

# 2010 SPRING MEETING of the AVS HUDSON MOHAWK CHAPTER

Thursday, March 25, 2010 3-7pm Upper Russell Sage Dining Hall Rensselaer Polytechnic Institute (RPI) 110 8th St, Troy, NY, 12180

### TALKS:

### T1. HIGH FIGURE OF MERIT NANOSTRUCTURED BULK THERMOELECTRICS FROM DOPED PNICTOGEN CHALCOGENIDE NANOPLATE CRYSTALS

<u>Rutvik J Mehta<sup>1,§</sup></u>, C. Karthik<sup>1</sup>, Binay Singh<sup>1</sup>, Yanliang Zhang<sup>2</sup>, Eduardo Castillo<sup>2</sup>, Damien West<sup>3</sup>, Yiyang Sun<sup>3</sup>, N. Ravishankar<sup>1</sup>, Shengbai Zhang<sup>3</sup>, Theo Borca-Tasciuc<sup>2</sup>, and Ganpati Ramanath<sup>1</sup>

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# T2. THE GLASS TRANSITION TEMPERATURE OF POLYMER NANOCOMPOSITES: WHAT IS HAPPENING AT THE INTERFACE?

Katelyn Parker, Ryan T. Schneider, Richard W. Siegel, Rahmi Ozisik<sup>†</sup>

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Juan Carlos Cabanelas, Berna Serrano, Claire Antonelli, Juan Baselga

Department of Materials Science and Engineering and Chemical Engineering, Universidad Carlos III de Madrid, Av. Universidad 30, 28911 Leganés, Madrid, Spain.

### T3. IR MICROSCOPY AS AN EARLY ELECTRICAL YIELD INDICATOR IN BONDED WAFER PAIRS USED FOR 3D INTEGRATION

Andrew C. Rudack, SEMATECH, Inc.

Pratibha Singh, SEMATECH/GLOBALFOUNDRIES, Inc.

J. Christopher Taylor, SEMATECH/Hewlett-Packard Company

Vadim Mashevsky, Olympus Integrated Technologies America, Inc.

# T4. NANOSCALE CHEMICAL CHARACTERIZATION WITH SCANNING AUGER MICROSCOPY

John S. Hammond, Dennis F. Paul, and David G. Watson Physical Electronics, 18725 Lake Drive East, Chanhassen, MN, USA 55317

### **T5. RESPONSIVE POLYELECTROLYTES ON SURFACE: FROM SINGLE MOLECULES TO SMART THIN FILMS**

<u>Y. Roiter</u>, I. Tokarev, O. Trotsenko, V. Gopishetty, S. Minko Department of Chemistry and Biomolecular Science, Clarkson University, 8 Clarkson Ave, Potsdam, NY 13699-5810

# **T6. VOLTAGE CONTROLLED BRANCHING OF TITANIA NANOTUBES AND ITS APPLICATION FOR PHOTOVOLTAICS**

<u>Gorun Butail</u>, P. Gopal Ganesan, R. Mahima, N. Ravishankar, Ganpati Ramanath Department of Material Science and Engineering, Rennselaer Polytechnic Institute, 110 Eighth Street, Troy, New York 12180, USA

### **POSTERS:**

### P1. A NEW TECHNIQUE TO MONITOR SURFACE TEXTURE OF NANOSTRUCTURES

<u>Gwo-Ching Wang</u> and Toh-Ming Lu Department of Physics, Applied Physics and Astronomy, Rensselaer Polytechnic Inst. 110, 8<sup>th</sup> Street, Troy, NY, USA 12180-3590

### P2. ANALYSIS OF WRITING INKS BY TOF-SIMS – A FORENSIC CASE STUDY

<u>Albert Schnieders</u><sup>1</sup>, Albert H. Lyter, III<sup>2</sup>

<sup>1</sup>Tascon USA, Inc, 100 Red Schoolhouse Road, Bldg. A-8, Chestnut Ridge, NY 10977 <sup>2</sup> Federal Forensic Associates, Inc., P.O. Box 31567, Raleigh, NC 27622

### **P3. CARBON DIOXIDE SEQUESTRATION BY CARBON NANOTUBES**

Deniz Rende<sup>1, 2</sup>, Nihat Baysal<sup>1</sup>, <u>Rahmi Ozisik<sup>3</sup></u>

<sup>1</sup>Department of Chemical Engineering, Yeditepe University, Istanbul 34755, Turkey

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<sup>3</sup>Department of Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, NY 12180, USA

### P4. CAPACITANCE-VOLTAGE AND X-RAY PHOTOELECTRON SPECTROSCOPY STUDY OF TiN/HfO<sub>2</sub>/La<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub>/Si GATE STACKS

<u>E. Bersch,</u><sup>a</sup> M. Di,<sup>a</sup> S. Consiglio,<sup>b</sup> R.D. Clark,<sup>b</sup> G. J. Leusink,<sup>b</sup> A. C. Diebold<sup>a</sup> <sup>a</sup>College of Nanoscale Science and Engineering, University at Albany, 255 Fuller Rd., Albany, NY 12203 <sup>b</sup>TEL Technology Center, America, 255 Fuller Rd., Suite 244, Albany, NY 12203

# P5. THE DIFFUSIVE AND DEFORMATIONAL DEGREES OF FREEDOM IN PROTEINS CONCURRENTLY FREEZE AT THE DYNAMICAL TRANSITION

Osman Burak Okan, Rahmi Ozisik

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Canan Atilgan Faculty of Engineering and Natural Sciences, Sabanci University, 34956 Istanbul, Turkey

# P6. CONFORMATION TRANSITIONS OF SINGLE POLYELECTROLYTE MOLECULES AT SOLID-LIQUID INTERFACE IN RESPONSE TO CHANGES IN pH AND SALT CONCENTRATIONS STUDIED USING AFM IN AQUEOUS SOLUTIONS

<u>O. Trotsenko</u>, Y. Roiter, S. Minko Department of Chemistry and Biomolecular Science, Clarkson University, 8 Clarkson Ave, Potsdam, NY 13699-5810

### P7. HYDROPHOBIC AND OLEOPHOBIC SURFACES MADE OF PIN-LIKE STRUCTURES

<u>A. Grigoryev</u>, Y. Roiter, I. Tokarev, S. Minko Department of Chemistry and Biomolecular Science, Clarkson University, 8 Clarkson Ave, Potsdam, NY 13699-5810

### **P8. ELECTRON SCATTERING AT SINGLE CRYSTAL Cu(001) SURFACES**

J.S. Chawla<sup>1</sup>, D. Gall<sup>2</sup>

<sup>1</sup>Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, NY 12180 <sup>2</sup>Rensselaer Polytechnic Institute, Troy, NY 12180

# **P9. EPITAXIAL CrN(001) LAYERS: SURFACE MORPHOLOGICAL EVOLUTION AND ELECTRONIC/OPTICAL PROPERTIES**

Xunyuan Zhang, Daniel Gall Department of Materials Science and Engineering Rensselaer Polytechnic Institute, Troy, NY 12180

# P10. TEXTURAL EVOLUTION OF ULTRATHIN CaF<sub>2</sub> NANORODS CHARACTERIZED BY RHEED SURFACE POLE FIGURES

<u>Yu Liu</u>\*, W. Yuan, C. Gaire, T.-M. Lu, and G.-C. Wang Department of Physics, Applied physics and Astronomy Rensselaer Polytechnic Institute, 110, 8<sup>th</sup> St., Troy, NY 12180-3590

