

10 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 $-O-O-$.

15 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 $-C(CH_3)_3$; and B is $-C(CH_3)_3$. In certain instances, the gaseous initiator of the invention is a compound of formula I, wherein A is $-C(CH_3)_3$; X is $-O-O-$; and B is $-C(CH_3)_3$.

20 The initiators described above are capable of being in a gas state. Note that a "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. SACVD Reactant Pressures and Optional Carrier Gases

25 For the SACVD methods described herein, the polymeric coating may be formed under any suitable total pressure in the reaction chamber or reactor. In some instances, the total pressure of all gaseous components during the flowing step ranges from between about 1 to 760,000 mTorr. Selection of partial pressures is 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.

30

In some other instances, the total pressure of all gaseous components during the flowing step ranges from between 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
5 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 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
10 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
15 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
20 mTorr). In some embodiments, the total pressure of all gaseous components present during polymerization may be atmospheric pressure.

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
25 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 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
30 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
5 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
10 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
15 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
20 than or equal to 10 mTorr, greater than or equal to 5 mTorr and less than or equal to 10 mTorr).

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)
25 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
30 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.

d. Polymeric Coatings

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 device, 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, or greater than or equal to 50 nm/min. In certain instances, the deposition rate may be less than or equal to 100 nm/min, less than or equal to 50 nm/min, less than or equal to 25 nm/min, 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
15 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 equal to 1 nm/min). In some instances, the initiation temperature, as discussed above, is selected to provide a
20 deposition rate of the polymer(s) to form a polymeric coating of at least 0.5 nm/min.

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 device, all of the surface(s), or on substantially all of the surfaces. Any suitable substrate or device may be used in suitable SACVD methods, as described below. As noted, in certain SACVD
25 methods the surface(s) to be coated by polymer(s) are those of a reactor itself, in which 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%,
30 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 device (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
5 described herein are formed as polymeric coatings on one or more surface(s) of, for example, a substrate or device. 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
10 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 μm , greater than or equal to 2.5 μm , greater than or equal to 5 μm , greater than or equal to 7.5 μm , greater than or equal to 10 μm , greater than or equal to 25 μm , or greater than or equal to 50 μm . In
15 certain instances, polymeric coatings may have an average thickness of less than or equal to 100 μm , less than or equal to 50 μm , less than or equal to 25 μm , less than or equal to 10 μm , less than or equal to 7.5 μm , less than or equal to 5 μm , less than or equal to 2.5 μm , less than or equal to 1 μm , 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
20 possible (e.g., greater than or equal to 50 nm and less than or equal to 10 μm , greater than or equal to 100 nm and less than or equal to 10 μm , or greater than or equal to 100 nm and less than or equal to 1 μm).

As explained above, the polymeric coatings formed by SACVD typically
25 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.

30 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 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.

e. Substrates and Devices

5 Substrates or devices 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 device may be of any suitable size. In some stances, the substrate or device includes a metal and/or a polymeric material (e.g., a plastic, an elastomer).

10 The substrates or devices may be or include a variety of suitable articles, non-limiting examples of which include seals, gaskets, o-rings, and molds. In some instances, the substrates or devices 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
15 references, frequency selective filters, miniaturized arrays, digital to analog converters, analog to digital converters, and/or low noise amplifiers.

In some instances, the device 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 bipolar transistors and
20 silicon CMOS. According to some cases, the device may include gallium nitride, gallium arsenide, and silicon. For instance, the device may comprise gallium nitride or gallium arsenide high-electron-mobility transistors and silicon CMOS. In some instances, the device may include indium phosphide, gallium nitride, gallium arsenide, and silicon. In certain instances, the device may include indium phosphide heterojunction bipolar
25 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 devices 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
30 through-silicon vias (TSVs).

The substrates or devices 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 device. In some cases, the maximum 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 nm, less than about 10 nm, less than about 1 nm, or less. The substrate or device may or may not be substantially planar. For example, the substrate or device 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 other instances, where the surface(s) to be coated by a polymeric film are those of the reactor, the reactor may have any suitable shape capable of performing the SACVD process. Non-limiting examples can include hollow tubes. These may include one or more depressions in its surface. The depressions may have any suitable depth.

In certain instances, the substrate, device, or reactor may undergo one or more 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 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, device, or reactor may be exposed to an elevated temperature and/or a reduced pressure in order to remove volatile contaminants. Suitable 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, device, or reactor 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-

limiting examples of such linkers include silane-containing compounds, organophosphate-containing compounds, and thiol-containing compounds.

f. Optional Annealing during SACVD Methods

In certain instances, the SACVD methods described herein may further include
5 an annealing step. The annealing step can occur during or after flowing step (iv). The annealing step may include transferring the substrate or device having the polymeric coating thereon into another chamber where the annealing step is carried out. The annealing step can occur 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
10 °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. The annealing step can be carried out under a process gas selected from nitrogen, argon, ammonia, hydrogen, syn gas, and combinations thereof; optionally wherein the process gas is free or substantially free of oxygen (O₂) gas; or where the process gas includes oxygen (O₂) gas or air. The annealing step can occur for a time period ranging
15 from about 5 minutes to about 3 hours.

In some instances, following the annealing step, the polymeric coating is denser, as compared to the polymeric coating formed in step (iv). In some instances, the annealing step occurs after step (iv) and following the annealing step, the mass of the polymeric coating is about 50%, 40%, 35%, 30%, 25%, 20%, 15%, 10%, 5%, or less
20 than the mass of the polymeric coating formed in step (iv).

g. Physical Properties of Conformal Polymeric Coating(s)

As noted above, the conformal polymeric coatings formed by the methods described herein may be capable of protecting a substrate or device from deleterious environmental and/or electrical effects/conditions. In some instances, environmental
25 effects/conditions can be biological environmental effects/conditions. 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 year, at least 10 years, at least 25 years, or at least 100 years.

In some instances, the polymeric coatings can have a water vapor permeability of
30 greater than or equal to 250 g/m²/day, greater than or equal to 500 g/m²/day, greater than or equal to 750 g/m²/day, greater than or equal to 1000 g/m²/day, greater than or equal to 1250 g/m²/day, greater than or equal to 1500 g/m²/day, greater than or equal to 1750

g/m²/day, greater than or equal to 2000 g/m²/day, or greater than or equal to 2250 g/m²/day. According to some instances, films may comprise a water vapor permeability of less than or equal to 2500 g/m²/day, less than or equal to 2250 g/m²/day, less than or equal to 200 g/m²/day, less than or equal to 1750 g/m²/day, less than or equal to 1500 g/m²/day, less than or equal to 1250 g/m²/day, less than or equal to 1000 g/m²/day, less than or equal to 750 g/m²/day, or less than or equal to 500 g/m²/day. Combinations of the above-referenced ranges are also possible (e.g., greater than or equal to 250 g/m²/day and less than or equal to 2250 g/m²/day, greater than or equal to 500 g/m²/day and less than or equal to 2000 g/m²/day, or greater than or equal to 1000 g/m²/day and less than or equal to 1500 g/m²/day). One of ordinary skill in the art would be familiar with methods for determining water vapor permeability. In some instances, water vapor permeability may be assessed using ASTM E398.

