



*Science and Technology
of Materials, Interfaces, and Processing*

**2011 FALL MEETING of the
AVS HUDSON MOHAWK
CHAPTER**

**Wednesday, Oct 5, 2011
4-8pm**

**General Electric Global Research Center
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Magnetic Materials
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Microelectronic Materials
Nanometer-Scale S&T
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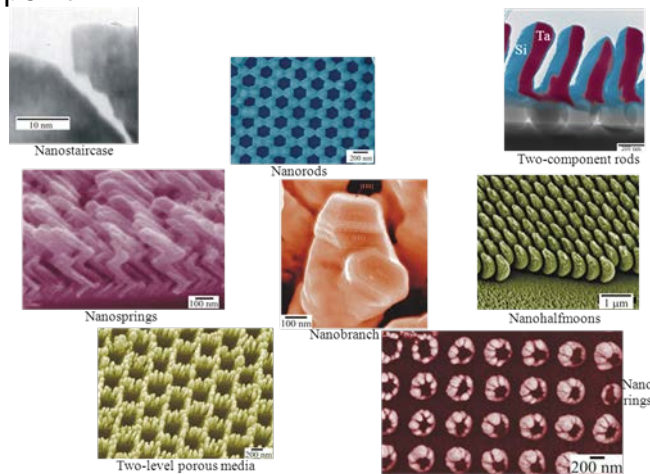
Verbal Presentations

NANORODS, NANOPIPES, NANOSMILES: NANOSTRUCTURE GROWTH FROM THE VAPOR PHASE

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Atomic shadowing during physical vapor deposition causes exacerbated growth of surface protrusions and leads to a chaotic 3D layer growth, which can result in the development of well-separated nanorods, nanosprings, or nanopipes, which are surprisingly regular and have potential applications ranging from fuel cell electrodes and pressure sensors to self-lubricating coatings and nanoactuation. Glancing angle deposition (GLAD) causes particularly strong atomic shadowing and can be used to systematically investigate the effect of shadowing on the morphological evolution. These extremely rough layers cannot be described as a chaotic perturbation from a flat surface. However, using a model which describes them as a nanorod array with an average rod width that follows power law scaling results in experimental curves where all metals converge on a single master curve which exhibits a discontinuity at 20% of the melting point, associated with a transition from a 2D to a 3D island growth mode, and a single homologous activation energy of 2.46 for surface diffusion on curved nanorod growth fronts, which is applicable to all metals at all temperatures. Also, under extreme shadowing conditions, the conventional structure zone model is simplified as there is a direct transition from an underdense (zone I) to a dense (zone III) structure at ~50% of the melting point.



INFLUENCE OF SELF-ASSEMBLED MONOLAYER CHAIN LENGTH ON THE SURFACE PROTECTION OF COPPER FOR LOW TEMPERATURE Cu-Cu BONDING

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Copper-copper thermocompression bonding is considered the method of choice for future generation three-dimensional integrated circuits. Copper is the preferred interconnect material because of favorable conductivity and electromigration resistance at reduced dimensions. However, due to the ease of copper oxide formation, obtaining a good quality copper bond is an issue. Oxide buildup require use of higher temperatures (>400 °C) and pressures for effective bonding, which is not favorable in sensitive ICs. The highly reactive copper surface requires extreme caution during cleaning and bonding processes; Cu-Cu thermocompression bonds are often formed under high vacuum or inert atmospheric conditions to reduce oxide formation. Environmental conditions during sample preparation and storage before the actual bonding needs to be controlled, as the time lag leads to an inevitable formation of an oxide layer.

In this work, self-assembled monolayers (SAMs) of thiol-terminated alkane chains are investigated for use as passivation layers to minimize oxidation of copper. These SAMs form nanometer thick protective films without increasing the surface roughness of the substrate. In addition, they tend to desorb under normal bonding conditions, allowing the copper atoms to diffuse and form a good metallic bond. Our goal is to use this SAM technique to reduce oxide formation and facilitate low temperature Cu-Cu thermocompression bonds for applications in 3D integration of ICs. The oxide protection properties are likely related to SAM surface stability and packing, both which are linked to alkane chain length.

