

PROCESSES FOR PHOTORESIST MATERIAL DEPOSITION**BACKGROUND****[0001] Field**

[0002] The disclosed and claimed subject matter relates to bismuth-based and antimony-based compositions useful for deposition of bismuth-containing and antimony-containing films on substrates. In particular, the disclosed and claimed subject matter relates to bismuth-based and antimony-based compositions and materials and processes for formation of metal-organic photoresists.

[0003] Related Art

[0004] A goal in the modern semiconductor industry is the development of nanolithography technologies and related materials for achieving higher resolution in lithography. This goal has been receiving increasing attention because fabricating integrated circuits with higher density of electrical components is required to realize more advanced electronics technologies.

[0005] The size of an elemental unit that composes a photoresist is considered the limit for realizing patterning feature size with desired quality in terms of line edge roughness (LER), line width roughness (LWR), and resolution. Chemically amplified resists (CARs) based on photoacids, and reactive organic polymers have been dominant in the semiconductor industry over the past decades. Hydrodynamic and/or gyration radii of polymers are large, making it inherently difficult to accomplish <10 nm feature size with polymer-based CARs. In addition, acid diffusion in the CARs can be another problem for realizing nanopatterns with desired low LER.

[0006] At present, the market demands non-CAR photoresist materials that are suitable for EUV photolithography and permit access to <20 nm node widths. However, developing such photoresists is a significant technical challenge, and several photochemical factors need to be considered. As the EUV light wavelength is very short (13.5 nm), an EUV photon carries a high energy of 92 eV, which is more than ten times higher than that of a deep UV (DUV) photon with a wavelength of 193-248 nm. Due to the high energy (92 eV), EUV photon can interact with atoms and eject one of their core electrons. The resulting photoelectron recombines with the photoresist material and scatters thereby ejecting another electron. These absorption and emission events, with energy dissipation at each step, continue in a cascade manner until the energy of electron drops below about 30 eV. Secondary electrons with low energies can finally cause bond cleavage to create radical species which can be useful for chemical events such as bond formation/crosslinking.

[0007] Recently, organometallic molecules, coordinative molecules and nanoclusters have been developed for efficient EUV photoresist materials. Specific metal-containing

photoresists can have a high EUV absorption cross-section and thus can improve the sensitivity and lessens the roughness of patterned structure induced by photon shot noise. Two primary design strategies have been adopted to develop coordinative EUV photoresists, with both strategies showing potential utility for EUV nanolithography. The recent investigations of EUV photoresists classify materials as either metal nanoclusters or organometallic/coordinative small molecules. Metal nanoclusters are composed of many metal atoms while organometallic or coordination complexes typically contain one or two metal centers along with associated ligands. In EUV photoresists, the size and composition of elementary unit particles are critical factors influencing dose, sensitivity, and pattern shape. For example, when a unit particle contains high-density metal atoms, it exhibits increased sensitivity and requires a lower dose for solubility transition. In addition, uniform and small unit particle sizes contribute to reduced line edge roughness in the final pattern.

[0008] Metal Nanoclusters

[0009] Metal nanoclusters with a diameter of a few nanometers (2-3 nm) are a promising class of EUV lithography photoresist materials to realize <20 nm half pitch lines. The key mechanism for photolysis of metal nanoclusters in EUV lithography process usually relies on radical generation via homolytic cleavage of metal–carbon bond and subsequent radical–radical coupling to induce agglomeration and aggregation of nanoclusters with solubility switch. To this end, the rational design of metal and organic ligand is essential. As the desired nanopattern size and LER become smaller, particularly in the <10 nm nodes, the size of nanoclusters needs to be further reduced. *See Coord. Chem. Rev.*, 493, 215307 (2023).

[0010] Tin oxo clusters have been used in EUV lithography processes. Photolysis reactions of tin-oxo nanoclusters with the structure $[(\text{RSn})_{12}\text{O}_{14}(\text{OH})_6]\text{X}_2$ have been induced by EUV light with 13.5 nm wavelength. *See Microelectron. Eng.*, 127, 44–50 (2014). The tin-oxo cluster was synthesized in a one-step reaction using alkylstannic acid $[\text{RSn}(=\text{O})\text{OH}]$, where R = aliphatic hydrocarbon group] or aryltin trichloride (RSnCl_3) where R = aryl group). The effect of the R and X structures on the EUV-induced photolysis was investigated. While patterning of ~18 nm lines was reported, it is unclear if smaller lines can be realized using tin-oxo nanoclusters.

[0011] Zr and Hf atoms can be used for producing EUV photoresists. HfO_2 -based nanoclusters capped by various organic ligands, with hydrodynamic diameter of 2-3 nm, can be prepared by a sol–gel process and employed for EUV photoresists. *See Proc. SPIE.*, 10146, 101460I (2017). Although the experimental data was not reported therein, the authors indicated that all the nanoclusters were patternable with 20–25 nm critical dimensions in 13.4-nm EUV photolithography. It is unclear if <20 nm patterns can be achieved with hafnium oxide nanoclusters.

[0012] Zinc nanoclusters have been studied for EUV lithography and have a high EUV absorbance compared to Zr and Hf atoms. Due to this reason, Zn nanoclusters have recently emerged as a new class of nanocluster photoresist. Zn-oxo nanocluster photoresist films were prepared via hydrolysis in a spin-coated aqueous solution containing methacrylic acid. *See J. Mater. Chem. C.*, 5, 2611 (2017). Deep-UV irradiation induced aggregation of nanoclusters, however, thermal annealing after the developing step was needed to cause nucleation and growth of zinc oxide crystals. Thermal annealing at high temperatures ($> 300^{\circ}\text{C}$) caused line patterns with indented surfaces (double-peak profile). This was attributed to a difference in thermal reactivity between the inner and outer structures, which exposed the surface experience to a contractive force.

[0013] Zinc-containing building blocks of a metal–organic framework were synthesized with monodentate ligands of benzoic acid derivatives. *See Chem. Mater.*, 30(12), 4124 (2018). The Zn-containing building blocks strongly interacted with soft X-rays at a wavelength of 13 nm. In contrast to previously reported resist materials based on ZrO_2 or HfO_2 nanoparticles, the Zinc m-toluic acid clusters enabled nanopatterns with good resolution (15 nm) due to their small size (1–2 nm), narrow size distribution, and uniform film formation.

[0014] Investigations of the potential application of silicon nanoclusters, based on hydrogen silsesquioxane (HSQ), for e-beam lithography have been disclosed in early work. *See J. Vac. Sci. Technol. B.*, 16, 69–76 (1998). The fabricated HSQ photoresist films had thicknesses of 50–100 nm, and their lithographic performance was compared with CAR-based resists. While HSQ-based Si clusters demonstrate good resolution in photolithographic nanopatterning, there is a need for improving their light sensitivity to make it more suitable for practical industrial applications. *See Front. Nanosci.*, Vol. 11, 349 (2016).

[0015] **Organometallic/Coordinative Small Molecules**

[0016] Low-molecular weight organometallic compounds (often called “molecular organometallic resists,” denoted as “MORE” in the literature) are smaller than nanoclusters in size but still contain EUV-absorbing metal atoms. By taking advantage of atomic-level structural design in organometallic synthesis, one skilled in the art can finely tune the structure of photoresist at the atomic scale to achieve optimal molecular photoresist for EUV photolithography. The strategies used to design low-molecular-weight organometallic photoresist are similar to the strategies used for metal-oxo nanoclusters. In many cases, using low-molecular-weight organometallic compounds, metal–carbon bond(s) undergo photochemical homolytic bond cleavage to produce radical species that are contained in the structure, while the rest of the chelating sites of metal centers are occupied by heteroatoms such as oxygen and nitrogen. The organometallic and inorganic complexes can form 1-dimensional,

2-dimensional and 3-dimensional structures known as coordination polymers.

[0017] Organometallic complexes with the structure, $R_2Sn(O_2CR')_2$ where R = butyl, phenyl, or benzyl, and O_2CR' = acetate, acrylate, methacrylate, pivalate, or benzoate were synthesized. One study examined the effects of ligand bulkiness and Sn-R bond energy on photosensitivity and lithographic performance. See *Mater. Chem. Front.*, 1, 2613–2619 (2017). The results indicated a tradeoff between the sensitivity and resolution. Most of the studied complexes exhibited poor sensitivity (dose = 50–600 mJ/cm²) but good resolution and LER. The complex where R = benzyl and O_2CR' = pivalate showed 16-nm half-pitch dense lines with an LER of 2.1 nm and 22-nm half-pitch dense lines with 1.4 nm LER in negative tone lithography by EUV.

[0018] Other studies have tested different metal atoms in the form of complexes $R_nM(O_2CR)_2$ where M is antimony, bismuth, tin, or tellurium. The studies revealed that antimony and tellurium complexes showed the best and worst sensitivity, respectively; the reason for this observation remains unclear. See *J. of Micro/Nanolithography, MEMS, and MOEMS*, Vol. 14, Issue 41, Article number 043503 (2015). Dense 35-nm lines with 5.6 mJ/cm² dosing was achieved using triphenylantimony diacrylate. The pattern size could be further decreased to 16-nm, however, pattern collapse was observed.

[0019] U.S. Patent Application Publication No. 2024/0210821A1 discloses precursors and methods related to bismuth oxycarbide-based photoresists. The precursors described in the disclosure are nitrogen-containing precursors having a formula $R'Bi(NR_2)_2$ or R'_2BiNR_2 where R and R' include a variety of alkyl groups and/or trialkylsilyl groups. Methods include thin-film-forming reactions of the bismuth precursors with oxygen-containing co-reagents.

[0020] U.S. Patent Application Publication No. 2022/0317572A1 discloses organometallic photoresists suitable for use in deep ultraviolet or extreme ultraviolet lithography. The photoresist precursors include organometallic molecules comprising one metal selected from bismuth or antimony having an oxidation state of 3 or higher and at least one group, R, which is a polymerizable group.

[0021] Triphenylbismuth has been reacted with a series of aromatic carboxylic acids (RCO_2H) of varying pKa and functionality [R = PhCH=CH, o-MeOC₆H₄, m-MeOC₆H₄, o-H₂NC₆H₄, o-O₂NC₆H₄, p-O₂NC₆H₄, 2-(C₅H₄N)] under reflux conditions in toluene to form bismuth tri(carboxylic acid) complexes. Several mixed phenyl/carboxylic acid complexes were also observed with certain carboxylic acids. See *Dalton Trans.*, 4852–4858 (2006). No reactivity with heteroleptic alkyl/aryl bismuth compounds was described in this report.

[0022] The presence of water during the reaction of triphenylbismuth and carboxylic acids leads to large Bi clusters rather than monomolecular complexes or coordination polymers.

See *Angew. Chem. Int. Ed.*, 45, 5638-5642 (2006).

[0023] Oxalic acid is the simplest form of dicarboxylic acid, and oxalate ($C_2O_4^{2-}$) can act as a multidentate ligand for various metals. While organotin compounds have received significant attention for potential EUV photoresists, different metal complexes such as platinum and palladium mononuclear complexes with the structure $L_2M(C_2O_4)$ (where $M = Pt$ or Pd and L is neutral phosphine ligand), have also been studied. See *J. of Micro/Nanolithography, MEMS, and MOEMS*, Vol. 14, Issue 4, 043511 (2015). The complexes were spin-coated and exposed to EUV as a positive tone photoresist. The best sensitivity was observed for $(dppm)Pd(C_2O_4)$, with 54 mJ/cm^2 ($dppm = \text{bis(diphenylphosphino)methane}$); a 30-nm half pitch was achieved at E_{size} of 50 mJ/cm^2 (E_{size} : dose-to-size, the amount of dose required to produce the proper dimension of resist feature). It should be noted that Pd and Pt are extremely expensive relative to other transition metals (*e.g.*, Co) and metalloids (*e.g.*, Sb/Bi).

[0024] Thus, while two primary strategies have been proposed to augment photosensitivity while reducing the patterning size in photolithography; namely, (1) molecular and (2) nanocluster designs based on organometallic coordination chemistry, photochemical reaction mechanisms, lithographic performance, and progress for resolving the resolution limit problem are all topics of active research in the semiconductor industry. Several concerns remain unresolved in the long journey to accomplish nanometer-scale patterns that the industry demands with high quality and yield, and many fundamental questions concerning the photochemical mechanisms need to be addressed.

[0025] Certain elements with good EUV atomic photoabsorption cross-sections at EUV wavelengths (*e.g.*, 13.5 nm) have not been extensively studied. These include antimony (Sb) and bismuth (Bi).

[0026] Most EUV photoresist materials developed so far rely on a top-down approach, specifically spin coating, which creates thin films with amorphous structures. In such films, the material's elemental unit particles are randomly distributed and react with each other through crosslinking, making it difficult to achieve the desired line edge roughness (LER) for sub-10 nm patterns. A new design paradigm for both materials and thin film structures is thus needed to overcome these problems.

SUMMARY

[0027] In one embodiment, the disclosed and claimed subject matter relates to bismuth-based and antimony-based compounds useful for deposition of bismuth-containing and antimony-containing films on substrates. In a further aspect of this embodiment, the disclosed

and claimed subject matter includes formulations that include the disclosed and claimed bismuth-based and antimony-based compounds.

[0028] In another embodiment, the disclosed and claimed subject matter includes deposition processes that include exposing a bismuth-containing and/or antimony-containing film to extreme ultraviolet light (EUV) where the film is formed from the disclosed and claimed bismuth-containing and antimony-containing compounds and/or formulations thereof. In one aspect of this embodiment, the film is deposited on a substrate by a spin-on process. In another aspect of this embodiment, the film is deposited on a substrate by a vapor deposition process such as CVD, CCVD, and ALD.

[0029] In another embodiment, the disclosed and claimed subject matter includes thin films formed from the exposure of the disclosed and claimed bismuth-containing and antimony-containing compounds and/or formulations thereof to extreme ultraviolet light (EUV).

[0030] In another embodiment, the disclosed and claimed subject matter includes the use of bismuth-based and antimony-based clusters to form films. A related embodiment is the use of thin-film-forming techniques such as spin-on deposition to form bismuth-containing and antimony-containing films.

[0031] In another embodiment, selective replacement of aryl ligands vs. alkyl ligands with new ligands is used to synthesize heteroleptic complexes which are used in metal-organic resist processes.

BRIEF DESCRIPTION OF THE DRAWINGS

[0032] 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 drawings:

[0033] FIG. 1 illustrates nanocluster synthesis and acid-catalyzed coupling of unsaturated groups in the form of aryl- and vinyl-sulfonic acids;

[0034] FIG. 2 illustrates the crosslinking of individual nanoclusters to form a network polymer film of nanoclusters;

[0035] FIG. 3 illustrates the use of functionalized nanoclusters in a patterning process;

[0036] FIG. 4 illustrates the use of functionalized nanoclusters in a patterning process;

[0037] FIG. 5 illustrates the molecular structure of $[\text{Bi}(\text{neo-pentyl})_2(\text{OAc})_2]_n$;

[0038] FIG. 6a illustrates the asymmetric molecular structures of $[\text{Bi}(\text{methyl})(\text{OAc})_2]_n$ (left), $[\text{Bi}(\text{isopropyl})(\text{OAc})_2]_n$ (center), and $[\text{Bi}(\text{neopentyl})(\text{OAc})_2]_n$ (right);

[0039] FIG. 6b illustrates the extended molecular structure of $[\text{Bi}(\text{methyl})(\text{OAc})_2]_n$; and

[0040] FIG. 7 illustrates the patterning of developed wafers of Example 23.

DETAILED DESCRIPTION

[0041] All references, including publications, patent applications, and patents, cited herein are hereby incorporated by reference to the same extent as if each reference were individually and specifically indicated to be incorporated by reference and were set forth in its entirety herein.

[0042] The use of the terms "a" and "an" and "the" and similar referents in the context of describing the disclosed and claimed subject matter (especially in the context of the following claims) are to be construed to cover both the singular and the plural, unless otherwise indicated herein or clearly contradicted by context. The terms "comprising," "having," "including," and "containing" are to be construed as open-ended terms (*i.e.*, meaning "including, but not limited to,") unless otherwise noted. Recitation of ranges of values herein are merely intended to serve as a shorthand method of referring individually to each separate value falling within the range, unless otherwise indicated herein, and each separate value is incorporated into the specification as if it were individually recited herein. All methods described herein can be performed in any suitable order unless otherwise indicated herein or otherwise clearly contradicted by context. The use of any and all examples, or exemplary language (*e.g.*, "such as") provided herein, is intended merely to better illuminate the disclosed and claimed subject matter and does not pose a limitation on the scope of the disclosed and claimed subject matter unless otherwise claimed. No language in the specification should be construed as indicating any non-claimed element as essential to the practice of the disclosed and claimed subject matter. The use of the term "comprising" or "including" in the specification and the claims includes the narrower language of "consisting essentially of" and "consisting of."

[0043] Embodiments of the disclosed and claimed subject matter are described herein, including the best mode known to the inventors for carrying out the disclosed and claimed subject matter. Variations of those embodiments may become apparent to those of ordinary skill in the art upon reading the foregoing description. The inventors expect skilled artisans to employ such variations as appropriate, and the inventors intend for the disclosed and claimed subject matter to be practiced otherwise than as specifically described herein. Accordingly, the disclosed and claimed subject matter includes all modifications and equivalents of the subject matter recited in the claims appended hereto as permitted by applicable law. Moreover, any combination of the above-described elements in all possible variations thereof is encompassed by the disclosed and claimed subject matter unless otherwise indicated herein or otherwise clearly contradicted by context.

[0044] For ease of reference, "microelectronic device" or "semiconductor device" corresponds to semiconductor wafers having integrated circuits, memory, and other electronic

structures fabricated thereon, and flat panel displays, phase change memory devices, solar panels and other products including solar substrates, photovoltaics, and microelectromechanical systems (MEMS), manufactured for use in microelectronic, integrated circuit, or computer chip applications. Solar substrates include, but are not limited to, silicon, amorphous silicon, polycrystalline silicon, monocrystalline silicon, CdTe, copper indium selenide, copper indium sulfide, and gallium arsenide on gallium. The solar substrates may be doped or undoped. It is to be understood that the term “microelectronic device” or “semiconductor device” is not meant to be limiting in any way and includes any substrate that will eventually become a microelectronic device or microelectronic assembly.

[0045] “Substantially free” is defined herein as less than 0.001 wt. %. “Substantially free” also includes 0.000 wt. %. The term “free of” means 0.000 wt. %. As used herein, “about” or “approximately” are intended to correspond to within $\pm 5\%$ of the stated value.

[0046] In all such compositions, where specific components of the composition are discussed in reference to weight percentage (or “weight %”) ranges including a zero lower limit, it will be understood that such components may be present or absent in various specific embodiments of the composition, and that in instances where such components are present, they may be present at concentrations as low as 0.001 weight percent, based on the total weight of the composition in which such components are employed. Note all percentages of the components are weight percentages and are based on the total weight of the composition, that is, 100%. Any reference to “one or more” or “at least one” includes “two or more” and “three or more” and so on.

