Spectroscopic Ellipsometry Focus Topic
Room: 19 - Session EL+TF+AS+EM+SS+PS+EN+NM-MoM

Spectroscopic Ellipsometry for Photovoltaics and Semiconductor Manufacturing

Moderator: M. Creatore, Eindhoven University of Technology, the Netherlands, H. Wormeester, MESA+ Institute for Nanotechnology, Univeristy of Twente, Enschede, The Netherlands

8:20am **EL+TF+AS+EM+SS+PS+EN+NM-MoM1 Multichannel Spectroscopic Ellipsometry: Applications in I-III-VI_2 Thin Film Photovoltaics**, ***R.W. Collins***, *D. Attygalle, P. Aryal, P. Pradhan, N.J. Podraza,* University of Toledo, *V. Ranjan, S. Marsillac*, Old Dominion University **INVITED**

Multichannel spectroscopic ellipsometry (SE) has been applied successfully as an in situ, real time tool for optimizing, monitoring, and controlling multi-stage deposition processes in various thin film photovoltaics (PV) technologies. A particularly challenging process optimization problem involves the thermal co-evaporation of individual elements of Cu, In, Ga, and Se in a three-stage process, which has proven to produce high quality $Cu(In_{1-x}Ga_x)Se_2$ (CIGS) materials and high performance PV devices. This three-stage process provides a high level of flexibility in determining the phase, composition, and microstructure of the film, but also generates greater challenges in run-to-run reproducibility of the optimized process. Information extracted from real time SE measurements includes the evolution of the bulk layer and one or more surface layer thicknesses, as well as layer dielectric functions. The layer dielectric functions can be analyzed further to extract the phase and alloy compositions and the defect density or grain size, which can assist in understanding the fabrication process, in optimizing solar cells, and ultimately in monitoring and controlling the optimized process for improved reproducibility. In this study, the focus is on analysis of ellipsometric (ψ, Δ) spectra acquired by real time SE in order to characterize (i) the structural and compositional evolution in $(In,Ga)_2Se_3$ film growth from In, Ga, and Se fluxes in the first stage, (ii) the transition from Cu-poor to Cu-rich CIGS at the end of the second stage, which occurs under Cu and Se fluxes, and (iii) the transition from Cu-rich to the desired Cu-poor CIGS, which defines the end of the third and final stage, and occurs under a second application of In, Ga, and Se fluxes. After the transition from Cu-poor to Cu-rich material in the second stage, a $Cu_{2-x}Se$ phase near the surface of the bulk layer is tracked. In the Cu-rich to Cu-poor transition, this $Cu_{2-x}Se$ phase has fully reacted with In, Ga, and Se to form CIGS. Studies using a standard Mo substrate and 2 µm thick CIGS for solar cells have also revealed features in the (ψ, Δ) spectra characteristic of the anticipated changes in the near surface phase composition as established by detailed modeling on thinner and smoother films. Although careful analysis of real time SE is expected to provide quantitative information on the surface properties and their evolution in this case of solar cells, control of the deposition has been successful simply by monitoring real time changes in the ellipsometric (ψ,Δ) spectra.

9:00am **EL+TF+AS+EM+SS+PS+EN+NM-MoM3 Contribution of Plasma Generated Nanoparticles to the Growth of Microcrystalline Silicon Deposited from SiF_4/H_2/Argon Gas Mixtures**, ***J.-C. Dornstetter***, *S. Kasouit, J.-F. Besnier,* Total S.a, France, *P. Roca i Cabarrocas*, LPICM-CNRS, Ecole Polytechnique, France

Despite the low fabrication cost of thin film silicon solar modules, this type of technology remains non competitive in main stream markets because of the high BOS costs, due to the low energy conversion efficiency of this type of modules (~10%).We have recently shown that microcrystalline silicon films deposited using SiF_4/H_2/Argon RF capacitive plasmas have excellent structural and transport properties, compared to films deposited using conventional SiH_4/H_2 mixtures, allowing for a very good carrier collection, even for thick cells, and Voc values of 0.55 V, without device optimization, thus opening up the path for the realization of high performance solar cells. However, little is known so far about the growth mechanism of this type of materials and the reason for such interesting properties.Studies of silicon thin films deposition from SiF_4/H_2 mixes, under conditions different from ours, suggested that the growth is due to the deposition of SiF_2 radicals, followed by the abstraction of fluorine by hydrogen. Previous work within our group has also shown that deposition occurs only when particles are present in the plasma, and that growth starts from crystallites without any amorphous phase.We present here a systematic study of the growth of microcrystalline films, together with the composition of nanoparticles attracted by thermophoresis to cold traps located both on the walls of the plasma chamber and in the fore line as a function of deposition conditions. The composition of the deposit on the traps is found to be amorphous at low power/ low hydrogen conditions and becomes crystalline when either of them increases. This correlates well with an increase in atomic hydrogen concentration in the plasma, as estimated by actinometry. The crystalline fraction of the deposited film was measured using in-situ ellipsometry and was found to correlate with the composition of the deposit on the cold traps. Deposition rate is drastically reduced when a water cooled trap is installed on the walls of the plasma chamber, and switches off at high H_2 flow rates. Under these conditions, TEM and AFM images, show that at the initial stages of the growth the film is constituted of sparse, hexagonal crystalline particles, having sizes on the order of few tens of nanometers. We interpret the data above as a result of plasma-generated nanocrystals being a significant contribution to the deposited film. This may explain the excellent electronic properties of the films, as the particles are formed in the bulk of the plasma region, free from energetic ions bombardment. We will correlate the structural properties and the film growth mechanisms to the properties of solar cells.

9:20am **EL+TF+AS+EM+SS+PS+EN+NM-MoM4 Multichannel Spectroscopic Ellipsometry for CdTe Photovoltaics: from Materials and Interfaces to Full-Scale Modules**, ***P. Koirala***, *J. Chen, X. Tan, N.J. Podraza,* The University of Toledo, *S. Marsillac,* Old Dominion University, *R.W. Collins*, The University of Toledo

Real time spectroscopic ellipsometry (RTSE) has been implemented in studies of the evolution of the semiconductor structural and optical properties during sputter deposition of thin film polycrystalline CdS/CdTe solar cells on transparent conducting oxide (TCO) coated glass substrates. Analysis of the real time optical spectra collected during CdS/CdTe deposition requires an optical property database as a function of measurement temperature for all substrate components. These include not only soda lime glass, but also an SiO_2 layer and three different SnO_2 layers. We report optical functions parameterized versus temperature for the glass substrate and its overlayers starting from room temperature and ending at elevated temperature above which the semiconductor layers are deposited. In fact, such a database has additional applications for on-line, through-the-glass monitoring applications of coated glass at elevated temperature. In the RTSE studies, knowledge of the temperature dependent optical functions of the substrate components enables an accurate substrate temperature determination before the onset of deposition and is critical for accurate extraction of the semiconductor layer optical properties. We implement RTSE to study the filling process of the surface roughness modulations on the top-most SnO_2 substrate layer and modification of the optical properties of this layer. This modification is further studied post-deposition by infrared spectroscopic ellipsometry. In addition to providing information on interface formation to the substrate during film growth, RTSE also provides information on the bulk layer CdS growth, its surface roughness evolution, as well as overlying CdTe interface formation and bulk layer growth. Information from RTSE at a single point during solar cell stack deposition assists in the development of a model that can be used for mapping the completed cell stack properties, which can then be correlated with device performance. Independent non-uniformities in the layers over the full area of the cell stack enable optimization of cell performance combinatorially.

9:40am **EL+TF+AS+EM+SS+PS+EN+NM-MoM5 Determination of Electronic Band Gaps from Optical Spectra**, ***R.A. Synowicki***, J.A. Woollam Co., Inc.

The band gap of a material Eg is defined theoretically as the lowest energy for electronic transition from the valence to conduction bands in a solid. For an ideal material free of defects this is the photon energy or wavelength where the optical properties change from transparent to absorbing. However, real materials contain defects which cause absorption to begin below the band gap (i.e. the Urbach Tail) making determination of the true band gap position difficult. For example, in a solar cell the measured absorption edge represents the onset of transitions first due to defects, then from band to band. Empirical methods used to determine the band gap in real materials with defects include the Tauc plot and the Mott-Davis plot. More theoretical mathematical dispersion models such as the Tauc-Lorentz, Cody-Lorentz, and Herzinger-Johs models have been developed which include an adjustable band gap parameter. The various plots and dispersion model methods will be discussed and applied to different materials measured optically via spectroscopic ellipsometry, intensity transmission, reflection, absorption, or a combination of these methods.