We are interested in comparing different alkane chain length and how they influence the copper surface state over an extended period of time (> 15 days). Toward this end we have compared three different alkane-thiol molecules of varying chain length and studied their stability and surface passivation properties over time using X-ray photoelectron spectroscopy (XPS) and contact angle measurements. We have also studied the effect of SAM chain length on Cu-Cu thermocompression bond strength using a pull tester. We found that the SAMs are stable for up to five days or more when exposed to ambient conditions. We also found the passivation of copper is more efficient when longer chain thiols are used.

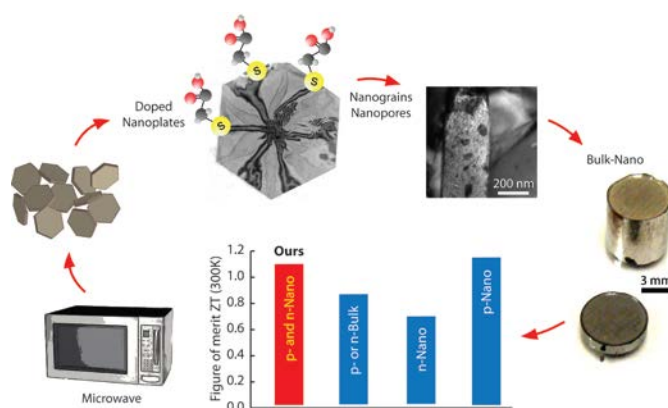
MICROWAVE-SOLVOTHERMAL SYNTHESIS FOR RAPID AND SCALABLE PRODUCTION OF TUNABLY DOPED NANOCRYSTALS AND THEIR ASSEMBLIES

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Scalable and cost-effective production of nanocrystals with control over structure, shape, chemistry and doping, and hence properties, by eco-sensitive bottom-up methods is key to harnessing nanotechnology for many applications including energy, catalysis and healthcare. Here, we report a novel wet-chemistry technique using inexpensive organic solvents and non-toxic metal salts as reactants to rapidly sculpt metal, semiconductor, and oxide nanocrystals of controllable shapes, sizes and doping by microwave-stimulated surfactant-mediated non-aqueous solvothermal synthesis. Our synthesis in recyclable high-boiling polar solvents allows multi-gram-per-minute synthesis with nearly 100% yields of nanocrystal powders for realizing thin-film and bulk nanostructured solids through further nanocrystal assembly and processing. Organic surfactants are used in our synthesis for serving multiple roles of shape-direction, surface-passivation and oxide-inhibition and doping agents. Our method is versatile, and can be used for the synthesis of a wide variety of materials through the selection of appropriate precursor-surfactant molecule combinations. We will describe the salient features of our method through illustrative examples of synthesis of nanoparticles, nanoplates, and nanowires of sulfur-doped pnictogen chalcogenides, aluminum-, bismuth-, indium-doped zinc oxide, and metal nanostructures such as gold, bismuth and antimony. We will show that our method can be used for morphing and heterostructuring the nanocrystals that allow control over properties such as Seebeck coefficient, and lead to up to billion-fold enhancement in electrical conductivity. We conclude with examples of how tuning the electron-crystal phonon-glass behavior (figure below) by adapting our bottom-up approach for designing nanoscale building blocks enable bulk nanostructured pnictogen chalcogenides and oxides with large enhancements in thermoelectric figure-of-merit for transforming thermoelectric refrigeration and power harvesting technologies.



CHARACTERIZATION OF GRAPHENE FILMS GROWN ON Cu(111)

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Previous studies have shown that graphene films can be grown on Cu substrates by the catalytic decomposition of hydrocarbon molecules. Because the Cu(111) surface has hexagonal symmetry and a lattice mismatch of 3.7% with graphene, growth on this surface termination has potential for producing films with a low defect density. There have been relatively few studies of graphene growth on single crystal Cu substrates, owing to the fact that hydrocarbon source pressures in the range of 100 millitorr are needed, which is incompatible with most UHV systems. In this study, graphene films were grown on Cu(111) substrates by first preparing the clean surface in UHV by sputtering with inert gas ions followed by annealing. The sample was then transferred to a conventional tube furnace where the graphene film was grown by annealing in forming gas to reduce the surface oxide, followed by annealing in ethylene to produce the graphene film.

