

Improved Deposition of High Quality Metal Oxide and Metal Nitride Layers

Related Applications

This application claims the priority benefit of United States Provisional Patent
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Introduction

Dielectric layers of oxides and some nitrides and metal electrodes are important for the performance and functionality of microelectronic devices such as transistors and memory
10 capacitors. For example, the gate dielectric layers and gate electrode layers are critical components that are necessary for the operation of a metal-oxide-semiconductor field-effect transistor (MOSFET) devices. Likewise, a dielectric layer and an inner electrode are needed in a dynamic random-access memory (DRAM) capacitor, where they are used for storage of charge and access to the charge stored within the capacitor. To accommodate shrinking devices, the improvement of
15 deposition processes for high-permittivity (high-k) materials has experienced increased demand, especially for high-k materials used as gate insulators and capacitor dielectrics as an alternative to SiO₂. Zirconium dioxide (ZrO₂) has already been proven as a suitable high-k material and is used industrially owing to its wide band gap (~5.8 eV), high dielectric constant (17–47), and high thermal stability. Hafnium dioxide, (HfO₂) is an emerging attractive material for use as a dielectric
20 barrier in high-power SiC and GaN electronics, both MOSFET and HEMT, due to its even higher band gap, dielectric constant and thermal stability. Silicon nitride (Si₃N₄, Si_xN_y, or SiN for short), zirconium nitride (Zr₃N₄, Zr_xN_y, or ZrN for short), other metal nitrides and a wider array of metal oxynitrides are also provide sufficient dielectric properties to be applicable for certain types of microelectronic devices. Shrinking device size is accompanied by increasing aspect ratios, which
25 means higher efficiency thermal ALD systems and processes will become increasingly favorable over plasma-based processes that comprise reactive species that may extinguish prior to exposure to high aspect ratio, hidden, or otherwise challenging to reach surfaces. As with many ALD processes, the success or failure of the coatings that can be produced for a particular device or feature is oftentimes linked to the specific apparatus used for the deposition.

30 Existing thermal ALD apparatuses have struggled with the trade-off between the need to shorten reaction times and improve chemical utilization efficiency, and on the other hand, the need

to minimize purge-gas residence and chemical removal times. Certain ALD systems of the prior art contain chemical delivery manifolds using synchronized actuation of multiple valves. In such systems, satisfactory elimination of flow excursions is impossible because valve actuation with perfect synchronization is itself practically impossible. As a result, the inevitable flow excursions are notorious for generating backflow of gas that leads to adverse chemical mixing.

As a conventional ALD apparatus is utilized, “memory” effects tend to reduce the efficiency of the ALD reactor. Such memory effects are caused by the tendency of chemicals to adsorb on the walls of the ALD reactor and consequentially release from the walls of the ALD reactor on a time scale that is dictated by the adsorption energy and the temperature of the walls. This phenomenon tends to increase the residence time of trace amounts of chemicals in the ALD reactor. As a result, memory effects tend to increase the purge-time required for removal of chemicals. Thus, a need exists for an ALD apparatus that minimizes memory effects.

Thus, a need exists for an ALD apparatus that can promote faster reaction times without sacrificing precursor utilization efficiency, one that minimizes purge-gas residence and chemical removal times, and one that can improve the deposition of high-k dielectric materials (oxides, nitrides and oxynitrides) using lower cost of ownership thermal ALD processes.

Current techniques for depositing many high-k materials by thermal atomic layer deposition (ALD) tend to produce low density and performing films, and many microelectronics manufacturers have adopted plasma enhanced ALD (PEALD) processes instead. PEALD is employed to improve the performance of the films, yet the high field and fast switching requirements of the device can make the resulting dielectric barriers derived from PEALD insufficient. In addition, not all applications can accommodate plasma, resulting in damage to the incoming substrate, degrading performance. Most critically, plasma processes will have an inherent limit to the aspect ratio that can be conformally coated. At some distance from the opening, usually no greater than 10:1, 10 times deeper than the opening diameter or distance, a sufficient concentration of plasma species will fail to interact with the surface. Since PEALD relies on the amount of radical species for a saturated amount of film per cycle, as well as for compositional tuning, the PEALD film will lose thickness conformality at this point or less (less than 10x the depth of the opening). More critically, the film composition will also be a gradient as one moves down the feature in step with the plasma active species concentration. This dynamic composition can cause device failure at critical parts, such as the bottom corners of a feature. As such, there is

a need to further improve and refine thermal ALD processes that can produce superior dielectric barriers at a reduced thermal footprint.

For example, Sneh et al. (US 2003/0180458 incorporated herein by reference in its entirety) taught of an apparatus that helped solve some of the problems described above using a Synchronous Modulation of Flow and Draw (“SMFD”) approach in a thermal ALD apparatus. In the SMFD approach, the flow of process gas into the ALD chamber is referred to as “flow”; the flow of gas out of the ALD chamber is referred to as “draw”. Under steady-state conditions, the draw generally matches the flow, and during transient flow conditions, the flow and the draw can be “mismatched”. An important aspect of Sneh’s invention was that it addressed the trade-off of conventional ALD systems between the contradictory requirements of a high flow rate during a purge of the deposition chamber, and of a low flow rate during chemical dosage. SMFD provides the ability to purge a process chamber at a low-pressure and a high purge-gas flow rate, and sequentially to conduct chemical dosage in the process chamber at a high-pressure and a low flow rate of chemical reactant gas, and to modulate pressures and gas flow rates with fast response times. Sneh’s apparatus taught of a means of modulating pressure drop (ΔP) between the ALD chamber and down-stream subsystems while being able to hold the ALD chamber pressure substantially constant. A draw control chamber was incorporated into the ALD apparatus, located downstream from the ALD chamber, and the draw control chamber has an outlet with conductance, C_{Draw} . By flowing control gas into and through the draw control chamber, P_{Draw} , can be controlled independently of the pressure in the ALD chamber upstream. The flow of gas into the draw control chamber is the total of the draw from the process chamber and the directly inserted draw-gas flow. Since the draw is a function of ΔP , independent control of ΔP provided substantial matching of draw to flow independent of the flow. Since, in principle, draw chambers can be made very small, modulation of ΔP in certain embodiments can be practiced with sub-millisecond speed. The selection of a small-volume draw control chamber facilitates process conditions with short transient times, while larger draw control chambers can be employed to advantageously sacrifice draw-control speed for a secondary benefit to the system (e.g. trapping or abatement of particularly hazardous or expensive chemicals). For Sneh’s apparatus, the draw-control response time was in the 10 msec to 20 msec range in a typical 200 mm wafer deposition system. As 300 mm wafer deposition systems are becoming ubiquitous in semiconductor manufacturing, it as been

determined that Sneh's apparatus that can achieve a 10 to 20 msec range yielded an insufficient cross-plate uniformity required in 300 mm wafer production.

Sneh's SMFD approach did however facilitate a new type of ALD method at the time, Catalyzing Reactions for Induced Surface Process ("CRISP"), taught in US2003/016800 and
5 incorporated herein by reference in its entirety. Catalyzing surface reactions (CSRs) can serve as a source for hydrogen atoms, as well as other reactive species, that are necessary for nonmetal ALD reactions. In this respect, a chemical process is enhanced by the addition of one or several continuous chemical reactions that are capable of producing intermediate reactive molecular fragments. These reactive intermediates further react in the chemical process. The sole purpose of
10 these additional side-reactions is to produce reactants for the original process. CRISPs are designed to provide a volatilization path for adsorbed reactive species when the surface reactive sites are depleted. Accordingly, CRISPs are robust and can be carried excessively beyond saturation to ensure reproducible and satisfactory results, yet were limited by the availability of suitable precursors, the speed and flexibility of the SMFD process in the apparatus available at the
15 time, and the ability to generate more desirable reactive intermediates that could achieve the more stringent technical requirements such as cross-plate uniformity, film density, refractive index, permittivity, etc., for 300 mm wafer production.

Sneh's original continuous CRISP process relied on non-saturating surface chemical reaction, referred to herein with the term "catalyzing reaction". Sneh's catalyzing reactions did not,
20 by themselves, deposit solid material on the surface. A catalyzing reaction requires two or more reactive chemicals, referred to herein as "catalyzing reactants", that react with each other, preferably vigorously, to produce a stable volatile by-product molecule and an unstable surface-adsorbed intermediate reactive molecular fragment. A catalyzing reaction is thermodynamically driven and is irreversible by virtue of volatilization of the stable by-product. The reactive
25 molecular fragments generated in catalyzing reactions generally form as adsorbed radical species. These adsorbed reactive molecular fragments are atomic or molecular sections, or both. Nevertheless, when the surface contains reactive sites, a reactive fragment reacts with a reactive site in a fragment-surface reaction, typically producing a volatile surface by-product or being incorporated into a growing film, or both. Thus, a catalyzing reaction generally proceeds (cascades)
30 from catalyzing reactants to a final volatile species from both the catalyzing reaction and from the reactive sites on the surface. Sneh's catalyzing reactions were distinctively continuous, as opposed

to intermittent. Nevertheless, in most methods including a continuous catalyzing reaction is part of a process at a substrate having a saturating nature, such as an ALD reaction stage, a surface treatment step, or a surface cleaning step. Therefore, Sneh's catalyzing reactions were uniquely different from saturating ALD or substrate treatment processes of the prior art. When a saturating process that is driven by a continuous catalyzing reaction reaches saturation, the catalyzing reactions possess an additional unique characteristic; namely, they have a non-damaging path for complete volatilization of all parts of the catalyzing reactants. While saturating processes are practically implemented only approaching saturation (since ideal saturation requires infinite time), they are clearly converging. In contrast, a catalyzing reaction continued as long as the corresponding catalyzing reactants are present. Though there was a clear technical benefit to this approach at the time, it has been discovered that this creates an inherent deficiency in cross-plate uniformity as the diameter of the substrate increases, which increases the path length between the catalyzing reactant input into the reactor, and the draw control of the catalyzing reactant that removes any reactive precursors or catalyzing reactants.