In some instances, the polymeric coating may be capable of passing the Military Specification for Insulating Compound, Electrical (for Coating Printed Circuit Assemblies), published as MIL-I-46058C on July 7, 1972, and incorporated herein by reference in its entirety and for all purposes. This specification describes properties that a film must have in order to be suitable for use as a coating on printed circuit assemblies by the Department of Defense.

In some instances, polymeric coatings that are suitable under MIL-I-46058C are free from deleterious substances, are chemically compatible with the materials used to form the printed circuit assembly, do not cause deterioration of any materials used to form the printed circuit assembly, and do not corrode any metals being coated.

In some instances, polymeric coatings that are suitable under MIL-I-46058C may be resistant to fungus. The coatings may show no fungal growth when assessed by ASTM G-21, which includes placing three samples of glass coated with the film into petri dishes filled with minimal salts agar, spraying fungal spores in a minimal salt solution onto the samples, sealing the samples, and incubating them for 28 days. Photographs are taken of each sample at regular intervals and compared to photographs taken of both a positive control (uncoated substrate) and a negative control (solid agar medium that was unexposed to the spores). The fungal spores include spores from the *Penicillium*, *Aspergillus*, *Chaetomium*, *Trichoderma*, *Aureobasidium*,

In some instances, polymeric coatings that are suitable under MIL-I-46058C may have an insulation resistance of greater than or equal to $1.5 * 10^{12}$ ohms and less than or equal to 10^{14} ohms, or greater than or equal to $2.5 * 10^{12}$ ohms and less than or equal to 10^{14} ohms. The insulation resistance may be measured using the procedure described in
5 MIL-STD-202 for method 302, test condition B. This test condition comprises coating the film on a megohm bridge, applying 500 +/- 10% V to the megohm bridge for one minute, and then measuring the insulation resistance across the film.

In some instances, polymeric coatings that are suitable under MIL-I-46058C may show no flashover, sparkover, breakdown, or leakage rate in excess of 10 microamperes
10 when tested using the procedure described in MIL-STD-202 for method 301. This procedure comprises applying 1500 V, alternating current, root mean square, at 60 Hz between two mutually insulated portions of the sample for 60 seconds.

In some instances, polymeric coatings that are suitable under MIL-I-46058C may have favorable properties after being subject to thermal shock as described in MIL-STD-
15 202, method 107. The coatings may be subject to the following temperatures in sequence 50 times: -70-65 °C, 20-35 °C, 200-205 °C, and 20-35 °C for a time as specified in MIL-STD-202, method 107 (e.g., 15 minutes for samples weighing less than or equal to 1 ounce; 30 minutes for greater than 1 ounce and less than or equal to 0.3 pounds; 1 hour for samples weighing greater than 0.3 pounds and less than or equal to 3 pounds; 2 hours
20 for samples weighing greater than 3 pounds and less than or equal to 30 pounds; 4 hours for samples weighing greater than 30 pounds and less than or equal to 300 pounds; 8 hours for samples weighing greater than 300 pounds). Then, the coatings may be held at 23-27 °C and 45-55% relative humidity for 35 hours. After this test, the coatings may show suitable properties after being inspected using microscopy and subject to MIL-
25 STD-202 method 301, as described above.

In some instances, polymeric coatings that are suitable under MIL-I-46058C may be capable of undergoing a modification of the procedure described in MIL-STD-202 for method 106 and then showing an insulation resistance of greater than or equal to $1.5 * 10^{12}$ ohms and less than or equal to 10^{14} ohms, or greater than or equal to $2.5 * 10^{12}$ ohms
30 and less than or equal to 10^{14} ohms, suitable properties after being inspected using microscopy, and may show no flashover, sparkover, breakdown, or leakage rate in excess of 10 microamperes when tested using the procedure described in MIL-STD-202

for method 301. The modified method comprises exposing the coating to a cycle with steps comprising defined humidities ranging from 80%-100% relative humidity and temperatures ranging from 25 °C to 65 °C. Then, the coating may be held at 25 +/- 2 °C and 50 +/- 5% relative humidity for 24 hours.

5 According to certain instances, polymeric coatings may be capable of meeting the requirements detailed in the publication “IPC-CC-830B with Amendment 1 Qualification and Performance of Electrical Insulating Compound for Printed Wiring Assemblies”, published October 2008 and incorporated herein by reference in its entirety and for all purposes. This publication details performance metrics for coatings.

10 In some instances, polymeric coatings may meet the requirements detailed in the publication “IPC-CC-830B with Amendment 1 Qualification and Performance of Electrical Insulating Compound for Printed Wiring Assemblies” with respect to appearance. The coatings may show no deleterious substances, bubbles, pinholes, whitish spots, blistering, cracking, peeling, crazing, mealing, evidence of reversion, or
15 evidence of corrosion. The coatings may be smooth, homogeneous, transparent or translucent, and tack-free. The films may be inspected to determine these properties at 10× magnification.

 In some instances, polymeric coatings may meet the requirements detailed in the publication “IPC-CC-830B with Amendment 1 Qualification and Performance of
20 Electrical Insulating Compound for Printed Wiring Assemblies” with respect to fungus resistance. The coatings may not contribute to or be attacked by biological growth after being inoculated with spores, incubated at 28 °C– 30 °C at 85% relative humidity for 28 days, and then assessed to determine fungal growth. The fungal spores may include spores from *Aspergillus niger*, *Chaetomium globosum*, *Gliocadium virans*,
25 *Aureobasidium pullulans*, and *Penicillium funiculosum*.

 In some instances, polymeric coatings may meet the requirements detailed in the publication “IPC-CC-830B with Amendment 1 Qualification and Performance of Electrical Insulating Compound for Printed Wiring Assemblies” with respect to the dielectric withstanding voltage. The coatings may not show flashover, sparkover,
30 breakdown, or a leakage current in excess of 10 microamperes after being subject to IPC-TM-650, Test Method 2.5.7.1. This test includes subjecting the coatings to a voltage of 1500 VAC at 50-60 Hz for one minute.

