

PCSI

Room Keauhou II - Session PCSI-WeA

Fabrication and Processing/New Approaches to Epitaxy II/2D Surfaces III/Growth

Moderators: Patrick Lenahan, The Pennsylvania State University, Erik Lind, Lund University, Robert Wallace, University of Texas at Dallas

2:00pm PCSI-WeA-1 Preparation and Characterization of Nanometer-thin Silicone Films for Dielectric Elastomer Transducers, *Bert Müller, B Osmani, T Töpfer*, University of Basel, Switzerland

Nanometer-thin silicone films are essential components of low-voltage dielectric elastomer transducers and will, for example, play a vital role in future artificial muscles [1]. Organic molecular beam deposition (MBD) is a versatile technique to prepare silicone films under well-defined conditions [2,3], but the achievable growth rates of about 1 μm per hour are too low for the fabrication of multi-layer devices. Therefore, we have developed electro-spraying as an alternative deposition method with one or two orders of magnitude faster rates [4,5]. For the two approaches, spectroscopic ellipsometry (SE) has been employed for *in situ* monitoring the film's optical properties, the film thickness and the surface morphology during deposition and ultra-violet (UV) light irradiation. The derived quantities were verified by means of atomic force microscopy (AFM).

Subsequent to the silicone deposition and the cross-linking by UV light curing, Au has been deposited using MBD and sputtering. This deposition process was also quantitatively characterized using SE and controlled by means of the plasmonic fingerprints of the metal nanostructures [6]. The *ex situ* AFM measurements revealed well-known modulations characteristic for strained surface layers [7]. Recent nano-indentation tests have demonstrated that the Au-layers on the silicone near the critical stress regime hardly contribute to the overall elastic modulus and are, therefore, a sound basis for smart electrodes [8]. The nano-mechanical probing of the powered thin-film dielectric elastomer transducers evidenced the importance of the thickness homogeneity for such devices [9]. The function of planar thin-film dielectric elastomer transducers can be precisely determined taking advantage of the cantilever bending approach [10].

In conclusion, spectroscopic ellipsometry and advanced atomic force microscopy with nano-indentation capability enables us to thoroughly characterize the film morphology as well as the optical and local mechanical parameters of silicone and Au/silicone nanostructures.

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- [2] F. M. Weiss, et al. *Mater Design* **105**, 106 (2016)
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- [4] F. M. Weiss, et al. *Adv Electron Mater* **2**, 1500476 (2016)
- [5] F. Weiss, et al. *Langmuir* **32**, 3276 (2016)
- [6] T. Töpfer, et al. *Adv Electron Mater* **3**, 1700073 (2017)
- [7] B. Osmani, et al. *Eur J Nanomed* **9**, 69 (2017)
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2:05pm PCSI-WeA-2 Improving Interfacial Adhesion Between Active Material and Solid Electrolytes in Thin Film Supercapacitors, *S Ahmed, N Korivi, Li Jiang, B Oni*, Tuskegee University

Solid-state thin film flexible supercapacitors are of interest for emerging applications including portable and wearable electronics. Adhesion between the electrolyte (e.g. ionic conductor in a polymer matrix) and the active electrode material (e.g. carbon nanomaterial) is an important factor influencing the performance of the supercapacitor. Typically, discrete electrode and electrolyte layers are fabricated and held together by pressure clamps or mechanical vises to improve electrode-electrolyte interfacial adhesion [1, 2]. However, this approach complicates the packaging of the devices for practical applications. There is a need for simple and scalable alternatives to improve the quality of electrode and electrolyte interface.

We report a facile method for improving adhesion between electrolyte and active electrode material in solid-state supercapacitors. The method involves dispersing active electrode material in a solvent, and depositing the dispersion on the surface of a solid electrolyte. The solvent causes swelling of the polymer matrix of solid electrolyte, which results in the active material being partially embedded on electrolyte surface. This allows

for enhanced adhesion between the electrode and electrolyte. The choice of solvent in the electrode material dispersion is influenced by the polymer matrix used in the solid electrolyte. The method reported here has been used to develop a flexible, solid-state thin film supercapacitor. This device was made by solution casting a dispersion of multi-walled carbon nanotubes (MWCNTs) and isopropyl alcohol (IPA) on one side of a solid electrolyte layer (composite of polyvinyl alcohol and phosphoric acid). The IPA swells the crosslinked PVA polymer matrix, and partially embeds the MWCNTs on the electrolyte surface. The process is repeated to fabricate an electrode layer on the other side of the electrolyte layer, resulting in a supercapacitor with an integrated structure. Consequently, there is no need for mechanical clamps to hold the structure together. Devices fabricated in this manner show capacitance of 1.8 F/g, with areal capacitance of 7 mF/cm². The energy and power densities are 0.25 Wh/kg and 1.25 kW/kg respectively. The devices are flexible and do not show appreciable degradation in performance over 2000 charge-discharge cycles and when operating at temperatures as high as 60°C. Electrode-electrolyte interface characterization shows good adhesion between MWCNTs and solid electrolyte.

