

VAPOR-PHASE THERMAL ETCH OF METAL OXIDES**BACKGROUND****[0001] Field**

[0002] The disclosed and claimed subject matter relates to vapor-phase processes for etching metal oxide films which do not require the use of plasmas or corrosive halogenating gases. The disclosed and claimed subject matter further includes a process for performing thermal selective vapor-phase etching of a thin layer of oxidized metal-containing material atop a metal. The disclosed and claimed subject matter further includes an atomic layer etch (ALE) process for etching metal oxide films that include ZrO_2 , HfO_2 , $(\text{Hf-Zr})\text{O}_2$ alloy or similar materials. The disclosed and claimed subject matter further includes a metal-insulator-metal capacitor (MIMcap) with unique properties enabled by the ALE process described herein.

[0003] Related Art

[0004] The miniaturization of features in the semiconductor industry is the main factor behind the continuous performance increase of devices. This trend is expected to continue for at least a few more generations of computer chips. In this regard, ultrathin ($< 5\text{nm}$) layers of high k dielectrics are needed for volatile and non-volatile memories, including DRAM, NAND Flash, and ferroelectric memories. Several technical challenges need to be successfully solved for this trend to continue. In the fabrication of microelectronic logic devices, highly selective etches are required to precisely remove one material or set of materials from a surface with many exposed materials, including metals, metal oxides, dielectric materials, and semiconductors.

[0005] The material to be etched may be a material with desirable properties which must be thinned or removed in certain areas. The material to be etched may also be an undesired byproduct of chemical treatment or air exposure, such as a native oxide on a metal surface. In such a case, the etch must selectively remove the undesired material while leaving intact the underlying desired material.

[0006] Atomic Layer Deposition (ALD) is one technique finding increased application in the semiconductor industry and it currently is the deposition method allowing the best control on the amount of material deposited. In ALD, a layer of atoms is deposited on *all* surfaces that are exposed to a precursor in the gas phase – this layer is at most as thick as the thickness of one atomic layer. By sequentially exposing the surfaces to two different precursors, a layer of material with the desired thickness will be deposited. The archetypical example of such a process is the deposition of aluminum oxide (Al_2O_3) from trimethylaluminum (TMA, $\text{Al}(\text{CH}_3)_3$) and water (H_2O), where methane (CH_4) is eliminated from the two reacting species. The coating of thin and narrow vias and other high aspect

ratio features by ALE have been demonstrated numerous times in the literature.

[0007] Atomic Layer Etching (ALE or ALEt) can be viewed as the layer-by-layer subtraction of material when ALD is the layer-by-layer addition of material. In ALE, a layer of atoms is removed from all surfaces that are exposed to a precursor in the gas phase – this layer is ideally also at most as thick as the thickness of one atomic layer. ALE is performed by sequentially exposing the surfaces to at least two different precursors, a 1st precursor that activates a layer of surface atoms and a 2nd precursor that promotes the sublimation of this activated layer of atoms; sometimes a 3rd precursor is used to regenerate the surface to the condition where the 1st precursor will be active. Several etching procedures have been described in which a metal is converted into a metal compound, followed by a volatilization step in which the metal compound is removed while the metal is not. *See, e.g., Zhao et al., Applied Surface Science*, 455, 438 (2018); Konh *et al., Journal of Vacuum Science & Technology A*, 37, 021004 (2019); Wang *et al., Journal of Vacuum Science & Technology A*, 38, 022611 (2020); and Kim *et al., Applied Surface Science*, 619, 156751 (2023). In one of these procedures, cobalt was etched at temperatures higher than 377 °C and exposing the cobalt surface (with a native oxide) to 1,1,1,5,5,5-hexafluoro-2,4,-pentanedione (Hhfac). The treated surface was then heated to produce sublimation of cobalt 1,1,1,5,5,5-hexafluoro-2,4,-pentanedionate. In a variant, cobalt was etched at temperatures higher than 140 °C by sequentially exposing the cobalt surface to:

- (A) chlorine which oxidizes a layer of cobalt into cobalt chloride (surface activation); and
- (B) an acetylacetone (such as 1,1,1,5,5,5-hexafluoro-2,4,-pentanedione (Hhfac)), which reacts with the cobalt chloride surface species to generate volatile cobalt chloro-acetylacetonate species (sublimation).

[0008] In another method, cobalt etching at temperatures higher than 80 °C was achieved with an etching rate was as high as 28 Å/cycle. *See, e.g., Chen et al., J. Vac. Sci. Technol., A* 35, 05C305 (2017). This process involved the sequential exposure of a cobalt surface to:

- (A) An oxygen plasma which oxidizes multiple layers of cobalt into cobalt oxide (surface activation); and
- (B) Formic acid, which react with the cobalt oxide surface species to generate volatile cobalt formate species (sublimation).

[0009] Another method reported etching copper at temperatures higher than 275 °C with an etch rate of 0.09 nm/cycle. *See, e.g., Mohimi et al., ECS Journal of Solid State Science and Technology*, 7, P491 (2018). This process involved the sequential exposure of a copper surface to:

- (A) oxygen which is a mild oxidizer and oxidizes a layer of copper into copper oxide (surface activation); and
- (B) an acetylacetone (such as 1,1,1,5,5,5-hexafluoro-2,4,-pentanedione (Hhfac), which reacts with the copper oxide surface species to generate volatile copper acetylacetonate species (sublimation).

[0010] Another method involved the etching of tungsten. *See, e.g.,* Johnson N. R. and George S. M., *ACS Applied Materials & Interfaces*, 9, 34435 (2017). In this process, tungsten could be etched (between 128 °C and 207 °C) by sequentially exposing a tungsten surface having a native oxide layer to:

- (A) A mixture of oxygen and ozone, which oxidizes an additional layer of tungsten into tungsten oxide (surface activation);
- (B) Boron trichloride, which reacts with some of the tungsten oxide to generate non-volatile boron oxide and volatile tungsten oxychloride (sublimation of tungsten-containing species; some tungsten oxide is still present below the boron oxide); and
- (C) Hydrogen fluoride, which reacts with the boron oxide to generate volatile water vapor, and volatile boron trifluoride (regeneration of fresh tungsten oxide surface).

[0011] Few-nanometer films of ZrO₂ and HfO₂ have different functional properties based on the thickness and crystal structure of the film. The high-k tetragonal crystal phase of ZrO₂, or the ferroelectric crystal phase of Hf_{0.5}Zr_{0.5}O₂, can only be stabilized above a certain minimum thickness of film, approx. 5 to 7 nm. If a thinner film than 5 to 7 nm is desired (*e.g.*, to maximize capacitance and/or reduce the device size), then a thicker film must first be grown and processed (*i.e.*, to crystallize the film), followed by the removal of some of the film material. Such a material removal method requires sub-nanometer precision, and the removal may need to be isotropic (*e.g.*, for conformally etching high aspect ratio features in 3D nano-architectures such as DRAM capacitors or 3D memory stacks). The best approach for this is isotropic ALE.

[0012] As noted above, isotropic ALE involves repeated cycles of dosing a reactant into a chamber, then purging the chamber to remove an excess of the reactant and any reaction products. In some implementations, there are two sequential dose-purge sub-cycles, each with a different reactant or combination of reactants. In some implementations, there are three or more sequential dose-purge sub-cycles, each with a different reactant or combination of reactants.

[0013] Some implementations of ZrO₂ ALE include cycling the following steps in a vacuum chamber tool, such as an atomic layer deposition (ALD) reactor: (1) dosing a first fluorinating agent

to convert surface ZrO_2 , which is a solid, into ZrF_4 , which is also a solid; (2) a first purge of the reactor; (3) dosing a second chlorinating agent to convert ZrF_4 , which is a solid, into ZrCl_4 , which is a gas, via a ligand-exchange reaction between ZrF_4 and the chlorinating agent; and (4) a second purge of the reactor. Optionally, (5) a surface modification step, and (6) a third purge, may be included in the cycle.

[0014] The fluorinating step (1) may use a metal-free fluorinating agent, such as anhydrous HF (aHF), XeF_2 , or SF_4 . See, e.g., J.A. Murdzek, S.M. George, “Effect of crystallinity on thermal atomic layer etching of hafnium oxide, zirconium oxide, and hafnium zirconium oxide”, *J. Vac. Sci. Technol. A*, 38, 022608 (2020). Alternatively, volatile metal fluorides, such as WF_6 , NbF_5 , TaF_5 , etc., may be used. See, e.g., U.S. Patent No. 10,283,319; U.S. Patent No. 10,273,584; P.C. Lemaire and G.N. Parsons, “Thermal Selective Vapor Etching of TiO_2 : Chemical Vapor Etching via WF_6 and Self-Limiting Atomic Layer Etching Using WF_6 and BCl_3 ” *Chem. Mater.*, 29, 6653-6665 (2017). The chlorination step (3) may use a volatile metal chloride, such as dimethylaluminum chloride (DMAC) or TiCl_4 . See, e.g., Y. Lee, C. Huffman, S.M. George, “Selectivity in thermal atomic layer etching using sequential, self-limiting fluorination and ligand-exchange reactions,” *Chem. Mater.*, 28, 7657-7665 (2016); J.A. Murdzek, S.M. George, “Effect of crystallinity on thermal atomic layer etching of hafnium oxide, zirconium oxide, and hafnium zirconium oxide”, *J. Vac. Sci. Technol. A*, 38, 022608 (2020).

[0015] Methods have been described for the thermal ALE of oxides, including ZrO_2 , HfO_2 , Al_2O_3 and TiO_2 . See, e.g., Y. Lee, C. Huffman, and S.M. George, *Chem. Mater.*, 28, 7657-7665 (2016); P.C. Lemaire and G.N. Parsons, *Chem. Mater.*, 29, 6653-6665 (2017); J.A. Murdzek and S.M. George, *J. Vac. Sci. Technol. A*, 38, 022608 (2020); H. Saare, *Ph. D. dissertation*, North Carolina State U., 2021. These methods typically involve two steps which are cycled: a fluoridation of the oxide surface in a first step, and a volatilization of the resulting surface fluoride in a second step. For the first step, fluoridating agents include hydrogen fluoride (HF), anhydrous hydrogen fluoride stabilized by pyridine (HF-pyridine), sulfur tetrafluoride (SF_4), sulfur hexafluoride (SF_6) remote plasma, tungsten hexafluoride (WF_6), or xenon difluoride (XeF_2). For the second step, volatilization agents include trimethylaluminum (TMA), dimethylaluminum chloride (DMAC), silicon tetrachloride (SiCl_4), or titanium tetrachloride (TiCl_4).

[0016] A method of thermal ALE of Al_2O_3 , ZrO_2 , HfZrO_4 , and HfO_2 was described by Lee *et al.* (Y. Lee, C. Huffman, and S.M. George, *Chem. Mater.*, 28, 7657-7665 (2016) and Murdzek and George (J.A. Murdzek and S.M. George, *J. Vac. Sci. Technol. A*, 38, 022608 (2020)).

[0017] In Lee, Huffman, and George, ALE testing was conducted at process temperatures ranging from 150 °C to 350 °C. These metal oxides were all effectively fluorinated using anhydrous

HF delivered from an ampule of HF-pyridine. Al_2O_3 could be etched by cycling doses of anhydrous HF and either tin(ii) acetylacetonate $\text{Sn}(\text{acac})_2$, trimethylaluminum (TMA), dimethylaluminum chloride (DMAC), or silicon tetrachloride (SiCl_4). ZrO_2 could be etched by cycling doses of anhydrous HF and either $\text{Sn}(\text{acac})_2$, DMAC, or SiCl_4 . HfO_2 could be etched by cycling doses of anhydrous HF and either $\text{Sn}(\text{acac})_2$, TMA, or DMAC.

[0018] In Murdzek and George, ALE testing was conducted at a process temperature of 250 °C. HF, SF_4 , and XeF_2 were used as fluorinating agents, and DMAC and TiCl_4 were used as ligand exchange agents. For all tested chemistries, crystalline ZrO_2 , HfZrO_4 , and HfO_2 etched at a lower rate than amorphous ZrO_2 , HfZrO_4 , and HfO_2 , respectively. XeF_2 was found to yield a much higher etch per cycle than HF or SF_4 .

[0019] A method of thermal ALE of TiO_2 and ZrO_2 was described by Lemaire and Parsons (P.C. Lemaire and G.N. Parsons, *Chem. Mater.*, 29, 6653-6665 (2017)) and Saare (H. Saare, *PhD dissertation*, North Carolina State U., 2021). In Lemaire and Parsons, ALE testing was conducted at process temperatures ranging from 120 °C to 220 °C. WF_6 was used as the fluorinating agent, and BCl_3 was used as the ligand-exchange agent. While the process yielded ALE of TiO_2 , residues of B or W remained on the surface. In Saare, ALE testing was conducted at process temperatures ranging from 160 °C to 325 °C. WF_6 was used as the fluorinating agent, and BCl_3 , TiCl_4 , and SOCl_2 were used as ligand-exchange agents. Each ALE process yielded ALE of TiO_2 and ZrO_2 .

[0020] Some chemicals used in the processes described above have drawbacks in practical use. Fluorinating gases such as aHF and SF_4 are toxic, corrosive, and require costly facilitization, with significant environmental health and safety concerns. Metal fluoride gases such as NbF_5 and metal chloride vapors such as TiCl_4 may leave undesirable residues on the surface of the work piece; these residues may be difficult to remove. As such, it may be desirable to use fluorinators and chlorinators which are metal-free and can be packaged in a condensed (liquid or solid) phase, *i.e.*, for easy adaptation onto an ALD, ALD-like, or ALE reactor, but which release a significant partial pressure (on the order of 1 – 100 Torr) of fluorinating or chlorinating chemical in the vapor phase. Examples of these from the art include HF-pyridine, thionyl chloride (SOCl_2), and sulfuryl chloride (SO_2Cl_2). *See, e.g.*, Y. Lee, C. Huffman, S.M. George, “Selectivity in thermal atomic layer etching using sequential, self-limiting fluorination and ligand-exchange reactions,” *Chem. Mater.*, 28, 7657-7665 (2016); H. Saare, “Investigations of Atomic Layer Deposition and Thermal Atomic Layer Etching: Nucleation Trends, Area-Selectivity, and Phase Change Memory Materials,” PhD dissertation, North Carolina State University, 2021-08-23; J.A. Murdzek, A. Lii-Rosales, S.M. George, “Thermal Atomic Layer Etching of Nickel Using Sequential Chlorination and

Ligand-Addition Reactions,” *Chem. Mater.*, 33, 9174-9183 (2021).

[0021] In contrast to some of the examples above, the disclosed methods do not require a plasma and do not require the use of corrosive halogenating gases.

SUMMARY

[0022] In one aspect, the disclosed and claimed subject matter relates to processes for the selective vapor-phase removal of a metal compound.

