Tuesday Morning, December 9, 2014

Thin Films
Room: Makai - Session TF-TuM

Interfaces in Multilayers & Nanocomposites
Moderator: Juan Luis Pena Chapa, CINVESTAV-IPN
Unidad Merida, Mexico

8:00am **TF-TuM1 Looking Below the Surface with Photoemission: Standing Waves and Hard X-rays**, *Charles Fadley*, University of California at Davis, USA **INVITED**
I will present some new directions in soft x-ray photoemission (XPS, SXPS) and hard x-ray photoemission (HXPS, HAXPES, HIKE) [1-5], with illustrative examples of applications to a range of sample types. These involve combined SXPS and HXPS studies of buried layers and interfaces in magnetic and transition-metal oxide multilayers [1], as well as semiconductor junctions [2]; solid-gas or solid-liquid interfaces with high ambient pressures [4,5]; and the use of standing waves from multilayer mirrors to enhance depth contrast in spectroscopy [1,3,4,5].

References

This work was supported by the U.S. Department of Energy under Contract No. DE-AC02-05CH11231, the Army Research Office, under MURI Grant W911-NF-09-1-0398, the Forschungszentrum Julich, Peter Grunberg Institute (PGI-6), and the LABEX-PALM, APTCOM project of Le Triangle de Physique, Paris.

[1] "Interface properties of magnetic tunnel junction La0.7Sr0.3MnO3/SrTiO3 superlattices studied by standing-wave excited photoemission spectroscopy", A. X. Gray et al., Phys. Rev. B 82, 205116 (2010); and A.X. Gray et al., Europhysics Letters 104, 17004 (2013).

[2] Nondestructive characterization of a TiN metal gate: chemical and structural properties by means of standing-wave hard x-ray photoemission spectroscopy", C. Papp, G. Conti, et al. J. Appl. Phys. 112, 114501 (2012).

[3] "Hard X-ray Photoemission with Angular Resolution and Standing-Wave Excitation", C. S. Fadley, invited review, J. Electron Spectrosc. 190, 165-179 (2013)

[4] "Some future perspectives in soft- and hard- x-ray photoemission", C.S. Fadley and S. S. Nemšák, invited review for a special issue of the Journal of Electron Spectroscopy dedicated to Structure Determination and Wave-Function Analysis, H. Daimon, A. Hishikawa, and C. Miron, Editors, available online at: http://authors.elsevier.com/sd/article/S036820481400139X .

[5] "Chemical-state resolved concentration profiles with sub-nm accuracy at solid/gas and solid/liquid interfaces using standing-wave ambient-pressure photoemission (SWAPPS)", S. Nemsak et al., submitted.

8:40am **TF-TuM3 ToF-SIMS and XPS Characterization of Plasma Polymerized ppAA/Teflon-like Thin Films Interfaces**, *V. Spampinato*, EC-JRC-IHCP Ispra (ITALY), Italy, *C. Desmet, A. Valsesia, P. Colpo, F. Rossi*, EC-JRC-IHCP Ispra (ITALY), *Giacomo Ceccone*, EC-JRC-IHCP Ispra (ITALY), Italy
The availability of the high energy cluster sources open new possibilities in the use of surface analysis techniques such XPS and ToF-SIMS to characterize organic films which are important in different application fields ranging from energy to food and medicine (1, 2). In particular the use of molecular depth profiling allows the investigation of the distribution of molecules within the different layers of organic films and nanostructured materials (3).

Plasma polymerization is a well establish method to deposit controlled thin films on different substrates and it is applied in many industrial and research activities (4, 5).

In this work we report the analysis of multilayers plasma polymerized polyacrylic acid (ppAA) and teflon-like (PTFE) films using XPS and ToF-SIMS. In particular, XPS has been used to verify the surface composition of the different polymeric films, whilst ToF-SIMS depth profiles have been obtained by means of Ar^+_n and Bi^+_n (n=1 and 3) polyatomic sources. Both single beam and dual beam analysis have been investigated and the different parameters (ion energy, analysis fluence and analysis area) have been studied to evaluate the degree of sample damage (6).

Finally, preliminary data on the use of ToF-SIMS depth profiling technique to identify the presence of nanoparticles at ppAA/PTFE interfaces will be also presented and discussed.

