Thin Films
Room 203 - Session TF+EL-WeA
In-situ Characterization of Thin Film Growth

Moderator: M.C.M. van de Sanden, Eindhoven University of Technology, The Netherlands

2:00pm **TF+EL-WeA1 Monitoring of Thin Film Metallization by Metastable He Atom Scattering***, G. Witte,* Lehrstuhl fuer Physikalische Chemie I, Germany*; P. Fouquet,* Physikalische Chemie I, RUB, Germany

Here we introduce metastable helium atom scattering (MHAS) to characterize metallization transitions occuring during the growth of ultrathin alkali metal (AM) films on metal and semiconductor surfaces. This technique combines the high sensitivity of HAS for measuring coverage and geometrical structure of the adlayer and the extreme surface sensitivity of the metastable atom deexcitation rate to detect modifications of the electronic surface structure.@footnote 1@ In case of Na, K and Cs on Cu(100) an onset of metallization was found at coverages of about half a monolayer. On the other hand for GaAs(110) somewhat larger coverages are required to produce metallic AM films, which are found to grow only below room temperature. These results are in good agreement with previous MDS experiments. Further experiments were carried out for alkali earth metal (AEM) films, where a particular attention is drawn to the comparison of Cs and Ba on Cu(100). It is shown that the onset of metallization for both systems is very similar and can be well described by a 2D Herzfeld model. Finally, MHAS can also be applied to characterize the demetallization of ultrathin AM and AEM films upon adsorption of CO or oxygen.@footnote 2@ @FootnoteText@ @footnote 1@ P.Fouquet and G. Witte, Phys. Rev. Lett. 83, 360 (1999). @footnote 2@ P.Fouquet and G. Witte, Surf. Sci. 454-456, 256 (2000).

2:20pm **TF+EL-WeA2 Ultraviolet Absorption Spectroscopy of Polytetrafluoroethylene Deposition by Pyrolytic CVD***, **B.A. Cruden**, K.K. Gleason, H.H. Sawin,* Massachusetts Institute of Technology

Polytetrafluoroethylene films have been deposited for use low dielectric constant materials in microelectronic chips. Deposition is performed through pyrolysis of hexafluoropropylene oxide (HFPO) to produce CF@sub 2@, which can then polymerize and deposit as a thin film. The variation of CF@sub 2@ concentration as a function of reactor conditions has been characterized by UV Absorption spectroscopy. CF@sub 2@ concentration is observed to go through a maximum with respect to both pressure and pyrolysis temperature when it is present in large amounts (~10@sup 14@ cm@sup -3@). The kinetics known for HFPO cracking and CF@sub 2@ recombination are not sufficient to describe these dependencies. An additional mechanism of particle formation, by CF@sub 2@ insertion into (CF@sub 2@)@sub n@ oligomers, has been introduced to produce a kinetic model for CF@sub 2@ concentration measurements. Deposition rates are seen to qualitatively track with CF@sub 2@ concentration variations. Attempting to develop a specific relationship between CF@sub 2@ concentration and deposition rate yields a sticking coefficient of ~4x10@sup -5@, which is consistent with what has been measured in a CF@sub 2@ beam experiment. However, this result does not adequately describe deposition profiles, and under some conditions, higher deposition rates than this sticking coefficient allows for have been observed. These results point to two important factors. First, under regimes of high CF@sub 2@ concentration, gas phase polymerization can produce species that contribute significantly to deposition. Second, it is possible that other properties of the deposition can affect the sticking coefficient. The final observation of note is that deposition only becomes detectable when CF@sub 2@ concentration approaches its maximum value. This might imply that (CF@sub 2@)@sub n@ species may be responsible for deposition.

