Thin Films Division
Room 615 - Session TF-TuM
Advanced Thin Film Formation Chemistry

Moderator: G.N. Parsons, North Carolina State University

8:20am **TF-TuM1 Coatings from Liquid and Supercritical Carbon Dioxide***, B.J. Novick, E.N. Hoggan,* North Carolina State University*; D. Flowers,* University of North Carolina*; Y. Chernyak,* North Carolina State University*; J.M. DeSimone,* North Carolina State University and University of North Carolina*; **R.G. Carbonell,*** North Carolina State University **INVITED**

Carbon dioxide offers several environmental as well as performance advantages over conventional solvents. The recent development of CO@sub 2@-soluble polymers and surfactants has broadened significantly the number of potential applications for supercritical and liquid carbon dioxide as a solvent for the formation of thin films and coatings. This paper discusses recent work on coatings of polymeric materials from both supercritical as well as liquid carbon dioxide. The rapid expansion of supercritical solution (RESS) process using CO@sub 2@ can produce thin films and sub-micron powders of a wide variety of inorganic and polymeric materials. The process involves the expansion of a solution through a nozzle to an ambient downstream pressure. The present work is aimed at gaining an understanding of the relationship between the morphology and dimensions of the precipitates and RESS operating conditions. A computational fluid dynamic analysis of the process path can help relate the rates of change of pressure and temperature in the nozzle to the thermodynamics of binodal and spinodal decomposition. These relationships govern deposition rates and the rates of droplet nucleation and growth. Liquid carbon dioxide also offers some advantages over conventional solvents for spin coating and free meniscus (dip coating) applications. Because of its low viscosity and low surface tension, it has the potential of forming thinner films and of penetrating into narrower features on the surfaces being coated. As examples, results are shown on the spin coating and development of CO@sub 2@-soluble polymers for photolithography, and the deposition of polymeric lubricants on the surface of hard disk drive materials by dip coating.

9:00am **TF-TuM3 Organic Films Prepared by Polymer Sputtering***, **H. Biederman**,* Charles University at Prague, The Czech Republic, Czech Republic **INVITED**

Deposition of organic films by means of radio frequency (rf) sputtering of conventional polymers became the center of attention in the seventies. The interest was particularly in polytetrafluoroethylene (PTFE)@footnote 1@ because of the prospect to prepare useful dielectric films and low friction coatings. Recently the interest in polymer sputtering was renewed and in addition to PTFE polyimide (PI) and polyethylene (PE) etc. were examined.Findings from these studies are concisely reviewed. Recent results are presented from our laboratory, obtained using balanced and unbalanced rf magnetron sputtering of PTFE and PE. The results of the kinetics of rf magnetron sputtering of PTFE by energy resolved mass spectrometry are shown. Various C@sub X@F@sub Y@ species were detected in the discharge, with the composition affected by the discharge parameters. It is assumed that CF, CF@sub 2@ and CF@sub 3@ fragments from the sputter process are the most important for film growth.@footnote 2@ The process was also monitored in situ by OES (Optical emission spectroscopy). The morphology of fluorocarbon plasma polymer films deposited on Si substrates at various temperature was observed by means of scanning electron microscopy. It was concluded that below +23 °C a columnar structure appears. The structure and basic properties of hydrocarbon plasma polymer films prepared by rf sputtering of PE are presented. @FootnoteText@ @footnote 1@ Biederman, H , Ojha, S M, and Holland, L:Thin Solid Films, Vol 41, pp 329- 339, 1977 @footnote 2@ Zeuner, M, Hirsch, D, Neumann, H, Zalman, J and Biederman, H, to be published in Proc. of ISPC 14, Prague August 2-6,1999 .

9:40am **TF-TuM5 Plasma Enhanced Atomic Layer Deposition of Ta for Diffusion Barrier Applications***, A. Sherman,* Sherman and Associates, Inc.*; S. Malhotra, **S.M. Rossnagel**,* IBM Research Division

Atomic Layer Deposition (ALD) is a variation of conventional CVD that uses sequential steps for the adsorption of a monolayer of one reactant and the subsequent exposure of this monolayer to a second reactant, which results in the deposition of roughly a monolayer of the desired elemental or molecular species. This paper describes the use of a free radical second reactant which is produced by a remote plasma source. Because of the high reactivity, it is possible to form films at moderate temperatures rather than the high temperatures of conventional CVD. In this paper, we describe the ALD of Ta, which is used in semiconductor interconect structures for diffusion, adhesion, or nucleation layers in high aspect ratio features which are subsequently filed with Cu. The ALD process is self-limiting in that each 2-step process results in approximately a single atomic layer and film thickness is built up in a controlled manner with a specific number of steps. This is unlike conventional CVD or PVD which are generally timed and require rate calibration. The Ta system uses moderate temperature adsorption of TaCl5 vapor followed by a reaction step using atomic hydrogen from an inductively-coupled rf plasma. The system has been extended to 200mm wafers using a modified Applied Materials Endura (PVD) system, compatible with existing manufacturing tools. Conformal Ta films with uniform thickness have been measured in high aspect ratio features and XRD, AES and RBS data sugget films of high purity adequate for interconnect applications.