# P11. GENERATION OF EQUILIBRATED POLYMER CONFORMATIONS IN COMPUTER SIMULATIONS

Gopinath Subramanian<sup>1,2,\*</sup> and Rahmi Ozisik<sup>1,3</sup> <sup>1</sup> Scientific Computation Research Center <sup>2</sup> Department of Mechanical, Aerospace and Nuclear Engineering <sup>3</sup> Department of Materials Science and Engineering Rensselaer Polytechnic Institute Troy, NY 12180

# P12. OPTIMIZED DNA MONOLAYER FORMATION ON GOLD FOR SIGNIFICANTLY IMPROVED HYBRIDIZATION EFFICIENCY

Andrew D. Pris, Sara G. Ostrowski, and Sarah D. Garaas General Electric-Global Research Center

### P13. ANGLE RESOLVED XPS INVESTIGATION OF HfZrO4 HIGH-K THIN FILMS

<u>S. Consiglio</u><sup>1</sup>, C. S. Wajda<sup>1</sup>, G. Nakamura<sup>1</sup>, R. D. Clark<sup>1</sup>, S. Aoyama<sup>2</sup>, and G. J. Leusink<sup>1</sup> <sup>1</sup>TEL Technology Center, America, LLC, 255 Fuller Road, Albany, NY, 12203, USA <sup>2</sup>Tokyo Electron AT, 650 Mitsuzawa, Hosaka-cho, Nirasaki, Yamanashi 407-0192, Japan

# P14. Quasi-SINGLE CRYSTAL GERMANIUM FILMS ON BIAXIALLY TEXTURED CaF<sub>2</sub>/GLASS SUBSTRATES

<u>C. Gaire</u>, H.-F. Li, P. Snow, G.-C. Wang, and T.-M. Lu Department of Physics, Applied Physics and Astronomy Rensselaer Polytechnic Institute, 110 8<sup>th</sup> Street, Troy, NY, 12180-3590

# P15. TEMPERATURE DEPENDANT BIAXIAL TEXTURE EVOLUTION IN Ge UNDER OBLIQUE ANGLE VAPOR DEPOSITION

<u>P. Snow</u>, C. Gaire, T.-M. Lu and G.-C. Wang Department of Physics, Applied Physics and Astronomy Rensselaer Polytechnic Institute, 110 8<sup>th</sup> St., Troy, NY 12180-3590

### P16. ANALYSIS OF SILICON NANOWIRES BY LASER ATOM PROBE TOMOGRAPHY PREPARED BY A PROTECTED LIFT-OUT PROCESSING TECHNIQUE

T.J. Prosa,\* R.A. Alvis,\* L. Tsakalakos,\*\* and V.S. Smentkowski\*\* \* Imago Scientific Instruments, Madison, WI 53711

\*\* General Electric Global Research, Niskayuna, NY 12309

# P17. THE EFFECT OF HUMIDITY ON THE ADHESION OF METAL-CERAMIC INTERFACES

<u>Vijayashankar Dandapani</u><sup>1</sup>, Saurabh Garg<sup>1</sup>, Ashutosh Jain<sup>1</sup>, Ranganath Teki<sup>1</sup>, Michael Lane<sup>2</sup>, Ganpati Ramanath<sup>1</sup>

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# P18. ADSORPTION AND DESORPTION OF DINITROTOLUENE ON FUNCTIONALIZED SURFACES

<u>Hui Li</u> and Brian G. Willis Department of Chemical, Materials & Biomolecular Engineering University of Connecticut, Storrs, CT 06269

### P19. MASS SPECTROMETER CALIBRATION FOR MEASUREMENT OF PHOTORESIST OUTGASSING SPECIES IDENTIFICATION AND QUANTIFICATION

<u>Alin O. Antohe</u><sup>1</sup>, Gregory Denbeaux<sup>1</sup>, Chimaobi Mbanaso<sup>1</sup>, Leonid Yankulin<sup>1</sup>, Yu Jen Fan<sup>1</sup>, Petros Thomas, Yashdeep Khopkar, Warren Montgomery<sup>2</sup> <sup>1</sup>College of Nanoscale Science and Engineering, University at Albany, NY

<sup>2</sup>SEMATECH, Albany, NY

**Abstracts for Talks** 

### High Figure Of Merit Nanostructured Bulk Thermoelectrics From Doped Pnictogen Chalcogenide Nanoplate Crystals

<u>Rutvik J Mehta<sup>1,§</sup></u>, C. Karthik<sup>1</sup>, Binay Singh<sup>1</sup>, Yanliang Zhang<sup>2</sup>, Eduardo Castillo<sup>2</sup>, Damien West<sup>3</sup>, Yiyang Sun<sup>3</sup>, N. Ravishankar<sup>1</sup>, Shengbai Zhang<sup>3</sup>, Theo Borca-Tasciuc<sup>2</sup>, and Ganpati Ramanath<sup>1</sup>

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Nanostructured forms of V-VI semiconductors based on bismuth telluride alloys are attractive for realizing high thermoelectric figure of merit (ZT) materials for solid-state refrigeration and efficient harvesting of electrical power from waste heat. We report single-component bulk assemblies of sulfur-doped nanostructured pnictogen chalcogenides (e.g., Bi<sub>2</sub>Te<sub>3</sub>, Bi<sub>2</sub>Se<sub>3</sub> and Sb<sub>2</sub>Te<sub>3</sub>) with 25% to 250% enhancement in the room temperature ZT, compared with their respective non-nanostructured bulk counterparts, and for the first time, a bulk *n-type* material with a room temperature ZT > 1. We synthesized ~5- to 20-nm-thick single-crystal hexagonal sulfur-doped nanoplates of the pnictogen chalcogenides by a rapid (<~ 60 seconds), scalable surfactant-assisted microwave synthesis approach, followed by compaction and sintering to obtain bulk nanostructured pellets. We show that <1% sulfur doping from thioglycolic acid, used as a nanoplate-sculpting and surface-passivating agent, not only enhances the electrical conductivity  $\sigma$  and Seebeck coefficient  $\alpha$ , but also reverses the majority carrier type in the bismuth chalcogenides. In particular, the  $\alpha$  values are negative for the bismuth chalcogenides and range between - 235 <  $\alpha$  < - 90  $\mu$ V/K for Bi<sub>2</sub>Te<sub>3</sub>, - 80 <  $\alpha$  < - 40  $\mu$ V/K for Bi<sub>2</sub>Se<sub>3</sub> and positive  $105 < \alpha < 125 \mu V/K$  for the Sb<sub>2</sub>Te<sub>3</sub>, while a high electrical conductivity ranges between  $3 \times 10^4 \le \sigma \le 2.5 \times 10^5 \,\Omega^{-1} \text{m}^{-1}$ . Electron spectroscopy and density functional theory calculations provide insights into the doping and majority carrier reversal mechanisms. The single-component nanostructured pellets exhibit 50% lower thermal conductivity  $\kappa$  and 5% higher power factor  $(\alpha^2 \sigma)$  when compared with that of the state-of-the-art alloys. Our electron microscopy analyses reveal that measured  $\kappa$  values as low as 0.7 – 1.4 W/mK are due to 50-100 nm grains with intragrain structural modulations with characteristic wavelengths between 3-10 nm. Such low  $\kappa$ values obtained without alloving provide an attractive means to preserve high intrinsic  $\alpha$  and  $\sigma$ . which collectively enables large increases in ZT. Our findings open up completely new possibilities for realizing novel high ZT thermoelectric materials through the assembly of doped single-crystal nanostructures.