1) Mahoney C, *Mass Spectrom Rev.,* **2010**, 29(2):247

2) Fletcher J.S. Vickerman J.C., *Anal. Chem.*, **2013**, 85 (2), 610

3) A. Shard, I. Gilmore, A. Wucher, In, ToF-SIMS: Materials Analysis by Mass Spectrometry Di John C. Vickerman and David Briggs (Eds), 2013, p311

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9:00am **TF-TuM4 A detailed Assessment of Indium Diffusion in InGaAs/high-k/TiN MOS Devices Employing ARXPS**, *Alberto Herrera-Gomez, O. Ceballos-Sanchez,* CINVESTAV-Unidad Queretaro, Mexico, *M. Vazquez-Lepe,* Universidad de Guadalajara, *T. Duong, R. Arroyave,* Texas A&M University, *A. Sanchez-Martinez,* CINVESTAV-Unidad Queretaro, Mexico, *F. Espinosa-Magaña*, Cimav-Unidad Chihuahua
The electrical performance of InGaAs-based MOS structures is affected by post deposition annealing. A proper characterization of the structural alterations associated with the degradation of the interface and electrical properties is important for understanding failure mechanisms [1]. While most of the results are focused in the control of interfacial passivation [2], phenomena such as diffusion of atomic species from the substrate has not been as widely examined. The samples employed in this study were TiN/high-k/InGaAs MOS structures with different thermal treatments. X-ray spectroscopy (XPS) studies revealed the appearance of an indium peak induced by annealing. Through a robust methodology based on angle-resolved XPS, it was found that the new peak is related to diffusion of indium through the dielectric into the metallic layer. This is the case when the high-k material is alumina [3], hafnia [4] and zirconia [5]. The transport of gallium is only patent in the case of hafnia and zirconia [4,5]. The structure of the samples was characterized employing the MultiLayer Method [6] and the experimental methodology described in Reference 7. Once the structure (thickness and composition) of the various layers constituting the nanofilms were assessed, it was possible to generate the expected angular behavior of the XPS signal from the indium peak under different scenarios. By employing this "scenarios" approach it was possible to robustly show the diffusion phenomenon and to quantify the amount of transported mass. These results, together with density function theory (DFT) calculations, allowed for the assessment of the activation energy for the diffusion of indium through the high-k dielectrics. It was surprising to find that, for all three dielectrics, the transport activation energy of indium is around 0.8 eV.

[1] R. V. Galatage et al. Appl. Phys. Lett. 99, 172901 (2011).

[2] S. A. Suleiman et al. Electrochem. Solid-State Lett. 13, H336–H338 (2010).

[3] O. Ceballos-Sanchez, A. Sanchez-Martinez, M. O. Vazquez-Lepe, T. Duong, R. Arroyave, F. Espinosa-Magaña, and A. Herrera-Gomez, J. Appl. Phys. 112, 053527 (2012).

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[5] O. Ceballos-Sanchez, E. Martinez, A. Herrera-Gomez. Submitted to Appl. Phys. Lett.

[6] http://www.qro.cinvestav.mx/~aherrera/reportesInternos/arxpsAnalysisSharpIntefaces.pdf.

[7] A. Herrera-Gomez, F.S. Aguirre-Tostado, P.G. Mani-Gonzalez, M. Vazquez-Lepe, A. Sanchez-Martinez, O. Ceballos-Sanchez, R.M. Wallace, G. Conti and Y. Uritsky. J. Elec. Spec. Rel. Phen. 184, 487 (2011).

9:20am **TF-TuM5 Electric and Thermoelectric Properties of Molecule-Nanoparticle Composite Structures Influenced by Surrounding Gases**, *ShienDer Tzeng, Y.S. Li, K.T. Chiang, I.C. Ni*, National Dong Hwa University, Taiwan, Taiwan, Republic of China
Nanocomposite structures formed by the assembly of nanoparticles with functional surface molecules have many interesting properties [1-3]. We found that these surface molecules at the interface between nanoparticles play very important role on the physical properties (e.g., resistance and Seebeck coefficient reported in this work) of the nanocomposite thin film. For instance, shorter length of surface molecules results in shorter interparticle gap distance and thus increases the electric and plasmonic coupling between nanoparticles. Besides, the barrier height could also be tuned by using different kinds of molecules. Furthermore, the interparticle gap distance or the barrier height of charge conduction could also be influenced by their surrounding gases. In this work, we show that Heme modified nanoparticle assembled films could be used for low water vapor