10:00am **EL+TF+AS+EM+SS+PS+EN+NM-MoM6 Optical Modeling of Plasma-Deposited ZnO: Extended Drude and its Physical Interpretation**, ***H.C.M. Knoops**, M.V. Ponomarev, J.W. Weber, N. Leick, B.W.H. van de Loo, Y.G. Melese, W.M.M. Kessels, M. Creatore*, Eindhoven University of Technology, the Netherlands

High-quality transparent conductive oxides such as ZnO are important due to their electrical and optical properties. To improve these properties the responsible physical processes have to be understood. Traditionally, charge-carrier-scattering processes are investigated by combining morphology data and Hall measurements. This contribution discusses the extensive optical modeling of plasma-deposited ZnO and how its interpretation directly provides insight into the relevant charge-carrier-scattering processes at different length scales. The interpretation is generalized to the concept of frequency-dependent resistivity, which is used to explain the applicability of different Drude models.

Thin films (50-1000 nm) of Al-doped and undoped ZnO were deposited using an expanding thermal plasma MOCVD process.[1] Conditions of high pressure and high diethyl zinc flow allowed for dense films with low electrical resistivities (e.g., 4×10^{-4} Ω cm at 300 nm). The films were analyzed with variable-angle spectroscopic ellipsometry (SE) (0.75 – 5.0 eV), FTIR reflection spectroscopy (0.04 – 0.86 eV), Four-point-probe (FPP), and Hall measurements.

The SE and FTIR data were combined and fitted with classical and extended Drude[2] models. The high intensity of the Drude in the FTIR range resulted in a high sensitivity with which the carrier concentration and mobility could even be determined for thin (~40 nm) undoped ZnO films. An extended Drude model was needed to correctly model the SE energy range, which was explained by the dominance of ionized impurity scattering and a reduction of this scattering for higher photon energies. The grain-boundary-scattering mobility could be determined by the difference between optical and Hall mobilities.[3] When combined with FPP results, the effective mobility can be determined from these optical techniques without the use of Hall measurements. The optical response above the band gap was modeled by a PSEMI or Tauc-Lorentz oscillator model, where a broadening and shift of the transition was seen for increasing carrier concentration.[4]

These insights and a generalized view of electron scattering in ZnO at different length scales will be presented.

1. Ponomarev et al., *J. Appl. Phys.* **Submitted** (2012)

2. Ehrmann and Reineke-Koch, *Thin Solid Films* **519**, 1475 (2010)

3. Steinhauser et al., *Appl. Phys. Lett.* **90**, 142107 (2007)

4. Fujiwara and Kondo, *Phys. Rev. B* **71**, 075109 (2005)

10:40am **EL+TF+AS+EM+SS+PS+EN+NM-MoM8 The Ellipsometric Response of Single-Crystal Silicon to Doping**, ***H.G. Tompkins***, Consultant

The current wisdom is that for ellipsometry in the UV-vis-NIR spectral range, doping of single-crystal silicon can be ignored. We study the ellipsometric response of silicon doped with arsenic at various levels. We also studied the response after implant (before activation) and after the activation (anneal). We find that for samples implanted with 1E18 atoms/cm3, the single-crystal silicon was not amorphized. Implants of 2E19 atoms/cm3 and higher left an amorphous layer on the surface of the wafer the thickness of which was about the depth of the implant. Activation of the sample implanted with 2E19 atoms/cm3 returned the sample to single-crystal silicon and the ellipsometric response in the UV-vis-near_IR is essentially that of undoped silicon. However, the response in the mid-IR is that the extinction coefficient is no longer zero. For samples implanted with 2.5E20 atoms/cm3 and greater, annealing did not return the UV-vis-near_IR ellipsometric response to that of single-crystal silicon. Although this amount of other material (arsenic) is still less that about one tenth of one percent, our conjecture is that the microstructure simply could not be returned to that of a single crystal. As with the lower doped sample, the mid-IR spectral region showed significant increase in the extinction coefficient.

11:00am **EL+TF+AS+EM+SS+PS+EN+NM-MoM9 The Effect of Stress on the Optical Properties Semiconductor Films**, ***A.C. Diebold**, G.R. Muthinti, M. Medikonda, T.N. Adam,* College of Nanoscale Science and Engineering, University at Albany, *A. Reznicek, B. Doris*, IBM Research at Albany Nanotech

Here we review the impact of stress on the complex dielectric function of semiconductor films measured using spectroscopic ellipsometry. Two relevant examples of stressed semiconductor layers are pseudomorphic epitaxial layers fabricated during semiconductor manufacturing and strained silicon on insulator (sSOI) wafers. Stress is known to shift the energies of direct gap critical point transitions in semiconductors. The biaxial stress in pseudomorphic films grown on silicon wafers can be as high as that used during opto-elastic studies of bulk semiconductors. The amount of stress in un-relaxed, pseudomorphic films of $Si_{1-x}Ge_x$ on Si (100) reaches 1 GPa for alloys with 20% Ge and is more than 3 GPa for films with > 50% Ge. The bi-axial stress in sSOI is typically ~1 GPa. An elastic theory approach for the effect of strain on the k*p determined band structure and optical transition energy is well known. Both low shear stress and high shear stress approximations can apply to the shift in transition energy depending on the magnitude of the spin orbit splitting energy vs the magnitude of the shear stress. Until recently it was difficult to obtain sets of samples that test both approximations. Here we discuss results from our recent study of pseudomorphic films of $Si_{1-x}Ge_x$ on Si (100) from x= 0.05 to 0.75 which covers both low and high shear regimes. We also present our recent study of the dielectric function of thinned sSOI which illustrates the impact of stress on the optical transitions for the Si layer on sSOI. All of these samples are examples of new materials being used in semiconductor research. The results of this study are directly transferred into cleanroom spectroscopic ellipsometry systems used for process control during manufacturing.

11:20am **EL+TF+AS+EM+SS+PS+EN+NM-MoM10 Numerical Ellipsometry: Spectroscopic n-k Plane Analysis of Thin Films Growing on Unknown Layered Substrates**, ***F.K. Urban**, D. Barton*, Florida International University

Spectroscopic ellipsometry measurements on thin films commonly make use of prior knowledge of the structure and optical properties of the underlying substrate. However, imprecision in substrate statistics propagates into the solution for the film of interest. Thus it is more accurate to have a method for solving for film properties which simultaneously obtains whatever is needed about the substrate. And it makes solutions possible whether or not book data or previous substrate solutions are available. In this work we apply Complex Analysis in the n-k plane to achieve solutions employing the well-know reflection equations. The method is carried out at each measured wavelength and does not necessitate an *a-priori* assumption of optical property dependencies on wavelength. The mean square error has been improved by many orders of magnitude, a selected limit of 10^{-14} as opposed to 1 to 30 or so for least squares. Thus the full accuracy of the ellipsometer is now available for more accurate measurements of film thickness and optical properties. The method requires six measurements during growth. The first is used to determine the relationship between Rp and Rs at the film-substrate interface. The following four are used to uniquely determine the values of Rp, Rs, and film n, k, and d. The final measurement confirms the unique solution. Suitability of the model is tested by comparing measurements at two of more wavelengths for self consistency. Results for n and k of the growing film are examined across the measurement spectrum in comparison with parameterizations in common use.

Nanomanufacturing Science and Technology Focus Topic
Room: 16 - Session NM+AS+MS-MoM

Metrology and Environmental Issues in Nanomanufacturing
Moderator: N.A. Burnham, Worcester Polytechnic Institute, L.J. Gamble, University of Washington

8:20am **NM+AS+MS-MoM1 Nanomanufacturing – Beyond Silicon**, ***J.A. Liddle***, National Institute of Standards and Technology **INVITED**

The fabrication of integrated circuits in silicon is the preeminent nanomanufacturing technology, and it occupies a very special niche in terms of functionality and value provided per unit area. As a consequence, it is economically viable to use very expensive fabrication processes to generate the required nanostructures. In addition, the degree of control over the manufacturing process that is required necessitates the use of complex and expensive metrology systems. In contrast the vast majority of other nanotechnology products cannot support the cost of comparably sophisticated manufacturing methods or the associated metrology schemes. In this talk I will give examples of how the complexity of the final product and its value dictate what type of nanomanufacturing approach is viable. In particular, I will describe the need for new metrology techniques that can provide nanoscale information, but do so at rates consistent with the high-volume manufacturing of low-cost products.