[0047] Where applicable, all weight percents unless otherwise indicated are “neat” meaning that they do not include the aqueous solution in which they are present when added to the composition. For example, “neat” refers to the weight % amount of an undiluted acid or other material (*i.e.*, the inclusion 100 g of 85% phosphoric acid constitutes 85 g of the acid and 15 grams of diluent).

[0048] Moreover, when referring to the compositions described herein in terms of weight %, it is understood that in no event shall the weight % of all components, including non-essential components, such as impurities, add to more than 100 weight %. In compositions “consisting essentially of” recited components, such components may add up to 100 weight % of the composition or may add up to less than 100 weight %. Where the components add up to less than 100 weight %, such composition may include some small amounts of a non-essential contaminants or impurities. For example, in one such embodiment, the formulation can contain 2% by weight or less of impurities. In another embodiment, the formulation can contain 1% by weight or less than of impurities. In a further embodiment, the formulation can contain 0.05% by weight or less than

of impurities. In other such embodiments, the constituents can form at least 90 wt%, more preferably at least 95 wt%, more preferably at least 99 wt%, more preferably at least 99.5 wt%, most preferably at least 99.9 wt%, and can include other ingredients that do not materially affect performance. Otherwise, if no significant non-essential impurity component is present, it is understood that the composition of all essential constituent components will essentially add up to 100 weight %.

[0049] In addition to known and understood representations for the attachment point of a covalent bond, the notation “ $\text{---}\ddot{\text{X}}\text{---}$ ” is intended to also designate the attachment point of a covalent bond.

[0050] The headings employed herein are not intended to be limiting; rather, they are included for organizational purposes only.

[0051] As noted above, the disclosed and claimed subject matter relates to bismuth-based and antimony-based compounds and compositions thereof (as described below) useful for deposition of bismuth- and antimony-containing films on substrates.

[0052] The complexes or compositions described herein are suitable for use as volatile precursors for ALD, CVD, pulsed CVD, plasma enhanced ALD (PEALD) or plasma enhanced CVD (PECVD) for the manufacture of semiconductor-type microelectronic devices. Examples of suitable deposition processes for the method disclosed herein include, but are not limited to, cyclic CVD (CCVD), MOCVD (Metal Organic CVD), thermal chemical vapor deposition, plasma enhanced chemical vapor deposition (“PECVD”), high density PECVD, photon assisted CVD, plasma-photon assisted (“PPECVD”), cryogenic chemical vapor deposition, chemical assisted vapor deposition, hot-filament chemical vapor deposition, CVD of a liquid polymer precursor, deposition from supercritical fluids, and low energy CVD (LECVD). In certain embodiments, the films are deposited via atomic layer deposition (ALD), plasma enhanced ALD (PEALD) or plasma enhanced cyclic CVD (PECCVD) process. As used herein, the term “chemical vapor deposition processes” refers to any process wherein a substrate is exposed to one or more volatile precursors, which react and/or decompose on the substrate surface to produce the desired deposition. As used herein, the term “atomic layer deposition process” refers to a self-limiting (*e.g.*, the amount of film material deposited in each reaction cycle is constant), sequential surface chemistry that deposits films of materials onto substrates of varying compositions. Although the precursors, reagents and sources used herein may be sometimes described as “gaseous,” it is understood that the precursors can be either liquid or solid which are transported with or without an inert gas into the reactor via direct vaporization, bubbling or sublimation. In some cases, the vaporized precursors can pass through a plasma generator. In one embodiment, the metal-containing film is deposited using an ALD process. In another

embodiment, the metal-containing film is deposited using a CCVD process. In a further embodiment, the metal-containing film is deposited using a thermal CVD process. The term “reactor” as used herein, includes without limitation, reaction chamber or deposition chamber.

[0053] Bismuth-containing and antimony-containing compositions can be used in several embodiments including but not limited to “single-source” precursors which demonstrate adequate vapor pressure and thermal stability to deposit thin bismuth-containing films on substrates via ALD or CVD. These compositions contain at least one photosensitive ligand that will promote either crosslinking and/or bond breaking upon EUV exposure. The method disclosed herein avoids pre-reaction of the metal precursors by using ALD or CCVD methods that separate the precursors prior to and/or during the introduction to the reactor. The method for depositing photoresist films generally includes, consists essentially of or consists of the following steps:

- (a) providing a substrate in a reaction chamber
- (b) providing one or more bismuth-containing reactant or antimony-containing reactant and one or more co-reactant to the reaction chamber to initiate a reaction between the reactant and co-reactant to deposit the photoresist film on the substrate.

[0054] The co-reactant is selected to preferentially react with at least one type of the ligands present in the bismuth-containing or antimony-containing reactants. The examples of co-reactants include but are not limited to molecular oxygen, ozone, water and carboxylic acids.

[0055] In one embodiment, the disclosed and claimed subject matter further includes a method of depositing a bismuth-containing film or an antimony-containing film on a substrate in a reactor that includes, consists essentially of or consists of the steps of:

- (a) providing the substrate to the reactor;
- (b) contacting the substrate with one or more of the bismuth-containing compounds and antimony-containing compounds disclosed herein and one or more coreactant; and
- (c) forming a bismuth-containing film or an antimony-containing film on the substrate.

In a further aspect of this embodiment, the substrate is contacted with one or more of the bismuth-containing compound. In a further aspect of this embodiment, the substrate is contacted with one or more of the antimony-containing compound. In a further aspect of this embodiment, the one or more coreactant includes, consists essentially of or consists of an oxygen-containing compound. In a further aspect of this embodiment, the one or more coreactant includes, consists essentially of or consists of one or more of water, oxygen, ozone, carboxylic acids, alcohols, peroxide compounds. In a further aspect of this embodiment, the substrate is selected from of metal, metal oxide, metal

nitride, metal silicide, silicon oxide, silicon nitride, fluorosilicate glass (FSG), organosilicate glass (OSG), carbon doped oxide (CDO), porous low-K material and combinations thereof.

[0056] In a further embodiment, the disclosed and claimed subject matter further includes a method of depositing a bismuth-containing film or an antimony-containing film on a substrate in a reactor that includes, consists essentially of or consists of the steps of:

- (a) providing the substrate to the reactor;
- (b) performing a pre-treatment to remove contaminants from surface of the substrate;
- (c) contacting the substrate with one or more of the bismuth-containing compounds and antimony-containing compounds disclosed herein and one or more coreactant; and
- (d) forming a bismuth-containing film or an antimony-containing film on the substrate.

In a further aspect of this embodiment, the substrate is contacted with one or more of the bismuth-containing compound. In a further aspect of this embodiment, the substrate is contacted with one or more of the antimony-containing compound. In a further aspect of this embodiment, the one or more coreactant includes, consists essentially of or consists of an oxygen-containing compound. In a further aspect of this embodiment, the one or more coreactant includes, consists essentially of or consists of one or more of water, oxygen, ozone, carboxylic acids, alcohols, peroxide compounds. In a further aspect of this embodiment, the substrate is selected from of metal, metal oxide, metal nitride, metal silicide, silicon oxide, silicon nitride, fluorosilicate glass (FSG), organosilicate glass (OSG), carbon doped oxide (CDO), porous low-K material and combinations thereof.

[0057] In a further embodiment, the disclosed and claimed subject matter further includes a method of depositing a bismuth-containing film or an antimony-containing film on a substrate in a reactor that includes, consists essentially of or consists of the steps of:

- (a) providing the substrate to the reactor;
- (b) contacting the substrate with one or more of the bismuth-containing compounds and antimony-containing compounds disclosed herein and one or more coreactant;
- (c) exposing the substrate, the one or more of the bismuth-containing compound and antimony-containing compound and the one or more coreactant to a plasma; and
- (d) forming a bismuth-containing film or an antimony-containing film on the substrate.

In a further aspect of this embodiment, the substrate is contacted with one or more of the bismuth-containing compound. In a further aspect of this embodiment, the substrate is contacted with one or more of the antimony-containing compound. In a further aspect of this embodiment, the one or more coreactant includes, consists essentially of or consists of an oxygen-containing compound. In a further aspect of this embodiment, the one or more coreactant includes, consists essentially of or consists of one or more of water, oxygen, ozone, carboxylic acids, alcohols, peroxide compounds. In a further aspect of this embodiment, the substrate is selected from of metal, metal oxide, metal nitride, metal silicide, silicon oxide, silicon nitride, fluorosilicate glass (FSG), organosilicate glass (OSG), carbon doped oxide (CDO), porous low-K material and combinations thereof.

[0058] In a further embodiment, the disclosed and claimed subject matter further includes a method of depositing a bismuth-containing film or an antimony-containing film on a substrate in a reactor that includes, consists essentially of or consists of the steps of:

- (a) providing the substrate to the reactor;
- (b) contacting the substrate with one or more contacting the substrate with one or more bismuth-containing compounds or antimony-containing compound and one or more coreactant; and
- (c) forming a bismuth-containing film or an antimony-containing film on the substrate.
- (d) exposing a portion of the film to extreme ultraviolet light (EUV)
- (e) removal of a portion of the film.

In a further aspect of this embodiment, the substrate is contacted with one or more of the bismuth-containing compound. In a further aspect of this embodiment, the substrate is contacted with one or more of the antimony-containing compound. In a further aspect of this embodiment, the one or more coreactant includes, consists essentially of or consists of an oxygen-containing compound. In a further aspect of this embodiment, the one or more coreactant includes, consists essentially of or consists of one or more of water, oxygen, ozone, carboxylic acids, alcohols, peroxide compounds. In a further aspect of this embodiment, the substrate is selected from of metal, metal oxide, metal nitride, metal silicide, silicon oxide, silicon nitride, fluorosilicate glass (FSG), organosilicate glass (OSG), carbon doped oxide (CDO), porous low-K material and combinations thereof.

[0059] In certain embodiments, the process employs a reducing agent. The reducing agent is typically introduced in gaseous form. Examples of suitable reducing agents include, but are not limited to, hydrogen gas, hydrogen plasma, remote hydrogen plasma, silanes (*i.e.*, diethylsilane, ethylsilane, dimethylsilane, phenylsilane, silane, disilane, aminosilanes, chlorosilanes), boranes (*i.e.*, borane, diborane), alanes, germanes, hydrazines, ammonia and/or mixtures thereof.

[0060] The deposition methods disclosed herein may involve one or more purge gases. The purge gas, which is used to purge away unconsumed reactants and/or reaction byproducts, is an inert gas that does not react with the precursors. Exemplary purge gases include, but are not limited to, argon (Ar), nitrogen (N₂), helium (He), neon (Ne) and/or mixtures thereof. In certain embodiments, a purge gas such as Ar is supplied into the reactor at a flow rate ranging from about 10 to about 2000 sccm for about 0.1 to 10,000 seconds, thereby purging the unreacted material and any byproducts that may remain in the reactor.

[0061] Energy may be applied to the at least one of the precursor, reducing agent, other precursors or combination thereof to induce reaction and to form the metal-containing film or coating on the substrate. Such energy can be provided by, but not limited to, thermal, plasma, pulsed plasma, helicon plasma, high density plasma, inductively coupled plasma, X-ray, e-beam, photon, remote plasma methods and combinations thereof. In certain embodiments, a secondary RF frequency source can be used to modify the plasma characteristics at the substrate surface. In embodiments wherein the deposition involves plasma, the plasma-generated process may include a direct plasma-generated process in which plasma is directly generated in the reactor, or alternatively a remote plasma-generated process in which plasma is generated outside of the reactor and supplied into the reactor.

[0062] The precursors may be delivered to the reaction chamber in a variety of ways. In one embodiment, a liquid delivery system may be utilized. In an alternative embodiment, a combined liquid delivery and flash vaporization process unit may be employed, such as, for example, the turbo vaporizer manufactured by MSP Corporation of Shoreview, MN, to enable low volatility materials to be volumetrically delivered, which leads to reproducible transport and deposition without thermal decomposition of the precursor. The bismuth-containing compounds and antimony-containing compounds (and/or compositions thereof) described herein can be effectively used as source reagents in direct liquid injection mode to provide a vapor stream of these precursors into an ALD or CVD reactor.

[0063] In certain embodiments, these compositions include those utilizing hydrocarbon solvents which are particularly desirable due to their ability to be dried to sub-ppm levels of water. Exemplary hydrocarbon solvents that can be used in the disclosed and claimed methods include, but are not limited to, toluene, mesitylene, cumene (isopropylbenzene), p-cymene (4-isopropyl toluene), 1,3-diisopropylbenzene, octane, dodecane, 1,2,4-trimethylcyclohexane, n-butylcyclohexane and decahydronaphthalene (decalin). The bismuth-containing compounds and antimony-containing compounds (and/or compositions thereof) described herein can also be stored and used in stainless steel containers. In certain embodiments, the hydrocarbon solvent

in the composition is a high boiling point solvent or has a boiling point of 100 °C or greater.

[0064] In certain embodiments, the gas lines connecting from the precursor canisters to the reaction chamber are heated to one or more temperatures depending upon the process requirements and the container comprising the composition is kept at one or more temperatures for bubbling. In other embodiments, a precursor is injected into a vaporizer kept at one or more temperatures for direct liquid injection.

[0065] A flow of argon and/or other gas may be employed as a carrier gas to help deliver the vapor of the at least one precursor to the reaction chamber during the precursor pulsing. In certain embodiments, the reaction chamber process pressure is between 1 and 50 torr, preferably between 5 and 20 torr.

[0066] The deposited films may contain varying levels of hydrogen, oxygen, carbon and nitrogen. Carbon content in the deposited films should preferably be >5 atomic percent (at.%), or more preferably, >10 at.%, and most preferably, >12 at.%. High carbon content in the film can yield films which may be reactive towards electron beams and/or ultraviolet light. The reactivity of the films towards electron beams and/or ultraviolet light may be enhanced by the presence of carbon-containing groups which are directly bound to bismuth in the deposited films.

[0067] Substrate temperature is an important process variable in the deposition of high-quality films. Typical substrate temperatures range from about 150 °C to about 350 °C. Higher temperatures can promote higher film growth rates. However, higher temperatures can lead to films with lower carbon content. It is therefore desirable to find film precursors and process conditions that can deposit films at high growth rates while maintaining suitable amounts of carbon in the films.

[0068] In another embodiment, the bismuth-containing film or antimony-containing film on a substrate are developed to produce a patterned substrate. The development processes include wet methods and dry methods.

[0069] One embodiment of a wet development method is contact of the film with one or more solvents which selectively dissolve a portion of the film thus forming a patterned substrate. In one aspect of this embodiment, the solvent contact time can be varied, for instance, from 1 second to 10,000 seconds. In another aspect of this embodiment, the solvent exposure may occur at a temperature ranging from 20 °C up to the normal boiling point of the solvent. In a further aspect of this embodiment, the one or more solvents includes one or more of THF, cyclohexanone, propylene glycol methyl ether (PGME), propylene glycol monomethyl ether acetate (PGMEA), anisole, 2-heptanone and 4-methyl-2-pentanol. In one aspect, such formulations are free of aromatic solvent.

[0070] One embodiment of a dry development method is contacting the film with a

vapor-phase or gas-phase reactant that selectively etches a portion of the film thus forming a patterned substrate. In one aspect of this embodiment, the reactant contact time can be varied, for instance, from 1 second to 10,000 seconds. In another aspect of this embodiment, the reactant exposure may occur at a temperature ranging from about 20 °C to about 350 °C. In a further aspect of this embodiment, the one or more reactants includes one or more inorganic acids such as HCl, HBr, and HI. In an additional embodiment, the one or more reactants includes one or more of organic acids. The organic acids of this embodiment include carboxylic acids such as formic acid, acetic acid, butyric acid, and pivalic acid.

[0071] In one embodiment, bismuth-containing films and/or antimony-containing films are fabricated using spin-on film deposition. Formulations of the bismuth-containing compounds and antimony-containing compounds are prepared by dissolving the precursor in a suitable solvent.

[0072] In another aspect, the disclosed and claimed subject matter includes formulations that include (i) one or more of the disclosed and claimed bismuth-containing compounds and antimony-containing compounds and (ii) one or more solvents suitable for use in a spin-coating process. In one embodiment, the formulation includes (i) two or more of the disclosed and claimed bismuth-containing compounds and antimony-containing compounds and (ii) one or more solvents suitable for use in a spin-coating process.

[0073] In another aspect, the disclosed and claimed subject matter includes preparing the target compounds in a spin-coating solvent (mixture) at the desired concentration, circumventing the isolation of the material and direct formation of the spin-coatable formulation.

[0074] In one embodiment, the one or more solvents suitable for use in a spin-coating process includes one or more of an alcohol, an ester, a ketone, a lactone, a diketone, a solvent with aromatic moieties, a solvent with a carboxylic acid, an amide and mixtures thereof.

[0075] In another embodiment, the one or more solvents suitable for use in a spin-coating process includes one or more of propylene glycol monomethyl ether acetate (PGMEA), propylene glycol methyl ether (PGME), butyl acetate, amyl acetate, cyclohexyl acetate, 3-methoxybutyl acetate, methyl ethyl ketone, methyl amyl ketone, cyclohexanone, cyclopentanone, ethyl-3-ethoxy propanoate, methyl-3-ethoxy propanoate, methyl-3-methoxy propanoate, methyl acetoacetate, ethyl acetoacetate, diacetone alcohol, methyl pivalate, ethyl pivalate, propylene glycol monomethyl ether, propylene glycol monoethyl ether, propylene glycol monomethyl ether propanoate, propylene glycol monoethyl ether propanoate, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, 3-methyl-3-methoxybutanol, N-methylpyrrolidone, dimethyl sulfoxide, gamma-butyrolactone, gamma valerolactone, cyclopentyl methyl ether, propylene glycol methyl ether

acetate, propylene glycol ethyl ether acetate, propylene glycol propyl ether acetate, methyl lactate, ethyl lactate, propyl lactate, tetramethylene sulfone, propylene glycol dimethyl ether, dipropylene glycol dimethyl ether, ethylene glycol dimethyl ether, diethylene glycol dimethyl ether, toluene, 2-heptanone, 1-hexanol, 4-methyl-2-pentanol and anisole. In a further aspect of this embodiment, the one or more solvents for use in a spin-coating process includes one or more of toluene, tetrahydrofuran (THF), cyclohexanone, PGME, PGMEA, anisole, 2-heptanone and 4-methyl-2-pentanol. In a further aspect of this embodiment, the one or more solvents for use in a spin-coating process includes one or more of THF, cyclohexanone, PGME, PGMEA, anisole, 2-heptanone and 4-methyl-2-pentanol. In one aspect, such formulations are free of aromatic solvent.

