Spectroscopic Ellipsometry I

Moderator: M.S. Wagner, Proctor and Gamble


III-VI compounds generally crystallize in layered-structures characterized by strong covalent interactions within the layers but weak Van der Waals binding between the layers. This unique structural characteristic has made III-VI compounds attractive for their potential applications in nonlinear optics. Among these compounds, InSe has been considered as a promising candidate for thin film photovoltaic (PV) material owing to its energy bandgap, optical and transport properties. Recently, high-quality epitaxial InSe thin films have been grown on GaSe substrates, and PV device structures containing n-InSe and p-GaSe have been successfully fabricated [1].

In order to design and optimize a high-performance PV device structure, knowledge of optical properties of constituent materials over a wide spectral range is required. However, large discrepancies were found in the properties of GaSe and InSe available in the literature, which have been measured mostly by reflectance methods with the Kramers-Kronig transformation employed to obtain the dielectric functions. Here, we present ellipsometrically determined pseudodielectric function $\varepsilon(\omega) = \varepsilon_1 + i\varepsilon_2$ spectra from 0.73 to 6.45 eV of bulk GaSe ($\varepsilon$-phase) and InSe ($\gamma$-phase) single-crystals grown by a vertical Bridgman method. The surfaces with minimum overlay were obtained by peeling off the top few layers from the sample surface and ellipsometric measurements were immediately followed under flowing N$_2$ environment, which yields good approximations to the intrinsic dielectric responses. The measured spectra exhibited a number of interband-transition critical-point structures, and their energy values were obtained precisely from numerically calculated second-energy-derivatives of $\varepsilon$ assuming the parabolic-band critical-point model.

Data obtained in this work can be used to model PV device structures utilizing GaSe and InSe, and the critical-point energies determined will be useful for theoreticians to perform fine band structure calculations of III-VI compounds.

The work done at Universitat de València was supported in part by the Spanish Project MAT2007-06841. This abstract is subject to U.S. government rights.


8:40am AS+EM+MS+TF-MoM2 Ellipsometric Porosimetry for the Microstructure Characterization of Plasma-Deposited SiO$_2$-Like Films. M. Creatore, N.M. Tertlinden, G. Arena, M.C.M. van de Sanden, Eindhoven University of Technology, The Netherlands

SiO$_2$ layers have been deposited from Ar/O$_2$-hexamethyldisiloxane mixtures in a remote expanding thermal plasma setup enabling a good control of both the ion flux (by changing the deposition chemistry and the arc plasma parameters) as well as the ion energy. This latter is achieved by an additional rf substrate biasing or a tailored ion biasing technique, i.e. a low frequency pulse-shaped bias. The role of the ion energy and ion-to-growth flux ratio on the film microstructure and densification at low substrate temperatures (100°C) has been investigated by means of ellipsometric porosimetry. This technique monitors the refractive index change due to the adsorption (and desorption) of ethanol vapors in the volume of macro-meso-micro pores in the SiO$_2$ layer. From the analysis of the adsorption isotherm and the presence of hysteresis during the desorption step as a function of the equilibrium partial pressure, the open porosity in the layer can be determined. It is found that both biasing techniques lead to densification of the deposited layer, which experiences a transition from micro- mesoporosity to microporosity and eventually non-porosity, as function of the increasing ion energy. Although both biasing techniques lead to a comparable critical ion energy value per deposited SiO$_2$ unit (about 100 eV), the ion-to-growth flux ratio and ion energy are not found to be interchangeable parameters. In fact, in the case of the rf bias, the meso- and large micropores are first affected leading to a quantitative decrease of porosity, i.e. from 11% to 3% at an ion energy less than 20 eV. A further increase in ion energy eventually reduces the presence of smaller micropores leading to non porous films at energy of 45 eV. When the pulse-shaped biasing technique is adopted, the micro- and mesopores are simultaneously affected over the whole range of available ion energy, leading to a non porous layer only at very high energy values, i.e. 240 eV. This difference is attributed to the increasing ion-to-growth flux ratio accompanying the rf biasing, as a consequence of the rf plasma generation in front of the substrate.

9:00am AS+EM+MS+TF-MoM3 Industrial Applications of Spectroscopic Ellipsometry. J.A. Woollam, J.A. Woollam Company Inc., J.N. Hilfiker, P. He, J.A. Woollam Company Inc. INVITED

Spectroscopic Ellipsometry (SE) has been used for decades for basic research on surfaces and thin films. Hundreds of articles, review papers, and books describe SE use in physics, chemistry and surface and materials engineering. Far less is available describing industrial applications because companies gain competitive advantage using SE and are not motivated to publish.

Without revealing anyone’s proprietary information, this talk reviews examples of SE use in industry. This involves both production quality control (QC), and product development. Best known is SE for QC in integrated circuit manufacturing. Others include integrated circuit critical dimension (CD) metrology, read-write heads, display technologies, optics, magnetics, photovoltaics, cryocoolers and thin films, optical coatings, web-coaters, wear surfaces, and protective coatings. Industrial SE applications include ex-situ, in-situ, and in-line metrology.


Vanadium oxide (VO$_x$) thin films have been used for the last twenty years as the imaging material in uncooled infrared imaging devices. The important material properties for this application are a high thermal coefficient of resistance (TCR), controllable resistivity ($\rho$), low electrical noise and process compatibility with standard IC fabrication. However, vanadium can adopt many different oxidation states, yielding a number of stable metal oxides, which can lead to difficulties in reliable and consistent device fabrication. In this work, VO$_x$ thin films were fabricated via pulsed-DC magnetron sputtering in an argon and oxygen atmosphere under variable total pressure and oxygen-to-argon ratio deposition conditions in order to investigate the variability in desired material properties. In situ real time spectroscopic ellipsometry (RTSE) has been applied to study films prepared under variable deposition conditions in order to evaluate the microstructural evolution of VO$_x$ during film growth and changes occurring to the surface and bulk material upon initial exposure to atmosphere. These films were characterized ex-situ using a number of complementary techniques including, Rutherford backscattering spectroscopy (RBS) in order to obtain the oxygen content, x; transmission electron microscopy (TEM) to determine film crystallinity; glancing incidence X-ray diffraction (GIXRD) was used to ensure localized measurements from the TEM were representative of the entire film; and I-V curve measurements as a function of temperature were used to determine the film resistivity and TCR. By varying deposition conditions, the film resistivity was varied over seven orders of magnitude from $\sim 10^{-3}$ to $10^4 \Omega$-cm and the TCR spanned from -0.1 to -3.5 %/K. The growth evolution, complex dielectric function spectra ($\varepsilon = \varepsilon_1 + i\varepsilon_2$), and structure are correlated to these electrical properties. Films produced at low oxygen-to-argon ratios exhibit nanocrystalline V, VO$_x$, and VO phase material dependent on the specific deposition conditions, while films produced at higher oxygen-to-argon ratios are amorphous. In both the nanocrystalline and amorphous phases, features in $\varepsilon$ obtained from spectroscopic ellipsometry have been shown to correlate with the oxygen content and resistivity and RTSE studies have been used to monitor changes occurring at the film / ambient interface after the vanadium oxide is exposed to air. This array of techniques were used to establish the roles deposition parameters play in the final structure and composition of each film, as well as to determine the resulting effects of these characteristics on the electronic transport and optical properties.


Thin film hydrogenated silicon (Si:H) and germanium (Ge:H) have been of wide interest as thin film semiconducting materials, and are now of growing interest for use in infrared sensing uncooled microbolometers, although the impact of the growth evolution and structure on device performance is only beginning to be determined. Ideal properties for incorporation of these layers in microbolometers include: a high temperature coefficient of resistance (TCR), controllable resistivity ($\rho$); low 1/f noise within frequencies of interest; and process compatibility with standard IC.
fabrication. In this work, n- and p-type doped Si:H and undoped Ge:H thin films have been prepared by plasma enhanced chemical vapor deposition (PECVD) with resulting resistivities ranging from 1.5 to 2500 Ω cm and TCR ranging from −0.8 to −4.0 %/K and studied using real time spectroscopic ellipsometry (RTSE). These films, monitored in situ during growth by RTSE, have been shown to exhibit changes in microstructure as a function of deposition conditions. For example, films prepared at low hydrogen dilution may remain amorphous throughout growth (a-Si:H), while films prepared at higher dilution may initially grow as amorphous until a bulk layer thickness where microcrystallites nucleate and eventually coalesce into a single-phase microcrystalline layer (μc-Si:H). A combination of in-situ RTSE, transmission electron microscopy (TEM), and electrical measurements (p, TCR, 1/f noise) have been used to study the effects of deposition conditions on the resulting microstructure during film growth and the dependence of the electrical properties on the microstructure. Studies of p-type a-Si:H have shown that both TCR and p increase with hydrogen dilution for fixed doping gas-to-silane ratio, which suggests that optimizing the TCR for a film of a given resistivity may potentially be obtained by varying both the hydrogen and dopant gas dilutions. n-type a-Si:H and mc-Si:H films were evaluated in order to quantify changes in TCR and p resulting from microstructural differences (a-Si:H: ρ = 250 Ω cm, TCR = −3.8 %/K; μc-Si:H: ρ = 1.5 Ω cm, TCR = −0.8 %/K). Growth evolution studies of undoped Ge:H films prepared under variable hydrogen dilution conditions show transitions from amorphous to microcrystalline material at higher hydrogen dilution and relatively high TCR values ranging from −2.2 to −3.6 %/K as dilution is increased within the amorphous growth regime.

10:40am A+EM+MS+TF-MoM8 Non-destructive Determination of Spatial Distributions of Free-Charge-Carriers in Low Doped Semiconductors using THz Ellipsometry. T. Hofmann, University of Nebraska-Lincoln, C.M. Herzinger, J. A. Woollam Co. Inc. and M. Schubert, University of Nebraska - Lincoln

The non-contact and non-destructive optical determination of spatial distributions of free-charge-carriers in low doped semiconductor homo- and heterojunctions addresses fundamental physical properties of device related structures. However, the optical characterization of low density free-carrier concentration, particularly for hole densities with their intrinsically lower mobility parameters than electron densities is very challenging. For low carrier densities the plasma frequencies are located at within the terahertz (THz) spectral region and measurements of plasma frequency properties in at THz frequencies have been used for determination of long-range free-carrier transport distances in single crystals (e.g. [1,2]). The characterization of free-charge carriers in low-doped homo- and heterostructures remains a challenge.

Here we report on the non-invasive optical measurement of hole diffusion profile in a p-p' Silicon homojunction by spectroscopic ellipsometry in the terahertz (0.2 to 1.5 THz) and mid-infrared (9 to 50 THz) spectral regions. In the terahertz region a surface guided wave resonance with transverse-electrical polarization is observed at the boundary of the p-p' homojunction, and it is found to be extremely sensitive to the low-dopant-type carrier concentration as well as to the hole diffusion profile within the p-p' homojunction. Effective mass approximations allow determination of homojunction hole concentrations as $p = 2.9 \times 10^{16} \text{cm}^{-3}$, $p = 5.6 \times 10^{13} \text{cm}^{-2}$, and diffusion time constant $D = 7.7 \times 10^{-9} \text{cm}^{2}$, in agreement with previous electrical investigations.


Interest has emerged in the development of devices based on organic materials and low cost, roll-to-roll fabrication techniques. Two specific target applications have received particular attention: organic transistors to enable macroelectronics (large area displays, RFID tags, etc.) and organic photovoltiax. Common to both applications is the development of optical inks: for macroelectronics, small crystallizable molecules in an inert polymer binder, and for photovoltaics, fullerene based acceptors blended in an aromatic polymer. Critical to the performance is an understanding of the vertical profile of the fabricated film. For thin film transistors, segregation of the small molecule semiconductor to the interfaces is essential. For PV, segregation of the fullerene can be both advantageous (if at the cathode) and deleterious (if at the anode). Spectroscopic ellipsometry studies of the vertical profile are daunting, as the systems are in general anisotropic with individual component absorption spectra that are strongly dependent on the local order. We present SE studies of both TFTs and OPV devices using a multiple sample approach to remove correlations in the resultant models. The optical depth profiles are compared to both NEXAFS studies of the interface composition and neutron reflectivity studies of similar processed films. We find good agreement between the SE and less model dependent techniques. The studies illuminate general principles of the interface of interfacial free energy on the resultant segregation of the species.

11:20am A+EM+MS+TF-MoM10 Thickness Variations Determined by Spectroscopic Ellipsometry in Organometallic Chemical Vapor Deposition: Connection to Growth Processes. X. Liu, D.E. Aspnes, North Carolina State University

Lateral thickness variations are commonly observed for films deposited by organometallic chemical vapor deposition (OMCVD). The variations are typically systematic near boundaries between growth and adjacent surfaces, for example mask edges. We use spectroscopic ellipsometry to study thickness variations for the heteroepitaxy of GaP by OMCVD on (001) GaAs, thermally generated SiO$_2$, (001) Si, and nanoscopically roughened Si surfaces using trimethylgallium (TMG) and phosphine (PH$_3$) sources, showing that the variations provide information about details of OMCVD growth that would be difficult to obtain in any other way. Our reference surface is the polycrystalline GaP inadvertently deposited on the Mo susceptor that surrounds the 2 in. wafers. We find that the thicknesses of the deposited GaP films increase or decrease accurately exponentially toward the edge. Using an analytic Green-function approach based on the one-dimensional diffusion equation, we show that for our growth conditions (4 Torr chamber pressure), the exponential thickness variations are due to differences in chemical reactivities of the various surfaces, especially on the different catalytic effects that they exert on PH$_3$ decomposition. The results show directly that different parts of the surface, including the susceptor, are in constant contact with each other through lateral gas-phase diffusion. The data are explained by assuming that growth occurs via a precursor that is formed by heterogeneous catalysis, largely desorbs, and involves both Ga and P. For example the H$_2$P=Ga-CH$_3$ dimer adduct. To distinguish this process from selective area growth (SAG), which takes place with a similar configuration, we also solve the SAG problem analytically, in this case using a conformal map. For SAG the thickness near mask edges is found to vary as $r^{-2}$, where $r$ is the lateral distance away from the edge. The distinctive differences in these thickness dependences indicate that SAG growth occurs via a different mechanism.

11:40am A+EM+MS+TF-MoM11 Optical Anisotropy Induced by Oblique Incidence Ion Bombardment of Ag(001). H. Wurmester, F. Everts, B. Poelsema, University of Twente, The Netherlands

Oblique incidence sputtering has become a widely used method for the creation of highly regular patterns of lines and dots. On a Ag(001) surface oblique incidence sputtering creates a ripple pattern that exhibits plasmonic features that depend on the incident angle, i.e. the periodically changing photon energy. The penetration depth of this plasmonic feature depends on the wavelength and wavelength distribution of the ion induced nanoripples. These spectra can be well described within the Rayleigh-Rice description for scattering from a slightly rough surface. The formation of nanoripples, i.e. a roughening of the surface perpendicular to the direction of the ion beam in one direction suffices to describe the measured optical data. The evolution of the rms, wavelength and wavelength distribution of the ion induced nanoripples is monitored using spectroscopic ellipsometry (SE) and neutron reflectivity studies of similar processed films. We find good agreement between the SE and less model dependent techniques. The optical depth profiles are compared to both NEXAFS studies of the interface composition and neutron reflectivity studies of similar processed films. We find good agreement between the SE and less model dependent techniques. The studies illuminate general principles of the interface of interfacial free energy on the resultant segregation of the species.
Graphene Topical Conference
Room: C3 - Session GR-MoM

Graphene and 2D Carbon Nanostructures
Moderator: M.Y. Zhu, College of William and Mary

8:20am GR-MoM1 Graphene-based Materials. R.S. Ruoff, The University of Texas at Austin

INVITED

Our top-down approaches [1] inspired physicists to study individual layers of graphene obtained by micromechanical exfoliation, but our current approaches include growth on metal substrates and judicious use of isotopic labeling (^{12}C vs. ^{13}C) to study the kinetics and mechanisms of deposition of large-area graphene and few layer graphene on metal substrates.[3] This talk will focus on our suggested path for obtaining large area growth of high quality graphene in ways compatible with methods of the semiconductor industry. In addition, I will present highlights of published work on polymer matrix composites with graphene as filler[4], on ultracapacitors based on graphene[5], on paper-like materials based on graphene[6], on the use of ^{13}C-labeled graphene (and ^{12}C-pure graphene and graphene) in a variety of areas[7], and on use of graphene as transparent but electrically conductive thin films[7]. Support of our work by SWAN-NRI, DARPA-CERA, DARPA-iMINT, and prior support by NASA, is appreciated.

(See also papers on http://bucky-central.me.uta.edu/publications.htm)

6. Cai, Weimei; Piner, Richard D.; Stadermann, Frank J.; Park, Sungjin; Shaibat, Medhat A.; Ishii, Yoshihata; Yang, Dongxing; Velamakanni, Aruna; An, Sung Jin; Stoller, Meryl; An, Jinho; Chen, Dongmin; Ruoff, Rodney S., Science (2008), 321(5897), 1815-1817.

9:00am GR-MoM3 Investigation of Process Dependence of Growth Graphene on Nickel Thin Film. J. Mun.

KAIST, Republic of Korea, C. Hwang, Korea Research Institute of Standards and Science, Republic of Korea, S. Lim, National Nano Fab Center, Republic of Korea, B.J. Cho, KAIST, Republic of Korea

Recent study on graphene synthesis on metal thin film by chemical vapor deposition in a hydrocarbon ambient has shown promising results for the feasibility of formation of graphene layer over a large area. However the deposition layer grown on metal thin film shows various kinds of defects on its surface such as islands of thick graphene layers, carbon dumps, and wrinkles from the different thermal expansion coefficient between metal and carbon, and so on. Control of such defects is critical for the technique to be useful, but the mechanism of the defect formation has not been well studied so far. In this work, the effect of various process conditions which affect the quality of graphene on nickel thin film is carefully investigated, including nickel thin film deposition process, ramping up ambient, annealing ambient, annealing temperature, thickness of nickel thin film, etc. During the high temperature annealing process, nickel thin film becomes highly agglomerated and thereby the surface becomes quite rough. Since the segregated carbon amount at nickel grain boundary is different from that segregated from crystalline nickel inside the grain, the agglomeration of nickel directly affects the thickness uniformity of graphene and roughness of graphene surface. It is found that the deposition process of nickel thin film affects the agglomeration and the e-beam evaporation of nickel has shown less agglomeration upon annealing, compared to physical sputtering. It is also found that the annealing temperature in CH4 is a critical factor to control the amount of thick graphite island on graphene. Furthermore, it found that the gas ambient during ramping up affects the deformation of nickel thin film. All such detailed process conditions on graphene formation on nickel thin film are carefully investigated and will be presented.

2. A. Reina et al., Nano Lett. 9, 31 (2009)

9:20am GR-MoM4 Evolution of Electrical, Chemical, and Structural Properties of Transparent and Conducting Chemically Derived Graphene Thin Films. C. Mattevi, G. Eda, Rutgers University, S. Agnoli, University of Padova, Italy, S. Miller, Rutgers University, A. Mkhoyn, University of Minnesota, O. Celik, D. Mastrogiovanni, Rutgers University, G. Granazzo, University of Padova, Italy, E. Garfunkel, M. Chhowalla, Rutgers University

An alternative path to graphene is represented by graphene oxide (GO) that can be readily exfoliated and then deposited from suspension on variety of substrates. GO is an insulator, but the nature of the electronic properties leading the possibility of accessing zero-band gap graphene. However, the GO structure and opto-electronic properties at different stages of reduction are largely unknown. Here we focus on a detailed description of opto-electronic properties, chemical state [1] and structure [2] of single and few-layered GO at different stages of reduction. The residual oxygen forms sp3 bonds with carbon atoms in the basal plane such that the carbon-carbon sp2 bonding fraction in fully reduced GO is ~0.80. The oxygen disrupts the transport of carriers delocalized in the sp2 network, limiting the mobility and conductivity of reduced GO thin films. Our analysis reveals that removal of oxygen to achieve sp2 carbon fraction of >0.95 in GO should lead to properties that are comparable to graphene.


9:40am GR-MoM5 Plasma-based Approach to Controlling the Oxygen Concentration in Graphene Oxide. S.G. Walton, M. Baraket, E.H. Lock, Naval Research Laboratory

Graphene and graphene oxide have attracted widespread interest because of their unique structural and electronic properties, which lend themselves well to the production of nanoscale electronic and sensing devices. Indeed, graphene is a single monolayer thick carbon sheet with remarkably high electron mobility. The addition of oxygen increases the sheet thickness and decreases this mobility and in most interestingly, determines both the conducting and reactivity properties of the material. One significant impediment to realizing the potential of graphene oxide is the development of an industrially viable approach to producing large area substrates of well-controlled concentration. In this respect, plasmas are an ideal candidate but problems associated with the large fluxes of energetic ions are a significant concern. The Naval Research Laboratory has developed a plasma processing system that is characterized by a uniquely low incident ion energy, in the range of a few eV, at or near the carbon-carbon and carbon-oxygen bond strength. We discuss the use of this system to reduce the oxygen concentration of graphene oxide. We examine the plasma processing conditions, plasma characteristics, and the resulting properties of the material in an effort to understand reduction mechanisms. This work was supported by the Office of Naval Research.

10:00am GR-MoM6 Graphene Growth on Transition-Metal Thin Films. P.M. Albrecht. E.A. Sutter, P.W. Sutter, Brookhaven National Laboratory

Epitaxy on transition metal substrates is a promising approach for the large-scale synthesis of graphene for potential applications in microelectronics and sensing. In particular, the controlled layer-by-layer growth of graphene on Ru(0001) has been shown to result in macroscopic monocrystalline graphene domains with lateral sizes greater than 260 microns, excellent thickness uniformity, and very low defect density [1]. Whereas the first graphene layer interacts strongly with the Ru(0001) template, the second layer is essentially decoupled from the metallic support, thus preserving the atomic structure and exotic electronic properties of isolated single-layer graphene [2]. A viable route towards large-area, free-standing graphene would be to grow on polycrystalline transition-metal thin films rather than single crystals, followed by the dissolution of the metal template to detach the graphene and transfer it to another support. Two groups have recently
demonstrated the growth of few-layer graphene on polycrystalline Ni films using this method [3, 4].

Here, we report a study of graphene growth on Ru thin films. The polycrystalline Ru substrate layers were deposited on SiO2 by magnetron sputtering in ultrahigh vacuum. We used in-situ annealing and scanning tunneling microscopy (STM) to study the recrystallization and grain growth of the Ru template, crucial to forming a starting surface suitable for the growth of macroscopic graphene domains. STM also provided a detailed understanding of the interaction of the growing graphene layer with Ru grains with different surface orientations, grain boundaries, as well as highly vicinal surfaces. Cross-sectional transmission electron microscopy (TEM) was used to directly image the graphene-metal interface for the first time. Our results provide a basis for the scalable synthesis of graphene on transition metal thin films.


10:40am GR-MoM8 Is Fullerene-Intercalation in Graphite a Vehicle to Graphene Surface Layer Doping?, P. Reinke, S. O'Donnell, University of Virginia

In order to exploit the extraordinary properties of graphene several materials-based challenges have to be addressed to reach full device functionality. The challenges include opening and control of a bandgap in and p-type doping while preserving the ambipolarity at the K-point, and sustaining the high mobility of charge carriers. We introduce here a novel and highly versatile method for the modulation of the electronic properties of graphene, which is based on fullerene (C60)-graphite intercalation compounds (C60-GIC). The goal is to electronically decouple the graphene sheet from its substrate through the introduction of an intercalated layer of fullerene molecules, which are a wide bandgap material and thus do not significantly perturb the bandstructure around the Dirac point of graphene. The fullerene layer can subsequently be doped and thus the charge transfer to the graphene is controlled via the modulation of the intercalated fullerene layer. The synthesis of the C60-GICs is achieved by an annealing process, where the supersaturation of the gasphase with fullerenes is used to drive the molecule into the graphite lattice. The parameter space for successful intercalation is controlled by the substrate temperature, fullerene concentration and the defect structure of the graphite. The intercalation process is observed with scanning tunneling microscopy and spectroscopy which is probes the geometric and electronic structure of the top layer. The presence of sub-surface fullerenes is detected through the appearance of a Moire pattern and a weak distortion of the topgraphy, usually presented in a well-defined area around step edges. The spatial distribution of intercalated regions is used to describe the kinetics of the intercalation process and to elucidate the mechanistic aspects of the material synthesis. The graphene doping through the incorporation of a second dopant (e.g. K) in the C60 layer is investigated with STM. The electronic structure of the top graphene layer is measured with STS, and the spatial distribution of charge-puddles and their relation to the sub-surface C60 lattice will be discussed.

11:00am GR-MoM9 1 nm Thin Carbon Nanosheets: Two-Dimensional Functional Materials. A. Gölzhäuser, University of Bielefeld, Germany

A route for the fabrication of 1 nm thin and free-standing carbon films and membranes, whose electrical and mechanical behavior as well as surface functionalization can be tuned, is presented. Self-assembled monolayers (SAMs) of aromatic bifunctional molecules are cross-linked by electron irradiation and carbon supports composed of graphitic materials is one of the most important need in development of electrocatalysts for fuel cell. We have studied the effects of the interface interaction on the catalytic properties using model catalysts of Pt-deposited highly oriented pyrolytic graphite (HOPG) by IETS-STS-STM, TPD, and molecular/atomic beam technique. The deposited Pt clusters show unique morphology and catalytic properties. That is, the shape of Pt clusters (1-5 nm) is a raft-like structure with one or few atomic heights. The Pt clusters show quite high catalytic activity for H2-D2 exchange reaction at 24 Torr. Desorption peak of CO from the Pt was observed at a low temperature of 300 K. The significant modification is ascribed to the interface interaction between Pt atoms and graphite surface. In the STM observation, it was found that Pt atoms are located on beta-carbon, indicating the shrinkage of Pt-Pt distance about 13% compared to that of the bulk Pt. The modification in the catalytic properties and the electronic structure of the flat Pt clusters is thus ascribed to the reduction in the lattice constant of Pt. It is explained that the d-band center of Pt shifts away from the Fermi level due to the reduction in the lattice constant. We show evidence of the interface interaction between Pt and graphite here. Distinct electronic states of the graphite near the Fermi level, “non-bonding α electronic states”, were observed at the carbon atoms in the vicinity of the Pt clusters by STS measurements, which is interpreted by our newly proposed model: the conjugated bond of graphite between alpha- and beta-carbon atoms are re-hybridized into two p-orbitals, where the p-orbital of beta-carbon would be hybridized with a d-orbital of the Pt atom and the other p-orbital of alpha-carbon becomes a non-bonding p-orbital. Consequently non-bonding p electronic states forms at the alpha-carbon atoms of graphene in the vicinity of the Pt cluster. The proposed model is consistent with our experimental result of scanning tunneling microscopy and inelastic electron tunneling spectroscopy (IETS) measurements as well as STS results and our first-principles density functional calculations of the graphene sheet with a Pt cluster.

Thin Film

Room: B3 - Session TF1-MoM

Thin Films: Growth and Characterization I

Moderator: S. Gupta, University of Alabama

8:40am TF1-MoM2 Photoluminescence Properties of SrAlO2:Eu3+·Dy3+ Thin Phosphor Films Grown by Pulsed Laser Deposition. O.M. Ntwaeaborwa, P.D. Nsimama, H.C. Swart, University of the Free State, South Africa

Thin films of SrAlO2:Eu3+·Dy3+ phosphor were grown on silicon substrates using a 248 nm KrF pulsed laser. The films were characterized by various techniques such as photoluminescence (PL), X-ray diffraction (XRD), scanning electron microscopy (SEM) and atomic force microscopy (AFM) were used to examine the structure, particle morphology and surface topography of the films. The chemical composition and thicknesses of the films were determined by Rutherford backscattering spectroscopy (RBS). Photoluminescence spectra of the films recorded by the Cary Eclipse spectrophotometer were characterized by varying the excitation wavelength and the emission maximum at ~520 nm and minor red shift to a maximum at 630 nm. The green and red photoluminescence at 520 and 630 nm are associated with the 4f5→4f4(5S2), 4f6→4f5(5D0) transitions of Eu3+ and residual Eu2+ respectively. The effects of processing parameters on the PL intensity and the possible mechanism of the green phosphorescence were discussed.

9:00am TF1-MoM3 Multifunctional Double Perovskite Thin Films and Heterostructures. A. Gupta, The University of Alabama

A double perovskite is a perovskite with the general formula of ABBO’6, where A is a divalent alkaline earth cation and B and B’ are transition metal ions. Depending on the relative size and oxidation state, the B and B’ ions can be crystalllographically completely ordered, making up a rocksalt-type lattice. La2NiMnO6 is an ordered double perovskite that is a ferromagnetic semiconductor with a Tc of 280 K. Recent studies of La2NiMnO6 in the bulk have revealed large magnetic-field induced changes in the resistivity and dielectric properties at temperatures as high as 280 K [1, 2]. This is a much higher temperature than previously observed for such a coupling between the magnetic, electric, and dielectric properties in a ferromagnetic
semiconductor. Substitution at the A site can also lead to multiferroic behavior in the double perovskites. Azuma et al. have succeeded in synthesizing the "designed" compound Bi$_2$NiMnO$_6$ in the bulk under high pressure and established its multiferroic properties, with ferroelectric and ferromagnetic transition temperatures of 485 K and 140 K, respectively [3]. We have synthesized epitaxial thin films of La$_2$NiMnO$_6$ [4], Bi$_2$NiMnO$_6$ [5], and their heterostructures using the pulsed laser deposition (PLD) technique. A related ferromagnetic semiconductor, La$_2$CoMnO$_6$, has also been epitaxially stabilized [6]. High quality epitaxial films of these double perovskites are grown on lattice-matched substrates such as SrTiO$_3$, NdGaO$_3$ and LaAlO$_3$. We have structurally characterized the double perovskite films using a variety of techniques. Additionally, the magnetic, electrical and magnetoelectric properties of the thin films and heterostructures have been studied in detail.


9:40am TF1-Mo5 Influence of Nanostructure on Charge Transport in RuO$_2$ Thin Films. M.M. Steeves, R.J. Lad, University of Maine

Ruthenium dioxide exhibits metallic electrical conductivity, and may have both electron and hole contributions to its charge transport. In this study, polycrystalline thin films of RuO$_2$ were grown on fused quartz substrates by RF reactive magnetron sputtering, and a parametric study was carried out to probe the influence of film nanostructure on the four-point Van der Pauw resistivity and Hall coefficient. The films were grown via reactive RF magnetron sputtering of a Ru target in an Ar/0$_2$ plasma using a range of deposition rates and with substrate temperatures ranging from 20-500°C. A wide variety of nanostructures and film textures were obtained as determined by high resolution x-ray diffraction for film thicknesses ranging from 40-180 nm as measured by x-ray reflectivity and profilometry. The films exhibited strain of the order of 0.5% and average crystallite sizes ranging from 20-70 nm. Room temperature resistivities varied between 200-400 μΩ cm and showed a relatively weak dependence on temperature. Hall coefficients ranged from +200 to -200 x10$^{-5}$ cm$^3$/C as a function of temperature, depending on exact nanostructure as well as the heating environment. The observation of both positive and negative Hall coefficients for different RuO$_2$ films is in contrast to the expected mirror symmetry of c-Sc$_{0.5}$Al$_{0.5}$N solid solutions predicted by first principles density functional theory calculations, only slightly deviating from Vegard’s law. On the contrary, the lattice parameters of the w-Sc$_{0.5}$Al$_{0.5}$N varied considerably less than predicted. Our calculated mixing enthalpies of c-, w-, and zinc blende Sc$_{0.5}$Al$_{0.5}$N solid solutions predict that the alloy is metastable with respect to phase separation for all temperatures below the melting points of AlN and ScN.


Low resistivity thin films of vanadium oxide with high temperature coefficient of resistance (TCR) are currently used as the imaging layer in uncooled infrared imaging. However, process control remains an issue because the films are formed under oxygen-starved conditions. In this paper, the influence of cathode current (target current) hysteresis on the properties of pulsed-dc reactive sputtered vanadium oxide thin films is investigated. VO$_x$ thin films were sputter deposited from a vanadium metal target under different Ar/O ratios. The gas flow rates and oxygen partial pressures were varied systematically, and the corresponding changes in the cathode current were monitored. Increasing the gas flow rate from 10 sccm to 100 sccm caused the cathode current to decrease by ~25%, but on reversing the flow rate, the cathode current did not go back up along the same curve, instead exhibiting a hysteretic behavior. A similar trend was observed for the change in oxygen partial pressure between 0 and 20% as well. The width and position of the hysteresis curve depends on the relative values of the gas flow rates and the oxygen partial pressures. VO$_x$ thin films deposited at various points along the hysteresis curve were evaluated using four-probe resistivity measurements over a wide temperature range. The room temperature resistivity of the films varied by more than six orders of magnitude and was found to have a progressive dependence on the cathode current. Structural characterizations such as X-ray diffraction and transmission electron microscopy studies indicated that the microstructure changes gradually from nanocrystalline to amorphous with the increase in total gas flow rate and/or oxygen partial pressure.


Ultrathin TiN films were grown by reactive dc magnetron sputtering on amorphous SiO$_2$ substrates and single-crystalline MgO substrates at various growth temperatures. The resistance of the films was monitored in-situ during growth to determine the coalescence and continuity thicknesses. TiN films grown on SiO$_2$ at 600°C are polycrystalline and have nominal coalescence and continuity thicknesses of 8 Å and 19 Å, respectively. TiN films grow epitaxially on the MgO substrates at 600°C. The nominal coalescence thickness is 2 Å and the thickness where the film becomes continuous cannot be resolved from the coalescence thickness. X-ray reflection measurements indicate a significantly higher density and lower roughness of the epitaxial TiN films.
Thin Film
Room: B4 - Session TF2-MoM
Metals and Nitrides (ALD/CVD)
Moderator: W.M.M. Kessels, Eindhoven University of Technology, the Netherlands

8:20am TF2-MoM1 ALD of Metal Chalcogenide Thin Films. M.A. Leskela, T. Hattanpaa, M.J. Heikkila, V.J. Porse, M.K. Ritala, University of Helsinki, Finland
INVITED
ALD of metal sulphide thin films has been known since the discovery of the technology in early 70s whereas ALD of metal selenide and telluride films has been limited because of a lack of precursors that would at the same time be safe and exhibit high reactivity as required in ALD. In this presentation we show that alkylsilylanes of tellurium and selenium can be used as tellurium and selenium precursors in thermal ALD. Compounds with a general formula (R₃Si)₂Te and (R₃Si)₂Se react with various metal halides producing metal telluride and selenide thin films. Sb₂Te₅, GeTe and GeCl₂·C₄H₈O₂ as precursors. All three precursors exhibit a typical saturative ALD growth behaviour. The Ge₂Sb₂Te₅ films show excellent conformality on a high aspect-ratio trench structure. Other metal selenide and telluride films can be deposited by ALD using alkylsilylides of tellurium and selenium as precursors. Those deposited in this work included ZnTe, Bi₂Te₃, ZnSe, Bi₂Se₃, InSe and CuSe. The growth temperature has in some cases been 400 °C showing the thermal stability of these new Se and Te precursors. Growth rates of these binary chalcogenide films are typically between 0.5 and 1 Å/cycle. Other metal precursors than chlorides are also possible in the selenide and telluride depositions, as exemplified by the use of GeBr₃ and Sb(OrEt)₃.

9:00am TF2-MoM3 Molybdenum ALD and Mo/W Alloy Growth Using MoF₆, WF₃ and SiH₄ as the Reactants, D. Seghete, A.S. Cavanagh, S.M. George, University of Colorado at Boulder
Metal ALD using thermal chemistry is limited and based on combustion reactions (Ru, Pt), organic or H₂ reduction (Cu, Pd) or fluorosilane elimination (W). Molybdenum (Mo) is a refractory metal that has many applications in alloys, catalysis and electronics. Mo ALD can be achieved with fluorosilane elimination chemistry using MoF₆ and SiH₄ as reactants. This process is similar to W ALD using WF₃ and SiH₄ as reactants. This study reports Mo ALD using a quartz crystal microbalance (QCM) to monitor the growth of the Mo ALD films and Mo/W alloy films in a hot wall viscous flow reactor. QCM studies showed that Mo ALD is self-limiting for both MoF₆ and SiH₄ reactants. MoF₆ produces a large mass gain and SiH₄ produces a small mass loss. A mass gain of 535 ng/cm² per cycle was observed at 120°C when both reactant exposures were in saturation. Although long MoF₆ residence times were observed on the surface, the Mo ALD growth per cycle was independent of purge time. The Mo film growth reached a linear regime after a short nucleation period of only 3-4 cycles on Al₂O₃ ALD surfaces. X-ray reflectivity (XRR) experiments confirmed linear Mo ALD growth versus number of cycles. A growth per cycle of 6.4 Å/cycle was measured at 120°C. The average density of the Mo films was 8.7 g/cm³ and there was excellent agreement between the QCM and XRR experiments. The temperature dependence of the Mo ALD growth per cycle was investigated from 90 °C to 150 °C. X-ray photoelectron spectroscopy confirmed negligible F concentrations in the Mo ALD films. However, higher Si concentrations were observed in the Mo ALD films compared with W ALD films. The variation of Si content in the Mo ALD films was examined versus growth temperature and dosing conditions. Various Mo/W alloys can be produced by alternating Mo ALD and W ALD. These alloys can eliminate crystalline grain growth that occurs in the pure metals. This reduction of crystalline grain growth relieves the internal mechanical stress that develops in pure W ALD films.

Ruthenium thin films were deposited by pulsed chemical vapor deposition from bis(N,N'-di-iert-butylacetamidato) ruthenium(II) dicarbonyl and O₂. Highly conductive, dense, conformal and pure thin Ru films can be deposited when oxygen exposure E₀ approaches a certain low threshold (Eₘₐₓ). When E₀ > Eₘₐₓ, the films peel off silica substrates, perhaps due to recombinitive desorption of O₂ at the film/substrate interface. Ruthenium films grown on tungsten substrates show very strong adhesion, > 17 J m², and no evidence for any oxidized interlayer between the Ru and the W. Thus the low oxygen exposure does not oxidize the tungsten substrate surface during Ru deposition. Analysis by an atomic probe microscope shows that the crystallites are nearly free of oxygen (<0.5 at.%), while a low level of carbon(≈0.3 at.%) is segregated near the grain boundaries. The atom probe microscope also shows that a small amount of O impurity (0.3 at.%) is distributed uniformly through the crystallites and the grain boundaries.

