AUTOMATIC CONTROL OF STOICHIOMETRY IN CVD OF METAL SILICATES BY ALTERNATING SURFACE REACTIONS

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ABSTRACT

Metal silicates, such as zirconium silicate, have recently been deposited by surface reactions between metal amide vapors and tris(*tert*-butoxy)silanol vapor.[1] When the vapors are brought to a heated surface either simultaneously (CVD conditions) or alternately (ALD conditions), metal silicate films form with compositions that are very uniform even over large areas of deposit. The ALD conditions also produce excellent thickness uniformity and conformal step coverage. This paper proposes a mechanism by which the films are formed by reactions on the surface of the growing film. The mechanism explains why the surface reactions are self-limiting and lead automatically to uniform stoichiometry and thickness. It also explains how the carbon and nitrogen in the precursors is eliminated, leaving pure films. The mechanism also rationalizes how the remarkably high growth rate, over 0.3 nm per cycle, is achieved from rather bulky precursors that by conventional arguments would be expected to produce a low growth rate.

INTRODUCTION

The vapor deposition of multicomponent materials can often produce different compositions on different areas of a substrate. Such variations in stoichiometry may arise from the different reactivities of different precursors used to supply the various components of the material. For example, in depositing strontium titanate, the strontium precursor is typically more reactive than the titanium precursor. Then strontium-rich films are deposited near the gas inlet, and titanium-rich films near the gas exhaust. These effects can be mitigated by careful design of the reactor. For example, rotating disk reactors can produce nearly uniform compositions, but at the cost of very low deposition efficiency resulting in the usage of large amounts of the precursors.

"Single source" precursors can be designed to contain all of the desired elements in the correct proportions, but the atoms in each molecule are not generally incorporated with equal efficiency and with spatial uniformity. Furthermore, the composition of a single-source precursor cannot be adjusted continuously to correct for differences in incorporation efficiency of different elements.

Another approach to controlling the stoichiometry is to use for each element precursors that chemisorb to a surface by self-limiting reactions. This means that even if different amounts of a reactant arrive at different parts of the substrate, the same amount of material will be deposited on each part of the substrate. After the surface is saturated with this reactant, any excess reactant that has not chemisorbed is removed from the

reactor by flow of carrier gas. Then a precursor vapor containing a second element is chemisorbed onto the surface by reactions that limit it to a certain saturated concentration. Then the cycle is repeated by dosing again with the first reactant, and then the second reactant. Each cycle deposits a layer whose composition and thickness are highly uniform over the surface. This alternating layer deposition (ALD) method has been demonstrated for certain reactants for a number of materials.[2] This method has commonly been called atomic layer deposition (ALD), even though layers of molecules, not atoms, are being chemisorbed onto the surface. Thus these processes should be termed molecular layer deposition. Re-intepreting ALD as "alternating layer deposition," rather than "atomic layer deposition," emphasizes that the essential feature of this method is the alternation of self-limiting chemisorption steps, without implying that the adsorbing species must be either single atoms or whole molecules. In the mechanisms that we propose in this paper, the chemisorbing species are always molecules, but in some cases subsequent surface reactions cause desorption of all but one atom in the molecule.

ALD processes can have many advantages: good step coverage, dense and pinhole-free films, excellent control of thickness and stoichiometry, and scalability to larger areas.

ALD processes are particularly suitable for forming ultrathin high-k dielectric layers needed in future generations of silicon microelectronics. Uniformity and good control of thickness and stoichiometry are readily achieved. ALD of high-k metal silicates can be done from metal chloride precursors in a non-oxidizing deposition atmosphere, so that the interface between the deposited layer and the silicon substrate remains abrupt and free of low-k interfacial oxides, but the films are contaminated with chlorine.[3]

New halogen-free metal alkylamide precursors avoid halogen contamination of metal silicate films and corrosion of deposition systems while also maintaining non-oxidizing deposition conditions.[1] They also provide remarkably high deposition rates of metal silicates (over 0.3 nm per cycle) at low deposition temperatures (200 to 300 °C). A typical reaction uses tetrakis(dimethylamino)hafnium and tris(*tert*-butoxy)silanol to deposit hafnium silicate:

$Hf(NMe_2)_4 + 2\,(^tBuO)_3SiOH \rightarrow HfSi_2O_6$ + volatile byproducts

For the case of lanthanide metals such as yttrium, lanthanum and praseodymium, the silicates are formed from reactions such as

$2\,Ln(N(SiMe_3)_4)_3 + 2\,(^tBuO)_3SiOH \rightarrow Ln_2Si_2O_7$ + volatile byproducts

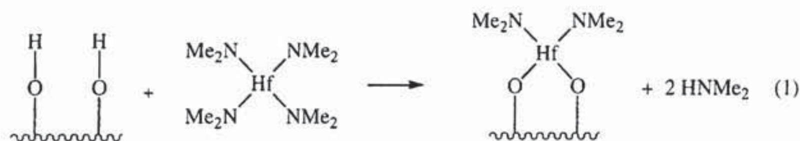
In this paper we propose mechanisms for the surface reactions in the ALD of these metal silicates.

THEORETICAL DESIGN OF THE PRECURSORS AND REACTION SEQUENCE FOR DEPOSITING HAFNIUM SILICATE

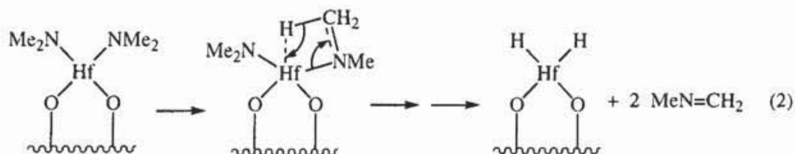
For a reaction to function effectively in ALD, it needs two precursors with specific chemical reactivity and physical properties. When the first reagent vapor is introduced

into the reactor, it must chemisorb rapidly onto the surface of the substrate, but only up to a monolayer coverage. The volatility of the precursor must be high enough so that multilayer physical adsorption does not occur. Then those atoms in the precursor that are not desired in the film must desorb rapidly into the gas phase as volatile species that are swept away with the flow of the carrier gas. Finally the surface must be left in a chemical state that is ready to chemisorb with the other reactant.

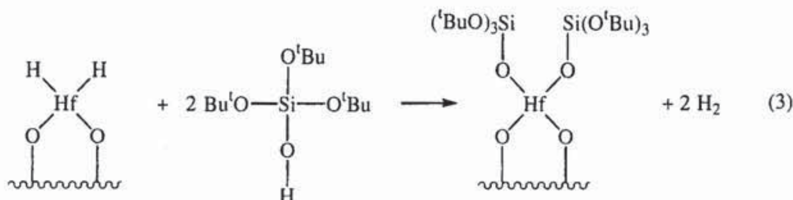
Prior to deposition, the substrate surfaces should be covered with hydroxyl groups that serve as the reactive sites for the first chemisorption reaction. Metal alkylamides are highly reactive toward hydroxyl groups. As an example, hafnium alkylamides can be used to deliver and bind hafnium to the surface. A monolayer of tetrakis(dimethylamino)hafnium is chemisorbed onto a hydroxyl-terminated surface by self-limiting reactions such as



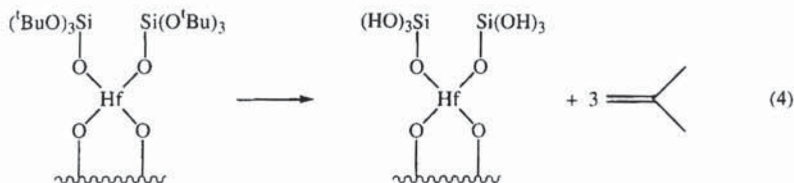
The vapors of the volatile byproduct amine (such as HL = $HNMe_2$) are swept out of the reactor by the flow of the carrier gas. Other hafnium precursor molecules may react with a single hydroxyl, or even three close hydroxyls. The remaining 1, 2 or 3 amide ligands then detach from the surface as N-methylimine vapor after a β-hydrogen shift:



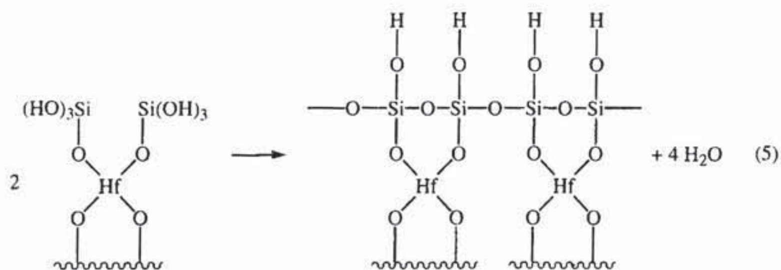
The next pulse of silanol precursor chemisorbs to this surface by the self-limiting reaction



Then the *tert*-butyl groups detach by β-hydrogen elimination to give surface hydroxyl groups and gaseous isobutene:[4]



Then water is eliminated by condensation between neighboring hydroxyls:



The remaining hydroxyls are ready to react with hafnium precursor molecules from the next pulse, to start the cycle of reactions (1) through (5) again. The net effect this complete cycle of reactions is to add material with the stoichiometry $HfSi_2O_6$ to the surface.

Using alternating pulses of metal amide and silanol, films were reproducibly formed on a substrates heated to between 200 and 300 °C. Rutherford backscattering spectroscopy (RBS) showed compositions containing only hafnium, silicon and oxygen, with silicon to hafnium ratios between 2.0 and 2.2, in fairly close agreement with the ratio of 2 predicted by this mechanism. No carbon or nitrogen was detected in the films by RBS or by X-ray photoelectron spectroscopy (XPS), showing that the proposed elimination reactions proceed to completion.[1]

When these vapors are brought simultaneously to a heated surface (CVD conditions), this stochiometry is preserved even where there is an excess of one or another reactant, because of the self-limiting nature of these reactions. However, the thickness generally varies over the surface, because the number of reaction cycles is limited only by the kinetics and the local concentration of the limiting reagent. When the vapors are supplied alternately to the surface under ALD conditions, then both the growth rate and the stoichiometry are the same over the whole surface, because the same number of reaction cycles take place everywhere on the surface. Ellipsometry showed that each ALD cycle of the two precursors adds about 0.3 nm to the thickness of the film. This is a remarkably high growth rate per cycle, particularly with precursors having such bulky ligands. This high growth rate supports this mechanism in which the bulky ligands desorb before the next pulse of reactant.

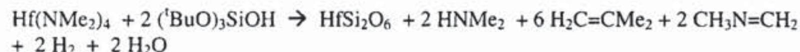
The net result of reactions (1) and (2) is the chemisorption of a hafnium atom onto the surface. Thus a pulse of hafnium dialkylamide molecules really does deposit an atomic layer. In contrast, the net result of reactions (3) – (5) is the chemisorption of a Si_2O_6 molecule from the tris(*tert*-butoxy)silanol. The ratio of the masses deposited in these two stages is thus predicted to be

(Atomic Mass of Hf)/(Molecular Mass of Si_2O_6) = 178.49 /152.17 = 1.17

The thermal decomposition of the amide ligands, reaction (2), may not go to completion, particularly at lower substrate temperatures. In such cases, the remaining ligands will nevertheless be removed later by reaction with the silanol. Then the ratio of the masses deposited in the two stages will be larger than in the case of complete thermal decomposition of the amide ligands.

If only the tris(*tert*-butoxy)silanol vapor is brought to a hydroxylated surface without any metal amide, then no material deposits because there is no reaction between the silanol and the hydroxyl groups. This prediction is in agreement with experiments. If only the metal amide vapor is used without any silanol at temperatures up to 300 °C, then only one molecular layer chemisorbs and the reaction stops because all of the surface hydroxyl sites have reacted. If, however, the surface temperature of the substrate is high enough to desorb hydrogen from hafnium hydride (over 300 °C[5]), then the bare hafnium metal atoms can insert into carbon-hydrogen bonds of additional precursors. Thus temperatures over 300 °C are predicted to give non-self-limiting growth of material containing hafnium, carbon and nitrogen, in agreement with experiment.[6] Thus 300 °C represents an upper limit to the range in which self-limiting ALD is possible with this precursor.

