

Wednesday Afternoon, November 2, 2011

Electronic Materials and Processing Division

Room: 210 - Session EM-WeA

Defects in Electronic Materials

Moderator: B.D. Schultz, University of California, Santa Barbara

2:00pm **EM-WeA1 Controlling Schottky Barriers and Doping with Native Point Defects**, *L.J. Brillson, Y. Dong*, The Ohio State Univ., *F. Tuomisto*, Helsinki Univ. of Tech., Finland, *B. Svensson, A.Yu. Kuznetsov*, Univ. of Oslo, Norway, *D. Doutt*, The Ohio State Univ., *H.L. Mosbacher*, Trayer Diagnostic, *G. Cantwell, J. Zhang, J.J. Song*, ZN Technology, *Z.-Q. Fang*, Univ. of Dayton, *D.C. Look*, Air Force Research Lab **INVITED**

Native point defects in semiconductors have until now not been considered a major factor in Schottky barrier formation or doping due to their relatively low bulk densities. Likewise, efforts to control doping type and density usually treat point defects as passive, compensating donors or acceptors. Recent advances in the rapidly emerging semiconductor ZnO include a deeper understanding into the nature of native point defects at its surfaces, interfaces, and epitaxial films. Key to ZnO Schottky barrier formation is a massive redistribution of native point defects near its surfaces and interfaces. It is now possible to measure the energies, densities and in many cases the type of point defects below the semiconductor free surface and its metal interface with nanoscale precision. Using depth-resolved cathodoluminescence spectroscopy (DRCLS) of deep level emissions calibrated with electrical techniques, we find that native point defects can (i) increase by orders-of-magnitude in densities within tens of nanometers of the semiconductor surface, (ii) alter free carrier concentrations and band profiles within the surface space charge region, (iii) dominate the Schottky barrier formation for metal contacts to ZnO, and (iv) play an active role in semiconductor doping. Among major roadblocks to ZnO optoelectronics have been the difficulty of both n- and p-type doping. Oxygen vacancies (V_O), V_O complexes, Zn interstitial-related complexes, and residual impurities such as H and Al are all believed to be shallow donors in ZnO, while Zn vacancies (V_{Zn}) and their complexes are acceptors. While their impact on free carrier compensation and recombination is recognized, the physical nature of the donors and acceptors dominating carrier densities in ZnO and their effect of carrier injection at contacts is unresolved. How these defects impact ZnO optoelectronics at the nanoscale is only now being explored. We address these issues using a combination of depth-resolved and scanned probe techniques to clearly identify the optical transitions and energies of V_{Zn} and V_{Zn} clusters, Li on Zn sites, Ga on Zn site donors, the effects of different annealing methods on their spatial distributions in ion-implanted as well as Ga grown-in ZnO, and how V_{Zn} , V_{Zn} clusters, and V_O complexes contribute to near- and sub-surface carrier density. Defects also couple to nanostructures, which form spontaneously on ZnO polar surfaces and create sub-surface V_{Zn} locally with Zn diffusion that feeds the growth. These results reveal the interplay between ZnO electronic defects, dopants, polarity, and surface nanostructure, and they highlight new ways to control ZnO Schottky barriers and doping.