Summary of the Invention

A novel conversion process, referred to as an "ICRISP" process (for Intermittent CRISP) has been developed to improve the deposition of metal oxides, metal nitrides, and metal oxynitrides with controllable O:N ratios, via thermal ALD. Utilizing the system's unique ability to intermittently introduce a small amount of non-metal catalyst during the conversion half-cycle, the new ICRISP process is able to further leverage surface catalysis to increase growth per cycle, improve stoichiometry, increase density, and modify crystal morphology compared to prior art metal oxide films. Prior art metal oxide films grown using conventional O_3 ALD, and prior art CRISP methods using O_3 with a continuous injection of a catalyst molecule, are shown in Figure 1 and Table 1 below for HfO_2 ; a comparison of the improvements to HfO_2 films grown using the ICRISP process deposited at the same temperature as the prior art films ($250^\circ C$) is shown.

The present invention overcomes the deficiencies of SMFD of the prior art in at least two ways: 1) by utilizing pressure controllers to improve the flow and flexibility of inlet gas sources, synchronously with the draw control of the prior art; and 2) by utilizing a substrate chuck having a controllable height to decrease the distance between the substrate and flow inlet(s), which increases the internal volume of the reaction chamber below the substrate.

The CRISP technique provides for superior time constant controls (1 ms to less than the 10 ms of the prior art for a 200 mm wafer system) as well as the ability to periodically pulse different gas compositions into the reaction chamber. By way of a non-limiting example of ICRISP, a small amount of monomethyl hydrazine (MMH) can be entrained periodically and/or intermittently, for
5 example ~0.03 Langmuir (from a 5 ms MMH pulse per each 45 ms of O₃) and produce superior film properties over the prior art.

ICRISP allows for substrates of various heights/dimensions to be handled without any external physical adjustments to the tool, and allowing the tool to be configured via computer control to reduce the distance between the substrate and the precursor delivery apparatus (e.g. a
10 showerhead) down to 24 mm or less or less than 10 mm, preferably less than 5 mm, more preferably 2-5 mm, and in some embodiments such as with the thermal ICRISP process, from 1.5 to 2.5 mm. In embodiments that include a plasma enhanced process, it may be advantageous for the distance between the plasma delivery apparatus and the substrate to be greater to facilitate deposition uniformity. In all embodiments, the inventive adjustable-height chuck facilitates the
15 use of alternative showerhead geometries such as a concave geometry and/or one with a slight dome, which enhances the draw control features of the system and apparatus. The concave geometry, in combination with the pressure control, facilitates a superior pressure differential between the draw control and ALD process zones that was unattainable with any prior art apparatus or system.

20 In one aspect, the invention provides an Intermittent Catalyzed Reaction Induced Surface Process (ICRISP) for producing an oxide or nitride film on a substrate, comprising: providing a substrate in a chamber; dosing the substrate with a metal-containing ALD precursor to make a first dosed substrate; purging or flushing the chamber; and either A or B: A) dosing the first dosed substrate with an oxidant and a nitrogen-containing reactant to form a metal oxide; or
25 B) dosing the first dosed substrate with a sulfur-containing reactant and a nitrogen-containing reactant to form a metal nitride; and purging or flushing the chamber.

In another aspect, the invention provides an Intermittent Catalyzed Reaction Induced Surface Process (ICRISP) for producing a film having a thickness T and composition M_xO_yN_z from a metal-containing precursor wherein x is 1 or 2, y is from 0 to 4, and z is from 0 to 2, an
30 oxygen-containing precursor, and a nitrogen-containing precursor, at a temperature of 300°C or lower, comprising the steps: a) dosing the metal-containing precursor for a pulse for time of 5

to 500 ms; b) purging and/or flushing the metal-containing precursor for a time of 250 to 30000 ms; c) if $y > 0$: i. dosing the oxygen-containing precursor for time t_3 ; ii. dosing the nitrogen-containing precursor entrained in the oxygen-containing precursor for time t_4 , wherein $t_4 < t_3$; iii. dosing the oxygen-containing precursor for time t_5 , wherein $t_5 > t_4$; iv. optionally repeating steps c.ii. and c.iii. as many times as required to convert at least 99% of the metal-containing precursor deposited in step a) to an $MxOy$ layer; d) if $z > 0$: i. dosing the nitrogen-containing precursor for time t_6 ; ii. dosing the oxygen-containing precursor entrained in the nitrogen-containing precursor for time t_7 , wherein $t_7 < t_6$; iii. dosing the nitrogen-containing precursor for time t_8 , wherein $t_8 > t_7$; iv. optionally repeating steps d)ii. and d)iii. as many times as required to convert at least 99% of the metal-containing precursor deposited in step a. to an $MxNz$ layer; and repeating steps a through d until a desired thickness T is obtained.

In any of its aspects, the invention can be further characterized by one or any combination of the following: the process produces a metal oxide or metal nitride film or metal-oxy-nitride film; the oxide film can have 0.1 mass% or less or 0.01 mass% or less nitrogen; the process of claim 1 for producing an oxide film comprising dosing the first dosed substrate with an oxidant and a nitrogen-containing reactant to form a metal oxide; wherein the dosing step comprises a sub-pulse with the oxidant without the nitrogen-containing reactant followed by a second sub-pulse with the oxidant and the nitrogen-containing reactant; followed by a third sub-pulse with the oxidant and without the nitrogen-containing reactant; wherein the oxidant comprises ozone and the nitrogen-containing reactant comprises a hydrazine; wherein the step of dosing the first dosed substrate with an oxidant further comprises the addition of H_2S ; the process of claim 1 for producing a nitride film comprising dosing the first dosed substrate with a sulfur-containing reactant and a nitrogen-containing reactant to form a metal nitride; wherein the dosing step comprises a sub-pulse with the nitrogen-containing reactant followed by a second sub-pulse with the sulfur-containing reactant and the nitrogen-containing reactant; followed by a third sub-pulse with the nitrogen-containing reactant; wherein the oxide film comprises: Al_2O_3 , SiO_2 , TiO_2 , Nb_2O_5 , Ta_2O_5 , La_2O_5 , Y_2O_3 , ZrO_2 , Ga_2O_3 , or In_2O_3 ; wherein the product comprises mixed oxynitrides and/or mixed metals; wherein the nitride film comprises: ZrN , GaN , YN , InN , or Si_3N_4 ; wherein the sulfur-containing reactant comprises: H_2S (hydrogen sulfide), H_2S_2 (dihydrogen sulfide), mercaptan ($HS(CH_3)$ or methane thiol), ethanethiol (ethyl mercaptan), $S(CH_3)_2$ (dimethyl sulfide), thionyl chloride ($SOCl_2$), sulfuryl chloride (SO_2Cl_2); wherein the

substrate comprises Si, SiO₂, Al₂O₃ (preferably in the form of corundum), SiC, GaN, AlGaIn, GaAs, or InP; wherein the oxidant comprises O₂, O₃, H₂O, H₂O₂, or N₂O (as with any category described as comprising, there may be additional components and the oxidants can be mixed); wherein the nitrogen-containing reactant comprises: hydrazine, monomethylhydrazine (MMH),

5 1, 1-dimethylhydrazine, 1,2-dimethylhydrazine, tert-butylhydrazine (tBuNNH), ammonia (NH₃), pyridine, 2,3-Lutidine (2,3-dimethylpyridine), 2,4-Lutidine (2,4-dimethylpyridine), 2,5-Lutidine (2,5-dimethylpyridine), 2,6-Lutidine (2,6-dimethylpyridine), 3,4-Lutidine (3,4-dimethylpyridine), or 3,5-Lutidine (3,5-dimethylpyridine); wherein the process is conducted for 10 to 5000 cycles, or 10 to 1000 cycles or 20 to 200 cycles; wherein the ALD precursor

10 comprises: Ti – TiCl₄, TTIP (titanium(IV) isopropoxide), Ti(NEtMe)₄ (titanium(IV)tetrakisethylmethylamine), Ti(NMe)₄ (titanium(IV)tetrakisdimethylamine); Hf – Hf(NEtMe)₄ (hafnium(IV)tetrakisethylmethylamine), HyALD (hafnium(IV)cyclopentadienyl-trisdimethylamine); Zr – Zr(NEtMe)₄ (zirconium(IV)tetrakisethylmethylamine), ZyALD (zirconium(IV)cyclopentadienyl-trisdimethylamine); Si – BEMAS (bisethylmethlamino silane), BDEAS

15 (bisdiethylaminosilane), 3DMAS (trisdimethylaminosilane); Y – ArYa (yttrium(III)bisethylcyclopentadienyl-isopropylamidinate); Al – TMA (trimethyl aluminum), AlCl₃, AlMeCl₂, and AlMe₂Cl (ALD precursors are typically metals having ligands of organo, alkoxy, and/or heteroatom groups; organo is typically alkyl, aryl, arylalkyl typically of C₁ to C₁₂ or C₁ to C₆; heteroatoms suitable for ALD precursors include H, amides, alkylamides, and halogen such

20 as Cl); wherein the step of dosing the substrate with a metal-containing ALD precursor comprises a step of introducing the precursor into the chamber followed by a pulse step of introducing precursor and draw control simultaneously; wherein draw control comprises flow of an inert gas and applying vacuum; wherein the pulse step is conducted for between 5 to 50 ms; followed by a step of from 10 to 500 ms in which no precursor flows into the system; wherein

25 the step of dosing is conducted for 150 ms or less; wherein an inert gas flows through the chamber for at least 200 ms; preferably wherein no precursor is introduced and no vacuum is applied to the chamber; wherein the sub-pulses with the oxidant without the nitrogen-containing reactant are conducted for a longer period of time than the sub-pulse with the oxidant and the nitrogen-containing reactant (the sub-pulses are summed together for this calculation); wherein

30 the sub-pulses with the oxidant without the nitrogen-containing reactant are conducted for a period of time at least two times longer than the sub-pulse with the oxidant and the nitrogen-containing reactant; wherein the sub-pulses with the oxidant without the sulfur-containing

reactant are conducted for a longer period of time than the sub-pulse with the oxidant and the sulfur-containing reactant (the sub-pulses are summed together for this calculation); wherein the sub-pulses with the oxidant without the sulfur-containing reactant are conducted for a period of time at least two times longer than the sub-pulse with the oxidant and the sulfur-containing
5 reactant.

