

## 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. Wiest, R.C. Davis, Brigham Young University, A. Dadson, 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 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 crosslinked with 1,2,5,6-diepoxyoctane 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 analyte loading capacity as measured in SPE than non-porous solid diamond particles. For example, for 50-70  $\mu\text{m}$  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.

2:20pm **TF2-MoA2 Plasma Polymer Film Behavior in Ethanol: A Multi-Technique Investigation**, L. Denis, D. Thiry, University of Mons, Belgium, D. Cossement, Materia Nova Research Center, Belgium, P. Gerbaux, University of Mons, Belgium, F. Brusciotti, I. Van De Keere, V. Goossens, H. Terryn, Vrije Universiteit Brussel, Belgium, M. Hecq, R. Snyders, 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 ( $\Delta d$ ) 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 ( $P_{\text{mean}}$ ). The PPF behavior in ethanol has been studied through analysis of both PPF and the resulting ethanol solution characteristics.

$\Delta d$  which is inversely proportional to  $P_{\text{mean}}$  has been measured by ellipsometry. This behavior has been attributed to the increase of the PPF cross-linking density ( $d_{\text{XL}}$ ) with  $P_{\text{mean}}$ . In order to evaluate  $d_{\text{XL}}$ , 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  $d_{\text{XL}}$  with  $P_{\text{mean}}$ , 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  $\Delta d$ , observed after PPF immersion in ethanol, is mostly related to reorganization of the PPF structure and not to material dissolution in the solvent.

2:40pm **TF2-MoA3 Controlled Growth of MOFs Thin Films 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. 1-3

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 IRRAS, SPR, and AFM. The IRRAS, SPR and AFM data showed a linear increase in the thickness of grown layers for each immersion cycle. The AFM and SEM data recorded for laterally patterned 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 [Cu3BTC2(H2O)n] MOF on both COOH and OH terminated surfaces, where the XRD out-of-plane (Figure 1) and the in-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

- (1) O. Shekhah, H. Wang, S. Kowarik, F. Schreiber, M. Paulus, M. Tolan, C. Sternemann, F. Evers, D. Zacher, R. A. Fischer and C. Wöll, J. Am. Chem. Soc., 2007, 129, 15118.
- (2) D. Zacher, O. Shekhah, Ch. Wöll, R. A. Fischer, Chem. Soc. Rev., 2009, 38, 1418–1429.
- (3) O. Shekhah, H. Wang, M. Paradinas, C. Ocal, B. Schüpbach, A. Terfort, D. Zacher, R. A. Fischer, Ch. Wöll, Nature Materials, in print. 2009. DOI:10.1038/nmat2445

3:00pm **TF2-MoA4 Counterion Dependent Swelling of Redox-Active Polyelectrolyte Multilayers**, R. Zahn, ETH Zurich, Switzerland, F. Boulmedias, Institut Charles Sadron, France, J. Voros, ETH Zurich, Switzerland, P. Schaaf, 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  $[\text{Fe}(\text{CN})_6]^{4-}$  to  $[\text{Fe}(\text{CN})_6]^{3-}$ , leading to a thicker and less rigid film. This was observed using electrochemical QCM-D (EC-QCM-D). 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 PAH-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 Fourier Transformed InfraRed (ATR-FTIR) spectroscopy. High ionic 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**

Al<sub>2</sub>O<sub>3</sub> 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. A reduction in these requires exploration of chemical deposition carried out in gas or liquid phases. Single Source Chemical Vapour Deposition (SSCVD) effectively delivers a metal organic package of stoichiometric Al<sub>2</sub>O in the form of aluminium(III) diisopropylcarbamate and reduces the temperature of formation to 500 °C. Amorphous Al(OH)<sub>n</sub> thin films with an average thickness of 200 nm can also be deposited at even lower temperatures by a simple solvothermal reaction. The decomposition of this carbamate precursor produces hydroxylated thin films at temperature of 65 °C. A subsequently high pressure hydrothermal reaction produces the dehydration of hydroxides and to promote the formation of polycrystalline oxide films. The chemical and structural integrity of these films are examined by XPS and NEXAFS.

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 readily undergo β-elimination decomposition pathways 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 phase 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 lack of detailed understanding of how 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 along the length of 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.

**4:20pm TF2-MoA8 Electron Scattering at Single Crystal Cu(001) Surfaces, J.S. Chawla, D. Gall, Rensselaer Polytechnic Institute**

We demonstrate specular electron scattering at single crystal Cu(001) surfaces and quantitatively show how Ta and Ta-oxide overlayers, and adsorbed O<sub>2</sub> molecules perturb the periodic surface potential, causing diffuse electron scattering. These findings are an important step towards narrow low-resistivity interconnect wires, and also provide the basis for a new type of gas sensor. Epitaxial Cu(001) layers with thickness *d* ranging from 20 nm to 1.4 μm were grown on MgO(001) substrates by ultra-high vacuum magnetron sputter deposition at 80 °C. X-ray diffraction  $\theta$ - $2\theta$  scans,  $\omega$ -rocking curves, and pole figures show the layers are single crystals with a cube-on-cube epitaxy. *In-situ* scanning tunneling microscopy shows