### THE GLASS TRANSITION TEMPERATURE OF POLYMER NANOCOMPOSITES: WHAT IS HAPPENING AT THE INTERFACE?

Katelyn Parker, Ryan T. Schneider, Richard W. Siegel, Rahmi Ozisik<sup>†</sup>

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Local glass transition temperatures ( $T_g$ ) were measured at the interfaces of solution blended silica/poly(methyl methacrylate) nanocomposites using florescence spectroscopy and were compared with  $T_g$  values measured by differential scanning calorimetry. It was found that the two types of measurements yielded significantly different information. Increases in the bulk  $T_g$  from the neat PMMA value were found upon the addition of silica nanofillers, but were independent of the nanofiller concentration when the filler concentration was above 2% by weight.

In order to measure the  $T_g$  at the interface, fluorescence probes were attached to silica nanoparticles via short poly(propylene glycol) chains of varying lengths, which allowed for controlled variation of the fluorescence probe distance from the nanofiller surface. As the distance of the fluorescence probe from the silica surface increased,  $T_g$  values were found to decrease and approach  $T_g$  of the neat polymer. The  $T_g$  measured at the interface was found to reach the bulk value within ~7 nm. This suggests that the confinement effect is not strong as previously suggested, and the deviation of  $T_g$  in nanocomposites must be due to increased surface area/volume ratio rather than confinement between nanoparticles.

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### IR MICROSCOPY AS AN EARLY ELECTRICAL YIELD INDICATOR IN BONDED WAFER PAIRS USED FOR 3D INTEGRATION

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Microscopy of 3D interconnect structures is challenged by the opaque nature of silicon. Infrared (IR) microscopy provides a way of "looking" through silicon where microscopes based on visible wavelengths fail. Perhaps the most prevalent application of IR microscopes in 3D manufacturing is imaging sub-surface features at the interface of a bonded wafer pair. The ability to see through silicon using IR microscopes enables a variety of metrology techniques, including the overlay of circuit layers (e.g., metal 2 to via). IR microscopy is a non-destructive technique and, as such, it is an ideal candidate for in-line metrology for the bonded wafer pairs required for 3D interconnects.

This paper reviews overlay metrology capability for an IR microscope. The ability to measure the overlay of bonded wafer pairs according to the 2009 *International Technology Roadmap for Semiconductors* (ITRS) is demonstrated. Overlay tolerances for a variety of copper interconnect test structures is predicted based on electrical designs, and overlay results are compared to electrical test results. The use of IR microscopy as an early indicator of electrical yield is clearly demonstrated.



### NANOSCALE CHEMICAL CHARACTERIZATION WITH SCANNING AUGER MICROSCOPY

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The recent increase in nanotechnology research has pushed the development of analytical techniques to study the growth mechanisms of nanostructures. Scanning Auger Microscopy provides valuable characterization tools for studying these structures including: 1) compositional analysis with nanometer surface sensitivity, 2) imaging with a spatial resolution better than 10 nm, and 3) depth profiling of nanometer structures with nanometer depth resolution. Current applications for this nanoscale characterization capability include the development of materials and processes for growing nanostructures (nanocones, nanowires, etc.) as well as the development of new materials for emerging technologies in microelectronics, energy conversion, metallurgy, and medical materials.

We will review the current capabilities of Scanning Auger Microscopy to provide nanoscale elemental and chemical characterization of surfaces. Examples with be presented on the dopant depth gradient on the surface of a Si nanowire characterized by Auger depth profiling and chemical state identification using high energy resolution Auger spectroscopy on nanostructures.

### RESPONSIVE POLYELECTROLYTES ON SURFACE: FROM SINGLE MOLECULES TO SMART THIN FILMS

Y. Roiter, I. Tokarev, O. Trotsenko, V. Gopishetty, S. Minko

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Polyelectrolytes (PE) represent a class of polymers whose repeating units carry functional groups capable of dissociation and, thus, the polymers bear electrical charges in aqueous media. Controlled ionization of flexible polymer chains provides a unique opportunity for the regulation of the PE chain's conformation in aqueous solutions (Fig.1). A list of major stimuli that could be used to change conformations of PE chains include ionic strength, pH, and quality of the solvent. These properties of PE are in the foundation of the mechanisms of responsiveness of smart nanostructured materials made of polyelectrolytes.



Polymer brushes, thin gel films, and membranes (Fig.2) are examples of such highly prospective materials for chemical, biomedical, textile, and environmental applications.

We report on recent developments of the Nanostructured Materials Group at Clarkson University. The emphasis of this presentation is made on the studies conducted using an *in situ* atomic force microscopy (AFM) at solid-liquid interfacial boundaries. AFM is the only research tool available to date that allows for the direct 3D-imaging of nanoand subnanoscale objects in liquid media with nanometer resolution. We demonstrate several examples from the stimuli-responsive behavior of single PE molecules to applications of the responsive materials for electrochemical gates and biosensors.

### VOLTAGE CONTROLLED BRANCHING OF TITANIA NANOTUBES AND ITS APPLICATION FOR PHOTOVOLTAICS

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Titania nanotubes are attractive for use in many emerging applications related to energy generation, storage and delivery, gas sensing, and water purification. Here, we demonstrate for the first time, the formation of branched titania nanotubes during potentiostatic anodization of titanium thin films or foils. Ramping down of anodization voltage, which we show, has a direct relationship with the nanotube diameter, induces branching. The realization of branched titania films provides a means to tune the electronic properties of titania and fill with multi-sized quantum dots and branched metallic/semiconducting nanostructures for applications. In particular, we quantitatively demonstrate the correlation between the potentiostatic anodization voltage and nanotube diameter, and exploit the relationship to create branches or merge tubes with diameters in the 30-110 nm range, by downscaling or increasing the voltage, respectively, in both stand-alone Ti foils and Ti films on substrates. We will then present the optical properties of branched titania nanotubes and compare light-harvesting efficiency of dye-sensitized solar cells fabricated with un branched and branched titania nanotubes. We will finally illustrate the formation of graded bandgap structures using branching, which opens up possibility for realizing rainbow solar cells to maximally harness sunlight for energy conversion.

### **Abstracts for Poster Presentations**

### A NEW TECHNIQUE TO MONITOR SURFACE TEXTURE OF NANOSTRUCTURES

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The supply of smart thin films and nanostructures is driven by the demand of high technology industries for vast applications in electronics, energy, magnetism, catalysis, etc. Microstructure, including the crystal orientation, controls many physical properties such as electrical, magnetic, and optical properties of the thin films. In reality most thin films and nanostructures are not single crystalline but polycrystalline with grains and grain boundaries. Often there exists preferred crystal orientation(s) or texture in polycrystalline thin films and nanostructures. To date the atomistic mechanism on the texture evolution remains a challenging task due to the lack of experimental techniques that allows one to measure quantitatively the surface texture evolution. In this work we will introduce a new surface pole figure technique using reflection high energy electron diffraction (RHEED) to characterize materials  $ex \ situ^1$  or *in situ<sup>2</sup>*. The electron used in RHEED has a few nanometer penetration depth and thus can probe the surface texture evolution of the growth front. An example of the surface texture evolution from random (Fig. a) to biaxial (Fig. d) during the oblique angle vapor deposition growth of unusual Mg nanoblades (for hydrogen storage) using RHEED surface pole figure will be presented. The impact of this new technique on nanostructure and thin film material research and its comparison with x-ray pole figure technique will be discussed.

