

METAL ORGANIC RESIST PHOTOSENSITIVITY IMPROVEMENT USING CARBOXYLIC ACID

[0001] Related Applications

[0002] This Application claims priority to U.S. Provisional Patent Application No. 63/515,921 filed on July 27, 2023, which is hereby incorporated by reference.

[0003] Field

[0004] The disclosed and claimed subject matter relates to a method for depositing tin-containing films. The method generally includes (i) contacting a substrate with organotin precursor vapor in a deposition reactor, (ii) purging the reactor vessel with inert gas, (iii) contacting the substrate with a water-containing vapor to form an organotin oxo network layer, (iv) purging the reactor vessel with inert gas, (v) contacting the substrate with a carboxylic acid-containing vapor and (vi) purging the reactor vessel with inert gas. The processing steps can be repeated may be repeated to provide a desired thickness of organotin oxo films.

[0005] BACKGROUND

[0006] Thin films, and in particular thin metal-containing films, have a variety of important applications, such as in nanotechnology and the fabrication of semiconductor devices. Examples of such applications include conducting metal oxides, EUV patterning, high-refractive index optical coatings, corrosion-protection coatings, photocatalytic self-cleaning glass coatings, biocompatible coatings, dielectric capacitor layers and gate dielectric insulating films in field-effect transistors (FETs), capacitor electrodes, gate electrodes, adhesive diffusion barriers, and integrated circuits. Metallic thin films and dielectric thin films are also used in microelectronics applications, such as the high- κ dielectric oxide for dynamic random-access memory (DRAM) applications and the ferroelectric perovskites used in infrared detectors and non-volatile ferroelectric random-access memories (NV-FerAMs).

[0007] Various precursors may be used to form metal-containing thin films and a variety of deposition techniques can be employed. Such techniques include reactive sputtering, ion-assisted deposition, sol-gel deposition, chemical vapor deposition (CVD) (also known as metalorganic CVD or MOCVD), and atomic layer deposition (ALD) (also known as atomic layer epitaxy). CVD and ALD processes are increasingly used as they have the advantages of enhanced compositional control, high film uniformity, and effective control of doping.

[0008] CVD is a chemical process whereby precursors are used to form a thin film on a substrate surface. In a typical CVD process, the precursors are passed over the surface of a

substrate (*e.g.*, a wafer) in a low pressure or ambient pressure reaction reactor. The precursors react and/or decompose on the substrate surface creating a thin film of deposited material. Volatile by-products are removed by gas flow through the reaction reactor. The deposited film thickness can be difficult to control because it depends on coordination of many parameters such as temperature, pressure, gas flow volumes and uniformity, chemical depletion effects, and time.

[0009] ALD is also a method for the deposition of thin films. It is a self-limiting, sequential, unique film growth technique based on surface reactions that can provide precise thickness control and deposit conformal thin films of materials provided by precursors onto surfaces substrates of varying compositions. In ALD, the precursors are introduced separately during the deposition. The first precursor is passed over the substrate surface producing a monolayer on the substrate surface. Any excess unreacted precursor is pumped out of the reaction reactor. A second precursor is then passed over the substrate surface and reacts with the first precursor, forming a second monolayer of film over the first-formed monolayer of film on the substrate surface. This cycle is repeated to create a film of desired thickness.

[0010] However, the continual decrease in the size of microelectronic components, such as semi-conductor devices, presents several technical challenges and has increased the need for improved thin film technologies. In particular, microelectronic components may include features on or in a substrate, which require filling, *e.g.*, to form a conductive pathway or to form interconnections. Filling such features, especially in smaller and smaller microelectronic components, can be challenging because the features can become increasingly thin or narrow. Consequently, a complete filling of the feature, *e.g.*, via ALD, would require infinitely long cycle times as the thickness of the feature approaches zero. Moreover, once the thickness of the feature becomes narrower than the size of a molecule of a precursor, the feature cannot be completely filled. As a result, a hollow seam can remain in a middle portion of the feature when ALD is performed. The presence of such hollow seams within a feature is undesirable because they can lead to failure of the device. Accordingly, there exists significant interest in the development of thin film deposition methods, particularly ALD methods that can selectively grow a film on one or more substrates and achieve improved filling of a feature on or in a substrate, including depositing a metal-containing film in a manner which substantially fills a feature without any voids.

[0011] CVD and ALD are specifically attractive for fabricating conformal metal containing films on substrates, such as silicon, silicon oxide, metal nitride, metal oxide and other metal-containing layers, using these metal-containing precursors. As noted above, in these techniques, a vapor of a volatile metal complex is introduced into a process reactor where it contacts the surface

of a silicon wafer whereupon a chemical reaction occurs that deposits a thin film of pure metal or a metal compound. CVD occurs if the precursor reacts at the wafer surface either thermally or with a reagent added simultaneously into the process reactor and the film growth occurs in a steady state deposition. CVD can be applied in a continuous or pulsed mode to achieve the desired film thickness. In ALD, the precursor is chemisorbed onto the wafer as a self-saturating monolayer, excess unreacted precursor is purged away with an inert gas such as argon, then excess reagent is added which reacts with the monolayer of chemisorbed precursor to form metal or a metal compound. Excess reagent is then purged away with inert gas. This cycle can then be repeated multiple times to build up the metal or metal compound to a desired thickness with atomic precision since the chemisorption of precursor and reagent are self-limiting. ALD provides the deposition of ultra-thin yet continuous metal containing films with precise control of film thickness, excellent uniformity of film thickness and outstandingly conformal film growth to evenly coat deeply etched and highly convoluted structures such as interconnect vias and trenches. Thus, ALD is typically preferred for deposition of thin films on features with high aspect ratio.

[0012] Suitable metal precursors for ALD include those which are thermally stable to preclude any thermal decomposition occurring during the chemisorption stage yet are chemically reactive towards added reagent. Additionally, it is important that the metal precursors are monomeric for maximum volatility and clean evaporation leaving only a trace of involatile residue. It is also desirable that the precursors are liquid at room temperature.

[0013] CVD/ALD processes using organotin compounds as precursors and an oxygen source such as water vapor or organic co-reactant to deposit MOR (metal organic resist) materials are known.

[0014] WO202016123 A1 discloses a film formed with a precursor and an organic co-reactant, as well as methods for forming and employing such films. The film can be employed as a photopatternable film or a radiation-sensitive film. In some embodiments, the carbon content within the film can be tuned by decoupling the sources of the radiation-sensitive metal elements and the radiation-sensitive organic moieties during deposition. In non-limiting embodiments, the radiation can include extreme UV (EUV) or deep UV (DUV) radiation.

[0015] WO202016128 discloses methods of forming photosensitive metal-polymer hybrid photoresist films for photolithography to improve extreme UV sensitivity and patterning quality are discussed. The method involves depositing a metal-containing layer on a surface of a substrate by providing a metal precursor to the surface, wherein the substrate is disposed within a chamber; purging the metal precursor from the chamber; and depositing an organic layer on a

surface of the metal-containing layer by providing an organic precursor to the surface, where the organic layer comprises a photosensitive organic moiety, thereby forming a patterning radiation-sensitive film.

[0016] US2022155689A discloses a method of depositing a photoresist onto a substrate in a processing chamber. In an embodiment, the method includes flowing an oxidant into the processing chamber through a first path in a showerhead and flowing an organometallic into the processing chamber through a second path in the showerhead. In another embodiment, the first path is isolated from the second path so that the oxidant and the organometallic do not mix within the showerhead. In yet another embodiment, the method further comprises that the oxidant and the organometallic react in the processing chamber to deposit the photoresist on the substrate.

[0017] US2022262625 discloses methods of depositing a metal oxo photoresist using chemical vapor condensation deposition processes over a substrate in a vacuum chamber includes providing a metal precursor vapor into the vacuum chamber from an ampoule maintained at a first temperature the method further includes providing an oxidant vapor into the vacuum chamber, where a reaction between the metal precursor vapor and the oxidant vapor results in the formation of the photoresist layer on a surface of the substrate. the photoresist layer is a metal oxo containing material. The substrate is maintained at a second temperature less than the first temperature during the formation of the photoresist layer on the surface of the substrate.

[0018] US2022002869 discloses methods of depositing a metal oxo photoresist using dry deposition processes for forming a photoresist layer over a substrate in a vacuum chamber comprises providing a metal precursor vapor into the vacuum chamber. In an embodiment, the method further comprises providing an oxidant vapor into the vacuum chamber, where a reaction between the metal precursor vapor and the oxidant vapor gave the photoresist layer on a surface of the substrate.