In some instances, polymeric coatings may meet the requirements detailed in the publication “IPC-CC-830B with Amendment 1 Qualification and Performance of Electrical Insulating Compound for Printed Wiring Assemblies” with respect to moisture and insulation resistance. Meeting these requirements may include having certain

5 desirable properties after testing the coatings in accordance with IPC-TM-650, Test Method 2.6.3.4. This test method includes forming the coating on a substrate comprising a test pattern, pre-conditioning the film at 50 +/- 2 °C for 24 hours, cooling the coating to room temperature, applying a 50 VDC polarizing bias to the test pattern, and exposing the coating to 20 cycles of temperature and humidity. At the conclusion of the test, the

10 coating may be held at 25 +/- 2 °C and 50 +/- 5% relative humidity for 24 hours. The temperature and humidity cycles comprise raising the temperature from 25 °C to 65 °C over a span of 1.75 +/- 0.75 hours, maintaining the temperature at 65 °C for 3-3.5 hours, and then lowering the temperature to 25 °C over 1.75 +/- 0.5 hours. The resistance of the coating may be measured after the first, fourth, seventh, and tenth cycles between the

15 second and third hour of the high temperature step. The resistance of the coating may also be measured at the conclusion of the test. In some instances, the coating may show an insulation resistance of at least 5000 megohms at the conclusion of the test, may have a dielectric withstanding voltage as described above at the conclusion of the test, and may meet the appearance requirements as described above at the conclusion of the test.

20 In some instances, polymeric coatings may meet the requirements detailed in the publication “IPC-CC-830B with Amendment 1 Qualification and Performance of Electrical Insulating Compound for Printed Wiring Assemblies” with respect to thermal shock. The coatings may show an acceptable dielectric withstanding voltage and an appearance after being subject to IPC-TM-650, Test Method 2.6.7.1. This test method

25 comprises exposing the coatings to 100 temperature cycles where the coatings are cycled from -65 °C to 125 °C, and then holding the films at 25 +/- 5 °C for 24 hours.

In some instances, polymeric coatings may meet the requirements detailed in the publication “IPC-CC-830B with Amendment 1 Qualification and Performance of Electrical Insulating Compound for Printed Wiring Assemblies” with respect to

30 hydrolytic stability. The coatings may meet the appearance standards described above and may be tack-free after being subject to IPC-TM-650, Test Method 2.6.11.1. This test method includes placing the coatings on a ceramic plate in a desiccator comprising a

saturated solution of deionized water and potassium sulfate at 85 +/- 2 °C, closing the desiccator, sealing the desiccator with high temperature silicone grease, and placing the sealed desiccator in an oven held at 85 +/- 2 °C for 120 days. After this treatment, the coatings may be held at 25 °C and 50% relative humidity for 7 days. The coatings may
5 also be brought to 25 °C and 50% relative humidity for two hours and then inspected on the 28th, 56th, and 84th days.

In certain instances, polymeric coatings may be capable of passing one or more of the tests detailed in methods 507.5 and 509.5 in the Department of Defense Test Method Standard Environmental Engineering Considerations and Laboratory Tests,
10 published as MIL-STD-810G on October 31, 2008 and incorporated herein by reference in its entirety and for all purposes.

Method 507.5 in Department of Defense Test Method Standard Environmental Engineering Considerations and Laboratory Tests, published as MIL-STD-810G on October 31, 2008 describes a procedure for determining the resistance of protective
15 coatings on materials to warm, humid atmospheres. In some embodiments, the coatings are capable of undergoing this procedure and having properties (e.g., water vapor permeability, freedom from defects, dielectric constant, dielectric breakdown voltage, adhesion strength, and the like) that fall within the parameters described herein after the test has concluded. In some instances, the coatings are capable of undergoing this
20 procedure and exhibiting a change in the dielectric breakdown voltage and/or dielectric constant of less than 25%, less than 10%, less than 5%, less than 2%, or less than 1%.

The aggravated cycle for method 507.5 in MIL-STD-810G on October 31, 2008 comprises placing the coated substrate or device in a chamber and exposing it to a temperature of 23 +/- 2 °C and a humidity of 50 +/- 5% relative humidity for a period of
25 at least 24 hours. Then, the temperature of the chamber is raised to 30 °C and the relative humidity of the chamber is raised to 95%. Next, the coated substrate or device is caused to undergo 10 cycles, where each cycle comprises raising the temperature from 30 °C to 60 °C over a period of 2 hours, holding the temperature at 60 °C for 6 hours, cooling the temperature to 30 °C over 8 hours, and holding the temperature at 30 °C for 8 hours. At
30 the conclusion of the 10 cycles, the temperature of the chamber is returned to 30 +/- 2 °C and the humidity of the chamber is returned to 50 +/- 5% relative humidity. The coated

substrate or device is maintained under these conditions until the coated substrate or device has reached temperature stabilization.

Method 509.5.5 in the Department of Defense Test Method Standard Environmental Engineering Considerations and Laboratory Tests, published as MIL-STD-810G on October 31, 2008 describes a procedure for assessing the effectiveness of protective coatings on materials when exposed to salt. In some embodiments, the films are capable of undergoing this procedure and having properties (e.g., water vapor permeability, freedom from defects, dielectric constant, dielectric breakdown voltage, adhesion strength, and the like) that fall within the parameters described herein after the test has concluded. In some instances, the coatings are capable of undergoing this procedure and exhibiting a change in the dielectric breakdown voltage and/or dielectric constant of less than 25%, less than 10%, less than 5%, less than 2%, or less than 1%.

Method 509.5.5 in MIL-STD-810G on October 31, 2008 includes placing the coated substrate or device in a chamber, adjusting the temperature to 35 °C, and conditioning the coated article at this temperature for at least two hours. Then, a 5% solution of sodium chloride in water is continuously atomized into the test chamber for 24 hours. The salt fog fallout rate and the pH of the fallout solution are measured every 24 hours, and the fallout is kept between 1 and 3 mL/80 cm²/hour. The coated substrate or device is then dried at standard ambient temperature and a relative humidity of less than 50 percent for 24 hours, after which the coated article is again exposed to the atomized salt solution for 24 hours and then dried for 24 hours once again. Then, the coated substrate or device is photographed, rinsed with running water under standard ambient conditions, and then examined for evidence of corrosion. The extent of salt deposits is noted, the substrate or device is tested for electrical malfunction, and any corrosion observed is assessed to determine its immediate and potential long term effects on the functionality and structural integrity of the substrate or device.

In some instances, polymeric coatings may be capable of passing one or more tests published by JEDEC. As used herein, a coating that passes a test published by JEDEC is capable of undergoing the JEDEC procedure and, at the conclusion of the procedure, having properties (e.g., water vapor permeability, freedom from defects, dielectric constant, dielectric breakdown voltage, adhesion strength, and the like) that fall within the parameters described herein. In some instances, polymeric coatings are

capable of undergoing one or more JEDEC procedures and exhibiting a change in the dielectric breakdown voltage and/or dielectric constant of less than 25%, less than 10%, less than 5%, less than 2%, or less than 1%.