The invention also includes any of the apparatus, systems (which may include apparatus and composition and conditions within the apparatus), and final or intermediate compositions described herein. For example, the invention includes an apparatus for an ICRISP process having a precursor showerhead, an ALD reaction zone, a dynamically-positionable chuck able to vary
10 the height of the ALD reaction zone (the distance between the showerhead and substrate) between 10 mm and 1.0 mm using computer control, a first series of fast pneumatic valves upstream of the precursor showerhead for pressure control; and a second series of fast pneumatic valves downstream of the ALD reaction zone for draw control. A dynamically-positionable chuck (see Fig. 6) floats on linear actuating pistons which are driven by single stepper motor and
15 belt assembly. The assembly gearing ratio allows for fine-tuned adjustments in real time with resolution down to 0.1 millimeters. The invention includes a system capable of carrying out a sequence of steps comprising a delay, pulse, dose, purge and pump purge for an ICRISP process. The invention also includes a film composition $M_xO_yN_z$ deposited using an ICRISP process wherein the deposition time of the ICRISP process is < 6 seconds per cycle, the film uniformity
20 is $> 92\%$, the $x:y$ and $x:z$ ratios and density are within $\pm 10\%$ of the bulk values of the M_xO_y metal oxide and the M_xN_z metal nitride.

The invention also includes a system comprising any of the compositions and conditions described herein. The invention can be further elucidated in the examples below. The invention may be further characterized by any features in the examples, for example, any of the inventive
25 aspects can be further characterized by values within $\pm 30\%$, $\pm 20\%$ (or within $\pm 10\%$) of any of the values in any of the examples, tables or figures; however, the scope of the present invention, in its broader aspects, is not intended to be limited by these examples. All ranges are inclusive and combinable. For example, when a range of “1 to 5” is recited, the recited range should be construed as including ranges “1 to 4”, “1 to 3”, “1-2”, “1-2 & 4-5”, “1-3 & 5”, “2-5”, any of 1,
30 2, 3, 4, or 5 individually, and the like.

The invention is often characterized by the term “comprising” which means “including,” and does not exclude additional components. In narrower aspects, the term “comprising” may be replaced by the more restrictive terms “consisting essentially of” or “consisting of.”

5 Brief Description of the Drawings

Fig. 1: X-ray diffraction pattern for HfO_2 from prior art (O_3 only – darker) and the new ICRISP process (orange) over 20 to $60^\circ 2\theta$. Note that the equivalent peaks are of higher intensity and since both films are equivalent thickness, this indicates a higher degree of crystallinity. In addition, the (002) peak at $\sim 35^\circ$ is sharper for the ICRISP film than the prior art, indicating a large grain size. Finally, two new peaks appear
10 in the HfO_2 ICRISP film compared to the prior art at 28.7 and $57^\circ 2\theta$. This indicates that the ICRISP modified the crystalline texture or orientation of the growing film.

Fig. 2 illustrates precursor flow into a deposition zone.

Fig. 3 illustrates a central pulse step with two inert gas flows on opposing sides.

Fig. 4 shows two cross-sectional views of one Fast Pneumatic Valve (FPV) used in the present
15 invention, in two different positions, an activated closed (100a) state and an activated open (100b) state.

Fig. 5 shows a cross-sectional view of two FPVs used in the present invention, for two different precursors, while FPV-1 is an activated closed state and FPV-2 is in an activated open state.

Fig. 6 illustrates a dynamically-positionable chuck.

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Metal Oxides by ICRISP

The time and cadence of the inventive ICRISP process can be described for a metal oxide, MO_x , using a metal-containing precursor MR_x where R represents an organic ligand, and non-metal containing O-containing precursor such as O_3 and non-metal containing N-containing co-
25 catalyst such as MMH:

Step 1: MR_x precursor pulse for time t_1

Step 2: purge and/or flush reaction stage for time t_2

Step 3a: O_3 sub-pulse 1 for time t_3

Step 3b: O_3 and MMH (entrained) sub-pulse 1 for time t_4

30 Step 3c: O_3 sub-pulse 2 for time t_5

Step 4: purge and/or flush reaction stage for time t_6

wherein t_3 and t_5 are greater than t_4 .

We have unexpectedly improved the rate of deposition and quality of metal oxide films deposited by thermal ALD using the ICRISP process at a given temperature by intermittent addition of a small amount of non-metal catalyst to the conversion step during the ALD process.

5 Specifically, a small amount, ~ 0.01 to 0.05 Langmuir, preferably 0.02 to 0.04 Langmuir, and more preferably 0.025 to 0.035 Langmuir, of monomethyl hydrazine (MMH) entrained periodically, every 30 - 60 ms, preferably every 35 - 55 ms, more preferably 40 - 50 ms, and sometimes 45 ms, into O_3 via a short pulse time of 2 to 10 ms, preferably 4 to 7 ms, more preferably 5 to 6 ms, and sometimes 5 ms, showed different growth kinetics and film properties than O_3 alone in the

10 deposition of HfO_2 with cyclopentadienyl trisdimethylamine hafnium ("HyALD"). In some embodiments, the ratio of the duration of the pulse time to the periodicity of the MMH entrainment ranges from $0.5:20$, preferably $0.75:15$, more preferably $1:10$, $1:9$ or $1:8$. For films grown at $250^\circ C$, the growth per cycle (GPC) increased by 29% , from 0.77 to 0.99 Å/cy, at saturation (as measured by spectroscopic ellipsometry). In addition, the refractive index at 633 nm increased from 1.977 to

15 1.993 . X-ray reflectivity (XRR) measurements and modeling showed a 7% increase, from 8.3 to 8.9 g/cm³. Bulk HfO_2 has a density of 9.63 g/cm and published density results for the HyALD/ O_3 process at $250^\circ C$ is 7.7 g/cm³ (<https://aip.scitation.org/doi/full/10.1063/5.0055847>). As noted in other data, films deposited on the ALD^x toolset appear to have higher density than the same ALD process deposited at the same temperature. An unexpected increase in density was also observed

20 for ICRISP processes based upon TiO_2 and Y_2O_3 as well. When compared to a cross-flow reactor, the HfO_2 CRISP process density increases 15.6% , 7.7 to 8.9 g/cm³. Films deposited at ~ 100 nm thickness for both the O_3 only and ICRISP process were polycrystalline in nature as deposited, as measured by x-ray diffraction (XRD). This is in contrast to multiple literature reports which showed amorphous films at $250^\circ C$ for the HyALD/ O_3 process. Although both processes on the

25 ALD^x tools were crystalline, the ICRISP process gave a film with higher crystallinity, as shown by the large peak intensity, when normalized for thickness, found in Figure 1. A rough comparison of the Scherrer equation also shows that the ICRISP process has 10 - 18% larger crystal grains. One interesting and unexpected observation was that crystalline textures between the O_3 and ICRISP processes were different. There are at least two peaks that exist in the ICRISP diffractogram, that

30 do not exist in the O_3 only diffractogram. These are located at 28.7° and 56.0° 2θ and are associated with the $(1\bar{1}11)$ and $(3\bar{1}11)$ orientations respectively. These data suggests that the

intermittent addition of MMH, a N based molecule, or potentially other Lewis Bases, can encourage a specific crystal orientation and suggests that surface mobility can be influenced by addition of other species during the ALD process. X-ray photoemission spectroscopy (XPS) was used to check carbon, nitrogen content and compare O:Hf ratio (stoichiometry). Films deposited with ICRISP had less carbon, 1.8 vs 3.2 atomic %, and a more ideal O:Hf ratio, 2.2 vs 2.4 (2.0 is ideal). Neither sample detected the presence of nitrogen, despite every ICRISP ALD cycle including the intermittent entrainment of the nitrogen-containing molecule MMH.

Table of HfO₂ process and film property comparison.

Oxygen Precursor	Density (g/cm ³)	GPC (Å/cy)	Refractive Index at 633nm	O%	Hf%	O:Hf	C%
Prior Art CRISP	8.3	0.77	1.977	54.7	23.3	2.4	3.2
ICRISP O ₃ /MMH	8.9	0.99	1.993	51.4	23.2	2.2	1.8
Bulk	9.68	N/A	2.1	50	25	2.0	0.0
Prior Art O ₃ ALD	7.7	0.70-0.77	Not Measured	67.0	27.8	2.4	2.8

Improvements in dielectric constant are directly related to crystalline grain size (<https://www.sciencedirect.com/science/article/abs/pii/S1359645403000521>) and impurities, both oxygen and carbon

(<https://www.sciencedirect.com/science/article/abs/pii/S0167931711003583?via%3Dihub>). Prior art CRISP films and ICRISP films of the present invention were crystalline as deposited, where multiple reports showed the process at 250°C to be amorphous. Even though the prior art O₃ process had higher density and was polycrystalline, the C content was roughly the same as published data. This suggests the C removal mechanism has a kinetic barrier that is driven by the temperature and not other factors that increase the density and packing of the growing film (such as the surface catalysis leveraged to form Hf-O bonds). The density of the ICRISP film however was higher than any prior art process and closer to bulk density than expected. The crystalline

texture of ICRISP being different than O₃ alone was very unexpected and suggests a potential mechanism to encourage crystalline orientation using ICRISP ALD, independent of substrate/template effects that are ubiquitous in the prior art, which is typically unattainable in a purely epitaxial growth process.

5 Given that this invention increases the crystalline grain size, decreases carbon content, and improved the Hf:O ratio, the dielectric constant of films derived using the ICRISP process is improved and more controllable. In addition, leakage current, a key property in high field dielectrics found in power electronics, improves with lower impurity content (<https://avs.scitation.org/doi/10.1116/1.5134135>), and the leakage current is also decreased using
10 ICRISP processing. We have further discovered that going to a deposition temperature of 300°C using the HyALD ICRISP process removed all impurities, further increased density, and improved crystallinity without forming intermediate metal nitride species embedded throughout the ICRISP layers.