9:00am **NM+AS+MS-MoM3 Use of Mueller Matrix – Spectroscopic Ellipsometry for Scatterometry based Measurement of Critical Dimensions during Semiconductor Manufacturing**, ***G.R. Muthinti***, *A.C. Diebold,* University at Albany-SUNY, *B. Peterson*, Nanometrics Inc.

Scatterometry is one of the most useful metrology methods for the characterization and control of critical dimensions (CD) during nanoelectronic manufacturing. Most Scatterometry is based on Spectroscopic Ellipsometry (SE) and Normal Incidence Reflectometry (NI) measurement and the simulation of the measured spectra through the Rigorous Coupled Wave Approximation. Evolution of better optical hardware and faster computing capabilities led to the development of Mueller Matrix (MM) based Scatterometry (MMS). Typically, spectroscopic ellipsometry based Scatterometry uses Y the D measured at each wavelength. In this presentation we discuss dimensional metrology using full Mueller Matrix (16 element) Scatterometry in the wavelength range of 245nm-1000nm measured using a dual rotating compensator spectroscopic ellipsometer. Unlike SE and NI, MM data provides complete information about the optical reflection and transmission of polarized light through a sample. The advantage of MMSE over traditional SE Scatterometry is its ability to measure samples that have anisotropic optical properties and depolarize light. We demonstrate this using a series of structures fabricated by e-beam lithography.

9:20am **NM+AS+MS-MoM4 Atomic Layer Deposition Monitored and Characterized by Joint *In Situ* Real-Time Spectroscopic Ellipsometry and Direct Surface Analysis**, ***M. Junige***, *M. Geidel, M. Knaut, M. Albert, J.W. Bartha*, Technische Universität Dresden, Germany

Atomic layer deposition (ALD) is a special kind of chemical vapor deposition, which pulses at least two chemical reactants into a vacuum reactor alternately and separated by purging steps. ALD has emerged as a powerful technique for the conformal and uniform coating of complex three-dimensional structures, even on large-sized substrates. Accordingly, ALD has a high potential for application throughout the entire field of nanotechnology.[1]

Since ALD alters the physical and chemical properties of a surface during a material's deposition, these changes are observable by direct surface analysis techniques like photoelectron spectroscopy (PES) or scanning probe microscopy (SPM) and also by spectroscopic ellipsometry (SE). As previously described in the References [2] - [4], we acquired ellipsometric spectra *in situ* and in real-time and thus monitored the ALD processes at exactly the place and the time of a sample's modification. In addition, we conducted PES as well as SPM measurements without breaking a high vacuum after the ALD. This revealed, among others, the chemical composition as well as the roughness of a coated surface without alteration in air and so enabled the generation of appropriate optical models, which translate the ellipsometric spectra into rather descriptive quantities like a film thickness or a surface roughness.

In the present work, we will demonstrate the capability of joint *in-situ* real-time SE and direct surface analysis based on the ALD of two exemplary materials: tantalum nitride and ruthenium. In the linear homogeneous film growth regime of both the ALD processes, the film thickness increment per cycle (also growth per cycle, GPC) was quantified and studied for varying process parameter sets. The initial ALD growth of TaN showed all the three possible growth modes according to Puurunen [5] depending on the starting substrate material. In the case of Ru, the ALD growth initiation indicated a substrate-inhibited island growth mode irrespective of the starting substrate.

[1] G. N. Parsons, S. M. George, and M. Knez, in *MRS Bulletin***36**, 865 (2011).

[2] M. Junige, M. Geidel, M. Knaut, M. Albert, J. W. Bartha, in *IEEE 2011 Semiconductor Conference Dresden* (Dresden, 2011). – DOI: 10.1109/SCD.2011.6068739

[3] M. Knaut, M. Junige, M. Albert, J. W. Bartha, *J. Vac. Sci. Technol. A* **30**, 01A151 (2012).

[4] M. Geidel, M. Junige, M. Albert, J. W. Bartha: In-situ analysis on the initial growth of ultra-tin ruthenium films with atomic layer deposition, *Microelectron. Eng.* (manuscript submitted).

[5] R. L. Puurunen, *J. Appl. Phys.* **97**, 121301 (2005).

10:40am **NM+AS+MS-MoM8 Transformation of Engineered Nanomaterials in the Environment: Effects of Size, Shape and Morphology on Nanomaterial Toxicity**, ***S. Obare***, Western Michigan University **INVITED**

Engineered nanomaterials (ENMs) are known to possess unique size and shape dependent chemical and physical properties. As a result of their properties, ENMs have been effective in several important applications including catalysis, sensor design, photonics, electronics, medicine, and the environmental remediation of toxic pollutants. Such properties and applications have led to an increase in the manufacture of ENMs and a rise in their presence in consumer products. The increase of ENMs in consumer products presents several opportunities and challenges, and necessitates a proactive study of their health and safety. An important and essential criterion toward a systematic study of the environmental safety of ENMs is the need to control their size, shape and morphology, and to produce them in high quantities. Synthetic procedures that produce gram-scale, well defined and monodisperse metallic nanoparticles with controlled size and shape, is not trivial and requires careful control of reaction conditions. This presentation will demonstrate our ability to develop new organic ligands that when used as stabilizers for metal nanoparticles, provide the ability to gain control of the particle size in one-step synthetic procedures. Monodisperse metallic nanoparticles were synthesized and characterized using spectroscopic, microscopic and x-ray techniques. The chemical composition, surface reactivity, solubility, and aggregation tendency of ENMs were studied under various environmental conditions. We will also discuss how ENMs interact with various components in the environment with an emphasis of their interaction with Gram-negative and Gram-positive bacteria. The results provide insights on the need for green manufacturing strategies of ENMs, their use and safe disposal practices.

11:20am **NM+AS+MS-MoM10 An Integrated Approach Toward Understanding the Environmental Fate, Transport, Toxicity and Occupational Health Hazards of Nanomaterials**, ***V. Grassian***, University of Iowa **INVITED**

Nanoparticles, the primary building blocks of many nanomaterials, may become suspended in air or get into water systems, e.g. drinking water systems, ground water systems, estuaries and lakes etc. Therefore, manufactured nanoparticles can become a component of the air we breathe or the water we drink. One important issue in understanding the environmental fate, transport, toxicity and occupational health hazards of nanoparticles is in characterizing the nature and state of nanoparticles in air, water or in vivo. For the nanoparticles of interest in these studies, metals and metal oxides, it can be asked: (i) will metal oxide and metal nanoparticles be present in air or water as isolated particles or in the form of aggregates? (ii) will metal oxide and metal nanoparticles dissolve in aqueous solution or in vivo? and (iii) under what conditions will metal oxide and metal nanoparticles aggregate or dissolve? As the size regime will be very different depending on the state of the nanoparticles, as dissolved ions, isolated nanoparticles or nanoparticle aggregates, these questions are important to address as it impacts the size regime that needs to be considered or modeled in for example environmental transport or lung deposition models. Furthermore, the effect on biological systems including nanoparticle-biological interactions and toxicity will depend on the state of nanoparticles. In the studies discussed here, macroscopic and molecular-based probes that includes quantitative solution phase adsorption measurements, molecular based probes, light scattering and zeta-potential measurements to investigate the behavior of nanoparticles in aqueous suspensions. We have focused on several different metal and metal oxide nanoparticles in including Fe, Ag, Zn, Cu, Ce and Ti. Some of our newest results which focus on aggregation and dissolution, including detailed size-dependent studies, in the presence and absence of organic acids will be discussed. This research is beneficial as it significantly contributes to the growing database as to the potential environmental and health implications of nanoscience and nanotechnology and how nanomaterials will behave in the environment and impact human health.

