

Thursday Afternoon, November 1, 2012

Thin Film

Room: 11 - Session TF+AS+SS-ThA

Thin Films: Growth and Characterization-III

Moderator: M.R. Davidson, University of Florida

2:00pm **TF+AS+SS-ThA1 Atomic Force Microscopy (AFM)-Based Nanografting for the Study of Self-Assembled Monolayer Formation of Organophosphonic Acids on Al₂O₃ Single Crystal Surfaces.** B. Torun, B. Oezkaya, G. Grundmeier, University of Paderborn, Germany

The surface chemistry of aluminum oxides plays a crucial role in the field of catalysis, corrosion and adhesion. Alumina (Al₂O₃) covered aluminum alloys are employed in the construction of lightweight automotive and aerospace parts. In order to protect these materials from environmental factors organic coatings are commonly used. In this context the adhesion between polymer and oxide surfaces is of utmost importance to improve the longevity of industrial parts. Using self-assembled adhesion promoting monolayers the complexity of surface pretreatment processes could be reduced tremendously. Long aliphatic phosphonic acids, such as octadecylphosphonic acid (ODPA), were found to be suitable for forming dense self-assembled monolayers on native oxide covered aluminum substrates. However in contrast to amorphous oxide films, single crystal surfaces provide a much more well-defined experimental and theoretical platform for studies on the adsorption mechanisms and the stability of organophosphonic acids.

In the presented study^[1], adsorption, stability, and organization kinetics of organophosphonic acids on single-crystalline alumina surfaces were investigated by means of atomic force microscopy (AFM)-based imaging, nanoshaving, and nanografting. The latter, nano-shaving and -grafting, are rather new techniques to study self-assembly processes. Since they were first reported^[2] in 1997, atomic force microscopy based nanografting has been used as a tool to investigate the adsorption of organic monolayers mostly on noble metals, such as gold.^[3] Moreover recent studies focused on influences of the confinement between AFM-tip and background monolayer on the adsorption of molecules during the grafting process. [about:blank#_ENREF_1]

AFM friction and phase imaging have shown that chemical etching and subsequent annealing led to heterogeneities on single-crystalline surfaces with (0001) orientation indicating differences in the local surface termination. These findings were supported by angle resolved X-Ray photoelectron spectroscopy (AR-XPS) measurements suggesting a partially hydroxide terminated surface. Self-assembly and stability of ODPA were shown to be strictly dependent upon the observed heterogeneities of the surface termination, where it was locally shown that ODPA can loosely or strongly bind on different terminations of the crystal surface. Furthermore, organization kinetics of ODPA was monitored with nanografting on (0001) surfaces. Supported by measurements of surface wettability and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), it was demonstrated that the lack of organization within the protective adsorbed hexylphosphonic acid (HPA) monolayer on alumina surfaces facilitated the reduced confinement effect during nanografting, such that kinetics information on the organization process of ODPA could be obtained.

[1] Torun, B. et al., *Langmuir* **2012**, 28, (17), 6919-6927.

[2] Xu, S. et al., *Langmuir* **1997**, 13, (2), 127-129.

[3] Yu, J. et al., *Langmuir* **2008**, 24, (20), 11661-11668.

[4] Xu, S. et al., *J. Amer. Chem. Society* **1998**, 120, (36), 9356-9361.

2:20pm **TF+AS+SS-ThA2 SIMS as a Method for Probing Stability of the Molecule-Substrate Interface in SAMs.** J. Ossowski, J. Rysz, Jagiellonian University, Poland, A. Terfort, Goethe University, Germany, P. Cyganik, Jagiellonian University, Poland

Despite the numerous structural studies of Self-Assembled Monolayers (SAMs) available nowadays, the structure and stability of the SAM-substrate interface is still poorly understood and controversial even for the most simple SAM system. As a consequence, the experimental and theoretical analysis of the bonding geometry and the stability of the molecule-substrate interface for technologically relevant, and therefore more complicated SAMs, is extremely difficult.

In this presentation we report extensive static secondary ion mass spectrometry (SIMS) studies¹ on homologous series of thiols (BPnS, CH₃-C₆H₄-C₆H₄-(CH₂)_n-S-Au(111), n = 2-6) and selenols (BPnSe, CH₃-C₆H₄-C₆H₄-(CH₂)_n-Se-Au(111), n = 2-6) where structure and stability of molecule-substrate interface was systematically modified as verified by

our previous experiments²⁻⁵. Correlating SIMS data with previous microscopic², spectroscopic³ and very recent neutral mass spectrometry studies^{4,5} we show that SIMS can be successfully applied to monitor fine changes in the molecule-substrate interface stability of these model SAMs. Further, to demonstrate general applicability of SIMS for such analysis, we report use of this method for monitoring influence of S versus Se substitution in purely aliphatic (heksadecanethiol/selenol) and aromatic (anthracenethiol/selenol) SAMs on Au(111). In summary our experiments show that a new approach for probing the stability of molecule-substrate interface in SAMs can be proposed by using SIMS. Importantly, this technique is relatively fast and can be applied for virtually all complicated and technologically relevant SAMs.