2:40pm **EM-WeA3 High Level of Mg Alloying Effects on the Deep Level Defects in $Mg_xZn_{1-x}O$** , *E. Gur*, The Ohio State University, *G. Tabares*, Ciudad Universitaria, Spain, *A. Arehart*, The Ohio State University, *J.M. Chauveau*, University of Nice Sophia Antipolis, France, *A. Hierro*, Ciudad Universitaria, Spain, *S.A. Ringel*, The Ohio State University
The $Mg_xZn_{1-x}O$ material system is very promising for ultraviolet emission and detection applications because of its direct band-gap, band-gap tunability, low lattice mismatch, and low polarization field. Using molecular beam epitaxy, a-plane 1.5 micron thick n-type $Mg_xZn_{1-x}O$ films ($x=0, 0.26, 0.36, 0.43, 0.52$) were grown on r-plane sapphire. Semi-transparent 100 Å thick Au Schottky contacts were used for deep level optical spectroscopy measurements (DLOS). The Schottky diodes (SD) exhibited rectification with low leakage currents and barrier heights between 1.00-1.19 eV from $Mg_{0.52}Zn_{0.48}O$ to ZnO. The frequency dependence of the capacitance caused by the high series resistance of the SDs required low frequency lock-in based capacitance measurements for accurate determination of capacitance. Lock-in 1kHz DLOS measurements revealed six deep levels in $Mg_xZn_{1-x}O$ samples while only three deep levels were observed in ZnO. In all samples, the energy of the deep levels relative to the conduction or valence band was independent of Mg content. The $\sim E_C-1.4$ eV, $\sim E_C-1.85$ eV, and $\sim E_C-2.50$ eV levels follow the conduction band while $\sim E_V+1.20$ eV, $\sim E_V+0.60$ eV, and $\sim E_V+0.28$ eV follow the valence band. Because of high concentration of two dominant deep levels, lighted capacitance-voltage measurements was applied on all the samples in

order to obtain true values of the concentration of the traps. The concentration of the two dominant compensating centers at $\sim E_V+0.28$ eV and $\sim E_V+0.60$ eV are $\sim 3 \times 10^{16} \text{ cm}^{-3}$ and $\sim 1 \times 10^{16} \text{ cm}^{-3}$, respectively.

3:00pm **EM-WeA4 Comparative Depth Resolved Cathodoluminescence and X-ray Excited Optical Luminescence Studies of $SrTiO_3$** , *R.A. Rosenberg, Y. Choi, V. Kalyanaraman*, Argonne National Laboratory, *M. Kareev, J. Tchakalian*, University of Arkansas at Fayetteville, *S. Balaz, L.J. Brillson*, Ohio State University

$SrTiO_3$ and related perovskite materials are increasingly being utilized in a wide range of electrical applications. Furthermore, $SrTiO_3$ is often used as a substrate for growth of thin film structures. Thus, knowledge of its defect structure and, in particular, their depth dependence is crucial for understanding their impact on conductivity and optical phenomena. In the present work we utilize the limited penetration depth of x-rays to study the near-surface properties of $SrTiO_3$ substrates and epilayers and compare the results to analogous measurements using electrons. For an incidence angle of 10 degrees, the x-ray penetration depth varies between 22 and 207 nm as the energy changes from 600 to 1500 eV. For electrons the mean penetration depth varies from 3 to 90 nm as the energy changes from 0.5 to 5 keV. Thus, by obtaining x-ray excited optical luminescence (XEOL) and cathodoluminescence (CL) spectra as a function of x-ray or electron energy, it is possible to probe the near-surface region with nm-scale resolution. We will present energy-dependent XEOL and CL data from several $SrTiO_3$ samples. The luminescence spectra show features that can be assigned to Ti^{3+} (~ 1.6 eV) and oxygen-related (1.9-2.9 eV) defects, but the relative intensities differ between XEOL and CL. We will discuss the results in terms of the respective mechanisms, previous CL studies [1,2] and theoretical models.

This work was performed at the Advanced Photon Source and was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Contract No. DE-AC02-06CH11357. We gratefully acknowledge

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1. J. Zhang, et al, J. Vac. Sci. Technol. B 26, 1456 (2008).
2. J. Zhang, et al, Appl. Phys. Lett. 94, 092904 (2009).

4:00pm **EM-WeA7 Quantifying the Surface Generation Rate for Bulk Point Defects in TiO_2** , *K. Pangan-Okimoto, A. Hollister, P. Gorai, E.G. Seebauer*, University of Illinois at Urbana Champaign

