Review of Recent Progress in Atomic Layer Deposition (ALD) of Materials for Micro- and Nano-electronics

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ABSRACT

We review processes that we discovered recently for ALD of transition metals, metal nitrides and metal oxides. Successful ALD requires pairs of precursors with high but self-limiting reactivity with surfaces prepared by the complementary co-reactant, along with high thermal stability, sufficient volatility and non-etching behavior toward substrates and the deposited films. New precursor pairs meeting all of these demanding requirements were found for depositing the transition metals iron, cobalt, nickel and copper, their oxides, tungsten nitride, silicon dioxide, and oxides of hafnium, zirconium, lanthanum, praseodymium, tantalum, and bismuth. The metal deposition may be applicable to interconnects and to magnetic devices. Tungsten nitride is an excellent diffusion barrier at nanometer thicknesses. The silica deposition is suitable for filling isolation trenches in microelectronics. The substrate temperatures are low enough so that applications of high-quality high-k dielectrics are possible to temperature sensitive substrates, such as carbon nano-tube transistors and photo-resist patterning by liftoff.

ALD OF TRANSITION METALS AND OXIDES

Atomic layer deposition is a process for depositing highly uniform and conformal thin films by alternating exposures of a surface to vapors of two chemical reactants. ALD processes have been successfully demonstrated for many metal compounds, but only for very few pure metals.

Recently, we discovered processes for ALD of transition metals including copper, cobalt, iron, and nickel.[1] Homoleptic *N,N'*-dialkylacetamidinato metal compounds[2]

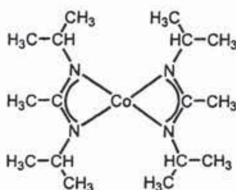

Figure 1. Structure of N,N'-diisopropylacetamidinato-cobalt(II)

and molecular hydrogen gas were used as the reactants. Their surface reactions were found to be complementary and self-limiting, thus providing highly uniform thicknesses and conformal coating of long, narrow holes. We propose that these ALD layers grow by a hydrogenation mechanism that should also operate during the ALD of many other metals. These processes should allow improved production of many devices for which ALD process had not been applicable. Using water as a co-reactant instead of hydrogen, the oxides of these transition metals can be deposited.

Our syntheses of the novel precursors for ALD of cobalt and copper have now been replicated and scaled up by chemists at Sigma-Aldrich Chemical Company, which is offering these materials for sale. Using these precursors, the new ALD processes for metals are currently being evaluated for use in microelectronic interconnects by companies in the semiconductor industry.

ELECTRICALLY CONDUCTIVE TUNGSTEN NITRIDE DIFFUSION BARRIERS

Diffusion barriers are key components in computer chips. They keep metals, such as copper and aluminum, from diffusing out of the wires that connect different parts of the chips. As the sizes of computer chips have been shrunk to provide faster computation and greater storage capacity, new materials are needed to make still thinner diffusion barriers. Another challenge is that the diffusion barriers must be spread uniformly inside extremely narrow holes.

Recently, we discovered a way to make thinner and more effective diffusion barriers out of tungsten nitride, WN.[3] We did this by synthesizing a new "precursor" compound, bis(*tert*-butylimido)-bis(dimethylamido)tungsten,[4]

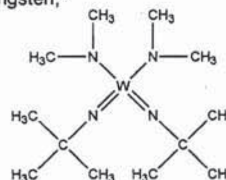

Figure 2. Structure of bis(*tert*-butylimido)bis(dimethylamido)-tungsten

that carries within it the desired tungsten and nitrogen atoms, along with other atoms that allow the precursor to exist as a vapor. We found that this precursor vapor could be converted into a tungsten nitride coating on a hot surface by exposure to ammonia gas. The WN coating demonstrated excellent properties as a diffusion barrier even when it is only 1.5 nanometers thick (just a few atomic layers thick, about 10 times thinner than currently used barriers). In addition, the coating spread uniformly inside extremely narrow holes that are more than 200 diameters deep, surpassing the projected requirements of the semiconductor industry. The ALD WN can also infiltrate crystals of silica micro-spheres, showing the feasibility of using ALD to form inverse opal photonic crystals.[5]

Our synthesis of the novel WN precursor has now been replicated and scaled up by chemists at Sigma-Aldrich Chemical Company, which is offering the material for sale. Using this material, the ALD process and the WN material are currently being evaluated for use as a diffusion barrier by companies in the semiconductor industry.