For example, the polymeric coatings may be capable of passing the JEDEC
5 Standard No. 22-A101C: Steady State Temperature Humidity Bias Life Test, published March 2009 and incorporated herein by reference in its entirety and for all purposes. JEDEC Standard No. 22-A101C: Steady State Temperature Humidity Bias Life Test comprises exposing the films to a stress condition comprising a temperature of 85 +/- 2 °C and a relative humidity of 85 +/- 5% for 976 – 1168 hours under 10 V dc bias
10 conditions. Then, the sample is cooled to ambient and held there for up to 48 hours. Electrical tests may then be performed on the coatings. Optionally, the coated substrates or devices may be returned to the stress condition within 96 hours of cooling.

According to certain instances, polymeric coatings may be capable of passing the JEDEC Standard No. 22-A110D: Highly Accelerated Temperature and Humidity Stress
15 Test (HAST), published January 2009 incorporated herein by reference in its entirety and for all purposes. JEDEC Standard No. 22-A110D comprises exposing the coatings to a stress condition of 130 +/- 2 °C and 85 +/- 5% relative humidity for 96-98 hours under 10 V dc bias conditions. Then, the sample is cooled to ambient and held there for up to 48 hours. Electrical tests may then be performed on the films. Optionally, the coated
20 substrates or devices may be returned to the stress condition within 96 hours of cooling.

In some instances, polymeric coatings may be capable of passing the JEDEC Standard No. 22-A100D: Cycled Temperature-Humidity-Bias Life Test, published July 2013 and incorporated herein by reference in its entirety and for all purposes. This test includes exposing the coatings to an experimental profile comprising an increase in
25 temperature from 30 °C to 65 °C at 80%-98% relative humidity over 2-4 hours, a constant temperature of 65 °C at 90%-98% relative humidity for 4-8 hours, and a decrease in temperature from 65 °C to 30 °C at 80%-90% relative humidity over the course of 2-4 hours. This cycle is repeated over a duration of time between 1084-1172 hours, while the coating is under 10 V dc bias conditions. The coatings are then cooled
30 to ambient and held there for up to 48 hours. Electrical tests may then be performed on the films. Optionally, the devices may be returned to the stress condition within 96 hours of cooling.

In some instances, polymeric coatings may be capable of passing a test conducted according to ASTM B117-16 Standard Practice for Operating Salt Spray (Fog Apparatus), published March 2016 and incorporated herein by reference in its entirety and for all purposes. In some instances, polymeric coatings may be capable of

5 undergoing the procedure outlined in ASTM B117-16 and, at the conclusion of the procedure, having properties (e.g., water vapor permeability, freedom from defects, dielectric constant, dielectric breakdown voltage, adhesion strength, and the like) that fall within the parameters described herein. In some instances, polymeric coatings are capable of undergoing the procedure outlined in ASTM B117-16 and exhibiting a change

10 in the dielectric breakdown voltage and/or dielectric constant of less than 25%, less than 10%, less than 5%, less than 2%, or less than 1%. Performing the ASTM B117-16 test comprises placing the coatings in a chamber held at 35 +/- 2 °C and exposing the coatings to a fog of a salt solution comprising 5 wt% sodium chloride at a pH between 6.5 and 7.2 for 24 hours twice.

15 In some instances, a polymeric coating's ability to pass one or more standard tests may be substantially unaffected by undergoing a stress test and/or undergoing elongation. In some instances, a percent elongation may be defined as the difference between the elongated length and the initial length divided by the initial length. According to certain instances, polymeric coatings may retain their ability to pass one or

20 more standardized tests after undergoing an elongation of greater than or equal to 1%, greater than or equal to 2%, greater than or equal to 3%, or greater than or equal to 5%. Coatings may be deposited on a flexible substrate (e.g., PET, a liquid crystalline polymer, and the like) including conductive traces. Then, a suitable property (e.g., dielectric breakdown voltage, dielectric constant, defect and/or pinhole concentration)

25 may be assessed prior to elongation. The coating may be elongated using an extensometer (e.g., an Instron 5900), and the suitable property may be measured again after elongation.

In certain instances, polymeric coatings synthesized by the SACVD methods described herein may include certain dielectric properties. It is believed that the dielectric

30 constant of a coating may be influenced by the composition of the coating. According to some instances, polymeric coatings including higher degrees of 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, greater than or equal greater
5 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 equal to 3.05, less than or equal to
10 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
15 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).

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
20 equivalent to 0.001 inches. In some instances, polymeric coatings may 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
25 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, polymeric coatings may exhibit a dielectric breakdown voltage of less than or equal to 10000 V/mil, less than or equal to 9500 V/mil, less than
30 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
5 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 10000 V/mil).

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
10 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.

15 In some instances, polymeric coatings may retain a percentage of their initial adhesion strength after undergoing mechanical cycling. The percentage of initial adhesion strength retained may be defined as the adhesion strength of the coating after undergoing flexing and/or elongation divided by the initial coating adhesion strength. In accordance with certain instances, percentage of initial adhesion strength retained may
20 be greater than or equal to 50%, greater than or equal to 75%, greater than or equal to 80%, greater than or equal to 85%, greater than or equal to 90%, greater than or equal to 95%, or greater than or equal to 99%. Flexing and elongating the coatings may include forming the coatings on a flexible substrate and then placing the flexible substrate over a hinge. The hinge then undergoes ten cycles, each of which comprise flexing the hinge to
25 130°, holding the hinge in this position for one second, returning the hinge to an unflexed position, and then holding the hinge in the unflexed position for one second. After this testing procedure, any suitable property of the coatings may be measured in a manner described herein.

The adhesion strength of a coating may be determined by a method as described
30 in ASTM D3359, which includes making cuts in the coating in a lattice pattern with eleven cuts in each direction, applying a pressure-sensitive tape over the cut, removing the pressure-sensitive tape, and assessing the adhesion by determining the extent of

removal of the coating. The percentage of adhesion strength retained after undergoing mechanical cycling is the ratio of the percent of the coating within the lattice pattern that is retained by a coating that has undergone mechanical cycling to the percent of the coating within the lattice pattern that is retained by a coating that has not undergone
5 mechanical cycling.

Regarding resistance to biological environments provided by the polymeric coatings discussed, those of ordinary skill in the art will be aware of methods and systems for exposing a coated substrate or device to a biological environment or biological fluid. The term “biological environment” is given its ordinary meaning in the
10 art and generally refers to the body of a subject (e.g., a mammalian patient such as a human patient). However, the term “biological environment” can also include an *in vitro* environment that models a desired *in vivo* environment (e.g., a temperature of about 37° C and saline or Ringer’s solution). In some instances, a coated substrate or device may be exposed to a biological environment or a biological fluid via implantation within or
15 on a subject (e.g., a human).