Nanomanufacturing Science and Technology Focus Topic
Room: 16 - Session NM+NS+MS+EM-MoA

ALD and Scalable Processes for Nanomanufacturing
Moderator: T.S. Mayer, Penn State University

2:00pm **NM+NS+MS+EM-MoA1 From R&D Towards Industrial Atomic Layer Deposition: Challenges in Scaling up**, ***M. Putkonen***, Beneq Oy, Finland

More and more ALD-enabled applications are emerging. Most of the ALD processes and applications are first demonstrated by small scale experiments. In optimal cases, the innovations lead to material-application combinations which have solid commercial interest. In the subsequent verification and pilot production phase, there is need for increased throughput and reduced costs also for the ALD processed materials.

There are two main features of ALD, that should be optimized when industrial scale production is being considered. Firstly, in large-area coating processes, more attention should be paid to the properties of the precursors. For large-area coatings, large doses of precursors are delivered to the substrates, preferably in very short pulses in order to keep the total cycle time as short as possible. This often requires either DLI-type sources or increased vapor pressure (i.e. increased thermal stability of metal precursors). In addition, although the ALD chemistry should be surface controlled and not dependent on the substrate surface area, deposition rates and film uniformities are habitually dependent on the tool configuration.

Secondly, ALD has so far been largely confined to laboratories due to non-availability of efficient, larger scale, high-throughput ALD systems. Whereas sputtering and CVD have been mainstream coating tools for decades, ALD has only recently started to gain acceptance as a mainstream industrial coating method. For example, ALD is widely seen as the desired manufacturing technology for producing high-quality functional layers for solar cells and packaging materials, but ALD is commonly considered too slow for high throughput manufacturing. However, large-area batch ALD tools, such as the Beneq P800, can operate up to 10 m^2 batch sizes and still maintain ALD cycle times in the range of 3-5 s. Currently, industrial ALD is diffusing into various industrial thin film areas where single wafer, batch or roll-to-roll ALD is the preferred coating method.

In this presentation, we discuss the different requirements for single wafer, conventional batch, cross-flow batch as well as spatial ALD deposition processes and tools for large throughput applications. In addition to conventional Al_2O_3 and TiO_2 processes, SiO_2 processes are used as examples when scaling up chemistry from single wafer to batch ALD. In addition, process transfer from an R&D scale Beneq TFS 200R rotating drum reactor to the true roll-to-roll Beneq WCS 500, developed for OLED encapsulation applications, is discussed in detail. Results of the studies using this system are presented including temperature dependence of growth rate, RI and WVTR measurements.

2:20pm **NM+NS+MS+EM-MoA2 Enabling ALD for Semiconductor Manufacturing**, ***D. Chu***, Applied Materials Inc. **INVITED**

Atomic layer deposition (ALD) is being extensively studied for semiconductor applications because of its precise, atomic level thickness control for very thin films; ALD is extremely conformal and the overall thermal budget is lower than its CVD alternatives. However, ALD is inherently slow which makes it cost prohibitive.

Adoption of ALD processes into manufacturing requires consideration of multiple factors. At Applied Materials, we focus on three main areas to enable ALD for volume manufacturing.

1. Atomic level engineering to create differentiated solutions that boost device performance.

2. Tool architecture and methods to allow integration of multiple films without vacuum break. This is particularly of importance when films scale to Angstrom level, stability of the film becomes an issue. Extendable tool architectures allow integration of other films such as capping layers and pre-post treatments to address this issue

3. Accelerate adoption of standalone ALD films by improving manufacturability and productivity while maintaining single wafer performance

Example applications and challenges for each area will be discussed in this paper.

3:00pm **NM+NS+MS+EM-MoA4 Migration to ALD Techniques in the Semiconductor Industry: Pattern Effects, Microloading and Film Thickness Variability in Dielectric Thin Films Deposition**, ***M.P. Belyansky***, IBM Semiconductor R&D Center

The continuation of scaling in the microelectronics industry is having a profound effect on thin film deposition techniques and processes. One of the consequences of the scaling is a decrease in average film thickness to accommodate the shrinking device dimensions which amplifies the problem of film thickness variability. Most of the CVD deposition techniques and tooling are reaching the limit of reliable thickness control of very thin films. At the same time, circuit designs are becoming more complex, which leads to significant pattern density variation on macro scale. Therefore CVD technology is facing a tremendous challenge in controlling film thickness and properties across variable pattern density which has been one of the major reasons that facilitated the transition to ALD-like deposition techniques and processes in the industry.

The paper discusses the microloading effect (dependence of thin film deposition rate on pattern density) as well as other manifestations of pattern effects in the semiconductor manufacturing. The data shows the effect of microloading on the variation of as deposited film thickness across features of different size as well as for identical features with different pattern density in the surrounding areas. The microloading performance of CVD and ALD silicon oxide and silicon nitride dielectric thin films is covered as well as methods aimed at quantifying and improving thin film variability. The effects of major process parameters, precursor chemistry and tool design on the thin films microloading performance are delineated. Thin films step coverage over a nano scale feature and pitch to pitch film thickness dependence for CVD and ALD dielectric processes are also discussed.

3:40pm **NM+NS+MS+EM-MoA6 Interface Analysis of PEALD TaCN Deposited on HfO_2 using Parallel Angle Resolved X-ray Photoelectron Spectroscopy for sub-20nm Gate Last CMOS Transistors**, ***F. Piallat***, ST Microelectronics, France, *V. Beugin, R. Gassilloud, P. Michallon,* CEA Grenoble, France, *L. Dussault, B. Pelissier,* LTM - MINATEC - CEA/LETI, France, *C. Leroux,* CEA Grenoble, France, *P. Caubet,* ST Microelectronics, France, *C. Vallée*, LTM - MINATEC - CEA/LETI, France

Sub-20 nm high-k/metal CMOS devices require about 2 nm thin metal gate electrode with adapted work function (WF) and chemical inertness regarding the high-k dielectric sub-layer. TaCN material deposited by Plasma Enhanced Atomic Layer Deposition (PE-ALD) has been investigated as a possible gate electrode candidate [1-2]. Depending on the carbon content TaCN can presents a *p-type* behavior with a WF from 4.5 to 4.7eV [3]. Besides plasma used for deposition may have an impact on the under-layer dielectric such as an increase of the EOT [4]. A deviation from bulk material characteristics of the metal gate WF is induced by the intimate bond linking environment at high-k/TaCN interface, but these chemical mechanisms are still unclear. Thus, in this work, interface of TaCN and HfO_2 dielectric is carefully analyzed by X-Ray Photoelectron Spectrometry (XPS), using Ta4f, Hf4f, O1s, C1s, N1s and Si2p core levels, and obtained bonding environments are correlated to work function extracted from MOS capacitors.

Thanks to chemical stability of SiO_2 [5], bonding environments of TaCN/SiO_2 and HfO_2/SiO_2 stacks were chosen as reference for XPS analysis. Then, by comparing TaCN deposited on HfO_2 spectra with these references, the evolution of the chemical environments can be determined, thus a mechanism of interaction between the two materials is proposed. Furthermore, it appeared that, when deposited on HfO_2, TaCN oxidation is higher than on SiO_2, which is attributed to the higher capacity of HfO_2 to have O deficiency [6].

In addition, TaCN/HfO_2/SiO_2 stack was measured using Parallel Angle Resolved XPS (PARXPS) in order to build a depth composition profile. This profile confirms the modifications of chemical environment such as oxidation of the electrode close to high-k/metal interface, it also shows N penetration in HfO_2, which could be induced by plasma densification.

Finally, electrical results from MOS capacitors with TaCN/HfO_2/SiO_2 stacks and TiN/W plug have shown an evolution of the *p-like* metal flat band voltage (Vfb) with plasma conditions. The modifications of chemical bonding environment observed at the high-k/metal interface can give insight on this deviation of Vfb with plasma.

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4:20pm **NM+NS+MS+EM-MoA8 Atmospheric Pressure Atomic Layer Deposition of Al_2O_3 using Trimethylaluminum and Ozone**, ***M.B. Mousa***, *D.H. Kim, C.J. Oldham, G.N. Parsons*, North Carolina State University

Atomic layer deposition (ALD) is used for nanoscale coatings with high uniformity and precise thickness control. Currently, most commercial ALD processes operate in batch mode. Expanding to ambient pressure can increase throughput and facilitate its integration for applications such as smart textiles, flexible electronics and synthetic polymer coatings. We find that under certain flow conditions in the trimethylaluminum (TMA)/water ALD process for Al_2O_3, increasing the reactor pressure from ~ 2 Torr to 760 Torr can produce excess film growth per cycle.