Ruthenium (Ru) is regarded as an electrode candidate for ultra-high-k SrTiO₃ dielectric films for future high-density trench capacitors. To achieve conformal film growth, atomic layer deposition (ALD) of Ru is investigated. To this end, the use of an oxidizing reactant is desired to avoid electronic degradation of the interface properties of SrTiO₃ as found when using a NH₃ plasma for Ru ALD or when using thermal ALD TiN as electrode. Thermal ALD of Ru using O₂ gas, however, generally results in a pronounced nucleation delay and high surface roughness. The current work aims at developing ALD of Ru using an O₂ plasma in order to improve the film nucleation and to try to obtain smoother films. Using the novel CpRu(CO)₂Et precursor and O₂, both thermal and remote plasma ALD of Ru were studied in the same reactor at wafers up to 200 mm. Unlike thermal ALD, the Ru film growth by remote plasma ALD does not rely on the dissociative chemisorption of O₂ on the Ru surface and good film nucleation is expected by providing O radicals from the gas phase. In situ spectroscopic ellipsometry, x-ray reflectometry and diffractometry, and electrical measurements clearly show this benefit of the O₂ plasma. The Ru films almost immediately nucleate for the plasma-based process, whereas the thermal process showed a nucleation delay of approximately 100 cycles. Once the film growth has started, the growth per cycle (1 Å/cycle), the electrical properties (20 μΩ cm for >5 nm films), and the polycrystalline structure are similar for both ALD processes. However, despite the drastically improved nucleation, the remote plasma ALD Ru films show higher roughness values than the thermal ALD Ru films (roughness of 13 nm and 8 nm for 20 nm thick films, respectively). To elucidate this unexpected phenomenon, the film nucleation and surface reactions were examined. Mass spectrometry provided insight into the reaction products (CO₂, CO, H₂O mainly) and, therefore, into the surface chemistry ruling both ALD processes. Optical emission spectroscopy delivered information on the species created during plasma exposure. A reaction mechanism will be proposed for these oxygen-based ALD Ru processes that accounts not only for the differences in nucleation, but also relates to the roughness development of the Ru films.

10:00am TF2-MoM6 Atomic Layer Deposition of Platinum-Iridium Mixed Metal Layers. J.W. Elam, S.T. Christensen, Argonne National Laboratory
Atomic layer deposition (ALD) provides the unique and powerful capability to blend materials at the atomic scale for tuning and optimizing the properties of the resulting mixed layers. The ALD of mixed metal-oxide layers to maximize the charge storage capacity of dielectric materials is well known, but the ALD of mixed metal films is less well explored. The capability to synthesize mixed-metal layers with tunable physical and chemical properties could benefit numerous applications such as catalysis, hydrogen storage, corrosion resistance, and microelectronics, and the ALD of metal laminate nanostructures offers the possibility of core-shell structures and near surface alloys. In this study, we examine the ALD of platinum-iridium (Pt-Ir) mixed metal layers. The platinum ALD uses alternating exposures to (methylcyclopentadienyl)trimethylplatinum and oxygen while the iridium ALD uses alternating exposures to iridium(III) acetylacetonate and oxygen. The similar chemistries and process conditions for these pure metals facilitates ALD of the mixed metal layers. Furthermore, the tendency of Pt to form discrete nanoparticles on oxide supports makes this material attractive for catalytic application. We examined the Pt-Ir mixed metal ALD using in situ quartz crystal microbalance and quadrupole mass spectrometry to investigate the growth mechanism for the pure and mixed materials as well as the effect of mixing on the metal nucleation and growth. In addition, ALD Pt-Ir films were prepared on planar substrates and examined with a variety of techniques to evaluate the thickness, morphology, crystal structure, and chemical composition of the films. These results demonstrate that the thickness and composition of the Pt-Ir films can be controlled precisely.
Selective CVD of Co Layer on SAM Treated Copper/Low-k surfaces. XPS showed complete coverage by Co films selectively on Cu surfaces. XPS and TEM characterizations indicate that low-k surfaces are refractory to Co deposition on Si coated with ~80 Å of ALD Al2O3. The tungsten growth nucleation period on the quartz surface is predicted to be similar to tungsten growth on Al2O3. Scanning electron microscopy showed only minor cracking of the tungsten film coating on the quartz fibers, even after handling. The resistivity of ALD tungsten thin films grown on Al2O3 was < 200 μΩcm, and measurements show similar resistivity values for the tungsten deposited on the quartz fiber. Electronic transport differences in measurement of resistivity and the subsequent mechanisms for conductive pathways through fiber bundles compared to monolithic structures will be discussed. These results suggest new opportunities in the use of ALD processing to create electronically active fiber systems.

Interconnect Reliability Improvement by Selective CVD of Co Capping Layer on SAM Treated Copper/Low-k Surfaces. H.B. Bhandari, H. Park, R.G. Gordon, Harvard University
Electromigration in copper interconnects is a surface phenomenon and therefore becomes a dominant reliability concern as the Cu line widths are narrowed to accommodate the continuing scaling of interconnect structures. Reliability can be improved by applying a layer of cobalt metal on the top surface of Cu lines, thereby improving its adhesion to an overlying etch-stop layer such as silicon nitride. Thus, selective deposition of Co metal on ultra narrow Cu lines integrated in low-k dielectric is of critical importance in preserving the electrical performance of future integrated circuits. Here we propose a chemical vapor deposition process for applying Co thin films selectively on Cu surfaces. XPS showed complete coverage by Co films less than 2 nm thick on Cu substrates. The selectivity of the Co deposition was confirmed by Cu line to line leakage measurements on long interdigitated comb structures. Further enhancement of Co selectivity was achieved by employing self-assembled monolayers (SAMs) to passivate low-k surfaces. XPS and TEM characterizations indicate that low-k surfaces treated with (heptadecafluoro-1,1,2,2,-tetrahydrodecyl)trimethoxysilane or (heptadecafluoro-1,1,2,2,-tetrahydrodecyl)dimethyl(dimethylamino)silane species on the porous dielectric increases both the initial uptake of Ta[N(CH3)2]5 in the first half cycle, and the growth rate per cycle. Here an important issue concerns the fate of the IOL—does the ALD thin film quickly and uniformly cover the IOL, or are there reactions between the ALD precursors and the IOL? We find that the fate of the IOL depends strongly on the density and spatial distribution of reactive groups in the organic layer. We will discuss the implications of these observations concerning the use of IOLs as nucleation promoters in ALD.

From Chemisorption to Steady-State Growth: Initial Stages of ALD Examined using In Situ X-ray Photoelectron Spectroscopy. K.J. Hughes, J.R. Engstrom, Cornell University
One of the least understood aspects of atomic layer deposition (ALD) is the initial stage of growth, which involves the first set of reactions between the thin film precursors and the substrate. As ALD growth is invariably conducted on foreign substrates, the surface must evolve from that representing the starting substrate, to that eventually representing the steady-state growth surface. Here we employ in situ x-ray photoelectron spectroscopy (XPS) to examine the initial stages of growth of TaN from the reactions of Ta[N(CH3)2]5 and NH3 on SiO2 and porous low-k substrates, and both of these substrates modified with interfacial organic layers (IOLs). In this presentation, first, we will examine the effect of the density of the reactive adsorption sites (–OH groups) on SiO2 and SiO2 based porous low-k substrates. Here we find that the saturation density (coverage) of Ta depends strongly on the initial density of –OH. Moreover, we find that there is a strong correlation between the amount of ligand loss in this first half-cycle, and the density of the reactive adsorption sites. For example, on porous low-k substrates, reactions involving the loss of a single ligand and formation of –O-Ta[N(CH3)2]5(µ2-OH) species dominate. In contrast, on surfaces with a high density of –OH (SiO2), ligand loss is much more significant. Second, another important feature that XPS can probe is the chemical state of the primary thin film constituents. One process observed in the first cycles of growth is the shift in the position of the N(1s) peak, from a binding energy of ca. 398.9 eV to 397.2 eV. The former binding energy corresponds well to that reported for –N(R2) species (398.6), while the latter is close to that reported for TaN (397.5) and TaN2 (396.9). As a final example, we will consider growth of TaN on SiO2 and porous low-k substrates modified with interfacial organic layers. We have found that adsorption of a branched polymer possessing a high density of –NH2 species on the porous dielectric increases both the initial uptake of Ta[N(CH3)2]5 in the first half cycle, and the growth rate per cycle. Here an important issue concerns the fate of the IOL—does the ALD thin film quickly and uniformly cover the IOL, or are there reactions between the ALD precursors and the IOL? We find that the fate of the IOL depends strongly on the density and spatial distribution of reactive groups in the organic layer. We will discuss the implications of these observations concerning the use of IOLs as nucleation promoters in ALD.
Finally potential sensor applications based on imaging and dynamic layers are presented. As an example, studies of thermally induced degradation of fibrinogen ellipsometry utilizing sub-nm thickness resolution are reviewed. The use of monitored and used to assess the conformational state in the protein layer. Optical Properties of Sculptured Thin Films

Spectroscopic Ellipsometry II

In this report, the use of various types of ellipsometry for studies of protein layers at air/solid and liquid/solid interfaces are reviewed. Among the methods included are spectroscopic, dynamic, internal reflection and imaging ellipsometry. Two examples of methodology for analysis are discussed in some detail. First we observe that in situ studies allow monitoring of the dynamics of protein layer growth. Modeling of layer structure by separation of refractive index and thickness from such in situ data recorded during adsorption of fibrinogen layers is presented as well as strategies for evaluation of surface mass density.

In a second example, a model dielectric function (MDF) concept for protein layers in the UV-VIS-IR spectral range is presented. The MDF contains model parameters like resonance energies and broadening of vibrational structures, e.g. in the amide bands. Changes in these parameters can be monitored and used to assess the conformational state in the protein layer. As an example, studies of thermally induced degradation of fibrinogen layers are presented.

Finally potential sensor applications based on imaging and dynamic ellipsometry utilizing sub-nm thickness resolution are reviewed. The use of surface-plasmon resonance enhancement to increase resolution of internal reflection ellipsometry to pm in thickness will be discussed.


Three-dimensional structure design on the nanoscale is in the focus of modern material science and engineering because intriguing applications are foreseen for such nanostructured films in various fields ranging from optics, electromechanics or electromagnetics. We utilize glancing angle electron-beam deposition, where physical shadowing and varying particle incidence azimuth are exploited for fabrication of three-dimensional individual nanostructures arranged in sculptured thin films with different morphologies. We will present the anisotropic (structure-related) optical and magneto-optical properties of sculptured thin films from cobalt. Generalized spectroscopic ellipsometry is employed to determine the anisotropic principal optical constants of slanted columnar and chiral nanocoil thin films in the spectral range from 400 to 1650 nm. These thin films show strong form birefringence and large dichroism and are distinctly different from their bulk material. We will also discuss why slanted columnar thin films have monoclinic optical properties [1]. Magneto-optic Kerr effect measurements in the polar configuration lead to the determination of the magneto-optical Q-values (Voigt parameters) of such highly anisotropic ferromagnetic sculptured thin films.


3:00pm AS+EM+MS+TF-MoA4 Development of Hybrid Quartz Crystal Microbalance / Ellipsometric Porosimetry for the Characterization of Anisotropic Optical Materials. R.A. May, D.W. Flatt, C.B. Mullins, K.J. Stevenson, University of Texas at Austin

Ellipsometric porosimetry (EP) relies on monitoring the change in optical properties during vapor adsorption/desorption and has been successfully applied to an array of materials using a variety of adsorbates both in vacuum and at ambient pressures. However, these studies typically avoid the analysis of optically complex systems with strong absorbance or optical anisotropy. Towards this end, a hybrid quartz crystal microbalance/ellipsometric porosimetry (QCM/EP) technique is being developed to facilitate the study of more complex optical materials and to quantitatively estimate parameters such as porosity, pore size distribution, and surface area. To highlight the power of this hybrid approach thin films of TiO2 and TiC, have been deposited using reactive ballistic deposition (RBD). RBD provides control over film parameters such as surface area, porosity, pore size, and birefringence through variation of the deposition angle. Combined with the QCM/EP technique these films provide a platform for understanding both novel material properties and the requirements for extracting valid optical constants from anisotropic optical materials.

3:40pm AS+EM+MS+TF-MoA6 Multichannel Ellipsometry for Thin Film Photovoltaics Applications: From Materials to Solar Cells. R.W. Collins, J. Li, M.N. Sestak, J.A. Stoke, L.R. Dahal, University of Toledo

Second generation or thin film photovoltaics (PV) technologies have achieved the lowest manufacturing costs in the PV industry. These technologies benefit from multichannel ellipsometric analysis for characterization of multilayered thin film materials and deposition processes, specifically for determination of component layer thicknesses and dielectric functions. From such results, predictions of the maximum achievable quantum efficiency of multilayered PV device structures are possible. In this presentation, the current applications and future prospects of multichannel spectroscopic ellipsometry (SE) will be discussed for optical characterization of PV materials and devices during fabrication in the research laboratory as well as for on-line and off-line evaluation in PV module production. First, this review will address the advances in instrumentation for multichannel SE. Second, this review will provide examples of the analysis of real time SE data acquired during film growth to obtain structural parameters and dielectric functions, as well as the subsequent analysis of the resulting dielectric functions in terms of parameterized models to deduce useful information on thin film materials properties. Recent applications to be discussed in this presentation involve (i) the analysis of grain size, strain, and void profiles from the dielectric functions of polycrystalline CdS and CdTe thin films used as heterojunctions in efficient solar cells; (ii) the analysis of amorphous and nanocrystalline volume fraction profiles from the dielectric functions of mixed-phase hydrogenated Si (Si:H) thin films also used in efficient solar cells; and (iii) the determination of interface dielectric functions and losses associated with Ag/ZnO structures used as back-reflectors in efficient thin film solar devices. In the latter studies, the optical features of confined plasmon resonances can be identified. Methods for dealing with microscopic (sub-wavelength order) and macroscopic (wavelength order) surface and interface roughness will be treated, as will its impact on prospects for analyzing PV device structures on-line during module manufacturing. The ability to extract polarization, depolarization, and irradiance information from the reflected beam by multichannel SE is advantageous in many such PV applications.

4:20pm AS+EM+MS+TF-MoA8 Universal Behavior of Light Scattering from Self-Affine Fractal Surfaces: A Quantitative Relationship between Roughness and EMA Models. A. Yanguas-Gil, B.A. Speiling, University of Illinois at Urbana-Champaign, J.R. Abelson, University of Illinois, Urbana-Champaign

The effective medium approximation (EMA) is typically used to model the influence of roughness on the optical response of a surface or buried interface as measured by ellipsometry. Although the standard assumption of 50% material - 50% void provides useful results, the relationship between the EMA layer thickness and the surface topography is not fully understood. For example, in thin film deposition many authors have found a good correlation between the thickness of the EMA layer and the rms surface roughness measured by the root mean square whereas other authors have found significant discrepancies between the time evolution of these two parameters.

Using first principles scattering models, we have analyzed the ellipsometric response of surfaces that exhibit a self-affine dependence of surface topography on the lateral scale of measurement. This type of surface
roughness is found for a wide variety of real surfaces, including many deposited thin films. The calculations show that when the surface correlation length evaluated from the height-height correlation function or the power spectral density is much smaller than the incident wavelength, a universal behavior is found in the ellipsometric response. Both the amplitude of the reflected fields in the p- and s-polarizations, and the thickness of the EMA layer, depend on the product of the rms surface roughness times the average surface slope. Therefore, the linearity between roughness and the thickness of the EMA layer holds only as long as the average surface slope remains constant. That is the case when the growth obeys the predictions of dynamic scaling theory, i.e., the rms roughness and the correlation length change with time as $\sigma \sim \tau^\beta$ and $\xi \sim \tau^{\eta}$, where $\alpha$ and $\beta$ are the roughness and the growth exponents, respectively. Results are presented for different materials whose optical properties cover a broad range from metals to dielectrics. An important consequence of this universality is that the ellipsometric response is mathematically separable into two independent functions, one depending only on the optical properties of the film and the other only on the surface topography.

4:40pm AS+EM+MS+TF-MoA9 Numerical Ellipsometry: Thin Absorbing Films Deposited on Opaque Substrates


A major challenge for those utilizing ellipsometry is numerical processing of the measured data. The transcendental, multivalued equations arising from the physics of simple reflection are problematic for the least-squares numerical methods in common use. These early numerical methods require fairly accurate initial guesses, leading to local minima, and only find solutions at the bottom of a relatively flat numerical topography. Previously we have applied Complex Analysis in the n-k plane to improve visualization of the mathematics and this has led to a growing array of new numerical methods avoiding these difficulties. The work presented here extends these new numerical methods for use beyond transparent substrates to include absorbing substrates. Results show that reflection ellipsometry alone can be sufficient for determination of thin absorbing film thickness and optical properties without the need for additional kinds of measurements.

Numerical processing considering surface layers such as air-formed oxides will also be presented.

5:00pm AS+EM+MS+TF-MoA10 In situ Spectroscopic Ellipsometry As a Versatile Tool to Study Atomic Layer Deposition

E. Langereis, H.C.M. Knoops, W. Keuning, A.J.M. Mackus, N. Leick, M.C.M. van de Sanden, W.M.M. Kessels, Eindhoven University of Technology, The Netherlands

Atomic layer deposition (ALD) is considered as one of the primary candidates for the deposition of ultrathin and conformal films with precise growth control. In this contribution, the merits of using in situ spectroscopic ellipsometry (SE) to address various aspects of ALD will be discussed. In particular, the versatility of this all-optical diagnostic will be demonstrated by results obtained on metal oxide (Al2O3, HfO2, Er2O3, TiO2, Ta2O5, and SrTiO3), metal nitride (TiN and TaN), and metal (Pt and Ru) films with thicknesses ranging from 0.1 to 100 nm [1]. By acquiring SE data within a short time range and energy range from 5.5 eV in between (half-cycles) and by analyzing the film thickness and the energy dispersion of the optical constants of the films, the layer-by-layer growth and material properties of the films can be studied in detail. It will be shown that the growth rate per cycle and the ALD saturation curves can be determined directly by monitoring the film thickness as a function of the number of cycles, while also the nucleation behavior of the film on various substrates can be probed. Furthermore, it is demonstrated that the energy dispersion relation can provide information on the optical properties, the crystalline phase, and the material composition of the films. For metallic films, electrical properties can be calculated from the Drude absorption yielding insight into the electrical resistivity and electron scattering effects in ultrathin films.


5:20pm AS+EM+MS+TF-MoA11 Mueller-Matrix Ellipsometry Studies of Optimally Active Structures in Scarab Beetles

C. Järrendahl, J. Landin, H. Arwas, Linköping University, Sweden

Ellipsometry is a valuable tool for general materials characterization but also for optical investigations of complex structures including multilayers, photonic crystals, metamaterials and other artificial materials. The complexity of these kind of structures has during the years promoted the use of spectroscopic, variable angle, generalized and Muller-matrix ellipsometry. In parallel more complex optical models and analysis algorithms have come into use. Naturally occurring structures may show even higher complexity than artificial structures but with a more narrow range of constituent materials, mainly chitin and various proteins. Many interesting structures are found in insects, especially in butterflies and beetles. Fascinating reflection properties result from intricate photonic structures in their wing scales and cuticles. Currently there is a large interest to explore such functional supramolecular architectures for exploitation in nanotechnology.

Even though the optical properties of natural structures are frequently investigated, ellipsometry rarely has been used to reveal structural and optical properties. In this study, Mueller-matrix spectroscopic ellipsometry is applied in the spectral range of 300 to 1700 nm to investigate structures in the cuticle of Scarab beetles, primarily Cetonia aurata (the rose chafers). The cuticle of Cetonia aurata is green with a metallic look and reflects circular polarized light. It has been suggested that the circular polarization of this metallic gloss is caused by a helical structure in the chitinous cuticle. We find that the circular polarization effect is limited to the narrow spectral range of 470-550 nm and for longer wavelengths the reflection properties are similar to those from a near-dielectric material. Furthermore, the light reflected from Cetonia aurata is left-handed circularly polarized and the beetle thus appears black if viewed through a right-handed circular polarizer. In addition to Mueller-matrix spectroscopic ellipsometry, reflectance and scattering measurements are used to characterize the cuticle of Cetonia aurata. Model calculations and parameterization of the nanostructure employing a helicoidal structure are discussed.

**Thin Film**

**Room: A8 - Session TF1+PV-MoA**

**Chalcogenide Photovoltaics**

Moderator: A. Rockett, University of Illinois, Urbana-Champaign

2:00pm TF1+PV-MoA1 Growth and Structure of RF Sputter-Deposited Cadmium Sulfide (CdS) Thin Films

R.S. Yemuri, D. Zubia, C. McClure, C.V. Ramana, University of Texas at El Paso

Cadmium sulfide (CdS) is a II-VI semiconductor of interest for various applications which finds many scientific and technological applications. CdS thin films are particularly interesting for application in large area photovoltaics in addition to field-effect transistors, visible spectral range photoconductors, optical filters and nonlinear integrated optical devices. However, growth and optimization of conditions to produce high-quality CdS layers is important for enhanced photovoltaic device performances. In the present work, ordered cubic structured CdS films for application in CdTe/CdS solar cells were produced using RF magnetron sputtering. Pure CdS target was employed for sputtering. Two sets of CdS films were deposited: (1) at varying powers, in the range of 70-130 W, at constant Ar pressure of 7 mTorr, and (2) at varying Ar pressures, in the range of 5-20 mTorr at a constant power of 100 W. A detailed structural characterization was made to understand the effect of processing conditions on the morphology evolution, grain size, and crystal structure of the CdS films. High-resolution scanning electron microscopy (HRSEM) measurements revealed the smooth surface morphology of the CdS layers both as a function of sputtering power and Ar-pressure. CdS films grown at 70-130 W were found to be nanocrystalline, exhibiting grain-size (L) dependence on the sputtering-power (W). L increased with W yielding the highest average L=145 nm at 105 W. Further increase in W resulted in decreasing L. Similarly, under varying Ar pressure, the highest L (<138 nm) values were found at 5 mTorr. X-ray diffraction (XRD) analysis indicated that the entire set of deposited CdS films exhibit highly oriented cubic structure. L values evaluated from XRD are in good agreement with the HRSEM results. The optical characterizations were evaluated and a functional relationship between growth conditions and band gap, useful to tailor the CdS films for desired solar-cell application, was found. The results obtained will be presented and discussed.

2:20pm TF1+PV-MoA2 Characterization of Photovoltaic Thin Films Materials Using RF GD-OES and LA ICP-MS

F. Li, S. Anderson, Air Liquide - Balazs, P. Hunault, HORIBA Jobin Yvon

Photovoltaic thin film materials have been characterized by a number of traditional vacuum techniques: Auger, XPS, SIMS, and GD-MS to name only a few. Depth profiles of solar cell modules, contamination in the sputtering targets or surface stoichiometry of photovoltaic thin films are specific application examples which predicate the technique best suited for the data requirement. The evolution of thin films with new chemistries and the importance of surface modification for photovoltaic applications provide a continuing need for thin film analyses along with an avenue for new analytical tools.
In this paper we will discuss the application of two non-traditional surface and material analysis techniques for the RF grid, photovoltaic devices, and the optimization of the interface for facile charge injection requires detailed knowledge of the band offsets, which cannot easily be determined by electrical transport measurements. We utilize high resolution X-ray photoelectron spectroscopy (XPS) to directly quantify the band offsets of heterojunctions relevant to photovoltaic cells. Nanostructured extremely thin absorber (ETA) photovoltaic devices have been proposed as an inexpensive alternative to current single-crystal device technology, although the devices reported thus far suffer from low conversion efficiency. Thus, material optimization is essential to improve the cell performance. We design the electron transporter, solid-state p-CuSCN as the hole conductor, and CdTe as the photon absorber. High quality ZnO thin films were deposited by pulsed laser deposition (PLD) on F:SnO2 glass substrates for XPS band offset measurements. The band offsets were determined as a function of ZnO conductivity, and strategies for improved electron conduction across the interface will be discussed. In addition, the materials properties of CuSCN were thoroughly characterized, and its electronic structure was compared to density functional theory (DFT) calculations. The calculations show an indirect bandgap of 2.7 eV and high anisotropic charge transport with the unusual prediction that hole mobility exceeds the electron mobility.

Avenues to improve hole conduction through the introduction of defects in CuSCN were explored. 3:40pm TF1+PV-MoA6 Effects of Cu Doping Level in ZnTe:Cu Back Contacts on Cu Diffusion and CdTe Solar Cell Performance, J.N. Duenow, R.G. Dhere, S.E. Asher, W.K. Metzger, J. Li, T. Moriarty, T.A. Gessert, National Renewable Energy Laboratory

CdTe photovoltaic (PV) cells require a low-resistance back contact for optimal device performance. Cu-doped ZnTe (ZnTe:Cu) has been implemented successfully as an ohmic back-contact interface layer to CdTe, enabling cells with efficiencies of 14% or higher. The key advantage of being easily manufactured by vacuum processes, which enables highly controlled, reproducible films. Although CdTe devices have been made without Cu-containing contacts, devices with Cu contacts have generally exhibited higher performance. Controlled Cu diffusion from the back contact is known to be critical for optimal performance. Sufficient Cu is required for doping the CdTe absorber to provide a strong electric field in the depletion region. Excessive Cu, however, can cause poor junction formation by narrowing the depletion region to the extent that few minority carriers are generated within a diffusion length of the depletion region. Cu may also adversely affect the junction by diffusing into the CdS window layer. Previous studies of Cu diffusion from ZnTe:Cu back contacts have been performed at NREL using a fixed doping level of Cu in ZnTe, but altering Cu diffusion by changing the deposition temperature or film thickness. In this study, we instead deposit ZnTe:Cu films from targets containing a range of Cu amounts—from 0.45 to 5 wt.-%—while holding the temperature and film thickness constant. Capacitance-voltage, red-light-biased quantum efficiency, and secondary-ion mass spectrometry depth-profile measurements will indicate the net acceptor concentration in the CdTe and the degree of Cu diffusion as a function of the Cu density in the back-contact interface layer. Minority-carrier lifetime measurements will be used to correlate the effects of Cu density to the carrier recombination rate.

4:00pm TF1+PV-MoA7 Surface and Interface Properties ZnTe-based Solar Cell, F. Fang, B.E. McCandless, R.L. Opila, University of Delaware

In order to substantially reduce the capital costs of present crystalline silicon photovoltaics, alternative thin film solar cell (TFSC) devices are favored because of the inexpensive materials, simple material preparation, and low-cost large area fabrication. There is interest in growing polycrystalline thin films of II-VI direct band gap semiconductors, such as CdS/CdTe. TFSCs are well studied and currently being used for manufacture of commercial scale solar modules. Here, we are proposing a heterojunction system ZnSe/ZnTe as a wide band gap TFSC (Eg > 2 eV) for potential application in tandem cells. This provides an efficiency enhancement for future generation photovoltaics, provided the wide band gap cell efficiency can be increased. In addition, we are using Close Space Sublimation (CSS), which is a low-cost evaporation technology method already demonstrated for high efficiency and commercial CdTe TFSC. Our ZnSe/ZnTe TFSC is a heterojunction device with a high density of defect states at interfaces which can provide interface recombination centers; also the grain boundaries in polycrystalline semiconductor films act as shallow and deep defect levels within the bandgap and create different recombination mechanisms than radiative band-to-band recombination in ideal crystalline devices. As a result, minority carrier collection relies on the build-in electric field, and not bulk voltage generated by collection of photo-generated current. Therefore, it is crucial to form a high quality diffusion junction. Some earlier work reported a diffusion voltage of 1.70 eV for single crystal ZnSe/ZnTe structure, which suggests that open circuit voltage, VOC > 1V is feasible. We have used Al-Ko X-ray photoelectron spectroscopy and Soft (Ultra-violet) X-ray photoelectron spectroscopy (Synchrotron Light Source) to investigate the surface chemistry and valence

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energy efficiency of multijunction cells due to it being lattice matched to GaAs and NREL, and Arizona State University. This abstract is subject to governmental review.

This work is supported by DOE-EERE grant DE-FG36-08GO18002, INVESTED.

5:00pm TF1+PV-MoA10 Novel Solar Cells based on a ZnGeAs2, T.J. Peshek, National Renewable Energy Laboratory, Nevada State University, T.J. Counts, T.J. Gessert, National Renewable Energy Laboratory, Arizona State University, T.J. Counts, T.J. Gessert, National Renewable Energy Laboratory, Arizona State University, T.J. Counts, T.J. Gessert, National Renewable Energy Laboratory, Arizona State University. We present the latest results on the development of a novel thin film solar cell based on the direct gap semiconductor ZnGeAs2. This material has long been viewed as a promising solar material for high efficiency multi-junction cells due to its unique absorption characteristics. We have fabricated devices with a single junction cell based on ZnGeAs2. Initial tests show that the devices have low efficiencies, possibly because the photogenerated currents are low. We find that the open-circuit voltage of our first tests is approximately 0.135 V. It is our hypothesis based on the J-V curves that the current sourced by the cell can be improved significantly at this point by reducing the series resistance of the device and minimizing any shunts that seem to be present in these devices. The cell is structured according to the superstrate configuration using RF sputtered CdS as the n-type buffer layer. The p-type ZnGeAs2 absorber was deposited at about 600 K by pulsed laser deposition. This work is supported by DOE-EERE grant DE-FG36-08GO18002, NREL, and Arizona State University. This abstract subject to governmental review.

TF2-MoA3 Controlled Growth of MOFs on Functionalized Organic Surfaces, S. Shekha, H. Wang, Ch. Woell, R. Fischer, Ruhr Uni. Bochum, Germany. The fabrication of thin film coatings of metal-organic frameworks (MOFs) on surfaces is of great importance for various applications, like smart membranes, catalytic coatings, chemical sensors, and many other related nano-technological devices. The main challenge for the fabrication of such thin films is to accurately control their growth. We will report on the development of a novel step-by-step approach for the synthesis of metal-organic frameworks (MOFs) and their deposition on functionalized organic surfaces. The approach is based on the sequential immersion of functionalized organic surfaces, alternately in solutions of the metal and the MOF building blocks. The MOF growth of the MOF layers is highly selective. Therefore, our set of data suggests that Ad, observed after PF immersion in ethanol, is mostly related to reorganization of the PP structure and not to material dissolution in the solvent.

TF2-MoA4 Plasma Polymer Film Behavior in Ethanol: A Multi-Technique Investigation, L. Denis, D. Thirty, University of Mons, Belgium, D. Cassemet, Materia Nova Research Center, Belgium, P. Gerbax, University of Mons, Belgium, F. Brusciotti, I. Van De Keere, V. Goossens, H. Terryn, Vrije Universiteit Brussel, Belgium, M. Hecq, R. Sniders, University of Mons, Belgium. Primary amine-based plasma polymer films (PPF) attract increasing interest in biotechnology since they have recently been reported to support cell growth and biomacromolecule (DNA, polysaccharides) immobilization. Since many years, the PPF chemistry has extensively been studied. Nevertheless, the behavior of these materials in solvents is not yet fully understood. For example, some works have reported the decrease of allylamine PPF thickness (Ad) after immersion in ethanol. Such a kind of observation is frequently attributed to the loss of material in the solvent. Up to now, however, such assumption remains unproved and therefore this phenomenon needs further investigations. In this work, allylamine PPF have been synthesized at low pressure (2.67 Pa) using pulsed radiofrequency discharges varying the mean power injected in the plasma (Pmean). The PPF behavior in ethanol has been studied through analysis of both PPF and the resulting ethanol solution characteristics. Ad which is inversely proportional to Pmean has been measured by ellipsometry. This behavior has been attributed to the increase of the PPF cross-linking density (Δd) with Pmean. In order to evaluate Δd, we have used Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) and further treatment of the data by Principal Component Analysis (PCA). The results suggest an increase of Δd with Pmean, hence supporting our assumption. Moreover, it should be noted that the PPF chemistry, evaluated by X-ray Photoelectron Spectroscopy (XPS), does not change significantly after ethanol immersion. On the other hand, the ethanol solution has been analyzed by Gas Chromatography – Mass Spectrometry (GC-MS), a highly sensitive method (10^-9 g/ml). The results show that there are no chemical species released by the PPF during immersion. Therefore, our set of data suggests that Ad, observed after PPF immersion in ethanol, is mostly related to reorganization of the PPF structure and not to material dissolution in the solvent.

TF2-MoA5 Controlled Growth of MOFs on Functionalized Organic Surfaces, O. Shekhah, H. Wang, Ch. Woell, R. Fischer, Ruhr Uni. Bochum, Germany. The fabrication of thin film coatings of metal-organic frameworks (MOFs) on surfaces is of great importance for various applications, like smart membranes, catalytic coatings, chemical sensors, and many other related nano-technological devices. The main challenge for the fabrication of such thin films is to accurately control their growth. We will report on the development of a novel step-by-step approach for the synthesis of metal-organic frameworks (MOFs) and their deposition on functionalized organic surfaces. The approach is based on the sequential immersion of functionalized organic surfaces, alternately in solutions of the building blocks of the MOF, i.e. the organic ligand and the metal precursor.

2:40pm TF2-MoA5 Controlled Growth of MOFs on Functionalized Organic Surfaces, O. Shekhah, H. Wang, Ch. Woell, R. Fischer, Ruhr Uni. Bochum, Germany. The fabrication of thin film coatings of metal-organic frameworks (MOFs) on surfaces is of great importance for various applications, like smart membranes, catalytic coatings, chemical sensors, and many other related nano-technological devices. The main challenge for the fabrication of such thin films is to accurately control their growth. We will report on the development of a novel step-by-step approach for the synthesis of metal-organic frameworks (MOFs) and their deposition on functionalized organic surfaces. The approach is based on the sequential immersion of functionalized organic surfaces, alternately in solutions of the building blocks of the MOF, i.e. the organic ligand and the metal precursor.

The synthesis and growth of different types of MOFs on substrates with different functionalization like COOH, OH and pyridine terminated were studied and characterized with different techniques like IR, NMR, and AFM. The IR, NMR, AFM and SEM data showed a linear increase in the thickness of grown layers for each immersion cycle. The AFM and SEM data recorded for laterally deposited substrates also demonstrated that the growth of the MOF-layers is highly selective. The dependence of MOF-deposition on the termination of the substrate was demonstrated in the case of [CuBTCc2(H2O)n] MOF on both COOH and OH terminated surfaces, where the XRD out-of-plane (Figure 1) and the

Thin Film

Room: B3 - Session TF2-MoA

Thin Films: Growth and Characterization II

Moderator: S.B. Sinnott, University of Florida

2:00pm TF2-MoA1 Creation of All-Diamond Core-Shell Particles by Layer-by-Layer Deposition for use in Solid Phase Extraction and Chromatography, G. Saini, L.A. West, R.C. Davis, Brigham Young University, University of Arizona, A. Dodson, M.A. Vail, U.S. Synthetic, M.L. Lee, M.R. Linford, Brigham Young University

We report the formation of all-diamond, core-shell particles based on chalcogenide materials for solid phase extraction (SPE) made via layer-by-layer deposition. The process begins with the amine functionalization of microdiamond by its immersion in an aqueous solution of an amine-containing polymer. The amine functionalized microdiamond is then immersed in an aqueous suspension of the nanodiamond, which leads to adsorption of nanodiamond. Alternating immersion in the solution of amine containing polymer and in the suspension of nanodiamond is continued until the desired number of nanodiamond layers is formed around the microdiamond. Finally, the core-shell particles are cross-linked with 1,2,5,6-diepoxychloroethane to increase their mechanical and chemical stability. Core-shell particles are characterized by diffuse reflectance infrared Fourier transform spectroscopy (DRIFT), environmental scanning electron microscopy (ESEM), X-ray photoelectron spectroscopy (XPS) and Brunauer Emmett Teller (BET) surface area and pore size measurements. Core-shell diamond particles have much higher surface area and loading capacity as measured in SPE than non-porous solid diamond particles. For example, for 50-70 μm core-shell particles containing 9 bilayers of poly(allylamine) (PAAM) and 100-250 nm nanodiamond, which can be made relatively easily, a ca. 21-fold increase in BET surface area and 80-fold increase in analyte loading capacity by SPE was observed in comparison to non-porous solid diamond particles.

Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) and further treatment of the data by Principal Component Analysis (PCA). The results suggest an increase of Ad with Pmean, hence supporting our assumption. Moreover, it should be noted that the PPF chemistry, evaluated by X-ray Photoelectron Spectroscopy (XPS), does not change significantly after ethanol immersion. Therefore, our set of data suggests that Ad, observed after PPF immersion in ethanol, is mostly related to reorganization of the PPF structure and not to material dissolution in the solvent.

The synthesis and growth of different types of MOFs on substrates with different functionalization like COOH, OH and pyridine terminated were studied and characterized with different techniques like IR, NMR, and AFM. The IR, NMR, AFM and SEM data showed a linear increase in the thickness of grown layers for each immersion cycle. The AFM and SEM data recorded for laterally deposited substrates also demonstrated that the growth of the MOF-layers is highly selective. The dependence of MOF-deposition on the termination of the substrate was demonstrated in the case of [CuBTCc2(H2O)n] MOF on both COOH and OH terminated surfaces, where the XRD out-of-plane (Figure 1) and the
plane data showed the presence of a highly ordered and a preferentially oriented crystalline material, that exhibits the same structure as observed for the bulk compound. [1] This was also demonstrated for the case of the (Zn2(bdc)2(dabco)) MOF on the pyridine terminated surface. [2]

References


3:00pm TF2-MoA4 Counterion Dependent Swelling of Redox-Active Polyelectrolyte Multilayers, R. Zahn, ETH Zurich, Switzerland. F. Boumilédas, Institut Charles Sadron, France, J. Voros, ETH Zurich, Switzerland, P. Schaub, Institut Charles Sadron, France, T. Zambelli, ETH Zurich, Switzerland

Polyelectrolyte Multilayers (PEMs), formed by alternating layer-by-layer (LBL) deposition of polyanions and polycations, have been widely studied during the last decade. The properties of these layers can be tuned by varying the PEM composition, and thus present a promising tool for a wide range of applications.

Here we present a PEM consisting of alternating layers of Poly-L-Glutamic Acid (PGA) and Poly-(Allylamine Hydrochloride) (PAH) containing Ferrocyanide (FC) ions as electrochemically active species. The PEM buildup was monitored in situ using Quartz Crystal Microbalance with Dissipation monitoring (QCM-D). Ferrocyanide (FC) ions were added to the film and cyclic voltammetry was performed to oxidize and reduce the ions.

We found that oxidation and reduction of the incorporated FC ions caused the expansion and contraction of the PEM films. Applying 0.6 V caused the FC ions to be oxidized from [Fe(CN)6]4− to [Fe(CN)6]3−, leading to a thicker and less rigid film. This was observed using electrochemical QCM-D (EC-QCM-D) and subsequent reduction of the ions caused the film to contract back to its original state. Measurements involving different counter ions showed a strong dependency on the anion species, charge, and molarity. No such effects could be shown for different cations. The swelling behavior of the PEM films is also influenced by changes in the pH of the buffer.