In some instances, polymeric coatings may 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 after being exposed to a biological environment or biological fluid for a time period of at least one
20 day, at least one week, at least one month, at least 1 year, at least 2 years, at least 3 years, at least 4 years, at least 5 years, at least 10 years, at least 20 years, at least 25 years, or at least 100 years. Leakage current may be determined by placing the coated device in salt water and measuring the current flow through the coating.

In some instances, polymeric coatings may exhibit a dielectric breakdown voltage
25 of greater than or equal to 5000 V/mil after being exposed to a biological environment or biological fluid for a time period of at least one day, at least one week, at least one month, at least 1 year, at least 2 years, at least 3 years, at least 4 years, at least 5 years, at least 10 years, at least 20 years, at least 25 years, or at least 100 years. In some instances, polymeric coatings may exhibit a dielectric breakdown voltage that is within
30 25%, within 10%, within 5%, within 2%, or within 1% of an otherwise identical film that has not been exposed to a biological environment or biological fluid after being exposed to a biological environment or biological fluid for a time period of at least one day, at

least one week, at least one month, at least 1 year, at least 2 years, at least 3 years, at least 4 years, at least 5 years, at least 10 years, at least 20 years, at least 25 years, or at least 100 years. The dielectric breakdown voltage of the coating may be measured by ASTM D149 as described above.

5 In some instances, polymeric coatings may retain at least 50%, at least 75%, at least 80%, at least 85%, at least 90%, at least 95%, or at least 99% of their initial adhesion after being exposed to a biological environment or biological fluid for a time period of at least one day, at least one week, at least one month, at least 1 year, at least 2 years, at least 3 years, at least 4 years, at least 5 years, at least 10 years, at least 20 years,
10 at least 25 years, or at least 100 years. In some instances, polymeric coatings may be a biocompatible material, such as a USP Class VI material.

 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
15 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 process may
20 be carried out in an SACVD system including:

 a reaction chamber comprising

 a platform able to support the at least one substrate or device in the reaction chamber; the platform including one or more heating elements for independently heating the platform to a first temperature;

25 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 independently heated to a second temperature which is lower than the first temperature;

30 at least one gas inlet port to introduce one or more gaseous reactants and optional gas carriers into the reaction chamber;

 at least one gas outlet port;

a first temperature controller for setting the first temperature of the platform;

a second temperature controller for setting the second temperature of the reaction chamber;

5 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
10 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 device is formed of a
15 material selected to possess a high degree of thermal uniformity and has a suitable configuration to provide good thermal contact with the substrate or device in order to ensure that the substrate or device 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
20 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
25 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.
30 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
5 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
10 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.
15 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.

20 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
25 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
30 absent such a throttling valve.

Use of a vacuum may be advantageous when, for instance, the reaction chamber initially comprises a combination of gases that it would be undesirable for the reaction

chamber to include during the deposition of a fluorinated 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

5 terminates further growth 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

10 coating. During 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

15 that 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

20 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.

25 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 device at the conclusion of a coating process.

In some other instances, a system can be configured such that one or more gases

30 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

5 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

10 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

15 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.

20 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

25 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

30 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
5 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
10 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
15 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
20 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
25 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
30 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
5 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%).

10 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
15 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
20 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
25 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 fluorinated 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.

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

The SACVD methods described above can be used to deposit/form polymeric coating(s) on surface(s) of a substrate or device having a degree of conformality, which

would otherwise be difficult or impossible to attain using other known deposition methods. Accordingly, in some instances, a substrate or device includes a polymeric coating formed using the SACVD methods described and includes:

a polymeric coating on at least one surface of the substrate or device;

5 wherein the polymeric coating has a conformality, as determined by the wafer stack method and has a step coverage of at least 50%, at least 60%, at least 65%, at least 70%, at least 75%, at least 80%, at least 85%, or at least 90% or more; and/or

10 wherein the polymeric coating has a microscale conformality, as determined by microtrench method, of at least 60%, at least 65%, at least 70%, at least 75%, at least 80%, at least 85%, or at least 90%, or more.

In some instances, such substrates or devices 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, 15 by adding electrical protection, by imparting optical effects, by modifying surface properties, and/or by enhancing biological or chemical compatibility.

EXAMPLES

20 **Example 1: Surface Activated Chemical Vapor Deposition (SACVD) of Siloxane-Based Polymer Coatings**

An SACVD synthesis of a siloxane ring-containing polymer coating was performed within a reactor chamber. A polymer coating was deposited on three different substrates: (1) a silicon wafer; (2) a microtrench feature; and (3) a silicon wafer stack. These substrates were selected for their high aspect ratio features at various length 25 scales. The microtrench feature had a depth of 57 μm , a width of 4.5 μm , and a length of 1 cm. The silicon wafer stack was formed of silicon wafer pieces 110 and 120 assembled into a 1-inch-long tunnel 150 with a height of 0.5 mm, as shown in Figures 1A and 1B.

Siloxane ring-containing polymer coatings were synthesized on these three 30 substrates in a pressure-controlled reactor chamber, shown schematically in Figure 2. As shown in the schematic representation in Figure 2, such an SACVD system 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. All components of the reactor chamber are equipped with heaters that can independently control the temperature of each component. The reactor chamber body, which has
5 diameter of 2" and length of 24" and is configured with temperature control capabilities. Housed within the reactor chamber body is an independently temperature-controlled stage where the three substrates were placed during the synthesis process. The temperature-controlled stage had a length of 4", a width of 1.5", and thickness of 0.31".

Monomer and initiator were vacuum purified at room temperature for a total of 2
10 minutes prior to use. The monomer was 1,3,5-trivinyl-1,3,5-trimethylcyclotrisiloxane and the initiator was di-tert-butyl peroxide. The monomer was heated to 80 °C to increase its volatility while the initiator was left at room temperature. Using dedicated metering needle valves, monomer gas was delivered into the chamber at a rate of 1.5 sccm and the initiator gas was delivered at a rate of 0.5 sccm. The pressure within the
15 chamber was maintained at 6 Torr using a throttle valve, resulting in a monomer partial pressure of 4.5 Torr and an initiator partial pressure of 1.5 Torr.

The reactor chamber body and sample stage were individually temperature controlled to 110 °C and 225 °C, respectively. The temperature of the reactor chamber body was selected such that the partial pressure of either gas species within the reactor
20 does not exceed the saturation pressures of the reactants at reactor body temperature. This was intended to prevent that gaseous precursors from condensing within the chamber. The sample stage temperature was set to a temperature that was greater than the temperature required for generating free radicals from the di-tert-butyl peroxide initiator. These conditions were maintained within the chamber for a total elapsed time
25 of 348 minutes to synthesize the polymer coating on the three substrates concurrently. After completing the polymer deposition process, the monomer and initiator vessels were isolated from the reactor chamber, the throttle valve was fully opened, and the stage heater and reactor chamber body heaters were turned off.

