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ALTERNATING LAYER CHEMICAL VAPOR DEPOSITION (ALD) OF METAL SILICATES AND OXIDES FOR GATE INSULATORS

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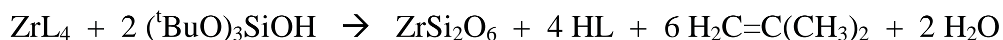
ABSTRACT

A new process was developed for deposition of the silicates and oxides of metals such as zirconium and hafnium at low substrate temperatures (100-300 ^oC). The silicon and oxygen source is tris(tert-butoxy)silanol, $(^tBuO)_3SiOH$, and the metal precursors are metal amides. A typical reaction is



$$ZrL_4 + 2\,(^tBuO)_3SiOH \rightarrow ZrSi_2O_6 + 4\,HL + 6\,H_2C{=}C(CH_3)_2 + 2\,H_2O$$

in which the ligand L is ethylmethylamide, -NEtMe. The precursor vapors were alternately pulsed into a heated reactor, yielding about 0.3 to 0.7 nm of metal silicate film for each cycle. Replacing the silanol pulses with water pulses yields pure metal oxides with a thickness of about 0.1 to 0.15 nm per cycle. The silicon content of the films can be adjusted to any desired value by replacing some of the silanol pulses by water pulses. This new process has a number of advantages over previous methods for depositing metal silicates. Uniformity of thickness and stoichiometry are readily achieved. The deposition atmosphere is non-oxidizing, so that formation of low-k interfacial oxides between the deposited layer and a silicon substrate is minimized. The new halogen-free precursors avoid halogen contamination of films and corrosion of deposition systems. This process is a promising method for forming the next generation of ultra-thin high-k gate dielectrics in silicon-based microelectronics.

INTRODUCTION

Alternating layer chemical vapor deposition (ALD) is a process for forming solid materials, such as coatings, from alternating pulses of reactant vapors. (A commonly used designation, atomic layer deposition, does not describe our new silicate process, in which one of the precursors adds a layer of molecular clusters, such as Si_2O_6, rather than a single atomic layer.) 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 of oxides has often been carried out using metal chlorides as precursors.[1] However, residual chloride contamination in the films may cause problems such as loss of adhesion, electrical instability or corrosion of metal gate electrodes. Metal alkyls and metal β-diketonates may leave carbon contamination in the films.

We have found that ALD using metal alkylamide precursors can produce very pure metal silicates and metal oxides under mild conditions. A novel silicon source, tris(tert-butoxy)silanol, facilitates ALD of metal silicates at high growth rates.

THEORETICAL DESIGN OF THE PRECURSORS AND REACTION SEQUENCE

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 the other reactant.

Prior to deposition, we chose to cover the substrate surfaces with hydroxyl groups that serve as the reactive sites for chemisorption. Metal alkylamides are highly reactive toward hydroxyl groups. As an example, zirconium alkylamides can be used to deliver and bind zirconium to the surface. A monolayer of the metal alkylamide is chemisorbed onto a hydroxyl-terminated surface by self-limiting reactions such as

$$2\ \text{Surface-OH} + ZrL_4 \rightarrow \text{Surface-}O_2ZrL_2 + 2\ HL, \qquad (1)$$

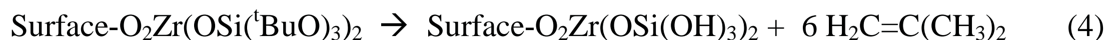
in which the ligand L is an alkylamide such as ethylmethylamide, -NEtMe. The vapors of the volatile byproduct amine (such as HL = HNEtMe) are swept out of the reactor by the flow of the carrier gas. Other zirconium amides may react with a single hydroxyl, or even three close hydroxyls. Some of the remaining 1, 2 or 3 amide ligands then detach from the surface by as imine vapor after a β-hydrogen shift by reactions such as the following:

$$\text{Surface-}O_2ZrL_2 \rightarrow \text{Surface-}O_2ZrH_2 + 2\ CH_3N{=}CHCH_3 \qquad (2)$$