For this work, we studied ALD of Al_2O_3 using TMA/O_3 and compared growth at ~ 2 Torr to that at 760 Torr in a flow tube reactor. We measured film thickness by ellipsometry and surface morphology by AFM. Also, we plan to monitor in-situ growth using a quartz crystal microbalance (QCM). At 2 Torr, by changing the ozone and TMA exposure times, we saw clear ALD saturation at ~ 0.45 Å/cycle at 170°C. A shorter purging time after the ozone exposure tends to increase the growth per cycle. Deposition at higher pressure results in growth rates between ~0.3 and 0.6 Å/cycle at 205°C, with lower growth rates obtained under higher gas flow rate conditions. For both the water and O_3 processes at 760 Torr, a low gas flow rate of 0.5 standard liters per minute (slm) in our flow-tube reactor leads to a high growth rates of ~3 Å/cycle (for water) and 0.6 Å/cycle (for O_3). For the water process at 760 Torr, increasing the flow rate to 10 slm somewhat decreases the growth per cycle to ~1.35 Å /cycle. However, for the O_3 processes at 760 Torr, we need only a relatively small increase to 1.5 slm to achieve growth of 0.3 Å/cycle. This could be due to enhanced ozone desorption kinetics compared to the rate of water desorption under the conditions used. Also interestingly, we find for the water process that films deposited at high pressure have higher surface roughness than films deposited at low pressure. These results will help to identify the key parameters for new continuous atmospheric pressure ALD reactors designs.

4:40pm **NM+NS+MS+EM-MoA9 An Industrial Solution for Surface Passivation of c-Si using AlO_x Film Deposited by In-line Atmosphere Chemical Vapor Deposition**, *K. Jiang,* Gebr. Schmid GmbH + Co, Germany, ***K.O. Davis,*** University of Central Florida, *C. Demberger, H. Zunft, H. Haverkamp,* Gebr. Schmid GmbH + Co, Germany, *W.V. Schoenfeld,* University of Central Florida, *D. Habermann*, Gebr. Schmid GmbH + Co, Germany

Among the different dielectric passivation layers for crystalline silicon (c-Si) solar cells, AlO_x has recently received a great attention due to its excellent chemical and field effect passivation performance for p-type c-Si surface. It offers great promise as a rearside passivation material for passivated emitter and rear cell (PERC) designs. However, up to this point in time, most of the development has been based on laboratory scale deposition systems and methods. Common approaches for synthesizing these passivation layers are thermal or plasma-assisted atomic layer deposition (ALD), whose deposition rates are typically too low (< 10 nm/min) to be compatible with high-volume manufacturing. Other deposition methods like PECVD or spatial separated ALD enable an increase in deposition rate by one order of magnitude (i.e. 100 nm/min). An industrially-compatible deposition technique with low processing cost, easy-handling, compact size, and high throughput that still retains comparable passivation performance to ALD films remains a challenging task.

Using an in-line atmosphere chemical vapor deposition (APCVD) tool, we have synthesized amorphous AlO_x films from precursors of trimethylaluminum and O_2, yielding a maximal deposition rate of up to 150 nm/min per wafer. Deposition rate is determined by the film thickness divided by wafer transportation time through the CVD injector. Both top view and the cross-sectional SEM images present an intact AlO_x/Si interface. A smooth surface is shown without any outgassing (blistering) after deposition and a subsequent firing step. The as-deposited layers exhibit an over stoichiometric O/Al ratio of 1.65~1.75 due to the incorporation of an OH group inside the layer. For both high and low doped p-type c-Si wafers deposited with APCVD AlO_x, excellent surface passivation is achieved with a maximum effective surface recombination velocities ($S_{eff.max}$) of 8 cm/s following by a firing step. These findings are attributed to the buildup of a large negative charge ($Q_f \approx -3 \times 10^{12}$ cm^{-2}) and low interface defect density ($D_{it} \approx 4 \times 10^{11}$ $eV^{-1}cm^{-2}$) following the firing process. It is believed that the incorporated OH group plays an essential role during the firing step. During the annealing/firing step, a certain degree of dehydration takes place (i.e. Al sites bonded OH termination start to bond via an O bridge), which may involve an octahedral to tetrahedral coordination change. This could facilitate the negative charge formation and release of atomic H for passivating the Si dangling bonds at the AlO_x/Si interface.

This data implies a high application potential of APCVD AlO_x for low cost industrial solar cell applications.

5:00pm **NM+NS+MS+EM-MoA10 Solution Based Processing of Floating Gate Memory using Additive-Driven Self-Assembly and Nanoimprint Lithography**, ***J. Watkins***, University of Massachusetts **INVITED**

Polymer and polymer-inorganic hybrid materials organized at the nanoscale are at the heart of many devices that can be created on flexible substrates for applications in energy generation and storage, microelectronics, optoelectronics, communications and sensors. The challenge is to produce these materials using process platforms and materials sets that are environmentally and economically sustainable and can be scaled for cost-effective, high value-added manufacturing. Here we describe a resource efficient, additive approach based on roll-to-roll coating of self-assembled hybrid materials. Specifically we report that nanostructured templates with periodic spherical, cylindrical, and lamellar morphologies exhibiting sub-10 nm domains can be easily obtained through the blending of commercially available disordered polymer surfactants with commodity homopolymers that selectively associate with one segment of the surfactant. We further demonstrate that order in the surfactant systems and in block copolymer templates can be induced by nanoparticle additives that undergo multi-point hydrogen bonding with one of the segments of the polymer template. These additives, which include metal and semiconducting nanoparticles, fullerenes, and other active components, impart functionality to the device. The strong interactions further enable particle loadings of more than 40% in the target phase, resolving a crucial constraint for many applications. These systems can be scaled in our newly constructed R2R processing facility, which includes a custom microgravure coater for hybrid materials that is equipped for in-line substrate planarization and a precision R2R UV-assisted nanoimprint lithography (NIL) tool.

We illustrate the capabilities of these approaches by the fabrication of floating gate field effect transistor memory devices. For this application, the charge trapping layer is comprised of well-ordered polymer/gold NP composites prepared via additive-driven self-assembly; the addition of gold nanoparticles that selectively hydrogen bond with pyridine in poly(styrene-*b*-2-vinyl pyridine) copolymers yields well-ordered hybrid materials at gold nanoparticle loadings of more than 40 wt.%. The charge trapping layer is sandwiched between a dielectric layer and a poly(3-hexylthiophene) semiconductor layer. We can achieve facile control of the memory windows by changing the density of gold nanoparticles. The devices show high carrier mobility (> 0.1 cm^2/Vs), controllable memory windows (0~50V), high *on/off* ratio (>10^5) between memory states and long retention times. Strategies for patterning of the device using NIL will be discussed.

Nanomanufacturing Science and Technology Focus Topic
Room: 16 - Session NM+MS-TuM

All Invited Session: Challenges of Nanomanufacturing from an Industrial Perspective
Moderator: S. Butler, Texas Instruments, B.R. Rogers, Vanderbilt University

8:00am **NM+MS-TuM1 Challenges of Nanomanufacturing from an Industrial Perspective**, ***A. Sekiguchi***, Tokyo Electron Limited **INVITED**

In the semiconductor industry, we have been able to benefit from cost reductions associated with physical scaling of memory and logic devices for decades. By reducing the physical dimensions of our devices from generation to generation, we have been able to drive bit cost of memory and processing power cost of our logic devices with ease. Today however, challenges associated with atomic scale manufacturing and control are daunting, to say the least. Dimensional controls are in the single nm range, six sigma, for lateral scales, and in the sub-Angstrom range for critical film thicknesses. The talk will describe the device level challenges that we face in this era of nano-scale manufacturing, explore options that we have in terms of patterning at 1x nm node and below, and discuss process options that will be needed in the next generation of devices.