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[2] X. Zhang, Z. Lin, B. Chen, S. Sharma, C. Wong, W. Zhang, Y. Deng, *J. Mater. Chem. A*, **1**, 5835 (2013).

2:10pm PCSI-WeA-3 Physical and Chemical Modification of Graphene for High Capacitive Energy Storage, *KwangBum Kim*, Yonsei University, Republic of Korea

Graphene, a one-atom-thick, two-dimensional (2D) sp² carbon structure, has attracted considerable interest as a next-generation electrode material. This can be attributed to a number of interesting properties of graphene, such as its good mechanical/chemical stability, high electrical/thermal conductivity, and a large surface area (over 2630 m²g⁻¹) due to its high surface-to-volume ratio. The combination of these unique physical and chemical properties means that graphene has significant potential to act as either an electrochemically active material in itself or as a conductive carbon template suitable for use in energy storage devices such as supercapacitors and Li-ion batteries.[1-4] At the same time, metal oxide/graphene nanocomposites are also of considerable interest for electrochemical energy storage applications owing to their outstanding properties. These excellent properties of metal oxide/graphene nanocomposites are generated from synergistic combination of graphene with metal oxide on the nanometer scale.[5-9] In this study, we report on the physical and chemical modification of graphene for energy storage applications.

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- [2] H.K Kim, and K.B Kim, *Chem. Mater* 2014, **26**, 4838
- [3] S.H Park, and K.B Kim, *Sci. Rep.*, 2014, **4**, 6118
- [4] S.H Park, and K.B Kim, *Chem. Mater.*, 2015, **27** (2), 457
- [5] H.K Kim, Kamali and K.B Kim, *Energy Environ. Sci.*, **9**, (2016) 2249
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2:15pm PCSI-WeA-4 Interface Analysis and Phase Transition of HfO₂ Film on Si Substrate after Thermal Treatment, *Hassan Siddique, D Rucheng, W Zhongping, D Zejun*, University of Science and Technology of China, China; *Z Zengming*, University of Science and Technology of China, Hefei, Anhui, China

Hafnium oxide (HfO₂) thin films on Si (100) substrate was prepared by radio frequency sputtering technique. XRD patterns show that the grown films are amorphous and transform into stable monoclinic phase after annealing treatment[1]. The position and width of Raman modes vary nonlinearly with increasing temperature due to the anharmonic interaction of hafnium and oxygen [2]. XPS of the film reveals that no silicide is found after thermal treatment. However, Si_{2p} suggests the occurrence of a SiO₂ interface between HfO₂ layer and Si substrate[3-4]. Ellipsometry spectroscopy results show that amorphous HfO₂ thin films crystallize into a monoclinic phase in the range of 300- 400 °C. This observation is consistent with that of XRD and Raman spectroscopy at variable temperature. Thickness and refractive index of HfO₂ thin film are obtained by fitting ES

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parameters. The total thickness of the HfO₂ thin film increases by 1.02 nm and refractive index decreases from 2.3 to 1.9 during the formation of the SiO₂ interface layer after thermal treatment. In this study, we investigated the temperature effects on the crystal structure, interface growth and optical properties of HfO₂ thin film. Furthermore, the correlations between temperature, interface growth, and optical properties have been established.

2:20pm PCSI-WeA-5 Machine Learning for Process Development for Semiconductor and Nanotechnology Product R&D, Mark Mueller, Georgia Institute of Technology

Machine Learning algorithms can be utilized to form analytic models for semiconductor or complex nanotechnology manufacturing processes. These serve as a means of mapping the process space for a manufacturing tool (such as metal deposition or oxide etch) within a manufacturing sequence. Methods described may also be extended to a “modules” or sequences of steps, such as deposition-lithography-etch-strip, and even to an entire manufacturing process.

To effectively leverage machine learning for data mining and inference formation, it is important to select variables or “attributes” for input, along with an output or predicted quantity for each set of inputs. This presentation describes how to construct an “X” matrix of inputs, along with how to process a “Y” matrix of outputs, where each row represents a wafer and each column represents an input/output variable.

Predictive modeling is compared to current methods of engineering and experiment execution. Typically, development data belongs to the engineer or group who runs an experiment, and the desired result is a report which provides technical progress or which may guide a business decision. Each experiment is designed around a particular focus, and “old” data lives in engineering notebooks or spreadsheets, while the “wisdom” derived lies in the reports and in professional experience of those involved. In contrast, by creating models based on continual collection of data, it is possible to mine this data with predictive models, such as classifier-based (example: in spec/out of spec) or regression-based machine learning algorithms.