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

$$2\ ({}^tBuO)_3SiOH + \text{Surface-}O_2ZrX_2 \rightarrow \text{Surface-}O_2Zr(OSi({}^tBuO)_3)_2 + 2\ HX, \qquad (3)$$

where X = H or NR_2. Any remaining alkylamide lignds also react with the silanol. Then the tert-butyl groups detach by β-hydrogen elimination to give surface hydroxyl groups and gaseous isobutene byproduct:



$$\text{Surface-}O_2Zr(OSi({}^tBuO)_3)_2 \rightarrow \text{Surface-}O_2Zr(OSi(OH)_3)_2 + 6\ H_2C{=}C(CH_3)_2 \qquad (4)$$

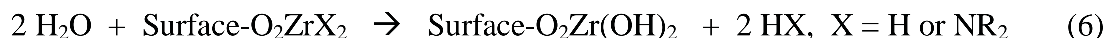
Some of the remaining hydroxyls attached to the silicon are then eliminated by condensation with neighboring hydroxyls, leaving (say) two surface hydroxyls on each silicon.

$$\text{Surface-}O_2Zr(OSi(OH)_3)_2 \rightarrow \text{Surface-}O_2ZrO_2Si_2O_2(OH)_2 + 2\ H_2O \qquad (5)$$

These two hydroxyls are ready to react with another zirconium precursor molecule, to start the cycle again.

Similar reactions were used to deposit silicates of hafnium, yttrium and lanthanum.

By using water pulses in place of the silanol pulses, pure 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 reactions with water, to produce zirconium dioxide, ZrO_2:



$2\ H_2O + \text{Surface-}O_2ZrX_2 \rightarrow \text{Surface-}O_2Zr(OH)_2 + 2\ HX,\ X = H \text{ or } NR_2$ (6)

SYNTHESIS OF PRECURSORS

The silanol precursor is readily synthesized from inexpensive reactants, by the following two reactions:

$SiCl_4 + 3\ {}^tBuOH \rightarrow ({}^tBuO)_3SiCl + 3\ HCl$

$({}^tBuO)_3SiCl + H_2O \rightarrow ({}^tBuO)_3SiOH + HCl$

Detailed experimental conditions follow.

Tri-*t*-butoxychlorosilane. One mole of silicon tetrachloride was added dropwise with stirring to an ice-cooled mixture of four moles of *t*-butyl alcohol, four moles of pyridine and 300 ml of toluene. The reaction mixture was then heated to reflux for 10 hrs. The precipitate of pyridine hydrochloride was filtered off and was thoroughly washed. 43.4% of tri-*t*-butoxychlorosilane was obtained by distillation (97 ºC at 12 Torr; bp 204 ºC). ^1H NMR (C_6D_6) ppm 1.35 (s, 9H, C**H**$_3$); ^{13}C NMR (C_6D_6) ppm 74.99 (**C**$(CH_3)_3$), 31.17 (C(**C**$H_3)_3$).

Tri-*t*-butoxysilanol. To a solution of one mole of pyridine and a large excess (22 moles) of water, one mole of tri-*t*-butoxychlorosilane was added. Then the mixture was stirred at 70-80 ºC for 1 hr and left standing overnight. After the white solid thus formed was filtered and washed with water, the solid was dissolved in ether and dehydrated with anhydrous magnesium sulfate. The solvent was removed and the residue gave (70%) of a white crystalline solid, mp 65.5 ºC. The solid was sublimed at 20 ºC in high vacuum. ^1H NMR (C_6D_6) ppm 2.29 (s, 1H, OH), 1.38 (s, 9H, C**H**$_3$); ^{13}C NMR (C_6D_6) ppm 72.71 (**C**$(CH_3)_3$), 31.44 (C(**C**$H_3)_3$). Tri-*t*-butoxysilanol is stable in contact with air and water at room temperature. It is now commercially available.[2]

The metal amides may be synthesized from the metal chlorides by published procedures.[3] Zirconium dimethylamide, ethylmethyamide and diethylamide are commercially available.[4] The metal amides are very reactive to moisture, and must be synthesized, handled and used in carefully-dried equipment and solvents.