Upon completing the synthesis process, the substrates were removed from the
30 reactor chamber. For the silicon wafer stack, it was disassembled to analyze the coating thickness inside of the tunnel feature. Thickness was measured using a Filmetrics MProbe 20 VIS reflectometer. The conformality of the coating on the wafer stack was

determined to be 70%. The conformality value was calculated, using the step coverage method, by comparing the thinnest portion of coating deposited within the tunnel feature (870 nm) as a percentage of the thickness coating on a wafer positioned at the opening of the tunnel (1240 nm). In contrast, a similar test was performed using initiated chemical vapor deposition (iCVD), which produced a conformality of 12% on an identical tunnel feature. The conditions for iCVD used are provided in Table 3 below:

Table 3. iCVD Conditions

Pressure	300 mTorr
Monomer (V3D3) flowrate	2.6 sccm
Initiator (TBPO) flowrate	0.6 sccm
Nitrogen flowrate	4.1 sccm
Filament temperature	475 °C

For the microtrench substrate, it was cleaved to produce a cross-sectional view of the microtrench. An exemplary microtrench substrate is shown in Figure 1C. Using the cross-section, coating thickness at various locations on the microtrench substrate’s side-walls and bottom were measured using scanning electron microscopy (SEM); SEM images not shown. The conformality of the coating was determined to be 70%, based on the step coverage method, and was calculated by comparing the thickness of the coating at the bottom of the microtrench (656 nm) to the thickness of the coating at the top of the trench (940 nm). The conformality observed from SEM micrographs revealed a step coverage of 18% for a microtrench cross-section having a coating produced by initiated chemical vapor deposition (iCVD), which was significantly lower, as compared to the step coverage of 70% produced using SACVD.

Prophetic Example: Surface Activated Chemical Vapor Deposition (SACVD) of Acrylic-Based Polymer Coatings

This example is a theoretical SACVD synthesis process of a co-polymer containing linear poly(methacrylic acid) and divinylbenzene cross-linker coating on the inner diameter of a stainless-steel tube that is 1’ long with an OD of 2” and an ID of 1.87”. The flow and concentration of chemical precursors will be controlled within the inner dimensions of the tube by attaching a gas deliver manifold and vacuum control

system. Seals will be formed directly on the tube to enable a vacuum pump to evacuate the inner volume of the tube. A temperature-controlled heater will be applied over the tube and connections to the gas delivery manifold and vacuum control system to control the surface temperature of the tube. The components of the manifold and reactor will be
5 equipped with heaters that can independently control the temperature of each component.

Monomer, cross-linker, and initiator will be vacuum purified at room temperature for a total of 2 minutes prior to use. In this case, the monomer will be cyclohexyl methacrylate, the cross-linker will be divinylbenzene, and the initiator will be tert-butyl peroxybenzoate. To increase volatility of each precursor, the monomer and cross-linker
10 will be heated to 55 °C and 65 °C, respectively. Initiator will be delivered by bubbling nitrogen as a carrier gas to achieve a total flow of 1 sccm. Three silicon wafers will be placed within the tube at positions that were 3", 6", and 9" from the inlet of the tube. Dedicated metering valves will be set to deliver the monomer and cross-linker at flow rates of 3 sccm and 1 sccm, respectively. The pressure within the chamber will be
15 maintained at 6 Torr using a throttle valve, resulting in a monomer partial pressure of 2.25 Torr and cross-linker partial pressure of 0.75 Torr. The temperature of the tube will be maintained at a temperature of 150 °C. This temperature will be selected to prevent condensation of either gas precursor at the operating pressure and to provide adequate thermal energy to decompose the tert-butyl peroxybenzoate initiator. These conditions
20 will be maintained within the chamber for a total of 2 hours.

Upon completion of the synthesis process, the silicon wafers will be analyzed using Fourier transform infrared measurements. A comparison of these spectra to monomer spectra will indicate successful polymerization, as suggested by the reduction of unsaturated carbon peaks. The spectra from these measurements will be used to
25 confirm the copolymerization of polycyclohexyl methacrylate and polydivinylbenzene, as indicated by the characteristic peaks summarized in Table 4 below.

Table 4. Characteristic Peaks

<i>Reactant</i>	<i>Functionality</i>	<i>Characteristic Peaks (cm⁻¹)</i>
Polycyclohexyl methacrylate	Cyclohexyl CH ₂ asymmetrical stretching	2939, 2861
Polycyclohexyl methacrylate	C=O	1714
Polycyclohexyl methacrylate	C-H	1350-1500
Polydivinylbenzene	sp ³ C-H	2850 - 3000
Polydivinylbenzene	Aromatic =C-H	3010 - 3084
Polydivinylbenzene	C=C	1630
Polydivinylbenzene	=C-H	903-990

Example 2 – Selective Heating Deposition of SACVD Coatings***Materials and Methods:***

5 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.

10 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
 15 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
 20 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 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.

5 **Results:**

Each polymer coating formed by SACVD was analyzed using Fourier transform 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
10 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.

Figure 4 shows the IR absorbance values as a function of wavenumber for the pV3D3 coatings of Example 2 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
15 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. Positive or
20 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 set-up.

The spectra shown in Figure 5 display IR absorbance values as a function of wavenumber for the pDVB coatings of Example 2 formed with TBPO or TBPA.
25 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 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
30 initiator incorporation.

The spectrum in Figure 6 displays IR absorbance values as a function of wavenumber for the pTBS coating of Example 2. 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 3 – 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.

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 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.

Example 4 – Conformality

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

Methods:

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 2 above. iCVD coatings were synthesized using a 0.0026 m³ reactor as shown in Figure 9 while iPECVD coatings were synthesized in a 0.210 m³ 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 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 5 below.

**Table 5. 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
5 shown) and a summary of the conformalities achieved by the various processes on microtrenches is shown in Table 6 below.

**Table 6. 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 %	--

10 **Example 5 – 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.

15 **Methods:**

Using a 0.0012 m³ reactor, as shown in 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 7. Condition 4A is an example of a deposition where the ratio of the
20 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 reactant condensation.

Table 7. 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

5

Results:

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.

10

Example 6 – Process Setup and Reactor Geometry Impacts on Coating Morphology

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

15

Methods:

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.

20

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.

Results:

A summary of the deposition rates is shown in Table 8. 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. 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.

Table 8. 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

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 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 claims.

We claim:

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

- (i) placing the at least one substrate or device 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 device 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 the one or more surfaces of the at least one substrate or device;

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

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.