Such models allow a thorough mapping of the process space for addressing challenges and future hardware/process development. Construction and continued extension of a model thus replaces the traditional approach of targeted experiments and design of experiments (DOE). Since the collection and analysis of data is a collaborative effort, this use of machine learning becomes a collaborative tool (such as Google Docs) where multiple team members may contribute.

Machine learning models may be utilized for more applications beyond process development. Such models can be used to measure differences between subsystems, for example, evaluating materials from different vendors or evaluating different power supplies. Machine learning can be leveraged to measure equivalence or non-equivalence between production tools within a high volume factory.

2:25pm PCSI-WeA-6 Interlayer Assisted Growth of Polycrystalline Germanium on Silicon at Low Temperatures, Naga Korivi, N Nujhat, S Ahmed, L Jiang, Tuskegee University; K Das, JBP Materials LLC

The growth of polycrystalline and heteroepitaxial germanium (Ge) on silicon (Si) is of interest for various electronic applications. Sputter deposition offers a simple and inexpensive process for deposition of homogenous Ge films on large-area substrates [1]. One challenge in growing high quality Ge on Si by sputtering method is the presence of native oxide on Si, formed during the pump down process. Also, the presence of excited and ionized oxygen created by plasma prior to Ge deposition can contribute to native oxide on Si. Our experimental observations indicate a native oxide of 1.5 - 2 nm thickness can form in the sputter chamber at mid-range vacuum ($\sim 10^{-6}$ – 10^{-7} Torr). This corresponds to observations made by others [2]. Some prior reports achieved high-quality heteroepitaxial Ge on Si by desorbing the native oxide from the Si substrate prior to sputtering of Ge [3]. The oxide desorption involves a high temperature in-situ anneal (> 1000 °C) in the sputtering chamber at ultra-high vacuum ($\approx 10^{-10}$ Torr). Desorption cannot be conveniently done in sputtering systems with a moderate vacuum. Also, desorption temperature is higher than the typical thermal budget for post-CMOS processing. It is relevant to investigate the growth of high-quality Ge films using a moderate pressure system without a high temperature step.

We report here a preliminary study of polycrystalline Ge film growth on Si by DC magnetron sputtering at moderate vacuum ($\sim 10^{-6}$ Torr) and at substrate temperature as low as 300 °C without a high-temperature in-situ oxide desorption step. Our approach involves the sputtering of a

nanometer scale Si interlayer on the Si substrate, prior to Ge deposition. This is designed to disrupt the surface oxide on the Si substrate and ultimately assist the growth of high quality Ge on Si substrate. X-ray diffraction and Raman spectroscopic studies indicate the formation of polycrystalline Ge at 300 °C when Si interlayer is incorporated. Sputtering Ge on Si at 300 °C without a Si interlayer resulted in amorphous Ge. Prior studies have reported amorphous Ge on Si at 320 °C under similar sputtering process conditions, but without any interlayer [2]. Currently, the Ge/Si interfaces in this work are being characterized further by high resolution transmission electron microscopy.

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2:35pm PCSI-WeA-8 Plasma-enhanced Atomic Layer Deposition of MoS₂: From 2-D Monolayers to 3-D Aligned Nanofins, Ageeth Bol, Eindhoven University of Technology, Netherlands

INVITED

Plasma-enhanced atomic layer deposition (PE-ALD) might prove to be a key enabler for tackling the current challenge of large-area growth of 2-D materials with wafer level uniformity and digital thickness controllability. In this contribution, we have implemented PE-ALD to synthesize large-area WS₂ and MoS₂ thin films with tuneable morphologies i.e. in-plane and vertically standing nano-scale architectures on CMOS compatible SiO₂/Si substrates. The large scale 2D in-plane morphology has potential applications in nanoelectronics, while the 3D nanofin structures could be ideal for catalysis applications such as water splitting.

The PE-ALD process was characterized over a wide temperature range between 150°C - 450°C by using a combination of a metal organic Mo or W precursor and a H₂S + H₂ + Ar plasma as the co-reactant. The use of plasma species as reactants allowed for more freedom in processing conditions and for a wider range of material properties compared with the conventional thermally driven ALD. The number of layers in the resulting films could be controlled accurately down to a mono-layer just by tuning the number of ALD cycles. HAADF TEM analysis of the showed that during the initial ALD cycles, MoS₂ islands expeditiously extended in the lateral direction and merged to form a film which continued to grow in a layer-by-layer fashion until a certain thickness. Thereafter, an aligned out-of-plane growth mode started to dominate as shown by cross-sectional TEM analysis. The origin of this transition from in-plane to out-of-plane growth mode might be attributed to the enhanced precursor adsorption on high surface energy locations such as grain boundaries, kinks or ledges. Due to crowding effects at these favourable adsorption sites subsequent vertical growth of MoS₂ is observed.