 We have also used the novel ICRISP process to deposit layers comprising other metal
15 oxides (Al₂O₃, SiO₂, TiO₂, Nb₂O₅, Ta₂O₅, La₂O₃, Y₂O₃, etc.) and have seen similar improvements to dielectric constant, leakage current, and breakdown voltage over prior art processes. The ICRISP process has superior dielectric properties, and given the speed of the ALD^x toolset with both pressure control and draw control, and low precursor consumption relative to other prior art tools, this process can be used in multiple applications for dielectric barriers, either as a monolith
20 or in a laminate structure. Given high refractive index (RI) and the added ability to precisely tune the RI based on the ICRISP parameters, there are also new applications for precision optics and mirrors. During development, the prior art CRISP process was studied using MMH, and it was determined that the RI could be shifted between the O₃ only and prior art CRISP states; subsequently upon development of the ICRISP process, e.g., developing the duration and
25 sequencing of the MMH, pressure control, draw control and chuck height could further increase the RI between prior art CRISP and novel ICRISP states. This invention provides an additional series of parameters to tune for optical and capacitive applications when deployed in the production of metal oxides using ICRISP monolayers and multilayers.

More examples of the ICRISP oxide process:

HfO ₂ at 250 °C	GPC (Å/cy)	Cycle time (s)	100 nm time (hrs)	Hf dose time (s)	Full range thickness uniformity (%)	Density (g/cm ³)	O:Hf ratio	Crystallinity
ICRISP	0.99	8.5	0.42	0.19	2	8.9	2.2	Polycrystalline
Prior Art	0.77	49.5	3.64	9	2	7.7	2.4	Amorphous

SiO ₂ at 300 °C	GPC (Å/cy)	Cycle time (s)	100 nm time (hrs)	Si dose time (s)	Full range thickness uniformity (%)	Density (g/cm ³)	O:Si ratio	Breakdown voltage (MW/cm)
ICRISP	1.2	0.9	0.7	0.05	2	2.32	2.0	>12
Prior Art	1.1	8.3	2.1	1	2	2.19	2.1	>9

TiO ₂ at 180 °C	GPC (Å/cy)	Cycle time (s)	100 nm time (hrs)	Ti dose time (s)	Full range thickness uniformity (%)	Density (g/cm ³)	O:Ti ratio	Crystallinity
ICRISP	0.44	2.3	1.48	0.032	9	4.0	2	polycrystalline
Prior Art	0.53	136.5	75.8	1	23	3.7	2.1	polycrystalline

Y ₂ O ₃ at 225 °C	GPC (Å/cy)	Cycle time (s)	100 nm time (hrs)	Y dose time (s)	Full range thickness uniformity (%)	Density (g/cm ³)	O:Y ratio	Carbon content (%)
ICRISP	0.90	9.2	2.8	0.135	2	4.8	1.50	0.0

Prior Art	0.46	281.5	169.9	8	10	3.6	1.62	12.6
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Metal Nitrides by ICRISP

More broadly, the time and cadence of the inventive ICRISP process can be described for a metal nitride, MN_x , using a metal-containing precursor MR^*_x where R^* represents an inorganic ligand such as a halide, a non-metal containing N-containing precursor such as MMH and non-metal containing S-containing co-catalyst such as H_2S :

- Step 1: MR^*_x precursor pulse for time t_1
 - Step 2: purge and/or flush reaction stage for time t_2
 - Step 3a: MMH sub-pulse 1 for time t_3
 - Step 3b: MMH and H_2S (entrained) sub-pulse 1 for time t_4
 - Step 3c: MMH sub-pulse 2 for time t_5
 - Step 4: purge and/or flush reaction stage for time t_6
- wherein t_3 and t_5 are greater than t_4 .

Metal nitride thermal ALD using halide precursors and non-metal containing N-containing precursors is ubiquitous in the prior art, but typically high temperatures are required to achieve quality nitride deposition. Higher quality nitride layers can be produced using plasma enhanced ALD, but as stated above, in embodiments that include a plasma enhanced process, the distance between the plasma delivery apparatus and the substrate should be greater to facilitate deposition uniformity, which eliminates the substantially reduced process time and precursor consumption afforded by the ICRISP process.

Extensive validation of the ability to reduce operating temperatures of a thermal ALD approach using the ICRISP process has been carried out using TiN as the metal nitride. $TiCl_4$ and NH_3 at $380^\circ C$ is the traditional process taught by the prior art. The ICRISP process can deposit high quality TiN films utilizing $TiCl_4$ and MMH at or below $300^\circ C$ with an intermittent entrainment of extremely short H_2S pulses. The further benefit of developing a process for nitrides that can operate at or below $300^\circ C$ is that these temperature ranges allow for the deposition of many other oxides without having to reduce the temperature in the ALD system from $380^\circ C$ or higher, down to $300^\circ C$ or lower for an oxide-included multilayered coating, and then back to $380^\circ C$ or higher if a subsequent nitride layer was required. For example, SiO_2 using ICRISP can

- be deposited using trisdimethylaminosilane with O_3 and intermittently entrained MMH; Si_xN_y (typically Si_3N_4) using ICRISP can be deposited using trisdimethylaminosilane with MMH and entrained H_2S at $300^\circ C$; Al_2O_3 using ICRISP can be deposited with trimethylaluminum with O_3 and intermittently entrained H_2S at $300^\circ C$; and AlN using ICRISP can be deposited with trimethylaluminum with MMH and entrained H_3S or trimethylaluminum with hydrazine and entrained H_3S at $300^\circ C$. Similar ICRISP processes have been demonstrated for ZrO_2 vs Zr_xN_y , Ga_2O_3 vs GaN , Y_2O_3 vs YN , In_2O_3 vs. InN , etc., on Si, SiO_2 (sapphire) and SiC substrates. Furthermore, the ICRISP process can easily produce multi-metallic materials with similar quality, such as $Al_xGa_{(1-x)}N$ and $In_xGa_{(1-x)}N$ using MMH as a nitrogen-containing precursor at $300^\circ C$ leveraging an intermittently entrained co-catalyst such as O_3 .

More examples of the ICRISP nitride process

TiN at $300^\circ C$	GPC ($\text{\AA}/\text{cy}$)	Cycle time (s)	100 nm time (hrs)	Ti dose time (s)	Full range thickness uniformity (%)	Refractive index at 633 nm	Extinction coefficient at 633 nm	Resistivity ($\Omega \cdot \text{cm}$)
ICRISP	0.53	2.8	1.47	0.035	5	1.96	1.17	1200
Prior Art (CRISP)	0.55	2.5	1.26	0.035	5	2.01	1.37	300

AlN at $275^\circ C$	GPC ($\text{\AA}/\text{cy}$)	Cycle time (s)	100 nm time (hrs)	Al dose time (s)	Full range thickness uniformity (%)	Refractive index at 633 nm	Extinction coefficient at 633 nm
ICRISP (MMH)	0.88	5	94.7	0.05	10	1.698	0.0
Prior Art	ALD not observed						

AlN at $275^\circ C$	GPC ($\text{\AA}/\text{cy}$)	Cycle time (s)	100 nm time (hrs)	Al dose time (s)	Full range thickness	Refractive index at 633 nm	Extinction coefficient at 633 nm
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					uniformity (%)		
ICRISP (hydrazine)	1.97	5	42.3	0.05	10	1.913	0.0
Prior Art	1.28	10	130.2	0.15	10	1.842	0.0

General Description of Prior Art Atomic or Molecular Layer Deposition

Atomic layer-controlled growth techniques permit the deposition of coatings of about 0.1 to about 5 angstroms in thickness per reaction cycle, and thus provide a means of extremely fine control over surface coverage or coating thickness. Thicker coatings can be prepared by repeating the reaction sequence to sequentially deposit additional layers of the coating material until the desired coating thickness is achieved.

The coating is deposited in an Atomic Layer Deposition (ALD) or Molecular Layer Deposition (MLD) process. In the ALD/MLD process, the coating-forming reaction is conducted as a series of (typically) two half-reactions. In each of these half-reactions, a single reagent (precursor) is introduced into contact with the substrate surface. Conditions are such that the reagent is in the form of a gas. In most cases, the reagent reacts with functional groups on the surface of the substrate and becomes bound to the substrate. Because the reagent is a gas, it permeates into pores in the substrate and deposits onto the interior surfaces of the pores as well as onto the exterior surfaces of the substrate. This precursor is designed to react with the surface at all of the available surface sites but not react with itself. In this way, the first reaction occurs to form a single monolayer, or sub-monolayer, and creates a new surface functionality. Excess amounts of the reagent are then removed, which helps to prevent the growth of undesired, larger inclusions of the coating material. Each remaining half-reaction is then conducted in turn, each time introducing a first reagent, allowing it to react at the surface of the substrate, and removing excess reagent before introducing the next reagent. Usually, an inert carrier gas is used to introduce the reagents, and the reaction chamber is usually swept with the carrier gas between successive reagent introductions to help remove excess reagents and gaseous reaction products. A vacuum may be pulled during and between successive dosing of reagents, to further remove excess reagents and gaseous reaction products.

After exposure to the first precursor, the surface is then exposed to the second precursor, also typically dispersed in an inert carrier gas. This precursor is designed to react with the functional groups put down in the first reaction step. This reaction also happens until all of the available surface sites are reacted. The second precursor also does not react with itself. Any
5 excess of the second precursor is also removed in an optional inert gas purge step. If the gases are metered properly, the purge step may be unnecessary. This may be at least a 4-step process (precursor 1, purge, precursor 2, purge) to deposit one monolayer of the film which is being grown. This is not meant to imply only a single precursor because some ALD and MLD processes use multiple reactants in a step, for example APTES/H₂O/O₃ for depositing SiO₂. This process is
10 repeated as many times as is necessary to build up the desired film thickness. The ALD/MLD process may start with a “linker” agent, or pre-treatment gas (such as ozone), that facilitates covalent bonding to the surface, or it may end with a terminating agent that may be hydrophobic, hydrophilic, or otherwise engineered for a specific purpose.