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

- (i) placing the at least one substrate or device 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 device 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 the one or more surfaces the at least one substrate or device;

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 one or more surfaces of the at least one substrate or device at the surface temperature; and

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.

3. The method of any one of claims 1-2, 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 become 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.

4. The method of any one of claims 1-3, wherein step (iv) is performed for a period of time ranging from about 30 to 800 minutes.

5. The method of any one of claims 1-4, wherein following step (iv) the reaction chamber is purged and allowed to cool to room temperature followed by venting of the reaction chamber.

6. The method of any one of claims 1-5, wherein the polymeric coating is formed under a pressure ranging from between about 1 to 760,000 mTorr.

7. The method of any one of claims 1-5, wherein the polymeric coating is formed under a pressure ranging from between about 100 mTorr to 10 Torr.

8. The method of any one of claims 1-7, 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.
9. The method of any one of claims 1-7, 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.
10. The method of claim 2, wherein the at least one substrate or device comprises a plurality of substrates and/or devices and optionally each of the substrates and/or devices in the plurality is independently placed on a separate temperature-controlled platform.
11. The method of any one of claims 1-10, wherein the at least one polymeric coating is formed continuously or semi-continuously on the at least one substrate or device.
12. The method of any one of claims 1-11, wherein step (iv) is repeated at least 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 step (iii) is optionally repeated before step (iv) is repeated, when the type of the one or more gaseous initiators is changed.
13. The method of claim 12, wherein at least one of the plurality of layers is formed of a polymer different from a polymer forming at least one other layer of the plurality of layers.
14. The method of any one of claims 1-13, wherein the polymeric coating forms via vinyl polymerization, wherein the one or more gaseous monomers comprise monomers having at least one vinyl moiety thereon.
15. The method of claim 14, wherein the vinyl polymerization is a free-radical vinyl polymerization.

16. The method of any one of claims 1-15, wherein the at least one polymeric coating is formed of one 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.

17. The method of any one of claims 1-16, wherein the one or more gaseous monomers are selected from the group consisting of acrylate monomers, methacrylate monomers, vinyl-containing monomers, paracyclophane monomers, oxirane-based monomers, and combinations thereof.

18. The method of claim 17, 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.

19. The method of claim 17, 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.

20. The method of claim 17, wherein the oxirane-based monomer is hexafluoropropylene oxide.

21. The method of any one of claims 1-20, wherein the initiation temperature ranges from about 50 °C to about 400 °C.

22. The method of any one of claims 1-20, wherein the initiation temperature ranges from about 100 °C to about 250 °C.

23. The method of any one of claims 1-20, wherein the initiation temperature is selected to provide a deposition rate of the polymeric coating of at least 0.5 nm/min, optionally wherein the initiation temperature is also sufficiently low to prevent defects in the polymeric coating.

24. The method of any one of claims 1-23, wherein the one or more gaseous initiators comprise at least one free-radical thermal initiator and/or at least one ionic (i.e. cationic or anionic) thermal initiator.

25. The method of claim 24, wherein the at least one free-radical thermal initiator is selected from the group consisting of a peroxide-based initiator, a paracyclophane-based initiator, an oxirane-based initiator, and combinations thereof.

26. The method of claim 25, wherein the peroxide-based initiator is selected from the group consisting of tert-butyl hydroperoxide, cumene hydroperoxide, di-tert-butyl peroxide, dicumyl peroxide, benzoyl peroxide, ammonium persulfate, and combinations thereof.

27. The method of claim 24, wherein the at least one free-radical thermal initiator is an azo nitrile-based initiator.

28. The method of claim 27, wherein the azo nitrile-based initiator is selected from the group consisting of azobisisobutyronitrile, 2,2'-azobis[2-(2-imidazolin-2-yl)-propane] dihydrochloride, and combinations thereof.

29. The method of claim 24, wherein the at least one ionic thermal initiator is 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, truphenylsulphonium nonaflate, and combinations thereof.

30. The method of any one of claims 1-29, wherein the polymeric coating formed on the one or more surfaces of the at least one substrate or device has a conformality of at least about 40%, as determined by wafer stack method.

31. The method of claim 30, wherein the conformality of the at least one substrate or device is at least about 45%, 50%, 55%, 60%, 65%, 70%, 75%, 80%, or 90%, as determined by the wafer stack method.

32. The method of any one of claims 1-29, wherein the polymeric coating formed on the one or more surfaces of the at least one substrate or device has a microscale conformality of at least about 50%, as determined by microtrench method.

33. The method of claim 32, wherein the microscale conformality of the at least one substrate or device is at least about 60%, 65%, 70%, 75%, 80%, or 90%, as determined by the microtrench method.

34. The method of any one of claims 1-33, 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.

35. The method of claim 34, wherein the annealing step occurs during the flowing step (iv).

36. The method of claim 34, wherein the annealing step occurs after the flowing step (iv).

37. The method of claim 36, 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.

38. The method of any one of claims 34-37, 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.
39. The method of any one of claims 34-38, 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.
40. The method of any one of claims 34-39, wherein the annealing step occurs for a time period ranging from about 5 minutes to about 3 hours.
41. The method of any one of claims 34 or 36-40, 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).
42. The method of any one of claims 34 or 36-40, wherein the annealing step occurs after step (iv) and wherein following the annealing step, the mass of the polymeric coating is about 80%, 70%, 60%, 50%, 40%, 35%, 30%, 25%, 20%, 15%, 10%, 5%, or less than the mass of the polymeric coating formed in step (iv).
43. The method of any one of claims 1-42, wherein the polymeric coating is free or substantially free of pin-holes and/or defects.
44. The method of any one of claims 1-43, 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.

45. The method of any one of claims 1-44, wherein the at least one substrate or device 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.

46. The method of any one of claims 1-45, further comprising treating the polymeric coating on the at least one substrate or device, 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.

47. A substrate or device comprising:

a polymeric coating on at least one surface of the substrate or device;

wherein the polymeric coating has a conformality, as determined by wafer stack method, of at least 40%, at least 45%, at least 50%, at least 60%, at least 65%, at least 70%, at least 75%, at least 80%, at least 85%, or at least 90%, or more; and/or

wherein the polymeric coating has a microscale conformality, as determined by microtrench method, of at least 50%, at least 55%, at least 60%, at least 65%, at least 70%, at least 75%, at least 80%, at least 85%, or at least 90%, or more.

48. A substrate or device comprising:

a polymeric coating on at least one surface of the substrate or device;

wherein the polymeric coating has a conformality, as determined by wafer stack method, of at least 40%, at least 45%, at least 50%, at least 60%, at least 65%, at least 70%, at least 75%, at least 80%, at least 85%, or at least 90%, or more; and/or

wherein the polymeric coating has a microscale conformality, as determined by microtrench method, at least 50%, at least 55%, of at least 60%, at least 65%, at least 70%, at least 75%, at least 80%, at least 85%, or at least 90%, or more;

wherein the substrate or device is made by the method of any one of claims 1-46.