ALD EXPERIMENTS

The precursors were vaporized by flash evaporation. For this purpose, each precursor was dissolved in liquid tetradecane at a concentration of 1 wt.%. This hydrocarbon solvent was chosen because its vapor pressure is low enough (about 5 milli-Torr) so that it does not boil at room temperature even when open to the full vacuum of the pump (about 10 milli-Torr). The solutions were placed separately in 2 reservoirs each pressurized with dry nitrogen gas. A dip tube in each reservoir lead to a 10 microliter sample loop of a chromatography valve (Valco Instruments, Houston, TX, model EP4C6WEPH). Under computer control, the solution in a sample loop was forced by a flow of 0.1 L/min of nitrogen gas into the end of a 2.5 cm diameter tube heated in a tube furnace. The entry zone into the tube contained a static mixer (Kenics,

model 1-09104, from Chemineer, Inc., North Andover, MA) on which the solution impacted and quickly vaporized. The static mixer also served to mix and distribute the vapors more uniformly in the tube furnace. The opposite end of the tube furnace was connected to a liquid nitrogen trap and a vacuum pump that typically maintained a pressure of 1 Torr in the tube.

The nitrogen gas flowed through a given sample loop for 0.3 seconds, although the solution was discharged from the loop in a time much shorter than this. Then the valve was turned back to the position in which it was refilled from the reservoir. After an adjustable time period, the computer directed the second valve to discharge the precursor in its sample loop, and then returned the valve to its refill position. The flow of 0.1 L/min of nitrogen continued through each valve in either position, although there is a brief instant (<0.05 sec) during which the nitrogen flow is interrupted during the time in which the valve is turning. During this interruption of one carrier gas flow, the other gas flow continues. The only effect of the flow interruption is a brief decrease of a few per cent in the pressure, followed by a brief increase caused by the expansion of the solvent vapor pulse. The vaporization zone in the tube furnace was typically held at temperatures from 100 to 200 °C, while the deposition zone and substrates were held at temperatures between 100 and 350 °C.

Silicon substrates were prepared by a standard RCA clean, followed by dipping in 1% HF solution until the surface became hydrophobic. Then the surface was exposed to UV-ozone until it became hydrophilic. The resulting surface is expected to have a hydroxyl-terminated silica layer about 0.8 nm thick.[5]

RESULTS

Control experiments using only one precursor showed no deposition on substrates at temperatures up to 300 °C. Above 300 °C, films were formed from zirconium ethylmethylamide alone. This temperature thus represents an upper limit to the range in which self-limiting ALD is possible with this precursor. No films were formed from tris(tert-butoxy)silanol alone at temperatures up to at least 400 °C.

Using alternating pulses of metal amide and silanol, films were formed reproducibly on substrates heated to between 250 and 300 °C. Rutherford backscattering spectra (RBS), such as the one shown in Figure 1, showed compositions containing only metal, silicon and oxygen, with silicon to metal ratios between 2 and 4 and no detectable impurities. The RBS detection limits were about 0.5 atomic % for nitrogen and 2 atomic % for carbon.

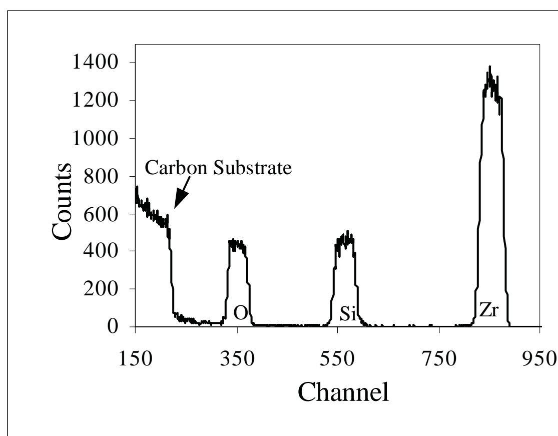


Figure 1. Rutherford Backscattering Spectrum of an ALD zirconium silicate film deposited on glassy carbon. The silicon to zirconium ratio is 2.85.

Ellipsometry showed that each cycle of the two precursors adds about 0.3 to 0.7 nm to the thickness of the film. Refractive index values were typically about 1.6. Thicknesses and refractive indices were constant over the length (30 cm) and width (2.5 cm) of the tube furnace. Variation of the solution concentration between 0.2 % and 1 % had negligible effect on the composition or thickness. These results indicate that the surface reactions are self-limiting under these conditions.

X-ray diffraction showed that these films are amorphous. Film density was found by combining RBS and ellipsometry to be about 3.5 g/cm^3. As expected, this value is smaller than the density, 4.6 g/cm^3, of $ZrSiO_4$, which has a higher zirconium content and is crystalline.