RAPID ALD OF SILICA

Highly uniform and conformal coatings may be made by the alternating exposures of a surface to vapors of two reactants, in a process commonly called atomic layer deposition (ALD). The application of ALD has, however, been limited because of slow deposition rates, with a theoretical maximum of one monolayer per cycle. We found that alternating exposure of a surface to vapors of trimethylaluminum and tris(*tert*-butoxy)silanol deposits highly conformal layers of amorphous silicon dioxide/aluminum oxide nanolaminates at rates of 15 nm (>40 mono-layers) per cycle.[6] This process allows for the uniform lining or filling of long, narrow holes with aspect ratios greater than 40. We propose that these ALD layers grow by a novel catalytic polymerization mechanism that also operates during the rapid ALD of many other metal silicates. It should allow improved production of many devices, such as trench insulation between transistors in microelectronics, planar waveguides, micro-electromechanical structures, multilayer optical filters and protective layers against diffusion, oxidation, or corrosion.

Synthesis of two different silanol precursors for this process have been scaled up to multi-kilogram quantities by Sigma-Aldrich Chemical Company, and are sold as tris(*tert*-butoxy)silanol, cat. # 55,346-8 and tris(*tert*-pentoxy)silanol, cat. # 55,344-1.

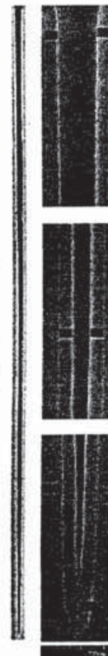

Figure 3. Cross section of a hole with diameter 0.13 micron and depth 8 microns, uncoated (left) and coated by ALD (right) with SiO_2.

After annealing under the expected conditions, the breakdown voltage of these films is about 10 MV/cm, in agreement with the best silica films. The films also show less stress than films made by the current technology. Because of the outstanding electrical and mechanical properties of these silica films, they are ideally suited to the requirements for shallow trench isolation of transistors and sealing pores in low-k dielectrics.[7] Several other applications of this rapid process for the ALD of silica are also currently under intense development by the semiconductor industry.

INSULATORS WITH HIGH DIELECTRIC CONSTANTS (HIGH-K)

Alternating Layer Deposition (ALD) of smooth and highly conformal films of hafnium and zirconium oxide was achieved using six metal alkyl amide precursors for hafnium and zirconium.[8] Water was used as an oxygen source during these experiments. As deposited, these films exhibited a smooth surface with a measured roughness equivalent to the substrate on which they were deposited. These films also exhibited a very high degree of conformality: 100% step coverage on holes with aspect ratios greater than 200. The films were completely uniform in thickness and composition over the length of the deposition reactor. The films were free of detectable impurities and had the expected (2 to 1) oxygen to metal ratio. Films were deposited at substrate temperatures from 50°C to 500°C from precursors that were vaporized at temperatures from 40°C to 140°C. The precursors were found to be highly reactive with hydroxylated surfaces.

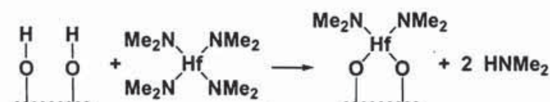

Figure 4. Schematic reaction of hafnium dimethylamide with a hydroxylated surface.

Their vapor pressures were measured over a wide temperature range. Deposition reactors and ALD cycle were designed using these precursors. Tetrakis(ethylmethylamido) hafnium was found to have the best combination of properties as a precursor for ALD of HfO_2. It is a liquid at room temperature and is more thermally stable than the solid tetrakis(dimethylamido) hafnium. It has greater volatility than liquid tetrakis(diethylamido) hafnium.

Atomic force microscopy was used to characterize the surface morphology of 10–100 nm thick films grown from 50 C to 300 C. X-ray diffraction was used to characterize the film crystallinity. Transmission electron microscopy was used to relate the surface morphology to the film crystallinity. A model for the nucleation and growth of crystallites during an ALD deposition leading to surface roughness was developed based on these findings. Analysis of the film properties in the context of this model suggested nanolaminate strategies that can control the surface roughness and crystallite sizes of ALD films. Nanolaminates of hafnium, zirconium and aluminum oxide were prepared and showed the reduction in roughness predicted by the model of film growth.[9]