Work supported by the US NSF 0853562 and 0506738.

**1.** F. Tang, G.-C. Wang, & T.-M. Lu, "Surface pole figures by reflection high-energy electron diffraction", Applied Physics Letters 89, 241903 (2006).

**2.** F. Tang, T. Parker, G.-C. Wang, and T.-M. Lu, "Surface texture evolution of polycrystalline and nanostructured films: RHEED surface pole figure analysis", Journal of Physics D: Applied Physics 40, R427 - R439 (2007).



### ANALYSIS OF WRITING INKS BY TOF-SIMS – A FORENSIC CASE STUDY

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The analysis of writing inks has garnered extensive interest by the forensic community in regards to differentiation, dating and the solving of problems such as line crossings and obliterations. Various assorted analytical techniques have been employed such as near infrared imaging, thin layer chromatography, chemical spot tests, high performance liquid chromatography, gas chromatography/mass spectrometry, Raman spectroscopy and capillary electrophoresis.

This presentation will evaluate the capabilities of surface mass spectrometry and especially ToF-SIMS in the analysis of writing inks. ToF-SIMS has besides its superb surface sensitivity several advantages that will be elucidated, including superior mass resolution, minimal sample destruction, and imaging capabilities. Because of the limited destruction ToF-SIMS is a desirable examination technique in those instances where the evidence is either extremely limited, as in the case of trace evidence, or extremely valuable, as in the case of antiquities or historical documents. The imaging capabilities of ToF-SIMS also allow this examination technique to be used in a court setting where examination results can be easily demonstrated to the trier of fact. One such instance where this circumstance arises is that of a "line crossing". The term "line crossing" refers to two intersecting lines, prepared by either writing or printing. Historically, microscopic examination has been the technique of choice for this problem, but high instances of inconclusive results and lack of ability to illustrate results has caused continuous research for a better solution. This work will illustrate a series of differences detected by ToF-SIMS among a group of ink formulations. These differences in mass spectra, combined with the surface sensitivity, allow for points of comparison that can be used to determine the sequence of application in a "line crossing" problem.

### CARBON DIOXIDE SEQUESTRATION BY CARBON NANOTUBES

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Carbon nanotubes (CNT) received remarkable attention in the last two decades since they were proven to possess unique electronic, mechanical and structural properties, and revealed to be effective and stable adsorbent materials that make them potentially useful for gas storage and separation of various gas mixtures.  $CO_2$  is one of the greenhouse gases and is released mainly by human activity due to fossil fuel usage, as well as emissions from volcanic eruptions and thermal resources. Removal of  $CO_2$  from atmosphere is necessary to stop global warming.

In this study, the influence of nanotube size, temperature, and composition on  $CO_2$  sequestration with single walled carbon nanotubes (SWNTs) was investigated with molecular dynamics simulations. All systems were simulated for at least 25 ns with a time step of 1 fs. The efficiency of the systems was measured via retention ratio,  $R_i$ , which is the fraction of  $CO_2$  molecules absorbed into the nanotube. To demonstrate the effect of SWNT size on  $CO_2$  retention, (10,10), (15,15) and (20,20) armchair carbon nanotubes with varying lengths were tested. The temperature of the systems was kept at 300 and 320 K. The composition of  $CO_2/N_2$  and  $CO_2/O_2$  binary systems was changed to demonstrate the effect of concentration on  $CO_2$  retention.



Figure 1. The absorption of  $CO_2$  molecules into single walled carbon nanotubes. From left to right: (10,10), (15,15), and (20,20) nanotubes.

Our results suggested that absorption of  $CO_2$  into the SWNTs was directly related to the internal volume of the SWNT, but the cross-sectional area of the tube entrance had a significant effect on the number of  $CO_2$  molecules retained. The temperature has an impact on the location of  $CO_2$  molecules, i.e. at 300K,  $CO_2$  molecules were absorbed into the SWNT and were adsorbed onto the outside of the SWNT; whereas at 320K, the  $CO_2$  molecules were mostly absorbed into the SWNT. These results indicate that the mechanism of  $CO_2$  retention can be controlled by temperature. Finally, our results showed that although the amount of absorbed  $CO_2$  increased with increasing  $CO_2$  concentration, the efficiency of absorption increased with decreasing  $CO_2$  concentration.

### CAPACITANCE-VOLTAGE AND X-RAY PHOTOELECTRON SPECTROSCOPY STUDY OF TiN/HfO<sub>2</sub>/La<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub>/Si GATE STACKS

E. Bersch,<sup>a</sup> M. Di,<sup>a</sup> S. Consiglio,<sup>b</sup> R.D. Clark,<sup>b</sup> G. J. Leusink,<sup>b</sup> A. C. Diebold<sup>a</sup>

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High-k Hf-based oxides have been shown to be effective replacements for SiO<sub>2</sub>-based gate dielectrics in metal oxide semiconductor field effect transistors (MOSFETs). A limitation in gate first processed HfO<sub>2</sub>/metal gate MOSFETs, however, is high threshold voltage  $(V_t)$ .<sup>1</sup> This problem has been addressed through the incorporation of V<sub>t</sub> tuning layers such as La<sub>2</sub>O<sub>3</sub> and  $Al_2O_3$  at the high-k/SiO<sub>2</sub> interface.<sup>2,3</sup> In order to investigate the effect of the La<sub>2</sub>O<sub>3</sub> layer on the TiN/HfO<sub>2</sub>/La<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub>/Si stack, we have grown and characterized several of these stacks where the thickness and the position of the La<sub>2</sub>O<sub>3</sub> layer within the HfO<sub>2</sub> layer, as shown in Fig. 1, has been varied. Both capacitance-voltage (C-V) and X-ray photoelectron spectroscopy (XPS) measurements were performed on these stacks. The C-V measurements showed decreasing flatband voltages with increasing bottom La<sub>2</sub>O<sub>3</sub> (at the HfO<sub>2</sub>/SiO<sub>2</sub> interface) thickness and increasing flatband voltages with increasing HfO<sub>2</sub> thickness between the La<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> layers. The band bending in the Si, as observed by XPS measurements, of the Si 2p core level correlates well with the C-V results. The XPS measurements have also been used to extract valence band offsets, as well as information about the chemical composition of the layers. The C-V and XPS results will be used to discuss possible explanations for the mechanism by which La<sub>2</sub>O<sub>3</sub> affects the Si band bending that have been given in the literature.<sup>4,5</sup>



**Fig. 1:** (a) Varying the thickness of bottom  $La_2O_3$  (b) Varying the position of the  $La_2O_3$  References:

- 1. S. Guha et al., Appl. Phys. Lett., 90, 092902 (2007).
- 2. K. Kakushima et al, Appl. Surf. Sci., 254, 6106 (2008).
- 3. K. Iwamoto et al., Appl. Phys. Lett., 92, 132907 (2008).
- 4. K. Kita et al., Appl. Phys. Lett., 94, 132902 (2009).
- 5. L. Lin et al., Appl. Phys. Lett., **95**, 012906 (2009).