The defect and surface properties of titania have been well-studied for its potential use in memory resistors and nanoelectronic gas sensors but the control of these properties in such fields has still not been fully realized. Such control of defect mobility and concentration in titania is essential for improving the operation of these technologies. Previous work in our research group has found that controlling the rutile (110) surface has opened up a new pathway for oxygen self-diffusion via an oxygen-interstitial mechanism in conditions where oxygen vacancies and titanium interstitials are thought to dominate. The present work models the detailed diffusion-reaction network of point defects in rutile to simulate interstitial-mediated self-diffusion of oxygen and to calculate a generation rate of bulk point defects at the surface. The model explicitly incorporates gas adsorption onto the (110) surface, interstitial generation at the surface/near surface, and diffusion of the oxygen in an interstitial-mediated mechanism through the bulk. In addition, the model employs techniques drawn from systems engineering to estimate the key kinetic parameters. Simulated diffusion profiles were compared to experimental profiles obtained by exposing annealing single-crystal rutile to isotopically labeled oxygen gas and then measuring isotopic oxygen concentration with secondary ion mass spectrometry. The simulated diffusion profiles matched experimental results, verifying that oxygen interstitials do indeed mediate oxygen self-diffusion in our experiment. More importantly, our model allows us to calculate the oxygen interstitial generation rate at the (110) surface, a first for titania.

4:20pm **EM-WeA8 Metastable Defects and Recoverable Degradation in InAs/AlSb HEMTs**, *X. Shen, S. DasGupta, R.A. Reed, R.D. Schrimpf, D.M. Fleetwood, S.T. Pantelides*, Vanderbilt University

It is known that some defects undergo a structural transformation to a metastable configuration when capturing a carrier. However, their roles in affecting device performance are not widely recognized. Here we show that metastable oxygen defects can cause recoverable degradation of InAs/AlSb HEMTs (high-electron mobility transistors).

Recently, we performed electrical stress tests on InAs/AlSb HEMTs and observed a recoverable degradation in some of the devices. The degradation is manifested as negative shifts of the transconductance peak and threshold voltage, which nearly completely recover after two days at room temperature. The recoverable nature of the degradation suggests that metastable defects are involved. The threshold shift indicates an increase of donor concentration or a decrease of acceptor concentration in the device. No degradation of mobility in the channel is observed, indicating that the responsible defects are in the AlSb barrier instead of the InAs channel.

We propose that the recoverable degradation is caused by a pre-existing defect in the top AlSb barrier being converted into more positive metastable configurations upon capturing the injected holes that are generated by impact-ionization in the channel. To identify the responsible defects, we performed a thorough survey of the defects in AlSb such as intrinsic defects, dopants, and contaminants, using first-principles calculations. We found that among all the candidates, oxygen impurities, both substitutional and interstitial, can account for the observed degradation. More specifically, both oxygen defects undergo large structural changes upon capturing two holes and the resulting states are metastable.

It is notable that the metastability of the oxygen defects in these devices does not originate from an energy barrier, but instead from a totally different mechanism. The Fermi level in the AlSb layer is pinned in the lower part of its band gap by the adjacent InAs layer, which ensures low electron concentration in AlSb. This leads to slow electron capture by the metastable defects. Furthermore, upon capturing two holes, the emptied electronic level associated with an oxygen defect is shifted far above the Fermi level due to the large structural relaxation. This energy-level shift ensures slow hole emission from the defect and slow electron tunneling from the adjacent layer. This mechanism results in lifetimes of metastable defects that are consistent with the experiments, and is further confirmed by additional annealing experiments that are done under bias.

The work was supported by ONR MURI under Grant No. N-00014-08-10665 and by the McMinn Endowment at Vanderbilt University.

4:40pm **EM-WeA9 Room-Temperature Native Defect Diffusion in Semiconductors**, *K.H. Warnick, Y.S. Puzyrev, T. Roy, D.M. Fleetwood, R.D. Schrimpf*, Vanderbilt University, *S.T. Pantelides*, Vanderbilt University and ORNL