The observed swelling behavior is attributed to charge compensation by counter ions. Upon oxidation of the FC, anions diffuse into the PEM and replace the missing negative charge. These ions, and their accompanying hydration shell, cause an increase in the osmotic pressure within the layer, which leads to the observed swelling behavior. Depending on their thermodynamic properties (charge, hydration shell thickness, and hydration entropy), a certain fraction of the counter anions can condensate on the PEM-FC complexes and decrease the swelling. This dependency of the swelling effect on the specific interaction of the polymer to the counter ion is also verified by Attenuated Total Internal Reflectance (ATR) Transformed InfraRed (ATR-FTIR) spectroscopy. High ion strengths and pH values result in partial Donnan breakdown, which allows water to enter and cations to leave the PEMs.

To conclude, we have investigated a system of electroactive PEMs. Their swelling response can be tuned by choosing different counter ions and pH conditions.

3:40pm TF2-MoA6 Gas and Liquid Media Approaches to Low Temperature Fabrication of Aluminum Oxide Thin Films. X.F. Duan, The University of Melbourne, Australia, N.H. Tran, University of Western Sydney, Australia, N.K. Roberts, The University of New South Wales, Australia, R.N. Lamb, The University of Melbourne, Australia

Al2O3 thin films are useful in a variety of applications from gate insulators to implant prosthetic devices. They can be made in a number of different ways but usually at high temperatures (> 800 °C) and considerable expense. The critical feature of these types of fabrication is the control of the thermal stability of the chemical precursor. In particular the selection of precursors which can be decomposed rapidly in a resistively-heated substrate and as a result will always produce highly volatile by-products. Resultant films are then always guaranteed to be relatively contaminant free.

4:00pm TF2-MoA7 Solution Growth of ZnO Nanowires and Thin Films in a Continuous Flow Microreactor. K. McPeak, J. Baxter, Drexel University

Crystal growth from solution is used in the optoelectronic and photovoltaic industries, as well as in the laboratory, for the production of oxide and chalcogenide thin films and nanowire arrays. Chemical bath deposition (CBD) offers advantages over high-temperature vapor phase growth in terms of both cost and compatibility with flexible substrates. However, its widespread use is limited by low process yield and excessive waste solvent, which result because precipitation in solution competes with deposition on the substrate and also by the initial adsorption of oxygen on growth surfaces. While CBD growth conditions impact material properties and morphology, We report on the implementation of a continuous flow microreactor, where the substrate serves as one reactor wall and the chemical bath is contained within a sub-millimeter channel. We have used these microreactors to grow dense arrays of well-aligned single-crystal ZnO nanowires and ZnO thin films. The smaller transport lengths offered by the microreactor design reduce mass transport limitations and mitigate homogenous precipitation, resulting in microreactor deposition yields that can be up to an order of magnitude higher than yields using CBD with conventional reactor geometries. Furthermore, the continuous flow microreactor operates in plug flow, where bath composition changes as a function of position but is time-invariant. Slow flow rates result in nanowires whose lengths, growth mechanisms, and optical properties vary even within a single substrate, while fast flow rates produce nanowires that are more uniform across the substrate. Spatially resolved characterization of the substrate enables rapid and direct correlation of material properties to growth conditions, which is not possible for batch growth where bath composition evolves with time. Here we explore growth at low flow rates to create combinatorial libraries of materials; and we describe the relationship between growth mechanism, strain, and photoluminescence of solution-deposited ZnO nanowire arrays and thin films in unprecedented detail.
In the last years, the semiconductor industry has shown a growing interest for the fabrication of nonvolatile memories based on a resistance switching mechanism to store information: Resistive Random Access Memories (RRAM). A basic RRAM cell consists in a Metal / Insulating oxide / Metal (MIM) structure where the oxide is a metal oxide (NiO, TiOx, ZrOx, CuO, Sr2MnO4…), a perovskite (BaTiO3, SrTiO3…) or a manganite (Pr1-xCaxMnO3, La1-xSrxMnO3…). A commonly admitted model to explain resistance switching is the formation of conducting filaments upon field-enhanced migration of cations or anions across the film's thickness. In this respect, oxygen vacancies seem to play an important role.

In this work, HfO2 MIM RRAM cells are elaborated and tested in two electrical modes: voltage sweep mode and constant voltage stress (CVS) mode. HfO2 choice is based on the fact that hafnia-based dielectrics are the most promising materials for the manufacturing of CMOS gates below the 45 nm technology node. Therefore, as far as integration and process compatibility are concerned, HfO2 would be an interesting candidate for the RRAM technology. HfO2 films (10 nm) were grown at 350 °C by atomic layer deposition (ALD) using alternate cycles of H2O and HfCl4 precursors (1 Torr) on Pt (100 nm) / Ti (10 nm) / Si wafers. The films are crystallized in the monoclinic phase and their gap is around 5.5 eV. Angle-resolved X-ray photoelectron spectroscopy (ARXPS) performed on thinner films (2 nm) reveals a homogeneous composition across the films thickness with a sharp HfO2/Pt interface (absence of PtO oxides). Top gold electrodes (100 nm) reveals a homogeneous composition across the films thickness with a sharp HfO2/Pt interface (absence of PtO oxides). A commonly admitted model to explain resistance switching is the formation of conducting filaments upon field-enhanced migration of cations or anions across the film's thickness. In this respect, oxygen vacancies seem to play an important role.

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The incorporation of an Al2O3 film for boron doped emitter passivation led to enhanced efficiencies of 23.2% for n-type c-Si solar cells [2]. From the cumulative research, various questions related to the thermal stability and other processing aspects of the Al2O3 films appeared. In this contribution we will show that a decrease of film thickness down to ~5 nm does not compromise the passivation quality, enabling a straightforward reduction of deposition time and providing freedom in the design of optimal front passivation/antireflection schemes. To activate the paper demonstrate the suitability of thin ALD-synthesised Al2O3 passivation recombination in the metalized area will be dominant. The findings in this paper show that the relative thermal stability and other processing aspects of the Al2O3 films are relatively thin. However, there are many industrial areas where substrate sizes as well as ensure good flow dynamics to obtain fast cycle times. New applications outside semiconductor industry where ALD can possibly be utilized include photovoltaics, diffusion barriers, wear resistant materials and optical coatings aiming to improve competitiveness of existing products and enabling new applications.

In this presentation different approaches to obtain uniform oxide films are discussed in detail. For example, optical thin film stack structures made by ALD there are several possibilities for high index materials but for low index materials the selection is still more limited. Scaling of the processes for batches up to 5-10 m2 of total area is required to obtain reasonable throughput. At the same time the deposition cycle should still be kept a well below 3-5 seconds. For example we have made TiO2 deposition in a large batch consisting of 36 shelves (240x500 mm2) double side coating using Beneq P400 A. Batch uniformity over 8 m2 area was ±2%.

In addition to process optimization to large batches we show preliminary data concerning the deposition of metal fluorides by using novel precursor chemistry based on the traditional metal oxide ALD chemistry using either fluorinated metal β-diketonates or fluorinated hydrocarbons as a fluorine source. According to the RBS film stoichiometry was CaF2.03 with oxygen contamination below the detection limit, i.e. below 5 at.%. The refractive index of films deposited at 300oC was 1.43.

The use of S-ALD to deposit films onto a range of substrates, both rigid and flexible, as well as webs, will be discussed. The ALD process also allows selective film growth by prepatterns substrates with growth inhibitors. These inhibitors can be applied to flexible substrates with conventional printing techniques. By leveraging selective area deposition, we combine the high quality of ALD films with printing-like patterning, all at atmospheric pressure. This combination is likely a key step in enabling high-quality printed electronics on flexible substrates. The performance of films deposited by the S-ALD approach will also be presented, functioning as barriers and components in patterned semiconductor devices. In general, performance of S-ALD films in terms of electrical and physical properties are consistent with the published performance of conventional ALD materials.
Glancing Angle Deposition I

Moderator: T. Karabacak, University of Arkansas at Little Rock

8:00am TF1+SE-TuM1 Nanorod Structures for Energy Conversion, N.A. Koratkar, Rensselaer Polytechnic Institute INVITED

Oblique angle deposition (OAD) is a technique which allows for fabrication of unique nanostructures, which cannot be grown by advanced lithographic techniques. OAD is simple, fast, cheap, has high mass production capability and can generate unique two- and three-dimensional nanostructures with large aspect ratio and controllable porosity, shape and symmetry. The fact that these nanostructures can be integrated onto a substrate platform makes them practical for many realistic applications. In this talk I will demonstrate the application of nanorods grown by OAD in various key device applications of today's energy starved society. The first is the use of Cu nanorods anodes for rechargeable Li-ion batteries with higher capacity. The second is the development of Zinc Oxide (ZnO) and Indium Tin Oxide (ITO) nanorods by magnetron sputtering at low temperatures and their use as enhanced transparent conducting electrodes for polymeric photovoltaic devices. The third is the use of Pt nanorod based electrode architectures for proton exchange membrane fuel cells and the fourth is the synthesis of TiO2 has been used as an efficient and effective photocatalyst material, with applications in water purification, water splitting for hydrogen generation, clean windows, and many others. The photocatalytic efficiency of TiO2 can be enhanced by increasing its surface area as well coupling it with another semiconductor which can create a charge separation effect. There are many methods to produce high surface area nano-sized TiO2 such as sol-gel, hydrothermal, and ball-milling, but these techniques are governed by surface chemistry and random aggregation, and are difficult to control the overall size and morphology of the nanoparticles. These results show that the GLAD based nanofabrication technique is a versatile tool to design new photocatalytic nanostructures. With more size- and structure-driven properties in such 3D metal nanostructures for controlled release and delivery of organics and synthetic molecules. Structured polymer brushes are envisioned to be useful in for specific controlled drug release, metallization (ERS and catalyst applications), tissue targeting as well as antifouling applications. [3-5]

Cetinkaya, M., Malvakdar, N., Demirel, M.C., “Photoconductivity Response of Indium Sulfide Nanorod Arrays”, University of Georgia

9:30am TF1+SE-TuM5 Oblique Angle Polymerization, M.C. Demirel, Penn State University

The growth of spatially organized structures is of considerable fundamental interest, since it may provide us with important clues to the way in which organized structures form in Nature. A closer look at complex structures in insect wings and lizard toes reveal organized structured features at the microscopic scale. The organized structures in Nature are formed through evolutionary processes, and these complex molecules and features are built using molecular templates. Synthesis of organized structures form in Nature. A closer look at complex structures in insect wings and lizard toes reveal organized structured features at the microscopic scale. The organized structures in Nature are formed through evolutionary processes, and these complex molecules and features are built using molecular templates. Synthesis of these structures has high aspect ratio and the production technique does not require any template, lithography method or a surfactant for deposition. This approach allows us to tune the chemical properties of nanostructured surfaces and film morphology to control the physicochemical properties of the resulting films, such as hydrophobicity, porosity, electrochemistry, chemical reactivity, surface energy and crystallinity. We have recently functionalized nanostructured polymer films for controlled release and delivery of organics and synthetic molecules. Structured polymer brushes are envisioned to be useful in for specific controlled drug release, metallization (ERS and catalyst applications), tissue targeting as well as antifouling applications. [3-5]


10:40am TF1+SE-TuM9 On the Uniformity of Films Fabricated by Glancing Angle Deposition, N.G. Wakefield, J.C. Slt, University of Alberta, Canada

Films fabricated using the glancing angle deposition technique are subject to significant variations in important film parameters across a sample due to varying geometric conditions at each point on the substrate. This is a serious fundamental problem, as non-uniformities in aspects such as film thickness or porosity can drastically change a film’s properties across even a small sample size. This means that film properties can vary rapidly, and undesirably, with position over a substrate and attempting to scale technologies based on glancing angle deposition to large areas presents a major challenge. An elegant way to quantify and control the non-uniformities in these quantities, starting from a simple geometric framework, applicable to physical vapor deposition at low pressures. In this work, this method is applied to glancing angle depositions done at a fixed deposition angle, but with arbitrary azimuthal substrate rotation. Quantities such as the effective deposition angle and the mass flux at any point on the substrate can be determined purely from the geometry of the deposition setup. Predicting further quantities such as the film porosity and thickness requires additional, material specific information that is easily obtainable.

For a TiO2 deposition at θ = 70° on a 10 cm substrate, dependent on the film’s structure, porosity and thickness non-uniformities are found to range from ±1.7% to ±8.2% and ±1% to ±30% respectively. Experimental values of thickness variation on a 10 cm × 10 cm substrate range from ±1% to ±3% for various deposition angles. A simple geometric model is used to predict deposition angle variations for films deposited at different angles on a 10 cm substrate. This model is validated experimentally using glancing angle deposition of TiO2 films at various angles on a 10 cm substrate and comparing the experimental results with the theoretical predictions. The model shows excellent agreement with experimental results, demonstrating the ability to accurately predict deposition angle variations for films deposited at different angles on a 10 cm substrate.

11:00am TF1+SE-TuM10 Nanostructured Tungsten and Tungsten Trioxide Films Prepared by Glancing Angle Deposition, D. Deniz, R.I. Lad, University of Maine

The sensitivity of chemiresistive metal oxide gas sensors can be markedly increased by fabricating nanostructured films with very high surface-to-volume ratio. In this work, nanostructured tungsten (W) and tungsten oxide (WO3) films were fabricated using pulsed direct current (DC) magnetron sputtering of a W target with a glancing angle deposition (GLAD) geometry. The major parameters that were varied included substrate temperature, deposition rate, substrate rotation, Ar/O2 plasma composition, and post-deposition thermal treatments. The stoichiometry of the nanostructured films was characterized by X-ray photoelectron spectroscopy (XPS), and the structure and morphology were investigated using X-ray diffraction (XRD) and high resolution scanning electron microscopy (SEM). Metallic W nanorods were formed by sputtering in a pure Ar plasma at room temperature and they crystallized in a simple cubic β-phase with W(100) texture. Subsequent annealing at 500 °C in air transformed the nanorods to textured triclinic WO3 structure but the nanorod morphology was retained. Stoichiometric WO3 films grown in Ar/ O2 plasma at room temperature had an amorphous structure and also exhibited a nanorod morphology. Post-deposition annealing at 500 °C in air induced crystallization of the triclinic WO3 phase and also caused a morphological change into a very porous nanowire network. The differences in the chemiresistive response to each of these high surface area nanoengineered films to CO2 and CH4 gas exposure will be presented.
Thin Film
Room: B4 - Session TF2-TuM

ALD/CVD: Basics, Organics, Electronics
Moderator: R.G. Gordon, Harvard University

8:00am TF2-TuM1 How Surface Reactions Afford Ultra-Conformal CVD: A Zone Diagram and the Application of Suppressor Species. J.R. Abeelson, University of Illinois at Urbana-Champaign

We present a unified description of conformal film growth in recessed features by low-pressure chemical vapor deposition. Experimental data on step coverage and growth rate are interpreted in terms of a Langmuirian kinetic model for the elementary surface processes. This model is combined with the continuity equation for gas transport and consumption to predict the values of precursor pressure and substrate temperature (p,T) that are necessary for conformal coverage to occur for a given precursor. We introduce a *conformal zone diagram* that considers the gas phase limitations (maximum precursor pressure, onset of secondary reactions), surface limitations (minimum reaction temperature, precursor adsorption and desorption rates, film growth rate) and the aspect ratio of the feature to be coated; the allowed intersection between the resulting boundaries defines the (p,T) zone for conformal growth. Sufficient precursor pressure is identified as a major requirement for conformal film growth, one that is not met by many commercially available molecules. We show that growth *inhibition*, the use of a second species to decrease the surface reactivity, can enlarge the conformal zone of low-pressure precursors. We incorporate the inhibition mechanism into the kinetic model; the theoretical predictions are in excellent agreement with experimental results. We also extend the kinetic model to the case of compound film growth from two reactants. Finally, we derive an approximate analytical solution to the inverse problem: what are the experimental conditions necessary to afford a desired degree of step coverage on a given aspect ratio feature at a desired growth rate. The solution depends on a set of rate constants in the kinetic model that can be extracted from measurements of the film growth rate as a function of precursor pressure and substrate temperature on trench or planar substrates.

8:40am TF2-TuM3 Functional and Conducting Polymer Thin Films by Vapor Deposition. K. Gleason, Massachusetts Institute of Technology

INVITED

Polymers provide extraordinary opportunities for functionalizing surfaces and creating thin films for integration into flexible devices. Vapor deposition is the method of choice for polymers having limited solubility or if the object to be coated degrades or swells upon exposure to solvent. Indeed, fluoropolymers, cross-linked materials, and electrically conducting polymers are three examples of organic materials which having little if any solubility, but which have been successful deposited by two new vapor phase methods: initiated chemical vapor deposition (iCVD) and oxidative chemical vapor deposition (oCVD). By depositing polymers from the vapor phase, many wetting and solution effects are avoided, and conformal films can be created. The iCVD method is a platform technology which has produced a number of different homopolymers. Random copolymers, alternating copolymers, and grafted polymer chains have all been demonstrated using the iCVD method. Surface properties achieved include non-leaching antimicrobial layers, flexible dielectrics with low leakage current, and coatings with specific ligand binding capability on porous substrates and particles, superhydrophobicity, and superhydrophilicity. Engineering of iCVD coatings has led to extremely stable and flexible biopassivation coatings for neural implants, reversible swellable hydrogel layers, and enteric coatings of drug particles for pH sensitive release. Mechanistic understanding of the oCVD growth mechanism led to the ability to propagate conductive polymer chains directly from the growth surface with the use of any additional linker molecules. The creation of covalent linkages between the substrate and the surface functionalization layer affords excellent adhesion and also enables 60 nm lithographic pattern formation. The demonstration of patterns in conducting polymer patterns grafted onto common plastic substrates is a potential breakthrough for integrated circuitry for flexible electronics where mechanical robustness is extremely important, requiring excellent interfacial properties and adhesion. Each organic thin film synthesized by iCVD and oCVD displays a well-defined chemical structure as a result of selectively limiting the reaction pathways available during processing through a judicious choice of reactants and minimizing the energy input that drives the CVD chemistry. The exquisite control over composition and conformality achieved by these new vapor phase methods enables precise organic functionality to be designed and applied to almost any type of substrate. The fundamental understanding of the processes accelerates both discovery of and scale-up.

9:20am TF2-TuM5 CVD of Three Aminoisalanes on Silicon Oxide: Effect of Silane Concentration, Surface Characterization and Stability, and Cyanine Dye Adsorption. M.R. Linford, F. Zhang, Brigham Young University, H. Samha, Southern Utah University, K. Sautter, Yield Engineering Systems, R.C. Davis, Brigham Young University

CVD of these reactants can be used to form functional materials. Of the various ways to deposit silanes, it is becoming increasingly recognized that CVD is the most reproducible and reliable. However, CVD of these important reagents is also much less studied than the less reproducible and much more widely practiced deposition from solution. We also stress the environmentally friendly and industrially viable nature of CVD silane deposition. Our work differs from that of most academic researchers because of the tool we use for silane deposition, which is a commercially available CVD system (the 1224P) from Yield Engineering Systems. This tool gives complete control over oven temperature, pressure, and reagent delivery, in addition to offering plasma pretreatment of the substrates at a range of powers and conditions. In our work we have explored the CVD at 150°C of 3-aminopropyltriethoxysilane (APTES), which has arguably the most widely used and important silane. We show how surface saturation leading to the same level of surface functionalization occurs over a very wide range of gas phase concentrations. This important result indicates that there is a wide process window for APTES deposition. We further compare CVD of APTES to the gas phase deposition of two of its aminoisalane analogs: one with two methyl groups (3-aminopropyl(dimethyl)silane), and the other with two isopropyl groups (3-aminopropyl(diisopropyl)oxysilane). X-ray photoelectron spectroscopy (XPS) shows a decrease in nitrogen concentration for these two molecules compared to APTES. All of these films are extremely flat by atomic force microscopy, and spectroscopic ellipsometry indicates the expected monolayer coverages of our silanes. Of particular significance is the stability against base of the disilopropyl aminoisalane, which should make it valuable in a number of applications. The interactions of our different amino surfaces with a cyanine dye are also probed, and the structure/adsorption of the dye seems to be well correlated to the amine density determined by XPS.

10:40am TF2-TuM9 Kinetic Study on InGaAsP-MOCVD Using Selective Area Growth and its Application to OEIC Device Fabrication. Y. Shimogaki, The University of Tokyo, Japan

INVITED

Metal-organic chemical vapor deposition (MOCVD) is a well developed deposition technology for the fabrication of InGaAsP compound semiconductors. If the substrate is partially covered by dielectric masks such as SiO2, selective growth will occur and take place on the mask during the MOCVD. Then reactants will be accumulated above the mask area and migrate towards the adjacent non-mask covered area, causing growth rate enhancement. This growth rate enhancement will be proportional to the size of the mask, because larger mask will accumulate more reactants. Thus we can control the selective growth rate by the area of the mask. This technique can be applied to both planar and mesa devices. We also recognize that CVD is the most reproducible and reliable. However, CVD of these important reagents is also much less studied than the less reproducible and much more widely practiced deposition from solution. We also stress the environmentally friendly and industrially viable nature of CVD silane deposition. Our work differs from that of most academic researchers because of the tool we use for silane deposition, which is a commercially available CVD system (the 1224P) from Yield Engineering Systems. This tool gives complete control over oven temperature, pressure, and reagent delivery, in addition to offering plasma pretreatment of the substrates at a range of powers and conditions. In our work we have explored the CVD at 150°C of 3-aminopropyltriethoxysilane (APTES), which has arguably the most widely used and important silane. We show how surface saturation leading to the same level of surface functionalization occurs over a very wide range of gas phase concentrations. This important result indicates that there is a wide process window for APTES deposition. We further compare CVD of APTES to the gas phase deposition of two of its aminoisalane analogs: one with two methyl groups (3-aminopropyl(dimethyl)silane), and the other with two isopropyl groups (3-aminopropyl(diisopropyl)oxysilane). X-ray photoelectron spectroscopy (XPS) shows a decrease in nitrogen concentration for these two molecules compared to APTES. All of these films are extremely flat by atomic force microscopy, and spectroscopic ellipsometry indicates the expected monolayer coverages of our silanes. Of particular significance is the stability against base of the disilopropyl aminoisalane, which should make it valuable in a number of applications. The interactions of our different amino surfaces with a cyanine dye are also probed, and the structure/adsorption of the dye seems to be well correlated to the amine density determined by XPS.

9:40am TF2-TuM6 Novel Precursors for CVD of Amorphous and Crystalline Cobalt Group Metal-Phosphide Films. J. Rivers, R. Jones, The University of Texas at Austin

INVITED

Volatile Cobalt group complexes were synthesized as single-source precursors for chemical vapor deposition of amorphous and crystalline metal-phospide thin films. Phosphide alloys of transition metals are of interest due to their use as barriers against corrosion, electrodes, catalysts, and as diffusion barrier layers in integrated circuits. Volatile precursors allow use of CVD which is advantageous to other physical methods such as PVD. Precursors were specifically designed and synthesized utilizing ligands which impart volatility such as 3,5-bis(trifluoromethyl)pyrazole and trimethylphosphine. Complexes studied include [Rh(CF3-Pz)(PMe3)], [Co(PMe3)], [Co(CF3-Pz)(PMe3)], and [Co(CF3-Pz)(PMe3)](HCO(PMe3)]. The nature of the films depends on reactor conditions such as flow rate, deposition time, substrate temperature, and annealing conditions. Films were grown at temperatures under 400 °C in a hot-wall reactor utilizing dynamic vacuum or Ar as a carrier gas and characterized using XPS, XRD, and SEM.
can be locally tailored by specifically designed mask patterns. For example, in the single-step growth of multiple-quantum-well structures (MQWs) on well-defined mask patterns, it is possible to control the effective band gap energy of the layers by changing the well width and composition. Thus, passive and active devices can be locally integrated simultaneously by designing the mask size and pattern. This technology will reduce the cost of fabrication and enhances production yield of opto-electronic integrated circuit (OEC).

Numerical simulation on growth rate non-uniformity of SAG in sub-millimeter scale can extract real surface kinetics in MOCVD process for InGaAsP-compounds, which is normally hindered by mass transport rate of film precursors [1]. SAG analysis with non-linear surface kinetics is introduced for the first time to analyze group-III precursor partial pressure dependency of InGaAsP-MOCVD [2]. Important kinetic parameters, such as surface reaction rate constant, adsorption equilibrium constant, and surface coverage, have been extracted. Such non-linear kinetic analysis using SAG (micro analysis) is combined with computational fluid dynamics (CFD) reactor-scale analysis (macro analysis) to elucidate the main reaction mechanism of InGaAsP-MOCVD process in the whole reactor. The design of photo- luminescence (PL) wave length for optical device by tailoring the mask pattern will be demonstrated.

References

11:20am TF2-TuM11 OLED Encapsulation by Room Temperature Plasma-Assisted ALD Al2O3 Films

H. Lifka, P. van de Weijer, Philips Research Laboratories, Netherlands, M.C.M. van de Sanden, W.M.M. Kessels, Eindhoven University of Technology, Netherlands

Organic light emitting diodes (OLEDs, both small molecule and polymer LEDs) require excellent gas and moisture permeation barrier layers to increase their lifetime. The quality of the barrier layer is ultimately controlled by the presence of defects in the layer. Although a barrier layer may be intrinsically excellent (water vapor transmission rate, WVTR ≤ 10-6 g·m-2·day-1) the protected device may fail in the presence of defects that lead to preferential diffusion pathways for H2O (e.g., defects caused by particles from the environment and/or production process). The state-of-the-art barrier coatings are micrometer-thick multi-layer structure, in which organic interlayers are alternated with inorganic barrier layers with the purpose of decoupling the above-mentioned defects. Recently, atomic layer deposition (ALD) has been successfully tested for the deposition of very thin (< 50 nm) single layer permeation barriers on pristine polymer substrates [1,2], showing the potential of this highly uniform and conformal deposition technique in the field of moisture permeation barriers. In this contribution the encapsulation of OLEDs by plasma-assisted ALD of thin (20-40 nm) Al2O3 layers is addressed. The layers are synthesized at room temperature by sequentially exposing the substrate to Al(CH3)3 vapor and a remote inductively coupled O2 plasma in Oxford Instruments FlexAL™ and OpAL™ reactors. The intrinsic quality of the deposited ALD layers was determined by monitoring the oxidation of a Ca film encapsulated by the Al2O3 film: WVTR values as low as 2·10-6 g·m-2·day-1 have been measured. The potential of ALD layers in encapsulating OLEDs, and therefore in successfully covering the defects present on the device, has been investigated by means of electroluminescence measurements of polymer-LEDs (effective emitting area of 5.8 cm2). The black spot density and area growth were followed as a function of the time under standard conditions of 20°C and 50% relative humidity. Within a 500 h test ALD-encapsulated OLEDs show approximately half the black spot density compared to devices encapsulated by plasma deposited a-SiNx:H (300 nm thick). The black spot density is further reduced by combining the a-SiNx:H and ALD Al2O3 layers. These results point towards a very promising application of ALD Al2O3 layers in the field of OLED encapsulation and will be interpreted in terms of possible mechanisms related to film growth in multi-layer structures.

Graphene: Characterization, Properties, and Applications
Moderator: M. Fuhrer, University of Maryland, College Park

2:00pm GR+TF-TuA1 Graphene Atomic Membranes, P.L. McEuen, Cornell University INVITED

Atmosically thin graphene membranes have exceptional electronic, optical, thermal and mechanical properties. Here we discuss our group’s measurements of graphene membranes made by either exfoliation, epitaxial growth on SiC, or chemical vapor deposition growth on Ni or Cu. For thermal and mechanical properties. Here we discuss our group’s efforts to understand the growth of graphene on metallic substrates, including the effects of growth temperature and pressure. We find that the morphology of argon-grown C-face films was markedly different from that of Si-face films, with the former having a higher degree of in-plane order and the latter exhibiting a more disordered structure.

The growth of graphene on metallic substrates allows us not only control the periodicity of the Moiré pattern but also tailor the interaction strength between the carbon atoms and the metallic substrate [1]. In this work we compare the results obtained on graphene overlayers grown on two different metallic substrates. We studied graphene/Ru(0001) and graphene/Ru(001) in the former there is a weak interaction between the graphene overlayer and the substrate and in the latter the strength of the chemical interaction is modulated by the Moiré pattern.

Field Emission Resonances (FERS), which are detected by STM when applying voltages larger than the work function, can be used to explore with nanometer resolution, the inhomogeneities in the local surface potential landscape. Operating the STM in constant current mode implies a constant electric field between tip and sample and the expected energy position for the FERS is given by the expression founded by Gundlach some time ago [2]. From that expression it is possible to determine experimentally the local work function of the surface. We applied this method to the Moiré pattern formed by graphene grown on Ir(111) and Ru(0001). For graphene on Ir(111) we did not find any modulation in the work function due to the Moiré pattern. On the contrary for graphene on Ru(0001) we have found a difference of 0.25 eV in the work function values depending on the position on the Moiré pattern. For graphene on Ru(0001) we also found that the energy position of the first FER presents strong spatial variations that can be measured by scanning tunneling spectroscopy. In fact, for the graphene/Ru(0001) system, the energy position of the first FER is not easily related with the local work function and is modified by the interaction between graphene and the Ruthenium underneath. The energy position of the higher FERS is only influenced by the variations in the local work function.


4:00pm GR+TF-TuA4 Mapping the Electronic Surface Potential of Graphene Grown on Ir(111) and Ru(0001), S. Barja, B. Borca, Universidad Autónoma de Madrid, Spain, M. Garmica, IMDEA Nanociencia, Spain, P. Hermanns, J.J. Hinojosa, Universidad Autónoma de Madrid, Spain, A.L. Vazquez de Parga, R. Miranda, UAM & IMDEA Nanociencia, Spain

Moiré patterns are generated by the superposition of two periodic structures with a lattice mismatch. They have been observed by means of Scanning Tunneling Microscopy (STM) on different systems and their interpretation, in some cases, is not straightforward. The influence, at the atomic scale, of these patterns in the local density of states of the overlayer is not clear and can be studied by STM.

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in elemental carbon deposition [3]. Thus, hydrocarbon decomposition only affects graphene growth through the rate of adatom formation; for ethylene, that rate decreases with increasing adatom concentration and graphene coverage. Graphene growth on Ir(111) is similar to that on Ru: the growth velocity is the same nonlinear function of adatom concentration (albeit with much smaller equilibrium adatom concentrations, as we explain with DFT calculations of adatom formation energies). When graphene is exposed to oxygen at high temperatures, it is etched. We observe the etching to proceed by the inverse of the graphene growth mechanism, i.e., by cluster detachment.


Advanced Surface Engineering Room: C4 - Session SE+TF-TuA

Glancing Angle Deposition II
Moderator: K. Robbie, Queen's University, Canada

2:00pm SE+TF-TuA1 Deposited Nanorod Films for Biosensor Applications. W. Zhang. University of Illinois at Urbana-Champaign, S.M. Kim, Chung-Ang University, Korea, N. Ganesh, Intel, I. Block, P. Mathias, B.T. Cunningham, University of Illinois at Urbana-Champaign

Plasmonic graphene films have been used as the basis of many biological sensing devices. Here, we successfully demonstrated that the combination of the plasmonic graphene structures and a dielectric nanorod coating prepared by the glancing angle deposition technique can lead to significant increases in the device sensitivity. By incorporating a TiO2 nanorod coating onto the label-free biosensor structure, the surface area of the device is increased. The sensitivity of high surface area sensors is compared with sensors without the high surface area coating. Results for detection of polymer films, proteins, and small molecules indicate up to a seven-fold enhancement of detected adsorbed mass density.

When a TiO2 nanorod coating is applied on top of the high index layer of an enhanced fluorescence biosensor, the emission intensity of a fluorescent dye on the device is increased by over one hundred times compared to a reference glass slide. The increased sensitivity is due to the combined effects of enhanced near-fields and enhanced surface area. The sensitivity is further increased by close to two hundred times when a TiO2 nanorod film is used as the high index layer of the photonic crystal structure.

The planar photonic crystal is also combined with a SiO2–Ag “post-cap” nanostructure for applications in surface-enhanced Raman spectroscopy (SERS). It is demonstrated that the resonant near fields of the photonic crystal could be used to efficiently couple light from a laser to the Ag nanoparticles to achieve a high SERS enhancement factor.

2:40pm SE+TF-TuA3 Surface Enhanced Raman Scattering from Silver Nanorod Array Substrates: Characteristics and Origin. Y. Liu, Z. Zhang, R.D. Dluhy, Y. Zhao, University of Georgia

Silver nanorod array substrates fabricated by oblique angle deposition can give a very strong SERS enhancement (>10^4). The SERS enhancement depends strongly on the length of nanorods, the incident angle of excitation light, the polarization states of excitation light, and the reflectance from substrate. A modified Greenler’s model based on the reflection from a single Ag nanorod and the substrate as well as dipole radiation is proposed to explain these SERS characteristics. The theoretical calculation qualitatively agrees well with the experimental results. However, the location of the strongest SERS enhancement and the nature of such an enhancement are still unknown. To answer this question, we have designed another set of experiments, by taking the advantage of oblique angle deposition, to put Raman probe molecules on different locations of Ag nanorod array substrates and found that the apparent SERS enhancement factor is about 50 ~ 200 times from the surface of the nanorods than that from the Ag thin film surface under Ag nanorods array. These effects cannot be interpreted directly by the local electric field enhancement effect. By combining the local electric field effect calculated by three dimensional finite-difference time-domain method and the anisotropic optical absorbance of the SERS signal from the anisotropic Ag nanorod array, the numerical calculations are semi-quantitatively agree with the experimental results.

* This work is supported by National Science Foundation (NO. ECS-0701787) and US Army Research Laboratory (W911NF-07-2-0065).

References:
We have successfully prepared multilayered sculptured thin films with various combinations of the layer thicknesses using a shutter system specially designed for the oblique angle deposition. A series of different thicknesses were realized on a single substrate by moving a step-shaped shutter incrementally across the sample during the oblique angle deposition, while an ordinary straight shutter was used during normal deposition. This deposition process has been applied to fabricate local plasmon resonators comprised of the sandwich of Au nanorod array (NRA)/structured dielectric layer/Ag mirror. The fundamental optical properties of the local plasmon resonators have been already reported [1]. Briefly, the reflectance in NIR layer/Ag mirror. The fundamental optical properties of the local plasmon resonators and the combinatorial approach is quite useful.

We present a semi-analytical model using mean-field nucleation and non-linear chaos theory that relates $p$ with the exponential divergence $\lambda$ from a surface diffusion limited material independent morphology that is controlled by atomic shadowing. $p$ is a function of the average island separation distance $<s>$, which is a measure of the diffusion length scale and varies with $\theta$, the activation energy $E_a$ for surface diffusion, the critical island size $i$, and the dimensionality of adatom surface diffusion. The model predicts a transition from a 2-d to a 3-d island growth mode at $\theta_c$. This transition, in turn, exacerbates differences between the atomic shadowing by the islands on the nanorod growth fronts, resulting in the higher growth exponents above $\theta_c$. The model also provides a single homologous activation energy $E_c/k_B = 2.46$ for surface diffusion on curved nanorod growth fronts, applicable to all studied metallic systems at all temperatures. $p$ follows a linear function with $<s>$, both in high and low temperature regimes and the model correlates with the slope of $4 \theta$ vs $\ln(4 \theta)$, indicating that the growth exponent and hence the morphology is intricately related to both shadowing and surface diffusion.

We have been investigating the performance and optimization of nanostructured relative humidity (RH) sensors produced by glancing angle deposition (GLAD) [1 – 2]. GLAD offers significant advantages for sensor applications, including extremely large surface areas, response times as low as 50 ms, and the use of any material compatible with physical vapour deposition. However, there remain a number of open questions regarding the underlying physics of GLAD RH sensor performance and response time, especially time and nutrient correlations with the shape and nature of pores in our sensors, and the interaction between the analyte and deposited material. To better understand the analyte-surface interactions, we have studied the performance of RH sensors with a thin coating of TiO$_2$ deposited by atomic-layer deposition (ALD).

Columnar thin films of Si and TiO$_2$ were produced by GLAD on interdigitated electrode substrates, creating a RH sensor. The GLAD sensing layer was conformally coated with TiO$_2$ films by atomic layer deposition. In this process, the deposition chamber is purged and oxygen is introduced. At the precursor-loaded substrate, this oxygen reacts with TiO$_2$ in a plasma-driven process to produce a thin layer of TiO$_2$ conformally surrounding the high surface area GLAD film. In this work, the ALD process is repeated cyclically to build up TiO$_2$ layers of different thicknesses.

Preliminary investigations have used 1.5 µm Si and TiO$_2$ GLAD films, coated with ALD TiO$_2$ films between 2 nm and 32 nm thick. The RH sensing properties of these devices were testing using a custom environmental chamber [1]. As expected, the uncoated Si and TiO$_2$ thin films exhibited different responses. However, once the different sensors were coated with ALD TiO$_2$ layers as thin as 2 nm, sensor response was very similar, indicating the same concentration and surface properties. To better investigate the transition between the GLAD post dominated response and ALD-layer dominated response, a series of films with thinner ALD coatings is underway. The sensor response will be characterized as a function of RH, electrical probe frequency, and ALD layer thickness. Current experimental results will be presented.

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constants of these films determined by ellipsometry. Analysis of the films by Scanning Electron Microscopy (SEM), and Atomic Force Microscopy (AFM) gives some hints to account for the evolution of porosity as a function of the evaporation angle.


We report on the magnetic monoclinic anisotropy behavior of cobalt sculptured GLAD structures. Exciting new physics are presented in a model showing the nanostructures result in a thin film with tunable properties dependent on orientation, tilt, and patterning of the slanted nanowires. These sculptured thin films can be further modified - non-magnetic structures are coated with ferroelectric polymers for novel surfaces. Alternatively, magnetic structures are modified using non-magnetic materials, once again creating hybridized structures with undiscovered properties.