### THE DIFFUSIVE AND DEFORMATIONAL DEGREES OF FREEDOM IN PROTEINS CONCURRENTLY FREEZE AT THE DYNAMICAL TRANSITION

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Dynamical transitions of proteins were studied through a series of 20 ns molecular dynamics simulations sweeping 160-300 K with 10 K decrements. To probe deviations from classical Brownian diffusion, the Hurst exponents (H) of single axis projected chain center-of-mass coordinates were calculated. The scaling exponents of chain diffusion follow an identical trend as the exponent of Kohlrausch (stretch exponential) function describing positional auto-correlations throughout the whole temperature range. Below ca. 200 K, the center-of-mass motion of the protein is driven to a fractional Brownian regime with lower H value bringing in prolonged memory effect due to solvent drag. It was observed that with supercooling, the frequency of side-chain torsional jumps also plummeted, and the protein surface ceased to screen the effect of increased solvent rigidity. Our findings necessitate a broader definition of dynamical transition wherein rigid body and deformation modes freeze concurrently below a single critical temperature. The results shed light upon the glassy dynamics of isolated globular macromolecular chains and nano-clusters in solvent environments.

### CONFORMATION TRANSITIONS OF SINGLE POLYELECTROLYTE MOLECULES AT SOLID-LIQUID INTERFACE IN RESPONSE TO CHANGES IN pH AND SALT CONCENTRATIONS STUDIED USING AFM IN AQUEOUS SOLUTIONS

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Conformational changes of synthetic and biological polyelectrolyte molecules are involved in many industrial processes and natural phenomena in living systems. Examples of such molecules are proteins and DNA. We study the response of PE molecules to changes in pH and ionic strength in aqueous solutions to provide the important information for engineering stimuli-responsive polymer systems.

In this work we use atomic force microscopy (AFM) for the direct visualization of single polyelectrolyte molecules of poly(2-vinylpyridine) - P2VP - hydrophobic weak cationic polyelectrolyte) in aqueous solutions. P2VP molecules were adsorbed on the solid substrates (mica) from very diluted solutions and studied using AFM in the same solutions (Fig. 1).





Conformation of poly(2-vinylpyridine) (P2VP) chain is balanced by the Coulomb repulsion and the short range van der Waals attraction. In our experiments, P2VP molecules underwent coil-to-globule transitions due to the changes in pH and/or ionic strength. The globule-to-coil transition takes place at pH  $\leq$  4. This transition occurs as a result of the increased fraction of protonated repeating units when the Coulomb repulsion exceeds van der Waals attraction. In the second example, the coil-to-globule transition was clearly observed in the presence of mono- and polyvalent salts. We were successful in the experimental demonstration study of the "re-extension" of the polymer chains in the conditions of a very high ionic strength (2-4.5 M) in accordance with theoretical and computer simulation studies.

We found a substantial conformationa changes of adsorbed P2VP globules in a wide range of pH and ionic strength of the aqueous solutions.

### HYDROPHOBIC AND OLEOPHOBIC SURFACES MADE OF PIN-LIKE STRUCTURES

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We developed a robust method for the fabrication of the arrays of metallic nanowires by the combination of a porous membrane template method and colloidal lithography. Anodic aluminum oxide (AAO) membranes (Whatman, Anodisc 13) with 200 nm pore size were used as templates for the electrochemical synthesis of the high-aspect-ratio nickel nanowires in the pores followed by the preparation of pin-like heads on the top of the wires (Fig.1a). The density of the particles deposited on the membrane surface was regulated by concentration of the polystyrene (PS) latex particles. The PS latex particles were spread on one side of the AAO membrane by depositing a specified volume of the particle dispersion in ethanol-glycerol medium. Afterwards, the sample was annealed above the glass transition temperature of PS to seal the pores with the latex particles. Electrochemical deposition of Ni-wires and caps were carried out in the Ni<sup>2+</sup>-containing electrolyte bath. The method allowed for the regulation of the density of Ni-nanowires arrays with a high aspect ratio and Ni-pin-head-like structures.



Fig.1. (a) SEM image of Ni-wires; (b) Contact angles on thiolized Ni-pin-head-like structures.

Prepared Ni-structures were sputter-coated with gold and then thiolized in the solution of perfluorodecanethiol. Obtained materials demonstrated hydrophobic and oleophobic properties (Fig.1b) due to the pin-head-like structure of the coatings.

### ELECTRON SCATTERING AT SINGLE CRYSTAL Cu(001) SURFACES

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We demonstrate specular electron scattering at single crystal Cu(001) surfaces and quantitatively show how Ta and Ta-oxide overlayers, and adsorbed O<sub>2</sub> molecules perturb the periodic surface potential, causing diffuse electron scattering. These findings are an important step towards narrow low-resistivity interconnect wires, and also provide the basis for a new type of gas sensor. Epitaxial Cu(001) layers with thickness d ranging from 20 nm to 1.4  $\mu$ m were grown on MgO(001) substrates by ultra-high vacuum magnetron sputter deposition at 80 °C. X-ray diffraction  $\theta$ -2 $\theta$  scans,  $\omega$ -rocking curves, and pole figures show the layers are single crystals with a cube-on-cube epitaxy. In-situ scanning tunneling microscopy shows 20 to 200 nm wide surface mounds with 0.35 to 0.60 nm wide atomically smooth terraces and atomic level roughness. In-situ electron transport measurements at room temperature show a resistivity increase with decreasing thickness, from  $1.70\pm0.06$  to  $2.65\pm0.09 \ \mu\Omega$ -cm for  $d = 1400\pm30$  to 20.0±0.4 nm, respectively. The data is consistent with the Fuchs-Sondheimer model and indicates specular scattering at the Cu-vacuum interface with an average specularity parameter p = 0.6±0.1. In contrast, layers measured *ex-situ* show completely diffuse surface scattering (p = 0)due to sub-monolayer oxidation. Samples that are immersed in liquid N<sub>2</sub> immediately after removal from the vacuum system do not oxidize and exhibit  $p = 0.7 \pm 0.1$  at 77 K. In-situ deposition of 0.3 to 7 nm thick Ta barrier layers on Cu(001) films leads to a resistance increase that indicates a transition to completely diffuse surface scattering, independent of the Ta thickness. Oxidation of the Ta layer leads to a partial recovery of the specularity, attributed to a reduced barrier density-of-states at the Fermi-level resulting in a lower scattering probability into barrier-layer states. In-situ exposure of Cu(001) layers to partial O<sub>2</sub> pressures  $P_{ox}$  between 10<sup>-8</sup> and 10<sup>-1</sup> torr cause distinct resistance changes that suggest a multiple step adsorption process: The initially adsorbed O<sub>2</sub> yields a resistance increase due to electronic roughening of the Cu surface, causing complete diffuse scattering at a coverage of 0.14 O<sub>2</sub> monolayers. Continued exposure results in a resistivity drop to the original value, as a complete monolayer is formed that yields specular scattering, followed by an increase associated with diffuse scattering at a chemically oxidized Cu surface. Data analysis provides values for the scattering cross-section of adsorbed molecules and shows that the rate in resistance-change is proportional to  $P_{or}$ , hence, these layers may become useful as thin metal film gas sensors.

