Electronic Materials and Photonics Division
Room 101A - Session EM+AN+MI+SS-WeM

Surface and Interface Challenges in Electronics and Photonics

Moderators: Andy Antonelli, Nanometrics, Michael Filler, Georgia Institute of Technology

8:00am **EM+AN+MI+SS-WeM-1 Few Monolayer Atomic Layer Deposition (ALD) to Engineer New Surfaces and Interfaces**, ***Parag Banerjee,*** Washington University in St. Louis **INVITED**

Atomically precise modification of surfaces and interfaces with few monolayer material leads to improved understanding and significant enhancements in properties, performance and reliability of heterogeneous materials and devices. This talk highlights the impact of few monolayer insulators, wide bandgap semiconductors and metals, deposited using atomic layer deposition (ALD) on a variety of surfaces and interfaces with direct relevance to electronic and photonic devices.

The first part of this talk deep dives into the process science of ALD in its early cycles. The nature and structure of few monolayer ALD films is highlighted. In particular, configurational state and entropy of adlayers during every half-cycle of ALD[1] is exploited to exquisitely manipulate nucleation and growth of metallic Ru thin films.[2]

In the second part of this talk, applied aspects of few monolayer engineering of surfaces and interfaces is discussed. Case studies included are the non-linear optical phenomena on Au-Al_2O_3 and Au-ZnO surfaces,[3] high performance photocatalysts for CO_2 photoreduction,[4] improved optoelectronic responses from surface passivated CuO nanowires[5] and few monolayer Ta_2O_5 to improve reliability of electrochromic windows.[6]

Regardless of the application, ALD at its ultimate thickness limit holds true potential for surface and interface engineering. The control of this process appears to be remarkably simple and yet, has hidden complexities that continue to push the boundaries of discovery of new materials and concept devices.

Relevant references:

[1] Zhengning Gao, Fei Wu, Yoon Myung, Ruixiang Fei, Ravindra Kanjolia, Li Yang, and Parag Banerjee, J. Vac. Sci. Technol. A **34** (1), 01A143 (2016); Lei Shi, Zhengning Gao, Zhaonan Liu, Yoon Myung, and Parag Banerjee, Chem. Mater. **29** (13), 5458 (2017).

[2] Zhengning Gao, Duy Le, Ravindra Kanjolia, Charles Dezelah, Jacob Woodruff, Talat Rahman, and Parag Banerjee, Under review (2018).

[3] Zhengning Gao, Mallik M.R. Hussain, Domenico de Ceglia, Maria A. Vincenti, Andrew Sarangan, Imad Agha, Michael Scalora, Joseph A. Haus, and Parag Banerjee, Appl. Phys. Lett. **111**, 161601 (2017).

[4] W-N. Wang, F. Wu, Y. Myung, D.M. Niedzwiedzki, H.S. Im, J. Park, Parag* Banerjee, and Pratim* Biswas, * co-corresponding authors, ACS Appl. Mater. Interfaces **7** (10), 5685 (2015).

[5] Sriya Banerjee, Zhengning Gao, Fei Wu, Yoon Myung, and Parag Banerjee, Under Review (2018).

[6] Yang Wang, Jongwook Kim, Zhengning Gao, Omid Zandi, Sungyeon Heo, Parag Banerjee, and Delia Milliron, Chem. Mater. **28**, 7198 (2016).

8:40am **EM+AN+MI+SS-WeM-3 Lattice-alignment mechanism of SiGe on Sapphire**, ***HyunJung Kim,*** National Institute of Aerospace*; S Choi,* NASA Langley Research Center

In the conventional heteroepitaxy processes, the deposition of dissimilar materials has been made with the same or similar crystal structure and perfect or nearly matching lattice constants, such as Ge/Si (diamond cubic), InAs/GaAs (zinc-blende), and GaN/Al_2O_3 (hexagonal/trigonal). On the other hand, the super-heteroepitaxy of two semiconductors with dissimilar crystal structures such as SiGe (diamond cubic)/Al_2O_3 (trigonal) is not readily achievable but requires scrupulous manipulation of growth conditions for single crystal formation. Epitaxial growth patterns of SiGe on *r*-plane and *c*-plane of sapphire substrates show 90°-rotated and 60°-rotated twin defects, respectively [1,2].