Cross-sectional transmission electron micrographs (TEM) showed that the interface between the silicon substrate and a hafnium silicate film is abrupt and smooth, and that the upper surfaces of the films are also smooth. TEM also verified the amorphous structure of the films. A typical TEM is shown in Figure 2.

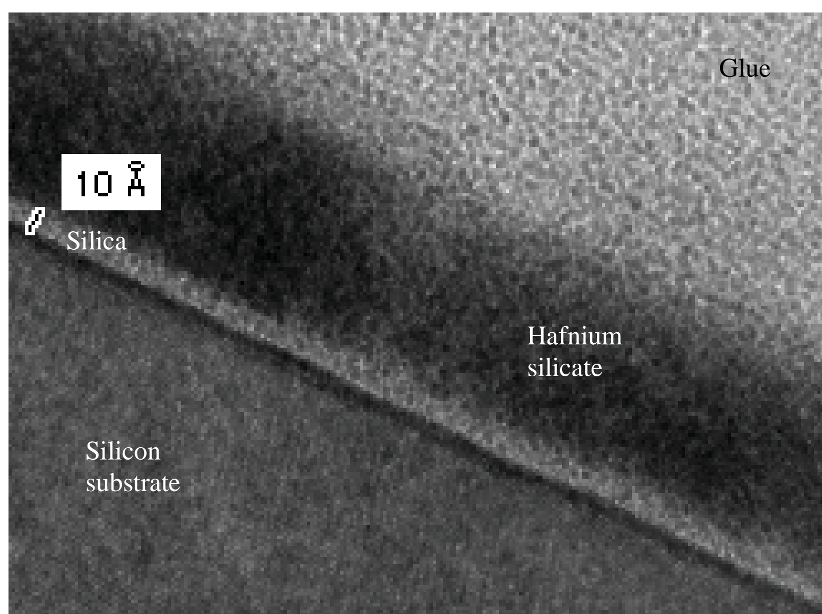


Figure 2. Transmission Electron Micrograph of the interface between a hafnium silicate film and the substrate silicon.

Zirconium oxide films were made by alternating pulses of zirconium(IV)ethylmethylamide (10 microliters of tetradecane solution/pulse, 2 wt. %) and neat water (0.5 microliter/pulse). The vaporization zone was held at 150 ^{o}C and the deposition zone at 200 ^{o}C. Films of zirconium oxide, ZrO_2, were deposited at a rate of 0.1 nm/cycle. Precursor doses less than 0.1 microliter gave thinner films. Increasing the precursor doses above 0.1 microliter/pulse did not cause any further increase in growth rate, showing that the surface reactions are saturated in this range. The refractive index of these films was about 2.1. No carbon or nitrogen was detected in the zirconium oxide films by RBS. Similar ZrO_2 films were formed at substrate temperatures from 100 ^{o}C (0.15 nm/cycle) to 300 ^{o}C (0.1 nm/cycle).

DISCUSSION

The zirconium silicate and zirconium oxide films are remarkably pure, considering that the precursors contain large amounts of carbon and nitrogen. The non-detectable level of these potential impurities in the films supports the idea that the ligands desorb rapidly, perhaps by the proposed β-hydrogen shift mechanism.

The growth rate/cycle of the silicate films is remarkably high, more than twice as high as previously reported ALD reactions.[1] This high growth rate is found despite the large sizes of the precursor molecules, which are normally found to produce low ALD growth rates for bulky ligands such as β-diketonates.[6] The difference appears to be the fact that the β-diketonates lack the facile β-hydrogen decomposition pathway open to the alkylamide ligands.

CONCLUSIONS

Zirconium silicate films were deposited by ALD from novel precursors: zirconium alkylamides and tris(tert-butoxy)silanol. These precursors have a number of advantages. The deposition reactions are rapid under mild deposition conditions, 250-300 ^{o}C in a non-oxidizing and non-corrosive atmosphere. They produce pure, amorphous films with well-controlled, uniform thicknesses and stoichiometries, and smooth, abrupt interfaces with substrates and smooth surfaces. Replacing the silanol with water produces pure zirconium oxide films at even lower substrate temperatures (100 ^{o}C to 300 ^{o}C).

Zirconium silicate and zirconium oxide are leading candidates for replacing silicon dioxide as a gate dielectric in the next generation of microelectronics.[7] The processes introduced in this paper are very suitable for making these high-k dielectrics.

ACKNOWLEDGMENTS

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