[0023] In another aspect, the disclosed and claimed subject matter relates to the selective vapor-phase volatilization of a metal-containing surface material which does not etch an underlying metal. In a further aspect, the selective vapor-phase volatilization consists essentially or consists of (a) a volatilization that includes exposing a metal oxide-containing surface or a metal fluoride-containing surface to one or more chlorine-supplying volatilizing agent to produce one or more chlorine-containing volatile byproduct containing one or more metals from the metal oxide-containing surface or the metal fluoride-containing surface and (b) a purge. In another aspect, the disclosed and claimed subject matter relates to the vapor-phase etch of a material (*e.g.*, an isotropic thermal ALE of metal oxides), including ZrO_2 , HfO_2 , $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ where x is a value between 0 and 1, including but not limited to 0.5, and other materials based on ZrO_2 and HfO_2 with engineered impurities or dopants, TiO_2 , Al_2O_3 and combinations thereof. The processes include, consist essentially of or consist of the steps of (i) a surface modification that includes exposing the surface of the metal oxide substrate to one or more fluorinating surface modifying agent to produce a fluorinated metal compound at the surface, (ii) a purge, (iii) a volatilization that includes exposing the fluorinated surface to one or more chlorine-supplying volatilizing agent to produce a chlorine-containing volatile byproduct containing one or more metals from the fluorinated metal compound, (iv) a purge, (v) a surface cleaning that includes exposing the surface to one or more oxidants to remove contaminants and convert at least a portion of the surface to a metal oxide and (vi) a purge. The steps in the processes can be cycled as many times as needed to remove a desired thickness of metal oxide. This process is cycled as many times as needed to remove the desired thickness of metal oxide. An optional step (vii) oxidizing post-treatment may be added to remove impurities remaining on the surface following a number of cycles.

[0024] In another aspect, the disclosed and claimed subject matter relates to a metal-insulator-metal capacitor (“MIMcap”) device made using the disclosed and claimed ALE processes. In a further aspect, the MIMcap devices ideally demonstrate a higher dielectric constant (k) and lower leakage current than an otherwise equivalent MIMcap made without using the disclosed and claimed ALE processes.

[0025] This summary section does not specify every embodiment and/or incrementally novel

aspect of the disclosed and claimed subject matter. Instead, this summary only provides a preliminary discussion of different embodiments and corresponding points of novelty over conventional techniques and the known art. For additional details and/or possible perspectives of the disclosed and claimed subject matter and embodiments, the reader is directed to the Detailed Description section and corresponding figures of the disclosure as further discussed below.

[0026] The order of discussion of the different steps described herein has been presented for clarity's sake. In general, the steps disclosed herein can be performed in any suitable order. Additionally, although each of the different features, techniques, configurations, etc. disclosed herein may be discussed in different places of this disclosure, it is intended that each of the concepts can be executed independently of each other or in combination with each other as appropriate. Accordingly, the disclosed and claimed subject matter can be embodied and viewed in many different ways.

BRIEF DESCRIPTION OF THE DRAWINGS

[0027] 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:

[0028] FIG. 1 illustrates an exemplary cycle of the disclosed and claimed ALE processes;

[0029] FIG. 2 illustrates an X-ray photoelectron spectroscopy (XPS) measured for the samples of Example 1; and

[0030] FIG. 3 illustrates an X-ray photoelectron spectroscopy (XPS) measured for the samples of Example 5.

[0031] DEFINITIONS

[0032] Unless otherwise stated, the following terms used in the specification and claims shall have the following meanings for this application.

[0033] For purposes of the disclosed and claimed subject matter, the numbering scheme for the Periodic Table Groups is according to the IUPAC Periodic Table of Elements.

[0034] The term "and/or" as used in a phrase such as "A and/or B" herein is intended to include "A and B," "A or B," "A" and "B."

[0035] The terms "substituent," "radical," "group" and "moiety" may be used interchangeably.

[0036] As used herein, the terms "metal-containing complex" (or more simply, "complex") and "precursor" are used interchangeably and refer to metal-containing molecule or compound which can be used to prepare a metal-containing film by a vapor deposition process such as, for example,

ALD or CVD. The metal-containing complex may be deposited on, adsorbed to, decomposed on, delivered to, and/or passed over a substrate or surface thereof, as to form a metal-containing film.

[0037] As used herein, the term “metal-containing film” includes not only an elemental metal film as more fully defined below, but also a film which includes a metal along with one or more elements, for example a metal oxide film, metal nitride film, metal silicide film, a metal carbide film, a metal halide film, and the like. As used herein, the terms “elemental metal film” and “pure metal film” are used interchangeably and refer to a film which consists of, or consists essentially of, pure metal. For example, the elemental metal film may include 100% pure metal or the elemental metal film may include at least about 70%, at least about 80%, at least about 90%, at least about 95%, at least about 96%, at least about 97%, at least about 98%, at least about 99%, at least about 99.9%, or at least about 99.99% pure metal along with one or more impurities. Unless context dictates otherwise, the term “metal film” shall be interpreted to mean an elemental metal film.

[0038] As used herein, the term “vapor deposition process” is used to refer to any type of vapor deposition technique, including but not limited to, CVD and ALD. In various embodiments, CVD may take the form of conventional (*i.e.*, continuous flow) CVD, liquid injection CVD, or photo-assisted CVD. CVD may also take the form of a pulsed technique, *i.e.*, pulsed CVD. ALD is used to form a metal-containing film by vaporizing and/or passing at least one metal complex disclosed herein over a substrate surface. For conventional ALD processes see, for example, George S. M., *et al.* *J. Phys. Chem.*, 1996, *100*, 13121–13131. In other embodiments, ALD may take the form of conventional (*i.e.*, pulsed injection) ALD, liquid injection ALD, photo-assisted ALD, plasma-assisted ALD, or plasma-enhanced ALD. The term “vapor deposition process” further includes various vapor deposition techniques described in *Chemical Vapour Deposition: Precursors, Processes, and Applications*; Jones, A. C.; Hitchman, M. L., Eds., The Royal Society of Chemistry: Cambridge, 2009; Chapter 1, pp. 1–36.

[0039] As used herein, the term “feature” refers to an opening in a substrate which may be defined by one or more sidewalls, a bottom surface, and upper corners. In various aspects, the feature may be a via, a trench, contact, dual damascene, *etc.*

[0040] The term “about” or “approximately,” when used in connection with a measurable numerical variable, refers to the indicated value of the variable and to all values of the variable that are within the experimental error of the indicated value (*e.g.*, within the 95% confidence limit for the mean) or within percentage of the indicated value (*e.g.*, $\pm 10\%$, $\pm 5\%$), whichever is greater.

[0041] The disclosed and claimed precursors are preferably substantially free of water. As used herein, the term “substantially free” as it relates to water, means less than 5000 ppm (by weight) measured

by proton NMR or Karl Fischer titration, preferably less than 3000 ppm measured by proton NMR or Karl Fischer titration, and more preferably less than 1000 ppm measured by proton NMR or Karl Fischer titration, and most preferably less than 100 ppm measured by proton NMR or Karl Fischer titration.

[0042] The disclosed and claimed precursors are also preferably substantially free of unintended presence of metal ions or metals such as, Li^+ (Li), Na^+ (Na), K^+ (K), Mg^{2+} (Mg), Ca^{2+} (Ca), Al^{3+} (Al), Fe^{2+} (Fe), Fe^{3+} (Fe), Ni^{2+} (Ni), Cr^{3+} (Cr), titanium (Ti), vanadium (V), manganese (Mn), cobalt (Co), nickel (Ni), copper (Cu) or zinc (Zn). These metal ions or metals are potentially present from the starting materials/reactor employed to synthesize the precursors. As used herein, the term “substantially free” as it relates to the unintended presence of Li, Na, K, Mg, Ca, Al, Fe, Ni, Cr, Ti, V, Mn, Co, Ni, Cu or Zn means less than 5 ppm (by weight), preferably less than 3 ppm, and more preferably less than 1 ppm, and most preferably 0.1 ppm as measured by ICP-MS.

[0043] Unless otherwise indicated, “alkyl” refers to a C_1 to C_{20} hydrocarbon groups which can be linear, branched (*e.g.*, methyl, ethyl, propyl, isopropyl, tert-butyl and the like) or cyclic (*e.g.*, cyclohexyl, cyclopropyl, cyclopentyl and the like). These alkyl moieties may be substituted or unsubstituted as described below. The term “alkyl” refers to such moieties with C_1 to C_{20} carbons. It is understood that for structural reasons linear alkyls start with C_1 , while branched alkyls and linear start with C_3 . Moreover, it is further understood that moieties derived from alkyls described below, such as alkyloxy and perfluoroalkyl, have the same carbon number ranges unless otherwise indicated. If the length of the alkyl group is specified as other than described above, the above-described definition of alkyl still stands with respect to it encompassing all types of alkyl moieties as described above and that the structural consideration with regards to minimum number of carbons for a given type of alkyl group still apply.

[0044] Halo or halide refers to a halogen, F, Cl, Br or I which is linked by one bond to an organic moiety. In some embodiments, the halogen is F. In other embodiments, the halogen is Cl.

[0045] Halogenated alkyl refers to a C_1 to C_{20} alkyl which is fully or partially halogenated.

[0046] Perfluoroalkyl refers to a linear, cyclic or branched saturated alkyl group as defined above in which the hydrogens have all been replaced by fluorine (*e.g.*, trifluoromethyl, perfluoroethyl, perfluoropropyl, perfluorobutyl, perfluoroisopropyl, perfluorocyclohexyl and the like).

[0047] The disclosed and claimed precursors are preferably substantially free of organic impurities which are from either starting materials employed during synthesis or by-products generated during synthesis. Examples include, but not limited to, alkanes, alkenes, alkynes, dienes, ethers, esters, acetates, amines, ketones, amides, aromatic compounds. As used herein, the term “free of” organic impurities, means 1000 ppm or less as measured by GC, preferably 500 ppm or less (by weight) as measured by GC,

most preferably 100 ppm or less (by weight) as measured by GC or other analytical method for assay. Importantly the precursors preferably have purity of 98 wt. % or higher, more preferably 99 wt. % or higher as measured by GC when used as precursor to deposit the ruthenium-containing films.

[0048] The section headings used herein are for organizational purposes and are not to be construed as limiting the subject matter described. All documents, or portions of documents, cited in this application, including, but not limited to, patents, patent applications, articles, books, and treatises, are hereby expressly incorporated herein by reference in their entirety for any purpose. In the event that any of the incorporated literature and similar materials defines a term in a manner that contradicts the definition of that term in this application, this application controls.

DETAILED DESCRIPTION

[0049] It is to be understood that both the foregoing general description and the following detailed description are illustrative and explanatory, and are not restrictive of the subject matter, as claimed. The objects, features, advantages and ideas of the disclosed subject matter will be apparent to those skilled in the art from the description provided in the specification, and the disclosed subject matter will be readily practicable by those skilled in the art on the basis of the description appearing herein. The description of any “preferred embodiments” and/or the examples which show preferred modes for practicing the disclosed subject matter are included for the purpose of explanation and are not intended to limit the scope of the claims.

[0050] It will also be apparent to those skilled in the art that various modifications may be made in how the disclosed subject matter is practiced based on described aspects in the specification without departing from the spirit and scope of the disclosed subject matter disclosed herein.

[0051] As noted above, the disclosed and claimed subject matter relates to processes for thermal vapor-phase treatment and etching. In a first embodiment, the process (“Process I”) includes, consists essentially of or consists of **(a)** a volatilization that includes exposing a metal oxide-containing surface or a metal fluoride-containing surface to one or more chlorine-supplying volatilizing agent to produce one or more chlorine-containing volatile byproduct containing one or more metals from the metal oxide-containing surface or the metal fluoride-containing surface. In a further aspect of this embodiment, Process I further includes, consists essentially of or consists of **(b)** a purge step. In a further aspect of this embodiment, Process I can include additional steps constituting a vapor-phase etch process and/or steps or be a part of other multi-step vapor-phase etch processes. In a further aspect of this embodiment, Process I selectively removes a metal oxide-containing surface or a metal fluoride-containing surface without removing an underlying metal or metal compound.

[0052] In a further aspect of this embodiment, the material to be etched includes a layer of metal oxide atop a metal. In a further aspect, the material to be etched includes a native oxide (*e.g.*, formed during exposure to an oxidizing environment such as atmosphere). In a further aspect, the metal includes cobalt, nickel, molybdenum, ruthenium, tungsten, and combinations thereof.

[0053] In one aspect, the disclosed and claimed subject matter relates to the selective vapor-phase etch process. In another aspect, the disclosed and claimed subject matter relates to the selective isotropic thermal ALE of metal oxides. The vapor-phase etch process ("Process 2") includes, consists essentially of or consists of the steps of:

- (i) a surface modification that includes exposing a metal oxide surface to one or more fluorinating surface modifying agent to produce one or more fluorinated metal compound at the surface;
- (ii) a purge;
- (iii) a volatilization that includes exposing the fluorinated metal compound to one or more chlorine-supplying volatilizing agent to produce one or more chlorine-containing volatile byproduct containing one or more metals of the fluorinated metal compound;
- (iv) a purge;
- (v) a surface cleaning comprising exposing the surface to one or more oxidants to remove contaminants and convert at least a portion of the surface to a metal oxide; and
- (vi) a purge.

In a further aspect of this embodiment, the method consists essentially of steps (i), (ii), (iii), (iv), (v) and (vi). In a further aspect of this embodiment, the method consists of steps (i), (ii), (iii), (iv), (v) and (vi). In a further aspect of this embodiment, the method consists essentially of steps (i), (ii), (iii), and (iv). In a further aspect of this embodiment, the method consists of steps (i), (ii), (iii), and (iv). In a further aspect of this embodiment, the method consists essentially of steps (iii) and (iv). In a further aspect of this embodiment, the method consists of steps (iii) and (iv). The steps in the processes can be cycled as many times as needed to remove a desired thickness of metal oxide. In a further aspect, any of the forgoing embodiments can further include a step (vii) oxidizing post-treatment to remove impurities remaining on the surface following a number of cycles.

[0054] In a further aspect of this embodiment, the material to be etched includes ZrO_2 , HfO_2 , $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ where x is a value between 0 and 1, and other materials based on ZrO_2 and HfO_2 with engineered impurities or dopants, TiO_2 , Al_2O_3 and combinations thereof.