The growth morphology of the graphene overlayer was characterized using low energy electron microscopy (LEEM), low energy electron diffraction (LEED), scanning electron microscopy (SEM), atomic force microscopy (AFM), and optical microscopy. The LEEM shows a mesa-like surface texture with relatively flat terraces covered with graphene and valleys between the terraces with low carbon coverage. Micro-Raman spectroscopy of the terrace regions produces a signal characteristic of a well-ordered graphene overlayer, whereas the Raman signal in the valleys is much weaker and shows a distinct D-peak. The typical lateral dimension of the terraces was ~10 μm . Micro-LEED performed on the terrace sites shows a sharp Moiré pattern. Conventional LEED, which probes a lateral area of ~1 mm, shows a ring structure with increased intensity in the six high symmetry directions of the Cu(111) substrate lattice. This indicates that for this growth procedure there is a quasi-epitaxial relationship between the graphene overlayer and the Cu(111) substrate with rotational disorder of the graphene from mesa to mesa. Synchrotron-based angle-resolved ultraviolet photoelectron spectroscopy (ARUPS) measurements have been performed to probe the electronic band structure of the graphene overlayer. A linear dispersion has been measured in the K direction with the Dirac point located near the Fermi level.

Prefer: Oral Presentation

Complete Analysis of ToF-SIMS Raw Data Files in a Research and Development Analytical Laboratory

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Time of flight secondary ion mass spectrometry (ToF-SIMS) raw data files contain a wealth of information since an entire mass spectrum is saved at each pixel in an ion image or at each depth in a depth profile. Currently, few tools are available to assist the analyst in visualizing the entire raw data set and as a result, most of the measured data are never analyzed. Typically, the ToF-SIMS analyst manually selects a few species to monitor based upon input from the customer, knowledge of results obtained from similar past analysis, high peak intensity and/or unusual species detected in the spectrum. Manual analysis is complicated by the fact that little is known about real-life samples prior to analysis. The analyst is expected to perform rapid, cost effective, analysis and provide a complete evaluation/description of the data set/sample. Automated, non-biased, multivariate statistical analysis (MVSA) techniques are useful for converting the massive amount of data into a smaller number of chemical components (spectra and images) that are needed to fully describe the ToF-SIMS measurement.

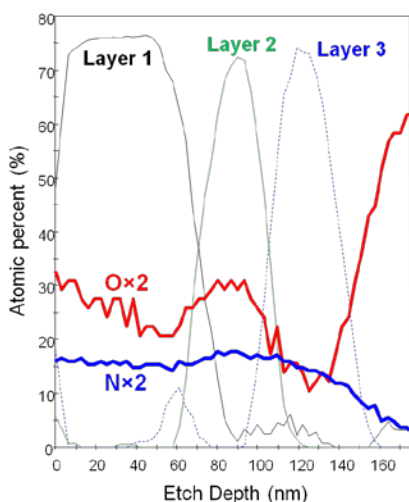
We are using the Automated eXpert Spectrum Image Analysis (AXSIA) tool-kit developed at Sandia National Laboratories to perform MVSA on ToF-SIMS raw data files. The advantages of AXSIA include: the ability to select the mass range of interest, the ability to bin the mass spectra from 0.001 amu to 1 amu, optimal scaling of the data to account for Poisson counting statistics, and the generation of intuitive results (e.g., negative peaks are not allowed in the spectral response). Examples will be selected to demonstrate these advantages. The analytical insight provided by MVSA analysis would be difficult, if not impossible, to obtain via other routes.

ARGON CLUSTER ION SOURCE FOR XPS DEPTH PROFILING OF ORGANIC/BIOLOGICAL MATERIALS

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Surface treatment of polymers produces materials that exhibit a wide range of surface compositions, properties, and structures. The chemical and structural properties of these novel materials can be exploited for the fabrication of devices for bio-medical, electronic, photovoltaic, and other applications. Knowledge of the surface and in-depth composition of these materials is required for the successful development of new processes and products. X-ray photoelectron spectroscopy (XPS) has been used for many years to characterize the elemental and chemical surface composition of organic and biological materials. However, XPS depth profiling of such materials using monomer argon ion sources is usually problematic because of chemical and structural damage caused by the ion beam sputtering process. In this study, a recently developed argon cluster ion source was used for soft XPS depth profiling of a variety of organic and biological materials to minimize ion-induced damage during the analyses. Comparisons were made to samples analyzed using monomer argon ion depth profiling. The materials examined include: a multi-layer, vapor-deposited, amino acid thin film structure; poly(methyl methacrylate) (PMMA) coatings; and fluoropolymer plasma coatings on different polymer substrates. The results obtained with the argon cluster ion source were consistent with minimal ion beam damage and preservation of the chemical state information throughout the profiles, as indicated by the film quantification data and analysis of the C 1s and other XPS peak shapes.