Surface Science

Room: C1 - Session SS1+PS+TF+AS+NS-TuA

Non-Thermal Chemistry / Ion, Electron Processes

Moderator: A.V. Walker, University of Texas at Dallas

2:00pm SS1+PS+TF+AS+NS-TuA1 Growth and Purification of Nanostructures Deposited by Electron Beam Irradiation: A Surface Science Perspective. H. Fairbrother, J. Wnuk, J. Gorham, S. Rosenberg, Johns Hopkins University, T. Madey, Rutgers, W.F. van Dorp, K. Hagen, Delft University of Technology, The Netherlands

Focused electron beam induced processing (FEBIP) of volatile organometallic precursors has emerged as an effective and versatile method of fabricating metal-containing nanostructures. However, to improve the material properties of FEBIP nanostructures, a more fundamental understanding is needed to aid the rational design of new precursors and improve the modeling of the FEBIP process. It is necessary to better understand the molecular level processes associated with the electron stimulated decomposition of organometallic precursors. To address this issue, we have employed a UHV/surface science approach to study the electron induced reactions of dimethyl(acetylacetonate) gold(III) (Au(acac)Me2), a common precursor used for Au deposition in FEBIP, adsorbed on solid substrates. Surface reactions, reaction kinetics and gas phase products were studied using incident electrons in the energy regime between 40-1500 eV, using a combination of XPS, RAIRS and MS. XPS data indicate that electron irradiation of Au(acac)Me2 is accompanied by the reduction of AuIII to a metallic Au0 species embedded in a carbon matrix while MS reveals the atomic hydrogen on Au-containing carbonaceous films deposited by electron beam irradiation of Au(acac)Me2, as a potential route to purify FEBIP deposits. Atomic oxygen was found to be the more effective of the two radical treatments in removing carbon, although a surface layer of gold oxide was formed. Subsequent exposure of this overlayer to atomic hydrogen rapidly removed the oxide, resulting in a pure Au film. AFM analysis of FEBIP deposits before and after radical treatment support the idea that carbon abatement is accompanied by a decrease in particle size.

2:20pm SS1+PS+TF+AS+NS-TuA2 Surface Morphology Control and 3D Structure Development with Cryogenic Assisted Electron Beam-Induced Deposition. M. Breslin, K.A. Dunn, University at Albany SUNY

Electron beam-induced-deposition (EBID) of platinum-containing materials was performed at cryogenic temperatures. Deposit morphology, microstructure and nanostructure have been characterized by scanning and transmission electron microscopy (SEM and TEM), and shown to be controllable by the electron fluence used for EBID. 3D structures were developed using a multilayer deposition method, facilitating the creation of hanging, suspended or incorporated-gap structures.

Experiments were performed using an FEI Nova 600 Nanolab dual beam system with a LN2 cryogenic stage, enabling substrate temperatures of -155 ± 5°C. A gaseous platinum precursor (MeCpPtMe3) was condensed onto the cooled substrate using a capillary-style gas injection system (GIS). Condensate thicknesses between 100nm-3mm were produced by adjusting the GIS-substrate gap and precipitable crucible temperature. Next, gas flow was terminated and the condensate was irradiated with an electron beam to induce precursor decomposition. When the substrate was returned to room temperature, any unreacted precursor desorbed and was removed by the pumping system, while irradiated regions showed clear evidence of successful deposition. The morphology of the deposited material depended on exact deposition conditions, and exhibited several distinct types absent from deposits made by conventional (room temperature) EBID.

3D structures were developed with a multilayer deposition method. In this method, multiple layers were used to take advantage of the electron penetration depth within the condensate, through which the depth of deposition could be controlled. An initial layer was first condensed and a region was deposited with the electron beam to act as a substrate-anchoring site. A second condensed layer was then applied such that electrons could only penetrate to the top of the initial condensed layer. The electron beam was then shifted, to deposit a section partially over the anchoring region (in the initial layer) with the remainder over unreacted area. After re-heating, part of the second deposit was found to adhere to the anchoring region, while the rest hung over vacuum. Using similar process, structures were also developed to create embedded gaps or tunnels.

Taken together, these observations have important implications for the creation of arbitrarily large or complex structures previously untenable by EBID fabrication. The growth mechanism and potential applications will be discussed, from nanotechnology to osteointegration.

2:40pm SS1+PS+TF+AS+NS-TuA3 Nanoscale Patterning and Graphene Film Deposition on Si using Low-energy Electron Beams. T.M. Orlando, D. Sokolov, D. Oh, K. Shepperd, Georgia Institute of Technology

The physics and chemistry associated with desorption induced by electronic transitions, particularly electron stimulated desorption (ESD), is the basis for many electron-beam induced processes in materials growth, etching, and lithography. We have demonstrated experimentally and theoretically that the total ESD yield of adsorbates can be a function of the incident low-energy electron-beam direction. We refer to this phenomena as Diffraction in Electron Stimulated Desorption (DESD). We have also explored three graphene growth strategies, a simple LB vapor deposition technique and two non-thermal reactions. The first uses electron beam irradiation in conjunction with chemical vapor deposition techniques to grow graphene directly on Si substrates. This approach utilizes unsaturated hydrocarbon precursor molecules and can be carried out at relatively low temperatures. The second involves electron-stimulated removal of oxygen and organic fragments from graphene-oxide flakes positioned on patterned Si substrates. This may allow for damage-free reduction of graphene-oxide to graphene. The third involves electron-beam removal of defects from graphene epitaxially grown from SiC(0001) substrates.

This study of the nucleation of Focused Electron Beam Induced Deposits: Growth Behavior on the Nanometer Scale. W.F. van Dorp, Delft University of Technology, The Netherlands

Focused electron beam-induced deposition (FEBID) is a technique where adsorbed precursor molecules are dosed by a focused beam of electrons to define metallic or semi-conducting patterns. The process has developed to the extent that the amount of deposited material can be controlled nearly to the level of single molecules. The highest resolution that is reported is 0.7 nm [1] using the precursor W(CO)6. At this scale, deposits contain no more than a few molecules on average. Our ultimate goal is to develop the ability to deposit single precursor molecules in a consistent manner. We perform our FEBID experiments in environmental scanning transmission electron microscopes (E-STEM) with a beam energy of 200 keV and a 0.2 nm probe. The annular dark field (ADF) signal is used for the imaging of the deposits. By recording the ADF signal during deposit growth we are able to monitor the growth process in situ. Thin, electron transparent...
graphite is used as a substrate and typical precursor gas pressures at the sample during the deposition were $10^{-3}$ to $10^{-5}$ Torr.

In the present study we used Me₃PtMeCp, a Pt-precursor that is often used in FEBID experiments [2]. To improve on the currently achieved resolution, it is important to study the nucleation stage of deposits. When using a graphite substrate we found that there is a significant difference in deposition behavior between the W(CO)₆ and Me₃PtMeCp precursors. Where the typical growth behavior for W(CO)₆ is to form nm-sized or even sub-nm sized deposits, the deposits fabricated from Me₃PtMeCp are a few nanometers in diameter and consist of individual sub-nm sized grains. We report on our study of this difference in growth behavior and strategies to increase the writing resolution.


4:20pm SS1+PS+TF+AS+NS-TuA8 Direct Local Deposition of High-Purity Pt Nanostructures by Combining EBID and ALD. A.J.M. Mackus, Eindhoven University of Technology, the Netherlands, H.J.J.L. Mulders, A.F. de Jong, FEI Electron Optics, the Netherlands, M.C.M. van de Sanden, W.M.M. Kessels, Eindhoven University of Technology, the Netherlands

Due to its ability to directly deposit nanostructures with sub-10 nm lateral dimensions electron beam induced deposition (EBID) has the potential to become a key nanomanufacturing technology. The technique suffers however from incomplete decomposition of the precursor gas and consequently a low material purity. Platinum EBID yields typically only a purity of ~15 at.% and consequently a low resistivity value of 10³ Ω cm [1]. The developed approach comprises seed layer deposition by EBID and area-selective ALD growth. For specific conditions the thermal ALD process of Pt (MeCpPtMe₂ precursor, O₂ gas) was found to start selectively on an EBID seed layer with a thickness equivalent to one monolayer Pt. It was established that the deposits have a uniform thickness and a high purity value (~93%), whereas the method has the potential to achieve sub-10 nm lateral dimensions. In addition to the approach the material properties the underlying reaction mechanism of the (area-selective) Pt ALD process will be discussed, including aspects such as the role of dissociative chemisorption of O₂ molecules on Pt and the formation of H₂O, CO₂, and CH₂, reaction products.


4:40pm SS1+PS+TF+AS+NS-TuA9 Anionic Surface Processes Induced by Low-Energy Electrons. P.A. Rowntree, University of Guelph, Canada

The historical development of surface chemistry has largely been based on the use of free-energy-driven processes; an enormous volume of literature exists that details the search for chemical control over these processes using the classical parameters of temperature, surface composition and reactions. However, as the interest in controlling the processes grows, and the need to produce structurally resolved reactive systems increases, alternative non-thermal mechanisms are increasingly being explored in order to drive the interfacial processes into reaction channels chosen by the needs of the operator instead of the principles of thermochemistry. Our specific interest is in the control of surface processes using low-energy electrons as specially 'reactive' that can be delivered to surfaces in a highly controlled manner, and interact with surface species according to understandable and reproducible mechanisms. The overall goal is to understand and manipulate these mechanisms to selectively interact with target molecules of our choosing to modify surfaces according to our needs.

This presentation will focus on two aspects of this ‘manipulative’ approach to surface chemistry. The first is our recent development of ways to selectively control where incident electrons interact with the organic monolayers that are deposited on Au(111) surfaces. These chemically homogeneous monolayers have a highly uniform electronic structure along the length of the chains, such that it is normally not possible to strongly enhance the dissociation probabilities at any given site. We have found that it is possible to selectively enhance the rupture of C-H bonds at the methyl terminations of these films by coupling the incident electron flux with anionic state terminations. The energy+charge transfer process that leads to bond rupture is extremely sensitive to the incident energy as well as the chemical nature of the target species, thus enhancing the selectivity of the local modifications to the organic surface. A second set of processes will be discussed that involves the electron-induced decarboxylation of metal carboxyls adsorbed on organic surfaces to produce atomic metal deposits. We have shown that low-energy electrons can induce surface polymerization reactions in Fe(CO)₅ films that lead to apparent CO-elimination cross-sections greater than 1 nm². This strong coupling to dissociative processes allows us to develop thin metal overlayers without the substrate damage that is usually associated with using thermal evaporation or sputtering processes.


Studies of low-energy electron-induced processes in nanoscale thin films serve to elucidate the pivotal role that low-energy electron-induced reactions play in high-energy radiation-induced chemical reactions in condensed matter. While electron-stimulated desorption (ESD) experiments conducted during irradiation have yielded vital information relevant to primary or initial electron-induced processes, analyzing the products following low-energy electron irradiation can provide new insights into radiation chemistry. We have used post-irradiation temperature-programmed desorption to identify labile radiolysis products as demonstrated by the first identification of methoxymethyl as a reaction product of methanol (CH₃OH) radiolysis. Although low-energy electron-induced oligomerization reactions have been previously reported for molecules such as thiophene and cyclopentene, electron-induced studies of CCL, represent the first study to specifically identify the products of such reactions, demonstrating the utility of post-irradiation temperature programmed desorption experiments to study the radiation chemistry of condensed matter. Results of post-irradiation studies have been used not only to determine the identity of radiolysis products, but also to determine the dynamics of electron-induced reactions. By comparing our post-irradiation results to previous electron stimulated desorption studies of anion production during irradiation of condensed CF₂Cl and CF₂I, we examine the relationship between desorbed anions and retained radicals during dissociative electron attachment in the condensed phase.

5:40pm SS1+PS+TF+AS+NS-TuA12 Cluster-induced Desorption and Ionization of Biomolecules for Application in Mass Spectrometry. M. Dürr, Hochschule Esslingen, Germany, C. Gehhardt, A. Tommies, H. Schröder, K. Kompa, MPI für Quantenoptik, Germany

Mass spectrometry of biological macromolecules has developed into a key technology for fast routine analysis in biotechnology. A critical issue is the efficient transfer of non-volatile biomolecules out of their sample solution into the gas phase in combination with their concomitant ionization. Here we show that a beam of neutral molecular clusters consisting of $10^3$ to $10^4$ SO₃ molecules can be used for the desorption and ionization of biomolecules. Cluster impact on arbitrary surfaces pre-treated with biomolecules efficiently creates cold, desolvated, gas phase biomolecular ions as large as 6000 u without any need for preparation of the biomolecules in a special matrix or post-ionization after desorption. Since the cluster provides not only the energy for the desorption process but also a transient matrix during the process, the molecules are found to be desorbed without any fragmentation.

As revealed by means of molecular dynamics simulations, high kinetic temperatures in the order of a few thousand Kelvin are reached during cluster impact on the surface. However, these extreme conditions prevail only for some picoseconds, since shattering of the initial cluster leads to very fast energy dissipation. Already after 20 ps, the SO₃ cluster fragments have reached a temperature colder than the original temperature of the adsorbates. This fast energy dissipation excludes efficient energy transfer into the vibrational degrees of freedom relevant for the cleavage of the relatively large biomolecules and thus allows for their soft, fragmentation-free desorption.
Thin Film
Room: B3 - Session TF1-TuA

Computational Modeling and Analysis of Thin Films
Moderator: M. Creatore, Eindhoven University of Technology, The Netherlands

2:00pm TF1-TuA1 First Principles Modeling of Hydrogen Diffusion in Thin Films: Crystalline Alloys, Amorphous Alloys, and Metal Hydrides, D. Sholl, S. H. L. Semidey-Flecha, C. Ling, S.-G. Kang, Georgia Institute of Technology

The diffusion of hydrogen through thin films is important in a variety of technological applications, including development of membranes for hydrogen purification and control of hydrogen uptake in solid state storage materials. First principles calculations play an important complementary role to experimental studies of these phenomena. Examples will be discussed of using first principles approaches in combination with cluster expansions and kinetic Monte Carlo to predict hydrogen permeation rates through crystalline and amorphous metal alloys used as membranes. In these materials, hydrogen exists as an uncharged interstitial atom. We will also discuss the diffusion mechanisms of hydrogen in ionic metal hydrides such as magnesium hydride and simple borohydrides. Understanding the diffusion mechanisms that exist in these materials has created opportunities for enhancing hydrogen transport rates in this important class of materials.

3:00pm TF1-TuA4 A Family of High Strength Ternary Titanium and Vanadium Nitride Thin Films, D.G. Sangiovanni, V. Chirita, L. Hultman, Linkoping University, Sweden

We use Density Functional Theory (DFT) calculations in the generalized gradient approximation (GGA) to predict the properties of a number of novel Ti-M-N and V-M-N thin films in the B1 (NaCl) structure. The new compounds are obtained by alloying TiN and VN, with Ta, Nb, V, Mo and W, respectively Nb and W, in concentrations of 50%. We evaluate the elastic moduli and constants for all these ternaries, perform a detailed analysis of their electronic structure, and compare these results with the corresponding properties of TiN and Ta50Nb50N. Our calculations show that, in terms of hardness, these ternaries compare with TiN and Ta50Al50N, as we obtain comparable, respectively increased values, for the Young and bulk moduli, in most cases. Significantly, however, these novel compounds exhibit substantially lower values of the C4 elastic constant and positive Cauchy pressures, i.e. they are considerably more ductile than TiN and Ta50Al50N. This unique combination of increased hardness and ductility, which is in contrast to the hardness/ductility relationship typically found in hard coatings, is certainly relevant for applications in which high strength thin films/coatings are desired. In terms of electronic structure, our results reveal a layered charge density for all these ternaries, consisting in alternating high and low electron density regions, similar to that reported for MAX phase materials and other nanolaminates. This combination of metallic and ceramic properties is also evident in the density of states analysis we report. In order to fully understand the mechanism responsible for this interleaved arrangement of electrons, we carry out an improved crystal orbital overlap population (COOP) calculation and succeed in resolving energetically the bonding and antibonding contributions, of the first and second neighbors, to the chemical bonds in these compounds. Herein, we present the results of our COOP analysis, and basically we explain the observed trend in hardness and ductility as a result of the interaction between the εg and t2g sets of d orbitals characteristic to these ternaries.

4:00pm TF1-TuA7 Study on the Influence of Ballistic and Diffusive Deposition Particles on the Evolution of the Surface Morphology of Thin Films, R. Alvarez, P. Romero-Gomez, J. Gil-Ruiz, A. Palmero, J. Cotino, P. Yubero, A.R. Gonzalez-Elpe, CSIC - University of Sevilla, Spain

The influence of ballistic and diffusive particles on the development of the surface morphology of plasma-assisted sputtered thin films is studied. Ballistic particles are sputtered from the cathode and are characterized by their high directivity towards the film surface as well as by typical kinetic energies in the order of 1 eV, whereas thermal diffusive particles follow the Maxwell velocity distribution function, with typical kinetic energies in the order of 0.01 eV. These factors influence the role of non-local surface shadowing and the surface sticking probability of the deposition particles, which, along with other fundamental mechanisms, strongly condition the development of the film morphology. In order to carry out this research, a combined theoretical and experimental approach has been followed: on one hand several thin films have been deposited in different experimental conditions which allow differentiating ballistic and diffusive contributions to the film growth, and, on the other hand, we have developed a basic Monte Carlo model of the depositions process. The comparison between experimental and theoretical results provides fundamental understanding of the effects of these two phenomena on the development of the thin film nanostructure.

4:20pm TF1-TuA8 DSMC Modeling of E-beam Metal Deposition, V. Ayyaswamy, A. Alexeenko, Purdue University

Electron-beam assisted physical vapor deposition (EBPVD) is now used in a wide variety of vacuum material processing applications for generation of thin films of metals and metallic compounds. The thickness uniformity, growth rate, grain size, texture, morphology and other physical properties of EBPVD thin films are highly dependent on the specifics of the system such as, for example, the geometric configuration and energy density of electron gun. A general capability to model the metal vapor flows encountered in EBPVD processes can greatly assist in the design and control of such deposition systems and processes. The main goal of this paper is to apply the direct simulation Monte Carlo (DSMC) method for modeling of a typical strip EBPVD system.

Under the conditions of high energy electron-beam deposition in ultra-high vacuum, the flow of metal vapor in EBPVD systems varies from high-density collisional flow in the proximity of the source to free-molecular flow at the deposition site. The application of the DSMC method for such flows requires a model for metal atom and cluster collisions. In this work, a model for copper-copper collisions is formulated and validated by comparison with experimentally measured deposition data reported by Sahu and Thakur (2006). The proposed molecular model can be used in DSMC simulations for the prediction of growth rates in thin film depositions of copper thereby leading to a more efficient designs of such deposition systems.

4:40pm TF1-TuA9 Electrochemical Capacitance in Cerium Oxide Thin Films and Its Relations to Anionic & Electronic Defects, W. Chaves, S. Hale, California Institute of Technology, USA

The electronic properties of thin film oxides are relevant in a broad range of phenomena and devices. In many instances, these properties are strongly influenced by the extent of deviation of the material stoichiometry away from that of the perfect crystal. Specifically, nonstoichiometry in oxides due to the formation of point defects can substantially impact electrical, electrochemical, and optical properties of thin films. However, the small samarium mass and the constrained nature of substrate materials, particularly with respect to the dissociation of oxygen nonstoichiometry, and, effectively, electronic carrier concentration. Even a relatively straightforward Hall effect measurement is precluded in the case of low mobility materials (typical of solid electrolytes). Thus, a reliable and highly accurate method for determining nonstoichiometry and carrier concentration in thin film oxides may be useful for a number of fields. In this work, we show that it is possible to accurately determine oxygen nonstoichiometry and electronic carrier concentration in nonstoichiometric samarium doped ceria thin films from an analysis of the capacitance measured by electrochemical impedance in a cross-plane configuration. For sufficiently thick bulk samples, it has been shown that a "chemical capacitance" arises from the change in the oxygen nonstoichiometry in response to the change in the oxygen chemical potential, analogous to the change in the polarization of a dielectric in response to the change in electric potential in an electrostatic capacitor. We extend this method to thin films and show that both interfacial and chemical capacitances contribute strongly to the observed capacitance and successfully decouple the two. The thin film oxygen nonstoichiometry and electronic defect concentration determined using chemical capacitance corresponds closely to bulk values in literature.

5:00pm TF1-TuA10 Virtual Sputter Chamber - Multiphysics Simulation of Magnetron Sputter & Deposition, C. Walton, G. Gilmer, M. McNenly, Lawrence Livermore National Laboratory, J. Verboncoeur, University of California, S. Wilks, L. Zepeda-Ruiz, T.W. Barbee, Lawrence Livermore National Laboratory

Lack of detailed process conditions knowledge remains a key challenge in magnetron sputtering, both for chamber design and for process development. Fundamental information such as the pressure and temperature distribution of the energetic gas and ions, and survival angles of the sputtered atoms and other energetic species is often missing, or is only estimated from general formulas. However, open-source or low-cost tools are available for modeling all the physics of the sputter process, which can give more accurate data from desktop computations than traditional empirical approaches.

To get a better understanding of magnetron sputtering, we have collected existing models for the 4 main physics steps: 1) dynamics of the plasma using Particle In Cell-Monte Carlo Collision (PIC-MCC), 2) impact of ions on the target using molecular dynamics (MD), 3) transport of sputtered...
atoms to the substrate using Direct Simulation Monte Carlo (DSMC), and 4) growth of the film using hybrid Kinetic Monte Carlo (KMC) and MD methods. All the models have been tested against experimental measurements. The spatial distribution and electron temperature $T_e$ of the plasma have been reproduced within $\pm 25\%$ for a scaled model of an example magnetron system. The rarefaction of the neutral gas in front of a magnetron observed by Rossnagel and others has been reproduced, and it is associated with a local pressure increase of $\pm 50\%$ which may strongly influence film properties such as stress and film density. Results on energies and arrival angles of sputtered atoms and reflected gas neutrals are applied to the Kinetic Monte Carlo simulation of film growth. Model results and applications to growth of Cu, Zr and Be films will be presented. Work underway on increasing computation speed with parallelization will also be discussed.

2:40pm TF2-TuA3 Atomic Layer Deposition of TiO$_2$ on Si (100) and GaAs (100) Surfaces, T. Gougoussi, J.W. Lacis, UMBC, J.D. Demaree, ARL

Atomic Layer Deposition (ALD) has been used to deposit TiO$_2$ films on Si (100) and GaAs (100) surfaces from tetrakis dimethylamino titanium (TDMA$_2$Ti) and H$_2$O at 200°C. The growth rate is measured at $\sim 6\AA$/cycle by Reflection Transmission Electron Microscopy (RTEM) and spectroscopic ellipsometry, and Rutherford Backscattering measurements indicate steady state Ti atom coverage of $\sim 1.4\times10^{15}$ cm$^{-2}$. As deposited films are slightly overoxidized (O/Ti~2.2) and are amorphous, but inert anneals above 500°C result in film crystallization mainly in the rutile phase. When films are deposited on native oxide GaAs surfaces an interface cleaning reaction is observed. The starting surface consists of $\sim 26\AA$ of gallium and arsenic native oxides. X-ray photoelectron spectroscopy indicates that the surface oxides are consumed gradually during the ALD process and that after 120 and 250 process cycles only about a monolayer of metallic arsenic-arsenic suboxide and gallium suboxide persists at the interface and the conclusions are corroborated by HRTEM data. The results for the TiO$_2$/GaAs interface will be compared to that obtained for the HIO$_2$/GaAs interface using two different but similar ALD chemistries that utilize amide precursors (TEMAHf and TDMAHf). All three ALD chemistries indicate the presence of an “interface cleaning” mechanism similar to what has been observed for other amide-precursor-based ALD processes.

3:00pm TF2-TuA4 Self-limiting Deposition of Anatase TiO$_2$ for Photocatalytic Applications, N.G. Kubala, C.A. Wolden, Colorado School of Mines

Titanium dioxide thin films were deposited using pulsed plasma-enhanced chemical vapor deposition at low temperature ($T < 200^\circ$C). Self-limiting deposition ($\sim 1 \AA$/cycle) was accomplished via simultaneous delivery of TiCl$_4$ and O$_2$. TiCl$_4$ is shown to be inert with molecular oxygen at process conditions, making it a suitable precursor for pulsed PECVD. The process was examined as a function of TiCl$_4$ exposure, plasma power, and substrate temperature. Crystalline anatase formation was observed at temperatures as low as 120°C. Depositions at high power also had a significantly greater refractive index. For process conditions, digital control over film thickness is demonstrated. Film uniformity is exceptional, with thickness variations less than 1% across 100 mm silicon wafers. Photocatalytic activity has been examined using methylene blue decomposition experiments, UV-vis spectroscopy, and electrochemical analysis. More specifically, we have quantified that the band edge position of these thin films is in agreement with measurements from anatase single crystals. The photocatalytic activity of these films for both hydrogen production and organic remediation is assessed. We also plan to present new results on the production of the titania-vanadia alloys with enhanced light response in the visible regime.

3:30pm TF2-TuA5 In situ X-ray Photoelectron Spectroscopy for the Study of Initial Stages of TiO$_2$ ALD on Silicon, R. Methaapanon, Stanford University

Titanium dioxide (TiO$_2$) is one of the widely studied atomic layer deposition (ALD) systems due to its outstanding electrical and optical properties that are suitable for a variety of applications. The properties of the deposited TiO$_2$, especially at the interface with the substrate, become more important as the size of required devices in each application approaches the nano-scale and are different chemical properties of the substrate and the deposited material, nucleation at the interface can be different from the steady state growth of the bulk.
In this work, TiO\textsubscript{2} ALD is carried out in an integrated ALD reactor/UHV chamber that allows for X-ray photoelectron spectroscopy (XPS) analysis after each process step without vacuum breaks. The substrate (TiCl\textsubscript{4}) and water (H\textsubscript{2}O) are selected as precursors due to their molecular simplicity and broad operating temperature range that result in several achievable TiO\textsubscript{2} phases. The initial growth at 100°C on two substrates – chemical oxide on silicon prepared by piranha treatment, and hydrogen-terminated silicon prepared by HF etch – is compared. The intensities and binding energies of characteristic peaks from the XPS spectra are used to analyze the elemental compositions and chemical state of each species as the deposition progresses. TiO\textsubscript{2} growth on both SiO\textsubscript{2} and H-Si surfaces exhibits linear behavior, as normally achieved by ALD, but the TiO\textsubscript{2} growth rate is lower on hydrogen-terminated surface than on silicon dioxide surface. Interestingly, no incubation period is observed on either surface.

The chemical shifts of the Si 2p, O 1s and Ti 2p XPS peaks after TiO\textsubscript{2} deposition on the SiO\textsubscript{2} substrate suggest bond formation between titanium and hydrogen. The oxygen signal at the interface also suggests that the titanium chloride is trapped at the SiO\textsubscript{2}/TiO\textsubscript{2} interface and that the titanium oxide right at the interface is sub-stoichiometric. The results on the hydrogen-terminated Si surface show different interfacial properties. There is no detectable amount of oxidized silicon species on hydrogen-terminated silicon after deposition under vacuum. Together with the results of \textit{ex situ} studies, we can conclude that interfacial silicon oxidation does not occur after exposure, not during ALD reactions. The absence of silicon oxide and a shift in the Si 2p binding energy in the \textit{as-grown} samples suggest the possibility of an ALD mechanism which involves direct bonding between titanium and silicon on the surface. The differences between the two substrates will be discussed.

4:20pm TF2-TuA8 Plasma-Assisted Atomic Layer Deposition of Titanium Dioxide: Reaction Mechanism Studies using Attenuated Total Reflection Fourier Transform Infrared Spectroscopy. Y. Rai, S. Agarwall, Colorado School of Mines

In this presentation, the authors will discuss the surface reaction mechanism during the plasma-assisted atomic layer deposition (ALD) of TiO\textsubscript{2} using titanium tetraisoproxide and an O\textsubscript{2}/Ar plasma at substrate temperatures ≤150°C. In situ attenuated total reflection Fourier-transform infrared (IR) spectroscopy was used to detect surface species generated or consumed during each half-reaction cycle with a sensitivity down to a fraction of a monolayer. Our IR data showed that the reactive species on the TiO\textsubscript{2} surface for TTIP chemisorption were both surface carbonates and –OH groups, identified in the 1450-1700 and 3400-3800 cm\textsuperscript{-1} regions, respectively. Based on this observation, we conclude that plasma-assisted ALD of TiO\textsubscript{2} involves a combination of the mechanisms previously reported for O\textsubscript{2}- and H\textsubscript{2}O-based ALD using TTIP as the metal precursor: we had previously reported surface carbonates as the reactive sites using O\textsubscript{2} as the oxidizing agent and –OH groups have previously been reported with H\textsubscript{2}O as the oxidant. We hypothesize the following reaction mechanism. Combustion products such as CO\textsubscript{2}, CO, and H\textsubscript{2}O are formed during the O\textsubscript{2} plasma cycle due to the plasma-assisted combustion of the isoproxy ligand in the gas phase. A fraction of this CO, CO\textsubscript{2} react with the surface to generate the carbonates, similar to the O\textsubscript{2}-based ALD mechanism. We explain the simultaneous presence of the surface –OH groups in addition to the carbonates due to the plasma activation of H\textsubscript{2}O, also generated during the O\textsubscript{2} plasma cycle, and the subsequent reaction of these activated species with the surface. The latter step does not occur when O\textsubscript{2} is used as the oxidant. In fact, the ratio of the carbonates and the surface –OH groups could be varied by controlling the residence time of the reaction products in the plasma. A growth per cycle of ~0.8 Å was obtained at 150°C, which was significantly higher compared to H\textsubscript{2}O- and O\textsubscript{2}-based ALD of TiO\textsubscript{2} at similar temperatures. In situ and ex situ IR measurements showed no significant carbon contamination in the films. Ex situ IR data showed the Ti-O CO\textsubscript{2} stretching vibration at 1450 cm\textsuperscript{-1}, characteristic of anhydride species. Ex situ x-ray diffraction measurements further confirmed anatase as the dominant crystal phase. The crystallinity of the films may be the reason for the higher growth per cycle compared to that observed for amorphous films deposited from the same metal precursor.

4:40pm TF2-TuA9 Molecular Layer Deposition of “Sugarcone” Hybrid Organic-Inorganic Films Using Saccharides and Metal Precursors. B. Young, H. Half, D. Seghete, A.S. Cavanagh, S.M. George, University of Colorado at Boulder

Molecular layer deposition (MLD) of hybrid organic-inorganic polymers is based on the sequential, self-limiting reactions of organic and inorganic reactants. Alumoxane HMLD has been reported based on the reaction between trimethylaluminium (TMA) and ethylene glycol (EG). Zincolate HMLD has also been demonstrated using diethylzinc and EG as the reactants. In this study, a new class of hybrid organic-inorganic films that can be called “sugarcone” was fabricated based on the reaction between saccharides and metal reactants. This strategy was demonstrated using sucrose and TMA.

The sugarcone MLD film growth was monitored using in situ transmission FTIR analysis. The FTIR spectra revealed that TMA reacts with hydroxy groups of the saccharides. The sintering of the AICH\textsubscript{4} species and deposits an organic moiety with available hydroxyl groups. Both the TMA and sucrose sequential reactions were self-limiting. Sequential exposures of TMA and sucrose led to the linear growth of the sugarcone film. X-ray reflectivity measurements were consistent with a growth rate of ~2.0 Å per cycle based on 300 MLD cycles on a Si wafer at 250°C. The TEM images of the ZrO\textsubscript{2} and TiO\textsubscript{2} MLD cycles at 150°C were in agreement with a MLD growth rate of ~2.3 Å per cycle. The sugarcone films were not stable in air and oxidized by adsorbing H\textsubscript{2}O. This reaction may be useful in gas diffusion barriers because the sugarcone film could serve as a chemical getter to adsorb any H\textsubscript{2}O that diffuses through the barrier.

5:00pm TF2-TuA10 In-situ Half-Cycle XPS Investigation of La-aluminate Formation during Atomic Layer Deposition. T.J. Park, H.C. Kim, M. Milojicic, B. Lee, R.M. Wallace, J. Kim, University of Texas at Dallas, X. Liu, M. Rousseau, J.H. Li, H. Li, D. Shenai, J. Suydam, Dow Electronic Materials

Lanthanum-based oxide (La\textsubscript{2}O\textsubscript{3}) having outstanding high dielectric constant of 30 has been extensively investigated because it can provide a generous thickness margin as well as a considerable leakage current reduction which is essentially required in modern device applications. However, the hygroscopic and catalytic nature of La ions leads to formation of either La-hydroxide (La(OH)\textsubscript{3}) or La-silicate (LaSiO\textsubscript{4}) resulting in degradation of dielectric properties. The formation of La-hydroxide can cause serious issues such as shifting of flat band voltage (V\textsubscript{fb}), increased gate leakage and increased the surface roughness. La-hydroxide may also cause a CVD reaction, causing the self-limiting nature of ALD reaction during conventional water based ALD process. Also, direct deposition of La\textsubscript{2}O\textsubscript{3} on Si substrate has a significant amount of La-silicate in the grown film by the interfacial reactions with the Si. In order to overcome these intrinsic problems of pure La-oxide, some of the researches have been carried out using an addition of aluminum oxide (Al\textsubscript{2}O\textsubscript{3}) layer in the pure La\textsubscript{2}O\textsubscript{3} film. La-aluminate is potentially stable on Si substrate having less opportunity to form an interfacial layer. In situ and \textit{ex situ} La-aluminate has enhanced stability to water ambient due to a gettering effect of Al\textsubscript{2}O\textsubscript{3}. In this presentation, we will focus on the detailed growth mechanisms of La-aluminate during a water ALD process. In order to investigate initial interfacial reactions during ALD, we investigate \textit{in-situ} half cycle reactions by means of x-ray photoelectron spectroscopy analysis following individual ALD pulses of (tris(N,N-diisopropylaminomethanid)lanthanum)[La(PrfAMD)\textsubscript{3}], triethyl- Al (TMA) and water (H\textsubscript{2}O) at a deposition temperature of 300°C. The La-aluminate sample was transferred from an ALD reactor after every individual pulse of La, Al and H\textsubscript{2}O to a monochromatic x-ray photoelectron spectroscopy (XPS) chamber via ultra high vacuum (UHV) chamber maintaining a vacuum level of less than 10\textsuperscript{-11} torr. This experimental technique enables us to investigate evolution of chemical bonding status without exposure to air as the number of ALD half cycle increases. Additionally, residual C and N in the films will be also discussed.

5:20pm TF2-TuA11 Engineering Optical Properties by Controlling Concentration and Proximity of Rare Earth Dopants in an Y\textsubscript{2}O\textsubscript{3} Host using Radical Enhanced ALD. J. Hoang, J. Chang, University of California, Los Angeles

The realization of compact fiber optic networks is limited by the control of the rare earth (RE) dopant ion’s identity and its distribution. Each RE ion contains spectral energy levels, whose transitions can be promoted by controlling the ion-ion proximity. In this work, a radical enhanced atomic layer deposition (RE-ALD) process, utilizing highly reactive radicals to activate surface reactions, is developed to design complex metal oxides with multiple dopants, whose concentration variation and spatial distribution can enable the synthesis of a wide range of functional hybrid materials with tunable properties including magnetic, spectral, and electronic. Specifically, the control of dopant proximity and concentration is used to enhance desirable spectral transitions related to amplification at 1.54 micron for compact planar optical amplifier applications. The spatial distributions between Er\textsuperscript{3+} and various rare earth sensitizers (e.g. Yb and Eu) are inverted to control the spacing of optical absorbance bands for a unique study of the correlation between energy transfer and dopant proximity. Thin films of approximately 10 nm are synthesized by sequential radical-enhanced ALD of Y\textsubscript{2}O\textsubscript{3}, Er\textsubscript{2}O\textsubscript{3}, Yb\textsubscript{2}O\textsubscript{3}, and Eu\textsubscript{2}O\textsubscript{3} at about 350°C. The composition, microstructure, cation distribution, local chemical bonding and optical properties of the as-synthesized thin films were determined by x-ray photoelectron spectroscopy, x-ray diffraction, micro-Raman and photoluminescence measurements. To optimize the effect of the sensitizer and minimize the concentration quenching, the concentration and spatial distance between Yb\textsuperscript{3+}/Eu\textsuperscript{3+} sensitizers and Er\textsuperscript{3+} were controlled by changing the global deposition cycle sequence. Extended x-ray absorption
fine structure analysis verified the spatial control of dopants in the Y$_2$O$_3$ host. It was found that multi-dopant spatial control allows for incorporation of minimal active sensitization sites, allowing for the possibility of maximizing the active Er concentration while maintaining efficient energy transfer. This additional degree of control allows for a class of complex materials that can potentially outperform their conventional counterparts by many-folds in luminescence.

TF2-TuA12  ALD of La Stabilized Amorphous HfO$_2$ High-k Dielectric Thin Films. T. Wang, J.G. Ekerdt, University of Texas at Austin

La$_2$O$_3$ was incorporated into hafnium dioxide grown by atomic layer deposition (ALD) to stabilize the amorphous phase during high temperature annealing. The incorporation was achieved by depositing HfO$_2$ and La$_2$O$_3$ alternatively in different ALD cycles. X-ray photoelectron spectroscopy compositional analysis shows that the Hf and La atomic percentage ratio can be controlled by varying the number of separate Hf and La ALD cycles. Microstructure was determined with X-ray diffraction and cross-sectional transmission electron microscopy. The introduction of La increases the film crystallization temperature from 500 °C for a HfO$_2$ film to 800 °C, 900 °C and 950 °C for 10 nm films containing 13% La (metal basis), 25% La and 43% La, respectively. Due to the ALD growth mechanism, the film is a HfO$_2$-HfLa$_{x}$O$_{y}$ periodic structure in which La just interacts with a limited thickness of HfO$_2$, and La-free layers mainly composed of HfO$_2$. The presence of periodic HfO$_2$ thin interval layers adds an extra advantage in amorphous stabilization during high temperature annealing over that found for homogeneous HfLa$_{x}$O$_{y}$ mixtures and less overall La is required. Therefore ALD incorporating La is a potential method to grow amorphous HfO$_2$-La$_2$O$_3$ high-$k$ dielectric thin films.
interaction between the plasma polymer BTSE film and the aluminum substrate. Ion etching by Xe+ 500 eV and 250 eV, depending on the plasma polymer BTSE film thickness, exposed the interfacial region, while Ga+ (15 keV) ions analysed the material composition. An AlOsi fragment was identified at nominal mass m/z = 70.9539 amu in high mass resolution spectra. The presence of this aluminium-oxygen-silicon ion fragment is a strong indication of an existing chemical interaction between the plasma polymer BTSE film and the aluminum substrate: the nature of this interaction implies the formation of a covalent bond between the silane and the aluminum substrate. Until now, this strong interaction silane-aluminum has never been observed in plasma polymer BTSE films. Ageing tests combined with X-ray photoelectron spectroscopy measurements allowed the evaluation of the adhesion performance of plasma polymerized BTSE films on aluminum. The Si2p signal intensity was measured before and after dipping the coated sample in an ultrasonic water bath for 30 min, at room temperature. The Si2p peak intensity remained constant after the sonication test, showing a strong adhesion between the deposited layer and the aluminum substrate. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) has been used for probing the metal/film interface. Ion etching by Xe+ 500 eV and 250 eV, depending on the plasma polymer BTSE film thickness, exposed the interfacial region, while Ga+ (15 keV) ions analysed the material composition. An AlOsi fragment was identified at nominal mass m/z = 70.9539 amu in high mass resolution spectra. The presence of this aluminium-oxygen-silicon ion fragment is a strong indication of an existing chemical interaction between the plasma polymer BTSE film and the aluminum substrate: the nature of this interaction implies the formation of a covalent bond between the silane and the aluminum substrate. Until now, this strong interaction silane-aluminum has never been observed in plasma polymer BTSE films.