[0055] **Number of Cycles**

[0056] As noted above, in the disclosed and claimed etch processes, the steps can be cycled as

many times as needed to remove a desired thickness of metal oxide. In the above-described embodiments, as well as the other embodiments described herein, the described steps define one cycle of the process. As those skilled in the art will understand (and as noted above), in the disclosed and claimed Process II will include a purge step (ii) when proceeding from step (i) to step (iii), a purge step (iv) when proceeding from step (iii) to step (v) as well as an additional purge step (vi) before beginning a new cycle (*i.e.*, proceeding from step (v) to step (i)). However, purge steps do not have to be performed between iterations of a single step (*e.g.*, between multiple iterations of step (i), between multiple iterations of step (iii) or between multiple iterations of step (v)). This is also true in Process I (*i.e.*, between multiple iterations of step (a)).

[0057] Thus, a single cycle in Process I is to be understood as the number of repetitions of step (a). A single cycle in Process II is to be understood as beginning when the first iteration of step (i) is performed and ending when the last purge step (vi) is performed before another iteration of step (i) is performed again regardless of the number of purging steps conducted during the process. It is to be understood that a cycle can be repeated until the desired thickness of a film is obtained.

[0058] In one embodiment, the number of cycles is from about 100 to about 1000. In one embodiment, the number of cycles is from about 20 to about 250. In one embodiment, the number of cycles is from about 10 to about 150. In one embodiment, the number of cycles is from about 5 to about 100. In one embodiment, the number of cycles is from about 5 to about 75. In one embodiment, the number of cycles is from about 5 to about 50. In one embodiment, the number of cycles is from about 5 to about 30. In one embodiment, the number of cycles is from about 5 to about 20. In one embodiment, the number of cycles is from about 15 to about 400. In one embodiment, the number of cycles is from about 20 to about 300. In one embodiment, the number of cycles is from about 25 to about 250. In one embodiment, the number of cycles is from about 35 to about 200. In one embodiment, the number of cycles is from about 45 to about 170. In one embodiment, the number of cycles is from about 50 to about 150. In one embodiment, the number of cycles is from about 75 to about 125. In one embodiment, the number of cycles is from about 25 to about 100. In one embodiment, the number of cycles is from about 50 to about 100. In one embodiment, the number of cycles is from about 75 to about 100.

[0059] In one embodiment, the number of cycles is about 5. In one embodiment, the number of cycles is about 10. In one embodiment, the number of cycles is about 15. In one embodiment, the number of cycles is about 20. In one embodiment, the number of cycles is about 25. In one embodiment, the number of cycles is about 30. In one embodiment, the number of cycles is about 35. In one embodiment, the number of cycles is about 40. In one embodiment, the number of cycles is about 45.

In one embodiment, the number of cycles is about 50. In one embodiment, the number of cycles is about 75. In one embodiment, the number of cycles is about 100. In one embodiment, the number of cycles is about 125. In one embodiment, the number of cycles is about 150. In one embodiment, the number of cycles is about 175. In one embodiment, the number of cycles is about 200. In one embodiment, the number of cycles is about 225. In one embodiment, the number of cycles is about 250. In one embodiment, the number of cycles is about 275. In one embodiment, the number of cycles is about 300. In one embodiment, the number of cycles is about 325. In one embodiment, the number of cycles is about 350. In one embodiment, the number of cycles is about 400. In one embodiment, the number of cycles is about 450. In one embodiment, the number of cycles is about 500. In one embodiment, the number of cycles is about 750. In one embodiment, the number of cycles is about 1000.

[0060] The steps of the disclosed and claimed processes are described in more detail as follows.

[0061] Step (i) Surface Modification

[0062] In the step (i) surface modification, the one or more fluorinating surface modifying agent is used to convert a surface including, consisting essentially of or consisting of one or more metal oxide (*e.g.*, ZrO_2 , HfO_2 , $Hf_xZr_{1-x}O_2$ where x is a value between 0 and 1, other materials based on ZrO_2 and HfO_2 with engineered impurities or dopants, Al_2O_3 or TiO_2) into the corresponding fluorinated species and thereby producing a fluorinated metal surface. In this step, the one or more metal oxide is exposed to the fluorinated agent for a period of time before moving to step (ii).

[0063] As those skilled in the art will understand, the initial exposure (not shown in FIG. 1) of the metal oxide surface to the fluorinated agent will produce by-products on the surface that contaminate the surface and that will, over time, slow down or halt the etching process. Accordingly, the disclosed and claimed processes include a step (v) in which such species are oxidized to species that can be readily volatilized upon exposure to the fluorinated agent when step (i) is repeated during the next cycle. For example, when Ishikawa's reagent (*N,N*-diethyl-(1,1,2,3,3,3-hexafluoropropyl)amine) is used for fluorination it may leave behind residues of *N,N*-diethyl-(*E*)-pentafluoropropenylamine or its decomposition products, which include C, N, and F. These light element surface contaminants may be combusted by oxidation to form carbon oxides (*e.g.*, CO, CO_2), nitrogen oxides (*e.g.*, NO, NO_2 , N_2O) and byproducts thereof (*e.g.*, N_2) and volatile fluorine compounds (*e.g.*, anhydrous HF). Similarly, hydrogen fluoride pyridine may leave behind residues of pyridine or its decomposition products, which include C and N, during a fluorination process step. These light element surface contaminants may be combusted by oxidation to form carbon oxides, nitrogen oxides, and byproducts thereof.

[0064] (a) Metal Oxide-Containing Surfaces and/or Metal Oxides

[0065] The metal oxide-containing surface and/or the metal oxide includes any acceptable, incidental, and/or desirable metal and/or metal oxide. Thus, the metal oxide-containing surfaces and/or metal oxides can include, consist essentially of or consist of one or more of zirconium (Zr), hafnium (Hf), aluminum (Al), titanium (Ti), cobalt (Co), nickel (Ni), molybdenum (Mo), ruthenium (Ru), tungsten (W) and combinations thereof. In one embodiment, the metal oxide-containing surface includes cobalt (Co). In one embodiment, the metal oxide-containing surface includes nickel (Ni). In one embodiment, the metal oxide-containing surface comprises molybdenum (Mo). In one embodiment, the metal oxide-containing surface includes ruthenium (Ru). In one embodiment, the metal oxide-containing surface includes tungsten (W). In one embodiment, the metal oxide includes one or more of ZrO_2 , HfO_2 , $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ where x is a value between 0 and 1, other materials based on ZrO_2 and HfO_2 with engineered impurities or dopants, TiO_2 , Al_2O_3 and combinations thereof. In one aspect of this embodiment, the metal oxide includes ZrO_2 . In one aspect of this embodiment, the metal oxide includes HfO_2 . In one aspect of this embodiment, the metal oxide includes $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ where x is a value between 0 and 1. In one aspect of this specific embodiment, $m = 0.1$. In one aspect of this specific embodiment, $m = 0.2$. In one aspect of this specific embodiment, $m = 0.3$. In one aspect of this specific embodiment, $m = 0.4$. In one aspect of this specific embodiment, $m = 0.5$. In one aspect of this specific embodiment, $m = 0.6$. In one aspect of this specific embodiment, $m = 0.7$. In one aspect of this specific embodiment, $m = 0.8$. In one aspect of this specific embodiment, $m = 0.9$. In one aspect of this specific embodiment, $m = 0.95$. In one aspect of this embodiment, the metal oxide includes materials based on ZrO_2 and HfO_2 with engineered impurities. In one aspect of this embodiment, the metal oxide includes TiO_2 . In one aspect of this embodiment, the metal oxide includes Al_2O_3 .

[0066] In one aspect of this embodiment, the metal oxide is in contact with a different material underlying the metal oxide. In one aspect, the metal oxide is deposited atop the underlying material by atomic layer deposition (ALD). In one aspect, the underlying material is a metal. In one aspect, the underlying material is a metal nitride. In one aspect, the underlying material is a different metal oxide. In one aspect, the underlying material includes one or of Ti, TiN, TiO_2 , Ta, TaN, W, Al, Ni, Ru, Pt, Al_2O_3 , ZrO_2 , HfO_2 , $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ where x is a value between 0 and 1, Si, Si_3N_4 , and SiO_2 .

[0067] (b) Fluorinating Surface Modifying Agents

[0068] The fluorinating surface modifying agent includes one or more metal-free or substantially metal-free fluorinating agent.

[0069] In one aspect of this embodiment, the fluorinating surface modifying agent includes

one or more of Ishikawa's reagent, ammonium bifluoride, sodium bifluoride, potassium bifluoride, hydrogen fluoride pyridine, triethylamine trishydrofluoride, hydrogen fluoride and combinations thereof. In one aspect of this embodiment, the fluorinating surface modifying agent includes two or more of Ishikawa's reagent, ammonium bifluoride, sodium bifluoride, potassium bifluoride, hydrogen fluoride pyridine, triethylamine trishydrofluoride or hydrogen fluoride. In one aspect of this embodiment, the one or more fluorinating surface modifying agent includes Ishikawa's reagent. In one aspect of this embodiment, the one or more fluorinating surface modifying agent includes ammonium bifluoride. In one aspect of this embodiment, the one or more fluorinating surface modifying agent includes sodium bifluoride. In one aspect of this embodiment, the one or more fluorinating surface modifying agent includes potassium bifluoride. In one aspect of this embodiment, the one or more fluorinating surface modifying agent includes hydrogen fluoride pyridine. In one aspect of this embodiment, the one or more fluorinating surface modifying agent includes triethylamine trishydrofluoride. In one aspect of this embodiment, the one or more fluorinating surface modifying agent includes hydrogen fluoride.

[0070] In one aspect of this embodiment, the fluorinating surface modifying agent is a liquid at room temperature. In one aspect of this embodiment, the fluorinating surface modifying agent is a solid at room temperature.

[0071] (c) Conditions

[0072] Dosing

[0073] The fluorinating surface modifying agent may be dosed as a vapor. In one aspect of this embodiment, the fluorinating surface modifying agent is dosed as a surface modifying vapor. In another aspect of this embodiment, the fluorinating surface modifying agent is decomposed in the vessel as a surface modifying vapor and a byproduct.

[0074] Time

[0075] As noted above, in step (i), the one or more metal oxide is exposed to the fluorinating surface modifying agent for a period of time ("exposure time") before moving to step (ii). In one embodiment, the step (i) surface modification exposure time is from about 0.5 seconds to about 30 seconds. In one embodiment, the step (i) surface modification exposure time is from about 0.5 seconds to about 10 seconds. In one embodiment, the step (i) surface modification exposure time is from about 1 second to about 7 seconds. In one embodiment, the step (i) surface modification exposure time is from about 7 seconds to about 10 seconds. In one embodiment, the step (i) surface modification exposure time is from about 10 seconds to about 20 seconds. In one embodiment, the step (i) surface modification exposure time

is from about 20 seconds to about 30 seconds. In one embodiment, the step (i) surface modification exposure time is about 0.25 seconds. In one embodiment, the step (i) surface modification exposure time is about 0.5 seconds. In one embodiment, the step (i) surface modification exposure time is about 1 second. In one embodiment, the step (i) surface modification exposure time is about 2 seconds. In one embodiment, the step (i) surface modification exposure time is about 3 seconds. In one embodiment, the step (i) surface modification exposure time is about 4 seconds. In one embodiment, the step (i) surface modification exposure time is about 5 seconds. In one embodiment, the step (i) surface modification exposure time is about 6 seconds. In one embodiment, the step (i) surface modification exposure time is about 7 seconds. In one embodiment, the step (i) surface modification exposure time is about 8 seconds. In one embodiment, the step (i) surface modification exposure time is about 9 seconds. In one embodiment, the step (i) surface modification exposure time is about 10 seconds. In one embodiment, the step (i) surface modification exposure time is about 12 seconds. In one embodiment, the step (i) surface modification exposure time is about 15 seconds. In one embodiment, the step (i) surface modification exposure time is about 17 seconds. In one embodiment, the step (i) surface modification exposure time is about 20 seconds. In one embodiment, the step (i) surface modification exposure time is about 25 seconds. In one embodiment, the step (i) surface modification exposure time is about 30 seconds.

[0076] Flow Rate of Fluorinating Surface Modifying Agent (Vapor)

[0077] In one embodiment, the fluorinating surface modifying agent vapor is flowed at from about 0.5 sccm to about 500 sccm. In one embodiment, the fluorinating surface modifying agent vapor is flowed at from about 0.5 sccm to about 100 sccm. In one embodiment, the fluorinating surface modifying agent vapor is flowed at from about 1 sccm to about 200 sccm. In one embodiment, the fluorinating surface modifying agent vapor is flowed at from about 1 sccm to about 100 sccm. In one embodiment, the fluorinating surface modifying agent vapor is flowed at from about 1 sccm to about 50 sccm. In one embodiment, the fluorinating surface modifying agent vapor is flowed at from about 5 sccm to about 25 sccm. In one embodiment, the fluorinating surface modifying agent vapor is flowed at from about 10 sccm to about 20 sccm. In one embodiment, the fluorinating surface modifying agent vapor is flowed at from about 15 sccm to about 25 sccm. In one embodiment, the fluorinating surface modifying agent vapor is flowed at about 5 sccm. In one embodiment, the fluorinating surface modifying agent vapor is flowed at about 10 sccm. In one embodiment, the fluorinating surface modifying agent vapor is flowed at about 15 sccm. In one embodiment, the fluorinating surface modifying agent vapor is flowed at about 20 sccm. In one embodiment, the fluorinating surface modifying agent vapor is flowed at about 25 sccm. In one embodiment, the fluorinating surface

modifying agent vapor is flowed at about 30 sccm. In one embodiment, the fluorinating surface modifying agent vapor is flowed at about 35 sccm. In one embodiment, the fluorinating surface modifying agent vapor is flowed at about 40 sccm. In one embodiment, the fluorinating surface modifying agent vapor is flowed at about 45 sccm. In one embodiment, the fluorinating surface modifying agent vapor is flowed at about 50 sccm. In one embodiment, the fluorinating surface modifying agent vapor is flowed at about 60 sccm. In one embodiment, the fluorinating surface modifying agent vapor is flowed at about 70 sccm. In one embodiment, the fluorinating surface modifying agent vapor is flowed at about 80 sccm. In one embodiment, the fluorinating surface modifying agent vapor is flowed at about 90 sccm. In one embodiment, the fluorinating surface modifying agent vapor is flowed at about 100 sccm. In one embodiment, the fluorinating surface modifying agent vapor is flowed at about 125 sccm. In one embodiment, the fluorinating surface modifying agent vapor is flowed at about 150 sccm. In one embodiment, the fluorinating surface modifying agent vapor is flowed at about 200 sccm. In one embodiment, the fluorinating surface modifying agent vapor is flowed at about 250 sccm. In one embodiment, the fluorinating surface modifying agent vapor is flowed at about 300 sccm. In one embodiment, the fluorinating surface modifying agent vapor is flowed at about 350 sccm. In one embodiment, the fluorinating surface modifying agent vapor is flowed at about 400 sccm. In one embodiment, the fluorinating surface modifying agent vapor is flowed at about 450 sccm. In one embodiment, the fluorinating surface modifying agent vapor is flowed at about 500 sccm.