XPS Argon Cluster Ion Depth Profile of Multi-Layer Amino Acid Thin Films on Silicon

Poster Presentations

SYNTHESIS AND THERMAL PROPERTIES OF Au-NANOWIRE NETWORK-FILLED POLYMER COMPOSITES FOR HEAT MANAGEMENT IN NANODEVICE PACKAGING

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We report the synthesis of a polymer composite filled with a metal nanowire network and investigate its thermal properties for exploring the use of the composite for heat management applications in nanoelectronics packaging. While polymeric composites filled with nanoparticles and carbon nanotubes have been widely studied, the use of high-aspect ratio metal nanostructures and their assemblies is new. We expect the interconnected mesh of metal nanowires to be more effective thermal channels due to inherent continuity, connectivity that can lead to percolation at lower filler loadings. Gold was chosen due to its high bulk thermal conductivity, high corrosion resistance, ease of nanostructure synthesis and its relatively low stiffness conducive for conformability at rough surfaces and interfaces.

Sub-gram quantities of several microns-long 3-10 nm diameter Au nanowires were synthesized in a microwave-stimulated solvothermal approach by reducing chloroauric acid with oleylamine in hexane. This process is easily scaled up to get gram quantities of 60% nanowires in minutes, with the rest of the product comprised of smaller aspect ratio nanostructures and aggregates. The wires are frequently looped or bent indicating high flexibility. We obtained the composites with low volume fractions of fillers (0.6-4%) by dispersing the nanostructures in polydimethylsiloxane(PDMS), evaporating the solvent and curing at 150 °C. The thermal properties of nanocomposites were measured in a modified ASTM D5470-06 standard set up. Our results show a substantial enhancement (6-10 fold) in the thermal conductivity of the PDMS composites filled with < 4% (by volume) of Au nanostructures and suggest the possibility of attaining percolation threshold and other attractive thermal properties at low volume fractions.

On the development of the CdS properties upon processing for CdTe devices

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CdS plays an important role in CdTe devices through both the thickness impact on J_{sc} and the less well understood effect on FF and Voc by impacting the minority carrier lifetime in the CdTe near the interface. In this study, two techniques are explored, chemical bath deposition and radio frequency sputtering, effectively exploring the role of film density. A multitude of characterization techniques have been exploited on CdS films after various stages in the process of device fabrication as the CdS properties change significantly upon processing of the films. For this purpose we compared the properties for as-deposited films, films that are exposed to a CdTe deposition heating profile without the actual CdTe deposition, as well as CdS films as they appear within completed devices. Especially the CdCl₂ process turned out to result in huge changes within the CdS film. From this study it is concluded that significant changes occur to the CdS film depending on its starting density. Change in electrical properties and intermixing occur during the CdTe deposition and are thus temperature related, while a change in optical properties and carrier lifetime near the interface is established after CdCl₂.

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Addressable Photo-Charging of Single Quantum Dots Assisted with AFM probe

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Atomic force microscopy (AFM) is a versatile technique that can be used to study the processes at subnanometer level in electronics, material science, biology, etc. Here we demonstrate a frequency-modulated electric force microscopy (FM-EFM) to study the process of photoemission of electrons from semiconductors. We obtain interesting results along two directions:

1. Photoemission is an important process in conversion of solar energy into electricity. Here we demonstrate how FM-EFM can be used to study electron photo emission from a nanoscale photo acceptor, single organically coated CdSe quantum dots (QDs). We demonstrate that the photoionization of QDs can be reliably measured with our method down to the level of single electron charge (e), with the error level of $0.1e$. *This method can be used for a fast screening of efficiency and defectivity of photoelectric materials in solar cells.*
2. Super Long-Living High-Density Memory. We further prove that the speed of ionization and discharge of QDs can be modeled as quantum tunneling through the organic coating layer. We also observe anomaly fast charging when photoionization happens during the AFM scanning. We show that such a behavior is in agreement with our model. The AFM probe is used to decrease/squeeze the coating barrier for the tunneling of photoelectron to either conductive substrate or the AFM probe. Based on this phenomenon, we suggest a memory device, in which each bit of information can be charged by touching with an AFM probe. Our model predicts that *such information can be recorded within microseconds and be stable for thousands of years. This method can be used for recording information at a density of $1\text{Tb}/\text{cm}^2$.*

ATOMIC FORCE MICROSCOPY AS A PROSPECTIVE TOOL IN THE DETECTION OF CANCER CELLS

3.

