Wednesday Afternoon, November 6, 2002

Thin Films
Room: C-101 - Session TF-WeA

Atomic Layer Deposition - Applications of ALD
Moderator: R.J. Carter, IMEC, Belgium

2:00pm **TF-WeA1 Influence of Film Roughness on the Electrical Properties of W / Al_2O_3 Films Grown on Si(100) by Atomic Layer Deposition**, ***F.H. Fabreguette***, *M.D. Groner, Z.A. Sechrist, S.M. George*, University of Colorado

The SiO_2 interfacial layer seriously impacts the electrical behavior of alumina high k dielectrics on silicon substrate, and produces a reduction of the overall dielectric constant with decreasing thickness of the high k dielectrics. To avoid the SiO_2 interfacial layer and probe the electrical properties of ultrathin dielectrics, Al_2O_3 layers were grown on tungsten on Si(100) using Atomic layer Deposition (ALD) technique. Si/W/Al_2O_3 structures are expected to exhibit a dielectric constant independent of the Al_2O_3 film thickness, because the tungsten layer should act as an equipotential electrode. These Si/W/Al_2O_3 structures were grown in a viscous flow ALD reactor using $Al(CH_3)_3$ and H_2O for the Al_2O_3 ALD, and WF_6 and Si_2H_6 for W ALD. The W thickness was kept constant while the Al_2O_3 thickness was varied. Ellipsometry was used to measure the Al_2O_3 ALD film thickness. Surface roughness was measured using Atomic Force Microscopy. The dielectric constant calculated from C-V curves was apparently reduced for the smaller Al_2O_3 thicknesses, even though impedance spectroscopy did not exhibit any interfacial oxide. By comparing this apparent dielectric constant reduction and the film roughness, the apparent reduction was discovered to be linked with the film roughness. The film roughness was then minimized using a Hadamard matrix optimization approach to adjust the various ALD parameters. With the surface roughness minimized, Si/W/Al_2O_3 structures were fabricated where the Al_2O_3 dielectric constant was almost independent of the Al_2O_3 layer thickness.

2:20pm **TF-WeA2 Growth and Structure of Al_2O_3/W Nanolaminates Fabricated Using Atomic Layer Deposition Techniques**, ***Z.A. Sechrist***, *F.H. Fabreguette*, University of Colorado, *O. Heintz*, Universite de Bourgogne, *S.M. George*, University of Colorado

Nanolaminates are expected to have unique thermal, mechanical, electrical and optical properties. Atomic layer deposition (ALD) methods have been used to grow Al_2O_3/W nanolaminates. Al_2O_3 ALD is based on the binary reaction: $2Al(CH_3)_3 + 3H_2O \rightarrow Al_2O_3 + 6CH_4$. W ALD is based on the binary reaction: $WF_6 + Si_2H_6 \rightarrow W + 2SiF_3H + 2H_2$. To optimize Al_2O_3/W nanolaminate growth, W ALD has been examined using in situ quartz crystal microbalance (QCM) investigations. The QCM measurements reveal extremely linear W growth versus the number of binary reaction cycles. The W deposition rates are dependent on substrate temperature and Si_2H_6 exposures. The W ALD deposition rates vary from ~4 Å per AB cycle at 177°C and ~10^5 L Si_2H_6 exposures to ~7 Å per AB cycle at 325°C and ~10^7 L Si_2H_6 exposures. QCM studies of Al_2O_3/W nanolaminate growth reveal that the nucleation of W ALD on Al_2O_3 surfaces is a critical variable. Atomic force microscope studies indicate that the shortest nucleation times yield the lowest surface roughnesses for the Al_2O_3/W nanolaminates. W ALD nucleation times were shortened by increasing Si_2H_6 exposures. Al_2O_3 nucleation times were shortened by finishing the W growth with a WF_6 exposure. The structural analysis of these nanolaminates using transmission electron microscopy (TEM) yields very well-resolved superlattice structures. X-ray reflectivity (XRR) measurements confirmed very conformal Al_2O_3 and W deposition with low interfacial roughness. Secondary ion mass spectrometry (SIMS) gave chemical confirmation of alternating oxide/metal nanolayers with regularly repeating AlO^+ and W^+ ion signals as the ion beam milled through the nanolaminate.