pressure sensing (as shown in Fig. 1). From high vacuum to ~0.01 Torr water vapor, the resistance of Heme device could increase 1%. By contrast, 8-mercaptooctanoic acid (MOA) or 6-mercaptohexanoic acid (MHA) modified nanoparticle assembled films need 1 Torr water vapor to cause 1% resistance change. Besides, we found that the response is proportional to P^γ, and the characteristic energy of water adsorbed in the nanocomposite structure could be calculated from the value of γ. Furthermore, the response time of such water vapor sensors could be less than 0.2 sec, much shorter than most known humidity sensors. We also found that the thermoelectric properties of these molecule-nanoparticle composite thin films were very sensitive to surrounding gases (as shown in Fig. 2). For instance, the Seebeck coefficient of MHA-modified gold nanoparticle assembled films was about 12.5 μV/K in high vacuum (10^{-5} Torr), but became 120 μV/K in 600 Torr O_2 gas. Such great change in Seebeck coefficient could be explain by the change of density of state contributed by the gas molecules adsorbed on the surface molecules.

References:

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2. Cheng-Wei Jiang, I-Chi Ni, Shien-Der Tzeng, and Watson Kuo, Applied Physics Letters 101, 083105 (2012).

3. Cheng-Wei Jiang, I-Chi Ni, Shien-Der Tzeng, Cen-Shawn Wu, and Watson Kuo, Nanoscale 6, 5887 (2014).

9:40am TF-TuM6 Laser Lift-Off of Single-Crystal GaAs Thin Films for Low-Cost, High-Performance Photovoltaics, Optics and Electronics, *Bruce Clemens*, Stanford University, *G. Hayes*, Stanford University, USA

GaAs and related III-V sphalerite materials offer a wide array of tunable characteristics that lend themselves to many advanced device technologies. However, the cost of GaAs substrates limits their use, specially for photovoltaics. Separating epitaxially-grown layers from a growth substrate can reduce costs, however the current approach, which uses an acid to laterally etch an epitaxial sacrificial layer, is slow and can damage other device layers. Here, we demonstrate laser lift-off as a new approach that is orders of magnitude faster, and that enables more freedom in the selection of other device layers. We grow a structure with a spatially-tuned optical absorption coefficient by growing a small-band-gap, pseudomorphic layer between the GaAs substrate and a GaAs film and device structure. By using InGaAsN with a band gap of 0.9 eV for this layer, we achieve high absorption of 1064 nm (1.17 eV) light from a Nd:YAG nanosecond laser pulse, while GaAs is essentially transparent for this wavelength. Illumination through the back of the GaAs substrate with laser fluences of about 0.7 J/cm^2 achieves transfer of the GaAs layer to a flexible polymer substrate. Transmission electron microscopy and x-ray diffraction show that the initial InGaAsN layer is coherently strained to match the GaAs substrate, and that the GaAs film is strain-free and free of dislocations, both before and after lift-off. Thermal modeling shows only modest heating outside of the InGaAsN layer, so that the film or device above the InGaAsN layer experiences minimum thermal exposure. Examination of the lift-off interfaces shows evidence of melting and re-solidification. We demonstrate a process using additional InGaP etch layers that allow for quick and easy clean-up of this melted region, resulting in restoration of the original GaAs wafer surface to a condition suitable for re-use. Thus our process can transform the GaAs substrate from a consumable to a manufacturing tool.

10:20am TF-TuM8 SIMS Depth Profiling and 3D characterization of Organic/Inorganic Surfaces by FIB Crater Wall Imaging and Tomography, *N.J. Havercroft,* ION-TOF USA, Inc.*, Felix Kollmer,* ION-TOF GmbH, Germany*, R. Moellers, D. Rading, S. Kayser, E. Niehuis*, ION-TOF GmbH

Information on the chemical composition, physical properties and the three dimensional structure of materials and devices is of major importance. Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) is known to be an extremely sensitive surface imaging technique which provides elemental as well as comprehensive molecular information on all types of solid surfaces. In the so-called dual beam mode the pulsed analysis beam is combined with a low energy sputter ion beam for the removal of material. This allows depth profiling of multilayers with high depth resolution as well as three-dimensional analysis.

However, the analysis of structures at greater depth (> 10μm) requires long measurement times and the build-up of surface roughness at the crater bottom limits the achievable spatial resolution. Moreover, extremely rough samples, samples with voids, and material that exhibits strong local variations in density or sputter yield are unsuitable for conventional depth profiling. Not only that the initial surface topography is unknown but it is also modified and in many cases even roughened by the sputtering process.