References

(1) J. Ossowski, P. J. Rysz, A. Terfort and P. Cyganik *in preparation*.

(2) P. Cyganik, K. Szelagowska-Kunstman, et al. *J. Phys. Chem. C* **2008**, *112*, 15466.

(3) K. Szelagowska-Kunstman, P. Cyganik, et al. *Phys. Chem. Chem. Phys.* **2010**, *12*, 4400.

(4) S. Wyczawska, P. Cyganik, A. Terfort, P. Lievens, *ChemPhysChem* (communication) **2011**, *12*, 2554.

(5) F. Vervaecke, S. Wyczawska, P. Cyganik, et al. *ChemPhysChem* (communication) **2011**, *12*, 140.

2:40pm **TF+AS+SS-ThA3 Wet Chemical Surface Modification of Silicon Oxide and Oxide Free Silicon by Aluminum Oxide.** P. Thissen, A. Vega, T. Peixoto, Y.J. Chabal, University of Texas at Dallas

Wet chemical surface modification is a powerful method to change the chemical properties of surfaces. Although it has been used extensively, there are still many issues that limit the applicability of these reactions. Substrate dip coating in aqueous solutions is particularly useful to facilitate both organic and inorganic layer functionalization. For instance, the bonding of phosphonic acid to silicon oxide is weak in water because the Si-O-P bond is easily hydrolyzed. We demonstrate here that this problem is alleviated by the addition of an ultra-thin aluminum oxide layer to the silicon oxide surface via dip-coating a silicon substrate in an aqueous solution of aluminum chloride. The growth kinetics of the aluminum oxide layer are characterized by several surface sensitive techniques and found to follow a Stranski-Krastanov mechanism. Once the aluminum oxide layer is in place, a self assembled monolayer (SAM) of octadecylphosphonic acid (ODPA) is attached by the "tethering by aggregation and growth" (T-BAG) method performed in a controlled environment. We demonstrate that this ODPA layer grafted on the aluminum oxide interlayer remains stable in water. We also show that, following the same wet chemical approach, we are able to attach aluminum hydroxyl directly on oxide-free silicon surfaces previously functionalized with 1/3 monolayer OH. [1] Finally, we show that our approach can easily be transferred to other metal oxides and discuss the most influencing parameters.

[1] Michalak, D. J.; Amy, S. R.; Aureau, D.; Dai, M.; Esteve, A.; Chabal, Y. J. *Nat. Mater.* **2010**, *9*, 266-271.

3:00pm **TF+AS+SS-ThA4 Static and Dynamic Depth Profiling of Thin Films with Low Energy Ion Scattering (LEIS).** H.R.J. ter Veen, M. Fartmann, Tascon GmbH, Germany, T. Grehl, ION-TOF GmbH, Germany, B. Hagenhoff, Tascon GmbH, Germany

With the ever increasing demand of thinner and better defined thin layer structures, good depth resolution becomes more and more critical in depth profiling techniques. Low Energy Ion Scattering (LEIS) is known as the most surface sensitive chemical analysis technique (see [1] for a review of LEIS technique). It is considerably less known that LEIS can also be applied for so called "static depth profiling" by interpreting the backgrounds on the low energy side of the LEIS peaks. The energy that the particles lose while travelling through the sample is a measure for the depth of the scattering atom, in a way similar to Rutherford Back Scattering (RBS) but for a much smaller depth range. New models have been developed to understand the process that gives rise to these backgrounds and that contains the information from layers below the surface up to depths of 10 nm. These models will be presented.

The models for this static depth profiling can be verified by dynamic (sputter) depth profiling. After each sputter step a full LEIS spectrum is recorded, which contains the surface information as well as the static depth profile at that point in the dynamic depth profile. In this way, the static depth profile can forecast the dynamic depth profile. This technique will be demonstrated for an Si/SiO₂/W/Al₂O₃ system.

LEIS is particularly suited for dynamic depth profiling. Since LEIS is so surface specific, the depth resolution is excellent, as long as the sputter conditions are chosen with care. Furthermore, LEIS can be quantified easily, in many cases - such as in depth profiles - without the use of references. However, any dynamic depth profile suffers from artifacts, such as preferential sputtering and ion beam mixing. By combining the dynamic depth profiling with static depth profiling there is an independent check on these artifacts. Furthermore, it will be shown how static depth profiling can give relevant information also at shallow depths where in a dynamic depth profile sputter equilibrium will not have been reached yet.