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Here we show that human cervical epithelial cells during progression to cancer develop appreciable changing of various physical properties. We are able to characterize the cell surface layer quantitatively; we used atomic force microscopy (AFM), a technique that allows studying mechanics of biological cells in their native environment. We found that the “brush” layer (microvilli, microridges, glycocalyx) on the surface of cancer cells was more heterogeneous and substantially less dense than in the case of normal cells.

Furthermore, using the AFM imaging of the surface of fixed cells, we found that cell surface can develop fractal behavior when cells become cancerous. Our analysis shows that this can only be seen at the nanoscale, when analyzing the distribution of adhesive properties over the two-dimensional surface of biological cells. This leads to an unusually high accuracy in identification of cancer at the single cell level, which is virtually 100% as tested in vitro on ~300 cells collected from 12 humans. Our results suggest that the fractal dimensionality could be used a fundamentally new potential biomarker for early detection of cervical cancer cells with accuracy and specificity surpassing existing methods.

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IN-SITU SURFACE CHARACTERISTIC METHODS INVESTIGATION OF 2, 4-Dinitrotoluene (DNT) ADSORPTION/DESORPTION ON GOLD SURFACES

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The adsorption and self-assembly of organic molecules on metal surfaces is fundamental to a large number of potential nanoelectronics applications. One of these applications is the trace detection of explosives via selective adsorption. Detection of TNT based explosives can be based on the sensing of dinitrotoluene (DNT) since it is a major impurity and decomposition product of TNT with a greater vapor signature. DNT is also an interesting model system for compounds with large dipole moments. Fundamentally, sensing requires an understanding of the adsorption, desorption, and bonding of DNT on sensor surfaces. In this paper we present a multi-technique study of the interaction of DNT vapor with Au, a commonly used electrode material. Temperature programmed desorption (TPD) experiments show that DNT multi-layers form at low temperatures and that desorption of the multi-layers occurs with zero order character near 0°C. A stable monolayer of DNT is observed above room temperature with desorption around 80°C on the Au (111) surface. Scanning tunneling microscopy (STM) data show that DNT forms well ordered (self-assembled) row structures aligned to the Au substrate. Two different structures are observed, and the stability of these structures is consistent with the TPD data. The mechanism for desorption from the monolayer shows that domains decrease in size with increasing temperature, but there are also indications of desorption from within the domains. X-ray photoelectron spectroscopy (XPS) was also utilized to investigate the adsorption, desorption, and orientation of the DNT molecules. The results are consistent with the TPD results and STM imaging in terms of an ordered monolayer. Angle-resolved XPS (ARXPS) was used to study the orientation of DNT on gold surface. The results indicate that monolayer DNT molecules orient with the central benzene ring near vertical to the surface and with the nitro groups closer to the Au (111) surface. The influence of the large dipole moment and its role on intramolecular interactions for DNT will be also discussed.

3D Interconnect: Sub-surface imaging Techniques for bonded wafer Pairs & Through Silicon Vias (TSVs)

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Abstract. 3D interconnects which stacks multiple chips in a single package significantly reduce interconnect delay and improve clock distribution. At the same time that research into 3D technology such as Through Silicon Vias (TSVs) is advancing quickly, the microscopy techniques used in the evaluation of TSV must also advance in capability. The stacked chips can be made through wafer bonding, direct die to die bonding, and die to wafer bonding. Copper-filled TSVs are used to provide electrical connection for the stacked chips. Defects inspection like void and overlay measurement at bonded interfaces and TSVs are important and challenging. Microscopy techniques for which silicon is opaque such as scanning acoustic microscope (SAM) and confocal infrared microscope (IR) are capable of inspecting the interface between bonded wafer pairs, while high resolution X-Ray techniques are used to detect voids in TSVs. SAM was able to resolve the 20 μ m alignment structure with 300MHz transducer on 300 mm wafer pair, while IR has sub-micron resolution for all bonded wafers. This paper discusses the current status of SAM, IR microscopy and x-ray microscopy (XRM) in terms of their application to process metrology for 3D interconnects.