[0019] US2022199406 discloses a method of forming a metal-oxo photoresist on a substrate. In one embodiment, the method includes repeating a deposition cycle, where each iteration of the deposition cycle includes: a) flowing a metal precursor into a chamber comprising the substrate; and b) flowing an oxidant into the chamber, where the oxidant and the metal precursor react to form the metal-oxo photoresist.

[0020] US10732505 discloses organometallic precursors for the formation of high-resolution lithography patterning coatings based on metal oxide hydroxide. The precursor compositions generally include ligands readily hydrolysable by water vapor or other oh source composition under modest conditions. The organometallic precursors generally include a radiation

sensitive organo ligand to tin that can result in a coating that can be effective for high resolution patterning at relatively low radiation doses and is particularly useful for EUV patterning.

[0021] Mullings, M. N., *et al.*, "Tin Oxide Atomic Layer Deposition from Tetrakis(dimethylamino)tin and Water." *J. Vac. Sci. Technol.*, 31(6) (2013) describes ALD of tin oxide by means of the precursor tetrakis(dimethylamino)tin and water as a counter-reactant at low temperature growth in the range of 30-200 °C on Si(100) and glass substrates. According to this article, high quality, amorphous SnO₂ films with moderately tunable optical properties are thus obtained by ALD at temps. as low as 30 °C using tin precursor and water.

[0022] US2021397085 discloses formation of imaging layers on the surface of a substrate which may be patterned using next generation lithog. techniques, and the resulting patterned film may be used as a lithog. mask, for example, for production of a semiconductor device.

[0023] US2021013034 discloses methods for making thin-films on semiconductor substrates, which may be patterned using EUV, including mixing a vapor stream of an organometallic precursor with a vapor stream of a counter-reactant so as to form a polymerized organometallic material; and depositing the organometallic polymer-like material onto the surface of the semiconductor substrate. the mixing and depositing operations may be performed by chem. vapor deposition (CVD), atomic layer deposition (ALD), and ALD with a CVD component, such as a discontinuous, ALD-like process in which metal precursors and counter-reactants are separated in either time or space.

[0024] Given the above, there is a need for improved deposition methods using organotin compounds as precursors for the deposition of photosensitive materials with better photosensitivity for certain applications in semi-conductor industry such as patterning process especially involving EUV for future technology nodes. As noted above, CVD and ALD have been employed as the main deposition techniques for producing thin films for semiconductor devices. These methods enable deposition of conformal films (*e.g.*, metal, metal oxide, metal nitride, metal silicide, and the like) through chemical reactions of metal-containing compounds (precursors) with a reactive gas in gas phase (CVD) or surface (ALD). This disclosed and claimed subject matter provides an improved deposition method through a combination of ALD and CVD (*i.e.*, an ALD-like process) in which three precursors (*i.e.*, organotin compound, water, and carboxylic acid) unlike a typical ALD process only involving two precursors. It is also worthwhile noting that CVD processes may have particle issues when water vapors are used as co-reactant.

[0025] Described herein is a method for deposition of organotin oxo films film via thermal ALD-like process such as, without limitation, a cyclic chemical vapor deposition process (CCVD)

employing three precursors vs related art processes which typically involves only two precursors. It is believed that reactions between an organotin compound and water vapor via sequentially introducing an organotin compound and water, followed by carboxylic acids can provide better photosensitive organotin oxo materials with improved photosensitivity, smoother film, and less particles. In addition, the ALD-like process described herein has the following advantages: (a) a growth rate ranging from about 2 Å/cycle to 50 Å/cycle, about 2 Å/cycle to about 30 Å/cycle, and about 2 Å/cycle to about 50 Å/cycle (compared to the growth rate of a typical ALD process which is in the range of about 0.1 Å/cycle to about 2 Å/cycle); (b) improved photosensitivity vs related art processes, *i.e.*, the improvement of EUV D50 Speed (mJ/cm²) in range of about 1 to 20 mJ/cm², about 5 to 20 mJ/cm², about 10 to 20 mJ/cm².

[0026] SUMMARY

[0027] In one embodiment, the disclosed and claimed subject matter relates to a method for depositing tin-containing films that includes (i) contacting a substrate with organotin precursor vapor in a deposition reactor vessel, (ii) purging the reactor vessel with inert gas, (iii) contacting the substrate with a water-containing vapor to form an organotin oxo network layer, (iv) purging the reactor vessel with inert gas, (v) contacting the substrate with a carboxylic acid-containing vapor and (vi) purging the reactor vessel with inert gas. The processing steps can be repeated to provide a desired thickness of organotin oxo films. In a further aspect, the method consists essentially of steps (i), (ii), (iii), (iv), (v) and (vi). In a further aspect, the method consists of steps (i), (ii), (iii), (iv), (v) and (vi).

[0028] This summary section does not specify every embodiment and/or incrementally novel aspect of the disclosed and claimed subject matter. Instead, this summary only provides a preliminary discussion of different embodiments and corresponding points of novelty over conventional techniques and the known art. For additional details and/or possible perspectives of the disclosed and claimed subject matter and embodiments, the reader is directed to the Detailed Description section and corresponding figures of the disclosure as further discussed below.

[0029] The order of discussion of the different steps described herein has been presented for clarity's sake. In general, the steps disclosed herein can be performed in any suitable order. Additionally, although each of the different features, techniques, configurations, etc. disclosed herein may be discussed in different places of this disclosure, it is intended that each of the concepts can be executed independently of each other or in combination with each other as appropriate. Accordingly, the disclosed and claimed subject matter can be embodied and viewed in many different ways.

[0030] BRIEF DESCRIPTION OF THE DRAWINGS

[0031] The accompanying drawings, which are included to provide a further understanding of the disclosed subject matter and are incorporated in and constitute a part of this specification, illustrate embodiments of the disclosed subject matter and together with the description serve to explain the principles of the disclosed subject matter. In the drawing:

[0032] FIG. 1 illustrates the dose curve for the oganotin-H₂O-carboxylic acid dosing sequence of Example 1.

[0033] DEFINITIONS

[0034] Unless otherwise stated, the following terms used in the specification and claims shall have the following meanings for this application.

[0035] For purposes of this invention and the claims hereto, the numbering scheme for the Periodic Table Groups is according to the IUPAC Periodic Table of Elements.

[0036] The term “and/or” as used in a phrase such as “A and/or B” herein is intended to include “A and B,” “A or B,” “A” and “B.”

[0037] The terms “substituent,” “radical,” “group” and “moiety” may be used interchangeably.

[0038] As used herein, the terms “metal-containing complex” (or more simply, “complex”) and “precursor” are used interchangeably and refer to metal-containing molecule or compound which can be used to prepare a metal-containing film by a vapor deposition process such as, for example, ALD or CVD. The metal-containing complex may be deposited on, adsorbed to, decomposed on, delivered to, and/or passed over a substrate or surface thereof, as to form a metal-containing film. In one or more embodiments, the metal-containing complexes disclosed herein are metal halide complexes, particularly molybdenum chloride complexes.

[0039] As used herein, the term “metal-containing film” includes not only an elemental metal film as more fully defined below, but also a film which includes a metal along with one or more elements, for example a metal oxide film, metal nitride film, metal silicide film, a metal carbide film and the like. As used herein, the terms “elemental metal film” and “pure metal film” are used interchangeably and refer to a film which consists of, or consists essentially of, pure metal. For example, the elemental metal film may include 100% pure metal, or the elemental metal film may include at least about 70%, at least about 80%, at least about 90%, at least about 95%, at least about 96%, at least about 97%, at least about 98%, at least about 99%, at least about 99.9%, or at least about 99.99% pure metal along with one or more impurities. Unless context dictates otherwise, the term “metal film” shall be interpreted to mean an elemental metal film.

[0040] As used herein, the term “vapor deposition process” is used to refer to any type of vapor deposition technique, including but not limited to, CVD and ALD. In various embodiments, CVD may take the form of conventional (*i.e.*, continuous flow) CVD, liquid injection CVD, or photo-assisted CVD. CVD may also take the form of a pulsed technique, *i.e.*, pulsed CVD. ALD is used to form a metal-containing film by vaporizing and/or passing at least one metal complex disclosed herein over a substrate surface. For conventional ALD processes see, for example, George S. M., *et al. J. Phys. Chem.*, 1996, *100*, 13121–13131. In other embodiments, ALD may take the form of conventional (*i.e.*, pulsed injection) ALD, liquid injection ALD, photo-assisted ALD, plasma-assisted ALD, or plasma-enhanced ALD. The term “vapor deposition process” further includes various vapor deposition techniques described in *Chemical Vapour Deposition: Precursors, Processes, and Applications*; Jones, A. C.; Hitchman, M. L., Eds. The Royal Society of Chemistry: Cambridge, 2009; Chapter 1, pp. 1–36.

