Friday Morning, October 29, 1999

Thin Films Division
Room 615 - Session TF-FrM

In-situ Characterization and Material Process Imaging

Moderator: J.S. Zabinski, Air Force Research Laboratory

8:40am **TF-FrM2 Ion Beam Induced Defects and Phonon Confinement in 2H-WS@sub 2@ by "In-situ/Real-Time" Raman Measurements***, **F.S. Ohuchi**,* University of Washington*; K. Ishioka, M. Kitajima,* National Institute for Metals, Japan

Ion beam bombardment induces chemical and structural changes in the solid surface. This occurs because a large fraction of the incident ion energy goes into bulk processes like atomic mixing, dissociation and reduction, forming defects in the material. Ra man scattering is sensitive to small changes that occur in the lattice symmetry of a crystal, thus it has been used as a sensitive structure probe to study the defects in solids. In this paper, we report "in-situ" and "real-time" Raman measurements on tu n gsten disulfide (WS@sub 2@) single crystals during the bombardment of 5 keV He@super +@ ion beam. Changes in the peak intensity, energy and broadening for the E@sub 2g@ phonon mode were measured as a function of ion dose (1x10@super 12@-4x10@super 16@ i o n s/cm@super 2@), and the phonon correlation lengths were obtained using "spatial phonon correlation (SPC)" model. The phonon correlation length decreased with ion irradiation dose, and their changes were correlated with our previous investigation on t h e surface stoichiometry change with ion bombardment (JVST A12(4) 2451, 1994). Appearance of a new shoulder peak at around 416 cm@super -1@ to the A@sub 1g@ peak became evident when the dose exceeded more than 10@super 14@ions/cm@super 2@. This peak is considered as a forbidden mode originated from defect-induced coupling of the longitudinal acoustic (LA) and transverse acoustic (TA) phonons at the K point in the Brillouin zone of the WS@sub 2@ lattice. .

9:00am **TF-FrM3 Toward 'Virtual' Materials Processing Research***, **S.R. LeClair**,* Air Force Research Laboratory **INVITED**

Of the many research challenges in materials science is the development of more comprehensive methods for materials process design and control ranging from bulk materials transformation at the macro scale to increasingly small systems at the nano scale. The unavoidable frontier of the future is 'small-systems', wherein thin-films and MEMs are merely the bow wave to a world of atomic-scale ordering and transitions which will manifest in the interfacial designs of nano-functional building blocks for more portable and efficient systems. Although small-systems have widespread application to Air Force pursuits in becoming a Space Force, the technology will be inevitably driven by the need for more powerful but compact computing and telecommunication devices. Let us assume the inevitability of small-systems, and focus on the more immediate and prerequisite issues relative to materials research and the methods for design, analysis and control of processes to realize small-systems. To enable these methods will require investments - first, in the area of molecular modeling - transforming the various molecular modeling methods from their current use as a limited means of atomic-scale perusal to the simulation of growth processes for the manufacture of small-systems. Also at issue, and potentially more pivotal, is atomic-scale sensing for in situ monitoring of the deposition and self-assembly of nano-functional building blocks and their associated interfaces. We will need in situ, but non-destructive, methods for imaging surfaces and subsurface structures to assess defect densities, electrical, optical and thermal conductivities, size and continuity of granular orientations, etc.

9:40am **TF-FrM5 Stress Evolution during Growth of Epitaxial and Polycrystalline Metal Multilayers***, **V. Ramaswamy**, W.D. Nix, B.M. Clemens,* Stanford University

A complete understanding of the relationship between film stress and microstructure at the various stages of growth and an ability to measure film stress in-situ during growth, provide an opportunity to study film microstructural evolution. In this study, stress evolution during growth of epitaxial and polycrystalline, (111)-oriented Pd/Pt and Pd/Ag multilayers is monitored by in-situ substrate curvature measurement. The initial stress behavior of Pd grown on Ag and Pt is similar in epitaxial and polycrystalline films, with Pd exhibiting a sharp tensile change when grown on Ag and a smaller compressive change followed by a tensile change when grown on Pt. This initial behavior is ascribed to the effects of coherency and surface energy differences between film and underlayer. However, with increasing Pd thickness, remarkable differences are observed in the stress behavior in the epitaxial and polycrystalline samples. In polycrystalline Pd/Pt and Pd/Ag, the tensile stress relaxes with increasing Pd thickness and eventually turns compressive at about 30 Å whereas in the epitaxial samples, the stress in Pd remains tensile even at large thicknesses. The stress behavior of Ag and Pt in Pd/Ag and Pd/Pt multilayers are similar in the epitaxial and polycrystalline cases, with Ag on Pd relaxing completely after the growth of the first monolayer and the development of compressive stress in Pt grown on Pd. The effects of the structural differences between epitaxial and polycrystalline films on the stress behavior are discussed in terms of strengthening mechanisms and susceptibility to the effects of atomic peening.