20 to 200 nm wide surface mounds with 0.35 to 0.60 nm wide atomically smooth terraces and atomic level roughness. *In-situ* electron transport measurements at room temperature show a resistivity increase with decreasing thickness, from 1.70±0.06 to 2.65±0.09 μΩ-cm for *d* = 1400±30 to 20.0±0.4 nm, respectively. The data is consistent with the Fuchs-Sondheimer model and indicates specular scattering at the Cu-vacuum interface with an average specular parameter *p* = 0.6±0.1. In contrast, layers measured *ex-situ* show completely diffuse surface scattering (*p* = 0) due to sub-monolayer oxidation. Samples that are immersed in liquid N<sub>2</sub> immediately after removal from the vacuum system do not oxidize and exhibit *p* = 0.7±0.1 at 77 K. *In-situ* deposition of 0.3 to 7 nm thick Ta barrier layers on Cu(001) films leads to a resistance increase that indicates a transition to completely diffuse surface scattering, independent of the Ta thickness. Oxidation of the Ta layer leads to a partial recovery of the specularity, attributed to a reduced barrier density-of-states at the Fermi-level resulting in a lower scattering probability into barrier-layer states. *In-situ* exposure of Cu(001) layers to partial O<sub>2</sub> pressures *P*<sub>ox</sub> between 10<sup>-8</sup> and 10<sup>-1</sup> torr cause distinct resistance changes that suggest a multiple step adsorption process: The initially adsorbed O<sub>2</sub> yields a resistance increase due to electronic roughening of the Cu surface, causing complete diffuse scattering at a coverage of 0.14 O<sub>2</sub> monolayers. Continued exposure results in a resistivity drop to the original value, as a complete monolayer is formed that yields specular scattering, followed by an increase associated with diffuse scattering at a chemically oxidized Cu surface. Data analysis provides values for the scattering cross-section of adsorbed molecules and shows that the rate in resistance-change is proportional to *P*<sub>ox</sub>, hence, these layers may become useful as thin metal film gas sensors.

**4:40pm TF2-MoA9 Current Fluctuations in Au/HfO<sub>2</sub>/PT Resistive Switching Memories, C. Vallee, Joseph Fourier University (UJF) - LTM, France, P. Gonon, Joseph Fourier University (UJF), France, C. Jorel, LTM, France, V. Jousseume, CEA/LETI, France**

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, TiO<sub>2</sub>, ZrO<sub>2</sub>, Cu<sub>x</sub>O...), a perovskite (BaTiO<sub>3</sub>, SrTiO<sub>3</sub>...) or a manganite (Pr<sub>1-x</sub>Ca<sub>x</sub>MnO<sub>3</sub>, La<sub>1-x</sub>Sr<sub>x</sub>MnO<sub>3</sub>...). 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, HfO<sub>2</sub> MIM RRAM cells are elaborated and tested in two electrical modes: voltage sweep mode and constant voltage stress (CVS) mode. The HfO<sub>2</sub> 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, HfO<sub>2</sub> would be an interesting candidate for the RRAM technology. HfO<sub>2</sub> films (10 nm) were grown at 350°C by atomic layer deposition (ALD) using alternate cycles of H<sub>2</sub>O and HfCl<sub>4</sub> 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 HfO<sub>2</sub>/Pt interface (absence of PtOx oxides). Top gold electrodes (100 nm thick, 2 mm in diameter) were deposited on the HfO<sub>2</sub> films by dc sputtering.

The voltage sweep mode shows that HfO<sub>2</sub> RRAM is bipolar and that the switching mechanism is probably due to the oxygen vacancies migration and accumulation through the electrical field to the Pt/HfO<sub>2</sub> interface. These positively charged vacancies may act as dopant and form a locally conductive channel in the dielectric. In the CVS mode the device's resistance was observed to be unstable, displaying fluctuations between the high resistance state and the low resistance state which are typical of random telegraph signals. The role played by oxygen vacancies on these fluctuations will be discussed and a mechanism based on a competition between the oxygen vacancies alignment by the electric field and their thermal redistribution by Joule heating will be proposed.

**5:00pm TF2-MoA10 Plasma Beam Deposition of Silver Mirrors, J.D. Barrie, C.T. Chu, P.D. Chaffee, C.J. Panetta, K.A. Folgner, P. Fuqua, The Aerospace Corporation**

The high reflectivity of silver coatings in the visible and infrared makes them the mirror of choice for many demanding applications. Unfortunately, these mirrors tend to be affected by exposure to atmospheric contaminants, resulting in corrosion that reduces reflectivity and increases scatter, limiting the mirrors' useful service life. Factors that can affect the stability of silver mirrors include interface adhesion, impurities and pinholes in the dielectric protection layers, and the microstructure and stress levels in the films. This paper examines the preparation of silver mirrors by plasma beam

deposition, a relatively new technique for thin film fabrication developed and patented by Plasma Quest, Ltd., and licensed by The Aerospace Corporation. In this method, a high-density inductively-coupled RF-plasma is created external to the deposition chamber, is electromagnetically steered towards a source target, and finally is accelerated towards the target by application of a bias on the target. The separation of plasma generation and transport offers significant advantages in process control. We will present data on how varied deposition conditions, such as plasma beam density and target bias, affect stress and durability of high reflectivity silver mirrors.

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