### **EPITAXIAL CrN(001) LAYERS: SURFACE MORPHOLOGICAL EVOLUTION AND**

### **ELECTRONIC/OPTICAL PROPERTIES**

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Single crystal CrN(001) layers with thickness t = 10-160 nm were grown on MgO(001) by ultra-high vacuum magnetron sputtering at growth temperatures  $T_s = 600-800$  °C. The surface morphological evolution was analyzed by in-situ scanning tunneling microscopy and quantitatively studied using the height-height correlation function. For  $T_s = 600$  °C, square mounds align along <110> directions, associated with nitrogen terminated step edges, and increase in width from 8 to 25 nm with increasing t = 10 to 40 nm. They coalesce to reach a quasi-equilibrium shape at t = 160 nm. In contrast,  $T_s = 800$  °C leads to surface mounds that elongate along <100>, associated with a Bales-Zangwill instability, to form long dendrites that develop for t < 40 nm, but are overgrown by wide square mounds during coalescence at t > 40 nm. The mound growth for  $T_s = 600$  °C is associated with kinetic roughening due to an Ehrlich-Schwoebel barrier, and results in increases in the root mean square surface roughness  $\sigma$  from  $0.7\pm0.2$  to  $2.4\pm0.5$  nm and in the lateral correlation length  $\xi$  from  $7.2\pm0.6$  nm to  $24\pm3$  nm as t increases from 10 to 40 nm. On the other hand, the dendritic growth at  $T_s = 800$  °C results in decreases of  $\sigma$  from 2.0±0.4 to 0.9±0.1 nm and of  $\xi$  from 20±4 to 10±0.5 nm. Optical properties of CrN over a large wavelength range, 250 nm - 20 µm, were determined using transmission and reflection measurements from layers with variable thickness t = 34 nm - 1000 mm8.5  $\mu$ m. Lattice vibration absorption dominates the spectra for photon energies  $h\nu < 0.1 \text{ eV}$ . The refractive index n exhibits a sharp transition from 1.4 for hv = 5 eV to  $\sim 5$  in the infrared range, with a peak of n = 5.5 at hv = 1.5 eV, associated with an interband transition with an onset of 0.69 eV. Electron transport data from 10 - 300 K are consistent with the optical results and indicate semiconductor behavior.

### TEXTURAL EVOLUTION OF ULTRATHIN CaF<sub>2</sub> NANORODS CHARACTERIZED BY RHEED SURFACE POLE FIGURES

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A thin film with biaxial texture is cost effective and may have physical properties comparable to that of a single crystal. Our previous work shows that CaF<sub>2</sub> nanorods grown by the oblique angle vapor deposition on amorphous substrates exhibit a biaxial texture. This  $CaF_2$  can be used as a buffer layer to grow biaxial thin films for various applications <sup>1-3</sup>. The understanding of the growth mechanism of the CaF<sub>2</sub> biaxial texture is not only of fundamental interest but also important for potential practical process engineering. In this poster, we present the texture evolution of ultrathin CaF<sub>2</sub> nanorods grown by oblique angle deposition on native oxide covered Si at room temperature and characterized by the reflection high energy electron diffraction (RHEED) surface pole figure technique which can probe the growth front starting from the very initial stage of thin-film growth. RHEED patterns at various thicknesses of CaF2 nanorods were collected. Continuous rings shown in Fig. 1(a) indicate a polycrystalline texture at 10 nm thickness. The broken arcs shown in Fig. 1(b) indicate that the biaxial texture has already developed at 20 nm thickness. The near vertical dashed lines indicate that the angle between the [111] direction (out-of-plane) of CaF<sub>2</sub> naorods with respect to the substrate normal also changes as the film thickness increases. Figure 2 shows the constructed RHEED {220} pole figures. The evolution of CaF<sub>2</sub> biaxial texture is clearly visualized through the changes of the surface-pole intensity distributions. The transition from highly dispersed poles from 20 nm CaF<sub>2</sub> nanorods to more well-defined poles from 200 nm CaF<sub>2</sub> nanorods reflects the reduced angular dispersions in both the out-of-pane and in-plane orientations.







Fig. 2 The {220} RHEED surface pole figures of the CaF<sub>2</sub> nanorods at various thicknesses.
"Biaxial CdTe/CaF<sub>2</sub> films growth on amorphous surface", Thin Solid Films 517 (24), 6623-6628 (2009).
2. "Growth of CdTe Films on Amorphous Substrates Using CaF<sub>2</sub> Nanorods as a Buffer Layer", J. of Electronic Materials 38 (8), 1600-1604 (2009).
3. "Small angle grain boundary Ge films on biaxial CaF<sub>2</sub>/glass substrate", J. of Crystal Growth 312, 607 (2009).

### GENERATION OF EQUILIBRATED POLYMER CONFORMATIONS IN COMPUTER SIMULATIONS

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Polymer brushes are used to modify the characteristics of a surface, and induce interesting and potentially useful behavior. Polymer brushes have been used as lubricants, adhesives, surfactants and chemical gates. In the form of patterned thin films, they have potential for use in microelectrics and biomimetic material fabrication. From a fundamental standpoint, it is important to understand the physics behind the functioning of polymer brushes. Computer simulations are a useful and inexpensive tool to do so, but require equilibrated conformations as their starting point. A new method of generating equilibrated polymer conformations is presented. In this method, the molecular weight of well--equilibrated conformations of polymers is successively doubled by affinely scaling the simulation box and adding beads. At each stage of molecular weight doubling, a substantial portion of the large--scale characteristics are preserved. Deformations are produced only on the smaller scales, thereby requiring relaxation times significantly smaller than the reptation time to fully equilibrate the melt. This method preserves the topological state of individual polymers in the melt, and its effectiveness is demonstrated for cyclic and linear polymers. The method requires simulation time that scales as N<sup>2</sup>, and is thought to be applicable to polymers with a variety of architectures.

### OPTIMIZED DNA MONOLAYER FORMATION ON GOLD FOR SIGNIFICANTLY IMPROVED HYBRIDIZATION EFFICIENCY

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Past literature investigations have optimized various single factors used in the formation of thiolated, single stranded deoxyribonucleic acid (ss-DNA) monolayers on gold. In this study a more comprehensive approach is taken, where a design of experiment (DOE) is employed to simultaneously optimize all of the factors involved in construction of the capture monolayer used in a fluorescence-based hybridization assay. Statistical analysis of the fluorescent intensities resulting from the DOE provides empirical evidence for the importance and the optimal levels of traditional and novel factors included in this investigation. We report on the statistical importance of a novel factor, temperature of the system during monolayer formation of the capture factor increased the hybridization signal 50%. An initial theory of how the physical factor of heat is mechanistically supplementing the function of the lateral spacer molecule is provided.