10:00am **TF-FrM6 Metallic Sputtered Film Evolution Via Real-time/In-situ X-ray Diffraction***, J.F. Whitacre, Z.B. Zhao, B.A. Rainey, **S.M. Yalisove**, J.C. Bilello,* University of Michigan

A laboratory-based in-situ x-ray diffractometer is described. This equipment allows the evolution of sputtered metallic films to be studied during growth. An 18kW rotating anode x-ray source is used in conjunction with an Inel(tm) curvilinear position sensitive detector, which is aligned in the asymmetric or symmetric grazing incidence x-ray scattering (GIXS) geometry. Complete diffraction patterns can be acquired in as little as 2 seconds from films of adequate thickness. The development of texture, stress, grain size, and phase content is observed in coatings consisting of Ta, Cr, and/or CrN. Traditional ex-situ analysis methods are applied to these films after growth and are correlated to the in-situ findings, providing a powerful tool for in-situ process control and optimization. Using this system, films and multilayer coatings can be tailored to have specific microstructural characteristics as they are grown. Data from a number of different experiments will be presented and discussed. This work funded by ARO contracts with numbers DAAH 04-95-1-0120 and 8c DAAG55-98-1-0382.

10:20am **TF-FrM7 In Line Measurement of Ti and TiN Thickness and Optical Constants using Reflectance Data through a Vacuum Chamber Window***, **M.F. Tabet**,* Nanometrics Inc.*; U. Kelkar,* Applied Materials

The thickness and optical constants of titanium and titanium nitride thin films were measured by visible reflectometry through a window of a vacuum deposition system while the wafer is cooling from deposition to room temperature. The measurement system is ultra-compact and was designed for integration into semiconductor processing equipment. This in-line metrology tool does not affect the system throughput. The Ti and TiN films were deposited on 3000 @Ao@ silicon dioxide film on 200 mm silicon wafers using an Applied Materials Endura PVD deposition system. The system was used to measure thin metal films with various thicknesses and deposited using conventional DC magnetron sputtering and Ionized Metal Plasma (IMP) techniques. The optical constants of the Ti and TiN films were modeled through the use of a Lorentz oscillator dispersion model. A standalone production metrology tool was used to measured both ellipsometer and reflectometer data from the same location on the wafer and simultaneously determined the thickness and optical constants model parameters. The dispersion model obtained from the analysis of the combined ellipsometry and reflectometry data was then used to fit the visible reflectance data measured in line. This measurement system can monitor Ti and TiN depositions on every wafer in a production environment.

10:40am **TF-FrM8 Morphology and Growth of Metal Thin Films on Si Probed by In Situ Spectroscopic Ellipsometry@footnote 1@***, **C. Liu**, J. Erdmann, A. Macrander,* Argonne National Laboratory

Here we present results of in situ spectroscopic ellipsometry studies of sputtered thin films of Au, Pt, Pd, Rh, Cr, Cu grown on Si wafers. This study was carried out systematically on incrementally grown metal thin films. Multiple data sets obtained for each film material with incremental thicknesses were analyzed using both flat-film and rough-film models. We found that the initial growth of these metal films on Si is correlated with their chemical bond strength with oxygen in the native oxide of Si. Metals with higher bond strength (such as Cr) grow smoother at the early stage of growth and have a better adhesion to the Si wafer. In metal/Si systems, a Cr thin film is thus commonly added as a "glue" layer between the metal and Si for better adhesion. The Cr film however, becomes rougher as its thickness increases. A glue layer of Cr should not exceed 10 nm to keep the film smooth. Rh films grow smoothly on a thin (6-nm) Cr-covered Si wafer. But on a thick (100-nm) Cr/Si film, they were initially as rough as the thick Cr film. The roughness decreases as the Rh film thickness increases. A relaxation effect was also observed on Rh/Si films. An increase of ~10% in measured Rh thickness was observed two hours after the growth when a flat-film model was used. This puzzle was solved when a rough-film model was applied. The Rh film simply became rougher in vacuum at room temperature and the total mass of Rh did not change. The same Rh film stored in air shrunk to small individual droplets 6 months later. These findings are important in our x-ray mirror applications. @FootnoteText@ This work is supported by the U.S. Department of Energy, BES, under contract no. W-31-109-ENG-38