Acknowledgements

The project partners VUB, ULB, FUNDP and CoIR gratefully acknowledge the Belgian Science Policy for funding the FOMOS project (P2/00/04) in the “Programme to stimulate knowledge transfer in areas of strategic importance”, www.belspo.be

8:20am PS2+TF-WeM2 Self-limiting Deposition of Nanolaminates by Pulsed PECVD, P.C. Rossette, C.A. Wolden, Colorado School of Mines

Self-limiting synthesis of alumina-titania nanolaminates (ATO, Al2O3/TiO2) was accomplished via pulsed plasma-enhanced chemical vapor deposition. At the synthesis temperature of 150 °C the alumina layers were amorphous, while TiO2 layers displayed a polycrystalline anatase structure. Digital control over nanolaminar structure was demonstrated through elemental analysis and TEM imaging. The optoelectronic properties of the ATO structures were examined as a function of composition and bilayer thickness. C-V measurements showed that the effective dielectric constant (κ) of the nanolaminates was consistent with treating the structure as individual capacitors in series. I-V measurements showed that leakage current deteriorated with TiO2 content, though low leakage was restored through interfacial engineering. With respect to dielectrics these results suggest that the best nanolaminate would employ Al2O3 interface layers deposited by PE-ALD to minimize leakage current, and that these two layers would sandwich a single TiO2 layer whose thickness would set the effective dielectric constant. We will also present work in SiO2 –TiO2 nanolaminates formed by the same technique at room temperature with applications as optical components. Finally, we will present recent findings in the area of inorganic/organic hybrid nanolaminates formed by alternating oxide and polymer layers.

8:40am PS2+TF-WeM3 Tailoring PECVD Ultra-Low-k Films for Nanoscale Interconnects, E.T. Ryan, GLOBALFOUNDRIES, S.M. Gates, S. Cohen, Y. Ostrovski, V. Patel, E. Simonyi, C. Dimitrakopoulos, IBM T.J. Watson Research Center, A. Madan, IBM Microelectronics, G. Dubois, IBM Almaden Research Center, A. Grill, IBM T.J. Watson Research Center

Ultra-low-k (ULK) insulating films are critical to reduce the resistance-capacitance (RC) delay in interconnect wires. This talk will briefly review the history of low-k materials that culminated with ULK nanoporous organosilicate glass (also called pSiCOH films deposited by plasma-enhanced chemical vapor deposition (PECVD). Nanoporous ULK pSiCOH films pose many interconnect fabrication challenges, and the needs of integration impose limits on the material properties of the films. For example, the pSiCOH film can be damaged by exposure to other plasma processes, and the degree of damage is related to material properties such as porosity, pore size, pore interconnection, carbon content, and bonding arrangement.

The stress and mechanical strength (modulus) of the pSiCOH film is critical for the structural stability of the interconnect wires. Spontaneous cracking is directly related to both modulus and stress. Packaging imposes additional stresses on the interconnect lines. Furthermore, if the modulus of the ULK film becomes too low, capillary forces during post-etch wet cleaning can cause the patterns in the pSiCOH film to collapse.

These integration needs require balancing various trade offs in material properties, and this constrains the process space for pSiCOH film deposition. The talk will review our work to design pSiCOH films with different properties to meet different integration needs. Examples of PECVD films with properties tailored to meet these interconnect needs illustrate the trade offs we face.

First we review our efforts to design films that are resistant to damage by the plasmas used for etch and ash and cap deposition. Mechanical properties were also maintained at favorable values. We modified a conventional pSiCOH film (V1) prepared from DEMS and BCHD porogen by adding a carbosilane skeleton precursor to incorporate new carbon structures. The modified films (V2, V3) can be adjusted by the choice of the carbosilane precursor. The films were characterized for electrical and mechanical properties, pore characteristics, and FTIR. The plasma damage of the films was characterized by thickness loss after HF etch of the damaged layer and depth profiling by ToF-SIMS. The new pSiCOH V2 and V3 films show reduced plasma damage. Our effort to optimize the pSiCOH modulus will be discussed, with the overall goals of reducing plasma induced damage and maintaining favorable stress and modulus.

9:20am PS2+TF-WeM5 Amplitude Modulated Pulse RF Discharges for Producing and Driving Nano-Blocks, S. Iwashita*, H. Miyata, H. Matsuizaki, K. Koga, M. Shiratani, Kyushu University, Japan

We have proposed a bottom-up nanosystem-fabrication method, which consists of production of nano-blocks and radicals (adhesives) in reactive plasmas, transport of nano-blocks towards a substrate, their arrangement on the substrate using pulse RF discharges with the amplitude modulation (AM) of the discharge voltage. For the method, control of the size of nano-blocks and their manipulation without their agglomeration are important. Up to now, we have succeeded in controlling the size of nano-blocks by pulse RF discharges, and have realized their rapid transport from their generation region towards a substrate with suppressing agglomeration by pulse RF discharges combined with AM. Here we report a criterion for driving nano-blocks rapidly and discuss their transport mechanisms.

Experiments were carried out using a capacitively coupled RF discharge reactor described elsewhere. Nano-blocks were formed in 13.56 MHz RF discharges of Si(CH3)2(OCH3)2 diluted with Ar. Nano-block transport in AM discharges is classified into two kinds: one is the rapid transport at a velocity more than 60 cm/s during the modulation period and the other is the slow transport at a velocity of 3-5 cm/s after turning off discharges due to temperature gradient. The key parameters to the rapid transport are the period Δt and voltage VAM of the modulation and asymmetry of the discharge, which is characterized by the dc self-bias voltage Vdc. The larger nano-blocks need longer Δt, higher VAM, and higher Vdc, for their rapid transport because of their large inertia. All nano-blocks of 26 nm in size, for instance, are transported rapidly during the modulation period for Vdc = -412 V, Δt = 100 ms and VAM = 1076 V, while 54 % of them transported rapidly during the modulation period and 46 % of them are transported after turning off discharges for Vdc = -350 V, Δt = 100 ms and
Methodologies and Plasmas (IMIP)- CNR, Italy

S. Martin, vapor deposition of amorphous carbon nitride (a-CNx) materials, which responsible for nitrogen incorporation are often obscured by the substituted into the amorphous film network, but the mechanisms exhibit a variety of interesting physical and chemical properties. These properties depend critically on the manner and extent to which nitrogen is content of Plasma-Deposited a-CNx Materials

9:40am PS2+TF-WeM6 Plasma Deposition of Platinum-Based Nanocomposite Films as Fuel Cell Electrocatalysts, A. Milella, E. Dilonardo, University of Bari, Italy, F. Palumbo, Institute for Inorganic Methodologies and Plasmas (IMIP)- CNR, Italy, S. Martin, CEA-G’/ Leti, France, R. D’Agostino, F. Fracassi, University of Bari, Italy

In Proton Exchange Membrane Fuel Cells (PEMFC) the electrode reactions rely heavily on the use of platinum catalysts. Since cost of this precious metal is one of the main barriers for commercialization of fuel cells, many research efforts are addressed to obtaining higher catalytic activity than the standard carbon-supported platinum particle catalysts used in current PEM fuel cells, with a reduced amount of metal. In this framework, plasma processes are particularly appealing since they allow the dispersion of catalyst in form of nanoparticles and the control of the film thickness to the nanoscale. Few examples are present in literature concerning the use of low pressure plasma for platinum-containing films as catalytic electrodes.

In this contribution we report our latest results on the one-step deposition of nanocomposite thin films containing platinum nanoclusters (high specific area), with definite concentration and uniform in size. Thin films are obtained from a simultaneous plasma-enhanced chemical vapour deposition of ethylene (C2H4) / argon gas mixtures and RF sputtering of a platinum target. The main advantages of this approach consist in the reduced thickness (less then 1 micron), the possibility to coat complex shapes, and the easy scale up in a continuous process. A comprehensive study on the effect of different parameters (RF power, deposition time, gas flow rates) on the film chemical composition and structure will be presented. In particular, it will be shown that the platinum content in the film, determined by X-ray Photoelectron Spectroscopy (XPS), can be continuously varied by properly controlling the RF power and the monomer flow rate. Field Emission Gun-Scanning Electron Microscopy (FEG-SEM) shows that films are porous with a cross-section characterized by columnar structures of different size and orientation, depending on the deposition parameters. Transmission Electron Microscopy (TEM) confirms that platinum aggregates in crystalline nanoclusters of diameters in the range 3-7 nm, uniformly distributed in the film. The electrochemical active area of the films, as determined from ex-situ Cyclic Voltammetry (CV) analyses, reaches a maximum correspondingly to a platinum load of about 60%. Preliminary results on device testing will be also presented.

Acknowledgments
This work was founded by the European Project NAPOLYDE (NMP2-CT-2005-515846).

10:40am PS2+TF-WeM9 Contribution of CN Radicals to the Nitrogen Content of Plasma-Doped a-CN, Materials, J.M. Stillahn*, E.R. Fisher, Colorado State University

This work details our efforts to explore the plasma-enhanced chemical vapor deposition of amorphous carbon nitride (a-CN,) materials, which exhibit a variety of interesting physical and chemical properties. These properties depend critically on the manner and extent to which nitrogen is substituted into the amorphous film network, but the mechanisms responsible for nitrogen incorporation are often obscured by the complexities of mixed-precursor systems (e.g., CH3/NH3) that are frequently used to study a-CN, deposition. Single-source precursors (e.g., CH3CN, BrCN) help to simplify the gas phase chemistry, and in this work we have employed such precursors to learn about nitrogen incorporation mechanisms in more complex systems. The CN radical is examined with particular interest as it exhibits near-unity surface reaction probabilities under all conditions, providing a stark contrast with other N-containing plasma species such as the less-reactive NH radical. Interestingly, this difference in surface reactivity is echoed by disparities in the molecules’ internal energies, which are characterized in this work by the rotational temperature. The distributions of the CN radical become especially evident with the addition of BrCN plasmas, yielding films that delaminate and buckle upon exposure to atmosphere. This behavior may reflect a high concentration of terminating groups in the film, leading to a porous material that is compressively stressed as it absorbs water. Data such as these can be used to form a more complete understanding of the chemical mechanisms that lead to a-CN deposition.

11:00am PS2+TF-WeM10 Comparison between a DC Reactive Magnetron Sputtering Discharge in an Ar/NH3 and Ar/H2/N2 Gas Mixture, F. Henry, A. Batan, F. Reniers, Université Libre de Bruxelles, Belgium

The reactive magnetron sputtering technique is widely used for thin films deposition. This one offers many advantages like: a large choice of composition of the deposited films, a low temperature of deposition that allows to use a large scale of substrates and a high speed of deposition. Other techniques used for thin films deposition like CVD often required the use of hazardous gases and required a high temperature of deposition. In this study, two different gas mixtures (Ar/NH3 and Ar/H2/N2) used for the deposition of silicon nitride thin films were compared. Optical Emission spectroscopy spectrum (OES) were recorded to characterize the plasma gas phase. X-ray Photon-electron Spectroscopy (XPS) was used to determine the stoichiometry of the deposited thin films and used to perform a depth profiling of the silicon target after exposure to the reactive magnetron sputtering discharge. Optical interferometry was used to measure the film thickness and current-voltage curves were plotted to determine the electric characteristics of the discharge.

The influence of the plasma parameters such as the molar fraction of reactive gas and the total pressure was studied. The same parameters were investigated for both kind of gas mixture and a detailed comparison was performed.

The experiments were performed in a stainless steel chamber equipped with a home-made magnetron cathode. The total pressure was set between 5 x 10-7 Torr and 2 x 10-2 Torr and the molar fraction varied between 0 and 0.6 in reactive gas. During all experiments the discharge current was set to 300 mA.

The excited species detected into the Ar/NH3 and Ar/H2/N2 plasma were the same, except for the NH radical that was not detected in the Ar/H2/N2 plasma. The stoichiometry of the thin films deposited with the two kind of gas mixtures was investigated by XPS, a N/Si ratio of 1.33 was determined for the Ar/H2/N2 plasma and 1.22 for the Ar/NH3 plasma.

The current voltage curves were plotted at different molar fractions of reactive gas and at different total pressures. A typical drop of the tension due to a poisoning of the target was observed for the Ar/NH3 plasma and for the Ar/H2/N2.

11:20am PS2+TF-WeM11 The Application of AC Diode Sputtering for Aluminum Thin Films in Small Apertures, D.R. Walters, Argonne National Laboratory

A thin conductive film was applied on the inner surface of a small-aperture vessel using the AC Diode Sputtering process. This paper describes the process and the technical equipment used in this thin-film method. The process configuration presented here employs a dual-electrode arrangement, which creates a glow discharge field around both electrodes, thereby spreading out the affected area. An example of coating performed in a 5 mm by 12.5 mm rectangular channel by 3.4 m in length is present along with examples of circular cross-sectional channels. A significant challenge of this configuration is how to get a homogeneous pressure throughout a long constricted channel; results show that the dual inlet-outlet gas flow circuit was able to achieve the uniformity needed for a satisfactory film. Analyses of the sample films confirm acceptable uniformity even in the pressure region of 600 mTorr. Further work has shown that the glow discharge can be maintained into a pressure regime of greater than 10 Torr.

11:40am PS2+TF-WeM12 3D Plasma Simulations of a High Density Plasma CVD Reactor using VIZGLOW, P. Kohnur, R. Kinder, Novellus Systems, Inc., X. Yuan, Esgee Technologies, Inc., L. Raja, The University of Texas at Austin

High-density plasma CVD (HDP-CVD) reactors are used to provide void-free gap fill of high-quality dielectric films in high aspect ratio device structures. The ability to accurately model a prototype or development design is a necessary capability of any equipment manufacturer in order to lower cost and shorten design cycle times. However, the ability to model an HDP-CVD tool accurately remains a difficult challenge due to the complex coupling of power deposition and plasma transport in a CVD chamber. To investigate issues related to power deposition and electron transport, we

* PSTD Coburn-Winters Student Award Finalist
have used the VIZGLOW simulation software developed at Esgee Technologies to simulate 3D geometries. The simulation software enables the solution of the energy equation for electron temperature, while solving for the electron density and electrostatic fields through a quasi-neutrality condition. Electron heating is produced by electromagnetic fields, while the energy equation is solved for all heavy species. The HDP-CVD tool considered is a hemispherical inductively coupled plasma (ICP) source. The simulation results are compared to previously published experimental measurements with Langmuir probes, voltage and current monitors, optical emission spectroscopy, ion mass spectrometry, and gas quadrupole mass spectrometry. Furthermore, results from VIZGLOW are benchmarked against simulation results obtained from the Hybrid Plasma Equipment Model (HPEM). Results for experimentally measured process gases (Ar, Ar/O₂, Ar/O₂/H₂) at low pressures (< 15 mTorr), operating at 3-6 kW’s of input power, and varying rf frequency (400 kHz -13 MHz) are discussed.

Thin Film
Room: B4 - Session TF-WeM

Nanostructuring Thin Films I
Moderator: A.V. Melechko, North Carolina State University

8:00am TF-WeM1 Growth of Thin Films of Nanomeshes on Solid Surfaces through Self-Assembly. F. Tao, S. Bernasek, Princeton University

The growth of homogeneous 2-D multi-component ordered thin films has attracted surprising interest because they may offer the multiple functions of organic materials and the flexibility in fine-tuning the chemical, physical and mechanical properties for desirable needs in a wide spectrum of technological areas. Controllable molecular self-assembly on solid surfaces is a promising approach to the design of such thin films. Coassembly of monolayers of 5-octadecylhexyloxyphosphoric acid (SOIA) and octanoic acid and of SOIA and terephthalic acid were fabricated on highly-ordered pyrolytic graphite (HOPG). The atomically-resolved morphology of these self-assembled monolayers was investigated using high-resolution scanning tunneling microscopy (STM). SOIA coadsorbs with terephthalic acid via a hydrogen-bonding network, forming ordered domains made of alternating SOIA and terephthalic acid lamellae. In the coadsorption of SOIA with octanoic acid, SOIA and octanoic acid alternately pack at the molecular level in each lamella, forming a homogeneous two-component crystal. Due to the different chain-lengths of the two components, a nano-hole with a size of 13.5 Å x 8.5 Å x 1.8 Å is formed in each lattice unit, producing homogeneous nano-meshes. The size of nano-hole in the meshes is tunable by using alkyl chain of either of the two components with different length. This coadsorbed molecule-by-molecule self-assembly is the first demonstration of a novel approach to fabricating multi-component 2-D to 3-D crystalline thin films at the molecular level. It suggests a new strategy to precisely and controllably grow homogeneous nano-structured composite thin films.

8:20am TF-WeM2 Nanometer-Size Direct-Write 3D-Patterning using Probes. A.W. Knoll, D. Pires, U. Drechsler, IBM Zurich Research Laboratory, Switzerland

Progress in nanotechnology is intimately linked to the existence of high quality methods for producing nanoscale objects and patterns at surfaces. Scanning probe technologies are intrinsically capable of addressing real space with atomic resolution and have been used to fabricate nanoscale devices with exceptional quality. However, high resolution patterning in combination with sufficient throughput remains challenging. We have discovered that organic molecular glasses can be reproducibly removed at the micro-second time scale with nanometer scale precision using heated probes, which opens up new perspectives for nanopatterning.

In our experiments, a thin film of molecular glass with a thickness of 10-100 nm is deposited on a substrate by spin-coating or evaporation. The material is locally desorbed by heating the tip to 300-500 °C and applying a mechanical force of 50-100 nN for a duration of 5 μs, leaving behind a well defined void. By laterally displacing the probe and repeating the process, any arbitrary pattern can be written whereby the resolution of the process is determined by the apex dimensions of the probe. Material removal can be cumulated thereby enabling the fabrication of three-dimensional structures. A replica of the Matterhorn was fabricated by consecutive removal of molecular glass layers. The almost perfect conformal reproduction of the original proves that the final structure is a linear superposition of well defined single patterning steps.

The created two and three-dimensional structures were transferred into silicon substrates using standard RIE technology. Additionally, to enhance the aspect ratio, a three layer nanoimprint process has been developed. It enables vertical amplification of the written structures by a factor of 50 without significant loss of lateral resolution. Using this new technology, one is able to fabricate complex three-dimensionally textured substrates, e.g. for the guided and directed assembly of shape-matching objects. The technique also offers a competitive alternative in terms of resolution and speed to high-resolution electron beam lithography.

8:40am TF-WeM3 Subwavelength Patterning of Organic Monolayers Via Nonlinear Laser Processing with fs-laser Pulses. N.O. Hartmann, S. Franzka, M. Mathieu, University of Duisburg-Essen, Germany, J. Koch, B.N. Chichkov, Laser Zentrum Hannover, Germany, A. Ostendorf, Ruhr-Universität Bochum, Germany

In the last decade, surface processing with ultra-short laser pulses has emerged as a powerful tool for nanofabrication. Here, fs-laser patterning of self-assembled organic monolayers offers a variety of particularly promising perspectives. The ultrathin nature of these coatings allows for single pulse processing and hence ensures short processing times. It also allows for well-defined irradiation and burn-free patterning of the coating and avoids bubble and particle formation. All off which are problems usually encountered in fs-laser processing. Moreover, varying the chemical structure of the monolayer allows for arbitrary cross-sections, incubation effects and resist properties and to enable chemical nanopatterning. Surprisingly, despite these promising perspectives, fs-laser processing of organic monolayers still is largely unexplored. In a recent study we investigated fs-laser patterning of alkylsiloxane monolayers on quartz glass substrates at λ=800 nm and pulse lengths below 30 fs [1]. Selective decomposition of the coating by single laser pulses at subwavelength resolution can be carried out over a wide range of fluences from 4.2 down to 3.1 J/cm². In particular, at a 1/e laser spot diameter of 1.8 μm, structures with a width down to 250 nm and below were fabricated. Very similar results were also obtained from multiple pulse patterning experiments suggesting that incubation effects are negligible. Hence precise fabrication of complex patterns appears feasible. This opens up a facile route towards laser fabrication. The in-plane and out-of-plane selectivity of the technique allow submicron single-dimensional structures down into the sub 100 nm regime. Such templates represent promising platforms for biotechnological applications, e. g. biosensor arrays. Processing at higher fluences, also provides a facile route towards combined chemical/topographic structures, e. g. for microfluidic applications. With a band gap of 9 eV, quartz glass, of course, represents an ideal platform for nonlinear fs-laser processing via multiphoton absorption processes. Further results, though, demonstrate that fs-laser processing also allows for subwavelength patterning of organic monolayers on thin gold films. A general account on recent achievements in nonlinear laser patterning of organic monolayers via multiphoton absorption and photothermal processes is given.


9:00am TF-WeM4 Alloy Destabilization Behavior of Cu-Ni Thin Films on Si during Solid State Dewetting. S. Subhakshat, North Carolina State University, P.D. Rack, R. Pearce, University of Tennessee, D.K. Hensley, M. Fuentes-Cabrera, J.D. Fowlkes, Oak Ridge National Laboratory, M.L. Simpson, Oak Ridge National Laboratory and University of Tennessee, A.V. Melechko, North Carolina State University

Synthesis of nanoparticles research witnessed a remarkable headway with techniques spanning a wide range of materials and offering good control over shape - size and composition. Top – down approaches have become successful in achieving controlled positioning of nanoparticles in pre-defined templates. A self-assembly method, however, is highly desirable because of its simplicity and compatibility with heterogeneous integration processes. Thin elemental or multicomponent films can be destabilized into self assembled arrays of nanoparticles. We will discuss how heating of ultrathin films can be a powerful but simple tool to fabricate functional nanostructures. Thin metal films on inert substrates are generally unstable, with their free energy resembling that of a spinodal system. Such films can spontaneously evolve into predictable morphologies with defined length scales. This process has been extensively used to prepare arrays of catalyst nanoparticles on Si surfaces for growth of vertically aligned carbon nanofibers. In this work we report on the behavior of Cu-Ni alloy thin films during solid state dewetting. Cu-Ni alloy thin films during solid state destabilization on Si is in contrast to behavior expected from isomorphous system. Thin films of Cu-Ni and Ti-Cu-Ni were formed on Si and subjected to annealing temperatures from 300 °C - 700°C. Scanning Electron Microscopy(SEM) micrographs of these films revealed the formation of Cu-rich clusters on the surface prior to complete dewetting of the film in the range of temperatures much lower than dewetting of Ni
The normalized concentration of the conducting phase atoms, where incorporated Ag nanoparticles gave only weak XPS signals from the Ag 3d peak (300 – 800 nm in transmission), showed with the presence of the Ag nanoparticles pronounced absorption peaks at around 420 to 480 nm, depending on the amount of incorporated Ag and different preparation conditions. This is related to us, in accordance with other authors, to the surface plasmon loss of the Ag nanoparticles where the loss energy depends on the particle size and form, the concentration of the particles and the nature (dielectric constant) of the surrounding matrix. HRTEM pictures showed the presence of Ag nanoparticles with sizes between 5 and 50 nm. The filling factor of Ag (within the fluorocarbon matrix) was about 0.3. Crystalline phases formed from the Ag films could be observed with (200) and (111) orientation. The evaluation of the lattice spacing resulted in d_{200} = 0.204 nm and d_{111} = 0.237 nm which is within 1% of the bulk Ag values. The surface free energy of our films was determined by the observation of the contact angle of liquid drops, using water, ethyl alcohol and olive oil. The evaluation was done following the method of Zisman. We obtained a value of 15 mNm, which is approximately 50% of the value reported for bulk Teflon.

**9:20am TF-WeM5 Electrical, Optical and Structural Studies of Shallow Buried Au-PMMa Composite Films formed by Very Low Energy Ion Implantation, F.S. Teixeira, M.C. Salvadori, M. Cattani, University of Sao Paulo, Brazil, I.G. Brown, Lawrence Berkeley National Laboratory**

We describe our electrical, optical and structural studies of sub-nanometer composite films formed using a pulsed cathodic arc plasma gun to implant 49 eV ions (palladium, copper, tantalum) to a depth of a few nanometers (palladium) or a few hundred nanometers (copper, tantalum) thick. Electrical resistance measurements in situ as a function of implantation dose (up to 2 x 10^{16} atoms/cm^2) show a conductivity increase that is well described by the percolation theory power law \( \sigma/\sigma_0 = (x-x_c)^\phi \), where \( \sigma_0 \) is the measured metal/insulator composite conductivity ratio, \( x \) is the normalized concentration of the conducting phase, \( x_c \) is the normalized critical concentration (percolation threshold) below which the composite has zero conductivity, and \( \phi \) is the critical exponent. For our Au/PMMa composite we found \( \sigma/\sigma_0 = (x-0.4)^{0.85} \), where \( x_c \) corresponds to a critical dose \( \phi = 1.0 \times 10^{16} \) atoms/cm^2. We point out that the low energy implantation used here does not create any target vacancies or carbonization, which can occur for incident ion energy greater than about 100 eV, and thus that the electronic transport properties of the composite form here are directly linked to the gold phase embedded in the original polymer. TEM (Transmission Electron Microscopy) images reveal that the gold phase is a shallow-buried sub-10 nm layer consisting of a distribution of nanoclusters (diameters \( 2 \) nm – 5 nm for implantation dose \( \phi < \phi_c \), spontaneously aggregated from the implanted gold ions, evolving to larger clusters as the dose increases. The computer simulation software TRIDYN, a dynamic version of the widely used TRIM (Transport and Range of Ions in Matter) that is more suitable when compositional changes are induced by the implantation itself as is the case here, gave very good predictions for the intermixed layer width and ion range, both with values lower than 10 nm. UV-Vis optical spectroscopy (ultraviolet to visible wavelength range) of the samples showed localized plasmon surface resonance effects from gold nanoparticles. SAXS (Small Angle X-ray Scattering) analysis was used to study the fractal character of the growth dynamics, the correlation lengths, and the size of agglomerates and elementary clusters. We related SAXS and UV-Vis data to percolation electrical behaviour. Note that the entire material is composed of a sequence, from substrate to surface, of PMMA thin film, shallow-buried composite film of nanoclusters, and an ultra thin film of unaltered polymer. These three layers can be electron beam lithographed at the same time, a highly desirable feature for application of the material for organic electronics/photonic.

**9:40am TF-WeM6 Preparation and Microstructure of Silver Nanoparticles Embedded into a Fluorocarbon Matrix Prepared by RF and DC Sputtering, D.G. Vásquez Mazzoti, A.F. Talledo Coronado, Universidade Nacional de Ingenieria, Peru, C. Bengdoff, University of Hamburg, Germany**

Composite materials consisting of metal nanoparticles embedded in transparent dielectric materials are interesting materials due to the size effects induced by the nanoparticles. We report about the preparation of fluorocarbon thin films with embedded silver nanoparticles and their characterization with UV-VIS spectroscopy, XPS (X-ray induced photoelectron spectroscopy), IR (infrared spectroscopy) and HRTEM (high resolution transmission electron microscopy). Further, the surface free energy is determined from contact angle measurements using different liquids. The metal-dielectric nanocomposites with a layered structure were prepared by switching alternatively the substrates (glass or stainless steel) from an RF powered Teflon target towards an Ag target powered by DC. The high resolution XPS spectra from the C 1s region displayed four peaks (on stainless steel substrates) with positions of 284.5, 286.5, 288.6 and 290.7 eV, related to C-H\(_2\), C-F, C-F\(_2\) and C-F\(_3\), bonds, respectively. For comparison, we measured the XPS spectrum from a Teflon surface (after scratching the surface). From this surface, the carbon 1 s region was dominated by two peaks, located at 284.6 (C-H\(_2\)) and 289.0 eV (C-F\(_3\)). The different composition of the sputtered films is due to the plasma process, which produces fragments like F, C, CF, CF\(_2\) and CF\(_3\) radicals and ions. The incorporated Ag nanoparticles gave only weak XPS signals from the Ag 3d doublet around 368 - 374 eV. UV-VIS Spectra, measured in the range of 300 - 800 nm in transmission, showed with the presence of the Ag nanoparticles pronounced absorption peaks at around 420 to 480 nm, depending on the amount of incorporated Ag and different preparation conditions. This is related to us, in accordance with other authors, to the surface plasmon loss of the Ag nanoparticles where the loss energy depends on the particle size and form, the concentration of the particles and the nature (dielectric constant) of the surrounding matrix. HRTEM pictures showed the presence of Ag nanoparticles with sizes between 5 and 50 nm. The filling factor of Ag (within the fluorocarbon matrix) was about 0.3. Crystalline phases formed from the Ag films could be observed with (200) and (111) orientation. The evaluation of the lattice spacing resulted in d_{200} = 0.204 nm and d_{111} = 0.237 nm which is within 1% of the bulk Ag values. The surface free energy of our films was determined by the observation of the contact angle of liquid drops, using water, ethyl alcohol and olive oil. The evaluation was done following the method of Zisman. We obtained a value of 15 mNm, which is approximately 50% of the value reported for bulk Teflon.
The dynamic stencil setup consists of an x-y moving stage with 20 nm encoding resolution each and three z-stages on which the stencil is attached, and a fixed part which holds the substrate, as described in [3]. The x-y stage is programmed to move along various trajectories. The movement parameters are the (x,y) coordinates of the start and end point (corners), the gap between stencil and substrate, and the stencil speed (0.04-5 µm/s).

By evaporating materials at a constant rate while changing the speed of the stencil, we obtained variable-height structures. We also varied substrate materials (SiO₂, SiN) and parameters such as the deposition rate and the stencil-substrate gap. These structures were characterized by scanning electron microscopy and atomic force microscopy. We also analyzed the pattern transfer integrity from the stencil to the substrate as a function of stencil-substrate gap and aperture size.

Dynamic stencils are used here for patterning two-dimensional variable-height structures by material deposition through a stencil at 4” wafer scale. The contamination-free, parallel-processing, and versatile nature of dynamic stencil lithography provides custom applications with a novel solution.


The PCD diodes were fabricated as follows. First, 100nm films of metal 1 and different materials were deposited followed by a 20nm thick oxide. The deposition parameters of the metal and the insulator films were optimized to obtain films that are pinhole free and have low surface roughness. The planar metal/insulator bilayer “sandwich” is contacted by a second metal in the form of a sharp tip, resulting in a diode contact area as small as \( \mu m^2 \). For our initial studies we are using blunt wire tips, since our initial work was using blunt wire tips, since our initial objectives are to optimize the planar metal/insulator layers. PCD devices with different metal 1, insulator and metal 2 (wire tip) combinations were fabricated and characterized for the desired I-V characteristics.

The PCD diodes were fabricated as follows. First, 100nm films of metal 1 candidates such as Ni, Nb, Sm, Hf were deposited by DC sputtering. The insulator layer (NiOx, NbOx, SmOx, HfOx) was grown by anodization of the metal films and by atomic layer deposition. Devices were characterized as a function of thickness of the insulator layer. In addition, dual insulators (MIM) were grown and compared with single insulator (MIM) devices. TiOx and AlOx were used for the second insulator layer. The deposition parameters of the metal and the insulator films were optimized to obtain films that are pinhole free and have low surface roughness. The films were characterized using scanning electron microscopy, atomic force microscopy, x-ray reflectivity and x-ray photoelectron spectroscopy. Pt, Au and Ag wire tips were used for Metal 2. PCD IV characteristics were analyzed in terms of non-linearity (NL) \([dI/dV]^2(V/I)_0\), asymmetry (AS), responsivity (RY) \([dI/dV]^2(dI/dV)\) and turn-on voltage (TOV) [based on positive current]. From the matrix of different material combinations and the fabricated MIM devices, an attempt was made to identify critical parameters that influence the desired I-V curve characteristics.

The NL, RY and TOV values for the Nb-NbOx (5.2 nm thick)-Pt system were 2.3, 3.8 A/V and 0.1 V respectively. But the AS value was not as good as found in Nb-NbOx (22.81 nm thick)-Pt system. At the same time, however, the turn-on voltage was relatively higher (1.7 V) in the latter system. Such results would help us fabricate a diode suitable for solar energy harvesting.

Coal gasification plants are advanced energy production systems. Inherent processes in these plants produce a lot of hazardous gases, such as hydrogen sulfide (H2S), which must be continuously and efficiently detected and removed before the syngas is used for power generation. The objective of the present work is to develop stable and reliable H2S sensors based on nanostructured tungsten oxide (WO3) thin films. The chemical sensing ability and high-temperature stability of WO3 is the motivation for the work. WO3 thin films have been fabricated by RF reactive magnetron-sputter deposition. A W-target has been employed for all the depositions and to investigate the effect of processing conditions on the growth and structure of resulting WO3 films. The fabrication has been made under varying substrate temperatures (T_s) in the range 30(RT)-400 °C. The argon to oxygen flow ratio is kept constant at 1:6 for reactive deposition and oxide formation. Investigations made using x-ray diffraction (XRD) and scanning electron microscopy (SEM) indicate that the effect of T_s is significant on the microstructure of WO3 films. XRD and SEM results indicate that the WO3-grown RT are amorphous, whereas films grown at higher temperatures are nanocrystalline. Thermally activated growth process of WO3 films is evident in the data. The average grain size increases with increasing substrate temperature, which is in agreement with the observations for structures (< 200 °C) while relatively rough at 400 °C. The optical measurements indicate that the films exhibit relatively high transmission and the band gap is dependent on the grain-size. The analyses indicate that the nanocrystalline WO3 films grown at 100-200 °C could be the potential candidates for H2S sensor development for application in coal gasification systems.

We installed and developed a large-bore CVD reactor for the growth of carbon nanotube materials on device substrates. The reactor was custom built by Tystar, Inc. and is capable of processing batches of up to thirty 150-mm wafers with industry-standard process controls. We synthesize vertically-aligned films of multi-walled carbon nanotubes by employing a Cr-Ni-Fe thin film catalyst stack pre-deposited on substrates. The kinetics of the growth process is studied by measuring the film thickness, the resistivity (indicative of the density), and the distribution of CNT diameters as a function of pre-growth catalyst treatment time, growth time, and growth temperature. It is found that pre-growth treatment times of about 200 min are needed before reaching steady-state catalyst conditions. Shorter pre-growth treatment times produce a more thick but less dense film. The CNT diameters are only weakly affected by the pre-growth treatment time (for at least greater than 30 min). A model is proposed to explain these results whereby the catalyst film quickly breaks up into catalyst particles but further treatment is needed to activate these particles. More activated particles leads to a more dense film but due to increased demand on feedstock also produces a less thick film. The kinetics of the film growth are studied as function of growth time and temperature under steady-state catalyst conditions.

Generation of strain in a silicon channel has been successfully used to increase performance of state-of-the-art CMOS devices. The most studied methods are embedded silicon germanium, stress liners and stress memory techniques. There have been relatively few studies of the effect of thin film dielectric materials in the Shallow Trench Isolation (STI) area on silicon strain. Raman spectroscopy has been used as a primary tool to measure silicon strain on a variety of STI structures. Different STI dielectric gap fill materials have been evaluated including high density plasma CVD, sub-atmospheric CVD and spin-on glass based oxide thin films. It has been shown that both intrinsic strain of thin film dielectric material and STI structure type affect strain in silicon. Ways of introducing new dielectric gap fill materials and generating high stress in STI are discussed. The most studied methods are embedded silicon germanium, stress liners and stress memory techniques.
Compressive stress can be applied by depositing films at elevated temperature on a high thermal expansion substrate and then letting the sample cool to room temperature. The critical compressive stress for cracking of Al2O3 ALD films was determined using Teflon FEP which is a flexible organic light emitting diodes (OLEDs) require barriers with extremely low water vapor transmission rates of < 1 x 10^-6 g/m2/day. Film cracking will severely impair the gas diffusion barrier.

The realised structures were made up of the stack of two couples of materials: amorphous hydrogenated silicon (a-Si:H) / silicon dioxide (SiO2), and - high elasticity in order to preserve a good adhesion when the substrate is deformations.

Our dichroic filters (transmission of one wavelength and reflection of another one) had to be deposited on shape memory substrates, with respect to several conditions:
- low thickness of the filter in order to minimize the weight supported by the substrate
- low internal stress in the structure to limit the mechanical action of the filter on the substrate
- high elasticity in order to preserve a good adhesion when the substrate is strongly deformed
- low light absorption in order to transmit the maximum of energy

The realised structures were made up of the stack of two couples of materials: amorphous hydrogenated silicon (a-Si:H) / silicon dioxide (SiO2), and a-Si:H / amorphous polyacrylic methacrylic (a-PAM), using the Bragg reflecting structure with seven layers only. These materials have been elaborated using two plasma techniques: a-Si:H and SiO2 were deposited by magnetron sputtering and the polymeric layers were deposited by inductive plasma enhanced chemical vapor deposition (PECVD). A brief study of the optical properties as a function of the deposition parameters has been performed for each material, and the chemical structure of the polymer was investigated with FTIR as a function of the RF power forwarded to the plasma. The internal stress of the optical filters has been calculated using the Stoney formula, and structures made up with polymeric layers have shown better mechanical properties than structures with silicon dioxide, with a lower value of residual stress. The elasticity of the realized optical filters has been tested on plastic substrate with a repeatedly deformation with a lower value of residual stress. The elasticity of the realized optical filters has been tested on plastic substrate with a repeatedly deformation with a lower value of residual stress. The elasticity of the realized optical filters has been tested on plastic substrate with a repeatedly deformation with a lower value of residual stress.

In this talk, we describe the use of pulsed plasma-enhanced chemical vapor deposition (PECVD) to modify AAO supports that offer a high pore density and a narrow pore size distribution. In this talk, we describe the use of pulsed plasma-enhanced chemical vapor deposition (PECVD) to modify AAO supports that offer a high pore density and a narrow pore size distribution. In this talk, we describe the use of pulsed plasma-enhanced chemical vapor deposition (PECVD) to modify AAO supports that offer a high pore density and a narrow pore size distribution.

5:00pm TF-WeA10 Single-Stage Deposition of Organic/Inorganic Multilayer by Plasma Enhanced and Initiated Chemical Vapor Deposition, A.M. Cooley, Massachusetts Institute of Technology, F. Palumbo, R. d’Agostino, University of Bari, Italy, K. Gleason, Massachusetts Institute of Technology Deposition techniques of multiple dense, inorganic layers alternated with soft, organic ones are widely investigated for several technological applications. Generally, a combination of two different deposition techniques is employed for deposition of organic/inorganic multilayered coatings. The possibility of a single-chamber vacuum-deposited system may greatly simplify the production and allows the quicker and cheaper roll-to-roll deposition. Here we propose a new technique for multilayer deposition, consisting of coupling initiated and plasma enhanced CVD, maintaining the same organosilicon precursor and the same reactor configuration.