### ANGLE RESOLVED XPS INVESTIGATION OF HfZrO<sub>4</sub> HIGH-K THIN FILMS

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In order to continue the scaling of MOSFET devices it is necessary to scale the gate dielectric in terms of equivalent oxide thickness (EOT) either by decreasing physical thickness or increasing effective dielectric constant (k-value). As a replacement for SiO<sub>2</sub> based gate dielectrics, which have reached their fundamental thickness scaling limit, high-k Hf-based dielectrics including HfO<sub>2</sub>, Hf silicate and nitrided Hf silicate have been chosen as viable materials.[1] Though the HfO<sub>2</sub>-based materials have generally been preferred, recent work has shown that HfO<sub>2</sub> with an admixture of ZrO<sub>2</sub>, which are both fully miscible, has the potential to provide a higher k by means of stabilization of tetragonal/cubic phases.[2,3] Moreover, the mixed oxide Hf<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> has been shown to exhibit improved device performance and reliability compared to HfO<sub>2</sub>.[4] We have recently demonstrated that HfZrO<sub>4</sub> with a higher-k (k>30) than HfO<sub>2</sub> processed under the same conditions can be obtained by chemical vapor deposition from a 1:1 molar mixture of Hf and Zr metallorganic sources.[5]

In this study we utilized angle resolved X-ray photoelectron spectroscopy (ARXPS) to probe the chemical species of these mixed high-k oxide films. ARXPS enables non-destructive measurements of key parameters of thin high-k stacks such as thickness, relative ordering of chemical species, and depth distribution of the species in a multilayer stack. An important parameter which is necessary for analyzing ARXPS data is the attenuation length ( $\lambda$ ) of emitted photoelectrons. In this regard, an internal calibration was performed to obtain  $\lambda$  for both Hf4f and Zr3d photoelectrons emitted from HfZrO<sub>4</sub>. Excellent agreement with  $\lambda$  obtained from the predictive formula proposed by Tanuma, Powell, and Penn (TPP-2M equation)[6] was obtained. Moreover, the ARXPS measurements allow for the measurement of interfacial (SiO<sub>2</sub>) layer thickness, which is not readily obtainable from conventional inline measurement techniques such as spectroscopic ellipsometry or X-ray reflectivity. This measurement is crucial for high-k containing MOS stacks because the lower-k value associated with the interfacial layer ultimately limits electrical scaling.

References:

- [1] D. G. Schlom et al., MRS Bull., 33, 1017 (2008).
- [2] X. Zhao et al., *Phys. Rev. B*, **71**, 085107 (2005).
- [3] D. H. Triyoso et al., J. Vac. Sci. Technol. B, 25, 845 (2007).
- [4] R. I. Hedge et al., IEDM Tech. Dig., pp. 35-38 (2005).
- [5] S. Consiglio et al., accepted, ECS Trans., 28, (2010).
- [6] S. Tanuma et al., Surf. Interface Anal., 21, 165 (1994).

# Quasi-SINGLE CRYSTAL GERMANIUM FILMS ON BIAXIALLY TEXTURED CaF<sub>2</sub>/GLASS SUBSTRATES

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Most of the high efficiency thin film photovoltaic devices are fabricated on a single crystal substrate, therefore making it inaccessible from a cost prospective. Fabrication of such devices on cheaper substrates such as glass has been shown to result in lower efficiencies. The semiconductor films grown on glass substrates are either amorphous or polycrystalline, in which the carrier scattering from the boundaries of misoriented grains have detrimental effects in achieving high efficiencies. If the grain orientation in the substrate can be highly aligned in both out-of-plane and in-plane (biaxially textured), the semiconductor film epitaxially grown on such a substrate would have a high level of orientation and approximate the properties of single crystal film and have electrically benign grain boundaries lowering the carrier scattering rate. In this poster we demonstrate that it is possible to grow quasi-single crystal Ge films on a glass substrate using a biaxially textured CaF<sub>2</sub> buffer layer at a low temperature of 400° C. The cross section scanning electron microscope image of one such film is shown in Fig. (a). The CaF<sub>2</sub> buffer layer was prepared by oblique angle vapor deposition technique. It has a biaxial texture orientation of {111} <121>. The {220} pole figure shown in Fig. (b) is similar to the theoretical projection of {220} poles along <111> direction of a cubic crystal tilted off the substrate normal.

Again, from X-ray pole figure analysis (Fig. (c)), it was determined that the heteroepitaxial Ge/CaF<sub>2</sub> films had a {111} <121> biaxial orientation rotated azimuthally by  $180^{\circ}$  about the <111>direction of CaF<sub>2</sub> (type B epitaxy). Transmission electron microscopy revealed that the Ge film grown at 400 <sup>o</sup>C has a quasi-single crystal like structure with small angle grain boundaries of  $<2^{\circ}$ misorientation [1]. This Ge



(a) Cross section image of Ge/CaF<sub>2</sub>/Glass sample taken by scanning electron microscope. (b) X-ray (220) pole figure of CaF<sub>2</sub> buffer layer. The out-of-plane orientation of this film is [111] tilted off the substrate normal by  $\sim 11^{\circ}$ . (c) X-ray (220) pole figure of Ge deposited on CaF<sub>2</sub>/Glass substrate. The (220) poles are seen to rotate by 180° about the [111] direction of the CaF<sub>2</sub> film.

film has mobility on the order of 40% of the mobility of the single crystal Ge substrates with similar carrier concentration.

Work supported by National Science Foundation of USA under grant number 0506738.

[1] C. Gaire, P. C. Clemmer, H.-F. Li, T. C. Parker, P. Snow, I. Bhat, S. Lee, G.-C. Wang, and T.-M. Lu, "Small angle grain boundary Ge films on biaxial CaF<sub>2</sub>/glass substrates", *J. Cryst. Growth* 312, 607-610 (2010).

### TEMPERATURE DEPENDANT BIAXIAL TEXTURE EVOLUTION IN Ge UNDER OBLIQUE ANGLE VAPOR DEPOSITION

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The morphology, texture and grain size of Ge films grown under oblique angle vapor deposition on oxide covered Si(001) substrates at various temperatures ranging from 230 °C to 400 °C were studied by SEM, x-ray diffraction and x-ray pole figure techniques. A transition from polycrystalline to biaxially textured films was observed within this temperature range. XRD demonstrated that the samples grown at <375 <sup>o</sup>C were polycrystalline (Fig. 1a). The Ge films consisted of isolated nanorods at 230 °C, and were continuous at all other temperatures. At the highest substrate temperatures used 375 °C and 400 °C a mixture of polycrystalline and preferred orientation was observed (Fig. 1b). The preferred orientation was a biaxial texture following the orientation of the Si(100) substrate as shown by the (111) x-ray pole figure shown in Fig. 1c for the 400  $^{0}$ C sample. In Fig. 1c, a, b, c, and d refer to twins about (111), (-111), (-1-11), and (1-11), respectively. For comparison a Ge film was deposited at normal vapor incidence at 400 °C. The normal incidence film was polycrystalline similar to films deposited obliquely at substrate temperatures < 375 <sup>o</sup>C. The biaxial texture is believed to be a result of the loss of interface oxide layer, resulting in epitaxial deposition on the Si. The loss of interface oxide is attributed to the interaction of the Ge with the Si oxide layer under oblique angle deposition. GeO<sub>2</sub> is known to become GeO at temperatures approaching 420 °C, and GeO can desorb at temperatures >420 °C. During the initial stages of an oblique angle deposition isolated islands will form. The isolated islands present during the initial stages of oblique angle deposition allows for the GeO to desorb as opposed to a normal incidence deposition which is a burial growth process.



**Fig. 1** (a) A XRD frame for Ge deposited at 230  $^{0}$ C substrate temperature, T<sub>s</sub>, the constant intensity of the diffraction rings indicate polycrystalline texture. (b) An XRD frame at T<sub>s</sub> = 400  $^{0}$ C where a preferred orientation is shown by the two high intensity regions, indicated by arrows, along the (111) diffraction ring. (c) A (111) pole figure of Ge deposited at T<sub>s</sub> = 400  $^{0}$ C. a, b, c, and d are twins about about (111), (-111), (-1-11), and (1-11), respectively.