We show that the in-plane grown 2D structures can be successfully applied in electronic devices, while the 3D aligned fins a very suitable catalysts for the Hydrogen Evolution Reaction. These results show that plasma enhanced ALD might be instrumental in realizing not only the large area growth of high-quality 2-D materials but can also be applied as a tool to control the morphology of thin films.

3:05pm PCSI-WeA-14 Phase Control of Ga₂O₃ Films Grown by Atomic Layer Epitaxy, V Wheeler, N Nepal, U.S. Naval Research Laboratory; L Nyakiti, Texas A&M University; D Boris, S Walton, D Meyer, Charles Eddy, Jr., U.S. Naval Research Laboratory

Ga₂O₃ has attracted significant interest as an ultra-wide bandgap material for next generation high-power, high-temperature electronic device applications. While there are five polymorphs of Ga₂O₃, the β -Ga₂O₃ (monoclinic) is the most stable and most widely studied to-date. By comparison, the α -Ga₂O₃ phase is less energetically favorable but has a similar bandgap (5.3 eV) and a rhombohedral corundum crystal structure. The ability to attain this metastable state can encourage bandgap engineering between α -Al₂O₃ and α -In₂O₃ similar to other III-V alloys. In addition, Schottky barrier diodes made with α -Ga₂O₃ films have shown improved performance over both β -Ga₂O₃ and SiC [1], demonstrating the benefit of this polymorph in next generation devices. Here, we use atomic layer epitaxy (ALE) to produce high-quality, heteroepitaxial Ga₂O₃ films and demonstrate phase selectivity with variations in growth temperature, plasma chemistry and gas pressure.

ALE Ga₂O₃ films were grown on c-plane sapphire substrates in a Veeco Fiji 200 reactor. All films were produced using trimethylgallium and O₂ plasma precursors with pulse/purge times of 0.015s/10s and 10s/10s, respectively.

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The growth temperature, plasma gas flow, and pressure were varied to assess their impact on resulting film crystallinity and phase composition. Independent of growth conditions, all films were crystalline and highly resistivity with Ga/O ratios between 0.68-0.70 and no indication of C contamination by XPS.

Decreasing chamber pressure an order of magnitude during the plasma step drastically effected the resulting phase, yielding pure β -Ga₂O₃ at 80 mTorr and pure α -Ga₂O₃ at 8 mTorr. Additionally, at 350°C and 8 mTorr, the phase could be altered by a varying the O₂ plasma flow from 5-100 sccm. For these conditions, optical emission spectroscopy and ion flux measurements were made to correlate the impact of ions and other plasma species on the preferential promotion of different phases. By varying the growth temperature from 300 to 500°C at 8 mTorr, films went from mixed phase, to pure α -Ga₂O₃ at 350°C, to pure β -Ga₂O₃ at 500°C. High-quality β -Ga₂O₃ films were produced at 5sccm O₂ that had an RMS roughness of 0.38nm and XRD FWHM of 268 arc-sec for a 30nm film. At 40sccm, high-quality α -Ga₂O₃ films were obtained with an RMS roughness of 0.15nm and XRD FWHM of 250 arc-sec for a 30nm film. Thus, using ALE high-quality, phase selective films can be achieved to satisfy application requirements.

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3:10pm **PCSI-WeA-15 Low-temperature Homoepitaxial Growth of Two-dimensional Antimony Superlattices in Silicon**, April Jewell, A Carver, S Nikzad, M Hoenk, Jet Propulsion Laboratory

Silicon-based imaging arrays have a variety of scientific and commercial applications, and are at the heart of NASA's optical space telescopes and instruments. Operation in space brings the challenge of dealing with radiation effects. For example, protons cause displacement damage within the silicon lattice, resulting in stable defects or "traps" within the device. Traps accumulate over time leading to increased dark current, hot pixels, and charge transfer inefficiency; adversely affecting performance and science return. JPL-invented delta-doped and superlattice-doped ("2D-doped") detectors offer high durability, high stability and high sensitivity to wavelengths spanning the UV, visible, and near IR spectral regions. Importantly, JPL's 2D-doped detectors offer a vast improvement in stability against damaging radiation over conventional devices.