[0078] In one embodiment, the fluorinating surface modifying agent vapor is supplied alone.

[0079] In one embodiment, the fluorinating surface modifying agent vapor is supplied with a suitable carrier gas. In one embodiment, the carrier gas includes argon. In one embodiment, the carrier gas includes nitrogen.

[0080] Pressure

[0081] The step (i) surface modification can be carried out at any suitable chamber pressure. In one embodiment, the pressure is from about 0.5 torr to about 100 torr. The step (i) surface modification can be carried out at any suitable chamber pressure. In one embodiment, the pressure is from about 5 torr to about 100 torr. In one embodiment, the pressure is from about 0.5 torr to about 15 torr. In one embodiment, the pressure is from about 1 torr to about 12 torr. In one embodiment, the pressure is from about 1 torr to about 10 torr. In one embodiment, the pressure is from about 1 torr to about 5 torr. In one embodiment, the pressure is from about 1 torr to about 2 torr. In one embodiment, the pressure is from about 0.5 torr to about 5 torr. In one embodiment, the pressure is from about 0.2 torr to about 2

torr. In one embodiment, the pressure is about 0.2 torr. In one embodiment, the pressure is about 0.5 torr. In one embodiment, the pressure is about 1 torr. In one embodiment, the pressure is about 1.5 torr. In one embodiment, the pressure is about 2 torr. In one embodiment, the pressure is about 2.5 torr. In one embodiment, the pressure is about 5 torr. In one embodiment, the pressure is about 10 torr. In one embodiment, the pressure is about 15 torr. In one embodiment, the pressure is about 20 torr. In one embodiment, the pressure is about 25 torr. In one embodiment, the pressure is about 30 torr. In one embodiment, the pressure is about 40 torr. In one embodiment, the pressure is about 50 torr. In one embodiment, the pressure is about 60 torr. In one embodiment, the pressure is about 75 torr. In one embodiment, the pressure is about 100 torr.

[0082] (d) Exemplary Step (i)

[0083] In an exemplary embodiment of the step (i) surface modification, and as illustrated in FIG. 1A, a ZrO_2 surface is exposed to anhydrous hydrogen fluoride (HF) (which can originate from, for example, ammonium bifluoride, sodium bifluoride, potassium bifluoride, or triethylamine trihydrofluoride) thereby converting the solid ZrO_2 at the surface into solid ZrF_4 and water vapor (*i.e.*, $\text{ZrO}_2(\text{s}) + 4 \text{HF}(\text{g}) \rightarrow \text{ZrF}_4(\text{s}) + 2 \text{H}_2\text{O}(\text{g})$). In another embodiment, shown in FIG. 1B, Ishikawa's reagent is used as the fluorinating surface modifying agent instead of HF.

[0084] Step (a) and/or Step (iii) Volatilization

[0085] In the step (a) and/or step (iii) volatilization, a fluorinated metal surface is exposed to one or more chlorine-supplying volatilizing agent to produce a chlorine-containing volatile byproduct containing one or more metals of the fluorinated metal compound.

[0086] (a) Volatilizing Agent

[0087] The chlorine-supplying volatilizing agent includes one or more chlorine-supplying ligands or species capable of exchanging fluoride ions with chloride ions. In one aspect of this embodiment, the one or more chlorine-supplying volatilizing agent includes one or more of thionyl chloride (SOCl_2), chlorine (Cl_2), dimethylaluminum chloride (DMAC, $\text{Al}(\text{CH}_3)_2\text{Cl}$), diethylaluminum chloride (DEAC, $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$), titanium tetrachloride (TiCl_4), boron trichloride (BCl_3) and combinations thereof. In one aspect of this embodiment, the one or more chlorine-supplying volatilizing agent includes DMAC. In one aspect of this embodiment, the one or more chlorine-supplying volatilizing agent includes DEAC. In one aspect of this embodiment, the one or more chlorine-supplying volatilizing agent includes TiCl_4 . In one aspect of this embodiment, the one or more chlorine-supplying volatilizing agent includes BCl_3 . In one aspect of this embodiment, the one or more chlorine-supplying volatilizing agent includes a combination of two or more of DMAC, DEAC, TiCl_4 and BCl_3 .

[0088] As those skilled in the art will recognize, DMAC, DEAC, TiCl_4 , and BCl_3 contain elements which may deposit on the etched surface, forming solid residues that may contain aluminum, titanium, or boron. Thus, in an embodiment, the chlorine-supplying volatilizing agent is free or substantially free of metals or boron. In another embodiment, the chlorine-supplying volatilizing agent contains thionyl chloride (SOCl_2). In another embodiment, the volatilizing agent contains chlorine (Cl_2).

[0089] (b) **Conditions**

[0090] **Time**

[0091] As noted above, in step (a) and/or step (iii), a fluorinated metal surface is exposed to one or more chlorine-supplying volatilizing agent for a period of time ("exposure time") before moving to the next step. In one embodiment, the step (a) and/or step (iii) exposure time is from about 0.5 seconds to about 30 seconds. In one embodiment, the step (a) and/or step (iii) exposure time is from about 0.5 seconds to about 10 seconds. In one embodiment, the step (a) and/or step (iii) exposure time is from about 1 second to about 7 seconds. In one embodiment, the step (a) and/or step (iii) exposure time is from about 7 seconds to about 10 seconds. In one embodiment, the step (a) and/or step (iii) exposure time is from about 10 seconds to about 20 seconds. In one embodiment, the step (a) and/or step (iii) exposure time is from about 20 seconds to about 30 seconds. In one embodiment, the step (a) and/or step (iii) exposure time is about 0.25 seconds. In one embodiment, the step (a) and/or step (iii) exposure time is about 0.5 seconds. In one embodiment, the step (a) and/or step (iii) exposure time is about 1 second. In one embodiment, the step (a) and/or step (iii) exposure time is about 2 seconds. In one embodiment, the step (a) and/or step (iii) exposure time is about 3 seconds. In one embodiment, the step (a) and/or step (iii) exposure time is about 4 seconds. In one embodiment, the step (a) and/or step (iii) exposure time is about 5 seconds. In one embodiment, the step (a) and/or step (iii) exposure time is about 6 seconds. In one embodiment, the step (a) and/or step (iii) exposure time is about 7 seconds. In one embodiment, the step (a) and/or step (iii) exposure time is about 8 seconds. In one embodiment, the step (a) and/or step (iii) exposure time is about 9 seconds. In one embodiment, the step (a) and/or step (iii) exposure time is about 10 seconds. In one embodiment, the step (a) and/or step (iii) exposure time is about 12 seconds. In one embodiment, the step (a) and/or step (iii) exposure time is about 15 seconds. In one embodiment, the step (a) and/or step (iii) exposure time is about 17 seconds. In one embodiment, the step (a) and/or step (iii) exposure time is about 20 seconds. In one embodiment, the step (a) and/or step (iii) exposure time is about 25 seconds. In one embodiment, the step (a) and/or step (iii) exposure time is about 30 seconds.

[0092] Flow Rate of Chlorine-Supplying Volatilizing Agent

[0093] In one embodiment, the chlorine-supplying volatilizing agent is flowed at from about 1 sccm to about 500 sccm. In one embodiment, the chlorine-supplying volatilizing agent is flowed at from about 5 sccm to about 500 sccm. In one embodiment, the chlorine-supplying volatilizing agent is flowed at from about 0.5 sccm to about 100 sccm. In one embodiment, the chlorine-supplying volatilizing agent is flowed at from about 1 sccm to about 50 sccm. In one embodiment, the chlorine-supplying volatilizing agent is flowed at from about 5 sccm to about 25 sccm. In one embodiment, the chlorine-supplying volatilizing agent is flowed at from about 10 sccm to about 20 sccm. In one embodiment, the chlorine-supplying volatilizing agent is flowed at from about 15 sccm to about 25 sccm. In one embodiment, the chlorine-supplying volatilizing agent is flowed at about 5 sccm. In one embodiment, the chlorine-supplying volatilizing agent is flowed at about 10 sccm. In one embodiment, the chlorine-supplying volatilizing agent is flowed at about 15 sccm. In one embodiment, the chlorine-supplying volatilizing agent is flowed at about 20 sccm. In one embodiment, the chlorine-supplying volatilizing agent is flowed at about 25 sccm. In one embodiment, the chlorine-supplying volatilizing agent is flowed at about 30 sccm. In one embodiment, the chlorine-supplying volatilizing agent is flowed at about 35 sccm. In one embodiment, the chlorine-supplying volatilizing agent is flowed at about 40 sccm. In one embodiment, the chlorine-supplying volatilizing agent is flowed at about 45 sccm. In one embodiment, the chlorine-supplying volatilizing agent is flowed at about 50 sccm. In one embodiment, the chlorine-supplying volatilizing agent is flowed at about 60 sccm. In one embodiment, the chlorine-supplying volatilizing agent is flowed at about 70 sccm. In one embodiment, the chlorine-supplying volatilizing agent is flowed at about 80 sccm. In one embodiment, the chlorine-supplying volatilizing agent is flowed at about 90 sccm. In one embodiment, the chlorine-supplying volatilizing agent is flowed at about 100 sccm. In one embodiment, the chlorine-supplying volatilizing agent is flowed at about 125 sccm. In one embodiment, the chlorine-supplying volatilizing agent is flowed at about 150 sccm. In one embodiment, the chlorine-supplying volatilizing agent is flowed at about 200 sccm. In one embodiment, the chlorine-supplying volatilizing agent is flowed at about 250 sccm. In one embodiment, the chlorine-supplying volatilizing agent is flowed at about 300 sccm. In one embodiment, the chlorine-supplying volatilizing agent is flowed at about 350 sccm. In one embodiment, the chlorine-supplying volatilizing agent is flowed at about 400 sccm. In one embodiment, the chlorine-supplying volatilizing agent is flowed at about 450 sccm. In one embodiment, the chlorine-supplying volatilizing agent is flowed at about 500 sccm.

[0094] In one embodiment, the chlorine-supplying volatilizing agent is supplied alone.

[0095] In one embodiment, the chlorine-supplying volatilizing agent is supplied with a suitable carrier gas. In one embodiment, the carrier gas includes argon. In one embodiment, the carrier gas includes nitrogen.

[0096] **Pressure**

[0097] Step (a) and/or step (iii) can be carried out at any suitable chamber pressure. In one embodiment, the pressure is from about 0.5 torr to about 100 torr. In one embodiment, the pressure is from about 5 torr to about 100 torr. In one embodiment, the pressure is from about 0.5 torr to about 15 torr. In one embodiment, the pressure is from about 1 torr to about 12 torr. In one embodiment, the pressure is from about 1 torr to about 10 torr. In one embodiment, the pressure is from about 1 torr to about 5 torr. In one embodiment, the pressure is from about 1 torr to about 2 torr. In one embodiment, the pressure is from about 0.5 torr to about 5 torr. In one embodiment, the pressure is from about 0.2 torr to about 2 torr. In one embodiment, the pressure is about 0.2 torr. In one embodiment, the pressure is about 0.5 torr. In one embodiment, the pressure is about 1 torr. In one embodiment, the pressure is about 1.5 torr. In one embodiment, the pressure is about 2 torr. In one embodiment, the pressure is about 2.5 torr. In one embodiment, the pressure is about 5 torr. In one embodiment, the pressure is about 10 torr. In one embodiment, the pressure is about 15 torr. In one embodiment, the pressure is about 20 torr. In one embodiment, the pressure is about 25 torr. In one embodiment, the pressure is about 30 torr. In one embodiment, the pressure is about 40 torr. In one embodiment, the pressure is about 50 torr. In one embodiment, the pressure is about 60 torr. In one embodiment, the pressure is about 75 torr. In one embodiment, the pressure is about 100 torr.

[0098] **(d) Exemplary Step (iii)**

[0099] In an exemplary embodiment of step (a) and/or step (iii), and as illustrated in FIG. 1, a layer of ZrF_4 atop the surface of ZrO_2 (as described above) undergoes ligand exchange with thionyl chloride (SOCl_2) to produce byproducts which may include volatile ZrCl_4 vapor and volatile thionyl fluoride (SOF_2) vapor (*i.e.*, $\text{ZrF}_4(\text{s}) + 2 \text{SOCl}_2 \rightarrow \text{ZrCl}_4(\text{g}) + 2 \text{SOF}_2(\text{g})$).

[0100] **Step (v) Surface Cleaning**

[0101] In the step (v) surface cleaning, the etched metal oxide surface is exposed to one or more oxidant for a period of time sufficient to oxidize metal byproducts present on the etched metal surface into species that can be readily volatilized upon exposure to the fluorinating agent when step (i) is repeated during the next cycle. As noted above, the fluorinating agents may produce surface contaminants that will, over time, slow down or halt the etching process. The oxidation step converts those byproducts to volatile species that can be readily reacted removed upon exposure to the

fluorinating agent when step (i) is repeated during the next cycle. In addition, exposure of the metal surface to the one or more oxidants converts at least a portion of the surface to a metal oxide prior to the next cycle of the process.

[0102] In one embodiment, the one or more oxidant includes one or more of oxygen (O_2), ozone (O_3), nitric oxide (NO), water (H_2O) vapor, hydrogen peroxide (H_2O_2), oxygen plasma (O^*), N_xO_y (where $x = 1$ or 2 and $y = 1, 2, 3$ or 4) and combinations thereof. In one aspect of this embodiment, the one or more oxidant includes oxygen. In one aspect of this embodiment, the one or more oxidant includes ozone. In one aspect of this embodiment, the one or more oxidant includes nitric oxide. In one aspect of this embodiment, the one or more oxidant includes water vapor. In one aspect of this embodiment, the one or more oxidant includes hydrogen peroxide. In one aspect of this embodiment, the one or more oxidant includes oxygen and ozone. In one aspect of this embodiment, the one or more oxidant includes oxygen plasma. In one aspect of this embodiment, the one or more oxidant includes N_xO_y where $x = 1$ or 2 and $y = 1, 2, 3$ or 4 . In one embodiment, the one or more oxidant is a vapor.

[0103] In one embodiment, the exposure of the etched metal oxide surface to the one or more oxidant includes the sequential exposure of a first oxidant followed by the exposure of second oxidant that is different than the first oxidant. In one aspect of this embodiment, the first oxidant is one of oxygen and ozone and the second oxidant is the other of oxygen and ozone.