2:40pm **TF+EL-WeA3 Near-edge Valence Band Structure of Amorphous Hydrogenated SiC Thin Films by a Combined use of Auger and Photoemission Processes***, **M.-H. Lee**, F.S. Ohuchi,* University of Washington

Although x-ray photoelectron spectroscopy (XPS) nominally provides useful information about the valence-band (VB) electron density of state (DOS), the VB leading edges for Si-C alloys are not adequately evaluated due to large difference in the photoionization cross-sections between Si-3p and C-2p. A core-valence-valance (CVV) Auger transition contains information about the local valence electronic structure of the probed atom due to the direct coupling of the core and valence levels in the Auger process. In addition, the Auger matrix elements give clear pictures of top and maximum of p-like local density of states (LDOS) around Si and C in the near-edge VB region. In this talk, a combined use of the Auger and photoemission processes for site-specific information about the local density of states (LDOS) and the leading edge in the VB will be described. Binding energy-corrected Auger line shape for each of Si and C was obtained to identify the valence electronic structure in the particular case of amorphous hydrogenated SiC (a-Si@sub 1-x@C@sub x@:H) thin films fabricated by plasma enhanced chemical vapor deposition. In the C-rich region (x @>=@ 0.6), the leading VB edge was defined by C-2p, while the VB edge was determined by both Si-3p and C-2p in Si-rich region (x < 0.6). The conduction band (CB) edge was assigned by electron energy loss spectroscopy (EELS) with Si-2p electron-associated energy loss. The band gap energies obtained from the VB and CB edges were compared to those from optical absorption measurements.

3:00pm **TF+EL-WeA4 Growth of Oxygen-rich Films on Ru(0001)***, **A. Böttcher**, B. Krenzer, W. Stenzel, H. Conrad,* Fritz-Haber-Institut, Germany*; H. Niehus,* Humboldt-Universität, Germany

The potential of photoemission electron microscopy (PEEM) has been utilized for monitoring the modifications of Ru(0001) induced by surface oxidation. The PEEM images of the initial oxidation stages exhibit bright patterns appearing on dark background. The former represent the precursor phases of regular oxides, Ru@sub x@O@sub y@. The background reflect the termination of the Ru(0001) surface by the chemisorbed oxygen layer. The growth of the Ru@sub x@O@sub y@ from nucleation centers to a thick oxide film strongly depends on the oxidation temperature. Three phases differing by characteristic morphologies have been distinguished. For low temperatures, TT@sub H@, the Ru@sub x@O@sub y@ phase manifests itself by very bright discs randomly distributed over large dark areas. For moderate temperatures, T@sub H@>T>T@sub L@, long stripes appear and grow along the main crystallographic directions of Ru(0001). This growth is initiated by formation of light grains. Further oxidation proceeds via a growth of star-shaped and linear islands following the hexagonal symmetry of the substrate and leads finally to the formation of an ordered network. The growth modes result from destabilization of the Ru surface.@footnote 1@ The thick oxygen-rich films created under low- and moderate-temperature oxidation regime are thermally unstable. PEEM images become gradually dark when keeping the sample at temperatures higher than the oxidation temperature. This transformation reveals the cluster formation of stoichiometric oxides as well as a rearrangement of Ru and O atoms across the thick oxygen-rich layer. All mesoscopic-scale structures studied offer adsorption sites for surplus atomic oxygen adsorbed when exposing them to oxygen at room temperature. @FootnoteText@ @footnote 1@A. Böttcher, H. Conrad, H. Niehus, J. Chem. Phys. 112 (2000) 4779.

3:20pm **TF+EL-WeA5 In-situ Characterization of Thin Film Growth***, **W. Fukarek**,* Research Center Rossendorf, Germany **INVITED**