In order to overcome these limitations we used a combined SIMS/FIB setup. Either a Bi cluster beam or a mono-atomic Ga beam is used to FIB mill a crater into the sample. Subsequently, a 2D TOF-SIMS image of the vertical crater wall is acquired. Since the crater wall is hardly affected by the aforementioned roughening problems this approach allows the in-depth distribution of elements to be determined by analyzing a plane perpendicular to the surface at high lateral resolution (Δl<50nm) [1].

Moreover, by serial slicing of the crater wall followed by intermediate analysis steps this approach can be extended in order to provide the full 3D characterization of the analyzed surface. We will present 2D and 3D data of reference material, multilayer samples and technically relevant real world samples such as fuel cells and battery electrodes. For thin multilayer samples the FIB process can be performed under grazing incidence in order to bevel the surface and hence magnify and accentuate thin layers in the plane of the analyzed crater wall.

However, FIB/SIMS approach fails when analyzing organic surfaces since the molecular structure is almost completely destroyed by the sputtering process. We will discuss methods to maintain the molecular structure under high dose sputtering conditions by performing the FIB milling with massive argon clusters.

[1] F. Kollmer, W. Paul, M. Krehl, E. Niehuis, SIMS XVIII proceedings paper, Surf. Interface Anal., 2012

10:40am TF-TuM9 Growth and Characterization of Heteroepitaxial III-N Semiconductor Films using Atomic Layer Epitaxy, *N. Nepal, Virginia Anderson, J.K. Hite, C.R. Eddy, Jr.*, US Naval Research Laboratory

Aluminum nitride (AlN), gallium nitride (GaN), and indium nitride (InN) semiconductors and their corresponding ternary films, such as InGaN, offer attractive properties, with high breakdown fields and widely tunable direct band gaps. Currently, III-nitrides are primarily deposited with molecular beam epitaxy and chemical vapor deposition. The addition of Atomic Layer Epitaxy (ALE) to the possible growth techniques is driven by the need for ever thinner films integrated into complex heterostructures, something that is increasingly difficult to achieve by conventional techniques. Furthering the attraction of ALE is the promise of lower growth temperatures that allow the deposition of a wider range of indium containing ternary films.

Here we report on ALE in a plasma-equipped Ultratech/Cambridge Nanotech atomic layer deposition system to grow AlN, GaN, and InN at temperatures significantly lower than needed for molecular beam epitaxy (MBE) and metalorganic chemical vapor deposition (MOCVD).[1] In growing epitaxial materials, the substrates and corresponding surface preparation procedures are important. The substrates include silicon(111), sapphire, and MOCVD gallium nitride on sapphire, as well as graphene.[2]

For InN on a-plane sapphire, the expected wurtzite hexagonal phase was heteroepitaxially grown for films deposited in the temperature window of 220 to 260 C, well below the typical minimum 450 C temperature used in MOCVD. At an even lower temperature, 183 C, the heteroepitaxial InN on a-plane sapphire was discovered to be cubic phase with a NaCl structure, a phase of InN that had before been unreported.[3] Heteroepitaxial AlN films were grown on GaN/sapphire at a much lower temperature (500 C) than by MOCVD, typically 1100 C or more. Finally, GaN has been included in ALE deposited ternaries in the relatively low temperature window of 250-400 C even as its optimization continues. The ALE grown III-N films have carbon and oxygen contamination that hinders their immediate use in many applications, and improving the film purity is a major focus. In addition, initial deposition of indium ternaries indicates that more stoichiometries are available by ALE than MOCVD.

The possibilities for greater use of III-nitrides are apparent even at the early stages of progress in atomic layer epitaxy. Further characterization during and after deposition of the films should lead to materials suitable for use in high electron mobility transistors, as well as optoelectronic devices.