[0104] (b) Conditions

[0105] Time

[0106] In one embodiment, the step (v) oxidant flow time is from about 0.5 seconds to about 30 seconds. In one embodiment, the step (v) oxidant flow time is from about 0.5 seconds to about 10 seconds. In one embodiment, the step (v) oxidant flow time is from about 1 second to about 7 seconds. In one embodiment, the step (v) oxidant flow time is from about 7 seconds to about 10 seconds. In one embodiment, the step (v) oxidant flow time is from about 10 seconds to about 20 seconds. In one embodiment, the step (v) oxidant flow time is from about 20 seconds to about 30 seconds. In one embodiment, the step (v) oxidant flow time is from about 30 seconds to about 60 seconds. In one embodiment, the step (v) oxidant flow time is from about 1 second to about 60 seconds. In one embodiment, the step (v) oxidant flow time is about 0.25 seconds. In one embodiment, the step (v) oxidant flow time is about 0.5 seconds. In one embodiment, the step (v) oxidant flow time is about 1 second. In one embodiment, the step (v) oxidant flow time is about 2 seconds. In one embodiment, the step (v) oxidant flow time is about 3 seconds. In one embodiment, the step (v) oxidant flow time is about 4 seconds. In one embodiment, the step (v) oxidant flow time is about 5 seconds. In one

embodiment, the step (v) oxidant flow time is about 6 seconds. In one embodiment, the step (v) oxidant flow time is about 7 seconds. In one embodiment, the step (v) oxidant flow time is about 8 seconds. In one embodiment, the step (v) oxidant flow time is about 9 seconds. In one embodiment, the step (v) oxidant flow time is about 10 seconds. In one embodiment, the step (v) oxidant flow time is about 12 seconds. In one embodiment, the step (v) oxidant flow time exposure is about 15 seconds. In one embodiment, the step (v) oxidant flow time is about 17 seconds. In one embodiment, the step (v) oxidant flow time is about 20 seconds. In one embodiment, the step (v) oxidant flow time is about 25 seconds. In one embodiment, the step (v) oxidant flow time is about 30 seconds. In one embodiment, the step (v) oxidant flow time is about 35 seconds. In one embodiment, the step (v) oxidant flow time is about 40 seconds. In one embodiment, the step (v) oxidant flow time is about 50 seconds. In one embodiment, the step (v) oxidant flow time is about 60 seconds.

[0107] Flow Rate

[0108] In one embodiment, the oxidant is flowed at from about 10 sccm to about 3000 sccm. In one embodiment, the oxidant is flowed at from about 50 sccm to about 3000 sccm. In one embodiment, the oxidant is flowed at from about 10 sccm to about 1000 sccm. In one embodiment, the oxidant is flowed at from about 500 sccm to about 1000 sccm. In one embodiment, the oxidant is flowed at from about 1000 sccm to about 2000 sccm. In one embodiment, the oxidant is flowed at about 50 sccm. In one embodiment, the oxidant is flowed at about 75 sccm. In one embodiment, the oxidant is flowed at about 100 sccm. In one embodiment, the oxidant is flowed at about 200 sccm. In one embodiment, the oxidant is flowed at about 300 sccm. In one embodiment, the oxidant is flowed at about 400 sccm. In one embodiment, the oxidant is flowed at about 500 sccm. In one embodiment, the oxidant is flowed at about 1000 sccm. In one embodiment, the oxidant is flowed at about 1500 sccm. In one embodiment, the oxidant is flowed at about 2000 sccm. In one embodiment, the oxidant is flowed at about 2500 sccm. In one embodiment, the oxidant is flowed at about 3000 sccm.

[0109] In one embodiment, the oxidant is supplied alone.

[0110] In one embodiment, the oxidant is supplied with a suitable carrier gas. In one embodiment, the carrier gas includes argon. In one embodiment, the carrier gas includes nitrogen.

[0111] Pressure

[0112] The step (v) surface cleaning step can be carried out at any suitable chamber pressure. In one embodiment, the pressure is from about 0.5 torr to about 100 torr. In one embodiment, the pressure is from about 5 torr to about 100 torr. In one embodiment, the pressure is from about 0.5 torr to about 15 torr. In one embodiment, the pressure is from about 1 torr to about 12 torr. In one embodiment, the

pressure is from about 1 torr to about 10 torr. In one embodiment, the pressure is from about 1 torr to about 5 torr. In one embodiment, the pressure is from about 1 torr to about 2 torr. In one embodiment, the pressure is from about 0.5 torr to about 5 torr. In one embodiment, the pressure is from about 0.2 torr to about 2 torr. In one embodiment, the pressure is about 0.2 torr. In one embodiment, the pressure is about 0.5 torr. In one embodiment, the pressure is about 1 torr. In one embodiment, the pressure is about 1.5 torr. In one embodiment, the pressure is about 2 torr. In one embodiment, the pressure is about 2.5 torr. In one embodiment, the pressure is about 5 torr. In one embodiment, the pressure is about 10 torr. In one embodiment, the pressure is about 15 torr. In one embodiment, the pressure is about 20 torr. In one embodiment, the pressure is about 25 torr. In one embodiment, the pressure is about 30 torr. In one embodiment, the pressure is about 40 torr. In one embodiment, the pressure is about 50 torr. In one embodiment, the pressure is about 60 torr. In one embodiment, the pressure is about 75 torr. In one embodiment, the pressure is about 100 torr.

[0113] (d) Exemplary Step (v)

[0114] In an exemplary embodiment of the step (v) surface cleaning, and as illustrated in FIG. 1, the etched metal oxide surface is exposed to an oxidant thereby converting surface contaminant atoms to a more oxidized form. In one embodiment, the surface contaminant atoms may include carbon, nitrogen, fluorine, sulfur or chlorine.

[0115] Steps (b), (ii), (iv) and (vi) Purges

[0116] In each of the steps (b), (ii), (iv) and (vi) purges ("purge steps"), any suitable inert purge gas can be used. In one embodiment, the purge gas includes argon. In one embodiment, the purge gas includes nitrogen. In one embodiment, the each of the purge steps uses the same inert gas.

[0117] Time

[0118] In one embodiment, the purge time is from about 0.5 seconds to about 30 seconds. In one embodiment, the purge time is from about 0.5 seconds to about 10 seconds. In one embodiment, the purge time is from about 1 second to about 7 seconds. In one embodiment, the purge time is from about 7 seconds to about 10 seconds. In one embodiment, the purge time is from about 10 seconds to about 20 seconds. In one embodiment, the purge time is from about 20 seconds to about 30 seconds. In one embodiment, the purge time is from about 30 seconds to about 60 seconds. In one embodiment, the purge time is from about 60 seconds to about 120 seconds. In one embodiment, the purge time is about 0.25 seconds. In one embodiment, the purge time is about 0.5 seconds. In one embodiment, the purge time is about 1 second. In one embodiment, the purge time is about 2 seconds. In one embodiment, the purge time is about 3 seconds. In one embodiment, the purge time is about 4 seconds.

In one embodiment, the time is about 5 seconds. In one embodiment, the purge time is about 6 seconds. In one embodiment, the purge time is about 7 seconds. In one embodiment, the purge time is about 8 seconds. In one embodiment, the step purge time is about 9 seconds. In one embodiment, the purge time is about 10 seconds. In one embodiment, the purge time is about 12 seconds. In one embodiment, the purge time exposure is about 15 seconds. In one embodiment, the purge time is about 17 seconds. In one embodiment, the purge time is about 20 seconds. In one embodiment, the purge time is about 25 seconds. In one embodiment, the purge time is about 30 seconds. In one embodiment, the purge time is about 35 seconds. In one embodiment, the purge time is about 40 seconds. In one embodiment, the purge time is about 50 seconds. In one embodiment, the purge time is about 60 seconds. In one embodiment, the purge time is about 75 seconds. In one embodiment, the purge time is about 90 seconds. In one embodiment, the purge time is about 120 seconds. In one embodiment, each of the purge steps uses about the same purge time.

[0119] Flow Rate

[0120] In one embodiment, the purge gas is flowed at from about 100 sccm to about 5000 sccm. In one embodiment, the purge gas is flowed at from about 500 sccm to about 2500 sccm. In one embodiment, the purge gas is flowed at from about 1000 sccm to about 2000 sccm. In one embodiment, the purge gas is flowed at about 100 sccm. In one embodiment, the purge gas is flowed at about 200 sccm. In one embodiment, the purge gas is flowed at about 300 sccm. In one embodiment, the purge gas is flowed at about 400 sccm. In one embodiment, the purge gas is flowed at about 500 sccm. In one embodiment, the purge gas is flowed at about 1000 sccm. In one embodiment, the purge gas is flowed at about 1500 sccm. In one embodiment, the purge gas is flowed at about 2000 sccm. In one embodiment, the purge gas is flowed at about 2500 sccm. In one embodiment, the purge gas is flowed at about 3000 sccm. In one embodiment, the purge gas is flowed at about 3500 sccm. In one embodiment, the purge gas is flowed at about 4000 sccm. In one embodiment, the purge gas is flowed at about 4500 sccm. In one embodiment, the purge gas is flowed at about 5000 sccm.

[0121] Pressure

[0122] The purge steps can be carried out at any suitable chamber pressure. In one embodiment, the pressure is from about 0.05 torr to 5 torr. In one embodiment, the pressure is from about 1 torr to about 5 torr. In one embodiment, the pressure is from about 1 torr to about 2 torr. In one embodiment, the pressure is from about 0.5 torr to about 5 torr. In one embodiment, the pressure is from about 0.05 torr to about 2 torr. In one embodiment, the pressure is about 0.05 torr. In one embodiment, the pressure is about 0.1 torr. In one embodiment, the pressure is about 0.2 torr. In one embodiment, the pressure is

about 0.5 torr. In one embodiment, the pressure is about 1 torr. In one embodiment, the pressure is about 1.5 torr. In one embodiment, the pressure is about 2 torr. In one embodiment, the pressure is about 2.5 torr. In one embodiment, the pressure is about 5 torr.

[0123] Post-Etch Treatment

[0124] As noted above, the disclosed and claimed Process II can further include, consist essentially of or consist of an optional step (vii) oxidizing post-treatment to remove impurities remaining on the metal oxide surface following a number of cycles. In one aspect of this embodiment, the optional step (vii) post-treatment includes treatment of the metal oxide surface with one or more oxidant for a desired period of time (*e.g.*, about 10 seconds to about 500 seconds). In one aspect of this embodiment, the optional step (vii) post-treatment includes treatment of the metal oxide surface with one or more of oxygen (O₂) and ozone (O₃) for a desired period of time (*e.g.*, about 10 seconds to about 500 seconds). In one aspect of this embodiment, the optional step (vii) post-treatment includes treatment of the metal oxide surface with oxygen (O₂). In one aspect of this embodiment, the optional step (vii) post-treatment includes treatment of the metal oxide surface with ozone (O₃). In one aspect of this embodiment, the optional step (vii) post-treatment includes treatment of the metal oxide surface with a combination of oxygen (O₂) and ozone (O₃).

[0125] Substrate Temperature

[0126] In one embodiment, the substrate is heated to a temperature from about 100 °C to about 450 °C. In one embodiment, the substrate is heated to a temperature of about 100 °C. In one embodiment, the substrate is heated to a temperature of about 150 °C. In one embodiment, the substrate is heated to a temperature of about 200 °C. In one embodiment, the substrate is heated to a temperature of about 250 °C. In one embodiment, the substrate is heated to a temperature of about 300 °C. In one embodiment, the chamber inner heater is set at about 350 °C. In one embodiment, the substrate is heated to a temperature of about 400 °C. In one embodiment, the substrate is heated to a temperature of about 450 °C.

[0127] Film Properties

[0128] The disclosed and claimed subject matter further includes films prepared by the methods described herein.

[0129] Film Aspect Ratio

[0130] In one embodiment, the films etched by the methods described herein have trenches, vias or other topographical features with an aspect ratio of about 0 to about 60. In a further aspect of this embodiment, the aspect ratio is about 1 to about 10. In a further aspect of this embodiment, the aspect ratio

is about 10 to 100. In a further aspect of this embodiment, the aspect ratio is about 0. In a further aspect of this embodiment, the aspect ratio is about 1. In a further aspect of this embodiment, the aspect ratio is about 2. In a further aspect of this embodiment, the aspect ratio is about 5. In a further aspect of this embodiment, the aspect ratio is about 10. In a further aspect of this embodiment, the aspect ratio is about 20. In a further aspect of this embodiment, the aspect ratio is about 30. In a further aspect of this embodiment, the aspect ratio is about 40. In a further aspect of this embodiment, the aspect ratio is about 50. In a further aspect of this embodiment, the aspect ratio is about 60. In a further aspect of this embodiment, the aspect ratio is about 80. In a further aspect of this embodiment, the aspect ratio is about 100.

[0131] Dielectric Constant

[0132] In another embodiment, the films etched by the methods described herein have a dielectric constant of between 5 and 10. In another embodiment, the films etched by the methods described herein have a dielectric constant of between 10 and 30. In another embodiment, the films etched by the methods described herein have a dielectric constant of between 30 and 50. In another embodiment, the films etched by the methods described herein have a dielectric constant of between 50 and 80. In another embodiment, the films etched by the methods described herein have a dielectric constant of about 1.5. In another embodiment, the films etched by the methods described herein have a dielectric constant of about 2. In another embodiment, the films etched by the methods described herein have a dielectric constant of about 3. In another embodiment, the films etched by the methods described herein have a dielectric constant of about 4. In another embodiment, the films etched by the methods described herein have a dielectric constant of about 5. In another embodiment, the films etched by the methods described herein have a dielectric constant of about 6. In another embodiment, the films etched by the methods described herein have a dielectric constant of about 7. In another embodiment, the films etched by the methods described herein have a dielectric constant of about 8. In another embodiment, the films etched by the methods described herein have a dielectric constant of about 9. In another embodiment, the films etched by the methods described herein have a dielectric constant of about 10. In another embodiment, the films etched by the methods described herein have a dielectric constant of about 12. In another embodiment, the films etched by the methods described herein have a dielectric constant of about 14. In another embodiment, the films etched by the methods described herein have a dielectric constant of about 16. In another embodiment, the films etched by the methods described herein have a dielectric constant of about 18. In another embodiment, the films etched by the methods described herein have a dielectric constant of about 20. In another embodiment, the films etched by the methods described herein have a dielectric constant of about 25. In another embodiment, the films etched by the methods described herein have a dielectric constant of about

30. In another embodiment, the films etched by the methods described herein have a dielectric constant of about 35. In another embodiment, the films etched by the methods described herein have a dielectric constant of about 40. In another embodiment, the films etched by the methods described herein have a dielectric constant of about 45. In another embodiment, the films etched by the methods described herein have a dielectric constant of about 50. In another embodiment, the films etched by the methods described herein have a dielectric constant of about 55. In another embodiment, the films etched by the methods described herein have a dielectric constant of about 60. In another embodiment, the films etched by the methods described herein have a dielectric constant of about 65. In another embodiment, the films etched by the methods described herein have a dielectric constant of about 70. In another embodiment, the films etched by the methods described herein have a dielectric constant of about 75. In another embodiment, the films etched by the methods described herein have a dielectric constant of about 80.