[0076] In another embodiment, the bismuth-containing compounds and antimony-containing compounds formulations have a concentration of about 1 mg/mL to about 1000 mg/mL. In another embodiment, the bismuth-containing compounds and antimony-containing compounds can be formulated into solutions having a concentration of bismuth-containing compounds and antimony-containing compounds of about 1 mg/mL to about 100 mg/mL. In another embodiment, the bismuth-containing compounds and antimony-containing compounds can be formulated into solutions having a concentration of Sn clusters of about 1 mg/mL to about 50 mg/mL. In another embodiment, the bismuth-containing compounds and antimony-containing compounds can be formulated into solutions having a concentration of Sn clusters of about 10 mg/mL to about 50 mg/mL. In another embodiment, the bismuth-containing compounds and antimony-containing compounds formulations have a concentration of Sn clusters of about 25 mg/mL to about 50 mg/mL. In another embodiment, the bismuth-containing compounds and antimony-containing compounds formulations have a concentration of bismuth-containing compounds and antimony-containing compounds of about 50 mg/mL to about 100 mg/mL.

[0077] The disclosed and claimed subject matter further includes using the disclosed and claimed bismuth-containing compounds and antimony-containing compounds formulations in EUV and E-beam processes. Such formulations are or can be used for patterning a radiation sensitive coating in a process that includes the steps of (i) forming a coating on a substrate surface with one or more of the disclosed and claimed bismuth-containing compounds and antimony-containing compounds formulations, (ii) drying the coating to produce a dried layer; and (iii) irradiating at least a portion of the dried layer to form a latent image.

[0078] In one embodiment, the substrate of step (i) includes silicon. In one embodiment, the substrate of step (i) includes silicon and at least one additional material layer (*i.e.*, a stack of materials) on top of which the material is deposited.

[0079] In one embodiment, the dried layer of step (ii) has a thickness of about 1 nm to about

500 nm. In one embodiment, the dried layer of step (ii) has a thickness of about 10 nm to about 100 nm. In one embodiment, the dried layer of step (ii) has a thickness of about 15 nm to about 50 nm.

[0080] In one embodiment, the irradiating of step (iii) includes exposing at least a portion of the dried layer to ionizing radiation. In one aspect of this embodiment, the ionizing radiation has a wavelength range of about 10 nm to about 365 nm. In one aspect of this embodiment, the ionizing radiation is generated via electron beams.

[0081] In another embodiment, the dried layer resulting from steps (i)-(iii) is developed to produce a patterned substrate. The development processes include wet methods and dry methods.

[0082] One embodiment of a wet development method is contact of the dried layer with one or more solvents which selectively dissolve a portion of the dried layer thus forming a patterned substrate. In one aspect of this embodiment, the solvent contact time can be varied, for instance, from 1 second to 10,000 seconds. In another aspect of this embodiment, the solvent exposure may occur at a temperature ranging from 20 °C up to the normal boiling point of the solvent. In a further aspect of this embodiment, the one or more solvents includes one or more of THF, cyclohexanone, PGME, PGMEA, anisole, 2-heptanone and 4-methyl-2-pentanol. In one aspect, such formulations are free of aromatic solvent.

[0083] One embodiment of a dry development method is contacting the dried layer with a vapor-phase or gas-phase reactant that selectively etches a portion of the dried layer thus forming a patterned substrate. In one aspect of this embodiment, the reactant contact time can be varied, for instance, from 1 second to 10,000 seconds. In another aspect of this embodiment, the reactant exposure may occur at a temperature ranging from about 20 °C to about 300 °C. In a further aspect of this embodiment, the one or more reactants includes one or more inorganic acids such as HCl, HBr and HI. In an additional embodiment, the one or more reactants includes one or more of organic acids. The organic acids of this embodiment include carboxylic acids such as formic acid, acetic acid, butyric acid, and pivalic acid.

[0084] One embodiment of photopatterning the materials is spin coating onto a substrate at 500 rpm/5 seconds followed by 800-5000 rpm for 15-120 seconds, exposing the substrate to E-beam at 2-100 keV for 1-10,000 μ C or EUV (13.5 nm) through a mask, baking the exposed wafer for 0.5-20 minutes at 100-200 °C, developing for 15-300 seconds in organic solvent (mixtures). Solvents and mixtures thereof include, but are not limited to, 2-heptanone, cyclohexanone, PGMEA, PGME, a mixture of anisole and PGMEA, a mixture of anisole and cyclohexanone and a mixture of anisole and 2-heptanone.

[0085] In one embodiment, the disclosed and claimed subject matter pertains to bismuth compounds including, consisting essentially of or consisting of at least one arene

ligand and at least one non-arene ligand having different reactivity toward co-reactant used to deposit the photoresist film.

[0086] Suitable bismuth-based and antimony-based compounds that can be used or be formulated for use in the disclosed and claimed methods include the following materials.

[0087] **Class 1 Compounds**

[0088] In one embodiment, the disclosed and claimed methods and formulations utilize bismuth compounds that include at least one arene (“Ar”) ligand and at least non-aromatic (“R^a”) ligand of the formula Bi(R^a)_x(Ar)_{3-x} where

- (i) $x = 1$ or 2 ;
- (ii) each R^a is independently one of an unsubstituted linear C₁-C₆ alkyl group, a linear C₁-C₆ alkyl group substituted with one or more halogen, a linear C₁-C₆ alkyl group substituted with an amino group, a linear C₃-C₆ alkyl group substituted with an alkoxy group, an unsubstituted branched C₃-C₆ alkyl group, a branched C₃-C₆ alkyl group substituted with one or more halogen, a branched C₃-C₆ alkyl group substituted with an amino group, a branched C₃-C₆ alkyl group substituted with an alkoxy group, an unsubstituted amine, a substituted amine, -Si(CH₃)₃, an unsubstituted cyclic C₃-C₆ alkyl group, a cyclic C₃-C₆ alkyl group substituted with one or more halogen, a cyclic C₃-C₆ alkyl group substituted with an amino group, an alkoxy group, a carboxylate group, an amino group, a diketone group, a ketoesterate group, an amidate group, a guanidinate group and an amidinate group; and
- (iii) each Ar is independently one of a C₃-C₈ unsubstituted aromatic group, a C₃-C₈ aromatic group substituted with one or more halogen, a C₃-C₈ aromatic group substituted with an amino group, a 5-member heterocyclic ring and a 6-member heterocyclic ring.

[0089] In some embodiments the R^a has a structure described in Table 1:

Linear Alkyl	Secondary Alkyl	Tertiary Alkyl
Methyl	Iso-propyl	Tert-butyl
Ethyl	Iso-butyl	Tert-pentyl
Propyl	Iso-pentyl	Allyl
n-Butyl	Sec-butyl	2-Methylallyl
n-pentyl	Sec-pentyl	Isopropenyl

Table 1

[0090] In some embodiments the R^a has a structure described in Table 2:

Secondary Alkoxy	Tertiary Alkoxy
Isopropoxy	Tert-butoxy
Sec-butoxy	Tert-pentoxy
--	1-Methoxy-2-methyl-2-propoxy
--	2,3-Dimethyl-2-butoxy

Table 2**[0091]**In some embodiments the R^a has a structure described in Table 3:

Carboxylate Group
Acetate
Trifluoroacetate
Pivalate
Formate
Propionate
Valerate
Butyrate
Iso-butyrate
2-Methylbutyrate
3-Methylbutyrate
Chloroacetate
Cyclobutanecarboxylate
Cyclopentanecarboxylate
Cyclohexanecarboxylate
Tetrahydro-3-furancarboxylate
Fluoroacetate
Chloroacetate
Trichloroacetate
Acrylate
Methacrylate
Salicylate

Table 3**[0092]**In some embodiments the R^a has a structure described in Table 4:

Amino Group
Dimethylamino

Ethylmethylamino
Diethylamino
Isopropylmethylamino
Diisopropylamino
Isopropyl-tert-butylamino
Di-tert-butylamino
Bis(trimethylsilyl)amino

Table 4

[0093] In some embodiments the R^a has a structure described in Table 5:

Amidinate Group
N,N'-di-isopropylformamidinate
N,N'-di-isopropylacetamidinate
N,N'-di-ethylformamidinate
N,N'-di-ethylacetamidinate
N,N'-di-tert-butylformamidinate
N,N'-di-tert-butylacetamidinate
N-ethyl-N'-tert-butyl-formamidinate
N-ethyl-N'-tert-butyl-acetamidinate

Table 5

[0094] In some embodiments the R^a has a structure described in Table 6:

Amidate/Guanidinate Group
N-tert-butylacetamidate
N-tert-butyl(tert-butyl)amidate
1,3,4,6,7,8-Hexahydro-2H-pyrimido[1,2-a]pyrimidinate
N,N'-diisopropyl-N'',N''-dimethylguanidinate

Table 6

[0095] In some embodiments the R^a has a structure described in Table 7:

Diketonate Group
Acetylacetonate
2,2,6,6-Tetramethyl-3,5-heptanedionate
Hexafluoroacetylacetonate

Table 7

[0096] In some embodiments the R^a has a structure described in Table 8:

Ketoesterate Group
Methyl 4,4-dimethyl-3-oxopentanoate
Ethyl 4,4-dimethyl-3-oxopentanoate
Tert-butyl 4,4-dimethyl-3-oxopentanoate

Table 8

[0097] In some embodiments, the Ar has a structure as illustrated in Table 9:

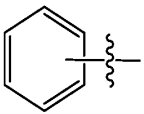
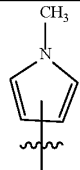
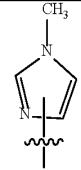
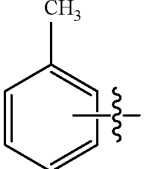
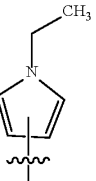
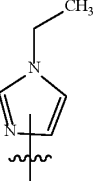
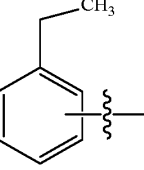
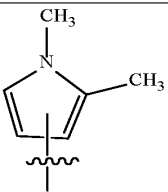
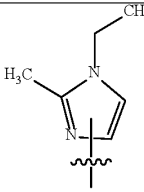
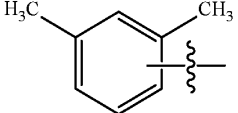
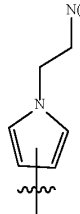
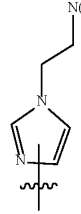
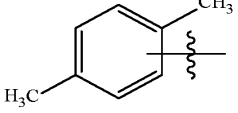
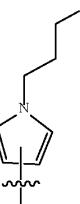
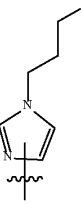
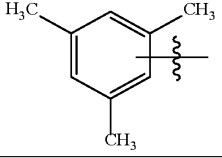
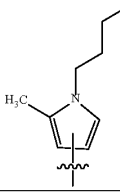
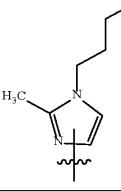
Aryl - Ar ¹	Pyrrolyl - Ar ²	Imidazolyl - Ar ³
		
		
		
		
		
		

Table 9

[0098] Specific examples of this embodiment include and are not limited to the examples shown in Table 10:

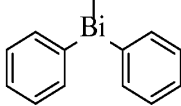
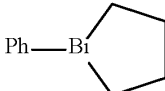
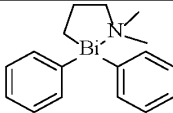
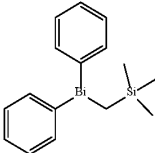
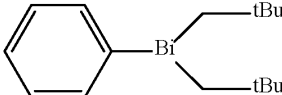
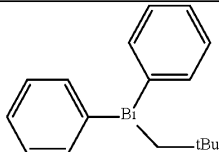
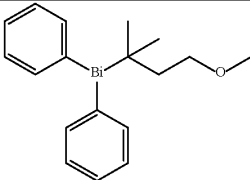
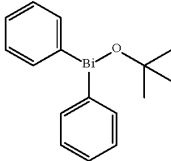
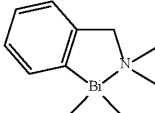
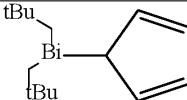
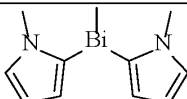
Structure	Compound
	Methylbisdiphenylbismuth
	1-Phenylbismolane
	1-Diphenylbismuthine-3-(dimethylamino)propane
	Trimethylsilylmethylene diphenylbismuth
	Di-neopentyl phenylbismuth
	Neopentyldiphenylbismuth
	(3-Methoxy-1,1-dimethylpropyl)diphenylbismuth
	Diphenylbismuth tert-butoxide
	Bis(2-N-methylpyrrolylino)methylbismuth
	Cyclopentadienylbis(neopentyl)bismuth
	Bis(2-N-methylpyrrolylino)methylbismuth

Table 10

[0099] Class 2 Compounds

[0100] In another embodiment, the disclosed and claimed subject methods and formulations utilize bismuth compounds including, consisting essentially of or consisting of at least one alkyl group and at least one other ligand having different reactivity toward co-reactant used to deposit a photoresist film. More specifically, the disclosed and claimed subject matter pertains to bismuth compounds of the formula $\text{Bi}(\text{R}^a)_x(\text{L})_{3-x}$ where

- (i) $x = 1$ or 2 ;
- (ii) each R^a is independently one of an unsubstituted linear C_1 - C_6 alkyl group, a linear C_1 - C_6 alkyl group substituted with one or more halogen, a linear C_1 - C_6 alkyl group substituted with an amino group, a linear C_3 - C_6 alkyl group substituted with an alkoxy group, an unsubstituted branched C_3 - C_6 alkyl group, a branched C_3 - C_6 alkyl group substituted with one or more halogen, a branched C_3 - C_6 alkyl group substituted with an amino group, a branched C_3 - C_6 alkyl group substituted with an alkoxy group, $-\text{Si}(\text{CH}_3)_3$, an unsubstituted cyclic C_3 - C_6 alkyl group, a cyclic C_3 - C_6 alkyl group substituted with one or more halogen and a cyclic C_3 - C_6 alkyl group substituted with an amino group; and
- (iii) each L is independently one of an alkoxy group, a carboxylate group, an amino group, a diketone group, a ketoesterate group, an amidate group, an amidinate group, and a guanidinate group.

[0101] In some embodiments the L has a structure described in Table 11:

Secondary Alkoxy	Tertiary Alkoxy
Isopropoxy	Tert-butoxy
Sec-butoxy	Tert-pentoxy
--	1-Methoxy-2-methyl-2-propoxy
--	2,3-Dimethyl-2-butoxide

Table 11

[0102] In some embodiments the L has a structure described in Table 12:

Carboxylate Group
Acetate
Trifluoroacetate
Pivalate
Formate
Propionate
Valerate

Butyrate
Iso-butyrate
2-Methylbutyrate
3-Methylbutyrate
Chloroacetate
Cyclobutanecarboxylate
Cyclopentanecarboxylate
Cyclohexanecarboxylate
Tetrahydro-3-furancarboxylate
Fluoroacetate
Chloroacetate
Trichloroacetate
Salicylate

Table 12

[0103] In some embodiments the L has a structure described in Table 13:

Amino Group
Dimethylamino
Ethylmethylamino
Diethylamino
Isopropylmethylamino
Diisopropylamino
Isopropyl-tert-butylamino
Di-tert-butylamino
Bis(trimethylsilyl)amino

Table 13

[0104] In some embodiments the L has a structure described in Table 14:

Amidinate Group
N,N'-di-isopropylformamidinate
N,N'-di-isopropylacetamidinate
N,N'-di-ethylformamidinate
N,N'-di-ethylacetamidinate
N,N'-di-tert-butylformamidinate
N,N'-di-tert-butylacetamidinate

N-ethyl-N'-tert-butyl-formamidine
N-ethyl-N'-tert-butyl-acetamidine

Table 14

[0105] In some embodiments the L has a structure described in Table 15:

Amide/ Guanidine Group
N-tert-butylacetamide
N-tert-butyl(tert-butyl)amide
1,3,4,6,7,8-Hexahydro-2H-pyrimido[1,2-a]pyrimidine
N,N'-diisopropyl-N'',N''-dimethylguanidine

Table 15

[0106] In some embodiments the L has a structure described in Table 16:

Diketonate Group
Acetylacetonate
2,2,6,6-Tetramethyl-3,5-heptanedionate
Hexafluoroacetylacetonate

Table 16

[0107] In some embodiments the L has a structure described in Table 17:

Ketoesterate Group
Methyl 4,4-dimethyl-3-oxopentanoate
Ethyl 4,4-dimethyl-3-oxopentanoate
Tert-butyl 4,4-dimethyl-3-oxopentanoate

Table 17

[0108] **Class 3 Compounds**

[0109] In another embodiment, the disclosed and claimed methods and formulations utilize bismuth compounds of the formula $(R^a)_2Bi-Bi(R^b)_2$ where each of R^a and R^b is independently one of an unsubstituted linear C_1 - C_6 alkyl group, a linear C_1 - C_6 alkyl group substituted with one or more halogen, a linear C_1 - C_6 alkyl group substituted with an amino group, a linear C_3 - C_6 alkyl group substituted with an alkoxy group, an unsubstituted branched C_3 - C_6 alkyl group, a branched C_3 - C_6 alkyl group substituted with one or more halogen, a branched C_3 - C_6 alkyl group substituted with an amino group, a branched C_3 - C_6 alkyl group substituted with an alkoxy group, an unsubstituted amine, a substituted amine, $-Si(CH_3)_3$, an unsubstituted cyclic C_3 - C_6 alkyl group, a cyclic C_3 - C_6 alkyl group substituted with one or more halogen, a cyclic C_3 - C_6 alkyl group

substituted with an amino group, a C₃-C₈ unsubstituted aromatic group, a C₃-C₈ aromatic group substituted with one or more halogen, a C₃-C₈ aromatic group substituted with an amino group, a 5-member heterocyclic ring and a 6-member heterocyclic ring.

[0110] Examples include, but are not limited to, the compounds set forth in Table 18:

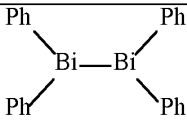
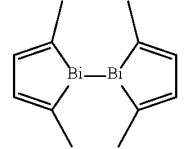
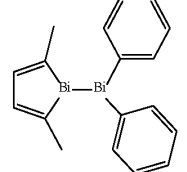
Structure	Compound
	Tetraphenyldibismuthine
	Tetramethylbibismole
	(Diphenylbismuthino)dimethylbismole

Table 18

[0111] **Class 4 Compounds**

[0112] In another embodiment, the disclosed and claimed methods and formulations utilize compounds of the formulas $M(R^a)_x(R^b)_{3-x}$ or $(R^a)_2M-M(R^b)_2$ where

- (i) M is independently Sb or Bi;
- (ii) X = 0, 1 or 2; and
- (iii) each R^a and R^b is independently one of an unsubstituted linear C₁-C₆ alkyl group, a linear C₁-C₆ alkyl group substituted with one or more halogen, a linear C₁-C₆ alkyl group substituted with an amino group, a linear C₃-C₆ alkyl group substituted with an alkoxy group, an unsubstituted branched C₃-C₆ alkyl group, a branched C₃-C₆ alkyl group substituted with one or more halogen, a branched C₃-C₆ alkyl group substituted with an amino group, a branched C₃-C₆ alkyl group substituted with an alkoxy group, an unsubstituted amine, a substituted amine, -Si(CH₃)₃, an unsubstituted cyclic C₃-C₆ alkyl group, a cyclic C₃-C₆ alkyl group substituted with one or more halogen, a cyclic C₃-C₆ alkyl group substituted with an amino group, a C₃-C₈ unsubstituted aromatic group, a C₃-C₈ aromatic group substituted with one or more halogen, a C₃-C₈ aromatic group substituted with an amino group, a 5-member heterocyclic ring, a 6-member heterocyclic ring, a trialkylstannyl group where the alkyl is a linear C₁-

C₆ alkyl group, a trialkylstannyl group where the alkyl is a branched C₃-C₆ alkyl group and a trialkylstannyl group where the alkyl is a cyclic C₃-C₆ alkyl group.