[0041] Throughout the description, the term “ALD or ALD-like” refers to a process including, but not limited to, the following processes: a) each reactant including organotin compound precursor and reactive gas is introduced sequentially into a reactor such as a single wafer ALD reactor, semi-batch ALD reactor, or batch furnace ALD reactor; b) each reactant including organotin compound precursor and reactive gas is exposed to a substrate by moving or rotating the substrate to different sections of the reactor and each section is separated by inert gas curtain, *i.e.*, spatial ALD reactor or roll to roll ALD reactor.

[0042] As used herein, the term “feature” refers to an opening in a substrate which may be defined by one or more sidewalls, a bottom surface, and upper corners. In various aspects, the feature may be a via, a trench, contact, dual damascene, *etc.*

[0043] As used herein, the terms “selective growth,” “selectively grown” and “selectively grows” may be used synonymously and refer to film growth on at least a portion of a first substrate and substantially no film growth on a remaining portion of the first substrate as well as more film growth on at least a portion of the first substrate compared to film growth on a remaining portion of the first substrate. For example, selective growth may include growth of a film on a lower portion of a feature while less film growth or no film growth may occur in an upper portion of that feature or outside that feature. With respect to more than one substrate, the terms “selective growth” “selectively grown” and “selectively grows” also encompass film growth on a first substrate and substantially no film growth on a second substrate (or a third substrate, or fourth substrate or a fifth substrate, *etc.*) as

well as more film growth on the first substrate than on the second substrate (or a third substrate, or fourth substrate or a fifth substrate, *etc.*).

[0044] The term “about” or “approximately,” when used in connection with a measurable numerical variable, refers to the indicated value of the variable and to all values of the variable that are within the experimental error of the indicated value (*e.g.*, within the 95% confidence limit for the mean) or within percentage of the indicated value (*e.g.*, $\pm 10\%$, $\pm 5\%$), whichever is greater.

[0045] “Halo” or “halide” refers to a halogen (*e.g.*, F, Cl, Br and I).

[0046] The section headings used herein are for organizational purposes and are not to be construed as limiting the subject matter described. All documents, or portions of documents, cited in this application, including, but not limited to, patents, patent applications, articles, books, and treatises, are hereby expressly incorporated herein by reference in their entirety for any purpose. In the event that any of the incorporated literature and similar materials defines a term in a manner that contradicts the definition of that term in this application, this application controls.

[0047] DETAILED DESCRIPTION

[0048] It is to be understood that both the foregoing general description and the following detailed description are illustrative and explanatory, and are not restrictive of the subject matter, as claimed. The objects, features, advantages and ideas of the disclosed subject matter will be apparent to those skilled in the art from the description provided in the specification, and the disclosed subject matter will be readily practicable by those skilled in the art on the basis of the description appearing herein. The description of any “preferred embodiments” and/or the examples which show preferred modes for practicing the disclosed subject matter are included for the purpose of explanation and are not intended to limit the scope of the claims.

[0049] It will also be apparent to those skilled in the art that various modifications may be made in how the disclosed subject matter is practiced based on described aspects in the specification without departing from the spirit and scope of the disclosed subject matter disclosed herein.

[0050] In one embodiment, the disclosed and claimed subject matter relates to a method for depositing tin-containing films that includes (i) contacting a substrate with organotin precursor vapor in a deposition reactor, (ii) purging the reactor vessel with inert gas, (iii) contacting the substrate with a water-containing vapor to form an organotin oxo network layer, (iv) purging the reactor vessel with inert gas, (v) contacting the substrate with a carboxylic acid-containing vapor and (vi) purging the reactor vessel with inert gas. The processing steps can be repeated may be repeated to provide a desired thickness of organotin oxo films. In a further aspect, the method consists essentially of steps

(i), (ii), (iii), (iv), (v) and (vi). In a further aspect, the method consists of steps (i), (ii), (iii), (iv), (v) and (vi).

[0051] Delivery of Organotin Precursor

[0052] As noted above, step (i) of the disclosed and claimed method includes contacting a substrate with organotin precursor vapor.

[0053] In one embodiment, the organotin precursor has the formula: $\text{RSn}(\text{NR}^1\text{R}^2)_3$ where R, R^1 and R^2 are each independently selected from a linear C_1 to C_6 alkyl group, a branched C_3 to C_6 alkyl group, a C_3 to C_6 cyclic alkyl group, a C_2 to C_6 alkenyl group, a C_2 to C_6 alkynyl group and a C_4 to C_{10} aryl group. In other embodiment, R, R^1 , and R^2 may contain at least one elements selected from the group consisting of oxygen, sulfur, nitrogen and halide (F, Cl, Br, or I).

[0054] In another embodiment, the organotin precursor includes one or more of $\text{MeSn}(\text{NMe}_2)_3$, $\text{MeSn}(\text{NEt}_2)_3$, $\text{EtSn}(\text{NMe}_2)_3$, $\text{EtSn}(\text{NEt}_2)_3$, $\text{n-PrSn}(\text{NMe}_2)_3$, $\text{i-PrSn}(\text{NMe}_2)_3$, $\text{n-BuSn}(\text{NMe}_2)_3$, $\text{i-BuSn}(\text{NMe}_2)_3$, $\text{s-BuSn}(\text{NMe}_2)_3$, $\text{t-BuSn}(\text{NMe}_2)_3$, $\text{cyclopentylSn}(\text{NMe}_2)_3$, $\text{MeSn}(\text{NEtMe})_3$, $\text{EtSn}(\text{NEtMe})_3$, $\text{n-PrSn}(\text{NEtMe})_3$, $\text{i-PrSn}(\text{NEtMe})_3$, $\text{n-BuSn}(\text{NEtMe})_3$, $\text{i-BuSn}(\text{NEtMe})_3$, $\text{s-BuSn}(\text{NEtMe})_3$, $\text{t-BuSn}(\text{NEtMe})_3$, $\text{cyclopentylSn}(\text{NEtMe})_3$ and combinations thereof. In one aspect of this embodiment, the organotin precursor includes $\text{MeSn}(\text{NMe}_2)_3$. In one aspect of this embodiment, the organotin precursor includes $\text{MeSn}(\text{NEt}_2)_3$. In one aspect of this embodiment, the organotin precursor includes $\text{EtSn}(\text{NMe}_2)_3$. In one aspect of this embodiment, the organotin precursor includes $\text{EtSn}(\text{NEt}_2)_3$. In one aspect of this embodiment, the organotin precursor includes $\text{n-PrSn}(\text{NMe}_2)_3$. In one aspect of this embodiment, the organotin precursor includes $\text{i-PrSn}(\text{NMe}_2)_3$. In one aspect of this embodiment, the organotin precursor includes $\text{n-BuSn}(\text{NMe}_2)_3$. In one aspect of this embodiment, the organotin precursor includes $\text{i-BuSn}(\text{NMe}_2)_3$. In one aspect of this embodiment, the organotin precursor includes $\text{s-BuSn}(\text{NMe}_2)_3$. In one aspect of this embodiment, the organotin precursor includes $\text{t-BuSn}(\text{NMe}_2)_3$. In one aspect of this embodiment, the organotin precursor includes $\text{cyclopentylSn}(\text{NMe}_2)_3$. In one aspect of this embodiment, the organotin precursor includes $\text{MeSn}(\text{NEtMe})_3$. In one aspect of this embodiment, the organotin precursor includes $\text{EtSn}(\text{NEtMe})_3$. In one aspect of this embodiment, the organotin precursor includes $\text{n-PrSn}(\text{NEtMe})_3$. In one aspect of this embodiment, the organotin precursor includes $\text{i-PrSn}(\text{NEtMe})_3$. In one aspect of this embodiment, the organotin precursor includes $\text{n-BuSn}(\text{NEtMe})_3$. In one aspect of this embodiment, the organotin precursor includes $\text{i-BuSn}(\text{NEtMe})_3$. In one aspect of this embodiment, the organotin precursor includes $\text{s-BuSn}(\text{NEtMe})_3$. In one aspect of this embodiment, the organotin precursor includes $\text{t-BuSn}(\text{NEtMe})_3$. In one aspect of this embodiment, the organotin precursor includes $\text{cyclopentylSn}(\text{NEtMe})_3$.