For device passivation by 2D-doping, dopant concentrations in the range of 10^{13} - 10^{14} cm⁻² are typically used, and delta layers are confined to within a few nanometers of the surface. P-type doping with boron from an effusion cell is relatively straightforward. Boron evaporates as an atomic beam, and the small boron atoms incorporate with the silicon crystal lattice. Conversely, n-type doping of silicon using antimony presents many challenges, arising primarily from the tendency of antimony to segregate to the surface. This phenomenon can be avoided by employing low temperature growth to kinetically limit dopant segregation. However, this approach may compromise epitaxial growth (leading to amorphous layers) and often results in poor dopant incorporation and activation.

Despite these challenges, it has been shown that at sufficiently slow silicon deposition rates it is possible to maintain epitaxial growth for finite thicknesses even at low temperatures [1]. We previously reported on the low-temperature growth of antimony delta-doped silicon [2]. We demonstrated ~85% dopant activation, activated dose concentrations as high as 2×10^{14} cm⁻², and sharp dopant profiles (~35 Å FWHM). We also showed that the low temperature antimony delta-doping process is effective for passivating back-illuminated, high-purity, p-channel CCDs [3,4]. In this presentation, we will discuss the extension of our n-type delta doping capabilities to the growth of n-type superlattices. Electrical characterization and preliminary device measurements will be included.

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3:15pm **PCSI-WeA-16 Unraveling Atomic-level Self-organization at the Plasma-material Interface**, Jean Paul Allain, A Shetty, B Holybee, M Cheng, C Jaramillo, University of Illinois at Urbana Champaign

The intrinsic dynamic interactions at the plasma-material interface and critical role of irradiation-driven mechanisms at the atomic scale during exposure to energetic particles require *a priori* the use of *in-situ* surface characterization techniques [1]. Characterization of "active" surfaces during modification at atomic-scale levels is becoming more important as advances in processing modalities are limited by an understanding of the

behavior of these surfaces under realistic environmental conditions. Self-organization from exposure to non-equilibrium and thermalized plasmas enable dramatic control of surface morphology, topography, composition, chemistry and structure yielding the ability to tune material properties with an unprecedented level of control. Deciphering self-organization mechanisms of nanoscale morphology (e.g. nanodots, ripples) and composition on a variety of materials including: compound semiconductors, semiconductors, ceramics, polymers and polycrystalline metals via low-energy ion-beam assisted plasma irradiation are critical to manipulate functionality in nanostructured systems.

By operating at ultra-low energies near the damage threshold, irradiation-driven defect engineering can be optimized and surface-driven mechanisms controlled. Tunability of optical, electronic, magnetic and bioactive properties is realized by reaching metastable phases controlled by atomistic-scale irradiation-driven mechanisms elucidated by novel *in-situ* diagnosis coupled to atomistic-level computational tools. In this work we present data *in-operando* the mechanisms responsible for low-energy (250-1000 eV) Ar, Kr and Ne irradiation of III-V semiconductors and Si nanopatterning. We conduct measurements of surface composition and chemistry with environmental XPS and low-energy ion spectroscopy (LEISS) illustrating the importance of *in-operando* and *in-situ* characterization of the surface and sub-surface regions from first ML down to about 10-nm. High-pressure low-energy ion scattering spectroscopy and mass spectrometry are also combined to elucidate mass redistribution and ion-induced desorption mechanisms at play during nanostructuring. Additional examples including ZnO nanoparticles on PDMS and nanopatterning of 70-nm TiO₂ thin films on biosensors are presented to illustrate *in-situ* PMI techniques.

[1] J.P. Allain and A. Shetty, *J. Phys. D: Appl. Phys.*, **50** (2017) 283002, *Invited Topical Review*

4:30pm **PCSI-WeA-31 Excitonic Linewidth Approaching the Homogeneous Limit in MoS₂ based Van der Waals Heterostructures**, Xavier Marie, Institut National des Sciences Appliquées, LPCNO, France **INVITED**

Transition metal dichalcogenides such as MoS₂ and WSe₂ are layered materials that are semiconductors with a direct bandgap when thinned down to one monolayer (ML). The strong light matter interaction and the valley selective optical selection rules make these monolayers an exciting 2D material for fundamental physics and optoelectronics applications. But so far optical transition linewidths even at low temperature are typically as large as a few tens of meV and contain large inhomogeneous contributions [1].

In this work we show that encapsulation of ML MoS₂ in hexagonal boron nitride can efficiently suppress the inhomogeneous contribution to the exciton linewidth, as we measure in photoluminescence and reflectivity a FWHM down to 2 meV at T = 4 K [2]. Similar results are obtained with encapsulated MoSe₂, WSe₂ and WS₂ monolayers [3,4]. This indicates that surface protection and substrate flatness are key ingredients for obtaining stable, high quality samples. These encapsulated monolayers allow accessing the optical and spin properties of these materials with unprecedented detail for neutral and charged excitons (trions).