[0113] Examples include, but are not limited to, the compounds set forth in Table 19:

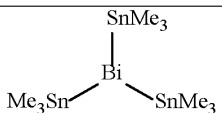
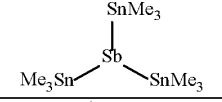
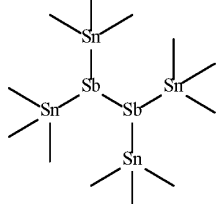
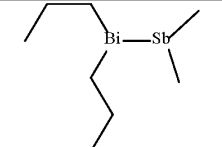
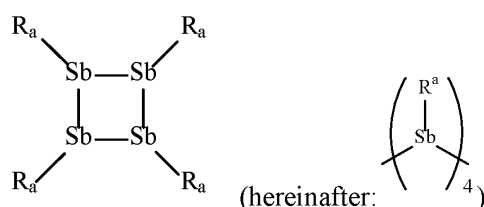
Structure	Compound	CAS#	Melting point (°C)
	Tris(trimethylstannyl) bismuth	81174-92-7	25-28
	Tris(trimethylstannyl) antimony	7029-29-0	39
	Tetrakis(trimethylstannyl) distibane	68354-51-8	93
	(Dipropylbismuthino) dimethylstibane	--	--

Table 19

[0114] **Class 5 Compounds**

[0115] In another embodiment, the disclosed and claimed subject methods and formulations utilize antimony compounds of the formula (R^a)₂Sb-Sb(R^b)₂ or cyclotetrastibane:



where each R^a and R^b is independently one of an unsubstituted linear C₁-C₆ alkyl group, a linear C₁-C₆ alkyl group substituted with one or more halogen, a linear C₁-C₆ alkyl group substituted with an amino group, a linear C₃-C₆ alkyl group substituted with an alkoxy group, an unsubstituted branched C₃-C₆ alkyl group, a branched C₃-C₆ alkyl group substituted with one or more halogen, a branched C₃-C₆ alkyl group substituted with an amino group, a branched C₃-C₆ alkyl group substituted with an alkoxy group, an unsubstituted amine, a substituted amine, -Si(CH₃)₃, an unsubstituted cyclic C₃-C₆ alkyl group, a cyclic C₃-C₆ alkyl group substituted with one or more halogen, a cyclic C₃-C₆ alkyl group substituted with an amino group, a C₃-C₈ unsubstituted aromatic group, a C₃-C₈ aromatic

group substituted with one or more halogen, a C₃-C₈ aromatic group substituted with an amino group, a 5-member heterocyclic ring and a 6-member heterocyclic ring.

[0116] Examples include, but are not limited to, the compounds set forth in Table 20:

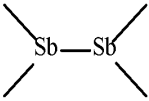
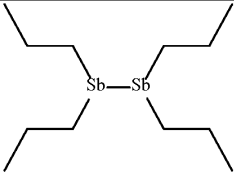
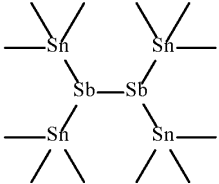
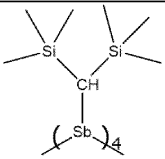
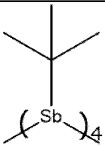
Structure	Compound	CAS#	Boiling point (°C)/ melting point (°C)
	Tetramethyldistibine	41422-43-9	45 @ 0.5 torr/16
	Tetrapropyldistibine	41422-45-1	112 @ 0.01 torr
	Tetrakis(trimethylstannyl) distibine	68354-51-8	93
	Tetrakis[bis(trimethylsilyl) methyl]cyclotetrasibane	91043-36-6	130
	Tetra-tert- butylcyclotetrasibane	4791-73-5	140

Table 20

[0117] **Class 6 Compounds**

[0118] In another embodiment, the disclosed and claimed subject methods and formulations utilize compounds of the formulas $M(R^a)_x(R^b)_{3-x}$ or $(R^a)_2M-M(R^b)_2$ where

(i) M is independently Sb or Bi;

(ii) X = 0, 1 or 2;

(iii) each R^a and R^b is independently one of a linear C₁-C₆ alkyl group, a unsaturated linear C₁-C₆ alkyl group substituted with one or more halogen, a unsaturated linear C₁-C₆ alkyl group substituted with an amino group, an unsaturated branched C₃-C₆ alkyl group, a unsaturated branched C₃-C₆ alkyl group substituted with one or more halogen, a unsaturated branched C₃-C₆ alkyl group substituted with an amino group, an unsubstituted amine, a substituted

amine, $-\text{Si}(\text{CH}_3)_3$, an unsaturated cyclic $\text{C}_3\text{-C}_6$ alkyl group, a unsaturated cyclic $\text{C}_3\text{-C}_6$ alkyl group substituted with one or more halogen, a unsaturated cyclic $\text{C}_3\text{-C}_6$ alkyl group substituted with an amino group, a 6-member aromatic ring, an aromatic with a $\text{C}_2\text{-C}_6$ unsaturated alkyl group, a 5-member heterocyclic ring and a 6-member heterocyclic ring; and

(iv) the compounds include at least one an unsaturated group.

[0119] Examples include, but are not limited to, the compounds set forth in Table 21:

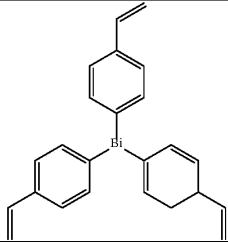
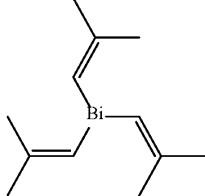
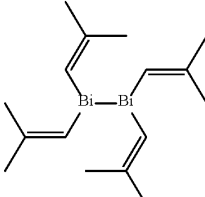
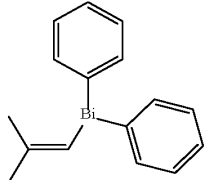
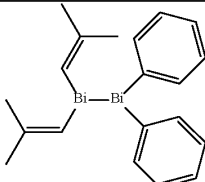
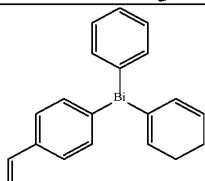
Structure	Compound	CAS#	Boiling point (°C)/ melting point (°C)
	Tri(p-styrene)bismuth	802-03-9	74
	Tri(propenyl)bismuthine	87432-62-0	85 @ 0.005 torr
	Tetrakis(propenyl)dibismuthine	87450-34-8	29
	Diphenylpropenyl bismuthine	--	--
	(Diphenylbismuthino) dipropenylbismuthine	--	--
	Diphenylstyrenyl bismuth	--	--

Table 21

[0120] The disclosed and claimed subject matter further includes the use of bismuth-containing and antimony-containing compositions with unsaturated alkyl ligands or imide/imine functional groups which demonstrate adequate vapor pressure and thermal stability to deposit thin films but will form polymers upon decomposition. Polymer formation can be triggered by thermolysis or exposure EUV light, among other process conditions. These compositions may include neutral compounds that have polymerizable ligands (for crosslinking); or could be self-initiating photocatalysts.

[0121] Another embodiment is a process which uses compounds that react in the liquid or gas phase with co-reagents, forming polymers or nanoclusters. An example of this embodiment are pre-formed, soluble nanoclusters that can be dispersed in uniform films. Another embodiment are pre-formed nanoclusters which are dispersed in an inert liquid with or without the use of dispersion aids such as surfactants.

[0122] Hydrolysis reactions and sol-gel reactions, among other processes, are used to prepare metal oxide nanoclusters which are preferably <10 nm, more preferably <5 nm, and most preferably <2 nm in diameter. The nanoclusters may be various shapes including spherical, square, hexagonal and irregular. The surfaces of the nanoclusters may be functionalized with groups that are useful for solubility and/or linking reaction chemistry to link nanoclusters into a 2-D or 3-D network. Examples of linking reaction chemistry include, but are not limited to, polymerization reactions, crosslinking reactions, homolytic- and heterolytic-coupling reactions, and condensation reactions. Polymerization reactions may be promoted by chemical catalysts, thermolysis, plasma treatments, and light exposure, among other conditions. Chemical catalysts may include the monomeric units themselves or added polymerization catalysts.

[0123] Bismuth-containing clusters may be formed starting with bismuth compounds such as bismuth nitrate, bismuth chloride, other bismuth salts and triphenylbismuth. Antimony-containing clusters may be formed starting with antimony compounds such as antimony nitrate, antimony chloride, other antimony salts and triphenylantimony.

[0124] The resulting nanoclusters may be further functionalized by subsequent reactions to append additional groups to the surface of the nanoclusters. These groups may contain reactive moieties such as functional groups with unsaturation, functional groups which undergo reduction or oxidation, functional groups that are reactive towards light, and functional groups that are activated with thermolysis to react with other functional groups.

[0125] Numerous reactions may be used to append functional groups which include, but are not limited to, polymerization reactions, crosslinking reactions, homolytic- and heterolytic-coupling reactions, and condensation reactions.

[0126] One embodiment of such reaction to append a functional group on a nanocluster is acid-catalyzed coupling. An example of nanocluster synthesis and acid-catalyzed coupling of unsaturated groups such as aryl- and vinyl-sulfonic acids is shown in FIG. 1. Addition of such unsaturated functional groups may be used in subsequent processing steps to promote cross-linking or other methods to form solid bismuth-containing thin films as shown in FIG. 2.

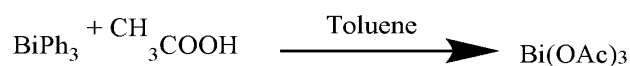
[0127] FIG. 3 illustrates the use of functionalized nanoclusters in a patterning process in which functionalized nanoclusters on a substrate are exposed to light through a patterning mask. The functionalized nanoclusters exposed to light are crosslinked. In the second step, non-light-exposed nanoclusters are removed from the substrate.

[0128] FIG 4 illustrates the use of functionalized nanoclusters in a patterning process in which crosslinked, functionalized nanoclusters on a substrate are exposed to light through a patterning mask. The crosslinked, functionalized nanoclusters exposed to light are uncrosslinked. In the second step, light-exposed nanoclusters are removed from the substrate.

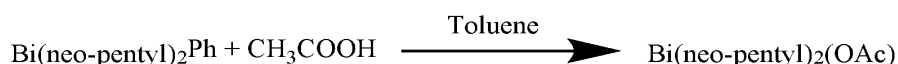
[0129] Suitable methods of dispersing pre-formed clusters onto a substrate include spin-on coating, spraying and aerosolization.

[0130] The disclosed and claimed subject matter further includes the formation of heteroleptic bismuth compounds from the selective replacement of aryl ligands on heteroleptic bismuth alkyl/aryl compounds to generate heteroleptic bismuth compositions which are useful as metal-organic photoresists. The aryl ligands can be replaced with ligands such as an alkoxide group, carboxylate group, diketonate group, a ketoesterate group, an amidate group and an amidinate group.

[0131] Although it is widely known in the art that alkyl groups on bismuth are more reactive towards certain reagents (*e.g.*, oxidants) than aryl groups, we have surprisingly found a very high selectivity for the replacement of aryl groups with oxygen-containing ligands starting with heteroleptic bismuth organometallic compounds. The reaction of triphenylbismuth with acetic acid results in the formation of bismuth triacetate, similar to literature reports of reactions of triphenylbismuth with other carboxylic acids:

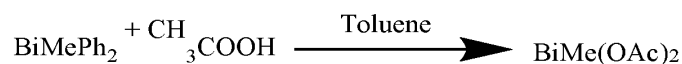


[0132] In contrast, the reaction of a heteroleptic bismuth organometallic compound, di(neo-pentyl)phenylbismuth, with acetic acid under the same conditions leads to selective replacement of only the phenyl ligand to form $[\text{Bi}(\text{neo-pentyl})_2(\text{OAc})]_n$:



[0133] FIG. 5 shows the molecular structure of the $[\text{Bi}(\text{neo-pentyl})_2(\text{OAc})]_n$ coordination polymer as determined by single crystal X-ray diffraction.

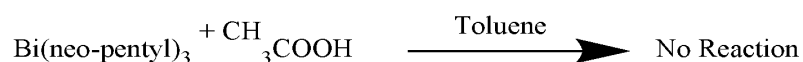
[0134] In a similar fashion, an unusually selective reaction occurs to replace the phenyl ligands of methylbisdiphenylbismuth with acetic acid under the same conditions to yield $[\text{Bi}(\text{methyl})(\text{OAc})_2]_n$:



[0135] FIG. 6a shows the asymmetric molecular structures of the $[\text{Bi}(\text{methyl})(\text{OAc})_2]_n$, $[\text{Bi}(\text{isopropyl})(\text{OAc})_2]_n$, and $[\text{Bi}(\text{neopentyl})(\text{OAc})_2]_n$ coordination polymers as determined by single crystal X-ray diffraction. Examination of the structural parameters shows that the molecular packing (packing group, symmetry, crystal density) is influenced by the R group bound to bismuth.

[0136] FIG. 6b shows the extended structure (A axis) of the $[\text{Bi}(\text{methyl})(\text{OAc})_2]_n$ coordination polymer as determined by single crystal X-ray diffraction.

[0137] The attempted reaction of a trialkylbismuth compound with acetic acid under forcing conditions (150 °C) leads to no reaction. Tri(neo-pentyl)bismuth was heated to 150 °C in the presence of glacial acetic acid. NMR analysis showed that no reaction occurred under these conditions:



[0138] Thus, the selective reaction of aryl ligands vs. alkyl ligands can be used in reactions to generate heteroleptic bismuth complexes which are useful for metal-organic photoresists.

[0139] Formulations comprising specific compounds derived from the selective reaction of aryl ligands vs. alkyl ligands can be used in metal-organic photoresist processes. The formulations may comprise part of a film coating on a substrate to be patterned.

[0140] FIG 7 shows a patterned film which was fabricated by spin-coating of methylbismuth diacetate to form a thin film which was selectively exposed to E-beam radiation and developed as described in Example 23.

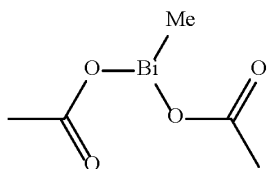
[0141] The disclosed and claimed subject matter further includes new bismuth-containing compounds as follows.

[0142] **Group 1**

[0143] In one embodiment, the disclosed and claimed subject matter includes bismuth compounds of the formula $\text{Bi}(\text{R}^a)_x(\text{L})_{3-x}$ where

- (i) $x = 1$ or 2 ;
- (ii) each R^a is independently one of an unsubstituted linear C_1 - C_6 alkyl group, a linear C_1 - C_6 alkyl group substituted with one or more halogen, a linear C_1 - C_6 alkyl group substituted with an amino group, a linear C_3 - C_6 alkyl group substituted with an alkoxy group, an unsubstituted branched C_3 - C_6 alkyl group, a branched C_3 - C_6 alkyl group substituted with one or more halogen, a branched C_3 - C_6 alkyl group substituted with an amino group, a branched C_3 - C_6 alkyl group substituted with an alkoxy group, $-\text{Si}(\text{CH}_3)_3$, an unsubstituted cyclic C_3 - C_6 alkyl group, a cyclic C_3 - C_6 alkyl group substituted with one or more halogen and a cyclic C_3 - C_6 alkyl group substituted with an amino group; and
- (iii) each L is a carboxylate group; and
- (iv) the compound where $x = 1$, R^a is $-\text{CH}_3$ and each L is acetate is excluded.

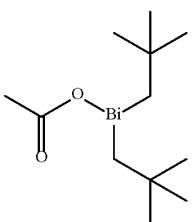
As those skilled in the art will understand, the disclosed and claimed bismuth compounds of this embodiment exclude the compound:



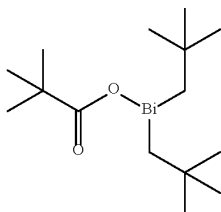
[0144] In one aspect of this embodiment, $x = 1$. In one aspect of this embodiment, $x = 2$.

[0145] In another aspect of this embodiment, each L is independently one of acetate, formate, pivalate, methacrylate and salicylate. In one aspect of this embodiment, each L is independently one of formate, pivalate, methacrylate and salicylate. In another aspect of this embodiment, each L is acetate. In another aspect of this embodiment, each L is formate. In another aspect of this embodiment, each L is pivalate. In another aspect of this embodiment, each L is methacrylate. In another aspect of this embodiment, each L is salicylate. In another aspect of this embodiment, when $x = 1$, each L is the same. In another aspect of this embodiment, when $x = 1$, each L is different from the other.