[1] H.H. Brongersma et al, Surf. Sci. Rep. 62 (2007)63

3:40pm **TF+AS+SS-ThA6 Paul Holloway Award Talk: Surface Chemistry and Structure of Alloy Thin Films under Reaction Conditions and their Correlations to Catalytic Performances of CO₂ Conversion and Methane Partial Oxidation, F. Tao***, University of Notre Dame **INVITED**

Formation of alloys is one of the important approaches to design of new catalysts with high activity and selectivity as a second metal could tune electronic structure of the first metal or/and create thermodynamically favorable sites for an ideal reaction channel. Co-Ru alloys are active catalysts for conversion of CO₂ into fuel molecules CH₄. Pd-based alloys are important catalysts for methanol partial oxidation to produce hydrogen. Thin films of model catalysts of alloys Co-Ru and Pd-Co were prepared through e-beam evaporation in UHV. In-house ambient pressure X-ray photoelectron spectroscopy using monochromatic Al K α were used to examine the evolution of surface compositions of alloy catalysts and the oxidation states of the constituting elements under reaction conditions and during catalysis in contrast to those before or after a reaction; Surface chemistry (composition and oxidation state) of active phases of Co-Ru and Pd-Co was revealed. High pressure STM provided visible information of surface structure at nano and atomic scale under reaction conditions. These studies clearly suggest a modification of Co electron state through coordinating Ru atoms and thus tuning the adsorption energy of intermediates on Co in CO₂ conversion, which enhances the selectivity to production of CH₄. The formed Co_{0.85}Ru_{0.15} alloy exhibits 100% selectivity to the production of CH₄ and a conversion of 40% which is higher than both pure Co and pure Ru. The promotion effect of the alloy film for CO₂ conversion was rationalized by electronic effects of Ru to Co in the alloy thin films under reaction conditions. In terms of Pd-Co alloy catalysts, segregation of Co to surface under reaction conditions was observed. Through the measurement of surface composition using AP-XPS and the coordination of Pd on surface visualized with STM, a correlation between surface chemistry and structure of Pd-Co alloy surface under reaction conditions and the corresponding catalytic performances were built. The modification of Co to the catalytic behaviors of Pd was identified.

4:20pm **TF+AS+SS-ThA8 Time-resolved and Surface Plasmon Resonance Studies in Metal-Insulator Phase Transition in VO₂ Thin Films, L. Wang, C. Clavero, K. Yang, E. Radue, M.T. Simons, I. Novikova, R.A. Lukaszew**, College of William and Mary

Vanadium dioxide (VO₂) is a prominent example for a material exhibiting a metal-insulator transition (MIT) as a function of temperature with a phase transformation around 340 K from a low-temperature insulator state to a high-temperature conducting state. During the MIT the lattice structure of VO₂ transforms from a monoclinic (insulator) to a tetragonal structure (conductor). Whether these structural changes are solely responsible for the nature of the transition or whether correlation effects also play a role, has been a subject of much debate. Two mechanisms have been generally considered to explain the origin of the MIT in VO₂. The Mott-Hubbard mechanism suggests that electron-electron correlation drives the first-order MIT whereas the Peierls mechanism proposes that a strong electron-lattice interaction leads to the MIT. In order to have a better understanding of the phase transition mechanism and the optical properties of this material across the MIT, we present our research studies on epitaxial VO₂ thin films. We have investigated the optical transmission of a VO₂ thin film during the thermally induced MIT in two different optical spectral regions, with cw THz light and low power (1 mW) IR light (1520 nm HeNe), to identify different mechanisms at play. We have found that the transmission of the THz light starts to decrease at higher temperature than that of the IR light thus probing different stages during the thermally induced MIT. We also investigated surface plasmon polariton excitation in VO₂ thin films in the IR region, and observed a clear trend from non-absorption in the insulator phase to a high absorption in the metallic phase while changing the VO₂ temperature. Our studies are aimed at helping to understand the evolution of the metallic phase in VO₂ thin films after the MIT and relaxation back to the insulator phase upon the MIT which is of paramount importance for

ultra-fast switch applications. Finally, we note that Cavalleri *et al.* [1] reported that the light-induced phase transition happens in less than half a pico-second thus hinting at electronic processes, although they also found that it strongly depended on pump-laser power which is suggestive of lattice interactions. We will compare our time-resolved measurements also using pump-probe techniques but with the sample held at low-temperature vs. room-temperature to illustrate the role of the pump-power on the photo-induced MIT.

[1] A. Cavalleri, Cs. Tóth, C.W. Siders, J. A. Squier, F. Ráksi, P. Forget and J. C. Kieffer, Phys. Rev. Lett. **87** (23), 237401 (2001).