11:00am **TF-FrM9 Stabilization of High Deposition Rate Reactive Magnetron Sputtering of Oxides by In-Situ Spectroscopic Ellipsometry and Plasma Diagnostics***, **M. Vergöhl**, N. Malkomes, B. Hunsche, B. Szyszka, T. Matthée,* Fraunhofer Institute for Surface Engineering and Thin Films, Germany

High deposition rates are of essential importance in reactive magnetron sputtering on architectural glass. To reach high deposition rates and a high transparency of oxide films with constant properties during the full target lifetime, it is required that the process can be stabilized in a specific window within the transition mode. In general, the control of the plasma parameters alone (i.e. partial pressure, optical emission intensity, plasma impedance) is not sufficient for the definition of an operating point with constant film parameters. Therefore, a control system is proposed that is based on a combination of a short-term stabilization of the plasma and a long-term stabilization employing an in-situ spectroscopic ellipsometer. For niobium and titanium oxide, both an optical emission monitor and reactive gas partial pressure measurement were employed. In addition, it turns out that the specific deposition rate, i.e. deposition rate divided by the power density, is a suitable control parameter. Compared to the oxide mode, the deposition rate of Nb2O5 and TiO2 films deposited in the transition mode could be enlarged by a factor of 3-4. The films were grown at different process parameters (oxygen partial pressure, target power, absolute pressure, mid-frequency and DC-technique) onto unheated substrates. Nearby in-situ ellipsometry, ex-situ spectroscopic ellipsometry at different angles of incidence was applied to study the optical properties and the morphology of the films.

11:20am **TF-FrM10 In-situ Structural, Chemical and Electrical Characterization of WO@sub 3@ Sensor Films***, **S.A. Ding**, C.S. Kim, R.J. Lad,* University of Maine, U.S.

Tungsten trioxide thin films are useful as active elements in semiconducting metal oxide conductance-type gas sensors. To explore the correlation between deposition parameters/post-deposition processing and sensing characteristics of the films, we have used a multi-chambered UHV system to deposit WO@sub 3@ films on r-cut sapphire. In-situ chemical and electrical characterizations of the films were then carried out before and after the exposure to target gases such as H@sub 2@S, Cl@sub 2@ and DMMP. The films were grown using rf magnetron sputtering of a W target in O@sub 2@/Ar mixtures ranging from 0 to 80% O@sub 2@. Additional deposition parameters included growth temperature, rf power and total pressure. Both in-situ RHEED and ex-situ XRD data indicate that a variety of film structures including amorphous, polycrystalline and highly textured films can be achieved by varying those parameters. In-situ conductivity measurements acquired using a four-point van der Pauw method show that the stoichiometry and microstructure have an influence on the electrical behavior of the sensor films. One other important parameter in dictating the electrical characteristics of the sensor films is found to be the deposition rate, which is altered by varying the rf power, O@sub 2@/Ar ratio and the total pressure. The conductivity measurements indicate that the higher rate yields higher baseline conductivity. In-situ XPS study of the films shows the formation of stable surface species upon exposure to the target gases. The observed chemical modification of the surface is discussed within the context of a dependence of sensor behavior on the post-deposition processing of the films.

11:40am **TF-FrM11 Growth and In Situ Characterization of Thin Films by a Dual-Plasma System***, **E.C. Samano**, G. Soto, R. Machorro,* CCMC-UNAM, Mexico

Thin films of CN@sub x@, SiO@sub x@Nsub y@ have a tremendous potential to be used in the mechanical and optical industry due to its unique mechanical and dielectric properties, respectively. The stoichiometric control of these films is highly important to manage their desired properties. A dual-plasma system has been set up to provide free radicals from a solid target by laser ablation, and atoms and ions in gas phase by an ECR source. These highly reactive species are deposited on a single crystal silicon substrate. The stoichiometry and properties of carbon nitride and silicon oxynitride films are studied as a function of N@sub 2@ and O@sub 2@ gas pressure, respectively, and the several PLD and ECR deposition parameters. The films are in situ analyzed in an adjacent analysis chamber by AES, XPS and EELS to determine the chemical stability and bonding of their compounds.

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