Diffusion mediated by native point defects does not generally occur in semiconductors at room temperature (RT) because of high activation energies. However, recent observations of plastic deformation in AlGaIn/GaN High Electron Mobility Transistors (HEMTs) in AlGaIn epilayers on GaN in the presence of strain and electric fields have been attributed to diffusive processes. Here we report the results of first-principles density-functional calculations of formation and migration energies of vacancies under strain and electric fields that allowed us to identify the enablers of self-diffusion at RT in AlGaIn/GaN structures: triply-negative cation vacancies with near-zero formation energy, driven by an electrostatic potential gradient. We show that the formation energies of Ga and Al vacancies in unstrained n-type AlGaIn are near zero but their migration energies are too large, >1.5 eV, for appreciable diffusion at RT (typically the diffusion activation energy, i.e., sum of formation and migration energies, must be ~1 eV or lower for diffusive processes to be appreciable at RT). We find that application of strain, even at substantial levels, has little effect on either formation or migration energies. However, the Ga and Al vacancies are triply negative, and application of an electric field lowers the barrier for migration by more than 0.5 eV. At the observed critical values of the field, the net activation energy is lowered down to approximately 1 eV which makes thermally-activated atomic migration possible at RT. Simulation of the AlGaIn/GaN HEMT shows that the electric field is highest in the region where the plastic deformation is observed. These results provide a mechanism for plastic deformation mediated by vacancies, much like Nabarro-Herring creep and dislocation climb, but with an electric field being the main driver (vacancy drift). In addition, unusually high local strain can also lead to dislocation glide and further dislocation formation via strain relaxation, compounding the role of vacancy migration processes.

The work was supported in part by ONR MURI grant N-00014-08-1-0655 and by the McMinn Endowment at Vanderbilt University.

5:00pm **EM-WeA10 Defect Interactions at Grain Boundaries in Polycrystalline Graphene**, *Y.S. Puzyrev, B. Wang*, Vanderbilt University, *S.T. Pantelides*, Vanderbilt University and ORNL

The properties of polycrystalline graphene largely depend on the properties of the grain boundaries (GB) [1,2]. Classical molecular dynamics simulations coupled with density functional calculations of vacancies and self-interstitials at grain boundaries show that lower formation energies are induced by the local strain near the GB. The vacancies interact with each other as well as the interstitials. Vacancies and interstitials [3] can diffuse in graphene due to their low migration barrier. We investigated the time scale of vacancy and interstitial dynamics in pristine graphene and at grain boundaries at the distances where defect-defect and defect-GB interactions are found to be significant. GB-558 consists of pentagon and octagon pairs, whereas GB-575 is formed by repeated pentagon-heptagon pairs. We show that recombination of vacancies and interstitials can occur at grain boundaries resulting in efficient annealing of defects. The compression (stretch) for GB-558 is up to 3%, while in GB-575, the stretch reaches 9% at the C-C bonds between pentagon and heptagon or between hexagon and heptagon. We find that single vacancies can diffuse towards a grain boundary, attach to a pentagon, then merge into the grain boundary to release the compressive strain and cause local reconstruction. Molecular dynamics simulations show that if a single vacancy exits at 1nm from the grain boundary GB-558, it diffuses towards the grain boundary and attaches at the pentagon ring after 160 ps at 3000 K. It takes another 40 ps to merge into the grain boundary. Similar phenomena occur in GB-575. Stretched C-C bonds at the heptagon, on the other hand, accumulate interstitials. An interstitial that was initially positioned 7 Å above the graphene sheet, was adsorbed on the grain boundary. Once the vacancy coalesces into the grain boundary, the carbon adatom fills the reconstructed vacancy and recovers the original grain boundary structure. This recombination takes only ~ 0.5 ns at 2000 K. The results suggest a new mechanism of defect annealing with a two-step procedure, i.e. point defects (single vacancies and interstitials) diffuse and recombine locally at grain boundaries. This work was supported by DTRA Grant No. HDTRA1-10-1-0016, the US Department of Energy, Basic Energy Sciences, and the William A. and Nancy F. McMinn Endowment at Vanderbilt University. The calculations were performed at ORNL's Center for Computational Sciences and the Air Force Research Laboratory DoD Supercomputing Resource Center

[1] P. Y. Huang et. al, *Nature* 469, 389-393, 2011.

[2] Q. X. Pei, Y. Z. Zhang, V. B. Shenoy, *Carbon* 48, 898-904, 2010.

[3] A. Hashimoto, et. al, *Nature* 430, 870-873, 2004.