[0133] Crystal Structure

[0134] In one embodiment, the films etched by the methods described herein are crystalline, with a desired crystal structure constituting the majority of the film. In one embodiment, a cubic crystal structure constitutes the majority of a film composed of ZrO_2 , HfO_2 , a combination of HfO_2 and ZrO_2 , or any of these materials with engineered impurities (*i.e.*, dopants). In one embodiment, a tetragonal crystal structure constitutes the majority of a film composed of ZrO_2 , HfO_2 , a combination of HfO_2 and ZrO_2 , or any of these materials with engineered impurities (*i.e.*, dopants). In one embodiment, an orthorhombic crystal structure constitutes the majority of a film composed of ZrO_2 , HfO_2 , a combination of HfO_2 and ZrO_2 , or any of these materials with engineered impurities (*i.e.*, dopants). In one embodiment, a noncentrosymmetric crystal structure constitutes the majority of a film composed of ZrO_2 , HfO_2 , a combination of HfO_2 and ZrO_2 , or any of these materials with engineered impurities (*i.e.*, dopants). In one embodiment, a desired crystal structure constitutes about 50% to about 90% of the film. In one embodiment, a desired crystal structure constitutes about 90% to about 95% of the film. In one embodiment, a desired crystal structure constitutes about 95% to about 100% of the film.

[0135] MIMcap Devices

[0136] In another aspect, the disclosed and claimed subject matter relates to a metal-insulator-metal capacitor (“MIMcap”) device including, consisting essentially of or consisting of a first electrode, a dielectric layer made using the disclosed and claimed ALE processes, and a second electrode. In a further aspect, the MIMcap devices ideally demonstrate a higher dielectric constant (k) and lower leakage current than an otherwise equivalent MIMcap made without using the disclosed and claimed ALE processes.

[0137] In a further aspect, the first electrode and the second electrode are independently selected from TiN, W, Ni, Ru, Pt, and Al.

[0138] In a further aspect, the first electrode and the second electrode are TiN. In a further aspect, the thickness of the starting dielectric layer prior to ALE is between about 5 nm and about 10 nm. In a further aspect, the thickness of the etched dielectric layer is between about 1 nm and about 6 nm.

[0139] In a further aspect, the capacitors have an ultrathin (< 5 nm) ZrO₂ dielectric layer with superior properties (*i.e.*, lower leakage current, higher *k*) vs. similar capacitors produced by other methods.

[0140] **EXAMPLES**

[0141] 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 below to more fully illustrate the disclosed subject matter and should not be construed as limiting the disclosed subject matter in any way.

[0142] 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.

[0143] **Materials and Methods:**

[0144] The ALE process includes repeated cycles of exposing the material to be etched to different vapor-phase reactants in a vacuum chamber. After each exposure, the chamber is purged by inert gas to remove excess reactants and reaction products.

[0145] The following Examples were performed in an ALD system with a showerhead lid which was heated to 130 °C. This ALD system has capability to accommodate up to 300mm diameter wafer sizes. This ALD system has a heated pedestal upon which the wafer is disposed. For each experiment, a 44mm x 44mm test substrate was disposed on a first 300mm silicon carrier wafer.

[0146] Ishikawa’s reagent and thionyl chloride were obtained from MilliporeSigma. Ishikawa’s reagent was maintained in a stainless-steel ampule at 35 °C. Thionyl chloride was maintained in a stainless-steel ampule at 30 °C.

[0147] **Experimental Conditions for Examples 1 and 2:**

Step	Conditions
(i)	Three 2-second doses of Ishikawa’s reagent vapor, diluted in 400 sccm of argon, with the chamber pressure maintained at 2000 mTorr

(ii)	A first reactor purge of about 2000 sccm of argon for 60 seconds
(iii)	One 5-second dose of thionyl chloride vapor, diluted in 600 sccm of argon, with the chamber pressure maintained at 2000 mTorr
(iv)	A second reactor purge of about 2000 sccm of argon for 60 seconds
(v)	One 15-second dose of 800 sccm 20% O ₃ + 80% O ₂ (<i>i.e.</i> , 160 sccm O ₃ + 640 sccm O ₂) with the chamber pressure maintained at 2000 mTorr
(vi)	A second reactor purge of about 2000 sccm of argon for 60 seconds

[0148] Experimental Conditions for Examples 3 and 4:

Step	Conditions
(i)	Three 2-second doses of Ishikawa's reagent vapor, diluted in 400 sccm of argon, with the chamber pressure maintained at 2000 mTorr
(ii)	A first reactor purge of about 2000 sccm of argon for 60 seconds
(iii)	One 5-second dose of thionyl chloride vapor, diluted in 600 sccm of argon, with the chamber pressure maintained at 2000 mTorr
(iv)	A second reactor purge of about 2000 sccm of argon for 60 seconds
(v)	One 15-second dose of either: 800 sccm O ₂ ; or, 800 sccm 4% O ₃ + 96% O ₂ (<i>i.e.</i> , 32 sccm O ₃ + 768 sccm O ₂) with the chamber pressure maintained at 2000 mTorr
(vi)	A second reactor purge of about 2000 sccm of argon for 60 seconds

[0149] Experimental Conditions for Examples 5 and 6:

Step	Conditions
(i)	Five 2-second doses of Ishikawa's reagent vapor, diluted in 400 sccm of argon, with the chamber pressure maintained at 2000 mTorr
(ii)	A first reactor purge of about 2000 sccm of argon for 60 seconds
(iii)	Five 5-second doses of thionyl chloride vapor, diluted in 600 sccm of argon, with the chamber pressure maintained at 2000 mTorr
(iv)	A second reactor purge of about 2000 sccm of argon for 60 seconds
(v)	Omitted
(vi)	Omitted

[0150] Experimental Conditions for Examples 7 and 8:

Step	Conditions
(i)	Three 2-second doses of Ishikawa's reagent vapor, diluted in 400 sccm of argon, with the chamber pressure maintained at 2000 mTorr
(ii)	A first reactor purge of about 2000 sccm of argon for 60 seconds
(iii)	One 2-second dose of dimethylaluminum chloride (DMAC) vapor, diluted in 700 sccm argon, with the chamber pressure maintained at 2000 mTorr

(iv)	A second reactor purge of about 2000 sccm of argon for 60 seconds
(v)	One 15-second dose of 800 sccm 20% O ₃ + 80% O ₂ (<i>i.e.</i> , 160 sccm O ₃ + 640 sccm O ₂) with the chamber pressure maintained at 2000 mTorr
(vi)	A third reactor purge using argon for 60 seconds

[0151] **Experimental Conditions for Examples 9 and 10:**

[0152] For prophetic Examples 9 and 10, the general form of steps (i) through (vi) is used, but with alternate chemicals, and without specific restriction on flows, concentrations, dose times, etc.

[0153] **Experimental Conditions for Example 11:**

Step	Conditions
(a)	One 5-second dose of thionyl chloride vapor, diluted in about 1700 sccm of argon, with the chamber pressure maintained at 2000 mTorr
(b)	A reactor purge of about 2500 sccm of argon for 60 seconds

[0154] **Example 1: ALE of ZrO₂ by Ishikawa's Reagent, SOCl₂ and Ozone**

[0155] Test substrates were prepared by ALD of ZrO₂ atop a 300 mm silicon wafer, which was subsequently cleaved into 44 mm x 44 mm test substrates. Film thicknesses were about 54–60 Å of ZrO₂. 10 to 30 ALE cycles were performed with the process chamber pedestal heater set at either 315 °C, 345 °C or 375 °C, corresponding to a calibrated sample temperature of about 300 °C, 325 °C or 350 °C, respectively. Results are shown in Table 1 below. Significant etch was observed from 300 °C to 350 °C, with increasing etch amount with increasing temperature. A linear fit to the data at 350 °C indicates an ZrO₂ etch per cycle of about 1.5 Å/cycle with an etch delay of about 3 cycles.

Number of ALE Cycles	Sample Temperature (°C)	ZrO ₂ Removed (Å)
30	300	4 ± 2
30	325	17 ± 2
10	350	11 ± 2
20	350	27 ± 2
30	350	43 ± 2
30 (repeat of above)	350	40 ± 2

Table 1

[0156] As shown in FIG. 1, X-ray photoelectron spectroscopy (XPS) was measured for samples that underwent 10, 20, or 30 ALE cycles at 350 °C. Compared to a similar sample that did not undergo ALE, each of these samples has a measurable quantity of fluorine. Without being bound by theory, this may be due to formation of a surface oxyfluoride which is not completely removed by

the chlorinating step. Increasing cycle counts result in slightly elevated surface carbon residues. Each of the samples is substantially free of nitrogen or sulfur surface residues.

[0157] Example 2: ALE of HfO₂ by Ishikawa's Reagent, SOCl₂ and Ozone

[0158] Test substrates were prepared by ALD of HfO₂ atop a 300 mm silicon wafer, which was subsequently cleaved into 44 mm x 44 mm test substrates. Film thicknesses were about 46–48 Å of HfO₂. 10 to 50 ALE cycles of process steps (i) through (vi) were performed with the process chamber pedestal heater set at either 315 °C, 345 °C or 375 °C, corresponding to a calibrated sample temperature of about 300 °C, 325 °C or 350 °C, respectively. Results are shown in Table 2 below. Significant etch was observed from 325 °C to 350 °C, with increasing etch amount with increasing temperature. A linear fit to the data at 350 °C indicates an HfO₂ etch per cycle of about 0.5 Å/cycle with an etch delay of about 4 cycles.

Number of ALE cycles	Sample temperature (°C)	HfO ₂ removed (Å)
30	300	~0
30	325	3 ± 2
10	350	3 ± 2
20	350	8 ± 2
30	350	12 ± 2
40	350	18 ± 2
50	350	23 ± 2

Table 2

[0159] Example 3: ALE of ZrO₂ by Ishikawa's Reagent and SOCl₂ with Alternate Oxidants

[0160] Test substrates were prepared by ALD of ZrO₂ atop a 300 mm silicon wafer, which was subsequently cleaved into 44 mm x 44 mm test substrates. Film thicknesses were about 65 Å of ZrO₂. 30 ALE cycles were performed with the process chamber pedestal heater set at 375 °C, corresponding to a calibrated sample temperature of about 350 °C. The oxidant used in step (v) was replaced with either O₂ or a mixture of about 4% O₃ + about 96% O₂. With O₂ as the oxidant, about 5 ± 2 Å ZrO₂ was removed. With a mixture of about 4% O₃ + about 96% O₂ as the oxidant, about 37 ± 2 Å ZrO₂ was removed.

[0161] Example 4: ALE of HfO₂ by Ishikawa's Reagent and SOCl₂ with Alternate Oxidants

[0162] Test substrates were prepared by ALD of HfO₂ atop a 300 mm silicon wafer, which was subsequently cleaved into 44 mm x 44 mm test substrates. Film thicknesses were about 47 Å of HfO₂. 30 ALE cycles were performed with the process chamber pedestal heater set at 375 °C,

corresponding to a calibrated sample temperature of about 350 °C. The oxidant used in step (v) was replaced with either O₂ or a mixture of about 4% O₃ + about 96% O₂. With O₂ as the oxidant, no significant amount of HfO₂ was removed. With a mixture of about 4% O₃ + about 96% O₂ as the oxidant, about 10 ± 2 Å HfO₂ was removed.

[0163] Example 5: ALE of ZrO₂ by Ishikawa's Reagent and SOCl₂ with No Oxidation Step

[0164] Test substrates were prepared by ALD of ZrO₂ atop a 300 mm silicon wafer, which was subsequently cleaved into 44 mm x 44 mm test substrates. Film thicknesses were about 56 Å of ZrO₂. Either 30, 60, or 90 ALE cycles were performed with the process chamber pedestal heater set at 375 °C, corresponding to a calibrated sample temperature of about 350 °C. Steps (v) and (vi) were omitted from the ALE process cycle, *i.e.*, only process steps (i) through (iv) were cycled. Dose counts for steps (i) and (iii) were increased as described above.

[0165] After 30 ALE cycles, about 16 ± 2 Å ZrO₂ was removed. After 60 ALE cycles, about 27 ± 2 Å ZrO₂ was removed. After 90 ALE cycles, about 32 ± 2 Å ZrO₂ was removed.

[0166] As shown in FIG. 2, X-ray photoelectron spectroscopy (XPS) was measured for samples that underwent 30, 60, or 90 ALE cycles of process steps (i) through (iv) at 350 °C. Compared to a similar sample that did not undergo ALE, each of these samples has a measurable quantity of fluorine. Without being bound by theory, this may be due to formation of a surface oxyfluoride which is not completely removed by the chlorinating step. There are measurable quantities of carbon, nitrogen, and sulfur residues which increase with increasing ALE cycle counts. This data suggests that without an oxidizing step (process step (v) above), accumulating light element residues prevent etch, either by blocking the surface and/or providing alternate surface reaction pathways which do not etch the surface.

[0167] Example 6: ALE of HfO₂ by Ishikawa's Reagent and SOCl₂ with No Oxidation Step

[0168] Test substrates were prepared by ALD of HfO₂ atop a 300 mm silicon wafer, which was subsequently cleaved into 44 mm x 44 mm test substrates. Film thicknesses were about 46 – 47 Å of HfO₂. Either 30, 60, or 90 ALE cycles were performed with the process chamber pedestal heater set at 375 °C, corresponding to a calibrated sample temperature of about 350 °C. Steps (v) and (vi) were omitted from the ALE process cycle, *i.e.*, only process steps (i) through (iv) were cycled. Dose counts for steps (i) and (iii) were increased as described above.

[0169] After 30 ALE cycles, about 3 ± 2 Å HfO₂ was removed. After 60 ALE cycles, about 5 ± 2 Å HfO₂ was removed. After 90 ALE cycles, about 6 ± 2 Å HfO₂ was removed.

[0170] Example 7: ALE of ZrO₂ by Ishikawa's Reagent, DMAC and Ozone

[0171] Test substrates were prepared by ALD of ZrO₂ atop a 300 mm silicon wafer, which

was subsequently cleaved into 44 mm x 44 mm test substrates. Film thickness was about 65 Å of ZrO₂. 30 ALE cycles were performed with the process chamber pedestal heater set at 375 °C, corresponding to a calibrated sample temperature of about 350 °C. As described above, the ALE cycle was modified such that in step (iii), dimethylaluminum chloride (DMAC) was dosed instead of SOCl₂.

[0172] After 30 ALE cycles, about 27 ± 2 Å ZrO₂ was removed.