[0055] In another embodiment, the organotin precursor vapor pulse time is from about 0.1 seconds to about 3 seconds. In another embodiment, the organotin precursor vapor pulse time is from about 0.3 seconds to about 3 seconds. In another embodiment, the organotin precursor vapor pulse time is about 0.1 second. In another embodiment, the organotin precursor vapor pulse time is about 0.25 second. In another embodiment, the organotin precursor vapor pulse time is about 0.5 second. In another embodiment, the organotin precursor vapor pulse time is about 1 second. In another embodiment, the organotin precursor vapor pulse time is about 1.5 seconds. In another embodiment, the organotin precursor vapor pulse time is about 2 seconds. Yet, in another embodiment, the organotin precursor vapor pulse time is longer than 2 seconds depending on the volume/design of the reactor chamber.

[0056] In one embodiment, the organotin precursor vapor is separated from other precursor materials prior to and/or during the introduction to the reactor. This process avoids pre-reaction of the metal precursor with any other materials.

[0057] In another embodiment, the organotin precursor vapor is alternatively exposed to the substrate with other reactants (*e.g.*, water vapor, and/or other precursors or reagents). This process enables film growth to proceed by self-limiting control of the surface reactions, the pulse length of each precursor or reagent and the deposition temperature. It should be noted, however, that film growth ceases once chemical reaction on the surface of the substrate is complete with organotin precursor vapor.

[0058] In another embodiment, a flow of argon and/or other inert gas is employed as a carrier gas to help deliver the organotin precursor vapor to the reaction reactor during the precursor pulsing.

[0059] **Organotin Precursor Vapor Purging**

[0060] As noted above, step (ii) of the disclosed and claimed method includes (ii) purging the reactor vessel with inert gas. Purging with an inert gas removes unabsorbed excess organotin precursor vapor from the process reactor. In one embodiment, the purge gas includes argon. In one embodiment, the purge gas includes helium. In another embodiment, the purge gas includes nitrogen.

[0061] In one embodiment, for example, the purge time varies from about 1 seconds to about 90 seconds. In one embodiment, for example, the purge time varies from about 15 seconds to about 90 seconds. In one embodiment, for example, the purge time varies from about 15 seconds to about 60 seconds. In another embodiment, the purge time is about 30 seconds. In another embodiment, the purge time is about 60 seconds. In another embodiment, the purge time is about 90 seconds.

[0062] Water-Containing Vapor Reactant

[0063] As noted above, step (iii) of the disclosed and claimed method includes contacting the substrate with a water-containing vapor to form an organotin oxo network layer.

[0064] In one embodiment, for example, the water-containing vapor pulse time varies from about 0.5 seconds to about 5 seconds. In one embodiment, for example, the water-containing vapor pulse time is about 2.5 seconds. In one embodiment, for example, the water-containing vapor pulse time is about 5 seconds. Yet, in another embodiment, the organotin precursor vapor pulse time is longer than 5 seconds depending on the volume/design of the reactor chamber.

[0065] Water-Containing Vapor Purging Step

[0066] As noted above, step (iv) of the disclosed and claimed method includes purging the reactor vessel with inert gas following the water-containing vapor treatment. Purging with an inert gas removes any remaining material used for the water-containing vapor treatment from the process reactor. In one embodiment, the purge gas includes argon. In one embodiment, the purge gas includes helium. In another embodiment, the purge gas includes nitrogen.

[0067] In one embodiment, for example, the optional inert gas purge time varies from about 15 seconds to about 90 seconds. In one embodiment, for example, the optional inert gas purge time varies from about 15 seconds to about 60 seconds. In another embodiment, the optional inert gas purge time is about 30 seconds. In another embodiment, the optional inert gas purge time is about 60 seconds. In another embodiment, the optional inert gas purge time is about 90 seconds.

[0068] Carboxylic Acid-Containing Vapor

[0069] As noted above, step (v) of the disclosed and claimed method includes contacting the substrate with a carboxylic acid-containing vapor. In one embodiment, the carboxylic acid has the formula: R^3COOH where R^3 is selected from hydrogen, a linear C_1 to C_6 alkyl group, a branched C_3 to C_6 alkyl group, a C_3 to C_6 cyclic alkyl group, a C_2 to C_6 alkenyl group, a C_2 to C_6 alkynyl group, and a C_4 to C_{10} aryl group. In another embodiment, R^3 contains at least one element selected from the group consisting of oxygen, sulfur, nitrogen and halide (F, Cl, Br, or I).

[0070] In another embodiment, the carboxylic acid includes one or more of formic acid, acetic acid, dihydroxyacetic acid, propionic acid, lactic acid, butyric acid, iso-butyric acid, valeric acid, 2-methylbutyric acid, 3-methylbutyric acid, pivalic acid, caproic acid, enanthic acid, caprylic acid, pelargonic acid, capric acid, fluoroacetic acid, chloroacetic acid, iodoacetic acid, dichloroacetic acid, 4,4,4-trifluorobutanoic acid, 3,3,3-trifluoropropanoic acid, heptafluorobutyric acid (aka perfluoro-n-butyric acid), perfluoropentanoic acid, 3,3,3-trifluoro-2,2-dimethylpropanoic acid, cyclobutanecarboxylic acid, cyclopentanecarboxylic acid, cyclohexanecarboxylic acid, 4,4-

difluorocyclohexanecarboxylic acid, tetrahydro-3-furancarboxylic acid and combinations thereof. In one aspect of this embodiment, the carboxylic acid includes formic acid. In one aspect of this embodiment, the carboxylic acid includes acetic acid. In one aspect of this embodiment, the carboxylic acid includes dihydroxyacetic acid. In one aspect of this embodiment, the carboxylic acid includes propionic acid. In one aspect of this embodiment, the carboxylic acid includes lactic acid. In one aspect of this embodiment, the carboxylic acid includes butyric acid. In one aspect of this embodiment, the carboxylic acid includes heptafluorobutyric acid. In one aspect of this embodiment, the carboxylic acid includes iso-butyric acid. In one aspect of this embodiment, the carboxylic acid includes valeric acid. In one aspect of this embodiment, the carboxylic acid includes 2-methylbutyric acid. In one aspect of this embodiment, the carboxylic acid includes 3-methylbutyric acid. In one aspect of this embodiment, the carboxylic acid includes pivalic acid. In one aspect of this embodiment, the carboxylic acid includes caproic acid. In one aspect of this embodiment, the carboxylic acid includes enanthic acid. In one aspect of this embodiment, the carboxylic acid includes caprylic acid. In one aspect of this embodiment, the carboxylic acid includes pelargonic acid. In one aspect of this embodiment, the carboxylic acid includes capric acid. In one aspect of this embodiment, the carboxylic acid includes fluoroacetic acid. In one aspect of this embodiment, the carboxylic acid includes chloroacetic acid. In one aspect of this embodiment, the carboxylic acid includes iodoacetic acid. In one aspect of this embodiment, the carboxylic acid includes dichloroacetic acid. In one aspect of this embodiment, the carboxylic acid includes 4,4,4-trifluorobutanoic acid. In one aspect of this embodiment, the carboxylic acid includes 3,3,3-trifluoropropanoic acid. In one aspect of this embodiment, the carboxylic acid includes heptafluorobutyric acid. In one aspect of this embodiment, the carboxylic acid includes perfluoropentanoic acid. In one aspect of this embodiment, the carboxylic acid includes 3,3,3-trifluoro-2,2-dimethylpropanoic acid. In one aspect of this embodiment, the carboxylic acid includes cyclobutanecarboxylic acid. In one aspect of this embodiment, the carboxylic acid includes cyclopentanecarboxylic acid. In one aspect of this embodiment, the carboxylic acid includes cyclohexanecarboxylic acid. In one aspect of this embodiment, the carboxylic acid includes 4,4-difluorocyclohexanecarboxylic acid. In one aspect of this embodiment, the carboxylic acid includes tetrahydro-3-furancarboxylic acid.

[0071] In another embodiment, the carboxylic acid includes, consists essentially of or consists of one more carboxylic acid having a boiling point of 250 °C or lower. In a further aspect of this embodiment, the carboxylic acid includes, consists essentially of or consists of one more carboxylic acid having a boiling point of 200 °C or lower.

[0072] In another embodiment, the carboxylic acid vapor is substantially free of any carboxylic acids having boiling points of greater 250 °C. In a further aspect of this embodiment, the carboxylic acid vapor is substantially free of any carboxylic acids having boiling points of greater 200 °C.

[0073] In another embodiment, the carboxylic acid vapor is free of any carboxylic acids having boiling points of greater 250 °C. In a further aspect of this embodiment, the carboxylic acid vapor is substantially free of any carboxylic acids having boiling points of greater 200 °C.