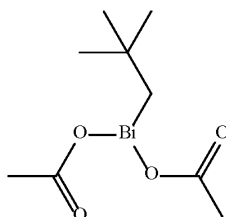
[0146] In one aspect of this embodiment, the bismuth compound of the formula $\text{Bi}(\text{R}^a)_x(\text{L})_{3-x}$ is:



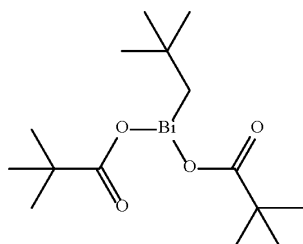
[0147] In one aspect of this embodiment, the bismuth compound of the formula $\text{Bi}(\text{R}^a)_x(\text{L})_{3-x}$ is:



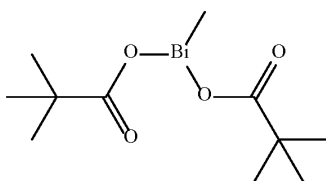
[0148] In one aspect of this embodiment, the bismuth compound of the formula $\text{Bi}(\text{R}^a)_x(\text{L})_{3-x}$ is:



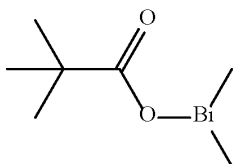
[0149] In one aspect of this embodiment, the bismuth compound of the formula $\text{Bi}(\text{R}^a)_x(\text{L})_{3-x}$ is:



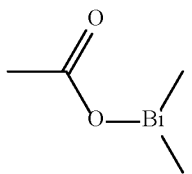
[0150] In one aspect of this embodiment, the bismuth compound of the formula $\text{Bi}(\text{R}^a)_x(\text{L})_{3-x}$ is:



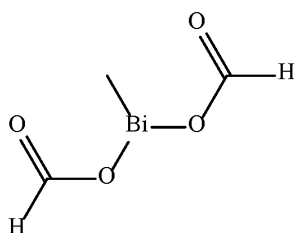
[0151] In one aspect of this embodiment, the bismuth compound of the formula $\text{Bi}(\text{R}^a)_x(\text{L})_{3-x}$ is:



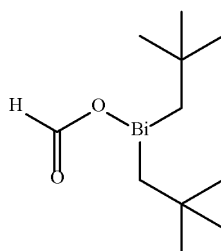
[0152] In one aspect of this embodiment, the bismuth compound of the formula $\text{Bi}(\text{R}^a)_x(\text{L})_{3-x}$ is:



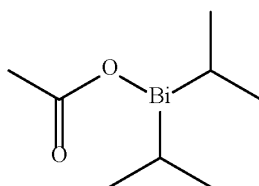
[0153] In one aspect of this embodiment, the bismuth compound of the formula $\text{Bi}(\text{R}^a)_x(\text{L})_{3-x}$ is:



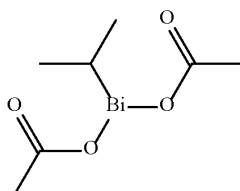
[0154] In one aspect of this embodiment, the bismuth compound of the formula $\text{Bi}(\text{R}^a)_x(\text{L})_{3-x}$ is:



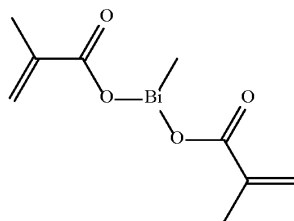
[0155] In one aspect of this embodiment, the bismuth compound of the formula $\text{Bi}(\text{R}^a)_x(\text{L})_{3-x}$ is:



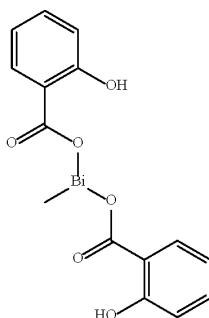
[0156] In one aspect of this embodiment, the bismuth compound of the formula $\text{Bi}(\text{R}^a)_x(\text{L})_{3-x}$ is:



[0157] In one aspect of this embodiment, the bismuth compound of the formula $\text{Bi}(\text{R}^a)_x(\text{L})_{3-x}$ is:



[0158] In one aspect of this embodiment, the bismuth compound of the formula $\text{Bi}(\text{R}^a)_x(\text{L})_{3-x}$ is:



[0159] **Group 2**

[0160] In another embodiment, the disclosed and claimed subject matter includes bismuth compounds of the formula $\text{Bi}(\text{R}^a)_x(\text{L})_{3-x}$ where

- (i) $x = 1$ or 2 ;
- (ii) each R^a is independently one of an unsubstituted linear C_1 - C_6 alkyl group, a linear C_1 - C_6 alkyl group substituted with one or more halogen, a linear C_1 - C_6 alkyl group substituted with an amino group, a linear C_3 - C_6 alkyl group substituted with an alkoxy group, an unsubstituted branched C_3 - C_6 alkyl group, a branched C_3 - C_6 alkyl group substituted with one or more halogen, a branched C_3 - C_6 alkyl group substituted with an amino group, a branched C_3 - C_6 alkyl group substituted with an alkoxy group, $-\text{Si}(\text{CH}_3)_3$, an unsubstituted cyclic C_3 - C_6 alkyl group, a cyclic C_3 - C_6 alkyl group substituted with one or more halogen and a cyclic C_3 - C_6 alkyl group substituted with an amino group; and
- (iii) each L is an amidinate, formamidinate or guanidinate group.

[0161] In one aspect of this embodiment, $x = 1$. In one aspect of this embodiment, $x = 2$.

[0162] In another aspect of this embodiment, each L is an amidinate group. In another aspect of this embodiment, each L is a formamidinate group. In another aspect of this embodiment, each L is a guanidinate group.

[0163] Group 3

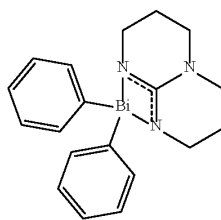
[0164] In another embodiment, the disclosed and claimed subject matter includes bismuth compounds of the formula $\text{Bi}(\text{Ar})_x(\text{L})_{3-x}$ where

- (i) $x = 1$ or 2 ;
- (ii) each Ar is independently one of a C_3 - C_8 unsubstituted aromatic group, a C_3 - C_8 aromatic group substituted with one or more halogen, a C_3 - C_8 aromatic group substituted with an amino group, a 5-member heterocyclic ring and a 6-member heterocyclic ring; and
- (iii) each L is an amidinate, formamidinate, or guanidinate group.

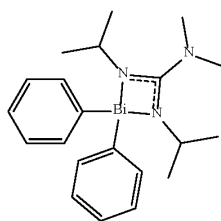
[0165] In one aspect of this embodiment, $x = 1$. In one aspect of this embodiment, $x = 2$.

[0166] In another aspect of this embodiment, each L is an amidinate group. In another aspect of this embodiment, each L is a formamidinate group. In another aspect of this embodiment, each L is a guanidinate group. In another aspect of this embodiment, each L is independently one of 1,3,4,6,7,8-Hexahydro-2H-pyrimido[1,2-a]pyrimidine, N,N'-diisopropyl-N'',N''-dimethylguanidinate and N,N'-diisopropylacetaminidate. In another aspect of this embodiment, each L is 1,3,4,6,7,8-Hexahydro-2H-pyrimido[1,2-a]pyrimidine. In another aspect of this embodiment, each L is N,N'-diisopropyl-N'',N''-dimethylguanidinate. In another aspect of this embodiment, each L is N,N'-diisopropylacetaminidate. In another aspect of this embodiment, when $x = 1$, each L is the same. In another aspect of this embodiment, when $x = 1$, each L is different from the other.

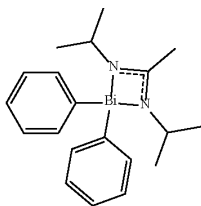
[0167] In one aspect of this embodiment, the bismuth compound of the formula $\text{Bi}(\text{Ar})_x(\text{L})_{3-x}$ is:



[0168] In one aspect of this embodiment, the bismuth compound of the formula $\text{Bi}(\text{Ar})_x(\text{L})_{3-x}$ is:



[0169] In one aspect of this embodiment, the bismuth compound of the formula $\text{Bi}(\text{Ar})_x(\text{L})_{3-x}$ is:



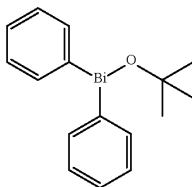
[0170] **Group 4**

[0171] In another embodiment, the disclosed and claimed subject matter includes bismuth compounds of the formula $\text{Bi}(\text{Ar})_x(\text{L})_{3-x}$ where

- (i) $x = 1$ or 2 ;
- (ii) each Ar is independently one of a $\text{C}_3\text{-C}_8$ unsubstituted aromatic group, a $\text{C}_3\text{-C}_8$ aromatic group substituted with one or more halogen, a $\text{C}_3\text{-C}_8$ aromatic group substituted with an amino group, a 5-member heterocyclic ring and a 6-member heterocyclic ring; and
- (iii) each L is an alkoxide group.

[0172] In one aspect of this embodiment, $x = 1$. In one aspect of this embodiment, $x = 2$.

[0173] In one aspect of this embodiment, the bismuth compound of the formula $\text{Bi}(\text{Ar})_x(\text{L})_{3-x}$ is:



[0174] **Examples**

[0175] Reference will now be made to more specific embodiments of the present disclosure and experimental results that provide support for such embodiments. The examples are given to illustrate the disclosed and claimed subject matter and should not be construed as limiting the disclosed subject matter in any way.

[0176] 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.

[0177] Materials and Methods:

[0178] All reactions and manipulations described in the examples were conducted under a nitrogen atmosphere using an inert atmosphere glove box or standard Schlenk techniques. Unless indicated otherwise, all reagents were purchased from Millipore Sigma and were used “as-is” without further purification. For single-crystal X-ray diffraction experiments, suitable crystals were selected and mounted on a Bruker APEX-II CCD diffractometer. The crystal was kept at ~100 K during data collection. Using Olex2 [Dolomanov, O.V., *et al.*, *J. Appl. Cryst.*, 42, 339-341 (2009)], the structure was solved with the SHELXT [Sheldrick, G.M., *Acta Cryst.*, A71, 3-8 (2015)] structure solution program using Intrinsic Phasing and refined with the XL [Sheldrick, G.M., *Acta Cryst.*, A64, 112-122 (2008)] refinement package using least squares minimization.

[0179] In the vapor-phase deposition processes, precursors were delivered to the reactor chamber by passing ~50-100 sccm argon via stainless steel containers filled with Bi precursor. The bismuth precursor container temperature varied from about 110-120 °C to achieve sufficient vapor pressure of the precursor. The wafer temperature varied between from about 130-200 °C. The reactor chamber pressure varied from about 5 to 25 torr. Deposition time varied from about 20 seconds to 20 minutes for achieving films of different thickness.

[0180] Bismuth-containing films were grown onto silicon substrates using a CN-1 showerhead style reactor.

[0181] Film thickness was measured by X-ray fluorescence (XRF), ellipsometry, and scanning electron microscopy (SEM).

[0182] Specific Examples

[0183] Example 1: Synthesis of Di-neopentylbismuth Acetate / Bi(neopentyl)₂(OAc). In an NMR tube was placed a 1:1 stoichiometric mixture of di(neopentyl)phenylbismuth and glacial acetic acid in d₈-toluene. NMR analysis showed no reaction at room temperature after 2 hours. The tube was heated to 90 °C for 4 hours and cooled to room temperature over 4 hours, forming colorless crystals. NMR analysis of the supernatant showed only traces of unreacted di(neopentyl)phenylbismuth. The molecular structure is shown in FIG. 5. Crystal data for C₁₂H₂₅BiO₂ (*M*=410.30 g/mol): orthorhombic, space group Pbca (no. 61), *a* = 14.6494(17) Å, *b* = 10.4636(13) Å, *c* = 21.400(3) Å, *V* = 3280.3(7) Å³, *Z* = 8, *T* = 100.15 K, *μ*(CuKα) = 20.974 mm⁻¹, *D*_{calc} = 1.662 g/cm³, 25306 reflections measured (8.262° ≤ 2θ ≤ 138.124°), 3040 unique (*R*_{int} = 0.0475, *R*_{sigma} = 0.0282) which were used in all calculations. The final *R*₁ was 0.0350 (*I* > 2σ(*I*)) and *wR*₂ was 0.0778 (all data).

[0184] Example 2: Synthesis of Methylbismuth Diacetate / Bi(methyl)(OAc)₂. In

an NMR tube was placed a 1:2 stoichiometric mixture of methyldiphenylbismuth and glacial acetic acid in d8-toluene. NMR analysis showed no reaction at room temperature after 2 hours. The tube was heated to 90 °C for 4 hours and cooled to room temperature over 4 hours, forming colorless crystals. NMR analysis of the supernatant showed only traces of unreacted methyldiphenylbismuth. The asymmetric crystal structure is shown in FIG. 6a (left). The extended crystal structure (A axis) is shown in FIG. 6b. Crystal data for $C_5H_9BiO_4$ ($M=342.10$ g/mol): tetragonal, space group $P4/nnc$, $a = b = 16.3676(10)$ Å, $c = 15.5112(10)$ Å, $V = 4155.4(6)$ Å³, $Z = 16$, $T = 100.15$ K, $D_{calc} = 2.187$ g/cm³, 21823 reflections measured, 2139 unique which were used in all calculations.

[0185] Example 3: Synthesis of Bi(OAc)₃. In an NMR tube was placed a ~1:2 stoichiometric mixture of triphenylbismuth and glacial acetic acid in d8-toluene. NMR analysis showed no reaction at room temperature after 2 hours. The tube was heated to 90 °C for 4 hours and cooled to room temperature over 4 hours, forming colorless crystals. NMR analysis of the supernatant showed Bi(OAc)₃ and traces of other compounds which may correspond to Bi(phenyl)_x(OAc)_y. The acetic acid was fully consumed during the reaction. Crystal data for $C_6H_9BiO_6$ (MW = 386.11 g/mol): monoclinic, space group $P2_1/c$ (no. 14), $a = 12.0052(4)$ Å, $b = 10.8168(4)$ Å, $c = 7.2433(3)$ Å, $\beta = 106.612(2)$, $V = 901.34(6)$ Å³, $Z = 4$, $T = 100.15$ K, $\mu(CuK\alpha) = 38.462$ mm⁻¹, $D_{calc} = 2.845$ g/cm³, 9819 reflections measured ($7.684^\circ \leq 2\theta \leq 139.482^\circ$), 1693 unique ($R_{int} = 0.0409$, $R_{sigma} = 0.0263$) which were used in all calculations. The final R_1 was 0.0223 ($I > 2\sigma(I)$) and wR_2 was 0.0575 (all data).

[0186] Example 4: Synthesis of Neopentylbismuth Diacetate. A 200 mL Schlenk flask was charged with diphenylbismuth chloride (10 g, 25.1 mmol) and 150 cc of toluene. This white suspension was cooled to -78 °C with stirring. A solution of Neo-pentylmagnesium chloride (2,2-Dimethylpropylmagnesium chloride, 1 M in diethyl ether; 25 cc, 25 mmol) was added dropwise with stirring at -78 °C. After the addition, the flask was allowed to warm to room temperature. The resulting light grey suspension was stirred overnight and filtered to yield a light-yellow solution. A portion of this crude neo-pentylbismuth (~1 g) was dissolved in 10 cc toluene. Glacial acetic acid (0.5 g) was added with stirring. The resulting colorless solution was allowed to stand at room temperature overnight forming colorless crystals. The crystals were washed with toluene (2 x 2 cc) and pentane (2 cc) and dried under vacuum. ¹H NMR (d₈-THF): 2.2 (s, 2H), 1.82 (s, 6H), 1.15 (s, 9H). X-ray diffraction of a selected crystal was performed to characterize the crystal structure of neopentylbismuth diacetate. The asymmetric crystal structure is shown in FIG. 6a (right). Crystal data for $C_9H_{17}BiO_4$ (MW = 398.2 g/mol): tetragonal, space group $I4_1/a$, $a = b = 23.0989(7)$ Å, $c =$

9.6411(4) Å, $V = 5144.1(4)$ Å³, $Z = 16$, $T = 100$ K, 44685 reflections collected, 2637 unique reflections which were used in all calculations.

[0187] **Example 5: Synthesis of Neopentylbismuth Dipivalate.** Neopentylbisdiphenylbismuth (~1 g) was dissolved in 10 cc toluene. Pivalic acid (0.5 g) was added with stirring. The resulting colorless solution was allowed to stand at room temperature overnight forming colorless crystals. The crystals were washed with toluene (2 x 2 cc) and dried under vacuum. ¹H NMR (d₈-Toluene): 2.31 (s, 2H), 1.18 (s, 18H), 1.09 (s, 9H).

[0188] **Example 6: Synthesis of Methylbismuth Diformate.** A 100 mL flask was charged with methylbisdiphenylbismuth (5 g, 13.2 mmol) in 50 cc toluene. Formic acid (1.38 g, 30 mmol) was added dropwise with stirring. After 2-3 minutes of addition, a white precipitate was observed. After standing overnight at room temperature, the white suspension was partially liquified with shaking and filtered. Hexanes (3 x 10 mL) was added to wash material from the flask and rinse toluene from the bright white solid. The solid was dried under vacuum at room temperature. The resulting bright white amorphous solid (3.6 g) was analyzed by TGA and DSC.

[0189] **Example 7: Synthesis of Methylbismuth Dipivalate.** A 100 cc Schlenk flask was charged with Methylbisdiphenylbismuth (5 g, 13.2 mmol) in 25 cc toluene. To this colorless solution, Pivalic acid (3.06 g; 30 mmol) was added dropwise with stirring. Under slight pressure of nitrogen (~2 psig) the solution was heated to 100 °C for 4 hours. The resulting colorless solution was allowed to slowly cool to RT. Upon standing overnight, a mass of fine colorless crystals formed in the flask. The colorless supernatant was removed via pipet. The crystals were washed with hexanes (2 x 2 cc) and the washes added to the supernatant. The crystals were dried under vacuum at room temperature for 1 hour. ¹H NMR (d₈-THF): 1.33 (s, 3H), 1.15 (s, 18H).

[0190] **Example 8: Synthesis of Dimethylbismuth Acetate.** Phenylbismuth dibromide (73 mmol) was suspended in toluene (150 cc) and cooled to -78 °C. Methylolithium (1.6M in ether, 160 mmol, 100 cc) was added dropwise with stirring. The resulting suspension was warmed to room temperature and stirred overnight. Grey precipitate was filtered and the resulting colorless solution concentrated under vacuum, resulting in the precipitation of additional solid. This solid was filtered and the resulting light-brown solution was distilled at 50 °C and 200 mTorr to yield a colorless liquid. A portion of this Dimethylphenylbismuth (5 g, 15.8 mmol) was dissolved in 10 cc toluene. Glacial acetic acid (1.2 g, 20 mmol) was added with stirring. The resulting colorless solution was allowed to stand at room temperature for 2 days. Large colorless crystals formed. The crystals were washed with toluene (2 x 2 cc) and pentane (2 cc) and dried under vacuum. ¹H NMR (d₈-THF): 1.8 (s, 6H), 1.36 (s, 3H).

[0191] **Example 9: Synthesis of Di-isopropylphenylbismuth.** Triphenylbismuth (39.6

g, 0.09 mol) was slowly added to a solution of Bismuth tribromide (89.8 g, 0.2 mol) in 400 cc diethyl ether. Yellow precipitate formed upon addition of solid Triphenylbismuth to the stirred solution. After stirring at room temperature overnight, the bright yellow suspension was cooled to -78 °C. To this cold suspension was added 2M isopropylMgCl in THF (300 cc, 0.6 mol) over 1 hour with stirring. The resulting suspension was allowed to warm to room temperature over several hours. The suspension was filtered, and the solids washed with Pentane (100 cc). The resulting combined solutions were concentrated under vacuum, precipitating additional grey solid. Filtration of the solid gave a pale-yellow liquid (72.1 g). A portion of this liquid was distilled under vacuum (200 mTorr) at 95 °C to yield a colorless, viscous liquid.