[0173] **Example 8: ALE of HfO₂ by Ishikawa's Reagent, DMAC and Ozone**

[0174] Test substrates were prepared by ALD of HfO₂ atop a 300 mm silicon wafer, which was subsequently cleaved into 44 mm x 44 mm test substrates. Film thickness was about 47 Å of HfO₂. 30 ALE cycles were performed with the process chamber pedestal heater set at 375 °C, corresponding to a calibrated sample temperature of about 350 °C. As described above, the ALE cycle was modified such that in step (iii), dimethylaluminum chloride (DMAC) was dosed instead of SOCl₂.

[0175] After 30 ALE cycles, about 8 ± 2 Å HfO₂ was removed.

[0176] **Example 9: ALE of ZrO₂ and HfO₂ Using Bifluoride Salts, a Chlorinator and Ozone**

[0177] In a prophetic example, test substrates can be prepared by ALD of a thin film of HfO₂ or ZrO₂ atop a silicon substrate. 5 to 100 ALE cycles can be performed with the sample at a temperature between about 200 °C and about 400 °C. The ALE cycle can include six steps: (i) a first dose of anhydrous HF vapor from a vessel containing a bifluoride salt; (ii) a first purge; (iii) a second dose of a chlorinator; (iv) a second purge; (v) a third dose of an oxidant; (vi) a third purge. The bifluoride salt can include ammonium bifluoride (NH₄HF₂), sodium bifluoride (NaHF₂), potassium bifluoride (KHF₂) or a mixture thereof. The chlorinator can include thionyl chloride or dimethylaluminum chloride. The oxidant can include ozone and oxygen gas. An etch per cycle of between about 0.5 Å/cycle and about 5.0 Å/cycle is expected.

[0178] **Example 10: ALE of ZrO₂ and HfO₂ Using a Liquid Source of Anhydrous HF, a Chlorinator and Ozone**

[0179] In a prophetic example, test substrates can be prepared by ALD of a thin film of HfO₂ or ZrO₂ atop a silicon substrate. 5 to 100 ALE cycles can be performed with the sample at a temperature between about 200 °C and about 400 °C. The ALE cycle can include six steps: (i) a first dose of vapor from a vessel containing a liquid fluorinator; (ii) a first purge; (iii) a second dose of a chlorinator; (iv) a second purge; (v) a third dose of an oxidant; (vi) a third purge. The liquid fluorinator can include triethylamine trifluoride (TREAT-HF), hydrogen fluoride pyridine (HF-pyridine), or a mixture of thereof. The chlorinator can include thionyl chloride or dimethylaluminum chloride. The oxidant can include ozone and/or oxygen gas. An etch per cycle of between about 0.5 Å/cycle

and about 5.0 Å/cycle is expected.

[0180] Example 11: Thermal Vapor-Phase Etch of Co, Mo and W Native Oxides Using a Chlorinator

[0181] Test substrates were prepared by physical vapor deposition (PVD) of Co, Mo, or W. For Co, about 165 – 180 Å of Co was deposited as a blanket film atop about 3000 Å of thermally grown SiO₂ on a 200mm silicon wafer, which was subsequently cleaved into 44 mm x 44 mm test substrates. For Mo, circular spots of about 200 Å of Mo, with diameter of about 45 mm, were deposited atop about 3000 Å of thermally grown SiO₂ on a 300mm silicon wafer, which was subsequently cleaved into 44 mm x 44 mm test substrates, with each test substrate centered on one Mo spot. For W, circular spots of about 200 Å of W, with diameter of about 45 mm, were deposited atop about 3000 Å of thermally grown SiO₂ on a 300mm silicon wafer, which was subsequently cleaved into 44 mm x 44 mm test substrates, with each test substrate centered on one W spot. All substrates had been exposed to ambient air at room temperature for over 1000 hours, resulting in formation of a native oxide. 20, 40, or 60 vapor etch cycles were performed with the process chamber pedestal set at 325 °C, corresponding to a calibrated sample temperature of about 310 °C. Results are shown in Table 3 below. The results are reported as measured using X-ray fluorescence calibrated to metal thickness, *i.e.*, the actual thickness of removed native oxide, with lower metal atom density vs. the metal, would be greater than reported below. The greatest etch was observed for Mo, followed by W. There is minimal effect on Co under the test conditions. The etch is limited to the surface layer, as indicated by the stable amount of material etched with increasing etch cycle count. No increase in metal resistivity was observed.

Number of ALE Cycles	Co removed (Å), metal equivalent	Mo removed (Å), metal equivalent	W Removed (Å), metal equivalent
20	1 ± 2	13 ± 3	8 ± 11
40	2 ± 1	17 ± 6	8 ± 8
60	2 ± 1	18 ± 4	10 ± 8

Table 3

[0182] As shown in Examples 1-10 above, the ALE process can be readily controlled (*i.e.*, tailored) to provide a specific amount of etch for desired applications. The choices of surface modification agent(s), volatilizing agent(s), and oxidant(s) are expected to influence the etch characteristics, including etch per cycle and selectivity. This flexibility enables etch of metal oxides for several applications, particularly in semiconductor devices, such as the thinning of high-*k* oxides in high aspect ratio structures or oxide ferroelectrics with strict requirements on composition and crystallinity.

[0183] Surface modification agents are proposed which either do not contain metals, or from which metal-free surface modification vapors may be obtained through decomposition of the original agent (*e.g.*, $\text{KHF}_2(\text{s}) \rightarrow \text{KF}(\text{s}) + \text{HF}(\text{g})$). Some of these agents, which are liquid or solid at standard temperature and pressure, may be packaged in a vessel such as an ampoule. This form of chemical storage & delivery may be safer and more readily deployed, compared to an agent which is a gas at standard temperature and pressure.

[0184] As shown in Example 11 above, the volatilizing agents disclosed & claimed herein are capable of selective removal of oxides formed on metal surfaces. These oxides may be byproducts, potentially formed due to air exposure of a metal. Such oxides can cause undesirable effects such as high contact resistance between the oxidized metal and a second metal deposited in contact with the oxidized metal. The selective vapor-phase volatilization of a surface compound such as a native oxide may be a convenient method of re-integrating an unfinished semiconductor device wafer which has been exposed to air.

[0185] Although the disclosed and claimed subject matter has been described and illustrated with a certain degree of particularity, it is understood that the disclosure has been made only by way of example, and that numerous changes in the conditions and order of steps can be resorted to by those skilled in the art without departing from the spirit and scope of the disclosed and claimed subject matter.

Claims

What is claimed is:

1. A vapor-phase etch process comprising the steps of:
 - (a) a volatilization that includes exposing a metal oxide-containing surface or a metal fluoride-containing surface to one or more chlorine-supplying volatilizing agent to produce one or more chlorine-containing volatile byproduct containing one or more metals from the metal oxide-containing surface or the metal fluoride-containing surface; and
 - (b) an optional purge.
2. A vapor-phase etch process comprising the steps of:
 - (i) a surface modification comprising exposing a metal oxide surface to one or more fluorinating surface modifying agent to produce one or more fluorinated metal compound at the surface;
 - (ii) a purge;
 - (iii) a volatilization comprising exposing the fluorinated metal compound to one or more chlorine-supplying volatilizing agent to produce one or more chlorine-containing volatile byproduct containing one or more metals of the fluorinated metal compound;
 - (iv) a purge;
 - (v) a surface cleaning comprising exposing the surface to one or more oxidants to remove contaminants and convert at least a portion of the surface to a metal oxide; and
 - (vi) a purge.
3. The process of claim 2, further comprising step (vii) an oxidizing post-treatment to remove impurities remaining on the surface.
4. The process of claim 1 or 2, wherein the metal oxide-containing surface, the metal fluoride-containing surface or the metal oxide surface comprises one or more of zirconium (Zr), hafnium (Hf), aluminum (Al), titanium (Ti), cobalt (Co), nickel (Ni), molybdenum (Mo), ruthenium (Ru), tungsten (W) and combinations thereof.
5. The process of claim 1, wherein the metal oxide-containing surface or the metal fluoride-containing surface comprises cobalt (Co).
6. The process of claim 1, wherein the metal oxide-containing surface or the metal fluoride-containing surface comprises nickel (Ni).
7. The process of claim 1, wherein the metal oxide-containing surface or the metal fluoride-containing surface comprises molybdenum (Mo).
8. The process of claim 1, wherein the metal oxide-containing surface or the metal fluoride-

containing surface comprises ruthenium (Ru).

9. The process of claim 1, wherein the metal oxide-containing surface or the metal fluoride-containing surface comprises tungsten (W).
10. The process of claim 2, wherein the metal oxide surface comprises cobalt (Co).
11. The process of claim 2, wherein the metal oxide surface comprises nickel (Ni).
12. The process of claim 2, wherein the metal oxide surface comprises molybdenum (Mo).
13. The process of claim 2, wherein the metal oxide surface comprises ruthenium (Ru).
14. The process of claim 2, wherein the metal oxide surface comprises tungsten (W).
15. The process of claim 2, wherein the metal oxide comprises one or more of ZrO_2 , HfO_2 , $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ where x is a value between 0 and 1, TiO_2 , Al_2O_3 and combinations thereof.
16. The process of claim 2, wherein the metal oxide surface comprises ZrO_2 .
17. The process of claim 2, wherein the metal oxide surface comprises HfO_2 .
18. The process of claim 2, wherein the metal oxide surface comprises $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ where x is a value between 0 and 1.
19. The process of claim 2, wherein the metal oxide surface comprises TiO_2 .
20. The process of claim 2, wherein the metal oxide surface comprises Al_2O_3 .
21. The process of claim 2, wherein the step (i) one or more fluorinating surface modifying agent comprises one or more metal-free fluorides.
22. The process of claim 2, wherein the step (i) one or more fluorinating surface modifying agent comprises one or more of Ishikawa's reagent, ammonium bifluoride, sodium bifluoride, potassium bifluoride, hydrogen fluoride pyridine, triethylamine trishydrofluoride, hydrogen fluoride and combinations thereof.
23. The process of claim 2, wherein the step (i) one or more fluorinating surface modifying agent comprises two or more of Ishikawa's reagent, ammonium bifluoride, sodium bifluoride, potassium bifluoride, hydrogen fluoride pyridine, triethylamine trishydrofluoride and hydrogen fluoride.
24. The process of claim 2, wherein the step (i) one or more fluorinating surface modifying agent comprises Ishikawa's reagent.
25. The process of claim 2, wherein the step (i) one or more fluorinating surface modifying agent comprises ammonium bifluoride.
26. The process of claim 2, wherein the step (i) one or more fluorinating surface modifying agent comprises sodium bifluoride.
27. The process of claim 2, wherein the step (i) one or more fluorinating surface modifying agent

comprises potassium bifluoride.

28. The process of claim 2, wherein the step (i) one or more fluorinating surface modifying agent comprises hydrogen fluoride pyridine.

29. The process of claim 2, wherein the step (i) one or more fluorinating surface modifying agent comprises triethylamine trishydrofluoride.

30. The process of claim 2, wherein the step (i) one or more fluorinating surface modifying agent comprises hydrogen fluoride.

31. The process of claim 2, wherein the step (i) exposure time of the one or more fluorinating surface modifying agent to the surface of the metal oxide is from about 0.5 seconds to about 30 seconds.

32. The process of claim 2, wherein the step (i) exposure time of the one or more fluorinating surface modifying agent to the surface of the metal oxide is about 0.5 seconds.

33. The process of claim 2, wherein the step (i) exposure time of the one or more fluorinating surface modifying agent to the surface of the metal oxide is about 1 seconds.

34. The process of claim 2, wherein the step (i) exposure time of the one or more fluorinating surface modifying agent to the surface of the metal oxide is about 5 seconds.

35. The process of claim 2, wherein the step (i) exposure time of the one or more fluorinating surface modifying agent to the surface of the metal oxide is about 10 seconds.

36. The process of claim 2, wherein the step (i) exposure time of the one or more fluorinating surface modifying agent to the surface of the metal oxide is about 15 seconds.

37. The process of claim 2, wherein the step (i) exposure time of the one or more fluorinating surface modifying agent to the surface of the metal oxide is about 20 seconds.

38. The process of claim 2, wherein the step (i) exposure time of the one or more fluorinating surface modifying agent to the surface of the metal oxide is about 25 seconds.

39. The process of claim 2, wherein the step (i) exposure time of the one or more fluorinating surface modifying agent to the surface of the metal oxide is about 30 seconds.

40. The process of claim 2, wherein the step (i) one or more fluorinating surface modifying agent is flowed at from about 0.5 sccm to about 500 sccm.

41. The process of claim 2, wherein step (i) is carried out at a pressure from about 0.5 torr to about 100 torr.

42. The process of claim 1, wherein the step (a) one or more chlorine-supplying volatilizing agent comprises one or more of dimethylaluminum chloride (DMAC; $\text{Al}(\text{CH}_3)_2\text{Cl}$), diethylaluminum chloride (DEAC; $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$), titanium tetrachloride (TiCl_4), boron trichloride (BCl_3), thionyl

chloride (SOCl_2), chlorine (Cl_2) and combinations thereof.

43. The process of claim 1, wherein the step (a) one or more chlorine-supplying volatilizing agent comprises dimethylaluminum chloride (DMAC; $\text{Al}(\text{CH}_3)_2\text{Cl}$).
44. The process of claim 1, wherein the step (a) one or more chlorine-supplying volatilizing agent comprises diethylaluminum chloride (DEAC; $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$).
45. The process of claim 1, wherein the step (a) one or more chlorine-supplying volatilizing agent comprises titanium tetrachloride (TiCl_4).
46. The process of claim 1, wherein the step (a) one or more chlorine-supplying volatilizing agent comprises boron trichloride (BCl_3).
47. The process of claim 1, wherein the step (a) one or more chlorine-supplying volatilizing agent comprises thionyl chloride (SOCl_2).
48. The process of claim 1, wherein the step (a) one or more chlorine-supplying volatilizing agent comprises chlorine (Cl_2).
49. The process of claim 1, wherein the step (a) exposure time of the one or more chlorine-supplying volatilizing agent to the surface of the metal oxide is from about 0.5 seconds to about 30 seconds.
50. The process of claim 1, wherein the step (a) exposure time of the one or more chlorine-supplying volatilizing agent to the surface of the metal oxide is about 0.5 seconds.
51. The process of claim 1, wherein the step (a) exposure time of the one or more chlorine-supplying volatilizing agent to the surface of the metal oxide is about 1 second.
52. The process of claim 1, wherein the step (a) exposure time of the one or more chlorine-supplying volatilizing agent to the surface of the metal oxide is about 5 seconds.
53. The process of claim 1, wherein the step (a) exposure time of the one or more chlorine-supplying volatilizing agent to the surface of the metal oxide is about 10 seconds.
54. The process of claim 1, wherein the step (a) exposure time of the one or more chlorine-supplying volatilizing agent to the surface of the metal oxide is about 15 seconds.
55. The process of claim 1, wherein the step (a) exposure time of the one or more chlorine-supplying volatilizing agent to the surface of the metal oxide is about 20 seconds.
56. The process of claim 1, wherein the step (a) exposure time of the one or more chlorine-supplying volatilizing agent to the surface of the metal oxide is about 55 seconds.
57. The process of claim 1, wherein the step (a) exposure time of the one or more chlorine-supplying volatilizing agent to the surface of the metal oxide is about 30 seconds.
58. The process of claim 1, wherein the step (a) one or more chlorine-supplying volatilizing agent

is flowed at from about 1 sccm to about 500 sccm.