Multi-layer coatings comprised of alternating inorganic (silica-like) and organic (organosilicon polymer) layers were deposited using hexamethyldisilazane as precursor. The organosilicon polymers were deposited by initiated CVD (iCVD) at filament temperature of 280°C. The silica-like layers were obtained by Plasma Enhanced CVD (PECVD) applying RF power to the same filament used in the iCVD process. The multilayers were obtained through layer by layer deposition, switching from one technique to the other without venting the system.

Chemical and morphological characterization of the organic single layer showed that the iCVD of poly-HVDSO resulted in a very crosslinked film with high carbon content (79 % from XPS analysis) and very low roughness (0.7 nm). PECVD of the same monomer, when highly diluted in Oxygen, gave inorganic coating with a low content of OH terminal groups and high deposition rate. X-ray photoelectron spectroscopy (XPS) depth profile, ellipsometric characterization and Secondary electron microscopic imaging of multilayer coatings clearly showed that the various layers do not mix or interdiffuse, but maintain the same chemical composition and refractive index in the single layers deposition. When the inorganic layer was deposited over the organic layer a graded interphase (around 40 nm thick) was detected, due to plasma ion bombardment of the underlayer.

The advantage of coupling iCVD and PECVD consists in the possibility of having dense inorganic coatings alternated with organic interlayers characterized by high crosslinking and high C content. Moreover the high smoothness of the iCVD layer is important to reduce the roughness of the underlayers in order to have conformal deposition on single layers. Hence, all these properties make this kind of multilayer coatings promising as ultrathin barriers (UHB) against the transmission of water vapor and oxygen through polymer substrates.

6:20pm TF-WeA11 Nonlinear Electro-optic Response and NLO Functionalization of Novel 3D Nanostructured Systems, R. D’Agostino, University of Bari, J.A. Bertrand, S.M. George, Massachussetts Institute of Technology Deposition techniques of multiple dense, inorganic layers alternated with soft, organic ones are widely investigated for several technological applications. Generally, a combination of two different deposition techniques is employed for deposition of organic/inorganic multilayered coatings. The possibility of a single-chamber vacuum-deposited system may greatly simplify the production and allows the quicker and cheaper roll-to-roll deposition. Here we propose a new technique for multilayer deposition, consisting of coupling initiated and plasma enhanced CVD, maintaining the same organosilicon precursor and the same reactor configuration.

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5:00pm TF-WeA11 The Role of Ammonia as an Inhibitor Species in Low Temperature CVD to Reduce Film Growth Rate and Enhance Conformal Coverage, S. Babar, P. Zhang, W. Wang, N. Kumar, J.R. Abelson, University of Illinois, Urbana-Champaign Our group recently demonstrated the phenomenon of growth inhibition in low temperature chemical vapor deposition of TiB2: a neutral molecule is added to the flow of precursor in order to reduce the growth rate and enhance the degree of conformal coverage; the atoms contained in the inhibitor are not incorporated into the film [JACS \textbf{130}, \textbf{52} (2008)]. Here, we demonstrate the inhibition behavior of ammonia on HfB2 growth using Hf[HB\textsubscript{3}]. The growth rate and surface roughness are measured in-situ by spectroscopic ellipsometry. At substrate temperatures below 350°C, ammonia reduces the growth rate of HfB2, down to zero at an ammonia pressure of ~ 1 mTorr. Upon cessation of the ammonia injection, growth resumes after 1-2 minutes. When ammonia is delivered as short pulses, the surface roughness appears to increase, then declines again after the ammonia is pumped out. With more investigation into the origins of this phenomenon, which may involve the formation of a dielectric surface layer or re-nucleation of HfB2 growth. We explain the role of ammonia using a site-blocking model in which ammonia adsorbs reversibly on the surface sites and reduces the rate of precursor adsorption. This simple rate model fits the data well. We show that growth inhibition by ammonia can be used to greatly enhance the degree of conformal coverage in a deep trench.

5:40pm TF-WeA12 Nanoscale Engineering of Ceramic Supports for High Permeance Ultrafiltration Membranes, R. Nahm, P.C. Rowlette, C.A. Wolden, Colorado School of Mines Anodized aluminum oxide (AAO) membranes are commercially available supports that offer a high pore density and a narrow pore size distribution. In this talk, we describe the use of pulsed plasma-enhanced chemical vapor deposition (PECVD) to modify AAO supports for arbitrarily designed molecular weight cuts or size cutoffs. PECVD is a deposition technique that provides digital control over the amount of deposited material (i.e. 1 Å/pulse). Specifically, we use pulsed PECVD to deposit SiO2 at room temperature to affect arbitrary pore size control. For this
work, pulsed PECVD is operated in a nonconformal mode, meaning that only the very pore opening is modified with no deposition occurring throughout the majority of the structure. Modified membranes are characterized by atomic force and electron microscopies. An advantage of this approach is that the modifications can be done very quickly. In addition, we demonstrate that the nominal pore size may be significantly reduced without any impact on the permeance. Moreover, these membranes provide a well-defined geometry that provides a unique experimental platform for studying hindered transport and nanofluidics. The modified membranes are characterized by gas permeance, water permeance, and measurements of solute rejection. SiO2 is the material of choice since it may be readily modified through addition of self-assembled monolayers to control the hydrophilicity of the surface and enhance biocompatibility. We will present preliminary work in this regard as well.
Magnetic Interfaces and Nanostructures

Room: C1 - Session MI-ThM

Magnetization Dynamics, Imaging and Spectroscopy

Moderator: A.T. Hanbicki, Naval Research Laboratory

8:00am  MI-ThM1 Correlated Magnetic Domain Structure and Magnetic Anisotropy Studies on Epitaxial Au / FePd(001) / MgO(001) Thin Films. J.R. Sklar*, C. Clavero, K. Yang, College of William & Mary, B. Wincheski, NASA Langley Research Center, R.A. Lukaszew, College of William & Mary

The FePd alloy system can exhibit the L10 ordered alloy phase when the Fe:Pd stoichiometry of the alloy is near 1:1.[1] The crystallographic structure of the L10 ordered alloy is characterized by alternating Fe and Pd atomic layers along a cubic stacking direction, which as a consequence suffers a tetragonal distortion. This tetragonal distortion induces a strong perpendicular magnetic anisotropy (PMA) when the layering is parallel to the film plane and the material is in thin film form. The origin of the strong PMA is the large spin-orbit coupling of the paramagnetic Pd atoms and a strong hybridization of their 4d bands with the highly polarized Fe 3d bands.[2] Although the mechanism of PMA is well known, controlling it in thin film form is non-trivial and warrants further study to be useful in applications such as magneto-recording media.

We will report on our correlated studies of the magnetic domain structure with the PMA in epitaxial Au / FePd(001) / MgO(001) thin films. Epitaxial FePd thin films were grown using magnetron sputtering in an ultra-high vacuum deposition system at elevated temperatures (400 – 600 °C) and on MgO(001) substrates to achieve highly ordered films with strong PMA. The films were subsequently capped with Au at room temperature (RT) to prevent oxidation, and alternative orientation of the [110] axis in the Au substrates was achieved by a Fe/Pd epitaxial lift-off process. High energy electron diffraction was used in situ to monitor the epitaxial growth and x-ray diffraction techniques were used ex situ to monitor the chemical ordering of the films. Magnetic anisotropy values were obtained from hysteresis loops measured at RT using a Superconducting Quantum Interference Device magnetometer and also by ferromagnetic resonance scans. The magnetic domain structure was investigated using a Nanoscope scanning probe microscope with a magnetically coated tip in non-contact mode. These studies have improved our understanding of these strong PMA materials, enabling correlations between the observed domain structure and the magnetic anisotropy, along with comparison to models of domain structure.[4]


This work was supported by the Virginia Space Grant Consortium, National Science Foundation (DMR Grant #0355171), the American Chemical Society (PRF Grant #41319-AC), and the Research Corporation Cottrell Scholar Award.

8:20am  MI-ThM2 Dependence of the Domain Wall Pinning Strengths to Lateral Constriction Size and Electrical Bias in GaMnAs. S.U. Cho, H.K. Choi, Yang, Park, Seoul National University, Korea, F. DaSilva, T. Osmin, D.P. Pappas, National Institute of Standards and Technology

Dynamics of domain wall (DW) motion and spin-polarized transport across DWs have received much attention due to their potential applications in large-scale memory storage and logic devices. Particularly for GaMnAs, spin-polarized current induced magnetization switching has been demonstrated.[1] Lateral nanoconstrictions (NC), from which DWs can form and be pinned, in GaMnAs have been utilized to demonstrate nonvolatile memory elements[2] as well as structures showing large magnetoresistance (MRs) [3]. Here, we investigate the size dependence of constrictions in GaMnAs epitfils, particularly the dependence of DW pinning strength and DW motion of lateral constriction size, as well as electrical bias across the constriction. A method to realize nanoconstrictions without plasma-assisted methods and nonlinear IV transport across NC junctions have been reported previously.[4] For this study, we present magnetotransport measurements on identically sized constrictions in series (up to five NC in series) equally spaced apart (~ 2 microns). For large constrictions, the overall resistance (~25 kΩ at room temperature) as function of applied field shows a background negative MR response which can be attributed to anisotropic magnetoresistance with distinct jump-down behavior. The number of distinct jump-down behavior corresponds to number of NC plus one with little dependence of jump field to bias current. Thus, for large constrictions, the geometrical lateral constrictions act to ‘seal’ DWs. For smaller constrictions (overall resistance > 25 kΩ at room temperature), the MR response is more complex as DW are formed and pinned at the lateral constrictions. MR responses show jump-up behavior along with a complex dependence on jump field to bias current. Furthermore, we will discuss the complex switching behavior observed in small constrictions in series in terms of effects attributed to DW motion and spin-polarized transport across DWs.


9:20am  MI-ThM3 Racetrack Memory: A Current Controlled Domain Wall Shift Register. S.S.P. Parkin, IBM Almaden Research Center

Invited

Racetrack Memory promises a novel storage-class memory with the low cost per bit of magnetic disk drives but the high performance and reliability of conventional solid state memories. Unlike conventional memories, the fundamental concept of Racetrack Memory is to store multiple data bits, perhaps as many as 10 to 100, per access point, rather than the typical single bit per transistor. In Racetrack Memory the data is stored in the form of a series of magnetic domain walls along magnetic nanowires which are oriented either parallel or perpendicular to the surface of a silicon wafer. These distinct structures form “horizontal” and “vertical” Racetrack Memories. Conventional CMOS devices and circuits are used to provide for the creation and manipulation of the domain walls in the magnetic nanowires or “racetracks”. The domain walls are shifted back and forth along the nanowires using nano-second long current pulses via the transfer of spin angular momentum from the spin polarized current. Note that the shifting of neighboring domain walls in the same direction along a nanowire is not possible using conventional means of manipulating domain walls with localized magnetic fields.

In this talk we discuss progress towards building a Racetrack Memory and the fundamental physics underlying it. In particular, we discuss the current and field controlled dynamical motion of magnetic domain walls in magnetic nanowires formed from permalloy and related materials.


Transport properties of mesoscopic Hall crosses in localized magnetic and electric fields have received considerable attention because of their potential application to detection of localized magnetic fields with nanometer resolution. We recently made the first measurement of the response of the Hall voltage to the localized magnetic and electric fields in Hall crosses down to 50 nm x 50 nm cross-sections[1]. Hall crosses, based on InAs quantum well heterostructures, were scanned with a magnetically-coated probe which was also electrically gated to generate both localized electric and magnetic fields. We found that Hall crosses were sensitive to magnetic fields at the center of the cross. Also, the sensitivity to the localized magnetic field was found to be much larger than that to the localized electric field.

In this work, we report the response to localized magnetic and electric fields of similar crosses configured electrically in “the bend resistance (BR) geometry”, where current is passed between adjacent arms of the cross and a voltage is measured between the remaining arms. To our knowledge the response of such heterostructures in the BR configuration to localized magnetic and electric fields has not been previously reported. Figure 1 shows the BR response when the gate voltage applied to the probe and the current applied to the Hall cross are 1 V and -600 μA, respectively. The magnetic field created by the magnetic tip at the InAs quantum well is ~ 600 Oe. The prominent feature in this image is that the BR is sensitive to the localized fields both at the center and the two corners. This is quite different from the response of the Hall resistance[1] where magnetic
sensitivity was predominant at the cross center. By using both non-magnetic and magnetic probes, we have found that the response to localized electric fields is comparable to localized magnetic fields. Thus, the mapping in Fig. 1 shows significant contributions from both fields. It may therefore be possible to combine the electric field sensitivity of BR measurements with conventional Hall measurements to obtain localized electric and magnetic field information on the nanometer size scale from the same device.


9:40am  MI-ThM6 Isolation of Exchange- and Spin-orbit- Driven Effects via Manipulation of the Axis of Quantization, T. Komesu, G.D. Waddill, Missouri University of Science and Technology, S.W. Yu, M.T. Butterfield, J.G. Tobin, Lawrence Livermore National Laboratory
Double Polarization Photoelectron Spectroscopy (DPSS), using circularly polarized x-rays and true spin detection, has been performed using the 2p core levels of ultra-thin films of Fe and Co. This includes both the separation into magnetization- and spin- specific spectra and an Instrumental Asymmetry analysis. By simply choosing different axes of quantization it is possible to selectively manipulate the manifestation of exchange and spin-orbit effects. Furthermore, the underlying simplicity of the results can be confirmed by comparison to a simple yet powerful single-electron picture. The interplay of spin-orbit and exchange effects is of crucial importance to the understanding of complex electronic structure. For example, in the highly relativistic 5f systems, this interplay may be the key to understanding electron correlation. [1] One way to address this crucial issue is via photon-helicity- specific and spin-polarized photoemission from core levels, which is strongly dependent upon each of the two effects. [2] In fact, it is possible to observe strongly spin polarized photoemission from completely non-magnetic systems. [3] Here, using circularly polarized x-rays and true spin detection, it will be demonstrated how each of the effects, exchange and spin-orbit, can be isolated and quantified, simply by choosing different axes of quantization within the same overall experimental geometry. Moreover, the underlying simplicity of the results will be illustrated by the utilization of separate magnetization- and spin-specific spectra, as well as a simple but powerful single-electron model.

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References

I will review recent achievements with focus on current induced wall [5] and vortex dynamics in ferromagnetic elements [6].

Future magnetic microscopies are faced with the challenge to provide both spatial resolution and magnetization dynamics at the nanometer regime, a time resolution on a ps to fs scale and elemental specificity to be able to study novel multicomponent and multifunctional magnetic nanostructures and their ultrafast spin dynamics. The unique features of soft X-ray microscopy and the current developments with regard to improved X-ray optics and high brilliant fsec X-ray sources seems to make this technique a strong candidate to meet this challenge.

Collaboration with M.-Y. Im, B.L. Mesler, W.Chao (CXR), G. Meier, L. Bocklage, M. Bolte, R.Eiselt, B. Krueger, D. Pfannschik, U. Merkt (U Hamburg), S. Kasai, K. Yamada, K. Kobayashi, T. Ono (U Kyoto), Y. Nakatani (U Choju), H. Kohno (U Osaka), A. Thivilae (U Paris-Sud), D.H. Kim (Chungbuk U) and S.-C. Shin (KAIST) is greatly appreciated. Supported by the Director, Office of Science, Office of Basic Energy Sciences, Materials Sciences and Engineering Division, of the U.S. Department of Energy.

References

Surface Science Room: M - Session SS1+AS+TF-ThM

Surface Science of Hazardous Materials
Moderator: V. Grassian, University of Iowa

8:00am SS1+AS+TF-ThM1 Interactions of Nerve Agents with Model Surfaces: Computational Approach, J.R. Leszczynski, Jackson State University Laboratory

The talk summarizes the results of recent studies performed by our group. They include modeling of interactions of selected nerve agents with model surfaces. Among studies nerve agents are soman, sarin, tabun and their surrogates. We investigated different types of surfaces: metals, metal oxides and clays. The study was performed using various techniques of non-empirical, ab initio methods. Among predicted characteristics are molecular geometries, their interaction energies, electrostatic potentials, and IR spectra. We identify the most promising surfaces that may be considered for decomposition of the selected nerve agents. Also, predicted differences between selected processes for nerve agents and their simulants will be discussed.

8:40am SS1+AS+TF-ThM3 Ab-Initio Computational Approaches to the Adsorption of Chemical Warfare Agents, V. Bermudez, Naval Research Laboratory

Computational chemistry can be used to great advantage in dealing with chemical warfare agents (CWAs). Computation can be applied to reagents which are much too dangerous for routine experimentation as well as to non-traditional species which have not yet been (but could be) synthesized. Examples will be given from recent work on the interaction of the simulant dimethyl methylphosphonate (DMMP) and the real CWAs Sarin and VX with γ-Al2O3 surfaces. The γ-Al2O3 surface is an excellent prototype for a wide range of other metal oxides. DMMP, Sarin and VX all adsorb in the same way and with a similar adsorption energy (ΔEads) which depends strongly on surface acidity. A coordinatively-unsaturated tetrahedral Al(T4) site, which is a strong Lewis acid, forms an Al−O−P dative bond to the phosphonyl group. This is always the most favorable site, and an agent adsorbed by hydrogen bonding at an OH site will migrate to a bare Al(T4) site if one is available. The γ-Al2O3 lowest unoccupied orbital is a surface state associated with the Al(T4) site which lies just below the conduction band minimum. The energy of this site relative to vacuum is a quantitative measure of Lewis acidity and is directly reflected in ΔEads. The highest occupied orbital of the molecule is a non-bonding orbital on the phosphonyl O atom. The one-electron energy of this orbital also directly affects ΔEads. The hydroxylated surface forms Type I, II and III OH sites with O bonded to one, two or three Al’s respectively. Brominated acidity, and ΔEads for OH−→O−P bond formation, increase in the order I<II<III with the Type I
interaction being almost negligible. The anionic group in VX is found to be a strong base, capable of deprotonating an acidic Type III OH site to form an ammonium ion even in the absence of a polar solvent. The electronic ex-
citations of DMMP, Sarin and VX have also been investigated with the goal of identifying possible photochemical effects due to terrestrial solar radiation (TSR). This issue has been largely overlooked in previous agent-
fate studies. DMMP and Sarin are insensitive at energies below ~7 eV; however, vapor-phase VX can be excited near 4.3 eV which is at the upper end of the TSR. The excitation threshold changes slightly for adsorbed VX,
shifting to the red or to the blue depending on the nature of the surface. These results provide a predictive framework for understanding the effects of surface condition on the adsorption of VX and G-series CWAs on oxide surfaces.

(1) Supported by the Defense Threat Reduction Agency (DTRA)

9:00am SS1+AS+TF-ThM4 Computational Prediction of Physical Properties and Environmental Reactivity of Nitro-aromatic and Hydrogen Reach Explosives, L.G. Gorb, F.C. Hill, SpecPro, Inc., E.V. Muratov, A.G. Arimenko, A.V. Bogatsky Physical-Chemical Institute, Ukraine, Y.I. Khodol, Jackson State University, V.E. Kuzmin, A.V. Bogatsky Physical-Chemical Institute, Ukraine, J.R. Leszczynski, Jackson State University

Prediction of chemical and physical properties of explosives and products of their environmental degradation, instead of expensive and toxic chemical experiments, is a very important task from many points of view. Among them, the solubility (SW) is an extremely important property of chemical compounds. It plays a major role in definition of migration and ultimate fate of chemicals in the environment. In particular, high solubility leads to expeditious distribution in water, i.e., chemicals that rapidly and completely dissolve in water will be transported along with the general flow of water. High SW is generally associated with a very low affinity for adsorption to solid-water, e.g., soil particles or sediment. In addition, high water solubility is associated with accumulation of contaminants in living organisms.

Water solubility values for twenty seven nitro-aromatic and hydrogen reach compounds with experimentally measured values were computed using the conductor-like screening model for real solvent (COSMO-RS) based on the density functional theory and COSMO technique. We have found that the accuracy of the COSMO-RS approach for prediction of water solubility of liquid nitro compounds is impressively high (the errors are lower than 0.1 LU). However, for some solid nitro compounds, especially nitramines, there is sufficient disagreement between calculated and experimental values. In order to increase the accuracy of predictions the quantitative structure–property relationship (QSPR) part of the COSMO-RS approach has been modified. The solubility values calculated by the modified COSMO-RS method have shown much better agreement with the experimental values (the errors are lower than 0.5 LU). Furthermore, this technique has been used for prediction of water solubility for an expanded set of twenty three nitro compounds including nitroaromatic, nitramines, nitrosoisobenzene, nitro rich compounds and some their nitroso and amino derivatives with unknown experimental values.

Finally, an application of COSMO-RS approximation to the prediction of environmental reactivity for hydrogen reach explosives (alkali hydrolysis in water) has been briefly discussed

9:20am SS1+AS+TF-ThM5 A Material Approach to Enable Detection of Toxic Chemicals in Water by IR Spectroscopy, C.P. Tripp, University of Maine

We are currently developing a detection system based on the principles of infrared (IR) spectroscopy that operates in heterogeneous aqueous environments and provides fast detection (< 10 min) and high sensitivity to chemical warfare agents and other toxic chemicals with minimal false alarms. The key enablers to using infrared spectroscopy for aqueous based detection are the development of materials that lead to selective and robust sampling protocols. In this talk, I will present new sampling methods that are based on the use of surface functionalized adsorbents and reactive thin films coated onto a porous and IR amenable support. The coatings chemically react with a predefined class of compounds and identification of the specific chemical is provided by IR spectral analysis. Examples of this approach for low level detection of cyanide, metals, pesticides, and chemical warfare agents in water will be demonstrated.

10:40am SS1+AS+TF-ThM9 Surface Science and its Application to Energetic Materials, V.J. Bellitto, J.M. Kelley, D.N. Sorensen, Naval Surface Warfare Center

Composite explosives and propellants are heterogeneous admixtures of crystalline powders in a rubbery binder. Materials such as aluminum are added to enhance specific performance criteria. The aluminum although improving performance in systems may not be efficiently consumed. Placement of explosives and propellants in closer proximity with the metal is expected to provide performance enhancements. The novel material should have more complete combustion and faster energy release rates as problems with heat transfer and diffusion rates are overcome.

We have undertaken a research effort to gain a fundamental understanding of the metal/explosive interaction. In performing experiments novel interfaces are produced which are not obtainable under ambient conditions. The research reveals possible avenues for the development of new energetic materials with improved performance.

In this work, X-ray photoelectron spectroscopy (XPS) was used to study the interaction of aluminum with cyclotrimethylene trinitramine (RDX) and the resultant products analyzed via Differential Scanning Calorimetry (DSC). For RDX, the spectrum of the N 1s region has two easily discernable peaks assigned to the nitro group and ring structure nitrogen. Upon the initial interaction of aluminum with RDX, the N 1s spectrum reveals that the nitrogen peak associated with the nitro group is diminished compared to that of the ring structure. This is an indication of the preferential reaction of the nitro group with the aluminum, leaving the ring structure intact. The data also shows the preferential formation of aluminum oxide species over aluminum nitride species. Continued deposition of aluminum produces aluminum layers over the initial oxide layer. The DSC data demonstrates an increase in decomposition energy through the placement of metal directly onto the explosive surface.

11:00am SS1+AS+TF-ThM10 Characteristics and Stability of Oxide Films on Plutonium Surfaces, H.G. Garcia Flores, University of Nebraska-Lincoln and Los Alamos National Laboratory, A.L. Broach, D.P. Moore, Los Alamos National Laboratory, D.L. Pugmire, Los Alamos National Laboratory and University of Nebraska-Lincoln

The oxidation of plutonium metal continues to be an area of considerable active research. The reaction chemistry has many implications for production use, storage, and disposition of this reactive material. Developing an accurate physical model of the structures, oxidation states, and oxygen concentration gradients present during oxidation are essential to understanding this process. Traditionally, the stable oxides of plutonium have been thought to be plutonium sesquisioxide (PuO2.0, O/Pu=1.5, Pu3+) and plutonium dioxide (PuO2, O/Pu=2.0, Pu4+), existing in a layered structure on oxidized plutonium metal. Many studies of this system are performed under ultra-high vacuum (UHV) using surface sensitive techniques to probe oxidation states, electronic structure, and surface chemistry.

Here, we report on a detailed study using x-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) to measure the relative concentrations of oxygen and plutonium, as well as the resulting oxidation states in the near-surface region. It has previously been shown that under UHV conditions, PuO2 undergoes an auto-reduction reaction to the more stable PuO2.0. The auto-reduction of PuO2 occurs as oxygen diffuses from the surface, through the oxide-film, to the metal-oxide interface.1 The results of this study show a much greater than anticipated extent of auto-reduction and challenge the commonly held notion of the stoichiometric stability of PuO2.0 thin-films, especially in the presence of plutonium metal. The data indicates that a hypo-stoichiometric plutonium oxide (Pu2O3-α) exists at the metal-oxide interface. A new model of the plutonium/oxygen thin-film system will be proposed and its applicability to thicker-films will be discussed.


Thin Film

Room: B4 - Session TF-ThM

Nanostructuring Thin Films II

Moderator: P.D. Rack, University of Tennessee

8:00am TF-ThM1 Nanostructure of Gold Film Over Vertically Aligned Carbon Nanotube Surface Impaction on Immobilization of Alkanethiols R. Desikan, North Carolina State University, T.E. McKnight, Oak Ridge National Laboratory, P.D. Rack, University of Tennessee, A.V. Melechko, North Carolina State University

Chemical self-assembly has been widely used for several applications including surface modification and functionalization. The physics and chemistry of alkanethiol self-assembled monolayers (SAM) has been extensively studied. It is well known that SAM structures of alkanethiol are strongly influenced both by the surface structure of the underlying gold
substrate. It has also been shown that the adsorption of alkanethiols onto gold surfaces having large, flat grains produces high-quality self-assembled monolayers. In this study, we have investigated the effect of O₂ partial pressure over carbon nanofibers coated with gold thin film. The film nanostructure is strongly affected by the morphology of the surface on these high aspect ratio 3D features. The thiolated molecules are chosen due to the strong affinity of sulfur head groups with the gold surface of the carbon nanofibers. The difference in surface stress response alkanethiol of adsorption on large-grain and small-grain size in Cu-Ag composite films as compared to pure copper or silver thin films. Not only is a stronger surface stress response alkanethiol of deposits film will be discussed. The characterization of molecular substrates. We will present observations of how the surface structure of the monolayer. In this study we have investigated the effect of SAM formation with differences in alkanethiol coverage and SAM structure on those substrates. We will present observations of how the surface structure of the underlying gold substrate influences the kinetics of SAM formation. It has been shown that in the case of gold surfaces with small grain sizes (<100 nm), access to the high coverage, standing-up phase is inhibited. A comparison of alkanethiol coverage on increasing the grain size on the gold surface was discussed. The characterization of molecular coverage as a function of the gold grain size with an x-ray photoelectron spectroscopy will be presented.

8:40am TF-ThM3 Spontaneous Growth of In-whiskers from In-Y Thin Films Prepared by Combinatorial Magnetron Sputtering Technique. T. Takahashi, A. Abdulkadhim, D. Music, J.M. Schneider, RWTH Aachen University, Germany

In-Y binary thin films with a composition gradient were prepared using a combinatorial magnetron sputtering technique. In-whiskers grow spontaneously from the film surface at room temperature upon exposure to air. Whisker morphology and population vary with the In to Y ratio. An appreciable amount of In-whiskers is formed at film compositions close to In:25 at.%Y. The In-whisker thickness ranges from a few hundreds of nanometers to a few micrometers. In order to identify the whisker growth mechanism, temporal changes of the film surface upon air exposure were captured using scanning electron microscopy. X-ray micro diffraction was employed for studying the structural evolution during the In-whisker growth in air. The results show that the In-whiskers grow not from the tip but from the root. The whisker growth rate was as high as 150 nm/s. The growth of In-whiskers is found to be related to the incorporation of oxygen into the film during air exposure. Correspondingly, the In concentration within the film decreases as In-whiskers grow. The mechanism of the spontaneous In-whisker growth presented here can be understood based on the stress-induced extrusion of In-whiskers due to the selective room temperature oxidation of Y in spattered In-Y thin films.

9:00am TF-ThM4 Photothermally Induced Microchemical Functionalization of Organic Monolayers. A. Schroeter, B. Klingebiel, N.O. Hartmann, University of Duisburg-Essen, Germany

Photochemical routines are widely recognized as a versatile means to fabricate multifunctional patterned organic monolayers with laterally alternating chemical terminations. The lateral resolution, in turn, usually is limited by optical diffraction, that is, the fabricated structures are not much smaller than the wavelength even when highly focusing optics are used. A simple routine for sub-wavelength patterning of organic monolayers relies on photothermal processes, which can utilize the advantage of nonlinear effects [1]. In photothermal processing a focused laser beam is used to locally heat the substrate and initiate thermal decomposition of the monolayer. Silane-based monolayers can be patterned from the micrometer-range down to the sub-100 nm range. In analogy to photochemical routines, it is tempting to explore photothermal procedures which allow to locally functionalize organic monolayers. Here we report on a simple photothermal procedure for local boronation of organic monolayers [2]. Surface-oxidized silicon samples are coated with alkylsiloxane monolayers. Local irradiation with a focused beam of an argon ion laser (λ = 514 nm) in gaseous bromine leads to boronation of the monolayer in a confined micrometer-sized reaction zone. While irradiation induces photolysis of bromine molecules in the gas phase, the local temperature rise of the substrate in the focal area allows for boronation of the alkyl chains. Thus locally brominated surface structures are fabricated. In conjunction with other chemical transformations this provides an efficient route to a broad variety of functional groups. This approach can be used to fabricate multifunctional patterned or ganic monolayers with laterally alternating chemical terminations which can be used for the selective room temperature oxidation of Y in spattered In-Y thin films.


TiO₂ and Fe₂O₃ nanoparticles are of significant importance in both chemical and biological applications. TiO₂ nanoparticles are used in paint, coatings, food, solar technology and many other areas. Fe₂O₃, as well as other magnetic nanoparticles, are used in the biomedical industry in drug delivery schemes as well as for magnetic resonance imaging contrast agents. Silica-coated TiO₂ and Fe₂O₃ nanoparticles have distinct functionalization properties over those of uncoated nanoparticles. Plasma-enhanced chemical vapor deposition (PECVD) was employed to conformally coat TiO₂ and Fe₂O₃ nanoparticles with SiO₂ and amine-containing films, thereby creating composite nanomaterials. Hexamethyldisiloxane (HMDSO)/O₂ plasmas were used to create SiO₂ and SiO₂–C₃H₇–coated nanoparticles and pulsed hexylamine (HexAm) plasmas were used to create amine-containing hybrid monolayers, all of which were analyzed using Fourier-transform infrared spectroscopy (FTIR), x-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and magnetic susceptibility. Films deposited on the NaNanomaterials showed little difference from those deposited on flat substrates. The performance of the TiO₂ nanoparticles was tested using UV-vis spectroscopy to determine dispersion characteristics of SiO₂-coated TiO₂ materials, which can give information about the agglomeration of the nanoparticles in solution. Notably, the coated materials stay dispersed longer in polar solvents, suggesting the coated nanoparticles may be better suited for applications involving colloidal suspensions. Magnetic susceptibility characterized the magnetic properties of the Fe₂O₃ nanoparticles before and after film deposition. Comparison of the mechanical and chemical properties of different composite nanomaterials will be discussed along with the influence of film composition on performance.

For more than 100 years the plasmonic periodic table has been dominated by two elements, Ag and Au. The change in the surface plasmon polariton (SPP) signal in Au thin films is currently one of the most widely used methods for detecting binding interactions in biological systems. Despite broad interest, there has been sparing fundamental research into new plasmonic materials. Here, we elucidate some equivalences regarding plasmonic phenomena in conducting metal oxides, specifically indium tin oxide (ITO), and Au. In contrast to Ag and Au, conducting metal oxides offer the possibility of tuning both the location of the metallic resonance and its width according to deposition conditions. We investigate properties of ITO and ITO/Au layers by reflectance spectra $R_p$ and $R_s$ obtained for light polarized parallel and perpendicular, respectively, to the plane of incidence. Data were obtained in the Kretschman configuration. These data reveal two distinct types of plasmonic phenomena, one due to a capacitive-type oscillation that can only occur for very thin conducting films and the second being the usual surface plasmon resonance. One or the other can be realized either by changing the ITO thickness or by depositing either metallic or nanostructured Au on the ITO to change boundary conditions. The results can be understood completely through a combination of the Drude model for free carriers in a metal, Bruggeman effective-medium theory, and the Fresnel equations. This provides a new dimension for engineering plasmonic phenomena for investigations of molecules adsorbed at interfaces.

11:20am  TF-ThM11 Micro and Nanostructured Interfaces for Therapeutic Delivery. T.A. Desai, University of California, San Francisco

Efficient drug delivery remains an important challenge in medicine. Continuous release of therapeutic agents over extended time periods and in accordance to a pre-determined temporal profile; local delivery at a constant rate to overcome systemic toxicity; improved ease of administration, and increasing patient compliance are some of the unmet needs of the present drug delivery technology. This talk will discuss in vivo drug delivery strategies that capitalize on the strengths of micro and nanofabrication. By taking advantage of our ability to control topography and chemistry at submicron size scales, we have developed organic and inorganic interfaces which modulate cell function while at the same time allow for controlled drug release kinetics. Due to our ability to create monodisperse features (pores, wires, and hollow tubes) as small as several nanometers in a variety of non-planar biocompatible materials, these interfaces offer advantages in their reproducibility, stability, and their ability to intimately contact cell and tissue surfaces. Such nanoengineered interfaces may be optimized for biomolecular selectivity and surface bioactivity, leading to unique interfacial properties not achieved through existing drug delivery approaches. Nanotechnology can add functionality to current drug delivery platforms while becoming an enabling technology leading to new basic discoveries in the biological sciences.
Advances in Microfluidics for BioMEMS
Moderator: G.W. Rubloff, University of Maryland

2:00pm BM+MN+MS+TF+Bi-ThA1 Advances towards Programmable Matter, D. Erickson, Cornell University

A dichotomy exists between the bottom-up self-assembly paradigm that seeks to create regular structures at the nanoscale, and top-down approaches used to fabricate arbitrary structures serially at larger scales. The former of these enables rapid, highly parallel assembly but lacks critically important features of the latter such as the ability to arbitrarily direct the assembly location and perform error correction. We and our collaborators have recently proposed an alternative approach which combines these two based on dynamically programmable self-assembling materials, or programmable matter. The uniqueness of our approach is that it uses dynamically-switchable affinities between accumulating components facilitating the assembly of irregular structures. In this talk I present an overview of our approach and detail some of the analytical and experimental advances towards a programmable matter system we have recently made. These include the development of a multi-layer microfluidic chip for improved far-field assembly, the demonstration of near-field inter-tile affinity switching using a thermoholographic assembly fluid and the ability to enhance assembly in three dimensions using unique fluid-structure interactions.

2:40pm BM+MN+MS+TF+Bi-ThA3 A Multilayered Microfluidic System with Buried Channels and Cell Compartmentalization for Engineering Heterogeneous Neural Networks, C. James, A. Greene, A. Schiess, G. Bachand, Sandra National Laboratories, M. Romero-Ortega, University of Texas at Arlington

Current technology for engineering in vitro neural networks utilizes cell guidance cues that yield only temporary networks (<1 month) as the cells rapidly diverge from their designed guidance cues during development of the culture. In addition, these engineered networks are typically comprised of homogeneous populations of neurons, thus the lack of multiple neuron types produces oversimplified networks that do not adequately represent in vivo networks. In addition, effective control over synaptic connections between different populations of neurons has not been demonstrated. Here, we describe a novel hybrid technology of multi-layered microfluidics with compartmentalized chambers containing multiple neuron types for engineering robust and complex neural networks with high resolution and organization of synaptic connections. The device contains a first level of microfluidic channels etched 1-2 microns into the base glass substrate. These channels are fabricated with a novel process using a silicon nitride mask for hydrofluoric acid undercut etching to create buried microfluidic channels for robust containment and guidance of neurons. After the etching process, photore sist lift off is performed to selectively adsorb poly-L-lysine (PLL) within the barried channels for improved neuron attachment and outgrowth at pre-defined locations. Polarity control of neurons is provided through a continuous set of guidance cues to promote axon development, while interrupted sets of guidance cues promote dendrite development. Current results show that axons and dendrites are positioned at predefined locations with a >45% accuracy. A second level of microfluidic channels and large (~mm) cell chambers are fabricated in polydimethylsiloxane (PDMS) from two-level SU-8 master molds. The base glass substrate and the PDMS substrate are aligned and bonded to create interconnects between channels in both substrates. These interconnects provide interaction regions for the development of synapses between growing neurites from cells in different chambers. We are currently applying this technology to engineer corticostriatal networks, an important region of the brain responsible for integrating multiple informational inputs crucial to complex decision-making in higher mammals. Specifically, we are using patch-clamp electrophysiology to track the development of synaptic memory in the form of long-term depression and potentiation (LTD/LTP) in these engineered networks.

3:00pm BM+MN+MS+TF+Bi-ThA4 Vesicle Production on a Microfluidic Platform using pH Sensitive Block Copolymers, L.E. Brown, The University of Sheffield, UK, S.L. McArthur, Swinburne University of Technology, Australia, G. Battaglia, P.C. Wright, The University of Sheffield, UK

The development of pH sensitive, biocompatible block copolymer vesicles has enabled the intracellular delivery of water soluble drugs and proteins. Improving the encapsulation efficiency of the vesicles is now a critical parameter. Transferring the production method to a microfluidic device creates the potential to vary the encapsulation conditions and improve this efficiency. In this work, a flow focussing microfluidic device is used. The self-assembly of PMPC-C-PDPA block copolymer vesicles is induced within the device by changing the pH of the flows within the microchannels. The use of pH shift eliminates the need for organic solvents currently required for glass capillary production methods. This enables the biocompatibility of the block copolymers to be maintained, an essential factor for their application as molecular delivery vehicles. The flow focussing microfluidic device was produced through standard soft lithography techniques. A three-channel flow system is used with the copolymer in solution at pH6 in the central channel and aqueous buffered solutions flowing in the channels either side. The laminar flow conditions within the microfluidic device result in a pH gradient at the interfaces where the three channels meet and where the block copolymers self-assemble into vesicles. These vesicle formation processes have been imaged using confocal microscopy via PRET with a block copolymer containing both rhodamine and fluorescein tags. Dynamic light scattering and TEM were used to confirm vesicle formation. With 50nm to 250nm vesicles continuously being produced within the device it was then possible to investigate whether higher encapsulation efficiencies can be achieved using the microfluidic device. The protein myoglobin was introduced through the central channel along with the copolymer. Spectrophotometric analysis indicated the overall efficiency of the encapsulation process within the device is not a significant improvement on the standard bulk methods currently used. Microfluidic sonication of the vesicle solution containing the molecule to be encapsulated. Despite this, the continuous nature of microfluidic devices, as well as the lack of organic solvents being used in the production process indicates that the development of these devices offers a viable alternative production method for polymer vesicles that may enable the increases in encapsulation efficiency to be achieved. Work is ongoing to achieve this using the same pH shift mechanism within a glass capillary microfluidic device.