Among the new possibilities offered by the well-defined optical transitions we evidence the optical selection rules for in-plane propagation of light. These studies yield a direct determination of the bright-dark exciton splitting, for which we measure 40 meV and 55 meV for WSe₂ and WS₂ monolayer, respectively [5]. The dark exciton fine structure is also revealed [6]. We also uncover new information on spin and valley physics and present the rotation of valley coherence in applied magnetic fields perpendicular to the ML [7].

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[4] Courtade *et al*, *PRB* **96**, 085302 (2017)

[5] Wang *et al*, *PRL* **119**, 047401 (2017)

[6] Robert *et al*, *ArXiv* 1708.05398 (2017)

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5:00pm **PCSI-WeA-37 Out-of-Plane Electromechanical Response of TMDs**, Christopher Brennan, K Koul, N Lu, E Yu, University of Texas, Austin

The electromechanical properties of materials are inherently interesting for sensors, actuators, and energy harvesters in which deformation is coupled with electronic or optical properties. 2D materials offer a promising

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platform for such devices because when atomically thin, they can withstand large strains and strain gradients. Theory [1] and experiments [2, 3] have revealed that transition metal dichalcogenides (TMDs) are intrinsically piezoelectric in-plane due to their lack of centrosymmetry in or close to the monolayer limit. Recently, we have shown that MoS₂ also exhibits an out-of-plane electromechanical response, potentially a result of the flexoelectric effect [4]. Theory suggests that flexoelectricity may depend on lattice constant, allowing for the opportunity to study the fundamental nature of the effect by looking at similar TMDs with varying lattice constants.

In this work, the out-of-plane electromechanical response of other monolayer TMDs is measured using piezoresponse force microscopy. A conductive atomic force microscope probe is used to apply an AC voltage across the sample and a lock-in amplifier is then used to measure the resultant deflection. Exfoliated WS₂ and WSe₂ are transferred onto gold for the measurements. Figure 1 shows optical images, topography, and piezoresponse (PR) amplitude and phase images for both WS₂ and WSe₂. Clear contrast between both TMDs and the underlying gold in the PR images confirms that out-of-plane electromechanical coupling is present. Preliminary analysis suggests a correlation between the magnitude of the response and the lattice constant as indicated by the stronger contrast in the WS₂. A more detailed analysis of the results will be presented as well as their possible flexoelectric origin.

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5:05pm PCSI-WeA-38 Infrared Problem in Cold Atom Adsorption on Graphene, Dennis Clougherty, University of Vermont

There has been some controversy [1] concerning the phonon-assisted adsorption of atomic hydrogen to suspended graphene at low energies; one numerical calculation predicts an enhancement of the adsorption rate in comparison to the rate on graphite [2], while another work has argued for a suppression of adsorption [3]. Recent theoretical results of the adsorption rate of atomic hydrogen to suspended graphene are presented using four different methods that include contributions from processes with multiphonon emission. We compare the numerical results of the atom self-energy obtained by: (1) the loop expansion of the atom self-energy, (2) the non-crossing approximation (NCA) [4], (3) the independent boson model approximation (IBMA) [5], and (4) a leading-order soft-phonon resummation method (SPR) [6].

The loop expansion reveals an infrared problem, analogous to the infamous infrared problem in QED. The 2-loop contribution to the sticking rate gives a result that tends to diverge for large membranes. The latter three methods remedy this infrared problem for a membrane at zero temperature and give results that are finite in the limit of an infinite membrane. At finite temperature, the divergence problems are exacerbated; only SPR gives a finite adsorption rate in the limit of an infinite membrane. For micromembranes (sizes ranging 100 nm to .01 mm) at zero temperature, the latter three methods give results that are in good agreement with each other and yield sticking rates that are mildly *suppressed* relative to the lowest-order golden rule rate; however, the SPR sticking rate decreases to *zero* with increasing membrane size for all temperatures. Thus, approximations to the sticking rate are sensitive to the effects of soft-phonon emission for large membranes, and multiphonon processes suppress the rate.

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[6] D. P. Clougherty and S. Sengupta, *Phys. Rev. A* **95**, 052110 (2017).

5:10pm PCSI-WeA-39 Measuring and Modeling Liquid-Filled Nanobubbles Trapped by 2D Materials, Daniel Sanchez, Z Dai, The University of Texas at Austin; P Wang, The University of Texas at Austin, China; A Cantu-Chavez, C Brennan, E Yu, R Huang, N Lu, The University of Texas at Austin

Layered systems of van der Waals bonded two-dimensional (2D) materials are widely explored for new physics and devices. In many cases, 2D atomic layers are transferred on a foreign substrate, including other 2D materials. It has been extensively reported that nanometer-scale interfacial bubbles form spontaneously after the transfer. So far, there is no consensus on whether these nanobubbles are filled by liquid, solid, or gas.