[0192] Example 10: Synthesis of Di-isopropylbismuth Acetate / Isopropylbismuth diacetate. Di-isopropylphenylbismuth (3.7 g, 10 mmol) was dissolved in 10 cc toluene. Glacial acetic acid (1.2 g, 20 mmol) was added with stirring. The resulting colorless solution was allowed to stand at room temperature for 2 days and colorless crystals formed. The crystals were washed with toluene (2 x 2 cc) and pentane (2 cc) and dried under vacuum. X-ray diffraction of a selected crystal showed the structure was isopropylbismuth diacetate. It is probable that this compound was formed *in situ* by disproportionation of di-isopropylbismuth diacetate to isopropylbismuth acetate and tri-isopropylbismuth. The asymmetric crystal structure is shown in FIG. 6a (center). Crystal data for $C_7H_{13}BiO_4$ (MW = 370.15 g/mol): trigonal, space group R-3, $a = b = 15.3049(15)$ Å, $c = 22.174(3)$ Å, $V = 4498.2(11)$ Å³, $Z = 18$, $T = 100$ K, 16140 reflections collected, 2054 unique reflections which were used in all calculations.

[0193] Example 11: Synthesis of Di-neopentylbismuth Formate. In a 50 cc round bottom flask was placed di-isopropylphenylbismuth (3.7 g, 10 mmol) and 10 cc toluene. To this colorless solution was added formic acid (0.5 g, 11 mmol) with stirring. The resulting colorless solution stood overnight at room temperature. During this time, a fluffy colorless solid formed. The toluene solution was decanted and 5 cc fresh toluene added with mixing. The toluene solution was filtered to yield a colorless solid which was dried under vacuum.

[0194] Example 12: Synthesis of Di-neopentylbismuth Pivalate. In a 100 cc Schlenk flask was placed di-neopentylphenylbismuth (10 g, 23.4 mmol) and 10 cc toluene. To this light-yellow solution was added an excess of pivalic acid (5.7 g, 55.9 mmol) with stirring. The resulting bright yellow solution was heated to 100 °C for 6 hours. During this time, a small amount of black solid precipitated and the solution color turned to yellow-green. The flask was cooled to room temperature and stood overnight. During this time, colorless crystals formed in the bottom of the flask. NMR (d_8 -THF): 1.09 (br s, 6.9H), 2.22 (br s, 1H). This matches with the expected structure if the tBu protons overlap with the methyl protons from the neo-pentyl groups (27 methyl protons

vs. 4 methylene protons; 4/27 = 6.75:1). The TGA analysis shows clean evaporation with about 0.5 wt.% non-volatile residue. The vapor pressure is low, however, with a $T_{1/2}$ of 187 °C. DSC analysis shows no significant exotherms but there are endotherms at 75 °C (v. small) and 235 °C (large).

[0195] Example 13: Synthesis of Methylbismuth Dimethacrylate. In a 100 cc round bottom flask was placed methylbisdiphenylbismuth (3.8 g, 10 mmol) and 10 cc toluene. To this colorless solution was added methacrylic acid (1.9 g, 22 mmol) with stirring. The resulting colorless solution stood overnight at room temperature. No solids formed during this time. The solution was heated to 90 °C for 2 hours. Upon cooling, a small amount of colorless solid was formed. The toluene was removed under vacuum to yield a white solid. The solid was washed with pentane (10 cc) and dried under vacuum. ^1H NMR (d_3 -Acetonitrile): 1.53 (s, 3H), 1.91 (s, 6H), 5.51 (br s, 2H), 6.0 (br s, 2H).

[0196] Example 14: Synthesis of Diphenylbismuth Hhpp (Hhpp = 1,3,4,6,7,8-Hexahydro-2H-pyrimido[1,2-a]pyrimidine). A solution of the sodium Hhpp (2.5 g, 15.5 mmol) in 50 cc THF was prepared. To this light orange solution was added diphenylbismuth chloride (6 g, 15 mmol) with stirring. The resulting suspension was stirred overnight, turning light grey. The THF was removed under vacuum and the resulting sticky grey solid extracted with pentane (50 cc). Upon evaporation of the pentane under vacuum, bright white precipitate formed. After drying, the crude solid was assayed by ^1H NMR. ^1H NMR (d_8 -Toluene): 1.62 (m, 4H), 2.68 (t, 4H), 3.29 (t, 4H), 7.09 (m, 2H), 7.17 (m, 4H), 7.67 (m, 4H).

[0197] Example 15: Synthesis of Diphenylbismuth iPrDMGD (iPrDMGD = N,N'-diisopropyl-N'',N''-dimethylguanidinate). In a 100 cc round bottom flask was combined diphenylbismuth chloride (330 mg, 0.83 mmol) and 10 cc toluene with stirring. To this suspension was added Lithium iPrDMGD (180 mg, ~1 mmol). As the Li iPrDMGD was added, the white solid diphenylbismuth chloride was rapidly consumed to yield a cloudy, pale-yellow solution. This solution was stirred overnight. The toluene was removed under vacuum with mild heating to yield a light brown oil. This oil was extracted with pentane and filtered. The pentane was removed under vacuum. The resulting off-white solid was dissolved in d_8 -toluene and analyzed. ^1H NMR (d_8 -Toluene): 1.30 (d, 12H), 2.49 (s, 6H), 3.60 (m, 2H), 7.08 (m, 2H), 7.15 (m, 4H), 7.67 (m, 4H) ppm.

[0198] Example 16: Synthesis of Diphenylbismuth iPrAMD (iPrAMD = N,N'-diisopropylacetaminidate). A solution of triphenylbismuth (10 g, 23 mmol) was prepared in 100 cc toluene. To this solution was added 4 M hydrogen chloride solution in dioxane (6.25 cc, 25 mmol). White solid precipitated upon addition of the hydrogen chloride solution. The resulting suspension was stirred at room temperature for 1 hour. Li(iPrAMD) was added slowly to the suspension with stirring (3.7 g, 25 mmol). Upon addition, the suspension turned

yellow. After stirring overnight at room temperature, the solids were filtered and washed with pentane. The solution was concentrated under vacuum to yield a sticky white solid. This solid was dissolved in a minimal amount of THF and added dropwise to pentane in order to precipitate solid. The solvents were slowly removed by evaporation, resulting in a colorless crystalline solid which was analyzed. ^1H NMR (d_8 -Toluene): 1.01 (d, 12H), 1.25 (s, 3H), 4.22 (m, 2H), 7.10 (m, 2H), 7.15 (m, 4H), 7.67 (m, 4H) ppm.

[0199] Example 17: Synthesis of Isopropenyldiphenylbismuth. Diphenylbismuth chloride (4 g, 10 mmol) was stirred in toluene (30 cc) to form a white suspension. To this suspension was added isopropenylMgBr solution (0.5 M in THF, 30 cc, 15 mmol) dropwise with stirring at room temperature. The solution rapidly turned dark, and the white solid was dissolved. The resulting dark grey solution was stirred overnight at room temperature. The solution was evaporated to dryness to form a dark grey sticky solid. This solid was extracted with pentane (20 cc). Evaporation of the pentane solution gave a mixture of needle-like crystals and liquid. The liquid was separated by filtration to yield a colorless viscous liquid (2.7 g) and needle-like crystals. ^1H NMR analysis of the needle-like crystals showed that the crystals were triphenylbismuth (by comparison to an authentic sample). The liquid product was a mixture of triisopropenylbismuth (signals compared to literature data) and two other compounds with NMR signals consistent with isopropenyldiphenylbismuth and di-isopropenylphenylbismuth. It is apparent from the NMR data that disproportionation of the isopropenyl and phenyl ligands has occurred at room temperature.

[0200] Example 18: Synthesis of Bi(methyl)(OSal)₂. Methylbismuth (1 g, 2.64 mmol) was dissolved in toluene (5 ml) and 2-hydroxybenzoic acid (HOSal, 0.8 g, 5.82 mmol, 2.2 eq.) was added dropwise at room temperature. The cloudy solution was stirred for 2 hours in the dark. The solid was filtered and washed 2 times with 2 ml of hexane. ^1H NMR (THF- d_8): δ 11.1 (s(br), Ph-OH, 2H), 7.8 (dd, Ph-H, 2H), 7.4 (m, Ph-H, 2H), 6.9 (m, 2 Ph-H, 4H), 1.7 (s, Bi-CH₃, 3H) ppm.

[0201] Example 19: Synthesis of BiPh₂(O^tBu). Diphenylbismuth bromide (1 g, 2.26 mmol) was dissolved in THF (10 ml) and potassium tert-butoxide (KO^tBu, 0.25 g, 2.26 mmol, 1 eq.) was slowly added at room temperature. The mixture was stirred for 16 hours, filtered and the solvent was removed in vacuum. The pale-yellow solid was sublimed at 70 °C and 0.02 mbar to yield a colorless solid. The NMR shows the target compound as the main species and small amounts of BiPh₃, Bi(O^tBu)₃ and BiPh(O^tBu)₂. ^1H NMR (THF- d_8): δ 8.0 (m, Ph-H, 4H), 7.4 (m, Ph-H, 4H), 7.2 (m, Ph-H, 2H), 1.2 (s, OC(CH₃)₃-H, 9H) ppm.

[0202] Example 20: Synthesis of BiPh₂(MODMP). Diphenylbismuth bromide (500 mg, 1.13 mmol) was suspended in toluene (10 ml) and cooled to -78 °C. A 0.4 M solution of 3-

methoxy-1,1-dimethylpropyl magnesiumchloride (MODMP-MgCl, 3 ml, 1.13 mmol, 1 eq.) was added dropwise. The solution turned black and was stirred for 16 h while warming to room temperature. Afterwards, the solvent was removed, and the residue extracted with pentane (20 ml). The mixture was filtered, and the solvent was removed to yield a yellow oil. ^1H NMR (500 MHz, THF- d_8): δ 7.8 (m, Ph-H, 4H), 7.3 (m, Ph-H, 4H), 7.2 (m, Ph-H, 2H), 3.5 (t, $\text{CH}_2\text{-OCH}_3$, 2H), 3.3 (s, OCH_3 , 3H), 2.3 (t, $\text{CH}_2\text{-CH}_2\text{-OCH}_3$, 2H), 1.9 (t, $\text{Sn-C-(CH}_3)_2$, 6H) ppm.

[0203] Example 21: Deposition of bismuth-containing films using Methylbismuth diacetate. Bismuth-containing films were deposited on silicon wafers using the process conditions shown in Table 22. The process sequence cycles consist of pulses of Bi precursor/purge/coreactant/purge (pulse times in seconds). Film thicknesses are shown as measured by ellipsometry and XRF for the same film samples. The results show that Bi-containing films are deposited using both ozone and water as coreactants. Using ozone, a combination of higher substrate temperature and chamber pressure gave thicker films. Increasing the ampule temperature resulted in thicker films using ozone as the coreactant. Bismuth-containing films were grown under a variety of process conditions using water as a coreactant.

Ampule temp. (°C)	Co-reactant	Substrate temp. (°C)	Pressure (Torr)	Bubbler flow rate (sccm)	Process Sequence (secs)	Thickness (ellipsometry /XRF)
110	Ozone	130	2	50	100 cycles of 5/2/2.5/30	22 / 15 Å
		130			100 cycles of 10/2/2.5/30	21 / 14 Å
		200			100 cycles of 5/2/2.5/30	24 / 20 Å
		200	25			32 / 26 Å
118	Ozone	200	25	50	100 cycles of 5/2/2.5/30	34 / 31 Å
					100 cycles of 25/2/2.5/30	65 / 81 Å
					300 cycles of 25/2/2.5/30	NA / 646 Å
118	Water	200	25	50	10 loops of 25/1/2.5/2, then 30 sec purge. Repeat 10 times.	58 / 68 Å
			2			56 / 67 Å
			10			87 / 109 Å
		130	10			58 / 55 Å

Table 22

[0204] Additional experiments were conducted using molecular oxygen as a coreactant.

The resulting film characterization showed that no films were formed with oxygen under thermal conditions (no plasma), however, films were deposited using oxygen plasma (Table 23).

Temp. (°C)	Plasma Power (W)	Sequence (secs.)	Pressure (T)	# of Cycles	Film Thickness (Å)
130	100	5/2/5/2	2	100	95
130	25	5/2/5/2	2	100	84
130	0	5/2/5/2	2	100	0
130	25	5/2/5/2	2	240	262

Table 23

[0205] Example 22: Etching of bismuth-containing films with acetic acid. Bismuth-containing films were deposited using methyldiphenylbismuth and ozone. These films are primarily bismuth oxide with low levels of carbon (<5 at. %). Upon exposure of these films to acetic acid at a substrate temperature of 200 °C, the acetic acid was observed to etch the bismuth oxide films at an etch rate of 0.25 Å/cycle (Acetic Acid/Ar; 1s/2s; 2T; 50 sccm Acetic Acid). Additional films were prepared with methylbismuth diacetate and water under conditions described in Example 21. These films were etched with acetic acid at 200 °C as shown in Table 24.

Etchant	Etch Time	XRF Thickness (pre-etch)	XRF Thickness (post-etch)	Etch Rate (XRF)
Acetic Acid	3.33 min	306	109	0.985 Å/cycle
		111	21	0.45 Å /cycle
	1.67 min	89	14	0.8 Å /cycle
		339	238	1.0 Å /cycle

Table 24

[0206] Example 23: Spin coating and E-beam exposure experiments. Solutions of methylbismuth diacetate were formulated in cyclohexanone (20 g/l concentration). The formulations were spin coated on Si wafers (800-4000 rpm), that were previously treated with oxygen plasma (400 W, 10 min). After a bake of 60 °C for 120 seconds, the wafers were exposed to E-beam radiation (30 keV) with dose levels from 10 to 5000 $\mu\text{C}/\text{cm}^2$. After exposure, the wafers were heated at 60 °C for 120 seconds. The wafers were then developed with 2-heptanone for 120 seconds at room temperature. Afterwards, the wafers were rinsed with water and dried under nitrogen. The unexposed films had a thickness of ~30 nm which was determined by profilometry. The developed structures were also determined via profilometry. The peak height vs. dose were translated into fitted dose level curves with D_{50} values between 500-5000 $\mu\text{C}/\text{cm}^2$. Profilometry shows that the developed wafers show sensitivity to the E-beam radiation (FIG. 7). Each line was exposed to the following doses

[from top (darkest spot, thickest film) to bottom (lightest spot, thinnest film)] in $\mu\text{C}/\text{cm}^2$: 5000, 4000, 3000, 2500, 2000, 1500, 1250, 1000, 950, 900, 850, 800, 750, 700, 600, 550 and 500.

[0207] Comparative Example 1: Attempted reaction of Tri(neo-pentyl)bismuth with glacial acetic acid. In a high-pressure NMR tube was placed a ~1:3 stoichiometric mixture of tri(neo-pentyl)bismuth and glacial acetic acid in d8-toluene. NMR analysis showed no reaction at room temperature after 2 hours. The tube was heated to 90 °C for 4 hours and analyzed by NMR, showing only unreacted tri(neo-pentyl)bismuth and glacial acetic acid. The tube was then heated to 150 °C for 4 hours and again analyzed by NMR, showing only unreacted tri(neo-pentyl)bismuth and glacial acetic acid.

[0208] Comparative Example 2: Film deposition experiments using Di-neopentylphenylbismuth. Bismuth-containing films were deposited on silicon oxide wafers and zirconium oxide wafers using the cyclic process conditions shown in Table 25. The pulse sequence cycles consist of pulses of Bi precursor/purge/coreactant/purge (pulse times in seconds). Film thicknesses are shown as measured by XRF. The results show that Bi-containing films are not deposited with water using di-neopentylphenylbismuth, unlike the deposition results observed for Methylbismuth diacetate where Bi-containing films were deposited under similar process conditions using water as a coreactant. The absence of film formation with acetic acid as a co-reactant may be indicative of simultaneous deposition and etching.

Reactant	T (°C)	Pulse Sequence (sec.)	Pulse No.	Pressure (T)	Film Thickness (Å)	
					SiO ₂	ZrO ₂
O ₂ thermal	200	5/2/5/2	100	2	2.0	1.3
O ₂ thermal	200	5/2/5/2	500	2	1.8	1.3
O ₂ plasma, 10 W	130	5/2/5/2	100	2	212.8	261.6
O ₂ plasma, 200 W	130	5/2/5/2	100	2	224.2	238.5
Water	130	5/2/5/2	200	2	1.1	1.4
Water	200	5/2/5/2	200	2	0.7	1.0
Ozone	130	5/2/5/2	200	2	244.6	237.5
Ozone	200	5/2/5/2	200	2	492.8	547.8
Acetic acid	130	5/2/1/2	200	2	1.5	1.7
Acetic acid	200	5/2/1/2	200	2	2.4	0.8
Acetic acid	300	5/2/1/2	200	2	2	0.6

Table 25

[0209] Although the disclosed and claimed subject matter has been described and illustrated with a certain degree of particularity, it is to be 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 disclosed and claimed subject matter.

Claims

What is claimed is:

1. A method of depositing a bismuth-containing film or an antimony-containing film on a substrate in a reactor comprising the steps of:
 - (a) providing the substrate to the reactor;
 - (b) contacting the substrate with one or more contacting the substrate with one or more bismuth-containing compounds or antimony-containing compound and one or more coreactant; and
 - (c) forming a bismuth-containing film or an antimony-containing film on the substrate.
2. A method of depositing a bismuth-containing film or an antimony-containing film on a substrate in a reactor comprising the steps of:
 - (a) providing the substrate to the reactor;
 - (b) performing a pre-treatment to remove contaminates from surface of the substrate;
 - (c) contacting the substrate with one or more contacting the substrate with one or more bismuth-containing compounds or antimony-containing compound and one or more coreactant; and
 - (d) forming a bismuth-containing film or an antimony-containing film on the substrate.
3. A method of depositing a bismuth-containing film or an antimony-containing film on a substrate in a reactor comprising the steps of:
 - (a) providing the substrate to the reactor;
 - (b) contacting the substrate with one or more contacting the substrate with one or more bismuth-containing compounds or antimony-containing compound and one or more coreactant;
 - (c) exposing the substrate, the one or more bismuth-containing compounds or antimony-containing compound and the one or more coreactant to a plasma; and
 - (d) forming a bismuth-containing film or an antimony-containing film on the substrate.
4. A method of depositing a bismuth-containing film or an antimony-containing film on a substrate in a reactor comprising the steps of:
 - (a) providing the substrate to the reactor;
 - (b) contacting the substrate with one or more contacting the substrate with

- one or more bismuth-containing compounds or antimony-containing compound and one or more coreactant; and
- (c) forming a bismuth-containing film or an antimony-containing film on the substrate.
 - (d) exposing a portion of the film to extreme ultraviolet light (EUV)
 - (e) removal of a portion of the film.
5. A formulation comprising one or more bismuth-containing compounds or antimony-containing compound.
6. A formulation comprising (i) one or more bismuth-containing compounds or antimony-containing compound and (ii) at least one solvent.
7. A deposition process comprising exposing a film formed from one or more bismuth-containing compounds or antimony-containing compound or a formulation thereof to extreme ultraviolet light (EUV).
8. A deposition process comprising exposing a film formed from one or more bismuth-containing compounds or antimony-containing compound or a formulation thereof to extreme ultraviolet light (EUV), wherein the film is deposited on a substrate by a spin-on process.
9. A deposition process comprising exposing a film formed one or more bismuth-containing compounds or antimony-containing compound or a formulation thereof to extreme ultraviolet light (EUV), wherein the film is deposited on a substrate by a vapor deposition process.
10. A deposition process comprising exposing a film formed from one or more bismuth-containing compounds or antimony-containing compound or a formulation thereof to extreme ultraviolet light (EUV), wherein the film is deposited on a substrate by a vapor deposition process selected from the group of CVD, CCVD and ALD.
11. A radiated film resulting from exposing a film formed from one or more bismuth-containing compounds or antimony-containing compound or a formulation thereof to extreme ultraviolet light (EUV).
12. A process for forming polymers or nanocluster comprising reacting one or more bismuth-containing compounds or antimony-containing compound or a formulation thereof with one or more co-reactants.
13. A polymer formed by reacting one or more bismuth-containing compounds or antimony-containing compound or a formulation thereof with one or more co-reactants.
14. A nanocluster formed by reacting one or more bismuth-containing compounds or antimony-containing compound or a formulation thereof with one or more co-reactants.
15. A process for forming a functionalized nanocluster comprising (i) reacting one or more

bismuth-containing compounds or antimony-containing compound or a formulation thereof with one or more co-reactants to form a non-functionalized nanocluster and (ii) functionalizing the non-functionalized nanocluster.