4:40pm **TF+AS+SS-ThA9 Growth, Microstructure and Optical Properties of Sputter-Deposited Gallium Oxide Thin Films, S.K. Samala, C.V. Ramana**, The University of Texas at El Paso

Gallium oxide (β -Ga₂O₃), which is a stable oxide of gallium, is a wide band gap material. The high melting point coupled with stable structure makes β -Ga₂O₃ the best candidate for high temperature sensing. β -Ga₂O₃ thin films can be used for developing oxygen sensors operating at higher temperatures (≥ 900 °C). This feature opens the possibility of developing the integrated β -Ga₂O₃ based oxygen sensors for power generation systems. The present work was performed on the analysis of growth behavior, microstructure, and optical properties of β -Ga₂O₃ films grown by sputter deposition. Ga₂O₃ thin film were deposited on Si(100) and quartz substrate by varying the growth temperature from room temperature to 800 °C. The characteristic analysis of the samples was performed employing grazing incidence X-ray diffraction (GIXRD), scanning electron microscopy (SEM), and spectrophotometry measurements. GIXRD analyses indicate that the samples grown at lower temperatures were amorphous while those grown at ≥ 400 °C. SEM results indicate that the morphology evolution is dependent on the temperature. The characteristic shape of the grains changed from triangular to square and finally to spherical morphology with increasing temperature. Optical characterization indicates that the band gap varies from 4.1 to 5.1 eV as a function of increasing temperature. The correlation between growth conditions, microstructure and band gap is established.

5:00pm **TF+AS+SS-ThA10 Optical and Structural Properties of Hafnium Oxide Thin Films Prepared Using Different Deposition Techniques, L. Sun, N.R. Murphy, J.T. Grant, J.G. Jones, R. Jakubiak**, Air Force Research Laboratory

The high dielectric constant and optical transparency of hafnium oxide makes it a useful component in leading-edge integrated circuitry and optical coatings. The optical and structural properties of stoichiometric HfO₂ films vary significantly depending on the deposition mechanism. We prepared 200 nm thick films of HfO₂ on silicon (100) substrates derived from DC magnetron sputtering (DCMS), high power impulse magnetron sputtering (HiPIMS) and pulsed laser deposition (PLD). Analysis of x-ray diffraction data revealed that films deposited via PLD are amorphous, while those deposited using the magnetron sputtering methods had peaks at 2θ of 28.3°, 31.3°, 34.3° and 50.0° indicative of polycrystalline monoclinic HfO₂. This is further supported by the FT-IR data collected in the far-IR regime where absorption bands at 258, 341, 410 and 514 cm⁻¹ were present. AFM and SEM images indicate that the sputtered samples had rougher surface morphology and larger grain sizes than the PLD films where the surface was uniform and smooth (RMS surface roughness less than 0.1 nm). The degree of surface roughness and grain size is inversely proportional to the refractive index. At 632 nm PLD films had an index of refraction of 2.10 while the index of the sputter coated films was 1.98, presumably due to presence of voids. The high refractive index and homogeneity of the PLD films indicate that they were highly packed without voids during growth. Additionally, the influence of the O₂/Ar ratio, working pressure, HiPIMS pulse profile and duty cycle on optical properties, surface roughness, particle size and structural properties of the HfO₂ thin films were characterized and evaluated.

5:20pm **TF+AS+SS-ThA11 Nitrogen Induced Changes in the Structure and Electronic Properties of WO₃ Thin Films, C.V. Ramana, R.S. Vemuri**, The University of Texas at El Paso, *M. Engelhard, S. Thevuthasan*, Pacific Northwest National Laboratory

Tungsten oxide (WO₃) is a wide band gap semiconductor (~ 3.2 eV), which exhibits excellent physical, chemical and electronic properties. WO₃ thin films have been widely used in electrochromics and chemical sensors. Recently, the band gap modification with anionic and cationic doping of WO₃ was gained importance to utilize these materials in photo-catalysis for energy production and utilization. The present work was performed on nitrogen incorporated WO₃ (N-WO₃) films to explore the options to engineer

* Paul Holloway Award Winner

the microstructure and electronic properties. Specifically, the effect of nitrogen incorporation and processing parameters on the microstructure evolution and band gap of WO_3 thin films is investigated. The samples were grown using reactive RF magnetron sputtering where the nitrogen concentration in the films is varied by varying partial pressure of nitrogen during deposition while keeping all other process parameters constant. Quantitative measurements employing X-ray photoemission spectroscopy indicate the nitrogen content increases with increasing nitrogen partial pressure. Structural analysis employing grazing incidence X-ray diffraction demonstrated that the nitrogen atoms embedded in WO_3 crystal matrix changes the crystal-texturing and thus induce changes in the physical properties. Optical spectrophotometry analysis on the N- WO_3 films revealed a shift in the fundamental absorption edge which is in linear relation with the corresponding nitrogen concentration. The correlation between microstructure, dopant profile, dielectric constant and band gap in WO_3 films will be presented and discussed.

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