Dark-Field Transmission Electron Microscopy and Spectroscopic Ellipsometry for the Structural and Optical Characterization of CVD Graphene

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Hydrocarbon-based Chemical Vapor Deposition (CVD) on copper has become one of the main graphene growth methods due to its ability to produce predominantly monolayer graphene in quantities determined by substrate area. Previous work has shown the presence of grains and grain boundaries in these films, the sizes of which may be controlled by growth process parameters. The mobility of CVD polycrystalline graphene samples has been shown to be lower than those values of essentially monocrystalline epi graphene and exfoliated graphene flakes due to scattering at boundaries between grains. The question of whether the optical response of CVD graphene is sensitive to the presence of grain boundaries has been investigated using Spectroscopic Ellipsometry (SE), in conjunction with Dark-Field Transmission Electron Microscopy (DF-TEM) and Raman Spectroscopy. Preliminary results based on updated optical dispersion modeling and PMMA-based transfer methods to SiO₂/Si substrates show differences in the complex refractive index for films of differing grain sizes. We preliminarily assign these differences to an increased density of states along grain boundaries in the films. This information enables in-line optical metrology.

*Submitted for: Poster

FACTORIAL INCREASES IN INTERFACIAL THERMAL CONDUCTANCE USING A MONOLAYER

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Manipulating interfacial thermal transport is a compelling need for a number of technologies including nanoelectronics and biomedical devices, solid-state lighting, energy generation, nanocomposites, and device packaging. Here, we demonstrate that introducing a strongly-bonding organic nanomolecular monolayer (NML) at a metal-dielectric interface leads to a factor of four increase in the interfacial thermal conductance to values as high as 450 MW/m²-K. Molecular dynamics simulation and a vibrational analysis of NML-tailored interfaces verify that this remarkable interfacial conductance enhancement is due to strong NML-silica and NML-metal bonding. The strong overlap of broadband low-frequency vibrational states at the interface further facilitates efficient heat transfer through the molecules comprising the NML. These results provide a rational means of increasing heterointerfacial thermal conductance through molecular functionalization with adhesion-enhancing functional groups for a wide variety of material systems and applications.

MOLECULAR MULTILAYERS USING “CLICK” CHEMISTRY FOR PHOTOVOLTAIC APPLICATIONS

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In an effort to improve the performance of molecular based solar cells, we have developed a novel molecular layer-by-layer (LbL) technique utilizing the copper-catalyzed azide-alkyne cycloaddition or “click” reaction.¹ This facile LbL technique requires inexpensive catalyst, easily introduced functional groups, is tolerant of a variety of solvents, and occurs on the timescale of minutes at room temperature. We have applied this LbL technique towards the construction of layered chromophores in an effort to develop multilayer light harvesting materials. These materials could be coupled with nanostructured crystalline semiconductors to improve the current performance of molecular based solar cells. Characterization of these covalently linked multilayer films on flat substrates using UV-Vis, x-ray reflectivity, ATR-IR and electrochemical methods provide insight into the molecular ordering and film properties which could affect device performance.^{2,3} Initial photocurrent results provide insight into the applicability of these films for use in p-type dye-sensitized solar cells.

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3. Palomaki, P. K. B.; Dinolfo, P. H. “Structural analysis of porphyrin multilayer films on ITO assembled using copper(I)-catalyzed azide alkyne cycloaddition by ATR IR” **2011** submitted to *ACS Applied Materials and Interfaces*.

NANOFERROFLUID-BASED THERMAL VALVES FOR GATING HEAT TRANSPORT

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Here we demonstrate a new concept of ferrofluid-based thermal valves based on magnetic nanofluids. For the first time we have measured effective thermal conductivity of a magnetic nanofluid in external non-uniform magnetic fields using a one dimensional steady state heat flow apparatus. We show that the effective thermal conductivity of a magnetite-based nanofluid can be increased up to 7 times in an external field with strength up to 68 mT providing a basis for switching thermal conductance states through the use of a magnetic field. We will present our results of the behavior of the conductivity switching at different magnetic field magnitudes and gradients to distinguish between effects arising from configurational alignment of the nanoparticles and magnetic field induced convection of the ferrofluid. We will show that the nanofluid effective thermal conductivity can be precisely tuned with an applied magnetic field. This behavior is explained both in terms of the changes in the network connectivity of the nanoparticles and enhanced convection in a magnetic field. We also reveal the dependence of the thermal conductivity-magnetic field nexus on the nanoparticle concentration, morphology and surfactant capping. These results open up a new way of gating heat transport in a variety of engineering systems and applications.