16. A functionalized nanocluster formed from one or more bismuth-containing compounds or antimony-containing compound or a formulation thereof.

17. A process for forming a functionalized nanocluster comprising (i) reacting one or more bismuth-containing or antimony-containing compounds or a formulation thereof with one or more co-reactants to form a non-functionalized nanocluster and (ii) functionalizing the non-functionalized nanocluster.

18. A process for forming a functionalized nanocluster comprising (i) reacting one or more bismuth-containing compounds or antimony-containing compound or a formulation thereof with one or more co-reactants to form a non-functionalized nanocluster and (ii) functionalizing the non-functionalized nanocluster with at least one group comprising at least one least one unsaturated bond.

19. The method, formulation, film, polymer, nanocluster or process of any of claims 1-18 comprising, consisting essentially of or consisting of bismuth compounds of the formula $\text{Bi}(\text{R}^a)_x(\text{Ar})_{3-x}$ wherein

(i) $x = 1$ or 2 ;

(ii) each R^a is independently one of an unsubstituted linear $\text{C}_1\text{-C}_6$ alkyl group, a linear $\text{C}_1\text{-C}_6$ alkyl group substituted with one or more halogen, a linear $\text{C}_1\text{-C}_6$ alkyl group substituted with an amino group, a linear $\text{C}_3\text{-C}_6$ alkyl group substituted with an alkoxy group, an unsubstituted branched $\text{C}_3\text{-C}_6$ alkyl group, a branched $\text{C}_3\text{-C}_6$ alkyl group substituted with one or more halogen, a branched $\text{C}_3\text{-C}_6$ alkyl group substituted with an amino group, a branched $\text{C}_3\text{-C}_6$ alkyl group substituted with an alkoxy group, an unsubstituted amine, a substituted amine, $-\text{Si}(\text{CH}_3)_3$, an unsubstituted cyclic $\text{C}_3\text{-C}_6$ alkyl group, a cyclic $\text{C}_3\text{-C}_6$ alkyl group substituted with one or more halogen, a cyclic $\text{C}_3\text{-C}_6$ alkyl group substituted with an amino group, an alkoxy group, a carboxylate group, an amino group, a diketone group, a ketoesterate group, an amidate group and an amidinate group; and

(iii) each Ar is independently one of a $\text{C}_3\text{-C}_8$ unsubstituted aromatic group, a $\text{C}_3\text{-C}_8$ aromatic group substituted with one or more halogen, a $\text{C}_3\text{-C}_8$ aromatic group substituted with an amino group, a 5-member heterocyclic ring and a 6-member heterocyclic ring.

20. The method, formulation, film, polymer, nanocluster or process of claim 19, wherein $X = 1$.

21. The method, formulation, film, polymer, nanocluster or process of claim 19, wherein X = 2.

22. The method, formulation, film, polymer, nanocluster or process of claim 19, wherein each R^a is independently one of:

Linear Alkyl	Secondary Alkyl	Tertiary Alkyl
Methyl	Iso-propyl	Tert-butyl
Ethyl	Iso-butyl	Tert-pentyl
Propyl	Iso-pentyl	Allyl
n-Butyl	Sec-butyl	2-Methylallyl
n-pentyl	Sec-pentyl	Isopropenyl

23. The method, formulation, film, polymer, nanocluster or process of claim 19, wherein each R^a is independently one of:

Secondary Alkoxy	Tertiary Alkoxy
Isopropoxy	Tert-butoxy
Sec-butoxy	Tert-pentoxy
--	1-Methoxy-2-methyl-2-propoxy
--	2,3-Dimethyl-2-butoxy

24. The method, formulation, film, polymer, nanocluster or process of claim 19, wherein each R^a is independently one of:

Carboxylate Group
Acetate
Trifluoroacetate
Pivalate
Formate
Propionate
Valerate
Butyrate
Iso-butyrate
2-Methylbutyrate
3-Methylbutyrate
Chloroacetate
Cyclobutanecarboxylate
Cyclopentanecarboxylate
Cyclohexanecarboxylate
Tetrahydro-3-furancarboxylate

Fluoroacetate
Chloroacetate
Trichloroacetate
Acrylate
Methacrylate
Salicylate

25. The method, formulation, film, polymer, nanocluster or process of claim 19, wherein each R^a is independently one of:

Carboxylate Group
Acetate
Trifluoroacetate
Pivalate

26. The method, formulation, film, polymer, nanocluster or process of claim 19, wherein each R^a is independently one of:

Amino Group
Dimethylamino
Ethylmethylamino
Diethylamino
Isopropylmethylamino
Diisopropylamino
Isopropyl-tert-butylamino
Di-tert-butylamino
Bis(trimethylsilyl)amino

27. The method, formulation, film, polymer, nanocluster or process of claim 19, wherein each R^a is independently one of:

Amidinate Group
N,N'-di-isopropylformamidinate
N,N'-di-isopropylacetamidinate
N,N'-di-ethylformamidinate
N,N'-di-ethylacetamidinate
N,N'-di-tert-butylformamidinate
N,N'-di-tert-butylacetamidinate
N-ethyl-N'-tert-butyl-formamidinate

N-ethyl-N'-tert-butyl-acetamidinate

28. The method, formulation, film, polymer, nanocluster or process of claim 19, wherein each R^a is independently one of:

Amidate/Guanidinate Group
N-tert-butylacetamidate
N-tert-butyl(tert-butyl)amidate
1,3,4,6,7,8-Hexahydro-2H-pyrimido[1,2-a]pyrimidine
N,N'-diisopropylacetaminidate
N,N'-diisopropyl-N'',N''-dimethylguanidinate

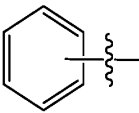
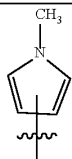
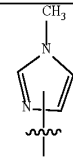
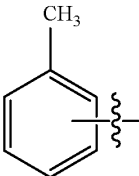
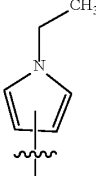
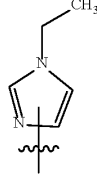
29. The method, formulation, film, polymer, nanocluster or process of claim 19, wherein each R^a is independently one of:

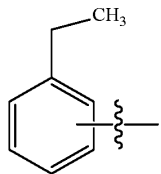
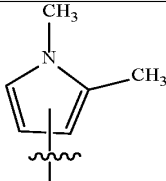
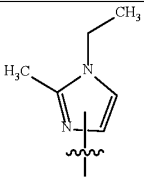
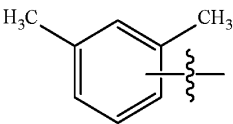
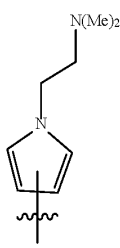
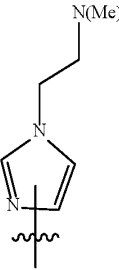
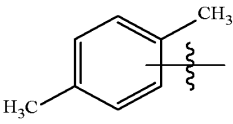
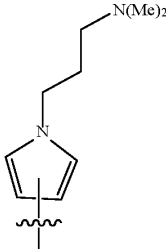
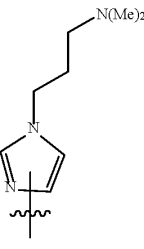
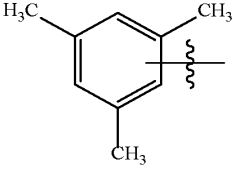
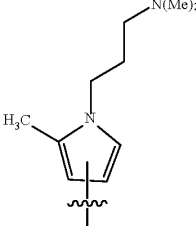
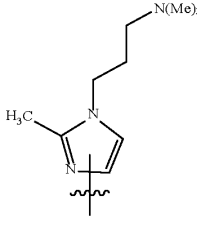
Diketonate Group
Acetylacetonate
2,2,6,6-Tetramethyl-3,5-heptanedionate
Hexafluoroacetylacetonate

30. The method, formulation, film, polymer, nanocluster or process of claim 19, wherein each R^a is independently one of:

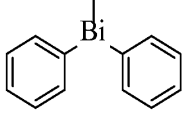
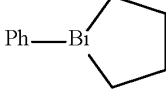
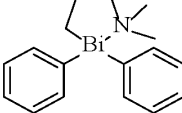
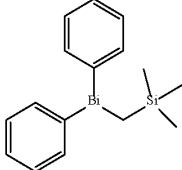
Ketoesterate Group
Methyl 4,4-dimethyl-3-oxopentanoate
Ethyl 4,4-dimethyl-3-oxopentanoate
Tert-butyl 4,4-dimethyl-3-oxopentanoate

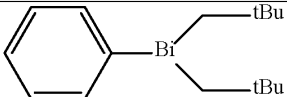
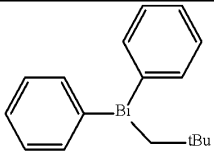
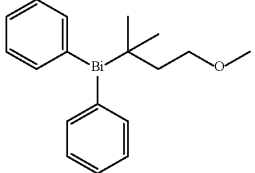
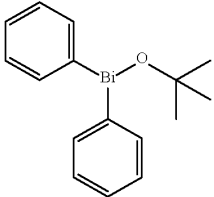
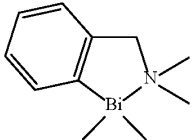
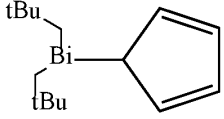
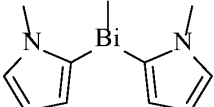
31. The method, formulation, film, polymer, nanocluster or process of claim 19, wherein each Ar is independently one of:

Aryl - Ar ¹	Pyrrolyl - Ar ²	Imidazolyl - Ar ³
		
		

32. The method, formulation, film, polymer, nanocluster or process of claim 19, wherein the compound is one of:

Structure	Compound
	Methylbisdiphenylbismuth
	1-Phenylbismolane
	1-Diphenylbismuthine-3-(dimethylamino)propane
	Trimethylsilylmethylene diphenylbismuth

	Di-neopentyl phenylbismuth
	Neopentyldiphenylbismuth
	(3-Methoxy-1,1-dimethylpropyl)diphenylbismuth
	Diphenylbismuth tert-butoxide
	Bis(2-N-methylpyrrollylino)methylbismuth
	Cyclopentadienylbis(neopentyl)bismuth
	Bis(2-N-methylpyrrollylino)methylbismuth

33. The method, formulation, film, polymer, nanocluster or process of any of claims 1-18 comprising, consisting essentially of or consisting of bismuth compounds of the formula $\text{Bi}(\text{R}^a)_x(\text{L})_{3-x}$ wherein

- (i) $x = 1$ or 2 ;
- (ii) each R^a is independently one of an unsubstituted linear $\text{C}_1\text{-C}_6$ alkyl group, a linear $\text{C}_1\text{-C}_6$ alkyl group substituted with one or more halogen, a linear $\text{C}_1\text{-C}_6$ alkyl group substituted with an amino group, a linear $\text{C}_3\text{-C}_6$ alkyl group substituted with an alkoxy group, an unsubstituted branched $\text{C}_3\text{-C}_6$ alkyl group, a branched $\text{C}_3\text{-C}_6$ alkyl group substituted with one or more halogen, a branched $\text{C}_3\text{-C}_6$ alkyl group substituted with an amino group, a branched $\text{C}_3\text{-C}_6$ alkyl group substituted with an alkoxy group, $-\text{Si}(\text{CH}_3)_3$, an unsubstituted cyclic $\text{C}_3\text{-C}_6$ alkyl group, a cyclic $\text{C}_3\text{-C}_6$ alkyl group substituted with one or more halogen and a cyclic $\text{C}_3\text{-C}_6$

alkyl group substituted with an amino group; and

(iii) each L is independently one of an alkoxy group, a carboxylate group, an amino group, a diketone group, a ketoesterate group and an amidate group.

34. The method, formulation, film, polymer, nanocluster or process of claim 33, wherein X = 1.

35. The method, formulation, film, polymer, nanocluster or process of claim 33, wherein X = 2.

36. The method, formulation, film, polymer, nanocluster or process of claim 33, wherein each L is independently one of:

Secondary Alkoxy	Tertiary Alkoxy
Isopropoxy	Tert-butoxy
Sec-butoxy	Tert-pentoxy
--	1-Methoxy-2-methyl-2-propoxy
--	2,3-Dimethyl-2-butoxide

37. The method, formulation, film, polymer, nanocluster or process of claim 33, wherein each L is independently one of:

Carboxylate Group
Acetate
Trifluoroacetate
Pivalate
Formate
Propionate
Valerate
Butyrate
Iso-butyrate
2-Methylbutyrate
3-Methylbutyrate
Chloroacetate
Cyclobutanecarboxylate
Cyclopentanecarboxylate
Cyclohexanecarboxylate
Tetrahydro-3-furancarboxylate
Fluoroacetate
Chloroacetate
Trichloroacetate

Acrylate
Methacrylate
Salicylate

38. The method, formulation, film, polymer, nanocluster or process of claim 33, wherein each L is independently one of:

Carboxylate Group
Acetate
Trifluoroacetate
Pivalate

39. The method, formulation, film, polymer, nanocluster or process of claim 33, wherein each L is independently one of:

Amino Group
Dimethylamino
Ethylmethylamino
Diethylamino
Isopropylmethylamino
Diisopropylamino
Isopropyl-tert-butylamino
Di-tert-butylamino
Bis(trimethylsilyl)amino

40. The method, formulation, film, polymer, nanocluster or process of claim 33, wherein each L is independently one of:

Amidinate Group
N,N'-di-isopropylformamidinate
N,N'-di-isopropylacetamidinate
N,N'-di-ethylformamidinate
N,N'-di-ethylacetamidinate
N,N'-di-tert-butylformamidinate
N,N'-di-tert-butylacetamidinate
N-ethyl-N'-tert-butyl-formamidinate
N-ethyl-N'-tert-butyl-acetamidinate

41. The method, formulation, film, polymer, nanocluster or process of claim 33, wherein each L is independently one of:

Amidate/Guanidinate Group
N-tert-butylacetamidate
N-tert-butyl(tert-butyl)amidate
1,3,4,6,7,8-Hexahydro-2H-pyrimido[1,2-a]pyrimidine
N,N'-diisopropylacetaminidate
N,N'-diisopropyl-N'',N''-dimethylguanidinate

42. The method, formulation, film, polymer, nanocluster or process of claim 33, wherein each L is independently one of:

Diketonate Group
Acetylacetonate
2,2,6,6-Tetramethyl-3,5-heptanedionate
Hexafluoroacetylacetonate

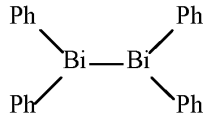
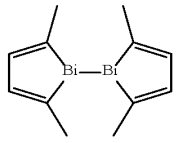
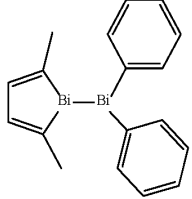
43. The method, formulation, film, polymer, nanocluster or process of claim 33, wherein each L is independently one of:

Ketoesterate Group
Methyl 4,4-dimethyl-3-oxopentanoate
Ethyl 4,4-dimethyl-3-oxopentanoate
Tert-butyl 4,4-dimethyl-3-oxopentanoate

44. The method, formulation, film, polymer, nanocluster or process of any of claims 1-18 comprising, consisting essentially of or consisting of bismuth compounds of the formula $(R^a)_2Bi-Bi(R^b)_2$ wherein each of R^a and R^b is independently one of an unsubstituted linear C_1 - C_6 alkyl group, a linear C_1 - C_6 alkyl group substituted with one or more halogen, a linear C_1 - C_6 alkyl group substituted with an amino group, a linear C_3 - C_6 alkyl group substituted with an alkoxy group, an unsubstituted branched C_3 - C_6 alkyl group, a branched C_3 - C_6 alkyl group substituted with one or more halogen, a branched C_3 - C_6 alkyl group substituted with an amino group, a branched C_3 - C_6 alkyl group substituted with an alkoxy group, an unsubstituted amine, a substituted amine, - $Si(CH_3)_3$, an unsubstituted cyclic C_3 - C_6 alkyl group, a cyclic C_3 - C_6 alkyl group substituted with one or more halogen, a cyclic C_3 - C_6 alkyl group substituted with an amino group, a C_3 - C_8 unsubstituted aromatic group, a C_3 - C_8 aromatic group substituted with one or more halogen, a C_3 -

C₈ aromatic group substituted with an amino group, a 5-member heterocyclic ring and a 6-member heterocyclic ring.