We have carried out time-lapse atomic force microscopy scans on nanobubbles trapped between graphene and SiO₂. The bubbles deflate slower than ideal-gas-filled 2D membranes over a course of 92 days indicating that liquid is likely trapped under the 2D membrane. We therefore develop a theoretical framework built upon the membrane equations for a thin, elastic membrane trapping incompressible liquid to form interfacial bubbles. Our final analytical solution suggests that adhesion between the 2D material and its substrate is related to the fourth power of the aspect ratio of the blister, which is a constant irrespective of the blister diameter. Our model is applied to estimate the adhesion energy of various 2D material interfaces using the experimentally measured aspect ratios of the bubbles. Good agreement between the estimated adhesion energies of graphene-SiO₂ and MoS₂-SiO₂, and those reported in the literature substantiates our model. In conclusion, liquid-filled nanobubbles trapped by 2D materials can be used as a simple but generic metrology for the adhesion of 2D materials.

5:15pm PCSI-WeA-40 Stress Relaxation Mechanism in the Si-SiO₂ System and its Influence on the Interface Properties, Daniel Kropman, T Laas, Tallinn University, Estonia; V Seeman, Tartu University; A Medvids, Riga University; J Kliava, University de Bordeaux

It is known that internal mechanical stresses (IMS) due to the differences in the thermal expansion coefficients between films and substrates and lattice mismatch appear in the Si-SiO₂ system during the process of its formation and that point defects (PD) generation and redistribution could be used to reduce partially the surface stress. However, this process on the atomic scale is still not studied. The goal of the present report is to investigate the stress relaxation mechanism in the Si-SiO₂ system using EPR, IR absorption spectroscopy, scanning electron microscopy (SEM) and samples deflection measurements. PD density and stresses in the Si-SiO₂ system were varied by oxidation condition (temperature, time, cooling rate, ambient) and by Si₃N₄ deposition on SiO₂. Different sign of the thermal expansion coefficient of the SiO₂ and Si₃N₄ on Si allow to modify the IMS at the interface. It has been found that samples deflection decreases or increases simultaneously with EPR signal intensity depending on the oxidation condition (temperature).

At oxidation temperature 1100°C the deflection of the samples(h) decreases with the increase of EPR signal intensity (vacancies), while at a oxidation temperature 1200°C EPR signal (I) and deflection increase simultaneously. Those allows to suggest that at lower oxidation temperature PD (vacancies) reduce the tensile IMS in Si, while at higher oxidation temperature compressive IMS created PD in SiO₂ (E' centers). At an intermediate oxidation temperature tensile stresses in Si and compressive stresses in SiO₂ may be equal and compensate each others. It has been found that at oxidation temperature 1130°C IMS at the Si-SiO₂ interface are lower than at 1100°C and 1200°C. Lower defect density on samples cross-section microphotos obtained by SEM and PD density diminishing in samples oxidized at 1130°C confirmed this suggestion. In Fig.2 the EPR signal and IR absorption line-width dependence on the oxidation time is shown. It can be seen, that EPR signal and IR absorption line-width at 1100 cm⁻¹ dependence on the oxidation time (oxide thickness) is nonmonotonous and depended on the cooling rate. In slowly cooled samples the increase of the EPR signal is accompanied by the decrease of Δv but, in fast cooled samples EPR signal and Δv increase simultaneously with increase oxidation time.

Absent of the cooling rate influence on the PD density and Δv dependence on the oxidation time at I(t) and Δv(t) dependence intersection points show, that IMS by an appropriate choice of the SiO₂ film thickness disappear. The obtained results may be explained by the PD generation kinetic model in the Si-SiO₂ system proposed by T.U.Tan and U.Gösele.

Wednesday Afternoon, January 17, 2018

5:20pm **PCSI-WeA-41 Characterization of Barium Hexaferrite Thick Films Deposited by Aerosol Deposition with an *in situ* Magnetic Field**, *Scooter Johnson*, U.S. Naval Research Laboratory; *D Park*, Korean Institute of Materials Science; *A Hauser*, *S Ranjit*, *K Law*, University of Alabama; *H Newman*, *S Shin*, *S Qadri*, *E Gorzkowski*, Naval Research Laboratory