[0074] **Carboxylic Acid-Containing Vapor Purging Step**

[0075] As noted above, step (vi) of the disclosed and claimed method includes purging the reactor vessel with inert gas following the carboxylic acid-containing vapor treatment. Purging with an inert gas removes any remaining material used for the carboxylic acid-containing vapor treatment from the process reactor. In one embodiment, the purge gas includes argon. In one embodiment, the purge gas includes helium. In another embodiment, the purge gas includes nitrogen.

[0076] In one embodiment, for example, the optional inert gas purge time varies from about 15 seconds to about 90 seconds. In one embodiment, for example, the optional inert gas purge time varies from about 15 seconds to about 60 seconds. In another embodiment, the optional inert gas purge time is about 30 seconds. In another embodiment, the optional inert gas purge time is about 60 seconds. In another embodiment, the optional inert gas purge time is about 90 seconds.

[0077] **Photosensitivity**

[0078] Radiation sensitive resists are films designed to change their solubility when exposed to radiation. In a further aspect, the disclosed and claimed process further includes exposing the tin-containing films to a radiation source selected from the group of KrF (248 nm), ArF (193 nm), VUV (157 nm), EUV (13 nm), E-beam, X-ray and ion beam. Patterns are formed by selectively exposing only the desired areas of the film. The films are exposed to radiation (photons in the case of EUV, electrons in the case of EBL), then the sample is then washed in a solvent (called a developer) that dissolves away either the exposed (positive-tone resists) or unexposed (negative-tone resist) region. In either the case, the pattern of radiation exposure has now become the pattern of presence or absence of resist on the substrate. The resist can then be used as a mask for further semiconductor processing steps, such as etching or deposition.

[0079] FIG. 1 shows a graph of a dose matrix test. This graph is generated by exposing an array of identical patterns on a sample with a resist film. The dose, or amount of radiation provided, is different at each point in the array. FIG. 1 provides a plot for each dose the height of the resist

remaining after development, but we could also use other measures of quality of the patterns produced. As can be seen, the sensitivity of the resist by looking at the lowest dose that still provides the desired patterns. Higher sensitivity (responding at a lower dose) is generally preferred. Also of interest is the contrast, a measure of how quickly the response of the film increases as the dose exceeds the minimum dose required.

[0080] Operating Conditions

[0081] As noted above, the disclosed and claimed tin deposition process can be effectively conducted under very favorable ALD conditions.

[0082] In one embodiment the substrate is one or more of amorphous carbon, silicon oxide (SiO₂), aluminum oxide (Al₂O₃), titanium nitride (TiN), hafnium oxide (HfO₂), zirconium oxide (ZrO₂), underlayer consist of two or more elements such as Si, O, C, N, Ge, Sn, Sb and Te) and combination thereof is heated on a heater stage in a reaction reactor that is exposed to the organotin precursor initially to allow the complex to chemically adsorb onto the surface of the substrate. In one embodiment, the substrate temperature is from about 25 °C to about 300 °C. In a further aspect of this embodiment, the substrate temperature is from about 25 °C to about 250 °C. In a further aspect of this embodiment, the substrate temperature is from about 25 °C to about 200 °C, or from about 50 °C to about 150 °C, or from about 50 °C to about 130 °C, or from about 60 °C to about 130 °C, or from about 70 °C to about 120 °C, or from about 80 °C to about 110 °C. Not bounded by theory, it is expected the substrate temperatures lower than 120 °C may facilitate the reaction of organotin precursor and water on the substrate surface, thus promoting formation of organotin oxo film.

[0083] In another embodiment, the reactor pressure for depositions according to the disclosed and claimed process is $\leq$ about 100 torr. In another embodiment, the reactor pressure for depositions according to the disclosed and claimed process is $\leq$ about 75 torr. In another embodiment, the reactor pressure for depositions according to the disclosed and claimed process is $\leq$ about 50 torr. In another embodiment, the reactor pressure for depositions according to the disclosed and claimed process is $\leq$ about 40 torr. In another embodiment, the reactor pressure for depositions according to the disclosed and claimed process is $\leq$ about 30 torr. In a further aspect of this embodiment, the reactor pressure is $\leq$ about 20 torr. In a further aspect of this embodiment, the reactor pressure is $\leq$ about 10 torr. In a further aspect of this embodiment, the reactor pressure is $\leq$ about 5 torr.

[0084] Cycles and Order of Steps

[0085] In the above-described embodiments, as well as the other embodiments described herein, the described steps (*e.g.*, (i) through (vi)) define one cycle of the method. It is to be understood that a cycle can be repeated until the desired thickness of a film is obtained.

[0086] In the embodiments described herein, it is understood that the steps of the methods may be performed in a variety of orders, may be performed sequentially or concurrently (*e.g.*, during at least a portion of another step), and any combination thereof. In addition, the respective steps of supplying the reactants (*i.e.*, the organotin precursor, the water-containing vapor and the carboxylic acid-containing vapor) and or the subsequent purges thereof may be performed by varying the duration of the time for supplying them to change film composition.

[0087] Exemplary Processes

In one exemplary embodiment of the disclosed and claimed subject matter, organotin oxo films are formed on a substrate using an ALD/ALD-like deposition method. The substrate and reactor are heated to a temperature of about 25°C to about 200°C and the reactor pressure is (optionally) maintained at a about 100 torr or less. The steps of the deposition include:

- (i) introducing into the reactor at least one organotin precursor vapor having the $\text{RSn}(\text{NR}^1\text{R}^2)_3$ where R, R^1 and R^2 are each independently selected from a linear C_1 to C_6 alkyl group, a branched C_3 to C_6 alkyl group, a C_3 to C_6 cyclic alkyl group, a C_2 to C_6 alkenyl group, a C_2 to C_6 alkynyl group and a C_4 to C_{10} aryl group;
- (ii) purging with inert gas;
- (iii) introducing a water-containing vapor;
- (iv) purging with inert gas;
- (v) introducing a carboxylic acid-containing vapor having the formula R^3COOH where R^3 is independently selected from hydrogen, a linear C_1 to C_6 alkyl group, a branched C_3 to C_6 alkyl group, a C_3 to C_6 cyclic alkyl group, a C_2 to C_6 alkenyl group, a C_2 to C_6 alkynyl group, and a C_4 to C_{10} aryl group; and
- (vi) purging with inert gas.

Steps (i) to (vi) may be repeated to provide a desired thickness of organotin oxo films which can range from about 50 Å to about 1000 Å, about 50 Å to about 500 Å, about 50 Å to about 300 Å or about 50 Å to about 200 Å. In one embodiment, the films formed by the methods described herein have a thickness of about 50 Å to about 1000 Å. In another aspect of this embodiment, the films formed by the methods described herein have a thickness of about 50 Å to 500 Å. In another aspect of this embodiment, the films formed by the methods described herein have a thickness of about 50 Å to 300

Å. In another aspect of this embodiment, the films formed by the methods described herein have a thickness of about, 50 Å to 200 Å.

[0088] In another exemplary embodiment of the disclosed and claimed subject matter, organotin oxo films are formed on a substrate using an ALD/ALD-like deposition method. The substrate and reactor are heated to a temperature of about 25°C to about 200°C and the reactor pressure is (optionally) maintained at a about 100 torr or less. The steps of the deposition include:

- (i) introducing into the reactor at least one organotin precursor vapor having the $\text{RSn}(\text{NR}^1\text{R}^2)_3$ where R, R^1 and R^2 are each independently selected from a linear C_1 to C_6 alkyl group, a branched C_3 to C_6 alkyl group, a C_3 to C_6 cyclic alkyl group, a C_2 to C_6 alkenyl group, a C_2 to C_6 alkynyl group and a C_4 to C_{10} aryl group;
- (ii) purging with inert gas;
- (iii) introducing a water-containing vapor;
- (iv) purging with inert gas;
- (v) introducing a carboxylic acid-containing vapor having the formula R^3COOH where R^3 is independently selected from hydrogen, a linear C_1 to C_6 alkyl group, a branched C_3 to C_6 alkyl group, a C_3 to C_6 cyclic alkyl group, a C_2 to C_6 alkenyl group, a C_2 to C_6 alkynyl group, and a C_4 to C_{10} aryl group; and
- (vi) purging with inert gas.