A team at NASA Langley Research Center developed a technique for super-hetero-epitaxy of single crystal SiGe growth; diamond-cubic structure of SiGe on trigonal structure of the *c*-plane sapphire substrate by a transformed lattice structure under a new lattice-alignment model [2]. Although the growth conditions were effective for the formation of single crystal film, how the mechanism or physics of single crystal formation of SiGe at the interface of sapphire was not theoretically and experimentally defined with the order of atomic scale level in arrangement. This work presents the interfacial image of SiGe/Al_2O_3 using high-resolution transmission electron microscope (HRTEM) to show the SiGe/Al_2O_3 interfacial bonding for superheteroepitaxy mechanism. The first two atomic layers of the SiGe are Si-rich where Si atoms match with the surface oxygen lattice of the Al_2O_3 substrate. After the Ge composition increases, the monolayer spacing is also increased due largely to the dominance of Ge composition since the lattice constant of Ge is bigger than that of Si. These results highlight the importance of a cleanliness of sapphire substrate, the Si-affinity to oxygen that ties up Si- of SiGe with the oxygen of sapphire, and eventually causing the deformation of SiGe cubic structure for super-heteroepitaxy [3]. From the essential understanding of the SiGe/Al_2O_3 interface mechanism, both low temperature SiGe super-heteroepitaxy and the III-V or II-VI semiconductor epitaxy are possible.

References:

[1] W.B. Dubbelday, K.L. Kavanagh, J. Cryst. Growth, 222 (2001), pp. 20-28.

[2] Y. Park, G.C. King, S.H. Choi, J. Cryst. Growth, 310 (2008), pp. 2724-2731.

[3] H. J. Kim, D. Adam, S. H. Choi, Acta Materialia, 145 (2018), pp. 1-7.

9:00am **EM+AN+MI+SS-WeM-4 An Effort to Resolve Band Offset Anomalies in ZnO/GaN Heterostructures**, ***Monu Mishra***[1]*, A Gundimeda, V Vandana, G Gupta,* CSIR-National Physical Laboratory, India

Gallium Nitride (GaN) and Zinc Oxide (ZnO) are well established wide band gap (WBG) semiconductors facilitating potential application in futuristic energy-efficient opto/micro-electronics technology. Despite of owing the merits of both semiconductors, the understanding of ZnO/GaN heterostructures is still posing challenges. The available reports display anomalies amongst calculated valence band offset (VBO) and defect state of ZnO/GaN interface. The influence of surface and interfacial properties perturbs the electronic structure, localized charge density and defect states at the interface, yet the impact of these properties on VBO requires more scientific attention. Hence, sharp interfaces of ZnO/GaN heterostructures (ZnO thickness = 2, 5 and 8 nm) were fabricated via atomic layer deposition (ALD) of ZnO on MOCVD grown highly crystalline GaN epilayer and further investigated by HR-XPS, UPS and PL spectroscopy. The impact of ZnO thickness on band bending (upwards & downwards), surface/interface dipole strength and defects states (vacancies, interstitials, donor/acceptors etc.) on valence & conduction band offsets (VBO/CBO) were thoroughly analysed. It was observed that the VBO at the interface was reduced via 0.6 eV as the ZnO thickness was increased from 2 nm to 8 nm which was ascribed to interface dipole strength along with dramatic change in localized BB (downwards-flatband-upwards). A type-II band alignment was perceived at all ZnO/GaN interfaces though the nature & contribution of defects states (especially oxygen vacancies and zinc interstitials) varied incommensurately. The defect band spectra revealed a blue shift (~502 eV) which correspond to the conversion of yellow-green emission in ultrathin ZnO/GaN heterostructure (2 nm ZnO) to characteristic green emission in bulk ZnO. The analysis revealed that the thickness of ZnO overlayer in ZnO/GaN heterostructure significantly alters the electronic structure and defect states at the interface and thus the resolution of anomalies in the present analysis would be useful for the fabrication of ZnO/GaN heterostructure based efficient optoelectronic devices.

9:20am **EM+AN+MI+SS-WeM-5 Stress Relaxation in the Si-SiO2 System and its Influence on the Interface Properties**, ***Daniel Kropman****, T Laas,* Tallinn University, Estonia*; A Medvids,* Riga Technical University, Latvia

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-SiO_2 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 till not studied. The goal of the present report is to investigate the stress relaxation mechanism in the Si-SiO_2 system using EPR, IR absorption spectroscopy, scanning elektron microscopy (SEM) and samples deflection measurements. PD density and stresses in the Si-SiO_2 system were varied by oxidation condition (temperature, time, cooling rate, ambient) and by Si_3N_4 deposition on SiO_2. Different sign of the thermal expansion coefficient of the SiO_2 and Si_3N_4 on Si allow to modifay 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).