Real time ellipsometry provides information on the dielectric function and dynamic film thickness when applied to film growth or etching. Density depth profiles can be derived either from refractive index depth profiles or from dynamic growth rate data if the flux of film forming particles is known and the sticking probabilities and sputter yield remain constant during growth. Absolute density depth profiles are obtained by scaling the integral to the areal mass density as obtained from ion beam analysis. In-plane stress in thin amorphous or nanocrystalline films, where diffraction methods can not or only hardly be applied, can be measured in situ also under harsh conditions employing optical sampling of cantilever bending. From real time film thickness and curvature measurement instantaneous stress depth profiles are derived with a depth resolution in the nanometer range. The synergistic effects on the information obtained from ellipsometry, particle flux, and cantilever bending data recorded simultaneously are demonstrated exemplarily for ion beam assisted deposition of boron nitride films. In turbostratic (tBN) films the density is found to increase slightly with film thickness whereas the compressive stress decreases, indicating an increasing quality and/or size of crystallites in the course of film growth. In the case of growth of cubic (cBN) films the density starts to increase rapidly from the value characteristic of tBN up to the density of cBN (3.6 g/cm@super 3@). Comparison with the dark field TEM graph recorded from the cBN reflex reveals that the increase in density coincides with the nucleation and increase in crystallite size of cBN. The density remains constant when coalescence of the cBN crystallites is observed in dark field TEM. In contrast to the growth of tBN the depth profile of the instantaneous compressive stress in cBN films is found to be very complex and not directly related to changes in crystalline structure.

4:00pm **TF+EL-WeA7 Characterization of the Phase Evolution of Boron Nitride Thin Films using Real Time Multichannel Ellipsometry from 1.5 to 6.5 eV***, **J.A. Zapien**, R. Messier, R.W. Collins,* The Pennsylvania State University

Cubic boron nitride (cBN) is the second hardest material after diamond. This property together with its superior chemical and thermal stability makes it a very promising candidate for hard coating applications. The layered structure of cBN films on crystalline silicon (c-Si) substrates is well documented. It is commonly accepted that a sequence of amorphous and hexagonal (hBN) layers grow prior to cBN nucleation. This sequence has been described by real time measurements including polarized infrared reflectance (PIRR) spectroscopy, and infrared spectroscopic ellipsometry (IRSE). The demand for real time characterization techniques is motivated by the use of complex deposition sequences used to optimize film characteristics. Recently, we have developed a rotating polarizer multichannel ellipsometer with spectral capabilities that extend well into the uv range. With this instrument, 132 spectral points in the ellipsometric parameters (@psi@, @DELTA@) covering the photon energy range from 1.5 to 6.5 eV can be collected with a minimum acquisition time of 24.5 ms, while maintaining sub-monolayer sensitivity. As a result of the uv-extended capabilities, the new multichannel ellipsometer is well suited to study wide band gap materials in real time during preparation. Here we report the use of the uv-extended multichannel ellipsometer to study the growth and layered structure of cBN films deposited on c-Si using two processes: i) rf magnetron sputtering of a BN target with pulsed dc substrate bias, and ii) pulsed dc sputtering of a B@sub 4@C target with rf substrate bias. The phase evolution of the BN films based on the optical response in the visible-uv spectral region has been found to be in good agreement with ex-situ Fourier Transform Infrared Spectroscopy (FTIR) performed at the end of the deposition. The effect of the deposition conditions on the phase evolution and optical properties of the films will be presented.

4:20pm **TF+EL-WeA8 Deposition of Hard Amorphous Hydrogenated Carbon Films from Hyperthermal Hydrocarbon Radicals, Studied by In Situ Real Time Infrared Spectroscopy***, **A. von Keudell**,* Max-Planck-Institut für Plasmaphysik, Germany*; K.Y. Letourneur,* TU Eindhoven, Netherlands*; M.C.M. van de Sanden,* TU Eindhoven, Netherlands, The Netherlands

Dense and hard amorphous hydrogenated carbon films are deposited from a cascaded arc discharge from argon and using remote acetylene (C@sub 2@H@sub 2@) injection. The film formation is monitored by means of real time in situ ellipsometry and real time in situ infrared spectroscopy. From an enhanced infrared absorption at 3300 cm@super -1@ at the surface during deposition, corresponding to the stretching mode of sp@super 1@ hybridized CH groups, it is concluded that C@sub 2@H is the dominant growth precursor. This surface enhancement of the concentration of sp@super 1@ hybridized CH groups increases with increasing growth rate and film density. This variation of the growth rate and the variation of the film properties like mass density, hardness and hydrogen content can be well described by the balance between the contribution of C@sub 2@H and C@sub 2@H@sub 2@ to the incorporated carbon flux.