2:40pm **TF-WeA3 Examination of New ALD Processes for Microelectronics**, ***M. Ritala***, *K. Kukli, T. Aaltonen, P. Alen, M. Vehkamäki, T. Hänninen, T. Hatanpää, R. Matero, A. Niskanen, A. Rahtu, V. Pore, M. Leskelä*, University of Helsinki, Finland

During the past years the atomic layer deposition (ALD) method has gained a lot of interest among semiconductor industry as a potential future manufacturing technology. Though the method has been widely examined by several groups, the studies have mainly focused to only a few processes: $Al(CH_3)_3$ - H_2O, $ZrCl_4$ - H_2O, $HfCl_4$ - H_2O and $TiCl_4$ - NH_3. While the $Al(CH_3)_3$ - H_2O process can be considered as a nearly ideal ALD process, the others have some limitations and drawbacks, thereby leaving room for improvement and calling for new chemical approaches for a deposition of the corresponding materials. In addition, there is a whole range of other materials, like metals and ferroelectrics, for which efficient ALD processes should be developed. In this presentation, our recent results on developing new ALD processes for microelectronic applications will be presented.

3:00pm **TF-WeA4 Temperature Effects during Quartz-crystal Microbalance Measurements of Thin Film Growth during Atomic Layer Deposition**, ***M.N. Rocklein***, *S.M. George*, University of Colorado, Boulder

The quartz-crystal microbalance (QCM) has become a very useful, in situ tool for monitoring atomic layer deposition (ALD) in viscous flow reactors. Mass changes can be measured for individual reactant pulses and for the entire ALD reaction cycle. These mass changes reveal information about the ALD reaction stoichiometry and the ALD film growth rate. Unfortunately, serious error in the QCM mass measurement can occur because of temperature effects. We will show that instantaneous apparent mass changes may be caused by differences in temperature between the reactant gas pulse and the QCM and that slow apparent mass drift may be caused by the integrated effect of many individual reactant gas pulses. These effects are clearly demonstrated by modifying the temperature profile along the length of the reactor tube and by using an exposure sequence of inert gases. These temperature effects are also illustrated using Al_2O_3 ALD as a model system. The primary factors influencing the magnitude and sign of the temperature-induced apparent mass change are determined to be the QCM temperature, the temperature profile of the reactor before the QCM, the type of gas, the gas flux, the ALD timing sequence and adiabatic cooling of the reactant gas. The results of this study also suggest methods to minimize these temperature-induced apparent mass changes for reliable QCM measurements of ALD in a viscous flow reactor.

3:20pm **TF-WeA5 Atomic Layer Deposition of Tribological Coatings for MEMS Devices**, ***T.M. Mayer***, *P.G. Kotula, R.S. Goeke*, Sandia National Laboratories, *J.W. Elam, S.M. George*, University of Colorado

Friction and wear are major concerns in the performance and reliability of micromechanical (MEMS) devices. However, the severe geometric constraints of many micromechanical systems (high aspect ratios, shadowed surfaces) make most deposition methods for friction and wear-resistance coatings impossible. We have produced highly conformal coatings of Al_2O_3 and ZnO, deposited by atomic layer deposition (ALD), for use on surface micromachined (SMM) and LIGA structures. We demonstrate extremely uniform deposition of 10 nm films of amorphous Al_2O_3 on micromachine structures with aspect ratio up to 50 (feature depth vs. width). Friction coefficient of the Al_2O_3 on flat surfaces is measured to be approx. 0.3, while wear resistance of the films is improved over that of the SiO_2/Si substrate. ZnO is a potentially lubricious film, whose tribological properties depend on the crystallite structure in the film. Thin, nm-thick films are shown to be nanocrystalline with low friction coefficient, while thicker films with larger grain size exhibit high friction coefficient. We can control crystallite size through thickness and temperature control in the deposition process, or by laminating the ZnO film with nm-thick layers of Al_2O_3 in the ALD process. We will report the tribological properties of ZnO films and nanolaminates as a function of crystallite size and preparation methods.