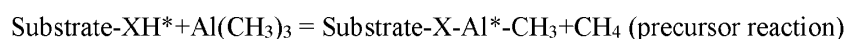
Reaction conditions are selected mainly to meet three criteria. The first criterion is that the
15 reagents are gaseous under the conditions of the reaction. Therefore, temperature and pressure conditions are selected such that the reactants volatilize before reaction. The second criterion is one of reactivity. Conditions, particularly temperature, are selected such that the desired reaction between the film-forming reagents (or, at the start of the reaction, the first-introduced reagent and the substrate surface) occurs at a commercially reasonable rate. The third criterion is that the
20 substrate is thermally stable, from a chemical standpoint and from a physical standpoint. The substrate should not degrade or react at the process temperature, other than a possible reaction on surface functional groups with one of the ALD precursors at the early stages of the process. Similarly, the substrate should not melt or soften at the process temperature, so that the physical geometry, especially pore structure, of the substrate is maintained. The reactions are generally
25 performed at temperatures from about 270 to 1000 K, preferably from 290 to 450 K, with specific temperatures in each case being below the temperature at which the substrate melts, softens or degrades.

Between successive dosings of the reagents, the substrates are subjected to conditions sufficient to remove reaction products and unreacted reagents. This can be done, for example, by
30 subjecting the substrates to a high vacuum, such as about 10⁻⁵ Torr or greater, after each reaction step. Another method of accomplishing this, which is more readily applicable for industrial

application, is to sweep the substrates with an inert purge gas between the reaction steps. This purge gas can also act as a fluidizing medium for the substrates and as a carrier for the reagents.

Several techniques are useful for monitoring the progress of the reaction. For example, vibrational spectroscopic studies can be performed using transmission Fourier transform infrared techniques. The deposited coatings can be examined using in situ spectroscopic ellipsometry. Atomic force microscopy studies can be used to characterize the roughness of the coating relative to that of the surface of the substrate. X-ray photoelectron spectroscopy and x-ray diffraction can be used to do depth-profiling and ascertain the crystallographic structure of the coating.

Aluminum oxide coatings are conveniently deposited using trimethylaluminum and water as the precursors, as illustrated by reaction sequence A1/B1. The illustrated reactions are not balanced, and are only intended to show the reactions at the surface of the substrate (i.e., not inter- or intralayer reactions).

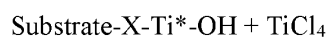
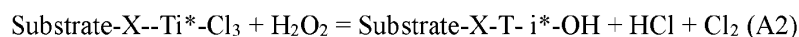
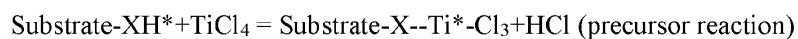


Substrate-X-Al^{*}-CH₃ + H₂O = Substrate-X--Al-OH^{*} + CH₄ (A1)



In reactions A1/B1, X is typically oxygen, nitrogen or sulfur, and the asterisk (*) represents the surface species at which the next half-reaction can occur. An aluminum oxide film is built up by repeating reactions A1 and B1 in alternating fashion, until the desired coating thickness is achieved. Aluminum oxide films tend to grow at a rate of approximately 0.1 nm/cycle using this reaction sequence.

Titanium oxide coatings are conveniently deposited using titanium tetrachloride and water and/or hydrogen peroxide as the precursors, as illustrated by reaction sequence A2/B2. As before, the illustrated reactions are not balanced, and are only intended to show the reactions at the surface of the substrates (i.e., not inter- or intralayer reactions).



Substrate-X-Ti-O-Ti^{*}-Cl₃ + HCl (B2)

In reactions A2/B2, X is typically oxygen, nitrogen or sulfur, and the asterisk (*) represents the surface species at which the next half-reaction can occur. A titanium oxide film is built up by repeating reactions A2 and B2 in alternating fashion, until the desired coating thickness is achieved. Titanium oxide films tend to grow at a rate of approximately 0.05-0.1 nm/cycle using this reaction sequence.

As is known for ALD/MLD processes, the order can be AB, ABC, ABCD, ABCDABABCD, or any desired order provided that the chemical entities react with each other in the desired order. Each of the reactants has at least two reactive moieties (this includes the possibility that the reactant is modifiable to have two reactive moieties such as having a first reactive moiety and a second reactive moiety that is temporarily blocked by a protecting group or requires activation for subsequent reaction such as UV activation). In some preferred embodiments, the reactants have exactly two reactive moieties since higher numbers of reactive groups may lead to lower packing density. In some preferred embodiments, the films have at least three repeating units (e.g., ABABAB), or at least 5, or at least 10, or at least 50, and sometimes in the range of 2 to 1000, or 5 to 100. By “reactive” it is meant under normal MLD conditions and commercially relevant timescales (for example, at least 50% reacted within 10 hours under appropriate reaction conditions). For control of film quality, the reactants may be singly reactive during each step of the MLD process to avoid reacting twice to the surface, and the reactants should not self-react and condense onto the surface.

In some preferred embodiments, the reactive moieties for Reactant A may comprise: isocyanates (R-NCO), acrylates, carboxylic acids, esters, epoxides, amides and amines, and combinations thereof. In some preferred embodiments, Reactant A comprises a diisocyanate, a diacrylate, a dicarboxylic acid, a diester, diamide or a diamine. In some preferred embodiments, the reactive moieties on Reactant B comprise: alcohols or amines, and combinations thereof. In some preferred embodiments, Reactant B comprises a diol, an amine alcohol, or a diamine.

In some cases, especially for MLD, the vapor phase reactants selected react only monofunctionally with the substrate or growing polymer chain, i.e., only one group or moiety on the vapor phase reactant is capable of reacting with the substrate or growing polymer chain under the conditions of the reaction. This prevents unwanted cross-linking or chain termination that can occur when a vapor phase reactant can react polyfunctionally. A reactant is considered to react “monofunctionally” if during the reaction the reactant forms a bond to only one polymer chain,

and does not self-polymerize under the reaction conditions employed. As explained more fully below, it is possible in certain embodiments of the invention to use a vapor phase reactant that can react difunctionally with the substrate or growing polymer chain, provided that the vapor phase reactant contains at least one additional functional group. Reactants that have exactly two
5 functional groups which have approximately equal reactivity are preferably avoided in this aspect of invention.

A first class of suitable vapor phase reactants are compounds having two different reactive groups, one of which is reactive with a functional group on the substrate or polymer chain and one of which does not readily react with a functional group on the polymer chain but is reactive with
10 a functional group supplied by a different vapor phase reactant. Examples of reactants of this class include:

a) Hydroxyl compounds having vinyl or allylic unsaturation. These can react with a carboxylic acid, carboxylic acid halide, or siloxane group to form an ester or silicone-oxygen bond and introduce vinyl or allylic unsaturation onto the polymer chain. Alternatively, the unsaturated
15 group can react with a primary amino group in a Michaels reaction to extend the polymer chain and introduce a hydroxyl group onto the chain.

b) Aminoalcohol compounds. The amino group can react with a carboxyl group, a carboxylic acid chloride, a vinyl or allylic group, or an isocyanate group, for example, to extend the polymer chain and introduce a hydroxyl group onto the chain. Alternatively, the hydroxyl
20 group can react with a siloxane species to form a silicon-oxygen bond and introduce a free primary or secondary amino group.

A second class of suitable vapor phase reactants includes various cyclic compounds which can engage in ring-opening reactions. The ring-opening reaction produces a new functional group which does not readily react with the cyclic compound. Examples of such cyclic compounds
25 include, for example:

a) Cyclic azasilanes. These can react with a hydroxyl group to form a silicon-oxygen bond and generate a free primary or secondary amino group.

b) Cyclic carbonates, lactones and lactams. The carbonates can react with a primary or secondary amino group to form a urethane linkage and generate a free hydroxyl group. The
30 lactones and lactams can react with a primary or secondary amino group to form an amide linkage and generate a free hydroxyl or amino group, respectively.

A third class of vapor phase reactants includes compounds that contain two different reactive groups, both of which are reactive with a functional group on the polymer chain, but one of which is much more highly reactive with that functional group. This allows the more reactive of the groups to react with the functional group on the polymer chain while leaving the less reactive group unreacted and available for reaction with another vapor phase reactant.

A fourth class of vapor phase reactants includes compounds that contain two reactive groups, one of which is blocked or otherwise masked or protected such that it is not available for reaction until the blocking, masking or protective group is removed. The blocking or protective group can be removed chemically in some cases, and in other cases by thermally decomposing the blocking group to generate the underlying reactive group, by radiating the group with visible or ultraviolet light, or in a photochemical reaction. The unprotected group may be, for example, an amino group, anhydride group, hydroxyl group, carboxylic acid group, carboxylic anhydride group, carboxylic acid ester group, isocyanate group and the like. The protected group may be one which, after removal of the protective group, gives rise to a functional group of any of the types just mentioned.

A reactant of this fourth class may, for example, have a hydroxyl group protected by a leaving group such as a benzyl, nitrobenzyl, tetrahydropyranyl, $-\text{CH}_2\text{OCH}_3$ or similar group. In these cases, the hydroxyl group can be deprotected in various ways, for example by treatment with HCl, ethanol, or in some cases, irradiation. Carboxyl groups can be protected with leaving groups such as $-\text{CH}_2\text{SCH}_3$, t-butyl, benzyl, dimethylamino and similar groups. These groups can be deprotected by treatment with species such as trifluoroacetic acid, formic acid, methanol or water to generate the carboxylic acid group. Amino groups can be protected with groups such as $\text{R}-\text{OOC}-$, which can be removed by reaction with trifluoroacetic acid, hydrazine or ammonia. Isocyanate groups can be protected with carboxyl compounds such as formic acid or acetic acid.

A fifth class of vapor phase reactants contains a first functional group, and a precursor group at which a further reaction can be conducted to produce a second functional group. In such a case, the first functional group reacts to bond to the polymer chain, and chemistry is then performed at the precursor group to generate a second functional group. The first functional group can be any of the types mentioned before, including a siloxane group, amino group, anhydride group, hydroxyl group, carboxylic acid group, carboxylic anhydride group, carboxylic acid ester

group, isocyanate group and the like. A wide variety of precursor groups can be present on this type of reactant.