59. The process of claim 1, wherein step (a) is carried out at a pressure from about 0.5 torr to about 100 torr.
60. The process of claim 2, wherein the step (iii) one or more chlorine-supplying volatilizing agent comprises one or more of dimethylaluminum chloride (DMAC; $\text{Al}(\text{CH}_3)_2\text{Cl}$), diethylaluminum chloride (DEAC; $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$), titanium tetrachloride (TiCl_4), boron trichloride (BCl_3), thionyl chloride (SOCl_2), chlorine (Cl_2) and combinations thereof.
61. The process of claim 2, wherein the step (iii) one or more chlorine-supplying volatilizing agent comprises dimethylaluminum chloride (DMAC; $\text{Al}(\text{CH}_3)_2\text{Cl}$).
62. The process of claim 2, wherein the step (iii) one or more chlorine-supplying volatilizing agent comprises diethylaluminum chloride (DEAC; $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$).
63. The process of claim 2, wherein the step (iii) one or more chlorine-supplying volatilizing agent comprises titanium tetrachloride (TiCl_4).
64. The process of claim 2, wherein the step (iii) one or more chlorine-supplying volatilizing agent comprises boron trichloride (BCl_3).
65. The process of claim 2, wherein the step (iii) one or more chlorine-supplying volatilizing agent comprises thionyl chloride (SOCl_2).
66. The process of claim 2, wherein the step (iii) one or more chlorine-supplying volatilizing agent comprises chlorine (Cl_2).
67. The process of claim 2, wherein the step (iii) exposure time of the one or more chlorine-supplying volatilizing agent to the surface of the metal oxide is from about 0.5 seconds to about 30 seconds.
68. The process of claim 2, wherein the step (iii) exposure time of the one or more chlorine-supplying volatilizing agent to the surface of the metal oxide is about 0.5 seconds.
69. The process of claim 2, wherein the step (iii) exposure time of the one or more chlorine-supplying volatilizing agent to the surface of the metal oxide is about 1 second.
70. The process of claim 2, wherein the step (iii) exposure time of the one or more chlorine-supplying volatilizing agent to the surface of the metal oxide is about 5 seconds.
71. The process of claim 2, wherein the step (iii) exposure time of the one or more chlorine-supplying volatilizing agent to the surface of the metal oxide is about 10 seconds.
72. The process of claim 2, wherein the step (iii) exposure time of the one or more chlorine-supplying volatilizing agent to the surface of the metal oxide is about 15 seconds.
73. The process of claim 2, wherein the step (iii) exposure time of the one or more chlorine-

supplying volatilizing agent to the surface of the metal oxide is about 20 seconds.

74. The process of claim 2, wherein the step (iii) exposure time of the one or more chlorine-supplying volatilizing agent to the surface of the metal oxide is about 55 seconds.

75. The process of claim 2, wherein the step (iii) exposure time of the one or more chlorine-supplying volatilizing agent to the surface of the metal oxide is about 30 seconds.

76. The process of claim 2, wherein the step (iii) one or more chlorine-supplying volatilizing agent is flowed at from about 1 sccm to about 500 sccm.

77. The process of claim 2, wherein step (iii) is carried out at a pressure from about 0.5 torr to about 100 torr.

78. The process of claim 2, wherein the step (v) one or more oxidants comprises one or more of oxygen (O_2), ozone (O_3), water (H_2O) vapor, hydrogen peroxide (H_2O_2), oxygen plasma (O^*), N_xO_y wherein $x = 1$ or 2 and $y = 1, 2, 3$ or 4 , nitric oxide (NO), and combinations thereof.

79. The process of claim 2, wherein the step (v) one or more oxidants comprises oxygen (O_2).

80. The process of claim 2, wherein the step (v) one or more oxidants comprises ozone (O_3).

81. The process of claim 2, wherein the step (v) one or more oxidants comprises nitric oxide (NO).

82. The process of claim 2, wherein the step (v) one or more oxidants comprises water (H_2O) vapor.

83. The process of claim 2, wherein the step (v) one or more oxidants comprises hydrogen peroxide (H_2O_2).

84. The process of claim 2, wherein the step (v) one or more oxidants comprises oxygen plasma (O^*).

85. The process of claim 2, wherein the step (v) one or more oxidants comprises N_xO_y wherein $x = 1$ or 2 and $y = 1, 2, 3$ or 4 .

86. The process of claim 2, wherein the step (v) exposure time of the one or more oxidants is from about 1 second to about 60 seconds.

87. The process of claim 2, wherein the step (v) exposure time of the one or more oxidants is about 1 seconds.

88. The process of claim 2, wherein the step (v) exposure time of the one or more oxidants is about 5 seconds.

89. The process of claim 2, wherein the step (v) exposure time of the one or more oxidants is about 10 seconds.

90. The process of claim 2, wherein the step (v) exposure time of the one or more oxidants is about 15 seconds.

91. The process of claim 2, wherein the step (v) exposure time of the one or more oxidants is about

20 seconds.

92. The process of claim 2, wherein the step (v) exposure time of the one or more oxidants is about 30 seconds.

93. The process of claim 2, wherein the step (v) exposure time of the one or more oxidants is about 60 seconds.

94. The process of claim 2, wherein the step (v) one or more oxidants is flowed at from about 10 sccm to about 1000 sccm.

95. The process of claim 2, wherein step (v) is carried out at a pressure from about 0.5 torr to about 100 torr.

96. The process of claim 1 or 2, wherein the substrate is heated to a temperature from about 100 °C to about 450 °C.

97. The process of claim 1 or 2, wherein the substrate is heated to a temperature of about 100 °C.

98. The process of claim 1 or 2, wherein the substrate is heated to a temperature of about 150 °C.

99. The process of claim 1 or 2, wherein the substrate is heated to a temperature of about 200 °C.

100. The process of claim 1 or 2, wherein the substrate is heated to a temperature of about 250 °C.

101. The process of claim 1 or 2, wherein the substrate is heated to a temperature of about 300 °C.

102. The process of claim 1 or 2, wherein the substrate is heated to a temperature of about 350 °C.

103. The process of claim 1 or 2, wherein the substrate is heated to a temperature of about 400 °C.

104. The process of claim 1 or 2, wherein the substrate is heated to a temperature of about 450 °C.

105. The process of claim 1 or 2, wherein the process comprises about 100 to about 1000 cycles.

106. The process of claim 1 or 2, wherein the process comprises about 25 to about 250 cycles.

107. The process of claim 1 or 2, wherein the process comprises about 5 to about 50 cycles.

108. The process of claim 1 or 2, wherein the process comprises about 5 cycles.

109. The process of claim 1 or 2, wherein the process comprises about 10 cycles.

110. The process of claim 1 or 2, wherein the process comprises about 20 cycles.

111. The process of claim 1 or 2, wherein the process comprises about 25 cycles.

112. The process of claim 1 or 2, wherein the process comprises about 35 cycles.

113. The process of claim 1 or 2, wherein the process comprises about 50 cycles.

114. The process of claim 1 or 2, wherein the process comprises about 75 cycles.

115. The process of claim 1 or 2, wherein the process comprises about 100 cycles.

116. The process of claim 1 or 2, wherein the process comprises about 200 cycles.

117. The process of claim 1 or 2, wherein the process comprises about 250 cycles.

- 118. The process of claim 1 or 2, wherein the process comprises about 300 cycles.
- 119. The process of claim 1 or 2, wherein the process comprises about 325 cycles.
- 120. The process of claim 1 or 2, wherein the process comprises about 400 cycles.
- 121. The process of claim 1 or 2, wherein the process comprises about 500 cycles.
- 122. The process of claim 1 or 2, wherein the process comprises about 750 cycles.
- 123. The process of claim 1 or 2, wherein the process comprises about 1000 cycles.
- 124. A metal-containing film etched by the process of any of claims 1-123, wherein the film comprises topographical features having an aspect ratio of about 0 to about 60.
- 125. A metal-containing film etched by the process of any of claims 1-123, wherein the film comprises topographical features having an aspect ratio of about 1 to about 10.
- 126. A metal-containing film etched by the process of any of claims 1-123, wherein the film comprises topographical features having an aspect ratio of about 10 to about 100.
- 127. A metal-containing film etched by the process of any of claims 1-123, wherein the film comprises topographical features having an aspect ratio of about 0.
- 128. A metal-containing film etched by the process of any of claims 1-123, wherein the film comprises topographical features having an aspect ratio of about 1.
- 129. A metal-containing film etched by the process of any of claims 1-123, wherein the film comprises topographical features having an aspect ratio of about 2.
- 130. A metal-containing film etched by the process of any of claims 1-123, wherein the film comprises topographical features having an aspect ratio of about 5.
- 131. A metal-containing film etched by the process of any of claims 1-123, wherein the film comprises topographical features having an aspect ratio of about 10.
- 132. A metal-containing film etched by the process of any of claims 1-123, wherein the film comprises topographical features having an aspect ratio of about 20.
- 133. A metal-containing film etched by the process of any of claims 1-123, wherein the film comprises topographical features having an aspect ratio of about 30.
- 134. A metal-containing film etched by the process of any of claims 1-123, wherein the film comprises topographical features having an aspect ratio of about 40.
- 135. A metal-containing film etched by the process of any of claims 1-123, wherein the film comprises topographical features having an aspect ratio of about 50.
- 136. A metal-containing film etched by the process of any of claims 1-123, wherein the film comprises topographical features having an aspect ratio of about 60.

- 137.** A metal-containing film etched by the process of any of claims 1-123, wherein the film comprises topographical features having an aspect ratio of about 80.
- 138.** A metal-containing film etched by the process of any of claims 1-123, wherein the film comprises topographical features having an aspect ratio of about 100.
- 139.** A metal-containing film etched by the process of any of claims 1-123, wherein the film has a dielectric constant of between about 5 to about 10.
- 140.** A metal-containing film etched by the process of any of claims 1-123, wherein the film has a dielectric constant of between about 10 to about 30.
- 141.** A metal-containing film etched by the process of any of claims 1-123, wherein the film has a dielectric constant of between about 30 to about 50.
- 142.** A metal-containing film etched by the process of any of claims 1-123, wherein the film has a dielectric constant of between about 50 to about 80.
- 143.** A metal-containing film etched by the process of any of claims 1-123, wherein the film has a dielectric constant of about 1.5.
- 144.** A metal-containing film etched by the process of any of claims 1-123, wherein the film has a dielectric constant of about 2.
- 145.** A metal-containing film etched by the process of any of claims 1-123, wherein the film has a dielectric constant of about 3.
- 146.** A metal-containing film etched by the process of any of claims 1-123, wherein the film has a dielectric constant of about 4.
- 147.** A metal-containing film etched by the process of any of claims 1-123, wherein the film has a dielectric constant of about 5.
- 148.** A metal-containing film etched by the process of any of claims 1-123, wherein the film has a dielectric constant of about 6.
- 149.** A metal-containing film etched by the process of any of claims 1-123, wherein the film has a dielectric constant of about 7.
- 150.** A metal-containing film etched by the process of any of claims 1-123, wherein the film has a dielectric constant of about 8.
- 151.** A metal-containing film etched by the process of any of claims 1-123, wherein the film has a dielectric constant of about 9.
- 152.** A metal-containing film etched by the process of any of claims 1-123, wherein the film has a dielectric constant of about 10.

- 153.** A metal-containing film etched by the process of any of claims 1-123, wherein the film has a dielectric constant of about 12.
- 154.** A metal-containing film etched by the process of any of claims 1-123, wherein the film has a dielectric constant of about 14.
- 155.** A metal-containing film etched by the process of any of claims 1-123, wherein the film has a dielectric constant of about 16.
- 156.** A metal-containing film etched by the process of any of claims 1-123, wherein the film has a dielectric constant of about 18.
- 157.** A metal-containing film etched by the process of any of claims 1-123, wherein the film has a dielectric constant of about 20.
- 158.** A metal-containing film etched by the process of any of claims 1-123, wherein the film has a dielectric constant of about 25.
- 159.** A metal-containing film etched by the process of any of claims 1-123, wherein the film has a dielectric constant of about 30.
- 160.** A metal-containing film etched by the process of any of claims 1-123, wherein the film has a dielectric constant of about 35.
- 161.** A metal-containing film etched by the process of any of claims 1-123, wherein the film has a dielectric constant of about 40.
- 162.** A metal-containing film etched by the process of any of claims 1-123, wherein the film has a dielectric constant of about 55.
- 163.** A metal-containing film etched by the process of any of claims 1-123, wherein the film has a dielectric constant of about 60.
- 164.** A metal-containing film etched by the process of any of claims 1-123, wherein the film has a dielectric constant of about 65.
- 165.** A metal-containing film etched by the process of any of claims 1-123, wherein the film has a dielectric constant of about 70.
- 166.** A metal-containing film etched by the process of any of claims 1-123, wherein the film has a dielectric constant of about 75.
- 167.** A metal-containing film etched by the process of any of claims 1-123, wherein the film has a dielectric constant of about 80.
- 168.** A metal-containing film etched by the process of any of claims 1-123, wherein a majority of the film has a cubic crystal structure.

- 169.** A metal-containing film etched by the process of any of claims 1-123, wherein a majority of the film has a tetragonal crystal structure.
- 170.** A metal-containing film etched by the process of any of claims 1-123, wherein a majority of the film has an orthorhombic crystal structure.
- 171.** A metal-containing film etched by the process of any of claims 1-123, wherein a majority of the film has a noncentrosymmetric crystal structure.
- 172.** A metal-insulator-metal capacitor (“MIMcap”) device comprising a first electrode, a dielectric layer made and a second electrode, where the dielectric layer is made using the process of any of claims 1-123.
- 173.** The metal-insulator-metal capacitor (“MIMcap”) device of claim 172, wherein the dielectric layer has a thickness of between about 5 nm and about 10 nm before etching using the process of any of claims 1-123.
- 174.** The metal-insulator-metal capacitor (“MIMcap”) device of claim 172, wherein the dielectric layer has a thickness of between about 1 nm and about 6 nm after etching using the process of any of claims 1-123.