This work is supported by ONR grant N00014-08-0453.

### ANALYSIS OF SILICON NANOWIRES BY LASER ATOM PROBE TOMOGRAPHY PREPARED BY A PROTECTED LIFT-OUT PROCESSING TECHNIQUE

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The determination of dopant profiles (concentration, distribution, segregation) and compositional interface characteristics (seed/nanowire, core/shell) in semiconducting nanowires (NWs) is a challenge (and in many cases not possible) for commonly employed techniques such as scanning transmission electron microscopy (TEM) and secondary ion mass spectrometry (SIMS). Atom Probe Tomography (APT) provides 3D atomic level position and composition appropriate for characterizations of this kind, but not without overcoming issues related to specimen preparation. We will discuss protection/lift-out processing techniques for preparing closely spaced NWs for subsequent APT analysis. Dopant distributions of Boron in prepared Silicon NWs will be presented.

Silicon NW arrays were fabricated on degenerately doped p-type Si <111> wafers. A layer of photoresist (PR) was spun on, followed by photolithography to produce an array of 500 nm diameter holes in the resist. A 5 nm thick Au film was then evaporated through the holes in the PR and standard lift-off was performed in acetone, leaving behind an array of 500 nm diameter Au dots on the Si substrate. Silicon nanowires were grown by chemical vapor deposition (CVD) using the vapor-liquid-solid growth mechanism. This process led to growth Si NWs that were generally vertically aligned with the Si substrate due to homoepitaxy.

Even though individual NWs have an ideal geometry for analysis via APT (proper length and radius), they cannot be analyzed in their native state. Lift-out preparation techniques developed for TEM have been utilized for APT specimen preparation with much reported success. Our variation utilized for APT of NWs was to incorporate a protective Nickel coating over the entire surface of the NW. This protective coating can be either removed after FIB milling is complete, or it can be shaped to allow manipulation of the NW volume available for analysis. The final step is to etch away the protective Ni coating leaving behind a single NW *without Gallium damage* from an extensive FIB milling procedure. Fig. 1 shows the reconstructed atomic positions for a >200 nm length of NW. The analysis volume accessible to APT is only some fraction of the entire tip volume (in this case, the central ~50 % of the diameter of the specimen). The central core portion of the NW is shown to be 99.9964 % Silicon, 0.0027 % Oxygen, and 0.0009 % Boron with no strong radial or axial dependence in concentration.



FIG. 1. 3D reconstruction of atomic positions: Silicon (gray dots), Boron (dark blue spheres), and Oxygen (light blue spheres).

### THE EFFECT OF HUMIDITY ON THE ADHESION OF METAL-CERAMIC INTERFACES

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The fracture toughness ( $\Gamma_{FT}$ ) of a bimaterial interface is often influenced by the local chemical environment, which alters the nature of interfacial bonding. The role of humidity in the adhesion of Cu/SiO<sub>2</sub> interfaces is of particular relevance to the durability of thin film interconnect structures that are widely used in the microelectronics industry. Previous studies of the Cu/SiO<sub>2</sub> interface have shown the susceptibility of the subcritical debonding process to the moisture content of the ambient environment. The crack growth behavior in these systems has been explained using a stress-corrosion mechanism that involves the fissure of Cu-O-Si linkages by hydrolysis (similar to that of Si-O-Si bonds in bulk silica glasses). In our current work we demonstrate the contribution of Cu-O-Si bond density to interfacial toughness by inducing the hydrolysis of Cu-O-Si bonds at the interface. We validate our experiment by using, as a control, a Au/SiO<sub>2</sub> system that is not susceptible to hydrolysis. We observe that the fracture energy of the Cu/SiO<sub>2</sub> interface can be partitioned into contributions due to bond-breaking and plasticity, following our previous work using a molecular nanolayer tailored Cu/SiO<sub>2</sub> interface.

Thin film sandwich structures were made by the deposition of Cu or Au on Si (001) wafers with an 85-nm thick thermal silica layer and tested on a four point bend test system in a temperatureand humidity-controlled environment. Our results show an 80% decrease in  $\Gamma_{FT}$  (5.4 J/m<sup>2</sup> to 1.1 J/m<sup>2</sup>) for the Cu/SiO<sub>2</sub> interface when increasing the water activity from 0.05 to 0.9 at 50 °C, while the effect on the Au/SiO<sub>2</sub> interface ( $\Gamma_{FT} = 0.58 \pm 0.1 \text{ J/m}^2$ ) is negligible. We estimate the onset of plasticity by the yield stress of Cu to be  $3.3 \pm 0.1$  GPa which is in excellent agreement with our previous results. Our findings show that the extent of Cu-O-Si bonding directly correlates with the toughness of Cu/SiO<sub>2</sub> interfaces and that environmental effects play a large role in the reliability of devices containing such interfaces.

### ADSORPTION AND DESORPTION OF DINITROTOLUENE ON FUNCTIONALIZED SURFACES

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Nanosensors, which are based on nanotechnology with small size and high sensitivity, are desirable for various applications, i.e. detecting atmospheric trace gas, contaminants, explosive, chemical and biological materials for environmental protection, homeland security and defense, healthcare and medical research. Surface science and engineering have the advantage in studying how a nanosensor works. Specifically, self assembled monolayers (SAMs) are widely used to modify the structure and functionality of a sensor surface, on which the adsorption and desorption of molecules have been extensively investigated.

For explosive detection using nanosensors, we have been examining in ultra-high vacuum the adsorption and desorption of dinitrotoluene (DNT) on various customized surfaces, including Au and SAMs with different functional groups. The temperature programmed desorption (TPD) results indicated that the interaction between DNT molecules and surfaces differed with the dose amount as well as the surface composition. The scanning tunneling microscope was utilized to study the structure of Au surface and with self-assembled hydrocarbon compounds. The morphology and distribution of adsorbed DNT on surfaces were also visualized in situ. Further work with the X-ray photoelectron spectroscopy (XPS) is on the way to quantitatively examine the surface composition and the adsorption/desorption of DNT.

### MASS SPECTROMETER CALIBRATION FOR MEASUREMENT OF PHOTORESIST OUTGASSING SPECIES IDENTIFICATION AND QUANTIFICATION

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Reduced Extreme Ultra Violet (EUV) optics lifetime, due to contamination caused by EUV irradiation with a wavelength near 13nm of lithographic imaging materials, continues to impact the timing of EUV exposure tool introduction. The Resist Outgassing and eXposure system (ROX) at the College of NanoScale Science and Engineering (CNSE) in collaboration with the vertically integrated Resist and Materials Development Center (RMDC) which is the newly formed Resist Center of Excellence within SEMATECH's lithography division, has been one of the key tools used to test resist outgassing.

One of most difficult tasks, when characterizing outgassing, continues to be the accurate calibration of the mass spectrometer in order to obtain the desired accuracy of the measurements for all species. In order to carefully characterize the molecular fragments, evolved during exposure, a quadrupole mass spectrometer is used. Use of noble gas mixtures or nitrogen are the standard for QMS calibration, however these methods can lead to inaccurate resist outgassing measurements due to C-C bond fragmentation.

The resist outgassing team has worked on species calibration using the very molecules that can be seen coming of the resist when exposed to EUV radiation. This careful effort will help refine the isolation of the signal produced by each outgas species as well as a more accurate quantification of the signal analyzed.