In some embodiments, steps (i) to (iv) may be repeated to provide a desired thickness of organotin oxo films which can range from about 50 Å to about 1000 Å, about 50 Å to about 500 Å, about 50 Å to about 300 Å or about 50 Å to about 200 Å, followed by steps (v) to (vi) are conducted to modify the resulting organotin oxo films. In some embodiments, a super-cycle ALD or ALD-like process may be performed, one super-cycle comprises the following: steps (i) to (iv) may be repeated to provide a desired thickness of organotin oxo films which can range from about 50 Å to about 1000 Å, about 50 Å to about 500 Å, about 50 Å to about 300 Å or about 50 Å to about 200 Å, followed by steps (v) to (vi) to modify the resulting organotin oxo films. The super-cycle can be repeated to provide a desired thickness of organotin oxo film. It is believed that reaction between the carboxylic acid and the resulting organotin oxo film from steps (i) to (iv) may improve/stabilize the organotin oxo film, thus allowing the organotin oxo films to be more resistant to environment changes such as moisture or carbon dioxide during semi-conductor fabrication processes.

[0089] Examples

[0090] Reference will now be made to more specific embodiments of the present disclosure and experimental results that provide support for such embodiments. The examples given below more fully illustrate the disclosed and claimed subject matter and should not be construed as limiting the disclosed subject matter in any way.

[0091] It will be apparent to those skilled in the art that various modifications and variations can be made in the disclosed subject matter and specific examples provided herein without departing from the spirit or scope of the disclosed subject matter. Thus, it is intended that the disclosed subject matter, including the descriptions provided by the following examples, covers the modifications and variations of the disclosed subject matter that come within the scope of any claims and their equivalents.

[0092] Example 1

[0093] Conditions: Deposition temperature was 90 °C; reactor pressure was about 2 torr; i-PrSn(NMe₂)₃ was employed as organotin precursor. Table 1 summarizes the results.

Ex.	Sequence		Growth/Cycle (Å/cycle)	EBL D50 Photospeed (μC/cm ²)	EUV D50 Photospeed (mJ/cm ²)
1	a	i-PrSn	12.0	160	21.5
	b	H ₂ O			
2	a	i-PrSn	0.2	NA	NA
	b	Acetic Acid			
3	a	i-PrSn	5.0	120	15.3
	b	H ₂ O			
	c	Acetic Acid			
4	a	i-PrSn	13.0	160	17.5
	b	Acetic Acid			
	c	H ₂ O			

Table 1

[0094] As shown in Table 1, the direct reaction between i-PrSn(NMe₂)₃ (“i-PrSn” above) and acetic acid (Ex. 2) was quite slow when compared to the growth rate between i-PrSn and water (Ex. 1). In ex. 2, for example, the GPC was only 0.2 Å/ cycle from direct reaction between i-PrSn-acetic

acid at 90 °C which is an extremely long film deposition time due to low precursor conversion efficiency. In comparison, the GPC for Ex. 1 was about 12 Å/ cycle. By comparison, GPC as high as 13 Å/ cycle can be achieved using i-PrSn-acetic acid-H₂O sequence (Ex. 4). The photosensitivity is measured using an electron beam; the smaller the photosensitivity value implies the resulting organotin oxo films are more sensitive (*i.e.*, higher photosensitivity) as photosensitive materials for future patterning applications. In Table 1, “NA” reflects that producing 250 Å films with 0.2 Å /cycle will consume too much precursor.

[0095] Table 1 also compared photosensitivity of the two sequences with carboxylic acid, with baseline sequence where no carboxylic acid was used. Even though adding carboxylic acid before H₂O vapor in the sequence resulted in higher GPC (Ex. 4), the photosensitivity (dosage) from EBL measurement was about the same as that of iso-propyl tris(dimethyl amido)tin-H₂O baseline (Ex. 1). In contrast, faster photosensitivity was achieved (as indicated by smaller D50 in the EBL Dose Curve) when carboxylic acid was added after the water (Ex. 3). The significant improvement (*ca.* 25%) in photosensitivity for organotin-H₂O-carboxylic acid sequence was unexpected and not disclosed by any prior studies as shown in FIG. 1. FIG. 1 is generated by exposing an array of identical patterns on a sample with a resist film. The dose, or amount of radiation provided, is different at each point in the array. The plot in FIG.1 for each dose the height of the resist remaining after development. The sensitivity of the resist is evaluated by looking at the lowest dose that still provides the desired patterns. Higher sensitivity (responding at a lower dose) is generally preferred. Also of interest is the contrast, a measure of how quickly the response of the film increases as the dose exceeds the minimum dose required.

[0096] Based on the above, it has been shown that the addition of the carboxylic acid (*e.g.*, acetic acid) after the organotin precursor and water, significantly and unexpectedly improves the photosensitivity over the baseline of reacting organotin and water alone. Although the growth per cycle is lower (*ca.* 40% of the baseline process), the new sequence provides the advantages of increased photosensitivity which directly translates into higher throughput and lower cost of ownership.

[0097] Example 2

[0098] Conditions: Deposition temperature was 90 °C and 130 °C, respectively; reactor pressure was about 2 torr; t-BuSn(NMe₂)₃ (t-BuSn) and n-BuSn(NMe₂)₃ (n-BuSn) were employed as organotin precursor, respectively. Table 1 summarizes the results. Acetic acid cap was carried in the same chamber immediately after organotin oxo film deposition was complete.

Process Splits	Pedestal Temp (°C)	GPC (Å/cyc)	EUV D50 Speed (mJ/cm ²)	EUV Contrast
t-BuSn – H ₂ O	130	2.3	12 to 12.6	3.3 to 4
t-BuSn – H ₂ O with Acetic Acid Cap	130	2.3	3.1	~ 7.2
n-BuSn – H ₂ O	90	4.6	22.8	5.9
n-BuSn – H ₂ O with Acetic Acid Cap	90	6.9	5.8	2.7

Table 2

[0099] As shown in Table 2, there is about 4x EUV photospeed improvement with the *in-situ* acetic acid cap demonstrated for both t-BuSn – H₂O and n-BuSn-H₂O – H₂O processes at different deposition temperatures, the improvement of EUV D50 Speed (mJ/cm²) for t-BuSn – H₂O with acetic acid cap vs t-BuSn – H₂O is about 9 mJ/cm² while n-BuSn – H₂O with acetic acid cap vs n-BuSn – H₂O is about 17 mJ/cm². The *in-situ* acetic acid capping steps were carried out at the same temperature as the deposition process. In this setup, the film thickness (and growth per cycles) remained the same or was even enhanced contrary to adding acetic acid to the deposition sequence as in Example 1. Therefore, EUV speed improvement could be achieved without sacrificing the growth per cycle and the throughput.

[0100] Example 3

[0101] Conditions: Deposition temperature was 130 °C; reactor pressure was about 2 torr; t-BuSn(NMe₂)₃ (t-BuSn) was employed as organotin precursor. Table 3 summarizes the results. Pivalic acid was employed in the same chamber immediately after organotin oxo film deposition was complete.

Process Splits	Pedestal Temp (°C)	EBL D50 Photospeed (μC/cm ²)
t-BuSn – H ₂ O	130	140
t-BuSn – H ₂ O with Pivalic Acid Cap	130	120

Table 3

[0102] Although the invention has been described and illustrated with a certain degree of particularity, it is understood that the disclosure has been made only by way of example, and that numerous changes in the conditions and order of steps can be resorted to by those skilled in the art without departing from the spirit and scope of the invention.