[1] N. Nepal et al., Appl. Phys. Lett. **103** 082110 (2013)

[2] N. Nepal et al., Cryst. Growth Des. **13** 1485 (2013)

[3] N. Nepal et al., Appl. Phys. Express **6** 061003 (2013)

11:00am TF-TuM10 Controlling Charges States at Nanoscale Schottky Contacts, *Tae-Hwan Kim,* Pohang University of Science and Technology, Republic of Korea*, H.W. Yeom*, Institute for Basic Science

Metal-semiconductor interfaces have drawn a lot of interest in the field of semiconductor surface and interface science, and have been one of the most essential parts in semiconductor electronic and optoelectronic devices. For example, the Schottky-barrier height experimentally observed at the metal-semiconductor interface appears to be nearly independent of the work function of the metal. Since the time of Bardeen, interface gap states seem to have been a primary mechanism of the Schottky-barrier height causing Fermi level pinning at metal-semiconductor interfaces. Recently, polarized

chemical bonds at metal-semiconductor interfaces have been recognized to lead to the apparent Fermi level pinning effect. When these interface bonds are formed underneath thin metal islands grown on a silicon substrate, a spontaneous charge transfer across the semiconductor-metal interfaces occurs as a result of the difference in the Fermi level positions between the metal and the semiconductor. These polarized chemical bonds can form a dipole layer. This dipole layer can play an important role in many areas of technology, for instance, in organic light emitting diodes. However, some of the fundamental aspects of the charge injection process into/from the interface dipole layer at the Schottky contact are yet not explored in any real detail.

In this work, we report the use of scanning tunneling microscopy (STM) to form a double-barrier tunneling junction (DBTJ) with thin metallic nanoislands grown on Si(111) and to control charges of the interface dipole layer formed between the metallic nanoislands and the Si(111) substrate. Reversible hysteric switching in their I−V and differential conductance spectra are observed due to the charging and discharging of the interface dipole layer in a similar fashion to molecular DBTJs. STM images clearly visualize the distinct charge states and scanning tunneling spectroscopy (STS) spectra reveal that quantum well states (QWSs) of the ultrathin islands act as the charging/discharging channels in analogy to the molecular orbitals in the case of the molecular DBTJs. This work demonstrates that the charges of the interface dipole layer at the nanoscale Schottky contact can be controlled by the electron transfer via the QWSs of the metallic islands.

11:20am **TF-TuM11 Enhancement of Contact Properties of Ytterbium Silicide by Alloying with Molybdenum**, *Sekwon Na, H. Lee*, Sungkyunkwan University, Korea, Republic of Korea

As scale-down of metal-oxide-semiconductor field effect transistors (MOSFETs) continues, the portion of resistance rising from the contact of total resistance has become burdensome. This has fueled a drive to find a new contact material with a low contact resistance. In particular, rare-earth (RE) metal silicides (Er, Yb, etc.) are promising as source/drain contact materials, since they have a very low Schottky barrier height (SBH) on n-type silicon (0.2~0.4eV).

Among several RE silicides, ytterbium silicide deserves much attention due to its some favorable characteristics for low SBH applications. In this study, we embarked full investigation of Yb silicide by thoroughly analyzing how the formation of the epitaxial silicide layer influences electrical properties including sheet resistance and SBHs. Moreover, we alloyed Yb with Mo to improve oxidation resistance of the material at high temperatures.

Ytterbium and molybdenum were deposited on an n-type silicon (001) substrate with a resistivity of 1-10ohm·cm using a radio frequency (rf) magnetron sputtering system. For the Mo-alloyed sample, the composition of Mo was found around 20 at. % from EDS analysis. To remove the native oxide of the silicon substrate, the wafer was dipped in 1% HF solution and then rinsed with deionized water. The films were deposited at room temperature and at a working pressure of 9mTorr in Ar ambient. Subsequently, a tantalum nitride (TaN) capping layer with the thickness of 50nm was deposited. To measure SBH, we fabricated Schottky diodes by forming circular dots (diameter: 50μm) of Yb via lift-off. The samples were annealed using rapid thermal annealing (RTA) at various temperatures (300°C ~800°C) for 1 minute in N_2 ambient. For characterization, we utilized transmission electron microscopy and X-ray diffraction. The electrical characteristics were examined using an HP semiconductor parameter analyzer.

Dynamic microstructural evolution of the Yb/Si contact, in which solid-state amorphization between Yb and Si, nucleation and growth of an epitaxial $YbSi_{2-X}$ layer, and disruption of the layer due to oxidation occurred successively with the temperature increasing. However, the microstructures of Mo-alloyed samples annealed at high temperatures show that the Mo-rich region is formed above the epitaxial layer, and it fended off oxygen diffusion. Thus, the epitaxial layer remained up to 800°C. While the epitaxial Yb silicide led to low SBHs, oxidation increased significantly SBHs at high temperatures in Yb/Si samples. Protection of epitaxial layer by Mo-segregated region helped to remain low SBHs over a wide temperature range (600~800°C).

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