9:00am **NM+MS-TuM4 PRINT® Nanomanufacturing Technology-Precisely Engineered Particles for Life Science Applications**, ***M. Hunter***, Liquidia Technologies, INC. **INVITED**

Nanomedicine, an offshoot of nanotechnology, refers to highly specific medical intervention at the molecular scale for treating and curing disease or repairing damaged tissues, such as bone, muscle, or nerves. At this size scale – about 500 nanometers or less –biological molecules and structures operate inside living cells. The pharmaceutical industry continues to evaluate the potential of these new technologies to alleviate the burden of rising research costs, improve the speed and efficiency of the discovery process, and create high-value new generation therapeutics. While nanotechnology is widely seen as having huge potential, the pharmaceutical industry remains skeptical that success at the bench scale can successfully be translated into high volume products.

Liquidia's PRINT® technology (Particle Replication in Non-Wetting Templates) is one example of a breakthrough in micro- and nanoparticle manufacturing that allows complete control over particle size, shape and chemical composition. Since its inception, Liquidia has been addressing nanoparticle manufacturing scale-up by adapting the PRINT particle fabrication process to merge the high-volume production methodologies of roll-to-roll processing and the high precision fabrication methods of the microelectronics industry. Using PRINT technology, Liquidia has the ability to rapidly scale up cGMP manufacturing of particles with unprecedented control over the composition and geometry. This creates the unique ability to manufacture high volumes of complex micro- and nanostructured objects in a number of particle geometries and a variety of materials in a cost paradigm that is very attractive. Using manufacturing methodologies developed and proven in other industries including the printing, film and medical device industries, Liquidia plans to scale its particle manufacturing capabilities to supply commercial quantities for a variety of industries, including diagnostics, vaccines and therapeutics.

10:40am **NM+MS-TuM9 High Productivity Combinatorial R&D Technologies for Cost-Effective Nanomanufacturing**, *D. Lazovsky*, ***C. Hunter***, Intermolecular, Inc. **INVITED**

Nanomanufacturing is inherently more challenging than the production of micron-scale and larger device structures, as interface effects increasingly dominate device performance for nano-scale devices. Theoretical understanding of such effects lags the results of practice, so empirical experimentation is necessary to simultaneously co-optimize multiple critical elements. Such co-optimization using traditional research and development (R&D) methods is typically inefficient, slow and expensive.

Cost-effective nanomanufacturing starts with the development of an optimized device structure, which depends upon our ability to learn about material interactions. For example, while a basic photovoltaic (PV) cell can be made with just 4 layers (n- and p-regions, two contacts), thin-film PV cells designed for optimum efficiency today use additional 10-50nm thick layers to modify band-gaps, optimize light reflection, and extract maximum current.

Even if an optimized nanodevice structure has been identified, it cannot be trivially transferred to high-volume manufacturing (HVM). Different tooling alters process conditions, which generally results in non-optimal final device performance as well as manufacturing yield losses. As an example, while the champion $Cu(In,Ga)Se_2$ (CIGS) cell from a lab has reached >20% conversion efficiency, the best reported from HVM lines today is only ~14%.

Once a nanomanufacturing line is running, experiments are needed to enhance device performance and improve line yield. However, it is inefficient to do R&D using the production line since the experiments must compete with manufacturing runs, and the HVM tools are generally not ideal for experiments. With inefficiency in R&D learning cycles, improving yield is slow and expensive.

A more efficient approach uses a high productivity combinatorial (HPC™) platform—such as that developed by Intermolecular—to dramatically accelerate R&D by 10-100x relative to traditional methods. With unique combinatorial process tools, throughput-matched characterization, and an informatics analysis and data management system, in less than a year we developed a world-class 17.7% active-area efficiency CIGS PV cell using a two-step sulfur-free process flow.

Intermolecular's HPC platform is purpose-built for the R&D of semiconductor and clean-energy products, and is used in Collaborative Development Programs (CDPs) with a growing number of customers. For example, leading-edge semiconductor memory chips today use dielectrics and metal electrode layers that are only 1-10 nm thick, and HPC technology has accelerated R&D learning-cycles and time-to-market for our customers producing such memory chips.

Nanomanufacturing Science and Technology Focus Topic
Room: Central Hall - Session NM-TuP

Topics in Nanomanufacturing Poster Session

NM-TuP1 Fabrication and Characterization of Nanoscale Carbon Nanotube Patterns on Nanostructured Aluminum Surfaces, ***Y. Watanabe***, *H. Kato, S. Asami, S. Sato, S. Takemura, K. Shimada, T. Hiramatsu*, Kanto Gakuin University, Japan

The aim of the present work is to develop the nanofabrication methods of highly-oriented patterns of carbon nanotubes on the various substrates and is to characterize the electronic and optical properties of the patterns. The authors proposed a nanoscale arrangement method using a nanostructured surfaces as a nanofabrication template. Single-walled carbon nanotubes (SWCNTs) were arranged in highly-oriented line pattern with nanoscale trenches fabricated on an aluminum surfaces by combined process of chemical treatments and anodization. SWCNTs dissolved in catechin containing solution. Then this solution were dropped on the nanostructures as a droplet utilizing micropipette and extended on the surface. SWCNTs were locally aligned along the line patterns. Dynamic force microscopy (DFM) observations and the cross section analysis were conducted on pre-aligned and aligned surfaces on the highly-oriented structures. Atomic force microscopy-current imaging tunneling spectroscopy (AFM-CITS) measurements were also conducted in order to investigate local conductive properties of CNTs. In the measurement of I-V characteristics by point contact, quantum conductivity of carbon nanotubes were observed. The proposed method can be applied for the CNT arrangement on different surfaces such as Si and glass substrates by nanoscale imprint which enables the prefabricated nanoscale pattern transcription. Nano-contact transcription was performed according to the following steps: CNTs dissolved in catechin containing solution were dropped with a micropipette on an aluminum line structure. The Al sample was placed on a silicon substrate and was pressed for 30 sec in order to transfer the CNTs pattern to the Si substrate. Then the Al template was removed and the Si substrate was dried naturally. In the case of the line pattern template, it was found that SWCNTs line pattern could be transferred to a Si wafer. Transcription of double wall carbon nanotubes (DWCNTs) was also the same result. Arrangement of multi-walled carbon nanotube (MWCNT) and cup-stacking CNT was also performed. Raman characterization of the fabricated patterns of SWCNT, DWCNT, MWCNT and cup-stacking CNT was conducted in order to investigate the detailed structures on the surface. Two types of Raman peaks which were characteristic of CNT were observed by Raman measurements. Several RBM peaks appeared in the low frequency region (80-400 cm-1). Asymmetric shaped G-band was confirmed (1500-1700 cm-1). A shoulder peak was observed in the low wavenumber side of the G-band.

This work was aided by MEXT-supported Program for the Strategic Research Foundation at Private Universities.

NM-TuP2 Topographical and Raman Studies of Nano-graphite Patterns on Nanostructured Al and Si Surfaces by Carbon Drawing, ***Y. Takarai***, *T. Hirakawa, K. Doi, H. Kato, A. Ishii, Y. Watanabe, S. Takemura, T. Hiramatsu*, Kanto Gakuin University, Japan

The authors performed carbon drawing and embossing methods in order to fabricate nanoscale structures on nanostructured Al surface and Si wafer. Carbon drawing is a nanofabrication method by gently pushing bulk graphite on the surface and drawing it. In the present study, the authors used HOPG and black carbon flakes for carbon drawing which performed on a nanostructured Al substrate. The surfaces were investigated by scanning probe microscopy (SPM) and Raman spectroscopy. The authors performed carbon drawing on the aluminum linked-crater structure. The AFM image demonstrated that each nanoscale crater was filled with carbon by the drawing and a unique carbon dots structure was created on the surface. A unique nanostructure was also fabricated by carbon drawing on the aluminum linked-crater structure. In the case of Si wafer, drawing with carbon flakes made stripe structure. The stripe separation was approximately 1 micrometer. Raman spectroscopy was used to characterize pre-drawing Si wafer and post-drawing Si wafer. Raman peaks due to Si were observed at around 500cm-^{1} and 1000cm^{-1}in the pre-drawing sample. Some characteristic peaks of carbon were observed in the post-drawing sample. A peak at 1360cm^{-1} can be assigned to D band. A peak at 1600cm^{-1} can be assigned to G band (Graphite band). Raman peaks due to glassy carbon appeared after carbon drawing on Si wafer. Furthermore, the authors performed embossing method with inserting carbon flakes between Si wafer and nanostructured Al. It was found that unique nanostructures were created on the Si surface by embossing method. In the case of aluminum highly-oriented line structure, the embossing made the nanoscale line pattern transfer to the Si wafer. The transferred line separation was estimated as several tens of nanometers.In the case of aluminum line structure, drawing a line perpendicular to the HOPG made arch-like structure. It was confirmed that the carbon was along the line in this structure. Raman spectroscopy was used to characterize pre-drawing and post-drawing nanostructured Al surfaces. A peak due to Al_2O_3 was observed at around 2900cm^{-1} in the Pre-drawing. Some characteristic peaks were observed in the post-drawing sample. A peak at 1360cm^{-1} can be assigned to D band due to defects in the crystal which is supposed to appear when crystallinity of thin graphene is distorted. A peak at 1600cm^{-1} can be assigned to G band, which appears when the measured object is allotrope of carbon. This peak intensity depends on wavelength of incident light. This work was aided by MEXT-supported Program for the Strategic Research Foundation at Private Universities.