3:40pm **TF-WeA6 Conformal Coating of Ultrahigh Aspect Ratio Anodic Alumina Membranes by Atomic Layer Deposition**, ***J.W. Elam***, University of Colorado, *D. Routkevitch, P.P. Mardilovich*, Nanomaterials Research Corporation, *S.M. George*, University of Colorado

Anodic alumina (AA) membranes are unique nanostructures that are permeated by highly uniform, nanometer-scale pores arranged in a hexagonal close packed array. The application of AA membranes to gas sensors requires that the nanopores with ultrahigh aspect ratios of L/d~1000 be coated by uniform films of chemoresistive materials such as ZnO. In this study, AA membranes were coated with Al_2O_3 and ZnO atomic layer deposition (ALD) films in a viscous flow ALD reactor. The coated membranes were analyzed using cross-sectional scanning electron microscopy (SEM) and electron probe microanalysis (EPMA). SEM analysis of individual nanopores revealed that the AA membranes with nanopore dimensions of d=65 nm and L=50 µm could be coated conformally by Al_2O_3 ALD using sufficient reactant exposure times. EPMA measurements with a spatial resolution of 3-5 µm were performed following ZnO ALD on the d=65 nm, L=50 µm AA membranes. The EPMA Zn concentration profiles showed the progr essive infiltration of the ZnO ALD into the nanopores with increasing exposure times. Monte Carlo simulations of these experiments assuming Knudsen diffusion accurately reproduced the experimental ZnO EPMA concentration profiles. Furthermore, this modelin g predicted that the diffusion-limited coating process would become

reaction-limited given a sufficiently low ALD reaction probability. To test this idea, Fourier transform infrared absorption measurements were performed during the coating of the AA membranes by Al_2O_3 and SiO_2 ALD. In agreement with the predictions, diffusion-limited behavior with a $t^{1/2}$ time dependence was observed for Al_2O_3 ALD during the AlOH* + $Al(CH_3)_3$ -> $AlOAl(CH_3)_2$* + CH_4 reaction. In contrast, reaction-limited behavior with a t^1 time dependence was observed for SiO_2 ALD during the SiOH* + $SiCl_4$ -> $SiOSiCl_3$* + HCl reaction.

4:00pm **TF-WeA7 Low Temperature Al_2O_3 Atomic Layer Deposition**, ***M.D. Groner***, *F.H. Faberguette, J.W. Elam, S.M. George*, University of Colorado at Boulder

Although Al_2O_3 is one of the most common dielectric materials grown by atomic layer deposition (ALD), very little is known about Al_2O_3 ALD at the low temperatures. Deposition at temperatures < 150°C is required for many important coating applications such as deposition of gas diffusion barrier layers on thermally sensitive polymers. Thin Al_2O_3 films were deposited by ALD at low temperatures in a viscous flow reactor using alternating exposures of trimethylaluminum and water. Deposition temperatures ranged from ~ 30°C to 125°C. The properties of Al_2O_3 ALD films grown on Si(100) substrates were studied versus growth temperature. Al_2O_3 film thicknesses, growth rates, densities, and optical properties were determined using surface profilometry, atomic force microscopy, quartz crystal microbalance, and ellipsometry measurements. In addition, current-voltage (IV) and capacitance-voltage (CV) measurements were employed to evaluate the electrical properties of the low temperature Al_2O_3 ALD films. The film densities and dielectric constants were reduced at the lower deposition temperatures. However, deposition at lower temperatures still achieved conformal Al_2O_3 growth. Low temperature Al_2O_3 ALD was also demonstrated on polymeric substrates. Preliminary measurements have characterized the effects of these Al_2O_3 ALD films on gas permeabilities.

4:20pm **TF-WeA8 Theoretical and Experimental Investigation of Atomic Layer Deposition of Copper(I) Oxide**, ***T. Törndahl***, *M. Ottosson, K.M.E. Larsson, J.-O. Carlsson*, Uppsala University, Sweden

Atomic Layer Deposition (ALD) of copper(I) oxide from copper(I) chloride and water has been investigated both theoretically and experimentally. The theoretical modeling was conducted on the reconstructed non-polar (111) surface of copper(I) oxide, using gradient corrected density functional calculations. Among the studied process steps related to the film growth were copper(I) chloride adsorption on different copper(I) oxide (111) surface sites and reactivity against water. The experimental studies have been carried out from 350 °C, were the films start to grow, up to 700 °C, where the deposition rate starts to decrease. The texture of the films was controlled to a large extent by the substrates. On fused silica no texture was observed while on aluminium oxide, (102) oriented, films with strong (110) texture were obtained. The experimental results will be discussed in connection to the theoretical modeling of the deposition process.

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