Claims

What is claimed is

1. A method for depositing tin-containing films comprising:
 - (i) contacting a substrate with organotin precursor vapor in a deposition reactor vessel;
 - (ii) purging the reactor vessel with inert gas;
 - (iii) contacting the substrate with a water-containing vapor to form an organotin oxo network layer;
 - (iv) purging the reactor vessel with inert gas;
 - (v) contacting the substrate with a carboxylic acid-containing vapor; and
 - (vi) purging the reactor vessel with inert gas.
2. The method of claim 1, wherein the organotin precursor of the step (i) contacting a substrate with organotin precursor vapor in a deposition reactor vessel comprises an organotin precursor of formula: $\text{RSn}(\text{NR}^1\text{R}^2)_3$ wherein R, R^1 and R^2 are each independently selected from a linear C_1 to C_6 alkyl group, a branched C_3 to C_6 alkyl group, a C_3 to C_6 cyclic alkyl group, a C_2 to C_6 alkenyl group, a C_2 to C_6 alkynyl group and a C_4 to C_{10} aryl group.
3. The method of claim 1, wherein the organotin precursor of the step (i) contacting a substrate with organotin precursor vapor in a deposition reactor vessel comprises one or more of $\text{MeSn}(\text{NMe}_2)_3$, $\text{MeSn}(\text{NEt}_2)_3$, $\text{EtSn}(\text{NMe}_2)_3$, $\text{EtSn}(\text{NEt}_2)_3$, $\text{n-PrSn}(\text{NMe}_2)_3$, $\text{i-PrSn}(\text{NMe}_2)_3$, $\text{n-BuSn}(\text{NMe}_2)_3$, $\text{i-BuSn}(\text{NMe}_2)_3$, $\text{s-BuSn}(\text{NMe}_2)_3$, $\text{t-BuSn}(\text{NMe}_2)_3$, $\text{cyclopentylSn}(\text{NMe}_2)_3$, $\text{MeSn}(\text{NEtMe})_3$, $\text{EtSn}(\text{NEtMe})_3$, $\text{n-PrSn}(\text{NEtMe})_3$, $\text{i-PrSn}(\text{NEtMe})_3$, $\text{n-BuSn}(\text{NEtMe})_3$, $\text{i-BuSn}(\text{NEtMe})_3$, $\text{s-BuSn}(\text{NEtMe})_3$, $\text{t-BuSn}(\text{NEtMe})_3$, $\text{cyclopentylSn}(\text{NEtMe})_3$ and combinations thereof.
4. The method of claim 1, wherein the organotin precursor of step (i) contacting a substrate with organotin precursor vapor in a deposition reactor vessel comprises an organotin precursor.
5. The method of claim 1, wherein the organotin precursor of step (i) contacting a substrate with organotin precursor vapor in a deposition reactor vessel comprises $\text{MeSn}(\text{NMe}_2)_3$.
6. The method of claim 1, wherein the organotin precursor of step (i) contacting a substrate with organotin precursor vapor in a deposition reactor vessel comprises $\text{MeSn}(\text{NEt}_2)_3$.
7. The method of claim 1, wherein the organotin precursor of step (i) contacting a substrate with organotin precursor vapor in a deposition reactor vessel comprises $\text{EtSn}(\text{NMe}_2)_3$.
8. The method of claim 1, wherein the organotin precursor of step (i) contacting a substrate with organotin precursor vapor in a deposition reactor vessel comprises $\text{EtSn}(\text{NEt}_2)_3$.
9. The method of claim 1, wherein the organotin precursor of step (i) contacting a substrate with organotin precursor vapor in a deposition reactor vessel comprises $\text{n-PrSn}(\text{NMe}_2)_3$.

10. The method of claim 1, wherein the organotin precursor of step (i) contacting a substrate with organotin precursor vapor in a deposition reactor vessel comprises $i\text{-PrSn}(\text{NMe}_2)_3$.
11. The method of claim 1, wherein the organotin precursor of step (i) contacting a substrate with organotin precursor vapor in a deposition reactor vessel comprises $n\text{-BuSn}(\text{NMe}_2)_3$.
12. The method of claim 1, wherein the organotin precursor of step (i) contacting a substrate with organotin precursor vapor in a deposition reactor vessel comprises $i\text{-BuSn}(\text{NMe}_2)_3$.
13. The method of claim 1, wherein the organotin precursor of step (i) contacting a substrate with organotin precursor vapor in a deposition reactor vessel comprises $s\text{-BuSn}(\text{NMe}_2)_3$.
14. The method of claim 1, wherein the organotin precursor of step (i) contacting a substrate with organotin precursor vapor in a deposition reactor vessel comprises $t\text{-BuSn}(\text{NMe}_2)_3$.
15. The method of claim 1, wherein the organotin precursor of step (i) contacting a substrate with organotin precursor vapor in a deposition reactor vessel comprises $\text{cyclopentylSn}(\text{NMe}_2)_3$.
16. The method of claim 1, wherein the organotin precursor of step (i) contacting a substrate with organotin precursor vapor in a deposition reactor vessel comprises $\text{MeSn}(\text{NEtMe})_3$.
17. The method of claim 1, wherein the organotin precursor of step (i) contacting a substrate with organotin precursor vapor in a deposition reactor vessel comprises $\text{EtSn}(\text{NEtMe})_3$.
18. The method of claim 1, wherein the organotin precursor of step (i) contacting a substrate with organotin precursor vapor in a deposition reactor vessel comprises $n\text{-PrSn}(\text{NEtMe})_3$.
19. The method of claim 1, wherein the organotin precursor of step (i) contacting a substrate with organotin precursor vapor in a deposition reactor vessel comprises $i\text{-PrSn}(\text{NEtMe})_3$.
20. The method of claim 1, wherein the organotin precursor of step (i) contacting a substrate with organotin precursor vapor in a deposition reactor vessel comprises $n\text{-BuSn}(\text{NEtMe})_3$.
21. The method of claim 1, wherein the organotin precursor of step (i) contacting a substrate with organotin precursor vapor in a deposition reactor vessel comprises $i\text{-BuSn}(\text{NEtMe})_3$.
22. The method of claim 1, wherein the organotin precursor of step (i) contacting a substrate with organotin precursor vapor in a deposition reactor vessel comprises $s\text{-BuSn}(\text{NEtMe})_3$.
23. The method of claim 1, wherein the organotin precursor of step (i) contacting a substrate with organotin precursor vapor in a deposition reactor vessel comprises $t\text{-BuSn}(\text{NEtMe})_3$.
24. The method of claim 1, wherein the organotin precursor of step (i) contacting a substrate with organotin precursor vapor in a deposition reactor vessel comprises $\text{cyclopentylSn}(\text{NEtMe})_3$.
25. The method of claim 1, wherein the step of (i) contacting a substrate with organotin precursor vapor in a deposition reactor vessel comprises pulsing the organotin precursor vapor for about 0.1 seconds to about 3 seconds.

26. The method of claim 1, wherein the step of (ii) purging the reactor vessel with inert gas comprises a purge time of about 1 seconds to about 90 seconds.
27. The method of claim 1, wherein the step of (ii) purging the reactor vessel with inert gas comprises a purge time of about 15 seconds to about 90 seconds.
28. The method of claim 1, wherein the step of (ii) purging the reactor vessel with inert gas comprises a purge time of about 15 seconds to about 60 seconds.
29. The method of claim 1, wherein the step of (ii) purging the reactor vessel with inert gas comprises a purge time of about 30 seconds.
30. The method of claim 1, wherein the step of (ii) purging the reactor vessel with inert gas comprises a purge time of about 60 seconds.
31. The method of claim 1, wherein the step of (ii) purging the reactor vessel with inert gas comprises a purge time of about 90 seconds.
32. The method of claim 1, wherein the step of (ii) purging the reactor vessel with inert gas comprises purging with an inert gas comprising argon.
33. The method of claim 1, wherein the step of (ii) purging the reactor vessel with inert gas comprises purging with an inert gas comprising nitrogen.
34. The method of claim 1, wherein the step of (ii) purging the reactor vessel with inert gas comprises purging with an inert gas comprising helium.
35. The method of claim 1, wherein the step of (iii) contacting the substrate with a water-containing vapor to form an organotin oxo network layer comprises pulsing the water-containing vapor from about 0.5 seconds to about 5 seconds.
36. The method of claim 1, wherein the step of (iii) contacting the substrate with a water-containing vapor to form an organotin oxo network layer comprises pulsing the water-containing vapor for about 2.5 seconds.
37. The method of claim 1, wherein the step of (iii) contacting the substrate with a water-containing vapor to form an organotin oxo network layer comprises pulsing the water-containing vapor for about 5 seconds.
38. The method of claim 1, wherein the step of (iii) contacting the substrate with a water-containing vapor to form an organotin oxo network layer comprises pulsing the water-containing vapor for longer than 5 seconds.
39. The method of claim 1, wherein the step of (iv) purging the reactor vessel with inert gas comprises a purge time of about 15 seconds to about 90 seconds.