5:20pm **EM-WeA11 X-ray Induced Defect Formation in Graphene**, *E.X. Zhang, A.K.M. Newaz, S. Bhandaru, M.L. Alles, D.M. Fleetwood, R.D. Schrimpf, K. Bolotin, R.A. Reed, R.A. Weller, S.M. Weiss, S.T. Pantelides*, Vanderbilt University

Graphene is a truly two-dimensional material that consists of carbon atoms connected by sp^2 bonding and arranged in a honeycomb lattice. Due to its unique properties and potential applications in future electronic devices, graphene has received much attention recently from the scientific community. Initial studies of the effects of electron-beam and proton irradiation have been performed on graphene materials, but there remain significant questions about the nature of the conductivity and of the defects.

In this work, the responses of graphene materials to 10-keV x-ray radiation are evaluated with Raman spectroscopy. A defect related peak (D-peak) appears (~1345 cm^{-1}) after x-ray irradiation in air; the intensity of the D-peak increases with increasing total dose, and decreases with post-irradiation vacuum annealing at 350 °C. (See supplemental figures.) These results suggest that new defects can be created and/or that weak bonds at defect precursor sites can be scissioned and decorated with impurities (e.g., H, O) during x-ray exposure. The charge neutral point of graphene transistors made from similar material shifts positively with increasing x-ray dose, suggesting that similar defects may contribute to shifts in the Dirac point and degradation in the conductivity.

It has been shown previously that ozone can react with C-C bonds to degrade graphene layers. We have measured significant ozone generation during x-ray irradiation, suggesting that the x-rays may not directly create the defects sensed by Raman, but that x-ray generated ozone may lead to at least some of the observed defects. However, it is likely that there is an additional source of degradation, since in previous work the ozone reaction typically has been shown to lead to irreversible degradation, but we find that vacuum annealing at elevated temperature leads to partial recovery. Hydrogen annealing treatments of graphene have shown reversible degradation. Thus, it seems likely that hydrogen released by x-ray exposure in the SiO₂ substrate reacts with defect precursors (e.g., weak bond sites) in the graphene. Hydrogen reactions with C-C bonds can enhance the intervalley scattering, thereby increasing the D line intensity. Much of the hydrogen may be driven out by annealing in vacuum at 350 °C, leading to recovery of the degradation, consistent with our experimental results.

This work was supported by the DTRA Basic Research Program through Grants HDTRA1-10-1-0016 and HDTRA1-10-1-0041.

5:40pm **EM-WeA12 Influence of Point Defects on the Properties of Highly Mismatched Alloys**, R.L. Field III, T. Dannecker, Y. Jin, C. Kurdak, C. Uher, R.S. Goldman, University of Michigan

It has been suggested that alloy films composed of highly immiscible solute atoms in a solvent, termed “highly-mismatched alloys” (HMAs), are promising for energy conversion devices due to their ability to efficiently absorb light and heat, and to subsequently transport charge carriers. The properties of HMAs are often described with models focusing on the influence of individual solute atoms, assuming that all solute atoms “see” the same atomic environment. In the case of GaAsN alloys, the single local environment models predict a N composition-dependence of the energy band gap which agrees *qualitatively* with experiment. However, such models do not *quantitatively* explain several extraordinary electronic and optical properties. In this talk, I will discuss our investigations of the growth [1], structure [2-3], and properties [4-6] of GaAsN alloys. I will focus on correlations between the presence of N-N, N-As, and N-Si pairs [2,5-6] and extraordinary physical phenomena, including non-monotonic composition-dependent effective masses [7] and persistent photoconductivity [8]. I will also discuss our preliminary work on complementary alloys in the GaAsBi system.

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- [2] M. Reason, et al, *Appl. Phys. Lett.* **85**, 1692 (2004).
- [3] M. Reason, et al, *J. Appl. Phys.* **97**, 103523 (2005).
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- [5] Y. Jin, et al, *Appl. Phys. Lett.* **95**, 062109 (2009).
- [6] Y. Jin, et al, *Appl. Phys. Lett.* **95**, 092109 (2009).
- [7] T. Dannecker, et al, *Phys. Rev. B* **82**, 125203 (2010).
- [8] R.L. Field III, et al., to be submitted (2011).

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