NM-TuP3 Photoluminescence Enhancement of Aluminum Surfaces with Various Shaped Nanostructures Filled with Metallopfthalocyanines and Organic Dye Molecules, ***A. Ishii***, *T. Shimizu, H. Kato, T. Kamino, S. Takemura, T. Hiramatsu*, Kanto Gakuin University, Japan

Nanostructures such as linked-crater and highly-oriented pillared structures made of anodized aluminum oxide were fabricated on an Al surface by combination process of chemical and electrochemical treatments. Crater–shaped structures were initially created on the alumnum surface by the chemical surface treatment. Successive anodization condition created the different sized linked-crater structures. A highly-oriented pillared structure was fabricated on an Al surface by chemical and electrochemical multi-process. Based on the initial structure fabricated by chemical surface treatments, successive anodization proceeded in the fabrication of well-ordered characteristic nanoscale patterns with highly-oriented aligned trenches on Al surface such as a groove-pattern structure. Successive surface treatment using Semi Clean assisted in fabrication of ordered finer nanoscale structures such as highly-oriented pillared structure. The present work also intended to make an organic nanoscale pattern using highly-oriented pillared structure as a template by filling of dye molecules, namely, rhodamine B (RB), brilliant green (BG) dissolved in acetonitrile, copper phthalocyanine (CuPc), iron phthalocyanine (FePc) and Cobalt phthalocyanine (CoPc) dissolved in toluene in order to functionalize the surfaces. The cross section analysis demonstrated that the dye molecules were filling the trenches along the linked-crater structure and the highly-oriented pillared structure by dynamic force microscopy (DFM) measurement. Photoluminescence measurements showed that RB emission peaks appeared in the wavelength range of 600-640 nm. In the case of BG emission peaks appeared in the wavelength range of 450-500 nm. In the case of metal phthalocyanines, CuPc, FePc and CoPc, the emission peaks appeared in the wavelength range of 450-550 nm. The authors confirmed that the significant emission enhancement happened to dye molecules filling linked-crater and highly-oriented pillared structures fabricated on the aluminum surface. The structure of RB filling aluminum nano-structures were investigated by FT-IR measurements. It was found that the intensity of Al-O mode at 800-1000 cm^{-1} in the case of highly-oriented pillared structure was larger than that in the case of the linked-crater structure while the intensity of Al-O mode at 1000 cm^{-1} was comparable between two structures. It was also found that the emission peaks appeared in the wavelength range of 1200-1700 cm^{-1} in both cases of linked-crater and highly-oriented pillared structures. This work was aided by MEXT-supported Program for the Strategic Research Foundation at Private Universities.

Scanning Probe Microscopy Focus Topic
Room: 16 - Session SP+AS+BI+ET+MI+NM+NS+SS+TF-WeM

Probe-Sample Interactions, Nano-Manipulation and Fabrication
Moderator: S. Allen, The University of Nottingham, UK, A.-P. Li, Oak Ridge National Laboratory

8:20am **SP+AS+BI+ET+MI+NM+NS+SS+TF-WeM2 Controlled Coupling of Silicon Atomic Quantum Dots at Room Temperature: A Basis for Atomic Electronics?**, ***R.A. Wolkow***, University of Alberta and The National Institute for Nanotechnology, Canada, *J. Pitters,* The National Institute for Nanotechnology, Canada, *G. DiLabio, M. Taucer, P. Piva, L. Livadaru*, University of Alberta and The National Institute for Nanotechnology, Canada **INVITED**

Quantum dots are small entities, typically consisting of just a few thousands atoms, that in some ways act like a single atom. The constituent atoms in a dot coalesce their electronic properties to exhibit fairly simple and potentially very useful properties. It turns out that collectives of dots exhibit joint electronic properties of yet more interest. Unfortunately, though extremely small, the finite size of typical quantum dots puts a limit on how close multiple dots can be placed, and that in turn limits how strong the coupling between dots can be. Because inter-dot coupling is weak, properties of interest are only manifest at very low temperatures (milliKelvin). In this work the ultimate small quantum dot is described – we replace an “artificial atom” with a true atom - with great benefit.

It is demonstrated that the zero-dimensional character of the silicon atom dangling bond (DB) state allows controlled formation and occupation of a new form of quantum dot assemblies - at room temperature. Coulomb repulsion causes DBs separated by less than ~2 nm to experience reduced localized charge. The unoccupied states so created allow a previously unobserved electron tunnel-coupling of DBs, evidenced by a pronounced change in the time-averaged view recorded by scanning tunneling microscopy. It is shown that fabrication geometry determines net electron occupation and tunnel-coupling strength within multi-DB ensembles and moreover that electrostatic separation of degenerate states allows controlled electron occupation within an ensemble.

Some speculation on the viability of a new “atomic electronics” based upon these results will be offered.

9:00am **SP+AS+BI+ET+MI+NM+NS+SS+TF-WeM4 Atomic Forces and Energy Dissipation of a Bi-Stable Molecular Junction**, ***C. Lotze,*** Freie Universtiät Berlin, Germany, *M. Corso, K.J. Franke, F.V. Oppen, J.I. Pascual*, Freie Universität Berlin, Germany

Tuning Fork based dynamic STM/AFM is a well established method combining the advantages of scanning tunneling and dynamic force microscopy. Using tuning forks with high stiffness, stable measurements with small amplitudes, below 1 Å can be performed. In this way, conductance and frequency shift measurements of molecular junction can be obtained simultaneously [1] with intramolecular resolution [2].

One of the most intriguing aspects of molecular junctions relates to the effect of structural bi-stabilities to the properties of the junction. These lead, for example, to conductance fluctuations, telegraph noise and the possibility to switch the electrical transport through the junction.

In this presentation, we characterize a model bi-stable molecular system using dynamic force spectroscopy. The effect of current-induced stochastic fluctuations of conductance are correlated with fluctuations in force. In our experiment we identified the last from both, frequency shifts and energy dissipation measurements, picturing a regime in which electrical transport and mechanical motion are coupled.

[1] N. Fournier *et. al*, PhysRevB 84, 035435 (2011),

[2] L. Gross *et. al*, Science 324, 1428 (2009)

9:20am **SP+AS+BI+ET+MI+NM+NS+SS+TF-WeM5 Acetylene on Cu(111): Imaging a Molecular Pattern with a Constantly Rearranging Tip**, ***Y. Zhu***, *J. Wyrick, K.D. Cohen, K. Magnone, C. Holzke, D. Salib, Q. Ma, D.Z. Sun, L. Bartels*, University of California Riverside

Abstract: Using variable temperature STM and DFT simulation, we identify the phases of acetylene adsorbed on the Cu(111) surface. Depending on the coverage, a diffraction-derived surface pattern of acetylene on Cu(111) is validated by STM. The modification of the STM image transfer function through the adsorption of an acetylene molecule onto the tip apex is taken into account. In this case, the images of acetylene patterns on Cu(111) also include direct evidence of **the rotational orientation and dynamics of the acetylene species attached to the tip apex**. DFT modeling of acetylene/Cu(111) reveals that the molecular orientation and separation is governed by a balance of repulsive interactions associated with stress induced in the top surface layer and attractive interactions mediated by the electronic structure of the substrate. Computationally modeling of the substrate with 3 layers obtains the periodicity of the intermolecular interaction that provides a theoretical underpinning for the experimentally observed molecular arrangement.

