ATOMIC LAYER DEPOSITION (ALD) OF OXIDES, NITRIDES, CARBIDES AND METALS

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Highly uniform and conformal coatings may be made by the alternating exposures of a surface to vapors of two reactants, in a deposition process commonly called ALD. The application of ALD has, however, been limited because of slow deposition rates, with a theoretical maximum of one monolayer per cycle. We show that alternating exposure of a heated surface (200-300 °C) to vapors of trimethylaluminum and tris(*tert*-butoxy)silanol deposits highly conformal layers of amorphous silicon dioxide/aluminum oxide nanolaminates at rates of 12 nm (>32 mono-layers) per cycle. This process allows for the uniform lining or filling of long, narrow holes with aspect ratios > 40:1. We propose that these ALD layers grow by a novel catalytic 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.[1]

Another potential application of this reaction is to sealing of the surfaces of pores in low-k dielectric materials. A catalytic monolayer of aluminum oxide is first deposited on the outer surface of the porous low-k material by a CVD process with poor step coverage. Then the activated surface is exposed to a single dose of the vapor of tris(*tert*-butoxy)silanol. A smooth layer of silica is formed that bridges and closes off the pores at the surface without infiltrating into the interior of the pores. In this way, a surface is created that allows the successful formation of utrathin barrier/seed layers by the ALD processes described below, without penetration of conductive material into the pores of the low-k insulator.[2]

Highly uniform, smooth and conformal coatings of tungsten nitride were synthesized by ALD from vapors of a novel precursor, bis(*tert*-butylimido)bis-(dimethylamido)tungsten, $(t\text{-BuN})_2(\text{Me}_2\text{N})_2\text{W}$, and ammonia at low substrate temperatures (250-350 °C). This tungsten precursor is a low-viscosity, non-corrosive liquid with sufficient volatility at room temperature to be a vapor source for ALD. These vapors were alternately pulsed into a heated reactor, where they added up to 0.1 nm to the thickness of tungsten nitride films for each cycle, with no initial delay or induction period. The films were uniform in thickness along the 30 cm length of the deposition zone, as determined by scanning electron microscopy. Successful depositions were carried out on all substrates tested, including silicon, glass, quartz, glassy carbon, aluminum and copper. The films are shiny, silver colored and electrically conducting. All of the films showed good adhesion to the substrates, were acid resistant and did not oxidize over time. The stoichiometry of the WN films was determined to be 1:1 by Rutherford back-scattering spectrometry and X-ray diffraction. The films were mainly amorphous as deposited, with some nano-crystallites (< 3 nm in size) embedded in the film as shown by X-ray diffraction and high-resolution transmission electron microscopy. 100 % step coverage was obtained inside holes with aspect ratios greater than 200:1. Annealing for 30 minutes at temperatures above 750 °C converted the WN to pure, polycrystalline tungsten metal. WN films as thin as 1.5 nm proved to be good barriers to diffusion of copper for temperatures up to 600 °C. ALD of copper onto the surface of the WN produced strongly adherent copper films that could be used as “seed” layers for CVD or electro-deposition of thicker copper coatings.[3]

Tungsten carbide, WC, films were grown at 250 °C by plasma-assisted ALD from bis(*tert*-butylimido)bis(dimethylamido)tungsten and H_2/N_2 plasma in a vertical flow reactor. The saturated growth rate was 0.05 nm/cycle and the film resistivity varied from 0.29 to 1 milliΩ-cm, depending on the plasma conditions. The films are generally smooth and the conformality of the films deposited in holes with an aspect ratio of 15:1 was 100%.[4]

Electrically conductive films of cobalt metal and copper metal were formed by atomic layer deposition from novel precursors. The syntheses and properties of the precursors will be described. Cobalt metal films were deposited on heated substrates (300 °C) by the reaction of alternating doses of cobalt(II) bis(*N,N'*-diisopropylacetamidinate) vapor and hydrogen gas. Smooth cobalt films nucleated uniformly and densely on hydroxylated silica surfaces and on tungsten nitride diffusion barriers. Copper metal films were deposited on heated substrates (200 °C) by the reaction of alternating doses of copper(I) *N,N'*-diisopropylacetamidinate vapor and hydrogen gas. Rough copper films nucleated sparsely and were agglomerated when grown on the same substrates. By growing a thin cobalt film followed immediately by a copper film, smooth and adherent copper films were produced. The films have very uniform thickness and excellent step coverage in narrow holes with aspect ratios over 60:1. These films appear to be very suitable as adhesion/seed layers in copper interconnects and as magnetoresistive multilayers in magnetic storage devices.[5]

A simple theory was developed for the conditions needed for ALD of coatings with uniform thickness in narrow holes of arbitrary cross section. Two conditions are found to be necessary: 1) certain minimum amounts of vapor must be supplied and 2) a certain minimum product of vapor pressure and its exposure time at the entrance to the hole. The theory is in good agreement with data from the reaction of hafnium dimethylamide vapor and water vapor to form hafnium dioxide films that are completely conformal in holes with an aspect ratio of 43. The theory provides a simple scaling law to predict the conditions needed to coat holes with other aspect ratios.[6]

REFERENCES

1. D. Hausmann, J. Becker, S. Wang, R. G. Gordon, Science **298**, 402 (2002).
2. P. de Rouffignac and R. G. Gordon, submitted.
3. J. Becker, S. Suh and R. G. Gordon, submitted.
4. D. H. Kim, Y. J. Kim, B. T. Lee, J. H. Kim, S. Suh and R. G. Gordon, submitted.
5. B. S. Lim and R. G. Gordon, submitted.
6. R. G. Gordon, D. Hausmann, E. Kim and J. Shepard, accepted for publication in Chemical Vapor Deposition.