45. The method, formulation, film, polymer, nanocluster or process of claim 44, wherein the compound is one of:

Structure	Compound
	Tetraphenyldibismuthine
	Tetramethylbibismole
	(Diphenylbismuthino)dimethylbismole

46. The method, formulation, film, polymer, nanocluster or process of any of claims 1-18 comprising, consisting essentially of or consisting of compounds of the formula $M(R^a)_x(R^b)_{3-x}$ or $(R^a)_2M-M(R^b)_2$ wherein

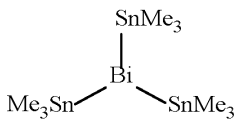
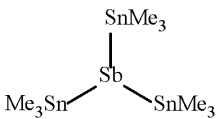
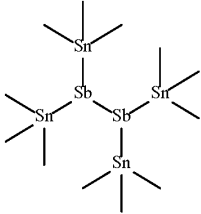
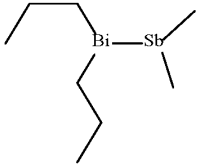
(iii) M is independently Sb or Bi;

(iv) X = 0, 1 or 2; and

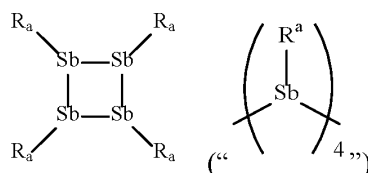
(iii) each R^a and R^b is independently one of an unsubstituted linear C₁-C₆ alkyl group, a linear C₁-C₆ alkyl group substituted with one or more halogen, a linear C₁-C₆ alkyl group substituted with an amino group, a linear C₃-C₆ alkyl group substituted with an alkoxy group, an unsubstituted branched C₃-C₆ alkyl group, a branched C₃-C₆ alkyl group substituted with one or more halogen, a branched C₃-C₆ alkyl group substituted with an amino group, a branched C₃-C₆ alkyl group substituted with an alkoxy group, an unsubstituted amine, a substituted amine, -Si(CH₃)₃, an unsubstituted cyclic C₃-C₆ alkyl group, a cyclic C₃-C₆ alkyl group substituted with one or more halogen, a cyclic C₃-C₆ alkyl group substituted with an amino group, a C₃-C₈ unsubstituted aromatic group, a C₃-C₈ aromatic group substituted with one or more halogen, a C₃-C₈ aromatic group substituted with an amino group, a 5-member heterocyclic ring, a 6-member heterocyclic ring, a trialkylstannyl group where the alkyl is a linear C₁-

C₆ alkyl group, a trialkylstannyl group where the alkyl is a branched C₃-C₆ alkyl group and a trialkylstannyl group where the alkyl is a cyclic C₃-C₆ alkyl group.

47. The method, formulation, film, polymer, nanocluster or process of claim 46, wherein M is Sb.
48. The method, formulation, film, polymer, nanocluster or process of claim 46, wherein M is Bi.
49. The method, formulation, film, polymer, nanocluster or process of claim 46, wherein X = 0.
50. The method, formulation, film, polymer, nanocluster or process of claim 46, wherein X = 1.
51. The method, formulation, film, polymer, nanocluster or process of claim 46, wherein X = 2.
52. The method, formulation, film, polymer, nanocluster or process of claim 46, wherein the compound is one of:

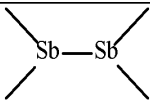
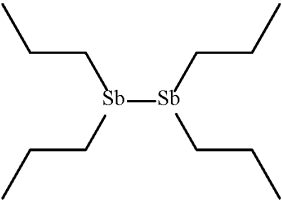
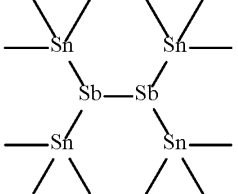
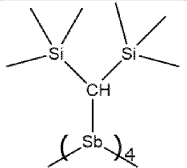
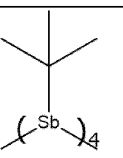
Structure	Compound
	Tris(trimethylstannyl)bismuth
	Tris(trimethylstannyl)antimony
	Tetrakis(trimethylstannyl)distibane
	(Dipropylbismuthino)dimethylstibane

53. The method, formulation, film, polymer, nanocluster or process of any of claims 1-18 comprising, consisting essentially of or consisting of antimony compounds of the formula (R^a)₂Sb-Sb(R^b)₂ or cyclotetrastibane



wherein each R^a and R^b is independently one of an unsubstituted linear C₁-C₆ alkyl group, a linear C₁-C₆ alkyl group substituted with one or more halogen, a linear C₁-C₆ alkyl group substituted with an amino group, a linear C₃-C₆ alkyl group substituted with an alkoxy group, an unsubstituted branched C₃-C₆ alkyl group, a branched C₃-C₆ alkyl group substituted with one or more halogen, a branched C₃-C₆ alkyl group substituted with an amino group, a branched C₃-C₆ alkyl group substituted with an alkoxy group, an unsubstituted amine, a substituted amine, -Si(CH₃)₃, an unsubstituted cyclic C₃-C₆ alkyl group, a cyclic C₃-C₆ alkyl group substituted with one or more halogen, a cyclic C₃-C₆ alkyl group substituted with an amino group, a C₃-C₈ unsubstituted aromatic group, a C₃-C₈ aromatic group substituted with one or more halogen, a C₃-C₈ aromatic group substituted with an amino group, a 5-member heterocyclic ring and a 6-member heterocyclic ring.

54. The method, formulation, film, polymer, nanocluster or process of claim 53, wherein the compound is one of:

Structure	Compound
	Tetramethyldistibine
	Tetrapropyldistibine
	Tetrakis(trimethylstannyl)distibine
	Tetrakis[bis(trimethylsilyl)methyl]cyclotetrasiloxane
	Tetra-tert-butylcyclotetrasiloxane

55. The method, formulation, film, polymer, nanocluster or process of any of claims 1-18

comprising, consisting essentially of or consisting of compounds of the formulas $M(R^a)_x(R^b)_{3-x}$ or $(R^a)_2M-M(R^b)_2$ wherein

- (i) M is independently Sb or Bi;
- (ii) $X = 0, 1$ or 2 ;
- (iii) each R^a and R^b is independently one of a linear C_1 - C_6 alkyl group, a unsaturated linear C_1 - C_6 alkyl group substituted with one or more halogen, a unsaturated linear C_1 - C_6 alkyl group substituted with an amino group, an unsaturated branched C_3 - C_6 alkyl group, a unsaturated branched C_3 - C_6 alkyl group substituted with one or more halogen, a unsaturated branched C_3 - C_6 alkyl group substituted with an amino group, an unsubstituted amine, a substituted amine, $-\text{Si}(\text{CH}_3)_3$, an unsaturated cyclic C_3 - C_6 alkyl group, a unsaturated cyclic C_3 - C_6 alkyl group substituted with one or more halogen, a unsaturated cyclic C_3 - C_6 alkyl group substituted with an amino group, a 6-member aromatic ring, an aromatic with a C_2 - C_6 unsaturated alkyl group, a 5-member heterocyclic ring and a 6-member heterocyclic ring; and
- (iv) the compounds include at least one an unsaturated group.

56. The method, formulation, film, polymer, nanocluster or process of claim 55, wherein M is Sb.

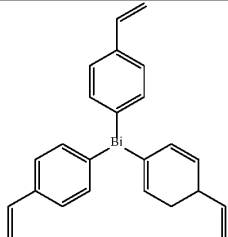
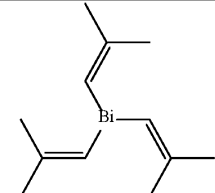
57. The method, formulation, film, polymer, nanocluster or process of claim 55, wherein M is Bi.

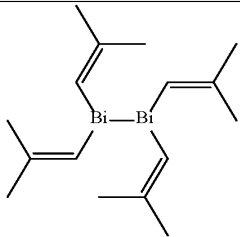
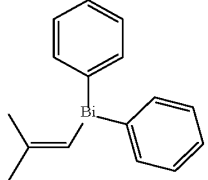
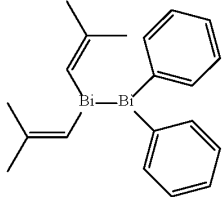
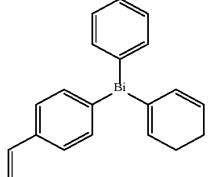
58. The method, formulation, film, polymer, nanocluster or process of claim 55, wherein $X = 0$.

59. The method, formulation, film, polymer, nanocluster or process of claim 55, wherein $X = 1$.

60. The method, formulation, film, polymer, nanocluster or process of claim 55, wherein $X = 2$.

61. The method, formulation, film, polymer, nanocluster or process of claim 55, wherein the compound is one of:

Structure	Compound
	Tri(p-styrene)bismuth
	Tri(propenyl)bismuthine

	Tetrakis(propenyl) dibismuthine
	Diphenylpropenyl bismuthine
	(Diphenylbismuthino) dipropenylbismuthine
	Diphenylstyrenyl bismuth

62. Bismuth compounds of the formula $\text{Bi}(\text{R}^a)_x(\text{L})_{3-x}$ wherein

(i) $x = 1$ or 2 ;

(ii) each R^a is independently one of an unsubstituted linear $\text{C}_1\text{-C}_6$ alkyl group, a linear $\text{C}_1\text{-C}_6$ alkyl group substituted with one or more halogen, a linear $\text{C}_1\text{-C}_6$ alkyl group substituted with an amino group, a linear $\text{C}_3\text{-C}_6$ alkyl group substituted with an alkoxy group, an unsubstituted branched $\text{C}_3\text{-C}_6$ alkyl group, a branched $\text{C}_3\text{-C}_6$ alkyl group substituted with one or more halogen, a branched $\text{C}_3\text{-C}_6$ alkyl group substituted with an amino group, a branched $\text{C}_3\text{-C}_6$ alkyl group substituted with an alkoxy group, $-\text{Si}(\text{CH}_3)_3$, an unsubstituted cyclic $\text{C}_3\text{-C}_6$ alkyl group, a cyclic $\text{C}_3\text{-C}_6$ alkyl group substituted with one or more halogen and a cyclic $\text{C}_3\text{-C}_6$ alkyl group substituted with an amino group; and

(iii) each L is a carboxylate group; and

(iv) the compound where $x = 1$, R^a is $-\text{CH}_3$ and each L is acetate is excluded.

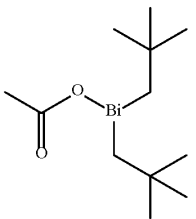
63. The compound of claim 62, wherein $x = 1$.

64. The compound of claim 62, wherein $x = 2$.

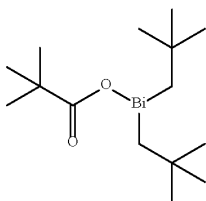
65. The compound of claim 62, wherein each L is independently one of acetate, formate,

pivalate, methacrylate and salicylate.

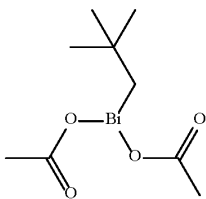
66. The compound of claim 62, wherein each L is independently one of formate, pivalate, methacrylate and salicylate.
67. The compound of claim 62, wherein each L is acetate.
68. The compound of claim 62, wherein each L is formate.
69. The compound of claim 62, wherein each L is pivalate.
70. The compound of claim 62, wherein each L is methacrylate.
71. The compound of claim 62, wherein each L is salicylate.
72. The compound of claim 62, wherein each L is the same.
73. The compound of claim 62, wherein each L is different from the other.
74. The compound of claim 62, wherein the compound of the formula $\text{Bi}(\text{R}^a)_x(\text{L})_{3-x}$ is:



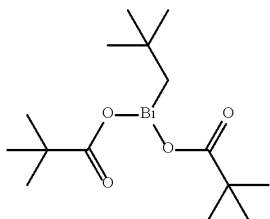
75. The compound of claim 62, wherein the compound of the formula $\text{Bi}(\text{R}^a)_x(\text{L})_{3-x}$ is:



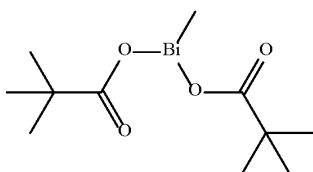
76. The compound of claim 62, wherein the compound of the formula $\text{Bi}(\text{R}^a)_x(\text{L})_{3-x}$ is:



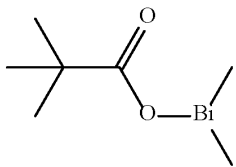
77. The compound of claim 62, wherein compound of the formula $\text{Bi}(\text{R}^a)_x(\text{L})_{3-x}$ is:



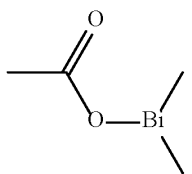
78. The compound of claim 62, wherein the compound of the formula $\text{Bi}(\text{R}^a)_x(\text{L})_{3-x}$ is:



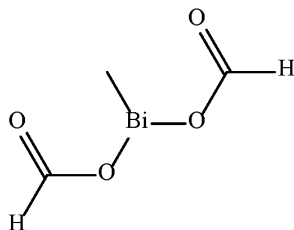
79. The compound of claim 62, wherein the compound of the formula $\text{Bi}(\text{R}^a)_x(\text{L})_{3-x}$ is:



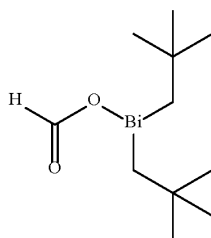
80. The compound of claim 62, wherein the compound of the formula $\text{Bi}(\text{R}^a)_x(\text{L})_{3-x}$ is:



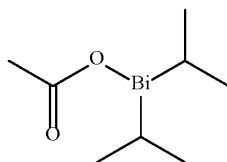
81. The compound of claim 62, wherein the compound of the formula $\text{Bi}(\text{R}^a)_x(\text{L})_{3-x}$ is:



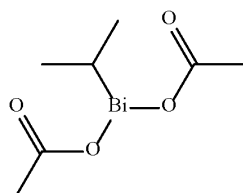
82. The compound of claim 62, wherein the compound of the formula $\text{Bi}(\text{R}^a)_x(\text{L})_{3-x}$ is:



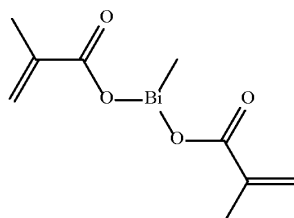
83. The compound of claim 62, wherein the compound of the formula $\text{Bi}(\text{R}^a)_x(\text{L})_{3-x}$ is:



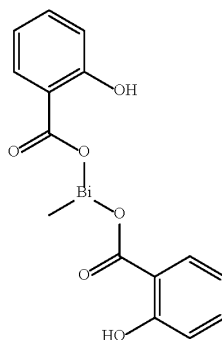
84. The compound of claim 62, wherein the compound of the formula $\text{Bi}(\text{R}^a)_x(\text{L})_{3-x}$ is:



85. The compound of claim 62, wherein the compound of the formula $\text{Bi}(\text{R}^a)_x(\text{L})_{3-x}$ is:



86. The compound of claim 62, wherein the compound of the formula $\text{Bi}(\text{R}^a)_x(\text{L})_{3-x}$ is:



87. Bismuth compounds of the formula $\text{Bi}(\text{R}^a)_x(\text{L})_{3-x}$ wherein

(i) $x = 1$ or 2 ;

(ii) each R^a is independently one of an unsubstituted linear C_1 - C_6 alkyl group, a linear C_1 - C_6 alkyl group substituted with one or more halogen, a linear C_1 - C_6 alkyl group substituted with an amino group, a linear C_3 - C_6 alkyl group substituted with an alkoxy group, an unsubstituted branched C_3 - C_6 alkyl group, a branched C_3 - C_6 alkyl group substituted with one or more halogen, a branched C_3 - C_6 alkyl group substituted with an amino group, a branched C_3 - C_6 alkyl group substituted with an alkoxy group, $-\text{Si}(\text{CH}_3)_3$, an unsubstituted cyclic C_3 - C_6 alkyl group, a cyclic C_3 - C_6 alkyl group substituted with one or more halogen and a cyclic C_3 - C_6 alkyl group substituted with an amino group; and

(iii) each L is an amidinate, formamidinate or guanidinate group.

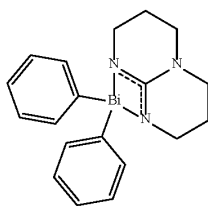
88. The compound of claim 87, wherein $x = 1$.

89. The compound of claim 87, wherein $x = 2$.

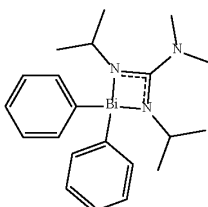
90. Bismuth compounds of the formula $\text{Bi}(\text{Ar})_x(\text{L})_{3-x}$ wherein

- (i) $x = 1$ or 2 ;
- (ii) each Ar is independently one of a C_3 - C_8 unsubstituted aromatic group, a C_3 - C_8 aromatic group substituted with one or more halogen, a C_3 - C_8 aromatic group substituted with an amino group, a 5-member heterocyclic ring and a 6-member heterocyclic ring; and
- (iii) each L is an amidinate, formamidinate, or guanidinate group.

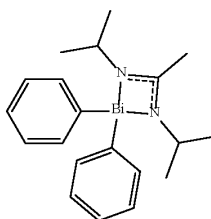
- 91. The compound of claim 90, wherein $x = 1$.
- 92. The compound of claim 90, wherein $x = 2$.
- 93. The compound of claim 90, wherein each L is an amidinate group.
- 94. The compound of claim 90, wherein each L is a formamidinate group.
- 95. The compound of claim 90, wherein each L is a guanidinate group.
- 96. The compound of claim 90, wherein each L each L is independently one of 1,3,4,6,7,8-Hexahydro-2H-pyrimido[1,2-a]pyrimidine, N,N'-diisopropyl-N'',N''-dimethylguanidinate and N,N'-diisopropylacetaminidate.
- 97. The compound of claim 90, wherein each L each L is 1,3,4,6,7,8-Hexahydro-2H-pyrimido[1,2-a]pyrimidine.
- 98. The compound of claim 90, wherein each L each L is N,N'-diisopropyl-N'',N''-dimethylguanidinate.
- 99. The compound of claim 90, wherein each L each L is N,N'-diisopropylacetaminidate.
- 100. The compound of claim 90, wherein each L is the same.
- 101. The compound of claim 90, wherein each L is different from the other.
- 102. The compound of claim 90, wherein the compound of the formula $Bi(Ar)_x(L)_{3-x}$ is:



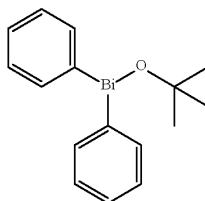
- 103. The compound of claim 90, wherein the compound of the formula $Bi(Ar)_x(L)_{3-x}$ is:



- 104. The compound of claim 90, wherein the compound of the formula $Bi(Ar)_x(L)_{3-x}$ is:



- 105.** Bismuth compounds of the formula $\text{Bi}(\text{Ar})_x(\text{L})_{3-x}$ wherein
- (i) $x = 1$ or 2 ;
 - (ii) each Ar is independently one of a $\text{C}_3\text{-C}_8$ unsubstituted aromatic group, a $\text{C}_3\text{-C}_8$ aromatic group substituted with one or more halogen, a $\text{C}_3\text{-C}_8$ aromatic group substituted with an amino group, a 5-member heterocyclic ring and a 6-member heterocyclic ring; and
 - (iii) each L is an alkoxide group.
- 106.** The compound of claim 105, wherein $x = 1$.
- 107.** The compound of claim 105, wherein $x = 2$.
- 108.** The compound of claim 105, wherein the compound of the formula $\text{Bi}(\text{Ar})_x(\text{L})_{3-x}$ is:



- 109.** The method, formulation, film, polymer, nanocluster or process of any of claims 1-18 comprising, consisting essentially of or consisting of the bismuth compounds of any of claims 62-108.