[1] **National Student Award Finalist**

At oxidation temperature 1100^0C the deflection of the samples(h) decreases with the increase of EPR signal intensity (vacancies),while at a oxidation temperature 1200^0C EPR signal (I) and deflection increase simultaneously. Those allows to suggest that at lower oxidation temperature PD (vacancies) reduce the tensil IMS in Si, while at higher oxidation temperature compressive IMS created PD in SiO_2 (E' centers).At an intermediate oxidation temperature tensil stresses in Si and compressive stresses in SiO_2 may bee equal and compensate each others. It has been find that at oxidation temperature 1130^0C IMS at the Si-SiO_2. interface are lower than at 1100^0C and 1200^0C. Lower defect dencity on samples crossection microphotos obtained by SEM and PD dencity diminishing.in samples oxidized at 1130^0C confirmed thise suggestion.In Fig,2 the EPR signal and IR absorbtion line-width dependence on the oxidation time is shown. It can bee seen ,that EPR signal and IR absorbtion 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 SiO_2 film thickness dissapear.

9:40am **EM+AN+MI+SS-WeM-6 Unique Sensitivity to Deep Trap States Demonstrated by CREM of Broad Bandgap Dielectric Layers***, **Hagai Cohen,*** Weizmann Institute of Science, Israel*; K Steirer,* Colorado School of Mines

Chemically resolved electrical measurements (CREM) present an efficient and sensitive means for studies of structural-electrical inter-relationships in heterostructures. Operated in-situ to x-ray photoelectron spectroscopy (XPS), the technique is yet far from being fully exploited. Recent progress in our CREM instrumentation has, however, opened new opportunities to which this report is dedicated. Using broad-bandgap dielectric layers, such as SiO_2, SiON and ZnOS, we tested the CREM resolving power and sensitivity to charge trap states. These experiments yielded band diagrams with fine details on charge traps, which typically require the application of advanced optical techniques combined with the electrical characterization tools.

In addition, an intriguing process of doubly triggered conductance in ZnOS was observed. The ZnOS layers exhibited very poor conductance under either electrical or optical input signals, whereas simultaneous application of the two yielded extremely high sample currents. Based on the in-situ derived band diagram, a comprehensive explanation of the effect is provided. Moreover, we show how the CREM analytical tool can also provide a potential activator of future related devices.

11:00am **EM+AN+MI+SS-WeM-10 Fabrication of Multilayered Optically Active Nanocrystal Solids by Surface Passivation using Metal Oxides: ALD vs CVD***, **Riya Bose**, A Dangerfield,* University of Texas at Dallas*; S Rupich,* University of Texas*; Y Chabal, A Malko,* University of Texas at Dallas

Semiconductor nanocrystal quantum dots (NQDs) provide a powerful platform for optoelectronic applications with their size/shape/composition tunable properties and inexpensive solution based synthesis techniques. Integration into solid state devices requires deposition of NQD films, and often a controlled assembly of multilayered NQD structures to ensure maximum light absorption and optimum efficiency of the devices. However, thin film fabrication is found to degrade its properties compared to NQDs in solution, especially a decrease in the photoluminescence (PL) quantum yield (QY) is frequently observed. Also, the bottleneck for fabrication of multilayer NQD films remains the use of solution phase deposition methods, where the solvent in the subsequent step of deposition dissolves the initial layer until each NQD layer is rendered insoluble by means of any surface passivation technique. Surface passivation techniques also play a critical role to protect the deposited layers from oxidation and deterioration. An attractive method to passivate NQD films during the deposition as well as from environmental exposure is to overcoat them with various metal oxides grown using atomic layer deposition (ALD). Though there are few reports of ALD encapsulation of NQD films, they mostly attend to charge transfer-based devices and aim to improve carrier moblities. Typically, such studies report a significant quenching of the PL intensity after encapsulation. In this study, we aim to investigate the exact growth mechanism of metal oxide layers by ALD on the surface of NQD films and how it, along with the ALD parameters, affects their PL properties. With the aid of in-situ FTIR and ex-situ XPS measurements during Al_2O_3 deposition on oleic acid capped CdSe-ZnS core-shell nanocrystals, it is observed that the interaction of the metal precursor trimethyl aluminium (TMA) with the surface of the NQDs leads to the reorganization of the ligands as well as replaces Zn, leading to PL intensity quenching. In order to prevent this, we opted for a pulsed chemical vapour deposition (CVD) like approach for metal oxide deposition where simultaneous purging of both the metal and oxygen precursors leads to formation of metal oxide in a gas phase in the immediate vicinity of the NQD surface. We found that minimization of TMA interaction with the NQDs' surface indeed leads to enhancement of the PL intensity and elongation of carrier PL lifetime. These measurements provide clear indication of defect-free surface passivation proving that CVD-like Al_2O_3 encapsulation is a suitable technique for controlled deposition of multilayered NQD structures that preserves its optoelectronic properties.