The precursor group may be one that it does not itself react with the polymer chain, but it can be converted to a functional group that can react with another vapor phase reactant to grow the chain. Two notable types of precursor groups are vinyl and/or allylic unsaturation, and halogen substitution, especially chlorine or bromine. Vinyl and allylic unsaturation can be converted to functional groups using a variety of chemistries. These can react with ozone or peroxides to form carboxylic acids or aldehydes. They can also react with ammonia or primary amino to produce an amine or imine. Halogens can be displaced with various functional groups. They can react with ammonia or primary amine to introduce an amino group, which can in turn be reacted with phosgene to produce an isocyanate group, if desired.

Reactants that are used to convert a precursor group to a functional group or to demask or deprotect a functional group, are introduced in the vapor phase. Excess reactants of this type are removed prior to the introduction of the next reactant, typically by drawing a high vacuum in the reaction zone, purging the chamber with a purge gas, or both. Reaction by-products are removed in the same manner, before introducing the next reactant into the reaction zone

In some preferred embodiments at least one or all of the reactants in the MLD repeating units have chain lengths between reactive moieties of from 2 to 20 atoms (typically carbon atoms although heterogroups such as oxygen may be present), or from 2 to 10 atoms, or from 2 to 5 atoms. In some preferred embodiments, the reactants have straight chains (i.e., no branching) between reactive moieties to enhance packing density. In some preferred embodiments, the chains between reactive moieties are non-reactive; however, in some embodiments, there may be moieties within the chains that are capable of cross-linking to adjacent chains. In some embodiments, the capping layer and/or the MLD layers at or very near the surface (e.g., within 5 cycles or within 2 cycles of the capping layer or surface) are branched for enhanced hydrophobicity.

An inorganic layer applied to the substrate in a first step preferably becomes covalently bonded to the substrate. Covalent bonding can occur when the first-to-be-applied precursor compound reacts under the conditions of the atomic layer deposition process with a functional group on the surface of the substrate. Examples of such functional groups are, for example, hydroxyl, carbonyl, carboxylic acid, carboxylic acid anhydride, carboxylic acid halide, primary or secondary amino.

Some ALD coatings are aluminum oxide and/or titanium oxide coatings. "Aluminum oxide" is used herein to designate a coating that is made up substantially entirely of aluminum and oxygen atoms, without reference to the specific stoichiometry. In many cases, it is expected that an aluminum oxide coating will correspond somewhat closely to the empirical structure of alumina, i.e., Al_2O_3 , although deviations from this structure are common and may be substantial. "Titanium oxide" is used herein to designate a coating that is made up substantially entirely of titanium and oxygen atoms, without reference to the specific stoichiometry. In most cases, it is expected that a titanium oxide coating will correspond closely to the empirical structure of titania, i.e., TiO_2 , although deviations from this structure are common and may be substantial. Similarly, considerations apply to understanding the other formulations described herein; although in some embodiments, the invention can be more specifically defined by the use of terms such as "consisting."

Except for the case of a half-reaction included in the broader aspects of the present invention, the atomic layer deposition process is characterized in that at least two different reactants are needed to form the coating layer. The reactants are introduced into the reaction zone individually, sequentially and in the gas phase. Excess amounts of reactant are removed from the reaction zone before introducing the next reactant. Reaction by-products are removed as well, between successive introductions of the reagents. This procedure ensures that reactions occur at the surface of the substrate, rather than in the gas phase.

A purge gas is typically introduced between the alternating feeds of the reactants, in order to further help to remove excess reactants. A carrier gas, which is usually but not necessarily the same as the purge gas, generally (but not always necessarily) is introduced during the time each reactant is introduced. The carrier gas may perform several functions, including (1) facilitating the removal of excess reactant and reaction by-products and (2) distributing the reactant through the reaction zone, thereby helping to expose all surfaces to the reactant. The purge gas does not react undesirably with the ALD reactants or the deposited coating, or interfere with their reaction with each other at the surface of the substrate.

Temperature and pressure conditions will depend on the particular reaction system, as it remains necessary to provide gaseous reactants. As is known for ALD/MLD processes, the temperature should be high enough to enable reactants in the gas phase but not so high that the product degrades.

The coating may comprise any coating that can be applied by molecular or atomic layer deposition. Some well-known coatings that can be applied to the metallic or other material core substrate may comprise: oxides or mixed oxides (e.g., Al_2O_3 , TiO_2 , ZnO , ZrO_2 , SiO_2 , HfO_2 , Ta_2O_5 , LiNb_xO_y), nitrides (e.g., TiN , TaN , W_2N , TiY_2N), sulfides (e.g., ZnS , CdS , SnS , WS_2 , MoS_2 , ZnIn_2S_4), and phosphides (e.g., GaP , InP , $\text{Fe}_{0.5}\text{Co}_{0.5}\text{P}$). Some lesser known materials that can be applied to the core substrate may comprise: transition metals (e.g., of Al, Cu, Co, W, Cr, Fe, Zn, Zr, Pt, Pd), metal fluorides (e.g., AlF_3 , MgF_2 , ZnF_2), oxy fluorides and oxy nitrides of transition metals, lanthanides in either elemental, oxide, fluoride, nitride, boride, or sulfide form (e.g., Y, YN, La_2O_3 , LaF_3 , Nb, Dy_2O_3 , Nd, LaB_6 , La_2S_3 etc), borides (e.g., TiB_2), carbides (e.g., B_4C , WC), silanes, silicides and other silicon containing materials, carbon-containing materials including, but limited to, polymers (e.g., polyamides, polyethylenes, polyamides, polyureas, polyurethanes), hydrocarbons, polymers or fragments of amino acids or other biological-related molecules and polymers, and other materials), fluorinated polymers (e.g., fluoro or perfluoro- polyamides, -polyethylenes, -polyamides, -polyureas, -urethanes, -hydrocarbons). This coating is highly uniform over the substrate; preferably, there is no more than a 20%, more preferably no more than 10%, or no more than 5% variation in coating thickness over the surface of the substrate. This high level of uniformity is a characteristic of the ALD/MLD process.

Detailed Description of the Invention

Each ICRISP process for oxides and nitrides was first verified on Si wafers due to the array of measurement tools and prior art reports available. Thickness during development was investigated with the single wavelength (633nm) Stokesmeter ellipsometer with a fixed refractive index (RI). Each process was first qualified with a thick film, >75 nm, for accurate thickness, RI, and extinction coefficient (k), both at 633 nm, measurements determined using spectroscopic ellipsometry (SE) at a fixed angle (75°). These data were modeled from $\cos(2\Psi)$ and $\sin(2\Psi)\cos(\Delta)$, measured from data generated using a dual light source over the range of 225-1000 nm (combined deuterium and halogen sources) and a Si based array detector. A regression analysis was explored via the Levenberg – Marquardt fitting algorithm employing a dispersion method (Cauchy, Exponential, Sellmeier, and Tauc-Lorentz) and the model was fit over the appropriate wavelength range from prior art reports (e.g. 250 to 1000nm for Al_2O_3 and SiO_2 ; 300 to 800nm for AlN and TiN ; etc.) Growth per cycle (GPC), RI, k are listed in *Table 3* below for the ALD processes

deposited on all samples, with data taken from those thick films. Goodness of Fit (GOF) is a term that measures the accuracy of the model to the raw data. A number greater than 0.97 is considered an accurate fit. Both TiN and AlN films have a slightly low GOF, so there is potential for error in the RI and k values, but this is due to the absorbing nature of the TiN and AlN films at the wavelength range of measurement. The thickness for both TiN AlN films was confirmed with thinner film, but RI and k require thicker films.

Table 3: Film properties of all ALD processes deposited on internal Si wafers as modeled from Spectroscopic Ellipsometry

Process	GPC (Å/cy)	Time/cy (s)	Refractive Index (RI)	Extinction Coefficient (k)	GOF
Al ₂ O ₃ (ICRISP) TMA/O ₃ -H ₂ S @ 300°C	0.77	2.5	1.63	0.0	0.99
SiO ₂ (ICRISP) BEMAS/O ₃ -MMH @ 300°C	1.29	6.0	1.44	0.0	0.98
SiO ₂ (Prior Art) 3DMAS/O ₃ @ 300°C	0.29	15.7	1.45	0.0	0.98
TiN (ICRISP) TiCl ₄ /MMH-H ₂ S @ 300°C	0.55	2.5	2.02	1.37	0.96
TiN (Prior Art) TiCl ₄ /NH ₃ @ 380°C	0.61	12.6	1.91	0.53	0.96
HfO ₂ (ICRISP) HyALD/O ₃ -MMH	0.99	8.9	1.99	0.0	0.97
HfO ₂ (Prior Art) HyALD/O ₃	0.63	49.5	1.79	0.0	0.97
Y ₂ O ₃ (ICRISP) ARYA-O ₃ -MMH	0.90	9.2	1.82	0.0	0.98
Y ₂ O ₃ (Prior Art)	0.46	281.5	1.76	0.0	0.97

ARYA-O ₃					
AlN (ICRISP) TMA/MMH-H ₂ S	0.88	~5	1.70	0.0	0.96
AlN (Prior Art) TMA/MMH	No film produced				
AlN (ICRISP) TMA/hydrazine-H ₂ S	1.97	~5	1.91	0.0	0.96
AlN (Prior Art) TMA/hydrazine	1.28	~10	1.84	0.0	0.96