3:40pm BM+MN+MS+TF+Bi-ThA5 Integration of a Microfluidic Flow Cell Array with SPR Microscopy for In Situ Microarray Formation and Biomolecule Interaction Analysis, J. Liu, M. Eddings, University of Utah, A. Miles, Wasatch Microfluidics, B. Gale, J. Shumaker-Parry, University of Utah

Analysis of biomolecule interactions based on surface plasmon resonance (SPR) microscopy provides a label-free approach to monitoring arrays of biomolecule interactions in real time. Typically the microarray sensing surface for these measurements is prepared ex situ and a single or few channel flow cell is used for the biomolecule interaction studies. The multiplexing nature then is derived from the microarray and the number of samples that can be run simultaneously is rather limited, diminishing the potential application for assays requiring a high-throughput approach due to a large number of samples. One example of this is the need to monitor for anti-drug antibodies from a large pool of patient samples during clinical trials of biotherapeutics. We demonstrate the capability of a multi-channel microfluidic flow cell array (MFCA) to expand the throughput capability when integrated with SPR microscopy. In addition, the MFCA provides an in situ approach to array fabrication that allows full characterization of the biomolecule immobilization process. We use the MFCA for delivery of sample solutions with continuous flow in 48 channels in parallel for rapid microarray creation and binding analysis while using SPR microscopy for real-time monitoring of these processes. Label-free measurement of antibody-antibody interactions demonstrates the capabilities of the integrated MFCA-SPR microsystem and establishes the first step towards the development of a high-throughput, label-free immunogenicity assay. We demonstrate a limit of detection (LOD) of ~80 ng/ml for the particular antibody pair we studied. This LOD is ~6 times lower than the industry recommended immunogenicity assay detection limit. The high-throughput nature of the integrated system allows a large number of replicate experiments, including control experiments, to be performed simultaneously on the same sensor surface in a short time. The integrated system also will be applicable for more general high-throughput protein-antibody based analysis.


Nanochannels with a diameter of about 100nm2 are a novel method for stretching DNA for genomic investigations. Such devices are implemented through standard nanolithography in fused silica. The elongation of DNA
results from an interplay of steric and entropic effects. Previous applications of nanochannel stretching included sizing, restriction mapping, and observation of transcription factor binding.

We show here that nanochannels can also be used to map the site-specific epigenetic state of DNA. In particular, we show here that the concept by nanofocusing can be extended to chromatins, or DNA complexed to histones, and that the stretching is within the range expected from the de Gennes theory. We also demonstrate that the location-resolution cytidine methylation state of DNA can be mapped by specific fluorescent labeling. We will discuss the basic operation of these technique, and the application to artificial substrates with predefined epigenetic marks.

4:40pm BM+MN+MS+TF+BI-ThA9 Microfluidic Models of Endothelial Cell Sprouting in Response to Biomechanical and Biochemical Microenvironments, A.M. Shamloo, S.C. Heilshorn, Stanford University

A novel microfluidic device was designed in order to generate stable, quantifiable concentration gradients of biomolecules in a cell culture chamber. We used the device to study 2-D and 3-D cell-cell and cell-matrix interactions in vitro. Endothelial cells form the inner lining of blood vessels and initiate a critical step in angiogenesis (the sprouting of new blood vessels) during wound healing and cancerous tumor growth. Therefore, a deeper understanding of the critical biomechanical and biochemical factors regulating endothelial cell sprouting can lead to improved clinical therapies for a wide range of diseases. Concentration distribution of soluble growth factors inside the microfluidic cell culture chamber was determined by simulation and experiment, and the stability of the gradient was verified over multiple hours. This device allows independent tuning of the matrix density, the growth factor absolute concentration, and the growth factor concentration gradient steepness within a single experimental platform. Sprout formation of dermal microvascular endothelial cells was studied within collagen gels of varying density (0.3–2.7 mg/mL, corresponding to shear moduli of 8–800 Pa) that contained stable gradients of soluble vascular endothelial growth factor (VEGF). These experiments revealed that endothelial sprouting into multi-cellular, capillary-like structures is optimized at an intermediate collagen matrix density (G’ ~ 100 Pa). At lower matrix densities, cells were more likely to lose their coordinated motion and migrate as individual cells through the matrix; while at higher matrix densities, the cells formed broad cell clusters that rarely elongated into a sprout. Sprout thickness directly correlated with matrix rigidity, with thicker and less frequent sprouts present in gels with the highest shear moduli. Intriguingly, our 3D experiments also found that endothelial sprouts alter their sensitivity to VEGF depending on the matrix density, suggesting a complex interplay between biochemical and biomechanical factors. As matrix stiffness increases, steeper VEGF gradients and higher VEGF absolute concentrations are required to induce directional sprouting. In more compliant gels, endothelial sprouts that originally misaligned were able to turn and properly reorient parallel to the VEGF gradient; however, this turning phenomenon was only rarely observed in stiffer gels. These results demonstrate that matrix stiffness is an effective factor in stabilization and elongation of endothelial cells during angiogenesis and suggests new anti-angiogenic strategies for potential cancer treatment as well as pro-angiogenic strategies for regenerative medicine scaffolds.

5:00pm BM+MN+MS+TF+BI-ThA10 Plasma Polymisation of PDMS for Microfluidic Applications, S. Forster, A.G. Pereira-Medrano, G. Battaglia, P.C. Wright, University of Sheffield, UK, S.L. McArthur, S.C. Heilshorn, Swinburne University of Technology, Australia

Polydimethylsiloxane (PDMS) has become the most popular material choice for a wide range of microfluidic bioengineering applications, including proteomics, protein separations and drug discovery and development. The reasons its popularity lie mainly in its highly advantageous fabrication requirements when compared to traditional materials such as glass and silicon. However, PDMS has some fundamental drawbacks, namely a lack of functionality present at the surface, high protein adsorption and an inability to retain stable surface modification due to its motile hydrophobic monomer. These factors can lead to the loss of specificity and sensitivity in many bioassays. Due to this reason much work has been completed looking into surface modification of PDMS for such applications. Here an alternative method of stable surface modification of PDMS for many microfluidic applications through enhanced curing conditions and plasma polymerisation is shown. Stable and functional surface coatings have been achieved on bulk PDMS and within microfluidic channels. Bulk surfaces were characterised using a combination of XPS and ToF-SIMS, while coated micro-channels were tested using confocal microscopy and various assays. This methodology has been used in many applications and one area where it has proven extremely useful is in microfluidic proteomics where surface properties are of paramount importance due to the inherently small volumes and quantities associated with biological samples. Firstly, plasma polymer coated PDMS micro-channels were utilised for on-chip IEF protein separations (i.e. separating proteins based on charge) and showed reduced electroosmotic flow (EOF) and protein adsorption in the device. Second, a µIMER (micro-immobilised enzyme reactor) was produced using plasma polymer coated PDMS devices. The µIMER was then used in ‘shotgun’ protein digestion applications in conjunction with Mass Spectrometry where it was shown to have numerous advantages over untreated PDMS devices, as well as comparing favorably to published work on other µIMER systems. The device was used to digest single protein and multiple protein samples as well as complex membrane protein samples. Finally, successful covalent bonding of plasma polymer coated devices has led to the completion of polymer vesicle immobilisation within a microfluidic channel. Initial work looking at the immobilisation of polymer vesicles with an encapsulated digestive enzyme has shown to increase proteomic digestion efficiency. This success opens up the possibility of translating this technique into many potential microfluidic applications through the extensive versatility of encapsulation within polymer vesicles.

Thin Film Room: B4 - Session TF-ThA

Next Generation Processing

Moderator: S. Gupta, University of Alabama

2:20pm TF-ThA2 Resonant Infrared Matrix-Assisted Pulsed Laser Ablation of Electroluminescent Dendrimer Thin Films, R.D. Torres, University of Florida, S.L. Johnson, Vanderbilt University, J. Hwang, University of Florida, P.L. Burn, University of Queensland, Australia, R.F. Haglund, Vanderbilt University, P.H. Holloway, University of Florida

The processing to create polymer thin films for organic light emitting diodes is limited to wet methods since molecular pyrolysis prevents the use of dry vacuum thermal evaporation methods. Wet methods have critical limitations such as poor thickness control, drying patterns, re-dissolution of previous layers, substrate limitations and others. In this work, a novel approach for the growth of thin polymer films, Resonant Infrared Matrix-Assisted Pulsed Laser Ablation (RIM-PLA), has been studied as a possible dry conformal deposition method for electroluminescent polymers. RIM-PLA was successfully used for the deposition of two model dendrimers: fluorescent and phosphorescent Ir-cored. A free-electron laser was tuned to the resonance frequency for the vibrational modes of two matrix solvents: toluene and chloroform. For chloroform, the alkyl C-H stretch (3.32 µm) and C-H bending (8.18 / 8.28 µm) modes were compared. For toluene, the C-H stretch (3.31 µm) and aromatic C=C stretch (6.23 µm) modes were compared. Targets made from flash-frozen, low-concentration solutions of the dendrimers were irradiated at each frequency while varying fluence and exposure times. The molecular structure integrity of the targets was characterized by NMR and FTIR spectroscopy, and MALDI-TOF mass spectrometry. The deposited film quality was characterized by surface roughness and topography measurements (AFM, stylus profilometry, optical/fluorescence microscopy), and luminescence (photoluminescent spectra and quantum yields). The RIM-PLA deposited films were compared with films that were spin-coated from solution. It was found that the ablation characteristics of each mode were dependent on the solvent and not the dendrimer. Calculations from a thermal-rise model show that FEL pulsed-irradiation results in heating rates on the order of 10⁶–10⁸ K/s depending on the absorption coefficient of the selected mode. As a result, localized temperatures in the melted focal volume approach the solvent’s superheat limit (~0.8 Tc), leading to spinodal decay and subsequent phase explosion. I.e. ablation occurs via a rapid spontaneous homogeneous nucleation of vapor bubbles within the melted solvent, which in turn develops a shockwave that propagates and ejects different size droplets from the target surface. The size and the frequency of the droplets depend on the absorption properties of the selected mode. The deposited films’ characteristics correlate well with the thermal-rise model.

2:40pm TF-ThA3 Etching Technology for Patterned Media used for Ultra High Density Hard Disk Drive, D.D. Djayaprawira, Shinde, Canon-ANELVA Corporation, Japan

INVITED Patterning of magnetic recording media is one of the proposed approaches for extending magnetic storage densities beyond 1Tbit/in². This approach is based on patterning the recording media into magnetically separated areas, which can be used for storing a single bit of information. Here we introduce the etching technology and equipment for discrete track recording media (DTM) mass-production. A unique requirement for magnetic recording media patterning system is that the system should be able to etch both sides of the media. Furthermore, since a typical media sputtering time in a process chamber is less than 4 seconds, a reasonably high etching rate
approach is necessary. To this end, we developed reactive ion etching (RIE) and ion beam etching (IBE) modules based on inductive coupled plasma (ICP) source. The advantages of using the ICP source are the high density plasma and the plasma are confined within the cavity. The high density plasma contributes to high etching efficiency. The confined plasma minimized the interference of ICP sources and enable the mounting of RIE or IBE modules facing each other. Recent etching results using RIE and IBE modules will be presented, and the feasibility of our approach for mass-production of DTM will be discussed.

We report the resonant infrared pulsed laser deposition (RIR-PLD) technique for depositing novel, functional polymers, small organic molecules and nanoparticle-loaded polymers. Film deposition based on resonant infrared (IR) laser ablation is enabled by resonant excitation of a localized, intra-monomer vibrational mode of the target material, such as a C-H stretch, this leads to low-temperature volatilization and deposition of undamaged small molecules, polymers and even nanoparticles. Because the mid-infrared photons used in this process have energies far below those required to break the bonds that connect monomer units, RIR laser irradiation ablates polymers without photofragmentation, unlike ultra-violet pulsed laser deposition (UV-PLD). In this paper, we will demonstrate successful RIR-PLD deposition of selected materials that are essential to organic light emitting diode (OLED) technology; (1) light emitting small-molecule and polymer materials such as Alq3 (Tri(is8-hydroxyquinolinate)aluminium), MEH-PPV and conducting polymer PEDOT-PSS (Poly(3,4-ethylenedioxythiophene) poly(styrene sulfonate)); (2) polymeric barrier film such as cyclic olefin copolymer (COC) and Teflon®; and (3) nanocomposite materials based on TiO2 and metal nanoparticles that serve as brightness enhancement layers and transparent conducting electrodes. The deposited films are characterized by SEM (scanning electron microscopy) and FTIR (Fourier-transform infrared spectroscopy), photoluminescence. We will also present the comparison of film properties as they depend on different mid-infrared laser choices, such as a picosecond, tunable free electron laser (FEL), Er:YAG laser and picosecond optical parametric oscillator (OPO).

4:00pm TF-ThA7 Room Temperature Synthesis of Silica and SiO2-TiO2 Composites for use as Barrier and Anti-Reflection Coatings. P.C. Rowlette, C.A. Wolden, Colorado School of Mines
Thin film oxides are ubiquitous in photovoltaics, serving as transparent electrodes, passivation layers, optical coatings, and moisture permeation barriers. Pulsed plasma enhanced chemical vapor deposition (PECVD) was used to deliver digital control of SiO2-TiO2 optical properties over room temperature. Sub-angstrom control of SiO2 deposition rate was demonstrated by varying the SiC1 density at low exposure levels (~250 L). No impurities were detected by XPS or FTIR, and the high film quality was confirmed by etch rate measurements. Crack-free SiO2 films have been deposited on polymer substrates, and we are currently assessing their barrier performance.

Next, SiO2-TiO2 composites were formed by pulsed PECVD using SiC1 and TiCl4 as precursors. The refractive index of the SiO2-TiO2 material system spans a large dynamic range (n: 1.4 – 2.4), and as such is of great interest for optical coatings. Alloy formation was investigated by maintaining constant delivery of one precursor while varying the second. Film composition was assessed by spectroscopic ellipsometry, XPS, and FTIR. It is shown that the alloy composition and refractive index can be tuned continuously over this broad range using pulsed PECVD. These two precursors were found to be highly compatible, with the alloy growth rate simply reflecting the sum of the contributions from the two individual precursors. The digital control over both thickness and composition offered by pulsed PECVD was demonstrated through room temperature synthesis of antireflection (AR) coatings for crystalline silicon solar cells. One, two, and three-layer AR coatings based on the range of indices offered by the SiO2-TiO2 system were designed and optimized to minimize the reflectance across the visible spectrum. AR coatings based on these designs were then fabricated, and in each case the measured optical performance was found to be in excellent agreement with model predictions. The integrated reflectance across the visible spectrum was reduced from 3% for uncoated wafers to 2.5% for the 3-layer AR coating.

We investigated the material properties of expanding thermal plasma deposited a-Si:H thin films, providing a record-low surface recombination velocity of 1.6 cm/s (at injection level of 1010 cm−2). a-Si:H thin films with different thicknesses have been deposited at a high deposition rate (1.2 nm/s) on both sides of low resistivity (1-5 Ohm cm), 260µm thick, n- and p-type c-Si FZ wafers. The material properties of a-Si:H films have been characterized by Fourier Transform Infrared diagnostic and Spectroscopic Ellipsometry. The surface passivation of the wafers has been determined by photoconductivity decay measurements of the effective carrier lifetime. The investigation points out that the growth of ETP a-Si:H films begins with the formation of a thin porous layer (~10 nm) with a refractive index of 3.9 (at 2 eV) and microstructure of Young's modulus parameter (R*) of 0.50. Despite the open network formation at the a-Si/c-Si interface, it has been found that the a-Si:H film achieves a recombination velocity as low as 12 cm/s (at 1·1017 m−3cm−1 injection level on n-type wafers). The good passivation is probably due to the large hydrogen content of the a-Si:H film, which terminates dangling bonds present on the c-Si surface. After this initial growth, a dense a-Si:H network develops with a refractive index of 4.5 (at 2 eV) and R* = 0.03. The surface recombination velocity decreases linearly with the a-Si:H thickness, achieving a record value of 1.6 cm/s (at 1·1017 m−3cm−1 injection level) for 90 nm thick a-Si film on n-type wafers. As compared to hot wire CVD and radiofrequency PECVD techniques, ETP is capable to deposit thin a-Si:H films with outstanding surface passivation at higher temperature (250°C) and higher deposition rate (1.2 nm/s). This reactivity in time stability has been investigated. Effective carrier lifetime is found to decrease following a stretched exponential. Photo-electronic properties of a-Si:H are known to relax in time in a similar fashion. These results therefore suggest a correlation between the photo-electronic properties of the a-Si:H/c-Si interface and a-Si:H bulk material.

The development of CdTe solar cells over the last 35 years has been advanced by introducing various modifications in the fabrication process such as post-deposition CdCl2 heat treatment and CdS deposited by chemical-bath deposition (CBD). The presence of oxygen during various stages of CdTe/CdS device fabrication has also been shown to be critical. In this work, we have investigated new methods to eliminate oxygen in the fabrication process while maintaining the advantages, such as post-deposition CdCl2 heat treatment and CdS deposited by both techniques as well as oxygen in the fabrication process. The first devices reported by Kodak to have efficiencies greater than 10% were fabricated by close-spaced sublimation (CSS) in oxygen ambient. CdCl2 heat treatment, crucial for achieving high efficiency, is usually carried out in ambient containing O2. In previous studies on devices fabricated using CBD CdS, CSS, and sputtering, the interfusion of the CdS/CdTe interface and a-Si:H layer has been investigated. We have fabricated devices with sputtered CdS films that have efficiencies near 14%, comparable to our baseline devices using CBD CdS. In this paper, we present our recent work on CdTe devices using CdS prepared by sputtering and CBD. For sputtered CdS films, we varied O2 content in the sputtering ambient from 0% to 3%. CdTe films were deposited by CSS in oxygen ambient and conventional physical vapor deposition in high vacuum. We will present detailed characterization of the CdS/CdTe interfusion at the interface. Specifically, we used secondary-ion mass spectrometry for samples fabricated under different conditions to investigate the dependence of interfusion characteristics on oxygen ambient during fabrication. We will also present the results of our transmission electron microscopy analysis on the structural properties of the CdS/CdTe interface and a correlation to the microstructure of CdS deposited by both techniques as well as oxygen in the fabrication process. We will fabricate devices using the samples from these studies and characterize the devices using standard current-voltage analysis. We will then analyze the results to correlate the device properties with the interface properties.

5:00pm TF-ThA10 Large-Scale Simulation of Nanoimprint Lithography. M. Chandross, G.S. Grest, Sandia National Laboratories
The production of surfaces with controllable/tunable nanostructures over large areas and at throughputs practical for commercial applications can be very difficult. Two processes of recent interest have been step-flash imprint lithography (SFIL) and nanoimprint lithography (NIL) in which nanoscale masks are imprinted into polymeric materials to create features with nm-scale resolution. Empirical approaches are currently the norm for industrial scale-up but are often time-consuming and expensive. Modeling and simulation can decrease manufacturing process design cycle time enormously, as has been proven in many industry segments.
Here we present our activities specifically with regard to nanopatterning by detailed large-scale simulations of nanolithographical processes in which rigid molds are imprinted into liquid oligomers that are subsequently hardened. We use a generic polymer model that can be applied to both SFIL, in which the oligomers are cross-linked by exposure to UV irradiation, and NIL, in which the liquid is hardened by lowering the temperature below the glass transition. Multiple stamps are inserted into melts of liquid oligomers at a temperature above the glass transition. The melts are either quenched or crosslinked and the systems are equilibrated. Stamps are then either removed at constant velocity to study the effects of stress and adhesion on resulting features, or simply deleted to study the effects in the limit of zero stress. We vary the size and pitch of the stamps in order to study the resolution limits of both methods.

5:20pm  TF-ThA11  All through Stencil MOSFET Fabrication  
L.G. Villanueva, O. Vazquez-Mena, EPFL, Switzerland, J. Montserrat, IMB-CNMCNM-CSIC, Spain, K. Sidler, V. Savu, EPFL, Switzerland, J. Brugger, EPFL, Switzerland

The fabrication of micro and nano devices using standard processing techniques is mainly based on the pattern transfer of designs onto a substrate. These standard techniques use pre-patterned resists that selectively expose certain parts of the substrate either to material deposition or implantation or to an etching process. The use of resist processes implies the coating, exposure, development and removal of the resist and also imposes certain restrictions regarding the materials and substrates to pattern (e.g. only flat substrates are acceptable). An alternative to resist-based processes is the use of stencil lithography (SL), which relies on the use of a shadow mask membrane, and has already been proved to achieve sub-micrometer resolution for metallization, and more recently for direct-etching and ion-implantation. In this abstract we present the combination of the three mentioned techniques to fabricate Metal-Oxide-Semiconductor Field Effect Transistors (MOSFET).

The proposed fabrication process flow of the MOSFETs follows the basic stages (Figure 1 in supplementary information) starting with a 100 mm diameter p-doped silicon wafer in which the n-doped regions for Source-Drain definition are implanted through stencil. Subsequently, the gate oxide is grown in a process that also activates the impurities in the lattice. Contacts for Source and Drain are opened in the oxide by means of dry etching through stencil and, finally, metal pads are deposited through stencil. All the stencils used were fabricated using standard microfabrication techniques (i.e. resist based processes) in 100 mm diameter wafers. However, for better compatibility with the processing equipment during MOSFET fabrication, the wafers were cleaved and the stencils were used in chip size.

Different designs were included in the fabrication: resistors, transistors and NOR gates. In addition, to demonstrate the capability of SL to pattern non conventional substrates, the transistors were fabricated not only on flat substrates, but also at the bottom of pre-patterned steps of 40 µm and 100 µm (Figure 2 of supplementary information).

The characterization shows that transistors have a linear I-V behavior. The square resistance decreases with the gap as expected (Figure 3, supplementary information). In addition, transistors also show the expected behavior (Figure 4, supplementary information), with a well defined saturation region.

The presented technique proposes a new concept for the fabrication of electronic devices, allowing the fabrication of structures on pre-patterned surfaces with resolutions close to the micrometer, which can be of great utility for some specific applications.
Diamond-like carbon (DLC) has the amorphous structure that is chiefly property was obtained by Ar + ion beam irradiation of 5 kV with 10 to 40 nm thick films were sputter deposited from CrSi-Cr-SiC targets by a dual cathode dc S-Gun magnetron. In addition to studying film resistance versus temperature using four point probe measurements, scanning electron microscopy and atomic force microscopy were also employed for analysis of the nanofilm structure features. This study has revealed that the cermet film TCR displays a significant increase when the deposited film thickness is reduced below 2.5 nm. An optimized sputter process consisting of wafer degassing, cermet film deposition at elevated temperature with rf substrate bias, and a double annealing in vacuum consisting of an in situ annealing following the film sputtering and an additional annealing following the exposure of the wafers to air has been found to be very effective for the film thermal stabilization and for fine tuning the film TCR. Cermet films with thicknesses in the range of 2.5 - 4 nm deposited using this process had sheet resistance ranging from 1800 to 1200 Ω and TCR from – 50 ppm/°C to near zero, respectively. A possible mechanism responsible for the high efficiency of annealing the cermet films in vacuum (after preliminary exposure the films to air) resulting in resistance stabilization and TCR reduction is discussed.

In this study, DLC films were formed using Ar + or He+ ion beam assist in a sputtering method. Commercial application of DLC has been already performed as engine parts of an automobile or surface coating of a hard material, it is possible to produce different structures; multilayers; amorphous carbon-Au (a-C:Au) composite thin films were synthesized by dc magnetron sputtering of a-C:H atmosphere. S. Narita, I. Takano, Kogakuin University, Japan Diamond-like carbon (DLC) has the amorphous structure that is chiefly composed by graphite (sp²) and disordered graphite (sp³) state. Therefore mechanical property of DLC generally shows high hardness and low friction. DLC films have been prepared by various method of chemical vapor deposition (CVD) or physical vapor deposition (PVD) including the sputtering method. Commercial application of DLC has been already performed as engine parts of an automobile or surface coating of a hard disk.

In this study, DLC films were formed using Ar+ or He+ ion beam assist in a naphthalene (C14H10) atmosphere. C9H6 is aromatic hydrocarbon with two benzene rings of a solidly in normal temperature and pressure. In our previous study, toluene (C7H8) of aromatic hydrocarbon with one benzene ring was used at same experimental process. By using C9H6 as an atmosphere gas, the higher deposition rate is expected than C7H8 gas. The formation conditions of DLC were changed with ion beam accelerating voltage and current density. Current dependence was performed by ion beam current density of 10 to 70 μA/cm² with a constant accelerating voltage of 5 kV, while voltage dependence was performed by 1 to 12 kV with a constant current of 10 μA/cm².

The mechanical properties of hardness and friction coefficient were determined using the dynamic micro Knoop hardness tester and the pin-on-disk tribio-tester with a SUJ2 ball of a 1/4 inches diameter, respectively. The conditions of examination were fixed at a load of 0.98 N, a revolution speed of 135 rpm, a sliding diameter of 10 mm and a sliding distance of 10 m. Atomic concentration and structure of the films were investigated by X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy, respectively.

The suitable property of Knoop hardness and friction coefficient were obtained by conditions of accelerating voltage of 5 kV with current density of 10 μA/cm². Knoop hardness of the film showed 5.37 GPa using Ar+ ion beam irradiation, while the friction coefficient of the film showed 0.117 using Hc+ ion beam irradiation. It was clear that property of DLC film was changed by ion species. In the case of He+ ion beam irradiation, low friction property was shown at 5 to 7 kV with 10 μA/cm², while high hardness property was obtained by Ar+ ion beam irradiation of 5 kV with 10 to 10 μA/cm².

As deposited films did not show any characteristic signal in the ellipsometric spectra related to the presence of gold, in agreement with the XRD results where no diffraction peaks were observed. Nevertheless, the RBS data showed that the gold concentration could be varied between 9 and 7 at% as the power increased. The samples were submitted to a thermal treatment in an Argon atmosphere at 600 °C, in order to promote the gold segregation. Ellipsometric spectra after the annealing clearly showed the absorption related to the interband transitions of gold (~ 2.5 eV). The spectra for each deposition power were modelled to obtain the variations in the optical properties of the films due to the gold incorporation, either as atomic inclusions (as-deposited samples) or particles (annealed samples) using the Drude-Lorentz model for the gold particles.

In this study, the sputtering method, which can improve the cost-efficiency and mass production of solar cells, was employed to deposit the CdTe thin film on the large-area substrates with the various processing conditions such as gas pressure, power, and the distance to the target. The non-uniformity and surface morphology were analyzed using AFM and SEM in the large-aread surface of CdTe thin-films deposited with the various processing conditions; likewise, the effects of the processing conditions on the non-uniformity and surface-morphology of the thin-film surface were compared. Also, the optical and electrical characteristics of CdTe thin films with the globally and locally difference in non-uniformity and surface morphology in a large-area were compared; thus, the effects of them on the efficiency of the sputter ing deposited thin film CdTe solar cells in a large-area were examined.
TF-ThP7 In-situ Analyses on Negative Ions in the Sputtering Process to Deposit Al doped ZnO Films. N. Tsukamoto, D. Watanabe, Aoyama Gakuin University, Japan. N. Ito, Panasonic Electric Works Co., Ltd., Japan. N. Oku, Y. Sato, Y. Shigesato, Aoyama Gakuin University, Japan

Magneton sputtering processes using ceramic oxide targets have been used to deposit transparent conductive Al doped ZnO films because of its advantages for large area uniform coatings with high packing density and strong adhesion. However, the degradations of electrical properties and crystallinity for ZnO films have similarly been observed at the positions opposite to the erosion track on the target. These are considered to be caused by the bombardment of high energy particles such as energetic Ar atoms (high energy neutrals) or negative oxygen ions. In this study, we tried to detect the flux and energy distributions of high energy negative ions during the dc magneton sputtering using an AZO target and discussed the influence of high energy negative ion bombardments on the structure and electrical properties of the films.

High energy negative ions were analyzed using a quadrupole mass spectrometer combined with an electrostatic energy analyzer, which was positioned at the substrate position opposite to the AZO (Al2O3: 2.0 wt%) target. The sputtering power during the analyses was maintained at 50 W. The O2 flow ratio [O2 / (Ar+O2)] were controlled from 0 to 5 %. For the analysis of the flux of the negative ions at the different substrate locations, the sputtering target was perpendicularly moved to the quadrupole mass spectrometer. In order to control the cathode voltage, the magnetic field strength was selected as 0.025, 0.06 and 0.1 T. In order to discuss the influence of the bombardments on the film properties, AZO films were deposited on unheated alkali-free glass substrate under the same condition of the fragment analysis. The atomic oxygen negative ion (O−) was observed as the high energy negative ions which possessed the energy corresponding to the double ion sheath voltage. The maximum flux of O− was observed at the location opposite to the erosion track on the target. The flux of O− decreased slightly with increasing O2 ratio. These results indicate that high energy negative ions were not formed by electron attachment in the cathode sheath region but should be sputtered from the target surface. Depending on the magnetic field strength, the cathode voltage varied from 337 V at 0.1 T to 403 V at 0.025 T. While the peak of O− shifted to lower energies with increasing the magnetic field strength, the flux of O− was hardly changed. The lower the energy of the peak of O− which AZO films is deposited at is, the lower both of resistivity and crystallinity for AZO films which are deposited at the positions opposite to the erosion track on the target are.

TF-ThP8 Influence of Microstructure and Surface Morphology on Photofunctional Properties of Titanium Dioxide Film Prepared by Reactive Magnetron Sputtering. K. Tanaka, I. Takano, Kogakuin University, Japan

Since the photoinduced decomposition of water on TiO2 electrodes was discovered, semiconductor based on photocatalyst has attracted extreme interest. TiO2 is anticipated as one of materials which are alternative for existing solar cell technology based on silicon. TiO2 shows relatively high reactivity under UV light which has the band gap of 3.2 eV in the anatase crystalline phase. The sun as an energy source can provide an abundant photons, however, UV energy in the sunlight accounts only for a small fraction (5%) compared to the visible region (45%). Many techniques have been examined to achieve the purpose, i.e. harness of the visible light. Improvement of TiO2 has been performed by doping transition metals or anionic species, but these doped materials induces increased instability and decreased photofunctional properties. On the other hand, the relationship between structure and photofunctional properties of TiO2 has some unclear points. Different TiO2 structures can be obtained in the reactive magneton sputtering method by control of O2 gas flow rate and formation temperature.

In this study, TiO2 was prepared by reactive magneton sputtering using Ti target in an Ar/O2 gas mixture. Composition and microstructure of these TiO2 films were investigated by XPS and XRD, respectively. The surface morphology of TiO2 was characterized by SEM analysis. The XRD and XPS analyses of a TiO2 film (Ti:20at%, O:80at%, as deposited) showed that the O2 flow rate of 0.06SCCM resulted in TiO2 with the band gap of 3.2 eV in the anatase crystalline phase. However, the O2 flow rate of 0.10SCCM showed TiO2 with the band gap of 3.0 eV in the rutile crystalline phase. The sun as an energy source can provide an abundant photons, however, UV energy in the sunlight accounts only for a small fraction (5%) compared to the visible region (45%). Many techniques have been examined to achieve the purpose, i.e. harness of the visible light. Improvement of TiO2 has been performed by doping transition metals or anionic species, but these doped materials induces increased instability and decreased photofunctional properties. On the other hand, the relationship between structure and photofunctional properties of TiO2 has some unclear points. Different TiO2 structures can be obtained in the reactive magneton sputtering method by control of O2 gas flow rate and formation temperature.

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A semiconductor with low electrical resistivity and high transparency in the visible region, fabricated by ion-beam assisted deposition, was reported on electrical and optical properties of Nb:TiO$_2$ films deposited on glass substrate by dc magnetron sputtering using a slightly reduced Nb-doped TiO$_2-x$ target with Nb$_2$O$_5$ pellets [2]. In this study, we investigated the effect of Nb doping on the electrical and optical properties of Nb:TiO$_2$ films with comparison of pristine TiO$_2$ films. Anatase TiO$_2$ and Nb:TiO$_2$ films were deposited on unheated quartz glass substrate by dc magnetron sputtering using a slightly reduced TiO$_2-x$ (with Nb = 9.5 at.%) targets [AGC Ceramics, Japan]. By using these reduced TiO$_2-x$ targets, stable dc discharge was maintained because of the sufficient resistivity of the reduced TiO$_2-x$, targets to avoid charge up of the target surface and hence to suppress arcing. X-ray diffraction patterns of all the as-deposited films exhibited amorphous structure, while they were crystallized into polycrystalline anatase structure after post-annealing in vacuum at 700°C for 1 hour. Electron probe microanalysis revealed that Nb concentration in the Nb:TiO$_2$ films remained almost constant at 7.4 at.%, regardless of O$_2$ flow ratio during the deposition. Resistivity of the TiO$_2$ films was larger than 1 ohm cm while the films were deposited at 5.0% of H$_2$ flow ratio. In contrast, resistivity of Nb:TiO$_2$ films exhibited 6.3×10$^4$ ohm cm while the films were deposited at 0.10% of O$_2$ flow ratio. Carrier density of the Nb:TiO$_2$ films was 2.0×10$^{14}$ cm$^{-3}$, where the doping efficiency was estimated to be about 90%. All the annealed films possessed transmittance of over 60-80% in the visible region of light. Ga$_2$O$_3$ was formed after heat-treatment over 500°C in nitrogen gas ambient. According to X-ray diffraction (XRD) analyses, the as-grown films being amorphous, polycrystalline Ga$_2$O$_3$ was formed after heat-treatment over 500°C in nitrogen gas ambient. Ga$_2$O$_3$ was formed after heat-treatment over 500°C in nitrogen gas ambient. Ga$_2$O$_3$ was formed.
400°C was found to be always lower than that of GZO thin films prepared using inductively coupled plasma source. Temperature silicon-nitride films deposited by internal linear TF-ThP16 Effect of DC bias on the Characteristics of Low-temperature silicon-nitride thin film transistors (TFT) and passivation layers for diverse microelectronics and as antireflection (AR) coating for solar cell. In addition, due to their chemical inertness, excellent dielectric properties, and thermal stability, they are limited by their intrinsic inflexibility, thickness, and weight. In general, of all TCO films, glass is the most commonly flat panels as well as flexible displays, due to their excellent electrical and optoelectronic devices such as light emitting diodes (LEDs), solar cells, and thin film transistors (TFTs). In this study, we carried out the deposition of silicon nitride thin films at the temperature of 200°C by either an rf superimposed dc or a conventional dc magnetron sputtering deposition technique (rf-de-MSD or dc-MSD). The obtained resistivities in AZO and GZO thin films prepared by rf-de-MSD were always lower than those in films prepared by dc-MSD. However, the obtained resistivity of the thin films prepared by an rf-de-MSD using lower resistivity targets was not decreased more sufficient than that of thin films prepared by a conventional dc-MSD with the same targets, whereas the obtained resistivity decreased as the resistivity of targets used was decreased. In moisture-resistant tests, resistivity change was measured over time with exposure to a highly moist environment (air at 85% relative humidity and 85°C). The resistivity stability of GZO thin films over long term testing was found to be always lower than that of AZO thin films prepared with the same thickness under the same deposition conditions. In heat-resistance tests, resistivity was measured both before and after heat treatment in an oxidizing atmosphere (air in a temperature range from 30 to 400°C). The resistivity stability of AZO thin films during heat testing at 400°C was found to be always lower than that of GZO thin films prepared with the same thickness under the same deposition conditions. It was also found that the increase of resistivity observed in AZO films was related to decreases of both the carrier concentration and the Hall mobility, but, in contrast, that observed in GZO films was mainly attributable to a decrease of carrier concentration. The difference of resistivity behavior in the heat tests was mainly attributed to the microstructural difference associated with the crystallinity of deposited films.

TF-ThP16 Effect of DC bias on the Characteristics of Low-Temperature Silicon-Nitride Films Deposited by Internal Linear Inductively Coupled Plasma Source. G.H. Gweon, J.H. Lim, S.P. Hong, G.Y. Keom, Sungkyunkwan University, Korea. There has been a growing interest in the dielectric material that can be deposited at low substrate temperatures for the applications such as organic devices and flexible display devices. Of diverse dielectric materials, silicon-nitride film has been widely used for various important applications from semiconductor to flat panel display, such as a gate dielectric material for thin film transistor (TFT), passivation layers for diverse microelectronics and as antireflective (AR) coating for solar cell. In addition, due to their chemical inertness, excellent dielectric properties, and thermal stability compared with those of silicon oxide, many researchers have been studied to develop high quality low temperature silicon-nitride films using various types of plasma sources. Generally, conventional technique for depositing SiN at a low temperature is plasma-Enhanced CVD (PECVD) (~300°C). In this study, we carried out the deposition of silicon nitride thin films at the temperature lower than 100°C by using an internal linear ICP source. To obtain high-quality film, several factors effects of the rate of the target, such as Al/SiH4 and DC bias on the properties of thin film were investigated. The results showed that, by using 2:1 ratio of NH3/SiH4 and by using -150V DC bias, the high quality silicon nitride film having the refractive index of 1.83, dielectric constant of 7.2 with negligible interface traps could be observed. The compositional, binding states, and the refractive indices of the films were measured using a XPS, FTIR, and an ellipsometer, respectively. In addition, metal/insulator/semiconductor (MIS) capacitors having Al/insulator/p-Si were fabricated and the flat-band voltage and hysteresis voltage were measured by the capacitance-voltage (C-V) method.

TF-ThP17 Characterization of Structural Modification in Columnar Thin Films Produced by Ion-Assisted Glancing Angle Deposition. J.B. Sorge, University of Alberta, Canada, M.J. Brett, NRC National Institute for Nanotechnology, Canada. In a traditional glancing angle deposition (GLAD) process, the column tilt angle and film density were both governed by the deposition angle α. It was later discovered that β could be controlled independently from the deposition angle by implementing an appropriately designed phisweep substrate rotation algorithm which reduces anisotropic shadowing. Ion-assisted deposition has also been demonstrated to alter columnar thin film morphology which has proven to be useful in humidity sensing applications. The influence of the phisweep process on β is inherently limited to producing tilt angles that are less than or equal to that of a traditional GLAD film grown without phisweep. Ion assisted GLAD is a procedure that can increase β above the maximum achievable tilt angle in a standard GLAD deposition and has been utilized in square spiral photonic crystal fabrication. The work presented here is focused on the influence of columnar to amorphous transition (CaT) thin films grown with an ion-beam assisted GLAD process. Our current capabilities in modifying β as a function of α with an ion assisted process will be described. In addition, we report on our efforts to decouple the film density ρ from α, a previously unstudied characteristic of the ion-assisted GLAD process. This latter result could enable partial decoupling of α and β, simultaneously and allow access to previously unattainable columnar film morphologies, improving the versatility of the GLAD process. Discussion will focus on the effect of ion assistance on ρ and β as measured by variable angle spectroscopic ellipsometry (VASE) and the influence of different α. The relationship between these parameters, the natural column broadening and effects on the resulting in-plane birefringence will also be discussed.