49. The substrate or device of claim 48, wherein the polymeric coating has a conformality, as determined by wafer stack method, of at least 50%, at least 60%, at least 65%, at least 70%, at least 75%, at least 80%, at least 85%, or at least 90%, or more; and/or wherein the polymeric coating has a microscale conformality, as determined by microtrench method, of at least 60%, at least 65%, at least 70%, at least 75%, at least 80%, at least 85%, or at least 90%, or more.

50. A method for forming a polymeric coating on a reactor surface, the method comprising the steps of:

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

51. The method of claim 50, wherein (ii) comprises heating for period of time of at least about 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, or 60 minutes prior to step (iii).

52. The method of any one of claims 50-51, wherein step (iii) is performed for a period of time ranging from about 30 to 800 minutes.

53. The method of any one of claims 50-52, wherein following step (iii) the reactor is purged and allowed to cool to room temperature followed by venting of the reactor.

54. The method of any one of claims 50-53, wherein the polymeric coating is formed under a pressure ranging from between about 1 to 760,000 mTorr.

55. The method of any one of claims 50-53, wherein the polymeric coating is formed under a pressure ranging from between about 100 mTorr to 10 Torr.

56. The method of any one of claims 50-55, wherein during step (iii), the one or more gaseous monomers, the one or more gaseous initiators, and/or the one or more carrier gases flow continuously through the reactor.
57. The method of any one of claims 50-55, wherein during step (iii), 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 reactor.
58. The method of any one of claims 50-57, wherein the at least one polymeric coating is formed continuously or semi-continuously on the one or more surfaces of the reactor.
59. The method of any one of claims 50-57, wherein step (iii) is repeated at least one or more times with the same or different types of the one or more gaseous monomers and the one or more gaseous initiators to form a polymeric coating comprising a plurality of layers wherein step (ii) is optionally repeated before step (iii) is repeated, when the type of the one or more gaseous initiators is changed.
60. The method of claim 59, wherein at least one of the plurality of layers is formed of a polymer different from a polymer forming at least one other layer of the plurality of layers.
61. The method of any one of claims 50-60, wherein the polymeric coating forms via vinyl polymerization, wherein the one or more gaseous monomers comprise monomers having at least one vinyl moiety thereon.
62. The method of claim 61, wherein the vinyl polymerization is a free-radical vinyl polymerization.
63. The method of any one of claims 50-62, wherein the at least one polymeric coating is formed of one 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 (iii);

and wherein one or more gaseous crosslinkers are further optionally flowed during step (iii), when forming the cross-linked polymers.

64. The method of any one of claims 50-63, wherein the one or more gaseous monomers are selected from the group consisting of acrylate monomers, methacrylate monomers, vinyl-containing monomers, paracyclophane monomers, oxirane-based monomers, and combinations thereof.

65. The method of claim 64, 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.

66. The method of claim 64, 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.

67. The method of claim 64, wherein the oxirane-based monomer is hexafluoropropylene oxide.

68. The method of any one of claims 50-67, wherein the initiation temperature ranges from about 50 °C to about 400 °C.

69. The method of any one of claims 50-67, wherein the initiation temperature ranges from about 100 °C to about 250 °C.

70. The method of any one of claims 50-67, wherein the initiation temperature is selected to provide a deposition rate of the polymeric coating of at least 0.5 nm/min, optionally wherein the initiation temperature is also sufficiently low to prevent defects in the polymeric coating.

71. The method of any one of claims 50-70, wherein the one or more gaseous initiators comprise at least one free-radical thermal initiator and/or at least one ionic (i.e. cationic or anionic) thermal initiator.

72. The method of claim 71, wherein the at least one free-radical thermal initiator is selected from the group consisting of a peroxide-based initiator, a paracyclophane-based initiator, an oxirane-based initiator, and combinations thereof.

73. The method of claim 72, wherein the peroxide-based initiator is selected from the group consisting of tert-butyl hydroperoxide, cumene hydroperoxide, di-tert-butyl peroxide, dicumyl peroxide, benzoyl peroxide, ammonium persulfate, and combinations thereof.

74. The method of claim 71, wherein the at least one free-radical thermal initiator is an azo nitrile-based initiator.

75. The method of claim 74, wherein the azo nitrile-based initiator is selected from the group consisting of azobisisobutyronitrile, 2,2'-azobis[2-(2-imidazolin-2-yl)-propane] dihydrochloride, and combinations thereof.

76. The method of claim 71, wherein the at least one ionic thermal initiator is 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, truphenylsulphonium nonaflate, and combinations thereof.

77. The method of any one of claims 50-76, wherein the polymeric coating formed on the one or more surfaces of the at least one substrate or device has a conformality of at least about 50%, as determined by wafer stack method.
78. The method of claim 77, wherein the conformality is at least about 60%, 65%, 70%, 75%, 80%, or 90%, as determined by the wafer stack method.
79. The method of any one of claims 50-76, wherein the polymeric coating formed on the one or more surfaces of the at least one substrate or device has a microscale conformality of at least about 50%, as determined by microtrench method.
80. The method of claim 79, wherein the microscale conformality is at least about 65%, 70%, 75%, 80%, or 90%, as determined by the microtrench method.
81. The method of any one of claims 50-80, wherein the method further comprises an annealing step.
82. The method of claim 81, wherein the annealing step occurs during the flowing step (iv).
83. The method of claim 81, wherein the annealing step occurs after the flowing step (iv).
84. The method of claim 83, 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.
85. The method of any one of claims 81-84, 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.

86. The method of any one of claims 81-85, 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.
87. The method of any one of claims 81-86, wherein the annealing step occurs for a time period ranging from about 5 minutes to about 3 hours.
88. The method of any one of claims 81 or 83-87, 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).
89. The method of any one of claims 81 or 83-87, wherein the annealing step occurs after step (iv) and wherein following the annealing step, the mass of the polymeric coating is about 50%, 40%, 35%, 30%, 25%, 20%, 15%, 10%, 5%, or less than the mass of the polymeric coating formed in step (iv).
90. The method of any one of claims 50-89, wherein the polymeric coating is free or substantially free of pin-holes and/or defects.
91. The method of any one of claims 50-90, 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.
92. The method of any one of claims 50-91, wherein the one or more surfaces of the reactor are 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.

93. The method of any one of claims 50-92 further comprising treating the polymeric coating on the reactor, following step (iii), with a treatment selected from the group consisting of electron beam, IR radiation, gamma radiation, plasma exposure, thermal treatment, laser exposure, and combinations thereof.