40. The method of claim 1, wherein the step of (iv) purging the reactor vessel with inert gas comprises a purge time of about 15 seconds to about 60 seconds.
41. The method of claim 1, wherein the step of (iv) purging the reactor vessel with inert gas comprises a purge time of about 30 seconds.
42. The method of claim 1, wherein the step of (iv) purging the reactor vessel with inert gas comprises a purge time of about 60 seconds.
43. The method of claim 1, wherein the step of (iv) purging the reactor vessel with inert gas comprises a purge time of about 90 seconds.
44. The method of claim 1, wherein the step of (iv) purging the reactor vessel with inert gas comprises purging with an inert gas comprising argon.
45. The method of claim 1, wherein the step of (iv) purging the reactor vessel with inert gas comprises purging with an inert gas comprising nitrogen.
46. The method of claim 1, wherein the step of (iv) purging the reactor vessel with inert gas comprises purging with an inert gas comprising helium.
47. The method of claim 1, wherein the carboxylic acid of the step (v) contacting the substrate with a carboxylic acid-containing vapor comprises a carboxylic acid of formula: R^3COOH wherein R^3 is selected from hydrogen, a linear C_1 to C_6 alkyl group, a branched C_3 to C_6 alkyl group, a C_3 to C_6 cyclic alkyl group, a C_2 to C_6 alkenyl group, a C_2 to C_6 alkynyl group, and a C_4 to C_{10} aryl group.
48. The method of claim 1, wherein the carboxylic acid of the step (v) contacting the substrate with a carboxylic acid-containing vapor comprises one or more of formic acid, acetic acid, dihydroxyacetic acid, propionic acid, lactic acid, butyric acid, iso-butyric acid, valeric acid, 2-methylbutyric acid, 3-methylbutyric acid, pivalic acid, caproic acid, enanthic acid, caprylic acid, pelargonic acid, capric acid, fluoroacetic acid, chloroacetic acid, iodoacetic acid, dichloroacetic acid, 4,4,4-trifluorobutanoic acid, 3,3,3-trifluoropropanoic acid, heptafluorobutyric acid (aka perfluoro-n-butanoic acid), perfluoropentanoic acid, 3,3,3-trifluoro-2,2-dimethylpropanoic acid, cyclobutanecarboxylic acid, cyclopentanecarboxylic acid, cyclohexanecarboxylic acid, 4,4-difluorocyclohexanecarboxylic acid, tetrahydro-3-furancarboxylic acid and combinations thereof.
49. The method of claim 1, wherein the carboxylic acid of the step (v) contacting the substrate with a carboxylic acid-containing vapor comprises formic acid.
50. The method of claim 1, wherein the carboxylic acid of the step (v) contacting the substrate with a carboxylic acid-containing vapor comprises acetic acid.
51. The method of claim 1, wherein the carboxylic acid of the step (v) contacting the substrate with a carboxylic acid-containing vapor comprises dihydroxyacetic acid.

52. The method of claim 1, wherein the carboxylic acid of the step (v) contacting the substrate with a carboxylic acid-containing vapor comprises propionic acid.
53. The method of claim 1, wherein the carboxylic acid of the step (v) contacting the substrate with a carboxylic acid-containing vapor comprises lactic acid.
54. The method of claim 1, wherein the carboxylic acid of the step (v) contacting the substrate with a carboxylic acid-containing vapor comprises butyric acid.
55. The method of claim 1, wherein the carboxylic acid of the step (v) contacting the substrate with a carboxylic acid-containing vapor comprises iso-butyric acid.
56. The method of claim 1, wherein the carboxylic acid of the step (v) contacting the substrate with a carboxylic acid-containing vapor comprises valeric acid.
57. The method of claim 1, wherein the carboxylic acid of the step (v) contacting the substrate with a carboxylic acid-containing vapor comprises heptafluorobutyric acid.
58. The method of claim 1, wherein the carboxylic acid of the step (v) contacting the substrate with a carboxylic acid-containing vapor comprises perfluoropentanoic acid.
59. The method of claim 1, wherein the carboxylic acid of the step (v) contacting the substrate with a carboxylic acid-containing vapor comprises 3,3,3-trifluoro-2,2-dimethylpropanoic acid.
60. The method of claim 1, wherein the carboxylic acid of the step (v) contacting the substrate with a carboxylic acid-containing vapor comprises pivalic acid.
61. The method of claim 1, wherein the carboxylic acid of the step (v) contacting the substrate with a carboxylic acid-containing vapor comprises 2-methylbutyric acid.
62. The method of claim 1, wherein the carboxylic acid of the step (v) contacting the substrate with a carboxylic acid-containing vapor comprises 3-methylbutyric acid.
63. The method of claim 1, wherein the carboxylic acid of the step (v) contacting the substrate with a carboxylic acid-containing vapor comprises caproic acid.
64. The method of claim 1, wherein the carboxylic acid of the step (v) contacting the substrate with a carboxylic acid-containing vapor comprises enanthic acid.
65. The method of claim 1, wherein the carboxylic acid of the step (v) contacting the substrate with a carboxylic acid-containing vapor comprises caprylic acid.
66. The method of claim 1, wherein the carboxylic acid of the step (v) contacting the substrate with a carboxylic acid-containing vapor comprises pelargonic acid.
67. The method of claim 1, wherein the carboxylic acid of the step (v) contacting the substrate with a carboxylic acid-containing vapor comprises capric acid.

68. The method of claim 1, wherein the carboxylic acid of the step (v) contacting the substrate with a carboxylic acid-containing vapor comprises fluoroacetic acid.
69. The method of claim 1, wherein the carboxylic acid of the step (v) contacting the substrate with a carboxylic acid-containing vapor comprises chloroacetic acid.
70. The method of claim 1, wherein the carboxylic acid of the step (v) contacting the substrate with a carboxylic acid-containing vapor comprises iodoacetic acid.
71. The method of claim 1, wherein the carboxylic acid of the step (v) contacting the substrate with a carboxylic acid-containing vapor comprises dichloroacetic acid.
72. The method of claim 1, wherein the carboxylic acid of the step (v) contacting the substrate with a carboxylic acid-containing vapor comprises 4,4,4-trifluorobutanoic acid.
73. The method of claim 1, wherein the carboxylic acid of the step (v) contacting the substrate with a carboxylic acid-containing vapor comprises 3,3,3-trifluoropropanoic acid.
74. The method of claim 1, wherein the carboxylic acid of the step (v) contacting the substrate with a carboxylic acid-containing vapor comprises cyclobutanecarboxylic acid.
75. The method of claim 1, wherein the carboxylic acid of the step (v) contacting the substrate with a carboxylic acid-containing vapor comprises cyclopentanecarboxylic acid.
76. The method of claim 1, wherein the carboxylic acid of the step (v) contacting the substrate with a carboxylic acid-containing vapor comprises cyclohexanecarboxylic acid.
77. The method of claim 1, wherein the carboxylic acid of the step (v) contacting the substrate with a carboxylic acid-containing vapor comprises 4,4-difluorocyclohexanecarboxylic acid.
78. The method of claim 1, wherein the carboxylic acid of the step (v) contacting the substrate with a carboxylic acid-containing vapor comprises tetrahydro-3-furancarboxylic acid.
79. The method of claim 1, wherein the carboxylic acid of the step (v) contacting the substrate with a carboxylic acid-containing vapor comprises one or more carboxylic acid having a boiling point of 250 °C or lower.
80. The method of claim 1, wherein the carboxylic acid of the step (v) contacting the substrate with a carboxylic acid-containing vapor comprises one or more carboxylic acid having a boiling point of 200 °C or lower.
81. The method of claim 1, wherein the carboxylic acid of the step (v) contacting the substrate with a carboxylic acid-containing vapor is substantially free of any carboxylic acids having boiling points of greater 250 °C.

82. The method of claim 1, wherein the carboxylic acid of the step (v) contacting the substrate with a carboxylic acid-containing vapor is substantially free of any carboxylic acids having boiling points of greater 200 °C.
83. The method of claim 1, wherein the carboxylic acid of the step (v) contacting the substrate with a carboxylic acid-containing vapor is free of any carboxylic acids having boiling points of greater 250 °C.
84. The method of claim 1, wherein the carboxylic acid of the step (v) contacting the substrate with a carboxylic acid-containing vapor is free of any carboxylic acids having boiling points of greater 200 °C.
85. The method of claim 1, wherein the step of (vi) purging the reactor vessel with inert gas comprises a purge time of about 15 seconds to about 90 seconds.
86. The method of claim 1, wherein the step of (vi) purging the reactor vessel with inert gas comprises a purge time of about 15 seconds to about 60 seconds.
87. The method of claim 1, wherein the step of (vi) purging the reactor vessel with inert gas comprises a purge time of about 30 seconds.
88. The method of claim 1, wherein the step of (vi) purging the reactor vessel with inert gas comprises a purge time of about 60 seconds.
89. The method of claim 1, wherein the step of (vi) purging the reactor vessel with inert gas comprises a purge time of about 90 seconds.
90. The method of claim 1, wherein the step of (vi) purging the reactor vessel with inert gas comprises purging with an inert gas comprising argon.
91. The method of claim 1, wherein the step of (vi) purging the reactor vessel with inert gas comprises purging with an inert gas comprising nitrogen.
92. The method of claim 1, wherein the step of (vi) purging the reactor vessel with inert gas comprises purging with an inert gas comprising helium.
93. The method of any of claims 1-92, further comprising exposing tin-containing films to a radiation source selected from the group of KrF (248 nm), ArF (193 nm), VUV (157 nm), EUV (13 nm), E-beam, X-ray and ion beam.
94. An organotin oxo material deposited by any of claims 1-93.