X-RAY PHOTOELECTRON SPECTROSCOPY STUDY OF GRAPHENE FILMS GROWN ON CU AND CU-NI FOILS

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Graphene is a single atomic layer of sp^2 -hybridized carbon that crystallizes in the honeycomb crystal structure. One of the primary reasons for the current interest in graphene is because of its unique electrical properties. The electronic structure of graphene depends on the number of graphene layers and the stacking sequence between the layers. Single-layer graphene is a semi-metal with a linear energy dispersion near the Dirac point, which results in a very small effective mass for the carriers. On the other hand, a small energy gap can be present in bi-layer graphene, and few-layer graphene films have electrical properties that differ from single- and bi-layer graphene films and bulk graphite. Therefore, it is important to have a non-destructive technique for analyzing the overlayer coverage of graphene directly on the growth substrate. Previous researchers have used Raman spectroscopy to estimate the number of graphene layers by analyzing the line shape of the G' peak. We have developed a technique using angle-resolved XPS to determine the average graphene thickness directly on metal foil substrates.

Since monolayer graphene films can be grown on Cu substrates by the catalytic decomposition of methane molecules, these samples can be used as a standard reference for a monolayer of graphene. Highly oriented pyrolytic graphite is used as a standard reference for bulk graphite. The electron mean free path of the C-1s photoelectron can be determined by analyzing the areas under the C-1s peaks of monolayer graphene/Cu and bulk graphite. After determination of the electron mean free path, the graphene coverage of a film of arbitrary thickness can be determined by analyzing the area under the C-1s of that sample. Analysis of graphene coverages for submonolayer graphene films on Cu substrates and graphene films grown on Cu-Ni substrates that are more than one monolayer thick will be presented.

Prefer: Poster Presentation

REAL-TIME SPECTROSCOPIC ELLIPSOMETRIC INVESTIGATION OF ADSORPTION AND DESORPTION IN ATOMIC LAYER DEPOSITION: A CASE STUDY FOR THE STRONTIUM BIS(TRI-ISOPROPYLCYCLOPENTADIENYL)/WATER PROCESS

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Atomic layer deposition (ALD), a self-limiting thin film deposition process, has attracted much attention due to its capability for accurate thickness control and superior conformal growth. A highly desirable application is the epitaxial growth of functional oxides on silicon for improving current microelectronic devices, like ferroelectric random access memories (FRAM). For example, ALD-grown strontium titanate (STO) has already been demonstrated to have relatively high dielectric constant (~210) and excellent conformality. Strontium oxide (SrO) plays a key role in achieving an atomically abrupt interface between epitaxial STO and silicon substrate. The atomic layer deposition (ALD) of SrO thin films from $\text{Sr}(\text{C}_5\text{H}_7\text{Pr}_3)_2$ (g) and H_2O (g) was studied using real-time spectroscopic ellipsometry (SE) investigations of adsorption and desorption during each half cycle. Adsorption of $\text{Sr}(\text{C}_5\text{H}_7\text{Pr}_3)_2$ was self-terminating at deposition temperatures of 150-350°C and the saturated growth per cycle (GPC) highly depended on the deposition temperature, ranging from 0.05 to 0.33 nm per cycle at the lower and upper limits, respectively. Submonolayer sensitivity of SE was demonstrated by examining changes in the ellipsometric parameters and apparent thickness before and after precursor pulses. Further interpretation of apparent thickness changes was assisted by using Bruggeman effective medium approximation (EMA) to simulate the roughness induced by adsorbed species. A comparison between experimental GPC and available theoretical models demonstrates that the deposition temperature has a marked effect on the reaction mechanisms and indicates more than one operation regime for the ALD process via $\text{Sr}(\text{C}_5\text{H}_7\text{Pr}_3)_2$ and H_2O .

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