Chem. Mater. **2001,** *13,* 2463−2464

Vapor Deposition of Metal Oxides and Silicates: Possible Gate Insulators for Future Microelectronics

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Received February 16, 2001
Revised Manuscript Received June 13, 2001

The speed and functionality of computers have followed "Moore's Law",[1] doubling every year or two for the past 40 years. This remarkable increase in performance has required shrinking the integrated circuits to smaller and smaller sizes. The smallest of the dimensions in modern circuits is the thickness of the gate insulator, which electrically separates the controlling electrode (the gate) from the controlled current in the silicon. This gate insulator has always been made from silicon dioxide, which in the most advanced devices has been reduced to a thickness of only about 1.5 nm or about 4 atomic layers of silicon and oxygen. Further reduction of this thickness would allow current to leak through the silicon dioxide insulator in unacceptably large amounts, by quantum-mechanical tunneling.[2,3] The computer industry projects that this technical barrier will repeal Moore's Law by about 2005.[4]

Intense efforts are underway worldwide to find a technical solution to this problem. Most efforts have focused on replacing silicon dioxide with a material having a higher dielectric constant "k". Such a high-k material could be made thicker than 1.5 nm to avoid the leakage by tunneling, but still would maintain the electric field needed for the gate to control the circuit because of its higher dielectric constant. Numerous materials do in fact have the required higher dielectric constant, but a potential high-k replacement must also satisfy many other stringent requirements. Leading candidates for meeting these requirements include the silicates and oxides of hafnium, zirconium, lanthanum, and yttrium.[2,3] Also necessary is a method for depositing these materials in highly pure form, with good control of stoichiometry, uniform thickness over large areas, conformal coverage of irregular surfaces, an abrupt interface with substrate silicon, a smooth surface, and no grain boundaries, cracks, or pinholes.

Chemical vapor deposition (CVD) and atomic layer deposition (ALD) are methods for depositing thin layers that may have these properties. In CVD, reactant vapors are brought together to the surface of the growing film, while in ALD they are brought separately in alternating pulses.[5] Previous methods for ALD of metal silicates and oxides have usually relied on metal chlorides as precursors for the metals. These precursors have either left chloride impurities in the film[6] or used conditions that oxidize the underlying silicon substrate to produce a low-k layer that degrades the performance of the high-k material.[7] Chloride precursors and the byproducts from their reactions also corrode materials such as stainless steel and aluminum that are commonly used to build deposition systems. Lack of sufficient volatility is another problem with the use of some metal chlorides, such as lanthanum and yttrium, as vapor precursors.

We present new deposition processes for metal silicates and oxides that provide excellent properties and avoid these difficulties. We find that metal alkylamides and tris(*tert*-alkoxy)silanols are very suitable precursors for vapor deposition of films of metal silicates. A typical example is the reaction of tetrakis(dimethylamino)-hafnium[8] vapor, $Hf(N(CH_3)_2)_4$, with tris(*tert*-butoxy)-silanol[9] vapor, $(t\text{-BuO})_3SiOH$. At substrate temperatures from about 250 to 350 °C these vapors react[10] to form films of hafnium silicate glass, $HfO_2(SiO_2)_x$, with silicon/hafnium ratios ranging from about $x = 2$ to $x = 3$, depending on deposition conditions. Films with similar composition have been prepared recently by remote plasma-enhanced CVD.[11]

These solid precursors were each dissolved in anhydrous tetradecane. A dip tube led each solution from a reservoir pressurized with nitrogen to a sampling valve normally used for gas or liquid chromatography.[12] When a valve turned, a 10-μL droplet of solution was ejected and carried by a 0.1 L/min flow of dry nitrogen into a 2.5-cm diameter tube furnace containing substrates of silicon and glassy carbon. The tube was evacuated from the opposite end to a pressure of 1 Torr. To perform ALD experiments, the valves for the two precursor solutions were actuated alternately (for 100−250 cycles) with a typical spacing of 15 s to purge the reactor of volatile byproducts and any excess reactants. For CVD experiments, the valves were pulsed simultaneously.

Analysis of the films by Rutherford backscattering spectroscopy (RBS) showed (Figure 1) that carbon and nitrogen impurities were less than 2 at. %. Under ALD conditions, the thickness (as determined by ellipsometry) of the films did not change by more than 2% along the 300-mm length of the tube furnace. Under

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10.1021/cm010145k CCC: $20.00 © 2001 American Chemical Society
Published on Web 07/10/2001