4:40pm **TF+EL-WeA9 In-Situ Monitoring of Adsorption and Film Growth Using Infrared Reflection Absorption Spectroscopy***, **V.M. Bermudez**, W.J. DeSisto,* Naval Research Laboratory

Chemical methods for thin-film growth and processing, such as CVD, suffer from a lack of techniques for surface-sensitive, chemically-specific diagnostics under steady-state conditions. Infrared reflection absorption spectroscopy (IRRAS) has been demonstrated as a viable approach to addressing this need. Polarization modulation (PM) has been coupled with a Fourier transform IR spectrometer, permitting the use of linear dichroism to distinguish weak, polarized surface absorptions from strong, isotropic gas-phase absorptions. Buried metal layers have been used both to increase the IRRAS sensitivity to adsorbates on nonmetallic surfaces and to impose the high degree of polarization needed for detection of surface species. Numerical modelling, via the Fresnel relations, has also been included as an integral part of the experiment. This approach has been used to observe the different @delta@@sub s@ frequencies of NH@sub 3@ adsorbed on Al nitride, oxide and oxynitride in a 200 Torr NH@sub 3@ ambient, which can be understood in terms of the different Lewis acidities of the surface Al cations. The optical system has been mated with a production CVD facility and used to observe the steady-state growth of Cr@sub 2@O@sub 3@ thin films on Al@sub 2@O@sub 3@ by reaction of Cr(CO)@sub 6@ and O@sub 2@ at @<=@270 °C. The T-dependence of the physisorbed Cr(CO)@sub 6@ coverage measured with PM-IRRAS gives a desorption energy of 11 Kcal/mol, indicating a weak interaction with the substrate. The growth rate of the Cr@sub 2@O@sub 3@ film is first-order in the Cr(CO)@sub 6@ pressure (both quantities having been obtained from IR data). Modeling of the IR data shows interfacial roughness to be important in this system.

5:00pm **TF+EL-WeA10 Investigation of the Subsonic Beam behaviour of an Expanding Thermal Plasma used to Deposit Silicondioxide like Films***, **M.F.A.M van Hest**,* Eindhoven University of Technology, The Netherlands, Eindhoven*; D.C. Schram,* Eindhoven University of Technology, The Netherlands, Netherlands*; M.C.M. van de Sanden,* Eindhoven University of Technology, The Netherlands

Silicondioxide like films are deposited using a remote thermal argon plasma generated by means of a cascaded arc (p=0.1 - 0.2 bar). Into this remote argon plasma, which expands into a vacuum vessel (p=0.1 mbar), two precursors are injected. First Oxygen is injected at the arc nozzle, and downstream HMDSO (hexamethyldisiloxane) is injected by means of an injection ring. By studying the behaviour of the expanding beam for various plasma conditions a better insight is created in the plasma chemistry. The plasma is analysed by means or Langmuir probe and Pitot tube measurements. Furthermore the growth is studied in situ by means of HeNe ellipsometry and infrared reflection absorption spectroscopy. By means of the Pitot tube the expanding gas velocity can be measured at various positions in the plasma reactor, and with this the gas flow pattern in the reactor can be determined. First of all the flow pattern is studied for a pure argon plasma. This is done as function of the carrier gas flow (argon) and arc current, but also for different background pressures. Second the flow pattern is studied when the depositing precursors are added to the expanding argon plasma. The Pitot tube measurements show that in the plasma reactor there is a recirculation flow on the outside of the expansion. The Langmuir probe measurements show the ion density in the plasma beam. From the combination of the Langmuir probe measurements and the Pitot tube measurements a possible dissociation mechanism for the deposition precursors will be derived. These results will be combined with the in situ measurements of the film growth to obtain insight in the film growth mechanism.

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