Devices utilizing magnetic materials such as circulators, inductors, and filters are critical components in many of today's electronics [1]. The need for ferromagnetic materials in these devices poses many difficulties for minimizing device size, weight, and cost. One issue that hampers integration of ferromagnetic materials is the high-melting temperature of the ferrite compared with the low-melting temperature component structure [2]. Furthermore, the need for low-loss and narrow bandwidth operation adds another significant barrier to the advancement of integration of ferromagnetic materials. The high-frequency operation regime and strong uniaxial anisotropy of barium hexaferrite ($\text{BaFe}_{12}\text{O}_{19}$, BaM) makes this material particularly interesting to utilize as an oriented film for microwave components. In this study, we characterize BaM films deposited onto sapphire by a room-temperature thick-film growth technique called aerosol deposition. We performed alternating gradient magnetometry depth studies on a series of as-deposited films that show a variation in magnetization with depth. Cross-sectional SEM images indicate laterally uniform film density. Electron dispersive spectroscopy of the interfacial region suggest significant Al_2O_3 mixing into the film volume. Fe XPS spectra indicate a change in peak weighting as a function of thickness, possibly indicative of modified structure or oxygen incorporation due to Al incorporation. To explore the possibility of magnetically orienting the films we deposited additional films in the presence of a 4 kOe static magnetic field. We report VSM, FMR, and XRD results of these films as-deposited and after sintering from 700C to 1000C. The Figure shows the results of VSM measurements of 5-um-thick films deposited with no applied field compared to films deposited in a 4 kOe applied field. The films deposited in the field presence show an increased saturation magnetization and remanence. Annealing improves the overall properties of the films further increasing the magnetic orientation and saturation.

[1] Adams, J., Davis, L., Dionne, G., Schloemann, E., and Stitzer, S., IEEE Transactions on Microwave Theory and Technology, **50** (2002), No. 3, pp.721.

[2] Johnson, S., Newman, H., Glaser, E., Cheng, S.-F., Tadjer, M., Kub, F., and Eddy, C., IEEE Trans. on Magnetics, **51**, (2015), No. 5, pp. 2200206.

5:25pm **PCSI-WeA-42 Surface Science Studies During Plasma-Assisted Atomic Layer Epitaxial Growth of InN on GaN Substrates**, *Samantha Rosenberg*, U.S. Naval Research Laboratory; *D Pennachio*, University of California, Santa Barbara; *V Anderson*, *S Johnson*, *N Nepal*, U.S. Naval Research Laboratory; *C Wagenbach*, Boston University; *M Munger*, SUNY Brockport; *A Kozen*, U.S. Naval Research Laboratory; *Z Robinson*, SUNY Brockport; *S Choi*, University of California, Santa Barbara; *J Hite*, U.S. Naval Research Laboratory; *K Ludwig*, Boston University; *C Palmstrøm*, University of California, Santa Barbara; *C Eddy, Jr.*, U.S. Naval Research Laboratory

III-N semiconductors such as GaN, AlN, and InN are the basis for creating many compound ternary and quaternary semiconductor materials well suited for applications in several important technological areas, including high current, normally-off power switches. [1-3] While atomic layer deposition (ALD) is a versatile technique and has gained wide use, it does not offer the required level of crystallinity and purity needed for high-performance III-N semiconductor devices. Therefore, we have developed a technique adapted from ALD, called low temperature plasma-assisted atomic layer epitaxy (ALEp). [2] Using surface science techniques we plan to develop a fundamental understanding of the ALEp growth process to further enable the method as a powerful new technique for growth of semiconductor materials.

Here we employ *in-situ* and *in-vacuo* surface studies of GaN substrate preparation and InN ALEp growth to advance fundamental understanding of the ALEp process as well as the effect of variation in nitrogen plasma pulse conditions on ALEp of InN. We conduct *in-situ* grazing incidence small angle x-ray scattering (GISAXS) experiments at the Cornell High Energy Synchrotron Source and The National Synchrotron Light Source-II at Brookhaven National Laboratory, utilizing morphological evolution monitoring to investigate the growth surface during sample preparation and film deposition, as well as using this technique to understand how the nitrogen plasma pulse affects nucleation and growth kinetics of InN on GaN substrate surfaces. GISAXS information is complemented with *in-vacuo* x-ray photoelectron spectroscopy and reflection high-energy electron diffraction studies conducted at the Palmstrøm Lab at UCSB, where we

consider traditional molecular beam gallium flash-off [4] in contrast to our ALEp based gallium flash-off as ways to produce the most suitable GaN surface for our ALEp-based approach. We have been able to determine with GISAXS that ALEp based gallium-flash off experiments run at higher temperatures (500°C) produce a less roughened starting surface than lower temperatures. We have also determined with *in-vacuo* XPS that traditional molecular beam gallium flash-off greatly reduces the oxygen content at the GaN interface (<40% remaining), while our ALEp based approach does not reduce the oxygen as effectively.

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

[2] C. R. Eddy, Jr, et al., J. Vac. Sci. Technol. A 31(5), 058501 (2013)

[3] R. S. Pengelly, et al., IEEE Trans. Microwave Theory Tech. 60, 1764 (2012)

[4] D.F. Storm et al. Journal of Crystal Growth 456 121–132, (2016)

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