The measured Al₂O₃ film values are within the expected range of what we have observed on this tool and what has been published in literature, so the measured values from the prior art Al₂O₃ process are not shown above. However as with all other films, the ultra-short cycle time for Al₂O₃ using the ICRISP process are unattainable using the prior art processes. In practice, this SiO₂ ICRISP process is currently being run at about 0.85-1.5s/cycle. The traditional prior art SiO₂ ALD process (3DMAS/O₃) was a struggle to bring up on the tool due to the low growth pressure and challenging reaction kinetics of the Si-O surface bond formation process. The GPC was lower than expected and the cycle times were very long, but the film properties were within expectation. The prior art 3DMAS/O₃ process prefers to run at higher pressure than the ICRISP process with pressure and draw control. As such, no significant cycle time improvement can be expected for the prior art process without adopting the ICRISP approach. The 300°C ICRISP TiN process had film properties within expectation, however surface oxidation (TiO₂ formation) artificially increases resistivity and should be capped prior to removal from the ALD tool. For the ICRISP TiN process, cycle times can likely be decreased further by 25-50% when optimized in a production tool. The prior art TiN process at 380°C was also a challenge, due to the high temperature interactions between the reactor components (e.g. the inventive chuck) and reaction by-products from the process. In effect, this caused non-uniformity issues at the edge of the wafer during development. The data in *Table 3* is taken from the center point of the high temperature TiN wafer to minimize any impact due to non-uniformity. HfO₂ has been discussed at length, in a previous section, but in brief, we see significant improvements with GPC, precursor dose exposure, and compositions with ICRISP. Prior art processes must use plasma to reach these density levels

or perform a post deposition anneal to induce crystallization. The Y_2O_3 ICRISP process is a significant improvement in speed, both GPC and cycle time, and film composition with increased density and reduced impurities. In addition, the crystalline nature of the ICRISP film is not observed in prior art. Finally, the two AlN ICRISP processes show the ability of the ICRISP process to activate an ALD process where one is not possible, as with the TMA/MMH- H_2S ICRISP process, true ALD without CVD of TMA/MMH does not exist, or a traditional improvement over prior art with speed and film property improvement, as with the TMA/hydrazine- H_2S ICRISP process. The AlN ICRISP process has increased GPC, lower cycle time, and a higher RI, which is used as a proxy for film density and crystallinity.

We have discovered a process to deposit ALD ZrN at low temperatures, without a CVD component. Using cyclopentadienyl tris(dimethylamine) zirconium (or “ZyALD” the equivalent of HyALD) and monomethyl hydrazine, we can perform ALD of ZrN. Growth rates saturate with higher precursor dose times, ~ 0.25 Å/cy at 225°C , and GPCs are stable with longer purge times (~ 10 s). Thickness increases with cycle number as expected (mostly linear, but metrology is lacking in our current setup). We believe that temperature window exists between 200 and 250°C (~ 0.2 to 0.35 Å/cy respectively). Precursor decomposition tests, dosing only ZyALD into the chamber, showed no decomposition at 225°C and significant decomposition at 275°C (250°C showed a small amount, but test was not definitive). Films have been deposited on Si wafers and have good nucleation and adhesion to the surface.

The Zr precursor, ZyALD, has been used in literature for ZrO_2 with H_2O and O_3 but has not been published in the literature for ZrN with any co-reactant. Processes for ALD of ZrN exist for a similar precursor, tetrakis(dimethylamine) zirconium and tetrakis(ethylmethylamine) zirconium, with ammonia (NH_3). However, we tested these tetrakis amine precursors and found that at temperatures including and above 200°C (tests were not performed below 200°C) there was significant decomposition, contrary to published records. Delivery of both tetrakis amine precursor at sub- 100°C temperatures resulted in decomposition in delivery lines. We have also tested ZyALD with NH_3 and found insufficient reactivity at temperatures below 275°C . Unfortunately, at 275°C , the ZyALD/ NH_3 process has a CVD component that influences the film. This appears to be the first true ALD process at 225°C for ZrN in the ALD^x tools. In addition, there is no work with a nitrogen-nitrogen bond (hydrazine or alkylated hydrazine) to grown ZrN, that we are aware

of, with any Zr precursor. This would be the first ZrN process deposited with a hydrazine type co-reactant.

ZrN has been used as a Cu diffusion barrier, a nuclear radiation barrier, and wear resistant coatings. PVD films of ZrN (with 5% TiN) have shown superior Cu barrier performance to TiN or TaN and being able to control composition and laminate thickness through ALD could find greater benefits. Additionally, ALD provides conformal coating, at consistent thickness, while PVD can struggle with conformality and composition. ZrN is a popular material in next-gen nuclear material. If the density of ZrN is sufficient by using an ICRISP process, applying a non-line-of-site wear resistant coating can have multiple applications.

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SYNCHRONOUSLY MODULATED FLOW AND DRAW (SMFD)

SMFD is executed with strategic inert gas routing. Flow out of the ALD space (Draw) is decoupled from the flow into the ALD space. Draw depends on gas conductance from the ALD space into the evacuation space, and on the pressure differential (DP) between these spaces.

15 SMFD enables the system to deposit ALD cycles at extreme speeds while maintaining a highly efficient use of precursor. Fig. 2 shows precursor gas (central down arrow) and outer arrows (Fig. 3) shows purge gas. During the purge step, both precursor and purge gas flow.

A **Delay Step** releases the desired precursor into the showerhead and ALD space. Draw Control gases are off allowing for precursor to be sole chemical flowed into the ALD space.

20 This is the least efficient use of precursor but aids in the initial saturation of the substrate surface. Typical processing time for this step is 0 – 10 milliseconds.

The **Pulse Step** follows the Delay Step. In this step, both precursor and draw control flow simultaneously. This will create a pressure differential between the draw control and ALD spaces. The precursor will exit the ALD space at a different rate than the draw control which creates a longer residence time for the precursor. Pulse efficiency is reduced as a function time as the pressures between the draw control and ALD spaces begin to equalize. However, the Pulse Step is the most efficient use of precursor due to the prolonged saturation of the ALD space. The Pulse Step is usually 5 – 50 milliseconds.

25 The **Dose Step** follows the Pulse Step. The Dose Step only uses Draw Control but takes advantage of any trapped precursor in the ALD space. Draw Control increases the overall residence time of any precursor still in the ALD space. This step acts to increase overall

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precursor utilization and induces turbulent flow to move precursor and remove reaction by-products. The Dose step ranges from 10 – 500 milliseconds in duration and can be gradually optimized as a new chemistry/process is developed. Longer Dose times, above 150 milliseconds, tend to have diminishing impact on precursor saturation. No precursor flows into the system during the dose step; typically, during the dose step purge (inert) gas continues to flow.

The **Purge Step** follows the Dose Step and is intended to remove all possible precursor vapors prior to the next half cycle. Inert gas (N₂) Purge runs with all draw control and precursor valves shut. The N₂ flow also purges the entire precursor valve stack for thorough evacuation. The cycle is normally 250 to 5000 milliseconds for easy processes and up to 30000 milliseconds for challenging chemistries.

An additional purge step, called the **Pump Purge Step**, can also run without any inert flowing. This is not as efficient as an inert driven purge but will bring the chamber to a lower base pressure if needed.

15 **Fast pneumatic valves (FPVs)**

Forge Nano produces fast acting pneumatic valves for the SMFD process. The FPV assembly is a normally closed diaphragm valve paired with a normally open solenoid valve. The solenoid valve regulates the pneumatic valves actuation. The FPV's come in two-way and three-way configurations depending on their role in the valve stack.

20 Figure 4 illustrates flow control valve 100 (represented by 100a or 100b), having a diaphragm 101 that is positioned such that it is operative to seal the flow path between valve seat 103 and fluid outlet port 105. Orifice 104 is formed between diaphragm 101 and valve seat 103. A sealed diaphragm control space 102 is formed above diaphragm 101. The diaphragm control space comprises control fluid inlet 123 and control fluid outlet 133. The flow control valve 100 also includes inlet fitting 110, outlet fitting 111, control fluid inlet 126, solenoid valve 120, solenoid valve 130, controller 108 and enclosure 109. Fluid from inlet 126 (e.g., compressed air) is fed into solenoid 120. In order to initially activate flow control valve 100, the inventors have determined that the diaphragm control space must be brought to a pressure threshold of at least 80 psi. From this threshold pressure, which keeps the diaphragm closed to precursor flow, small fluctuations in pressure can be used to transport fluid into and out of the diaphragm control space very rapidly, allowing for millisecond control over processing steps.

During operation, when solenoid 120 is activated, plunger 121 opens a flow path through inlet 123 to raise the pressure inside diaphragm control space 102 and deflect diaphragm 101 towards valve seat 103 to reduce orifice 104. The flow rate is thereby reduced or can be stopped entirely. Conversely, when solenoid 130 is activated, normally closed plunger 131 opens a flow path through outlet 133 and lowers the pressure inside diaphragm control space 102 by allowing control fluid to flow out of vent port 135. Diaphragm 101 responds to the reduced pressure by deflecting away from valve seat 103 to increase orifice 104 and restart or further increase the flow rate, as desired. Each flow control valve 100 representing an individual FPV comprises shutoff valve 150 to provide failsafe shutoff of diaphragm 101 via stem 152 when, for example, the pressure of control fluid is lost due to a system failure. Stem 152 can slide into control space 102 via opening 157. At the same time, seal 158 maintains the overall fluid tightness of control space 102. Stem 152 is retained to shutoff valve 150 by the force of spring 153, which is adapted to bias the stem 152 towards the diaphragm 101. The shutoff valve 150 is actuated open when pressurized control fluid (e.g., compressed air) is injected into actuator space 159 so as to translate the piston 151 against the spring 153 and away from the diaphragm 101. Piston 151 is equipped with sliding seal 154. Once shutoff valve 150 is actuated open, control fluid from actuator space 159 feeds into solenoid 120 via inlet 126, where it is available to modulate the position of diaphragm 101. Preferably, in use, the retraction of stem 152 is adjusted to the minimum needed to allow diaphragm 101 a full range of motion by plunger 156, as set by adjustment screw 155. That limited motion is desirable for minimizing the acceleration of stem 152 when control fluid pressure is lost, and the consequent impact when stem 152 translates into diaphragm 101 over valve seat 103. This impact is further reduced by restricting the vent of air out of actuator space 159 when the air supply at inlet 112 is deactivated. In actual reduction to practice, both measures were found to be very effective in preventing the generation of particles by the failsafe shutoff valve 150.