11:20am **EM+AN+MI+SS-WeM-11 The Role of Surface Oxides for the Optoelectronic Performance of III-V Semiconductor Nanowires***, J Colvin, A Troian, O Persson, A Mikkelsen, **Rainer Timm**,* Lund University, Sweden

III-V semiconductor nanowires (NWs) have a large technological potential within electronics, optoelectronics, and energy harvesting [1,2], mainly due to their flexibility in creating heterostructures by axial stacking during epitaxial growth. Because of their small diameter and their very large surface-to-volume-ratio, the performance of NW devices is strongly determined by surface properties. We have previously studied surfaces and surface oxides of semiconductor NWs by scanning tunneling microscopy and spectroscopy (STM/S) [3] as well as X-ray photoemission spectroscopy [4]. Here, we will correlate the surface properties of InAs and InP NW heterostructures with their electrical and photovoltaic behavior, which has been measured for individual upright-standing NWs using the STM tip as local nanoprobe [5].

InP and GaInP pin-junction NWs have been cleaned from their native oxide by annealing under atomic hydrogen background and re-oxidized by exposure to ambient conditions. By illuminating the InP NWs that were contacted by the STM nanoprobe, we observed a decrease of the open-circuit voltage from 0.75 V to 0.70 V upon native oxide removal and an increase back to 0.76 V upon re-oxidation, confirming the need of surface passivation for improving InP solar cells. However, the ideality factor of the NW pin-diodes remained constant at n = 1.82 upon oxide removal, but improved to n = 1.67 upon re-oxidation. Furthermore, our XPS results indicate the outdiffusion of Zn dopants from the p-doped NW segments, forming a Zn-rich shell around the NW.

A more significant effect of the presence of native surface oxide was found for InAs NWs which consist of one segment of wurtzite and one segment of zincblende crystal structure. Upon removal of the native surface oxide, we obtained an increase in conductivity of these NWs by two orders of magnitude, while reference NWs with pure wurtzite structure showed a slight decrease in conductivity with the same surface treatment. This effect can be explained by a staggered type-II surface band alignment at the wurtzite/zincblende interface of oxidized NWs, which turned into flat-band conditions upon oxide removal, as confirmed by nano-focus XPS measurements.

[1] E. Lind *et al.,* IEEE J. El. Dev. Soc. **3**, 96 (2015).

[2] J. Wallentin *et al*., Science **339**, 1057 (2013).

[3] M. Hjort *et al.,* ACS Nano **8**, 12346 (2014).

[4] R. Timm *et al.,* Appl. Phys. Lett. **99**, 222907 (2011); J. Webb *et al.,* Nano Lett. **15**, 4865 (2015).

[5] R. Timm *et al.,* Nano Lett. **13**, 5182 (2013).

11:40am **EM+AN+MI+SS-WeM-12 Photonic Annealing of 2D Transition Metal Dichalcogenides for Tailored Optical Properties***, **Rachel Rai**, K Gliebe,* University of Dayton; Air Force Research Laboratory*; N Glavin, R Kim, A Jawaid, R Wheeler, L Bissell,* Air Force Research Laboratory*; C Muratore,* University of Dayton

Thin layers of transition metal dichalcogenides (TMD) have attracted significant interest in the field of optoelectronics due to their unique light absorption and emission properties in the visible frequency range. Development of bright, flexible, large area emission sources based on 2D materials using photonic annealing represents an exciting opportunity for future quantum systems. Here we introduce new correlations relating the optical properties of WSe_2, a well-known single photon emitter, to post-processing annealing techniques to include lasers, broadband radiation, and nanoscale electron beams. Modulation of the total energy flux during growth of amorphous TMD material to develop purely amorphous materials or materials with nanoscale nuclei was employed by the authors to examine effects of pre-existing nuclei on crystallization kinetics (i.e.,

activation energy) and the resulting optical properties. We correlate the wavelength and intensity of photoluminescence from WSe_2 deposited on plasma treated and as-received flexible substrates and present techniques to control film continuity and the areal density of free edges from islands on discontinuous films for tuning the intensity of optical emission. A significant increase in photoluminescence intensity is accompanied by a change in domain boundary density, correlating well to theory. Furthermore, examination of quantum confinement effects by producing nanoscale crystalline areas (between 5-50 nm) with precisely controlled volumes via electron beam radiation provides insight on light emission mechanisms.