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TF-ThP18 Structural and Electrical Characterization of rf Magnetron Sputtered Aluminum Doped Zinc Oxide. K. Braum, M. Kyslinger, J. Doyle, Macalester College. We present a study of the relationship between structural properties and opto-electronic quality of aluminum doped zinc oxide produced by rf magnetron sputtering. Thin films (300-400 nm thick) were deposited as a function of substrate temperature, working gas (argon) pressure, and oxygen partial pressure. Structural and optical measurements included X-ray diffraction scans, electron microscopy, Raman spectroscopy, and infrared spectroscopy. Electrical measurements included resistivity, Hall effect, and optical transmission. Substrate temperature had a strong effect on the crystalline quality of the films as inferred from xrd, infrared, and Raman measurements. Working gas pressure and oxygen partial pressure had a much weaker effect on the crystal structure. Good opto-electronic properties were not always correlated with good crystal quality. In particular good electronic quality films could be produced under deposition conditions that resulted in poor crystal quality. A simple model is presented that relates the crystal quality to the electronic properties accounting for dopant activation, grain boundary scattering, and ionized impurity scattering.

TF-ThP19 Effect of Silicon Content on the Resistivity of Tungsten Silicon Film. C. Lo, D. Draper, P. McDonald, R. Mathew, Praxair Electronics. Tungsten (W) – silicon (Si) alloy has been used for many applications in the semiconductor. Resistance layer is one of the applications. In this study, five sputtering targets with composition ranged from WSi1.6 (W=20wt%) Si to WSi4 (W=38wt% Si) have been prepared. By controlling the sputtering power and Argon (Ar) gas pressure, the film resistivity as a function of target composition and sputtering parameters has been established. The results are able to provide helpful information to the alloy design of WSi for new thin film applications.

TF-ThP20 Effect of Process Parameters on the Growth and Properties of ATO Films Prepared on Flexible Substrate at Room Temperature. S.U. Lee, B.Y. Hong, Sungkyunkwan University, Korea. Transparent conducting oxide (TCO) have found applications in several optoelectronic devices such as light emitting diodes (LEDs), solar cells, and flat panels, as well as flexible displays, due to their excellent electrical and optical properties. In general, all of TCO films, glass is the most commonly selected substrate. However, for future development in flexible devices, glass is limited by its intrinsic inflexibility, thickness and weight characteristics. The objective of this study was to characterize the electrical, structural and optical properties of antimony-doped tin oxide (ATO) films prepared by a polycrystalline (PC) sputtering technique by the radio frequency (RF) magnetron sputtering method for applications to transparent electrodes using a SnO2 target mixed with Sb of 6 wt% at room temperature. The process parameters were working pressure and RF power. The working pressure was varied from 1 to 7 mTorr in steps of 2 mTorr, and the RF power was varied from 100 to 175 W in step of 25 W at room
The thickness of the deposited ATO films was about 150 nm ± 10. X-ray diffraction (XRD) measurements showed ATO films to be crystalline with a (101) preferred orientation at the RF power increased. The spectra revealed that the deposited films were polycrystalline and they retained the tetragonal structure. The grain size was calculated from the XRD spectra using the Scherrer equation. The change in FWHM reflects the change in the grain size of the film, that is, the decrease in FWHM corresponds to the increase in grain size. ATO film deposited at a PES substrate at optimized condition showed the lowest resistivity of 7.4 x 10⁻⁷ ohm-cm and the optical transmittance was 85% in the visible range. The possibility as the next-generation transparent electrode is also studied.

TF-ThP24 Photoelectric Emission Properties and Work Function of Sn-doped InOₓ Films. A. Takasaki, Y. Sato, N. Oka, Aoyama Gakuin University, Japan, F. Utsuno, K. Yano, Idemitsu Koso Co., Ltd., Japan, Y. Shigesato, Aoyama Gakuin University, Japan

Sn-doped InOₓ (ITO) films have been used as a transparent electrode for various applications including organic light-emitting diodes (OLEDs) since it combines good conductivity and transparency in the visible region. The work function control of ITO film plays an important role in device parameters such as operating voltage or lifetime for OLED. The work function of ITO film has been controlled by surface treatments by plasma or UV-ozone treatment. However in such methods the work function of ITO film is unstable and can change over time. On the other hand, it is expected that the work function could be controlled by a variation in carrier density. In this study, we investigate how the work function depends on the carrier density of ITO films. The ITO films with various carrier densities were deposited by dc magnetron sputtering on glass substrates heated at 300 °C and 400 °C using high-density ceramic ITO targets with various SnO₂ concentrations. Total gas pressure and dc power were maintained at 1.0 Pa and 300 W, respectively, for all the depositions. The film thickness of all the ITO films was adjusted to 300 nm. Carrier density was controlled from 3.06 x 10¹⁹ to 2 x 10¹⁹ cm⁻³ from the deposited on the substrates heated at 300 °C or 400 °C, respectively, by using the ITO targets with the different SnO₂ concentrations from 0 to 10 wt. %. The increase in the carrier density should be caused by the increase in the substitutional Sn⁺ at In⁺ sites of InOₓ. Optical band gap of the films increased with the increasing SnO₂ concentration of the target, where work function decreased. This must be explained quantitatively in terms of the shift of Fermi level with varying carrier density within a parabolic conduction band. The optical gap or work function of the films showed clearly positive or negative relationships to the two-thirds power of carrier density, respectively. Furthermore, a detailed analysis was performed using hard X-ray photoemission spectroscopy (HXS) in order to investigate the electronic state between the Fermi level and the valence band of ITO films deposited on the substrates heated at 400 °C. As a result, the density of state near the Fermi level was found to vary systematically with the carrier density. The synchrotron radiation experiments were performed at the BL47XU in the SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal No. 2015).
organic solar cells, organic thin film transistor, and organic sensors, and organic smart window devices. Here, we reported on the new hole-only contact system of 2-TNATA / MoOx. The organic light-emitting diode with a glass / ITO (85 nm) / MoOx (5 nm) / 2-TNATA (30 nm) / NPB (18 nm) / Alq3 (52 nm) / LiF (1 nm)/Al (100 nm) structure showed higher luminous efficiency as two times than the device of the same structure with MoOx of 0 nm-thick. The improvement of the luminous efficiency by inserting a MoOx layer between thin-doped indium oxide (ITO) and 2-TNATA is attributed to the lowering of the barrier height by a hole injection (Φin) as well as the raising the band bonding by pinning of Fermi level in the interfaces between two layers. The mechanism for a hole-injecting efficiency from anode to a MoOx / 2-TNATA layer was proved by analyzing an ultraviolet photoemission spectroscopy (UPS) spectra. Φin in the 2-TNATA / MoOx interface with MoOx of 20 nm-thick was decreased about 2.0 eV, when compared to Φin of the pure layer with only 2-TNATA.

Keywords: organic light-emitting diode, electronic structure, interface, MoOx, 2-TNATA

TF-ThP26

Unusual Properties of InN Epilayers Probed by Photoluminescence, F.I. Lai, W.T. Lin, Yuan-Ze University, Taiwan, W-C. Chen, C.N. Hsiao, National Applied Research Laboratories, Taiwan, S.Y. Kuo, Chang Gung University, Taiwan, Y.K. Liu, J.L. Shen, Chung Yuan Christian University, Taiwan

In this paper, we report the studies on the hetero-epitaxial growth of wurtzite indium nitride (InN) thin films on oxide buffer layer by plasma-assisted chemical beam epitaxy (CBE) system with different III/V ratios. Oxide buffer layer was pre-sputtered using RF sputtering technique before InN deposition. The structural and optical properties of InN films samples were investigated by X-ray diffraction (XRD), field-emission scanning electron microscopy (FE-SEM) and temperature-dependence photoluminescence (PL) measurements. The near-infrared emission peak value of samples was between 0.74 and 0.78 eV, which are higher than those pre-reported values explained by the Moss-Burstein effect. While increasing the III/V ratio, the emission PL peak red-shifted. In addition, the temperature-dependence PL spectra exhibit blue-shifted as the measurement temperature increased. We suggest that the blue shift in PL spectra with temperature may result from the variation in concentration of InN films.

TF-ThP27

Thermophysical Properties of Alq3 and α-NPD Films Measured by Nanosecond Thermoreflectance Technique, N. Oka, K. Kato, Aoyama Gakuin University, Japan, N. Ito, Panasonic Electric Works Co., Ltd., Japan, T. Yagi, N. Taketoshi, T. Baba, National Metrology Institute of Japan, AIST, Japan, Y. Sato, Y. Shigesato, Aoyama Gakuin University, Japan

Organic light-emitting diodes (OLEDs) are promising for future lighting and display applications. It has been reported, however, that the thermoluminescence properties are degraded by self-heating during operation [1,2]. In order to determine the heat propagation mechanism in OLEDs, it is important to measure the thermophysical properties precisely for the components of OLEDs, such as Tris-(8-hydroxyquinoline) aluminum (Alq3) and N,N,N',N'-Diphenyl-1-naphthyl-N',N'-diphenylbenzidine (α-NPD) films. Alq3 and α-NPD are used as the electron-transport/emitting materials and the hole-transport material, respectively. In this study, the thermal diffusivity of both the films was characterized quantitatively by ‘rear heating / front detection (RF) type’ nanosecond thermoreflectance system. During the deposition of the α-NPD films, the thermal diffusivity of Alq3 and α-NPD was 2.8×10⁻⁴ m²/s and 1.0×10⁻⁴ m²/s, respectively. It is expected that the Alq3 is a promising material for OLEDs because of its high thermal diffusivity compared to those pre-reported values explained by the Moss-Burstein effect.

TF-ThP29

Damage to Fatigue and Retention Characteristics of BLT Capacitors Fabricated by Damascene Process with High-pressure Process, W. Lee, S Shin, Chosun University, Korea, N. Kim, Chonnam National University, Korea

Damascene process of mechanical polishing (CMP) process was proposed to fabricate the BLT ferroelectric capacitor instead of plasma etching process for the vertical profile without plasma damage. However, the authors also reported in the previous study that the electrical damages to leakage current and P-T characteristics of BLT capacitor induced by high-pressure process of damascene process although the high-pressure process had shown the better removal rate (high yield) and the sufficient surface characteristics including non-uniformity for BLT-CMP [1,2]. BLT thin films deposited on Pt/Ti/SiO2/Si substrate is well known to have good fatigue endurance and retention characteristics; however, the fatigue process in damascene process of BLT capacitor degraded the fatigue behavior and retention characteristics. Therefore, the CMP pressure was controlled in damascene process for BLT capacitor although the yield and the surface characteristics became somewhat lower. Fatigue behavior and retention characteristics of BLT capacitor were recovered with the good P-T and leakage current characteristics. [1] N.-H. Kim, et al., Thin Solid Films, Vol. 515, Iss. 16, p. 4654 (2007), [2] N.-H. Kim, et al., Electronics Letters, Vol. 44, Iss. 24, p. 1429 (2008).

TF-ThP30


ZnO films were deposited by atomic layer deposition (ALD) on glass at 40°C. The films were studied by Atomic force microscope (AFM), X-ray diffraction (XRD), and contact angle measurements. The root mean square (RMS) roughness of ZnO increases with increasing the number of growth cycles. According to the XRD analysis, the crystalline phase becomes apparent when the growth cycle is increased. The contact angle decreases substantially at 400 cycles and the film reveals a hydrophilic surface. The surface roughening of ZnO films can be turned by the growth cycle at this lower temperature due to the presence of ZnO nanocrystals.
TF-ThP31 Glancing Angle Deposited Metallic Nano-Structured Thin Films for Surface Enhanced Fluorescence and Biosensing in Water. C. Khare, Leibniz-Institut of Surface Modification, Germany. A. Karachevsky, I. Abdalhalim, Ben Gurion University of the Negev, Israel, C. Patzig, Leibniz-Institut of Surface Modification, Germany. B. Fuhrmann, Martin-Luther-University Halle, Germany, B. Rauschenbach, Leibniz-Institut of Surface Modification, Germany.

Metallic nanophotonic structures demonstrate surfaced enhanced phenomena, thus find application in optical biochips. To facilitate this, we report on the improvement in the already successful panoply of optical biosensors in general and in the field of water quality in particular, nanophotonic structures such as sculptured thin films (STF) can be used. The existence of localized surface plasmon resonance (LSPR) was observed within metallic STFs. The glancing angle deposition technique (GLAD) by ion beam sputtering and electron beam evaporation was employed to sculpt thin films as a means for surface enhanced fluorescence (SEF). The self-similar growth mechanism is responsible for the growth of non-close films which consist of needles grown in the direction of the incoming flux of the particles. This thin film deposition method, coupled with an appropriate substrate rotation scheme, enabled to deposit nanorods with less than 30° and greater than 80° inclination with respect to the substrate surface. A multitude of structures were prepared by depositing materials like Ag, Au and Si with GLAD on different substrates such as fused silica, Si(100), Si(110) coated with 15 nm Ti, and on nanosphere lithography pre-patterned substrates that consist of Au and Al nanodots in hexagonal arrangement. The reference (compact) thin films of each material were prepared with the vapor incidence parallel to the substrate normal.

With the integration of a fluorescence microscope with a spectrometer, the green Gg line at 546 nm was used for excitation in most of the SEF experiments and the emission was detected using the red filter at 590 nm. STFs spin coated with a Rhodamine 123 layer of thickness (30-50 nm) were observed to show enhancement factors up to few tens. A higher degree of surface enhancement was observed with Ag nanorod STFs inserted in an aqueous solution of E. coli in comparison to corresponding dense Ag reference film.

TF-ThP33 Molecular Layer Deposition of Organic Films for EUV Photoresists. H. Zhou, P.W. Locstoff, S.F. Bent, Stanford University. Lithography at the sub-22 nm length scale will require resist films under 50nm thick with a high degree of homogeneity. Current resists that are in use for ultraviolet lithography may not be suitable for the projected transition to extreme ultraviolet (EUV) wavelengths, leading to active study of alternative materials solutions. One method for gaining sub-nanometer control over the thickness and composition of photoresist film is molecular layer deposition (MLD), which utilizes a series of self-limiting reactions of organic molecules. In this study, a variety of nanoscale organic films were deposited by MLD via a urea coupling chemistry, which occurs by reaction of isocyanates and amines. Films were deposited on substrates that were first prepared by vapor deposition of 3-aminopropyltriethoxysilane on hydroxylated SiO2 surfaces to yield an amine-terminated surface, as confirmed by XPS and XPS. The amination and amine termination were dosed in a binary cycle, and this cycling was repeated to yield the desired thickness of organic film. Ellipsometry indicates a linear growth rate of 4.5 Å/cycle for the standard coupling of phenylene disiocyanate (PDC) and ethylenediamine (ED). The urea coupling moiety is confirmed by infrared spectroscopy, and films are shown to have stoichiometric composition by XPS. Temperature dependent measurements show that the films have good thermal stability. To fabricate EUV films, we have explored a variety of backbones contained within the amine and isocyanate linking groups to tune the functions of the organic films. By changing the backbone of the MLD precursors, we have incorporated ketal-based acid-labile groups into the film and have shown that after incorporation of photocatalytic generator (PAG), UV exposure, post-exposure bake and development, the films are cleaved, leaving behind the photoresist. The chemical composition and impurity content were investigated by Auger electron spectroscopy (AES). The phase identifications of the samples were performed by X-ray diffraction (XRD). A modern alternative for EUV photoresists, we report a variety of nanoscale oligoureas films for EUV resists. We have applied the nanoscale oligoureas for exposure bake and development, the films are cleaved, leading to potential process optimization faster and more cost-efficient. Additionally, it permits use as photoresists. Results of applying the nanoscale oligoureas films for advanced photoresist application will be presented.

TF-ThP34 Time-Resolved FTIR Spectroscopy During ALD. B.A. Sperling, J.E. Maslar, W.A. Kimes, D.R. Burgess, Jr., E.F. Moore, National Institute of Standards and Technology. In situ monitoring of atomic layer deposition (ALD) could potentially make possible to perform ALD in a faster and more cost-efficient way. Additionally, it permits computational models for chemistry and fluid dynamics to be tested and refined; these validated models, in turn, could also be useful tools for process development and equipment design. We have been developing real-time diagnostics for gas-phase concentrations using a number of methods including mass spectroscopy, distributed-feedback diode laser absorption spectroscopy, and quantum cascade laser absorption spectroscopy. This work focuses on our work with time-resolved Fourier transform infrared (FTIR) spectroscopy, which we use to monitor gas-phase species during ALD of hafnium oxide from tetra(ethylmethylo)-hafnium and water. Results are compared to other measurement techniques applied to the same warm-walled, single-wafer reactor. Additionally, our efforts to model the system using computational fluid dynamics and a detailed kinetic reaction mechanism are discussed.

TF-ThP35 Characteristics of Thin Films Deposition of Ruthenium on Various SiO2 Substrates by Remote Plasma Atomic Layer Deposition. J.S. Lee, T.Y. Park, D.O. Kim, H.T. Jeon, Hanyang University, Republic of Korea, J.K. Lee, B.C. Cho, IPS R&D Center, Korea, M.S. Kim, H.B. Ahn, Air Product Korea. High-k dielectrics, such as HfO2, ZrO2, Ta2O5, and (Ba, Sr) TiO3, have been studied for the application in storage capacitors of next generation dynamic random access memory (DRAM). Ruthenium is one of the promising electrode materials which are compatible with these high-k dielectrics. Ruthenium exhibits characteristics of high work function, good etching property with oxygen plasma and low resistivity. For these reasons, ruthenium thin film has been extensively studied for the next candidate material as an electrode for capacitors of DRAM. However, the Ru deposition shows long incubation time before actual deposition. Thus, the detail investigation of this incubation time and correlation with initial growth mechanism is very important to monitor the growth mechanism. To study the growth mechanism of Ru, we prepared several different SiO2 substrates grown under different conditions by CVD method, thermally grown, and grown in wet atmosphere. Ruthenium films were deposited on these various SiO2 substrates by remote plasma ALD method. We used bis(ethyl-cyclopentadienyl) ruthenium [Ru(η5Cp)], Ru(η5C5H4CH3)2 as a ruthenium precursor and NH3 plasma as the reactant. In this experiment, the remote plasma atomic layer deposition (RPALD) method with NH3 plasma is used to deposit ruthenium films. The thin-film characteristics and initial growth of Ru on the different SiO2 substrates were measured with many analysis tools. The characteristic of differently grown SiO2 was investigated by X-ray reflectivity (XRR). And the surface morphologies of ruthenium films were examined by field emission scanning electron microscope (FESEM) and atomic force microscopy (AFM). We also analyzed chemical states of the ruthenium films with X-ray photoelectron spectroscopy (XPS). The chemical composition and impurity content were investigated by Auger electron spectroscopy (AES). The phase identifications of the samples were performed by X-ray diffraction (XRD).

TF-ThP36 Electrical Characteristics of Lanthanum Oxide with SiO2 Buffer Layer using Remote Plasma Atomic Layer Deposition (RPALD) Method. H.R. Lee, S.H. Woo, H.C. Kim, J.S. Lee, H.G. Kim, Y.C. Kim, H.T. Jeon, Hanyang University, Republic of Korea. Conventional SiO2 has been used as a gate dielectric in complementary metal oxide semiconductor (CMOS) devices. When high-k materials are used as new gate oxides instead of SiO2, the film thickness can be increased to reduce the tunneling leakage current while scaling the equivalent oxide thickness (EOT). Atomic layer deposition (ALD) method has been studied in an effort to deposit high-k materials. Especially, the plasma-enhanced atomic layer deposition (PEALD) method is applied for deposition of high-k dielectrics due to its advantages such as an increased reactivity, reduced impurities, and a good uniformity. Lanthanum oxide (La2O3) is considered as one of the most promising materials among these high-k materials for the following reasons. It has high dielectric constant (k=20-30), large band gap, and good thermal stability on Si substrate. However, one of the difficulties in the application of the La2O3 to MOSFETs is a large flat-band voltage shift. The undesirable large flat-band voltage shift results from two kinds of defects. One is a fixed oxide charge located at the interface between the oxide and Si, and the other is an oxide trap charge in the oxide. Lanthanum silicate interlayer, which is formed between La2O3 and silicon substrate, has defects that can shift flat-band voltage. Therefore, it is desirable to reduce impact of these defects for the application of lanthanum oxide. In this study, a SiO2 buffer layer was used to improve the electrical properties of La2O3 gate oxides. The SiO2 buffer layer retards the formation of lanthanum silicate interlayer and oxide charge defects. We have examined the La2O3 films which were deposited on Si substrate and thermally grown SiO2 buffer layer using PEALD method, respectively. La2O3 growth rate was 0.3 nm/cycle at 300 °C on Si substrate and flat-band voltage was 0.29 V. Leakage current was 5.67E-8 A/cm2 at . We analyzed a composition and chemical bonding of the films with X-ray photoelectron spectroscopy (XPS). Electrical characteristics were also measured using an Agilent B1500A semiconductor parameter analyzer to investigate the flat-band voltage and the equivalent oxide thickness (EOT).
TF-ThP37 Chemical Vapor Deposition of Samarium Doped Ceria from Metal-Organic Solid Precursors, T.-S. Oh, D. Boyd, S. Haile, Caltech

Samarium doped ceria (SDC) thin films are grown via metal-organic chemical vapor deposition (MOCVD) as a first step towards high power density SDC based fuel cells.

TF-ThP38 Characterization of OTFT Fabricated Using Ink Jet Combined with Imprint Technology, K.H. Kim, K.H. Eum, I.S. Chung, Sungkyunkwan University, Korea

We fabricated organic thin film transistor using ink jet printing combined with a nano imprint. The channel length of OTFT were in the range from 2 μm to 7 μm. TIPS pentacene was used as an active material to achieve the better mobility. Additionally, Poly-4-vinylphenol (PVP) was chosen as a gate insulator. All materials including Ag electrode were prepared using ink jet printer (IJ-200) on polyethersulphone (PES) substrate. The physical properties were analyzed using SPM and SEM. The electrical characterization was done usingKeithley 4200.

TF-ThP39 Fabrication and Characterization of Ink Jet Processed Organic Thin Film Transistors with Poly-4-Vinylphenol (PVP) Dielectric, K.H. Eum, K.H. Kim, Y.K. Son, I.S. Chung, Sungkyunkwan University, Korea

We fabricated organic thin film transistor using ink jet printing combined with a nano imprint. The channel length of OTFT were in the range between 2 μm and 7 μm. TIPS pentacene was used as an active material to achieve the better mobility. Additionally, Poly-4-vinylphenol (PVP) was chosen as a gate insulator. All materials including Ag electrode were prepared using ink jet printer (IJ-200) on polyethersulphone (PES) substrate. The physical properties were analyzed using SPM and SEM. The electrical characterization was done using Keithley 4200.

TF-ThP40 Improvement of Ohmic Contact Property of a Inkjet Printed TIPS-pentacene Schottky Diode by Employing SAM and PEDOT:PSS Layers, J.M. Kwon, K.H. Kim, J.H. Heo, I.S. Chung, Sungkyunkwan University, Korea

Inkjet printing technology has attracted a large of attention increasing because of its low cost fabrication, capability with flexible substrate and high-throughput. Especially, organic schottky diode is thought to play an important role to operate a Radio Frequency Identification (RFID) at high frequency. In this paper, we fabricated organic schottky diodes using inkjet printer with two different sizes of diameters, namely, 50 μm and 30 μm. Au was deposited on polyethersulphone (PES) substrate, and then printed 6,13-bis(trisopropylsilylethynyl) pentacene (TIPS - pentacene ) using ink-jet printer. Finally, Silver was form schottky contact with TIPS-pentacene layer. In an effort to improve ohmic contact, we utilized self-assembled-monolayer (SAM) and Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) between gold and TIPS- pentacene layer, respectively. Keithley 4200 and Scanning probe microscopy (SPM) were used to examine the physical and electrical properties.

TF-ThP41 Solution-derived Nanocomposite Materials for Photovoltaetics, E. Ryabova, NVIA, M. Shkolnikov, ADCO-Engineering

Photovoltaics are in a verge of expansion challenged with the grid parity requirement. Three generations of solar cell technologies are racing for the better $$/Wp numbers.

c-Si, mc-Si, micromorph, Thin film (CdTe, CIGS), Organic – all use thin film processing in order to create absorber, emitter, light trap-assisting layer, back side field-passivating layer, barriers, metallization, etc.

In order to achieve grid parity ($$/Wp) PV-technology strives to increase Power Conversion Efficiency (PCE) coupled with reduced Cost of Ownership (CoO).

Former is done by minimizing losses -optical and electrical and implies advanced interface engineering.

Later entails low cost material and technology utilization that places verdict on industry trend toward innovative technologies.

Wet chemistry based thin film deposition routing is proposed to replace high vacuum ones for several critical layers, such as ARC, TCO, BSF and surface modification.

This low cost method features:

High deposition rate
High material utilization
Simple equipment capable of very large substrate handling.

Ideal for roll-to-roll operation
Full confromity with complex shape surfaces

Highly uniform films of various compositions with the thickness range 6-600 nm have been deposited using dip coating, slot die and microgravure coating, spray coating.

With the proper surface activation film forms covalent bonds with the substrate and has no interfacial imperfections.

When used for solar cell fabrication – can add up to couple of percent to PCE compare to traditionally processed cells.

Precursor for the specific layer can be purchased or mixed in-house depends on formulation.

Solution Derived Nanocomposites are already on their way to mass production at many PV-houses with the increasing popularity among large size, flexible substrate, and concentrating solar users.


Only a limited amount of semiconductor materials have been deployed on a wide-spread basis for terrestrial solar energy production. Single crystalline silicon has held the majority of the market share, with other technologies emerging over the years with lower production costs. Some of the materials used in many of these technologies possess clear long-term disadvantages with regards to economics, availability, and environmental consequences. A recent study of 23 potential semiconductors ranks the potential of each in regards to their annual electricity production potential and their raw material cost [1]. Detailed experimental research on the photovoltaic potential of many of these individual compounds is very sparse or non-existent.

In this experimental study, seven of the best candidates were selected for further investigation, including FeSe2, ZnP2, PbS, CuO, CuO2, NiS, and ZnSe. Transmission, reflection, and absorption measurements were performed on these binary compounds. Solar cells were also fabricated at the Florida Solar Energy Center to measure photovoltaic properties, including conversion efficiency under Standard Test Conditions, quantum efficiency, and spectral response. The measured optical and electrical properties of these semiconductor materials provides a better understanding of the potential of each for wide-spread deployment. Future work will be focused toward optimizing device design and fabrication processes to maximize the energy conversion of the best potential compounds.
Pt$_{1-x}$Ir$_x$ films with $x = 22.76$-$63.25$ are fabricated on (100) Si substrates at 400 °C by magnetron sputtering deposition. Effects of Ir content on the microstructure, morphology and hardness of PtIr films are investigated by field emission scanning electron microscopy, X-ray diffraction, atomic force microscopy and nanoindentation system. The columnar structures are observed by field emission scanning electron microscopy. X-ray diffraction analysis revealed that PtIr films had preferred orientation along Pt(111) as Ir content is below 50.84 at.%. When the Ir content is more than 50.84 at.%, the PtIr film had another preferred orientation, Ir(111). The surface morphology is analyzed by atomic force microscopy. Roughness of PtIr films is decreased with increased Ir content. The hardness of all PtIr films is under 20 GPa. It is found the maximum hardness of PtIr films is about 14.9 GPa as Ir content is 57.9 at.%.

In this work, effects of hydrogen plasma pretreatment on superconformal Cu gap-filling of the nano-scale trench with atomic-layer –deposited (ALD) Ru barrier metal were investigated. For this purpose, hydrogen plasma pretreatments on ALD-Ru layer were carried to control the nucleation and growth of Cu during metal-organic chemical vapor deposition (MOCVD). As the plasma pretreatment time increases, Cu nucleation is suppressed increasingly. XPS and thermal desorption experiments of the pretreated ALD Ru surface showed that hydrogen atoms passivate the Ru surface, which leads to suppression of Cu nucleation presumably due to inhibition of adsorption of Cu MO precursors. During Cu gap-filling of the sub 60-nm and ALD-Ru deposited trenches without the plasma pretreatment, the entrance of the trenches during copper deposition was easily blocked. On the contrary, for the plasma pretreated trenches, evolution of Cu layer in the trenches showed a dramatic reduction of over-hang near the entrance of the trench leading to superconformal filling of the nano-scale trench.
and the amount varied slightly with \( f_{O_2} \), which could be expected to promote charge transfer complex should be generated at an interface of the bilayers.

A flexible multi-layer ultra-barrier stack consisting of stacked silicon nitride layers interleaved by planarization layers has been developed for encapsulation of OLEDs on foil.

For this purpose a low temperature (<120°C) silicon nitride, deposited using a RF-driven parallel plate plasma reactor, has been optimized both on c-Si and on PEN foil by using spectroscopic ellipsometry (SE) and Fourier transform infrared spectroscopy (FTIR).

However, while intrinsically very low water vapour transmission rates (WVTR <10^-10 g/m²/day at room conditions) of the SiN can be achieved, the total flux of water through the barrier stack is eventually determined by the presence of local defects or pinholes. To gain insight in the transport mechanism of water in the barrier stack, both modelling and a method to trace pinholes in the barrier stack has been applied. On samples (both Ca-mirrors and OLEDs) excellent correspondence of local decay to local presence of water in the barrier stack has been shown.

Ca mirror tests of these barriers on PEN foil have yielded spotless devices after several weeks of accelerated lifetime testing at 60°C and 90% RH and even at 85°C/85% climates. Accelerated lifetime testing at 60%/90% of encapsulated OLEDs resulted in a significant yield of 6 cm² OLED devices without visible black spots due to cathode oxidation for over 3 weeks in this harsh climate.

Mechanical compatibility of the barrier coating with respect to R2R processing has been verified by means of bending tests of SiN layers on foil. As a next step towards R2R processing of barriers, the feasibility of R2R compatible plasma deposition by means of in-line microwave driven plasma sources is investigated. Barrier layer quality is monitored as a function of deposition rate and thickness.

This work was supported by New Energy and Industrial Technology Development Organization (NEDO) as a project of "Development of High-efficiency Lighting Based on the Organic Light-emitting Mechanism".


9:00am TF-FrM3 Amorphous and Crystalline Metaloxide Semiconductors for Transistor Applications, A. Facchetti, Northwestern University

INVITED

In this presentation I will discuss our latest results in developing semiconductor metal oxide (SMO) formulations for solution-processed thin-film transistors based on crystalline and amorphous metal oxide films.

Solution-processed amorphous semiconductor film fabrication by spin-coating and eventually printing is advantageous because of process simplicity, low cost, high reproducibility, chemical composition/structure control, and possible high throughput enabling inexpensive electronics. Regarding crystalline SMO films, InOₓ thin-film transistors (TFTs) were fabricated on various dielectrics [SiO₂ and self-assembled nanodielectrics (SANs)] by spin-coating InOₓ film precursor solutions consisting of methoxyethanol (solvent), ethanolamine (EAA, base), and InCl₃ as the In⁺ source. Importantly, an optimized film microstructure characterized by the high-mobility InOₓ 0.04 phase, is obtained only within a well-defined base: In⁺/n/Si/SiO₂, metal ratio after annealing at 400°C. The greatest electron mobilities of ~ 44 cm²/Vs, for EAA-doped In⁺/n−/SiO₂, are measured for n-Si/SiO₂/InOₓ/Au devices. This result combined with the high InOₓ/n−/SiO₂ mobilities of ~ 10 cm²/Vs and very low operating voltages (< 5 V) is encouraging for high-speed applications. We have also developed amorphous Sn-In-O and Zn-Ga-In-O formulations in which the corresponding films can be annealed at far lower temperatures (< 250 °C). For instance, solution-processed amorphous tin-doped indium oxide (ITO) films for TFT fabrication at temperatures < 250 °C can be achieved by controlling film precursor solution In₁−xSnₓO₀.₅+x ratio versus Sn₁−xO₁−x ratio resulting in electron mobilities > 2 cm²/Vs for ITO and > 10 cm²/Vs for TFTs using SnO₂ as the gate dielectric. Furthermore, we demonstrate that hybrid integration of solution-processed ITO semiconductor films SAND enables m ~ 20 cm²/√Vs.

8:00am TF-FrM1 Thin-film Barrier on Foil for Roll-to-Roll OLEDs, F.J.H. van Assche, E.W.A. Young, J.J. Michels, TNO Holst Centre, The Netherlands

Y. Shigesato, Aoyama Gakuin University, Japan

The amount of oxygen in the films was controllable by appropriate adjustment of \( f_{O_2} \). In order to evaluate the chemical reaction between each MoO₃ thin-film and HTL by Raman spectroscopy, bilayer films were fabricated by subsequent vacuum evaporation of N,N'-di(1-naphthyl)-N,N'-diphenylbenzidine (α-NPD) as HTL. The electronic state of the MoO₃/x [2] and forming a charge-transfer complex into the organic layer have been discussed actively. It has been reported that the hole-injection performance of MoO₃ films would be dependent on the amount of oxygen and zirconia content. Temperature-dependent Hall measurements indicate a critical point at which the films are non-degenerate. We further correlate the optical and electrical data with structural and compositional analysis.

is not so high and also the cost for the high quality ceramic targets is high.

On the other hand, reactive sputtering using Zn-Al alloy targets is considered to be one of the most promising techniques to achieve much higher deposition rate for various industrial applications because sputtering yield of the metallic surface is much larger than oxide surface and also the higher sputtering power density can be applied for metallic targets because of their higher thermal conductivity. The reactive sputtering process, however, is strongly affected by the O2 flow ratio; the deposition rate exhibited hysteresis with respect to the O2 reactive gas flow rate. Such behavior originates in the oxidation state of the target surface, resulting in the marked decrease in deposition rate with the increasing O2 flow.

Therefore, the sputtering conditions should be precisely controlled so as to obtain high-quality AZO films by reactive sputtering with a high deposition rate and with high reproducibility. In this study, AZO films were deposited on quartz glass substrates, unheated and heated at 200°C, using reactive sputtering with a specially designed feedback system. The plasma impedance combined with mid-frequency (mf) pulsing [1]. A planar Zn-Al target (AI: 1.5wt.%) was connected to the switching unit, which was operated in a 50 kHz unipolar pulse mode [2]. Oxidation of the target surface was precisely controlled by the feedback system control, the entire O2 flow ratio in the “transition region”. The deposition rate was about 10-20 times higher than the one deposited by conventional sputtering depositions using oxide ceramic targets. For the AZO films deposited on the glass substrates heated at 200°C with a discharge power of 4000 W, the deposition rate was 390 nm/min, where the resistivity of the films was 3.8×10^-4 Ωcm and transmittance in the visible region was 85%.

Due to recent shortages [1] and toxicity issues [2] of indium, Al-doped ZnO (AZO) have attracted much attention as alternatives to transparent conductive materials, such as Sn-doped In2O3 (ITO) films and indium zinc oxide (IZO). In general, AZO films deposited by magnetron sputtering showed large spatial distributions of electrical properties. Several investigations have suggested that such electrical property distributions should originate in the bombardment of the high-energy negative oxygen ions accelerated in cathode sheath region [3] or the oxidation enhancement by the activated oxygen sputtered from the oxide targets and reaching at the growing film surface [4], both of which should take place at the locations in front of the erosion area of the magnetron cathode. In order to clarify the mechanisms of the degradation in the electrical properties, we investigated the dominant factors determining the electrical property distributions of AZO films deposited by dc magnetron sputtering with various sputtering gases, such as Ar, Kr or Xe. The spatial distributions clearly showed the dependence on a variety of the sputtering gases when the films were deposited on unheated glass substrate. In the cases of using Kr or Xe gases, the tendency to increase in the resistivity at the location in front of the erosion area was enhanced extremely compared with the case of using Ar. This could be attributed to the bombardment damages enhanced by the increasing sputtering voltages, because the plasma impedance increased by the smaller secondary electron emission coefficients for Kr or Xe impingements. We will also discuss on the oxidation effect of the activated oxygen or the bombardment effects by the high energy neutrals (Ar, Kr or Xe) on the electrical property distribution of AZO films. This work was partially supported by a High-Tech Research Center project for private universities with a matching fund subsidy from the Ministry of Education, Culture, Sports, Science, and Technology (MEXT) of Japan.

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TF-FrM8 Study on Spatial Distribution of Electrical Properties for Al-doped ZnO Films Deposited by DC Magnetron Sputtering using Various Inert Gases. Y. Sato, K. Ishihara, N. Oka, Y. Shigesato, Aoyama Gakuin University, Japan

Due to recent shortages [1] and toxicity issues [2] of indium, Al-doped ZnO (AZO) have attracted much attention as alternatives to transparent conductive materials, such as Sn-doped In2O3 (ITO) films and indium zinc oxide (IZO). In general, AZO films deposited by magnetron sputtering showed large spatial distributions of electrical properties. Several investigations have suggested that such electrical property distributions should originate in the bombardment of the high-energy negative oxygen ions accelerated in cathode sheath region [3] or the oxidation enhancement by the activated oxygen sputtered from the oxide targets and reaching at the growing film surface [4], both of which should take place at the locations in front of the erosion area of the magnetron cathode. In order to clarify the mechanisms of the degradation in the electrical properties, we investigated the dominant factors determining the electrical property distributions of AZO films deposited by dc magnetron sputtering with various sputtering gases, such as Ar, Kr or Xe. The spatial distributions clearly showed the dependence on a variety of the sputtering gases when the films were deposited on unheated glass substrate. In the cases of using Kr or Xe gases, the tendency to increase in the resistivity at the location in front of the erosion area was enhanced extremely compared with the case of using Ar. This could be attributed to the bombardment damages enhanced by the increasing sputtering voltages, because the plasma impedance increased by the smaller secondary electron emission coefficients for Kr or Xe impingements. We will also discuss on the oxidation effect of the activated oxygen or the bombardment effects by the high energy neutrals (Ar, Kr or Xe) on the electrical property distribution of AZO films. This work was partially supported by a High-Tech Research Center project for private universities with a matching fund subsidy from the Ministry of Education, Culture, Sports, Science, and Technology (MEXT) of Japan.

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