9:40am **SP+AS+BI+ET+MI+NM+NS+SS+TF-WeM6 Atomic Scale Imaging and Electronic Structure of Trimethylaluminum Deposition on III-V Semiconductor (110) Surfaces**, ***T.J. Kent***, *M. Edmonds, E. Chagarov, A.C. Kummel*, University of California San Diego

Silicon based metal oxide semiconductor field effect transistors (Si-MOSFETs) are quickly approaching their theoretical performance limits, as a result many semiconductors are being explored as an alternative channel material for use in MOSFETs. III-V semiconductors are an appealing alternative to Si because of their higher electron mobilities. The limiting factor in III-V based MOSFET performance is defect states which prevent effective modulation of the Fermi level. The InGaAs (001) As-rich (2x4) surface contains two types of unit cells: ideal unit cells with double As-dimers and defect unit cells with single As-Dimers. The missing As-dimer unit cells, which comprise ~50% of the surface, are believed to cause electronic defect states at the semiconductor-oxide interface, specifically at the conduction band edge of the semiconductor. *In-situ* scanning tunneling microscopy and spectroscopy (STM/STS) and density function theory (DFT) modeling show that TMA readily passivates the As-As dimers in the ideal unit cell but the missing InGaAs(001)-2x4 may not be fully passivated by TMA. To improve the electronic structure of the interface, the sidewalls of the finFETs on InGaAs(001) can be fabricated along the (110) direction. The (110) surface contains only buckled III-V heterodimers in which the lower group III atom is sp2 hybridized with an empty dangling bond and the upper group V atom is sp3 hybridized with a full dangling bond. This results in an electrically unpinned surface.

To investigate the benefits of using a (110) surface as a channel material, the atomic and electronic structure of the ALD precursor trimethylaluminum (TMA) monolayer deposited on III-V (110) surfaces has been studied using *in-situ* STM and STS. Both GaAs and InGaAs samples were studied. GaAs wafers were obtained from Wafertech with a Si doping concentration of 4x1018/cm3. The (001) samples were cleaved *in-situ* to expose the (110) surface. Samples were transferred to the STM chamber (base pressure 1x10-11 torr) where the atomic bonding structure of the precursor monolayer unit cell was determined. STS, which probes the local density of states (LDOS), was used to determine Fermi level pinning. A model of TMA chemisorption was developed in which TMA chemisorbs between adjacent As atoms on the surface, giving a highly ordered monolayer with a high nucleation density which could allow for aggressive effective oxide thickness (EOT) scaling.

10:40am **SP+AS+BI+ET+MI+NM+NS+SS+TF-WeM9 A New Experimental Method to Determine the Torsional Spring Constants of Microcantilevers**, ***G. Haehner***, *J.D. Parkin*, University of St Andrews, UK

Cantilever based technologies have seen an ever increasing level of interest since the atomic force microscope (AFM) was introduced more than two decades ago. Recent developments employ microcantilevers as stand-alone sensors by exploiting the dependence of their oscillating properties on external parameters such as adsorbed mass [1], or the density and the viscosity of a liquid environment [2,3]. They are also a key part in many microelectromechanical systems (MEMS) [4]. In order to quantify measurements performed with microcantilevers their stiffness or spring constants have to be known. Following calibration of the spring constants a change in oscillation behavior can be quantitatively related to physical parameters that are probed. The torsional modes of oscillation have attracted significant attention due to their high sensitivity towards lateral and friction forces, and recent developments in torsional-tapping AFM technology [5]. However, the methods available to determine the torsional spring constants experimentally are in general not simple, not very reliable, or risk damage to the cantilever [6].

* ASSD Student Award Finalist

We demonstrate a new method to determine the spring constants of the torsional modes of microcantilevers experimentally with high accuracy and precision. The method is fast, non-destructive and non-invasive. It is based on measuring the change in the resonance frequencies of the torsional modes as a function of the fluid flow escaping from a microchannel. Results for rectangular cantilevers will be presented and compared to results obtained with other methods [7].

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11:00am **SP+AS+BI+ET+MI+NM+NS+SS+TF-WeM10 A Torsional Device for Easy, Accurate and Traceable Force Calibration of AFM Cantilevers**, ***J.F. Portoles***, *P.J. Cumpson*, Newcastle University, UK

Accurate measurement of biologically-relevant forces in the range of pN to µN is an important problem in nanoscience.

A number of force probe techniques have been applied in recent years. The most popular is the Atomic Force Microscope (AFM). Accuracy of force measurement relies on calibration of the probe stiffness which has led to the development of many calibration methods[1], particularly for AFM microcantilevers. However these methods typically exhibit uncertainties of at best 15% to 20% and are often very time consuming. Dependency on material properties and cantilever geometry further complicate their application and take extra operator time. In contrast, one rapid and straightforward method involves the use of reference cantilevers (the "cantilever-on-cantilever" method) or MEMS reference devices. This approach requires that a calibrated reference device is available, but it has been shown to be effective in providing measurement traceability[2].

The main remaining difficulty of this approach for typical users is the positional uncertainty of the tip on the reference device, which can introduce calibration uncertainties of up to around 6%. Here we present a new reference device based on a torsional spring of relatively large dimensions compared to the typical AFM cantilever and demonstrate how it is calibrated. This method has the potential to calibrate the reference device traceably[3] to the SI with a 1% accuracy by applying techniques typically used for the characterisation of micromechanical devices. The large dimensions of the device reduce the positional uncertainty below 1% and simultaneously allow the use of the device as an effective reference array with different reference stiffnesses at different positions ranging from 0.090 N/m to 4.5 N/m

[1] P J Cumpson, C A Clifford, J F Portolés, J E Johnstone, M Munz Cantilever Spring-Constant Calibration in Atomic Force Microscopy, pp289-314 in Volume VIII of Applied Scanning Probe Methods, Ed. B Bhushan and H Fuchs (Springer, New York, 2009)

[2] P J Cumpson PJ, J Hedley, Nanotechnology 14 (2003) pp. 1279-1288

[3] J F Portolés, P J Cumpson, J Hedley, S Allen, P M Williams & S J B Tendler, Journal of Experimental Nanoscience 1 (2006) pp51-62.

11:20am **SP+AS+BI+ET+MI+NM+NS+SS+TF-WeM11 Nanoscale Surface Assembly by Single-Molecule Cut-and-Paste**, ***H.E. Gaub***, Ludwig-Maximilians Universitat, Germany **INVITED**

Bottom up assembly of functional molecular ensembles with novel properties emerging from composition and arrangement of its constituents is a prime goal of nanotechnology. With the development of Single-Molecule Cut-and-Paste (SMC&P) we provided a platform technology for the assembly of biomolecules at surfaces. It combines the Å-positioning precision of the AFM with the selectivity of DNA hybridization to pick individual molecules from a depot chip and allows to arrange them on a construction site one by one. An overview on different applications of this technology will be given in this talk. One recent example demonstrates the functional of receptors for small molecules. By SMC&P we assembled binding sites for malachite green in a molecule-by-molecule assembly process from the two halves of a split aptamer. We show that only a perfectly joined binding site immobilizes the fluorophore and enhances the fluorescence quantum yield by several orders of magnitude. To corroborate the robustness of this approach we produced a micron-sized structure consisting of more than 500 reconstituted binding sites. To the best of our knowledge this is the first demonstration of a one by one bottom up functional bio-molecular assembly. Figure included in supplemental document. S. Kufer, Puchner E. M.,Gumpp H., Liedel T. & H. E. Gaub *Science* (2008), Vol 319, p 594-S. Kufer, Strackharn, M., Stahl S.W., Gumpp H., Puchner E. M. & H. E. Gaub *Nature Nanotechnology* (2009), Vol 4, p 45-M. Erdmann, R. David. A.N. Fornof, and H. E. Gaub, *Nature Chemistry* (2010), Vol 2, p 755-M. Strackharn, S. Stahl, E. Puchner & H.E. Gaub, *Nanoletters* (2012) in press

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