12:00pm **EM+AN+MI+SS-WeM-13 Polarity Control of GaN Nanowires on Diamond: Experiment and Theory***, **Karin Larsson,*** Uppsala University, Sweden*; M Hetzl, M Kraut, T Hoffmann, M Stutzmann,* Technical University Munich, Germany

III-nitride nanowires on diamond substrates are of current interest for two different potential applications: (i) selectively grown n-type AlGaN nanowires on p/i – diamond are promising for the electrical control and the efficient optical and electrical readout of individual NV-centers in diamond as qubits and (ii) AlGaN/diamond n/p-heterodiodes are an interesting option for future ultraviolet LEDs and laser diodes. For both applications, the polarity of AlGaN nanowires grown on diamond has a strong influence on the optoelectronic properties of the heterojunctions, because the polarization-induced interface charge strongly influences the details of the diamond/III-nitride band alignment. Thus, the growth of nanowire arrays with randomly fluctuating polarity will have a negative influence on the electronic properties of the heterojunctions.

In this presentation, we will discuss recent experimental results concerning the control of GaN nanowire polarity on diamond (111) substrates via different surface termination treatments (hydrogenation, oxygen termination, nitrogen radical exposure [1]). Systematic experimental investigations have shown that even very well ordered periodic nanowire arrays deposited by Selective Area Growth exhibit a high degree of polarity disorder. Diamond is a well-suited substrate for these investigations, since it supports several different types of stable surface structures which only differ by about one monolayer and have a strong influence on the preferred nanowire polarity. The effect of different surface terminations on nanowire polarity will be recapitulated. Furthermore, we complement these experimental investigations by theoretically studying the effect of diamond surface termination on the energetically preferred GaN polarity. First principle DFT-calculations are used to calculate the interface energies and the corresponding atomic configurations of the different diamond/GaN interfaces. Strong variations observed in the interface chemistry between diamond and GaN nanowires will be discussed based on the available experimental and simulation data.

[1] M. Hetzl et al., Nano Lett. 17, 3582 (2017)

Author Index

Bold page numbers indicate presenter

— B —
Banerjee, P: EM+AN+MI+SS-WeM-1, **1**
Bissell, L: EM+AN+MI+SS-WeM-12, 2
Bose, R: EM+AN+MI+SS-WeM-10, **2**
— C —
Chabal, Y: EM+AN+MI+SS-WeM-10, 2
Choi, S: EM+AN+MI+SS-WeM-3, 1
Cohen, H: EM+AN+MI+SS-WeM-6, **2**
Colvin, J: EM+AN+MI+SS-WeM-11, 2
— D —
Dangerfield, A: EM+AN+MI+SS-WeM-10, 2
— G —
Glavin, N: EM+AN+MI+SS-WeM-12, 2
Gliebe, K: EM+AN+MI+SS-WeM-12, 2
Gundimeda, A: EM+AN+MI+SS-WeM-4, 1
Gupta, G: EM+AN+MI+SS-WeM-4, 1
— H —
Hetzl, M: EM+AN+MI+SS-WeM-13, 3
Hoffmann, T: EM+AN+MI+SS-WeM-13, 3
— J —
Jawaid, A: EM+AN+MI+SS-WeM-12, 2
— K —
Kim, H: EM+AN+MI+SS-WeM-3, **1**
Kim, R: EM+AN+MI+SS-WeM-12, 2
Kraut, M: EM+AN+MI+SS-WeM-13, 3
Kropman, D: EM+AN+MI+SS-WeM-5, **1**
— L —
Laas, T: EM+AN+MI+SS-WeM-5, 1
Larsson, K: EM+AN+MI+SS-WeM-13, **3**
— M —
Malko, A: EM+AN+MI+SS-WeM-10, 2
Medvids, A: EM+AN+MI+SS-WeM-5, 1
Mikkelsen, A: EM+AN+MI+SS-WeM-11, 2
Mishra, M: EM+AN+MI+SS-WeM-4, **1**
Muratore, C: EM+AN+MI+SS-WeM-12, 2
— P —
Persson, O: EM+AN+MI+SS-WeM-11, 2
— R —
Rai, R: EM+AN+MI+SS-WeM-12, **2**
Rupich, S: EM+AN+MI+SS-WeM-10, 2
— S —
Steirer, K: EM+AN+MI+SS-WeM-6, 2
Stutzmann, M: EM+AN+MI+SS-WeM-13, 3
— T —
Timm, R: EM+AN+MI+SS-WeM-11, **2**
Troian, A: EM+AN+MI+SS-WeM-11, 2
— V —
Vandana, V: EM+AN+MI+SS-WeM-4, 1
— W —
Wheeler, R: EM+AN+MI+SS-WeM-12, 2