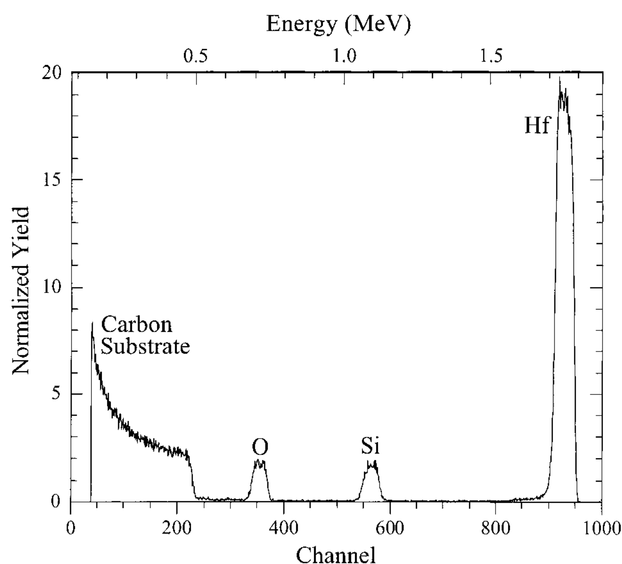

Figure 1. Rutherford backscattering spectroscopy (RBS) data for a hafnium silicate film deposited on a glassy carbon substrate at a temperature of 250 °C. The peaks integrate to give a Si/Hf ratio of 2.1 ± 0.1.

CVD conditions, the thickness decreased along the gas flow direction.

Scanning electron microscopy showed the hafnium silicate films are smooth, free of cracks or pinholes, and conformal over holes with an aspect ratio of 6:1.[13] Atomic force microscopy found surface roughness <0.5% of the film thickness. Transmission electron microscopy showed that the films are amorphous and have <1 nm of interfacial oxide (mostly native silicon oxide) between the film and the substrate silicon, confirming that an abrupt silicon to film interface is preserved by the nonoxidizing deposition conditions.[14]

The self-limiting nature of this reaction under ALD conditions was established by runs using solutions with different concentrations of the precursor. The film growth per cycle increased as the concentration increased from 0.1 to 1 wt %. For concentrations higher than 1% each ALD cycle added between 0.3 and 0.4 nm to the thickness of the film. This is an astonishingly high value, higher than any other previously reported ALD reaction,[15] despite the fact that the ligands are rather bulky. (For example, 36 of the 37 atoms in the hafnium precursor are converted to volatile byproducts.) It has generally been assumed that precursors with bulky ligands must lead to low growth rates, as for example in the case of magnesium oxide deposition from a bulky β-diketonate precursor at a rate 40 times slower than for this new hafnium silicate reaction.[16]

An indicator of the efficiency of the chemisorption reactions is that a majority of the input hafnium, silicon, and oxygen atoms (measured by RBS) are found in the film on the substrates and the exposed walls of the tube furnace, even though the average residence time of the flowing vapors in the reactor is only about 0.05 s. The initial rise in mass recorded for each pulse by a quartz crystal microbalance[17] was very rapid (<0.25 s, its time resolution), confirming the high speed of the chemisorption reactions.

Metal oxide films were grown using water pulses in place of the tris(*tert*-butoxy)silanol pulses. Films of HfO_2 were grown by this reaction at temperatures from 250 to 350 °C at about 0.1 nm/cycle, a rate also much larger than expected for such a bulky precursor.

Volatile alkylamides are also known for the metals Be, Al, Ga, Ti, Zr, V, Nb, Ta, Cr, Mo, W, Ge, Sn, Sb, U, and Th.[18] Thus, we expect that it is possible to deposit silicates and oxides of these metals by similar reactions with alkoxysilanols or water. Preliminary data have been obtained for the deposition of zirconium silicate and zirconium oxide at temperatures even lower than those used for hafnium.

There are no known volatile alkylamides of the lanthanide metals, but volatile tris(bis(trimethylsilyl)amido)lanthanide compounds are known. We found that tris(bis(trimethylsilyl)amido)lanthanum[19] vapor reacts with tris(*tert*-butoxy)silanol vapor to deposit films of amorphous lanthanum silicate, $(La_2O_3)(SiO_2)_x$, under either CVD or ALD conditions. Using water in place of the silanol gave films of lanthanum oxide, La_2O_3.

Volatile bis(trimethylsilyl)amide compounds are also known for the metals Li, Na, K, Be, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ge, Sn, Pb, Y, and all the lanthanide metals.[18] Thus, we expect that silicates and oxides of these metals can also be formed by reactions similar to the one for lanthanum.

We conclude that vapor deposition from metal amides and tris(alkoxy)silanols and/or water is a versatile method for making films of pure metal silicates and metal oxides under mild and noncorrosive conditions. These reactions should be applicable to the majority of the available metals, providing smooth films with uniform thickness and stoichiometry over large areas, and no grain boundaries, cracks, or pinholes. These properties are well-suited for production of the next generation of gate insulators.

Acknowledgment. The authors appreciate discussions with M. Ritala and M. Leskela. We thank Vidya Kaushik and Motorola for providing TEM images. This work was supported in part by the U.S. National Science Foundation and the U.S. Department of Energy.

Supporting Information Available: Figures of a scanning electronic micrograph and transmission electron micrograph of a hafnium silicate film (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) A cross-sectional scanning electron micrograph showing the conformality of the coating is available as Supporting Information.

(14) A cross-sectional transmission electron micrograph showing the native silica interlayer under the coating is available as Supporting Information.

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