Figure 5 shows a cross-sectional view of two FPVs used in the present invention, for two different precursors, while FPV-1 is in an activated closed state and FPV-2 is in an activated open state. Gas delivery is accomplished through FPV stacking. Each FPV is stacked in series onto one another, such that each outlet 111 of each FPV is in fluid communication with the main gas delivery line that feeds into the ALD showerhead. Due to the rapid nature of the precursor steps required by the ICRISP process, a plurality of gas exposure sequences must be entrained into the

gas delivery line prior to the precursors arriving at the substrate surface. As such, the control sequence, and in particular the communication between solenoids 120 and 130 of FPV-1 and solenoids 120 and 130 of FPV-2 must be entirely fluid and robust.

During operation of an FPV stack using the inventive ICRISP process for a metal nitride, MN_x , where FPV-1 is used to deliver a metal-containing precursor MR^*_x , FPV-2 is used to deliver a non-metal containing N-containing precursor such as MMH, FPV-3 is used to deliver a non-metal containing S-containing co-catalyst such as H_2S , and FPV-4 is used to deliver an inert gas such as nitrogen or argon.

Step 1: Provide a MR^*_x precursor pulse for time t_1 by activating solenoid 120 of FPV-1, then activating solenoid 130 of FPV-1 after the time t_1 ;

Step 2: purge and/or flush reaction stage for time t_2 by activating solenoid 120 of FPV-4, then activating solenoid 130 of FPV-4 after the time t_2 ;

Step 3a: Provide a non-metal containing N-containing precursor such as MMH sub-pulse 1 for time t_3 by activating solenoid 120 of FPV-2;

Step 3b: Simultaneously activate solenoid 130 of FPV-2 and solenoid 120 of FPV-3 to intermittently pause the delivery of MMH and initiate the delivery of the non-metal containing S-containing co-catalyst such as H_2S for time t_4 ;

Step 3c: Simultaneously activate solenoid 130 of FPV-3 and solenoid 120 of FPV-2 to intermittently restart the delivery of MMH and pause the delivery of the non-metal containing S-containing co-catalyst such as H_2S for time t_5 ;

Step 4: repeat Steps 3b and 3c as many times as are required to convert at least 99% of the MR^* surface sites deposited in Step 1 to an M_xN_y metal nitride layer; and

Step 5: purge and/or flush reaction stage for time t_6 ;
wherein t_3 and t_5 are greater than t_4 .

What is claimed:

1. An Intermittent Catalyzed Reaction Induced Surface Process (ICRISP) for producing an oxide or nitride film on a substrate, comprising:
providing a substrate in a chamber;
5 dosing the substrate with a metal-containing ALD precursor to make a first dosed substrate;
purging or flushing the chamber; and either A or B
A) dosing the first dosed substrate with an oxidant and a nitrogen-containing reactant to form a metal oxide; or
10 B) dosing the first dosed substrate with a sulfur-containing reactant and a nitrogen-containing reactant to form a metal nitride; and
purging or flushing the chamber.
2. The process of claim 1 for producing an oxide film comprising dosing the first dosed
15 substrate with an oxidant and a nitrogen-containing reactant to form a metal oxide;
wherein the dosing step comprises a sub-pulse with the oxidant without the nitrogen-containing reactant followed by a second sub-pulse with the oxidant and the nitrogen-containing reactant; followed by a third sub-pulse with the oxidant and without the nitrogen-containing reactant.
20
3. The process of claim 2 wherein the oxidant comprises ozone and the nitrogen-containing reactant comprises a hydrazine.
4. The process of claim 2 wherein the step of dosing the first dosed substrate with an
25 oxidant further comprises the addition of H_2S .
5. The process of claim 1 for producing a nitride film comprising dosing the first dosed substrate with a sulfur-containing reactant and a nitrogen-containing reactant to form a metal nitride;

wherein the dosing step comprises a sub-pulse with the nitrogen-containing reactant followed by a second sub-pulse with the sulfur-containing reactant and the nitrogen-containing reactant; followed by a third sub-pulse with the nitrogen-containing reactant.

5 6. The process of claim 2 wherein the oxide film comprises: Al_2O_3 , SiO_2 , TiO_2 , Nb_2O_5 , Ta_2O_5 , La_2O_5 , Y_2O_3 , ZrO_2 , Ga_2O_3 , or In_2O_3 .

7. The process of claim 5 wherein the nitride film comprises: ZrN , GaN , YN , InN , or Si_3N_4 .

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8. The process of claim 5 wherein the sulfur-containing reactant comprises: H_2S (hydrogen sulfide), H_2S_2 (dihydrogen sulfide), mercaptan ($\text{HS}(\text{CH}_3)$ or methane thiol), ethanethiol (ethyl mercaptan), $\text{S}(\text{CH}_3)_2$ (dimethyl sulfide), thionyl chloride (SOCl_2), sulfuryl chloride (SO_2Cl_2).

15 9. The process of any of the above claims wherein the substrate comprises Si , SiO_2 , Al_2O_3 (preferably in the form of corundum), SiC , GaN , AlGaN , GaAs , or InP .

10. The process of any of the above claims wherein the oxidant comprises O_2 , O_3 , H_2O , H_2O_2 , or N_2O . As with any category described as comprising, there may be additional
20 components and the oxidants can be mixed.

11. The process of any of the above claims wherein the nitrogen-containing reactant comprises: hydrazine, monomethylhydrazine (MMH), 1, 1-dimethylhydrazine, 1,2-dimethylhydrazine, tert-butylhydrazine (tBuNNH), ammonia (NH_3), pyridine, 2,3-Lutidine (2,3-dimethylpyridine), 2,4-Lutidine (2,4-dimethylpyridine), 2,5-Lutidine (2,5-dimethylpyridine),
25 2,6-Lutidine (2,6-dimethylpyridine), 3,4-Lutidine (3,4-dimethylpyridine), or 3,5-Lutidine (3,5-dimethylpyridine).

12. The process of any of the above claims conducted for 10 to 5000 cycles, or 10 to 1000
30 cycles or 20 to 200 cycles.

13. The process of any of the above claims wherein the ALD precursor comprises:
- Ti – TiCl₄, TTIP (titanium(IV) isopropoxide), Ti(NEtMe)₄ (titanium(IV)tetrakisethylmethylaniline), Ti(NMe)₄ (titanium(IV)tetrakisdimethylamine)
 - 5 ○ Hf – Hf(NEtMe)₄ (hafnium(IV)tetrakisethylmethylaniline), HyALD (hafnium(IV)cyclopentadienyl-trisdimethylamine)
 - Zr – Zr(NEtMe)₄ (zirconium(IV)tetrakisethylmethylaniline), ZyALD (zirconium(IV)cyclopentadienyl-trisdimethylamine)
 - 10 ○ Si – BEMAS (bisethylmethlamino silane), BDEAS (bisdiethylaminosilane), 3DMAS (trisdimethylaminosilane)
 - Y – ArY₃ (yttrium(III)bisethylcyclopentadienyl-isopropylamidinate)
 - Al – TMA (trimethyl aluminum), AlCl₃, AlMeCl₂, and AlMe₂Cl.
14. The process of claim 1 wherein the step of dosing the substrate with a metal-containing
- 15 ALD precursor comprises a step of introducing the precursor into the chamber followed by a pulse step of introducing precursor and draw control simultaneously; wherein draw control comprises flow of an inert gas and applying vacuum; wherein the pulse step is conducted for between 5 to 50 ms;
- followed by a step of from 10 to 500 ms in which no precursor flows into the system.
- 20
15. The process of claim 14 wherein the step of dosing is conducted for 150 ms or less.
16. The process of claim 13 wherein an inert gas flows through the chamber for at least 200 ms; preferably wherein no precursor is introduced and no vacuum is applied to the chamber.
- 25
17. The process of claim 2 wherein the sub-pulses with the oxidant without the nitrogen-containing reactant are conducted for a longer period of time than the sub-pulse with the oxidant and the nitrogen-containing reactant. (the sub-pulses are summed together for this calculation)

18. The process of claim 17 wherein the sub-pulses with the oxidant without the nitrogen-containing reactant are conducted for a period of time at least two times longer than the sub-pulse with the oxidant and the nitrogen-containing reactant.
- 5 19. The process of claim 5 wherein the sub-pulses with the oxidant without the sulfur-containing reactant are conducted for a longer period of time than the sub-pulse with the oxidant and the sulfur-containing reactant. (the sub-pulses are summed together for this calculation)
20. The process of claim 17 wherein the sub-pulses with the oxidant without the sulfur-
10 containing reactant are conducted for a period of time at least two times longer than the sub-pulse with the oxidant and the sulfur-containing reactant.
21. An Intermittent Catalyzed Reaction Induced Surface Process (ICRISP) for producing a film having a thickness T and composition $M_xO_yN_z$ from a metal-containing precursor wherein
15 x is 1 or 2, y is from 0 to 4, and z is from 0 to 2, an oxygen-containing precursor, and a nitrogen-containing precursor, at a temperature of 300°C or lower, comprising the steps:
- a) dosing the metal-containing precursor for a pulse for time of 5 to 500 ms;
 - b) purging and/or flushing the metal-containing precursor for a time of 250 to 30000 ms;
 - c) if $y > 0$:
 - 20 i. dosing the oxygen-containing precursor for time t_3 ;
 - ii. dosing the nitrogen-containing precursor entrained in the oxygen-containing precursor for time t_4 , wherein $t_4 < t_3$;
 - iii. dosing the oxygen-containing precursor for time t_5 , wherein $t_5 > t_4$;
 - iv. optionally repeating steps c.ii. and c.iii. as many times as required to convert at least
25 99% of the metal-containing precursor deposited in step a) to an M_xO_y layer;
 - d) if $z > 0$:
 - i. dosing the nitrogen-containing precursor for time t_6
 - ii. dosing the oxygen-containing precursor entrained in the nitrogen-containing precursor for time t_7 , wherein $t_7 < t_6$;
 - 30 iii. dosing the nitrogen-containing precursor for time t_8 , wherein $t_8 > t_7$;

iv. optionally repeating steps d)ii. and d)iii. as many times as required to convert at least 99% of the metal-containing precursor deposited in step a. to an M_xN_z layer; and
repeating steps a through d until a desired thickness T is obtained.