10:00am **TF-TuM6 Atomic Layer Deposition of Tungsten and Tungsten Nitride Using Sequential Surface Reactions***, **J.W. Klaus**, S.J. Ferro, S.M. George,* University of Colorado, Boulder

The deposition of ultrathin and conformal films on high aspect ratio structures is important for forming conducting layers and diffusion barriers. Thin films of tungsten (W) and tungsten nitride (W@sub 2@N) were deposited with atomic layer control using sequential surface reactions. The tungsten growth was accomplished by separating the binary reaction WF@sub 6@ + Si@sub 2@H@sub 6@ --> W + 2SiHF@sub 3@ + 2H@sub 2@ into two half-reactions. The tungsten nitride growth was performed by dividing the binary reaction 2WF@sub 6@ + NH@sub 3@ --> W@sub 2@N + 3HF + 9/2F@sub 2@ into two half-reactions. Successive exposure to WF@sub 6@ and Si@sub 2@H@sub 6@ (NH@sub 3@) in an ABAB... binary reaction sequence produced W (W@sub 2@N) deposition at substrate temperatures between 425-600 K (600-800K). The W deposition rate was 2.49 Å/AB cycle for WF@sub 6@ and Si@sub 2@H@sub 6@ reactant exposures > 800 L and 1600 L, respectively. The WN deposition rate was 2.55 Å/AB cycle for WF@sub 6@ and NH@sub 3@ reactant exposures > 3000 L and 10,000 L, respectively. Atomic force micrographs of the deposited films on Si(100) were remarkably flat indicating smooth and conformal deposition. These results for W represent the first demonstration of atomic layer deposition of conformal single-element films using sequential surface reactions. Similar surface chemical strategies may facilitate the atomic layer growth of other metals besides tungsten.

10:20am **TF-TuM7 Relating Phase Content to Deposition Kinetics in Ultra-Thin Sputtered Tantalum Films***, **J.F. Whitacre**,* University of Michigan*; Z.U. Rek,* Stanford Synchrotron Radiation Laboratory*; S.M. Yalisove, J.C. Bilello,* University of Michigan

How phase and stress formation relate to adatom kinetics in extremely thin sputtered Ta films was examined. This was accomplished by controlling the adatom kinetic energy distribution at the substrate during growth. If low sputter gas (Ar) pressures are used (less than 5 mTorr), arriving adatoms have kinetic energies on the order of 10 eV as they impinge upon the substrate. At pressures above 15 mTorr, the energy distribution shifts to the thermal regime, where all atoms have energies less than 1 eV. For this experiment, Ta films 25 to 500 Å in thickness were DC magnetron sputter deposited using Ar pressures ranging from 2 to 20 mTorr. The films were analyzed using a synchrotron x-ray source (SSRL beamline 7-2) in conjunction with a four-circle diffractometer aligned in the grazing incidence x-ray scattering (GIXS) geometry. The stress in these films was calculated using double crystal diffraction topography (DCDT, a wafer curvature method) data. Film nanostructure was examined using TEM analysis. Phase content was determined by modeling ideal polycrystalline x-ray diffraction patterns and comparing them with corrected (for air scattering) diffraction data. It was found that films grown at progressively higher pressures displayed a systematic increase in amorphous content. Film grown using 20 mTorr of Ar were 100% amorphous to thicknesses as great as ~150Å. Residual stress analysis showed that all films less than 100 Å thick had compressive stresses on the order of -2 GPa. These results are discussed in context of a model that relates adatom kinetics, surface diffusion, and grain development during the early stages of film growth. Work supported by ARPA under contract No. DAAH-04-95-1-0120. Work done (partially) at SSRL, which is operated by the Department of Energy, Office of Basic Energy Sciences.

10:40am **TF-TuM8 Atomic Layer Controlled Growth of SiO@sub 2@ and Al@sub 2@O@sub 3@ on BN Particles Using Sequential Surface Chemistry**, ***J.D. Ferguson***, *A.W. Weimer, S.M. George,* University of Colorado, Boulder

BN particles have a high thermal conductivity and are relatively inert. To improve BN particle coupling in polymer composites for thermal management applications, ultrathin coatings can be deposited that are more reactive and do not degrade the BN thermal properties. SiO@sub 2@ and Al@sub 2@O@sub 3@ were grown on BN particles with atomic layer control using sequential surface reactions of SiCl@sub 4@/H@sub 2@O@footnote 1@ and Al(CH@sub 3@)@sub 3@/H@sub 2@O,@footnote 2@ respectively. The sequential surface chemistry was monitored in vacuum using transmission Fourier transform infrared vibrational spectroscopy. The initial BN particles displayed B-OH and B-NH@sub 2@ surface species. These groups reacted with SiCl@sub 4@ or Al(CH@sub 3@)@sub 3@ and converted the surface species to Si-Cl or Al-CH@sub 3@. The subsequent reaction with H@sub 2@O converted the surface species to Si-OH or Al-OH. By repeating the sequential surface reactions, SiO@sub 2@ and Al@sub 2@O@sub 3@ bulk vibrational modes increased with number of reaction cycles. Transmission electron microscopy studies revealed conformal coatings on the BN particles. X-ray photoelectron spectroscopy analysis was also consistent with uniform and conformal deposition. These results illustrate the potential of sequential surface reactions to deposit conformal and atomic layer controlled coatings on particles. @FootnoteText@ @footnote 1@ J.W. Klaus, A.W. Ott and S.M. George, Appl. Phys. Lett. 70, 1092 (1997). @footnote 2@ A.W. Ott, J.W. Klaus and S.M. George, Thin Solid Films 292, 135 (1997).

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