Analysis of these ALD HfO_2 films showed that carbon, nitrogen and chlorine impurities are near the detection limits of very sensitive Secondary Ion Mass Spectroscopy (SIMS) analysis. The dielectric constant of the HfO_2 is about 20, in agreement with the high density of the films (95% of bulk crystalline value). The leakage currents are as low as the best values reported previously for HfO_2: $< 10^{-8}$ A/cm^2 at 1 MV/cm and an equivalent oxide thickness (EOT) of 2 nm. These values meet the specifications for capacitors in advanced DRAMs. Excellent transistors have been made using this process on carbon nanotubes.[10] Synthesis of tetrakis(ethylmethylamido) hafnium has been scaled up by several chemical suppliers, including Sigma-Aldrich, Tri Chemical, Epichem and Praxair. Using this new material, commercial production of HfO_2 insulators for DRAMs is expected to start in 2004.

ALD of highly conformal films of tantalum oxide were studied using tantalum alkylamide precursors and water as the oxygen source.[11] These films also exhibited a very high degree of conformality: 100% step coverage on holes with aspect ratios greater than 35. As deposited, the films were free of detectable impurities with the expected (2.5 to 1) oxygen to metal ratio and were smooth and amorphous. The films were completely uniform in thickness and composition over the length of the reactor used for depositions. Films were deposited at substrate temperatures from 50°C to 350°C from precursors that were vaporized at temperatures from 50°C to 120°C. As deposited, the films showed a dielectric constant of 28 and breakdown field consistently greater than 4.5 MV/cm.

Using these highly reactive ALD precursors, we found a novel method for depositing patterned dielectric layers with sub-micron features using ALD.[12] The patterned films are superior to sputtered or evaporated films in continuity, smoothness, conformality, and minimum feature size. Films were deposited at 100–150 C using several different precursors, patterned using either PMMA or photoresist. The low deposition temperature permits uniform film growth without significant outgassing or hardbaking of resist layers.

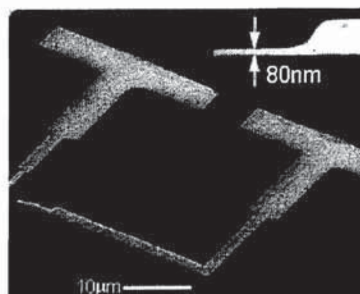

Figure 5. Nanoscale pattern of hafnium oxide produced by liftoff.

The liftoff technique presented here gave sharp step edges with edge roughness as low as ~10nm. We also measured dielectric constants (k) and breakdown fields for the high-k materials aluminum oxide (k ~ 8–9), hafnium oxide (k ~ 16–19) and zirconium oxide (k ~ 20–29), grown under similar low temperature conditions.

Thin films of lanthanum oxide/ aluminum oxide nanolaminates were grown by atomic layer deposition from a new volatile lanthanum precursor, tris(*N,N'*-diisopropylacetamidinato)lanthanum, trimethylaluminum and water.[13] Smooth, amorphous $La_xAl_{1-x}O_3$ films were deposited on HF-last silicon and measured without post-deposition annealing. The films contained less than 1 at. % of carbon. A thin (9.8 nm) film showed low leakage current ($<5*10^{-8}$ A/cm^2 at 1 V at an equivalent oxide thickness of 2.9 nm), flat-band voltage of -0.1 V and low hysteresis (20 mV). Thicker films had even lower leakage currents ($<10^{-8}$ A/cm^2 at 2 MV/cm) but larger flat-band shifts and more hysteresis.

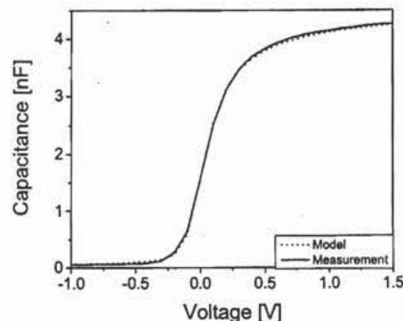

Figure 6. C-V curve of a lanthanum aluminum oxide nanolaminate film

The permittivity of the films was 13 and the dielectric strength 4 MV/cm. Cross sectional HRTEM showed a sharp interface between the film and the silicon substrate. The new ALD process for lanthanum

aluminate is being studied for use as an insulator in DRAM capacitors and in transistor gates.

ACKNOWLEDGEMENT

This work was supported in part by the National Science Foundation.

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