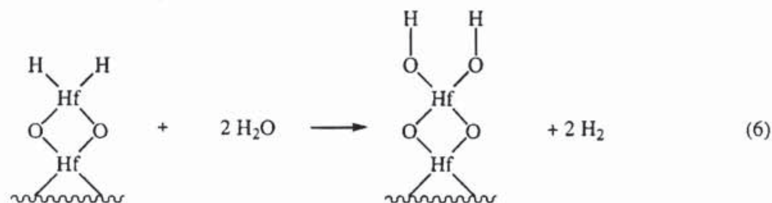
This mechanism also predicts that the volatile byproducts of this reaction cycle should be dimethylamine, isobutene, N-methylimine, hydrogen and water:



$$Hf(NMe_2)_4 + 2\,(^tBuO)_3SiOH \rightarrow HfSi_2O_6 + 2\,HNMe_2 + 6\,H_2C{=}CMe_2 + 2\,CH_3N{=}CH_2 + 2\,H_2 + 2\,H_2O$$

If the amide ligands do not undergo thermal decomposition, then N-methylimine and hydrogen will not be byproducts, and twice as much dimethylamine will appear instead.

By using water pulses in place of the silanol pulses, metal oxides, rather than silicates, can be grown by ALD using the metal alkylamide sources. The reactions (1) and (2) are the same as above, followed by the reaction with water:



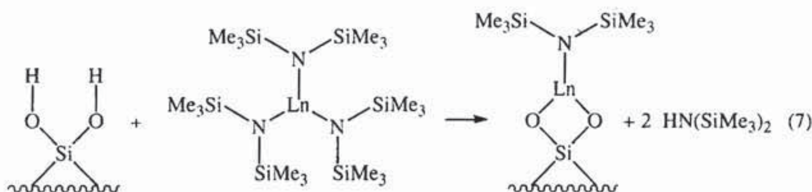
This cycle of alternating hafnium alkylamide and water pulses produces hafnium oxide, HfO_2. Films of hafnium oxide with this stoichiometry were deposited by this ALD reaction at a rate of 0.15 nm/cycle.[6]

The silicon content of the films can be adjusted in a well-controlled way by replacing some of the silanol pulses by water pulses, to produce $HfSi_{2-x}O_{6-2x}$ for any x in the range $0 < x < 2$.

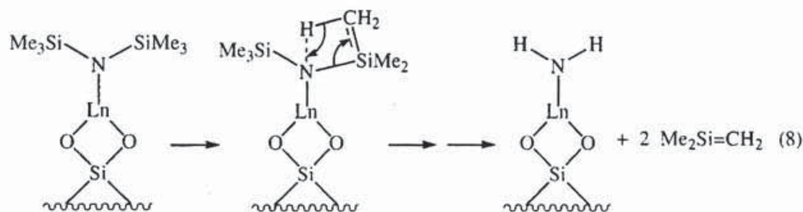
Similar reactions can be used to deposit zirconium silicate and zirconium oxide.

THEORETICAL DESIGN OF THE PRECURSORS AND REACTION SEQUENCE FOR DEPOSITING SILICATES OF THE LANTHANIDE METALS

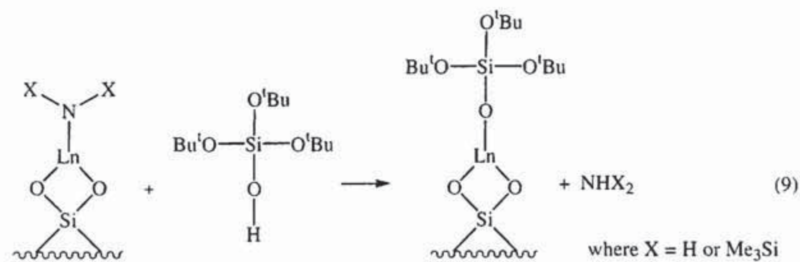
The tris(bis(trimethylsilyl)amides) of the lanthanides are water-sensitive and volatile, so they should react with silanols to form silicates in a manner somewhat analogous to the alkylamides of the group 4 metals zirconium and hafnium. The first step involves chemisorption onto a hydroxylated surface:



Because these compounds do not have a hydrogen β to the metal, they cannot produce metal hydrides by reactions like equation (2) for hafnium. The lanthanide compounds do, however, have hydrogens β to the nitrogens, so some of the trimethylsilylamide li β-elimination can desorb dimethylsilene leaving a metal amide:

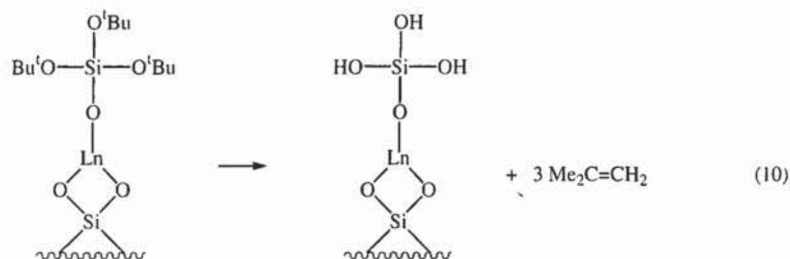


The acidic proton in tris(*tert*(butoxy)silanol reacts readily with the metal amide, or with the undecomposed metal trimethylsilylamide:



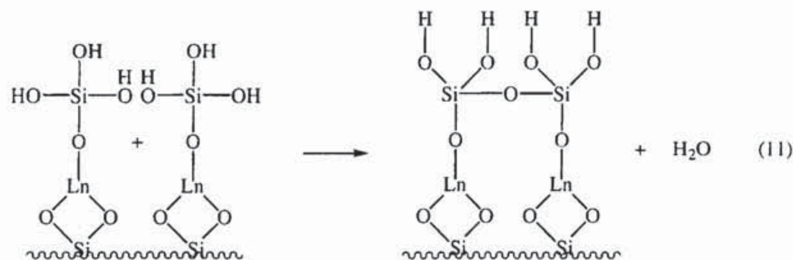
(9)

The *tert*-butyl groups can then desorb as isobutene by β-hydrogen elimination:



(10)

Elimination of water between some neighboring hydroxyls then produces a surface with the same number of hydroxyls as it had at the start of the cycle, so that the same cycle can be replicated:



(11)

This cycle of reactions (7) through (11) predicts the deposition of material with stoichiometry $Ln_2Si_2O_7$. The silicon content can be lowered (or eliminated) in a controlled way by replacing some (or all) of the silanol pulses with water pulses to deposit material with stoichiometry $Ln_2Si_{2-x}O_{7-2x}$ for any x between 0 and 2.

The effect of a pulse of a lanthanide amide precursor is to chemisorb the molecule LnN by reactions (7) and (8). Following a silanol pulse, reactions (9) – (11) remove a nitrogen atom and add a $SiO_{3.5}$ molecule. The ratio of these masses is predicted to be

(Molecular mass of LnN)/(Molecular mass of $SiO_{3.5}$ - Atomic mass of N)

CONCLUSIONS

A theoretical mechanism is proposed for surface reactions between metal amides and tertiary alkoxysilanols to form metal silicates with well-defined stoichiometry. The reactions lead to complete elimination of the bulky organic ligands as volatile byproducts. Applying alternating pulses of these reactants to a surface is predicted to lead to films with uniform thicknesses and stoichiometries with smooth surfaces. The reactions take place under non-oxidizing and non-corrosive conditions at moderate temperatures, so that damage to substrates is minimized and abrupt interfaces between film and substrate can be preserved. Using alternating pulses of water and metal amides can form metal oxides by similar reactions.

These predictions have been verified experimentally for zirconium and hafnium silicate films deposited from the metal alkylamides and tris(*tert*-butoxy)silanol at substrate temperatures from 200-300 °C. Similar reactions of water with zirconium and hafnium alkylamides produced films of the metal oxides.

Silicates and oxides of metals such as hafnium, zirconium, lanthanum and yttrium have higher dielectric constants than silica, and are considered likely materials to replace silica in gate oxides in future microelectronic devices. The excellent uniformity of stoichiometry and thickness make these new ALD reactions good candidates for this application.

ACKNOWLEDGMENTS

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