Thursday Afternoon, October 31, 2013

Electronic Materials and Processing
Room: 101 B - Session EM2-ThA

Non-traditional Inorganic Semiconductors
Moderator: S. Durbin, University at Buffalo-SUNY, D.O. Scanlon, University College London, UK

2:00pm **EM2-ThA1 Electronic Structure and Defect Chemistry of II-IV-V_2 Semiconductors**, ***D.O. Scanlon***, University College London, UK **INVITED**

The drive to replace indium in optoelectronic devices, and to move away from toxic materials such as CdTe in photovoltaics has focused attention on semiconductors featuring affordable and abundant elements. Recently, both $ZnSnP_2$ and $ZnSnN_2$ have emerged as leading candidates for earth abundant photovoltaics.[1,2] In this presentation we discuss the electronic structure and defect chemistry of these two materials, and specifically the role of intrinsic defects in controlling the native conductivity. The possibility of tuning the polarity of the conductivity by varying growth environments or via incorporation of extrinsic impurities will also be discussed.

1) [1] D. O. Scanlon and A. Walsh, "Bandgap engineering of ZnSnP2 for high efficiency solar cells", Applied Physics Letters, 100, 251911 (2012)

2) [2] N. Feldberg, B. Keen, J. D. Aldous, D. O. Scanlon, P. A. Stampe, R. J. Kennedy, R. J. Reeves, T. D. Veal and S. M. Durbin, "ZnSnN2: A new earth-abundant element semiconductor for solar cells", Photovoltaic Specialists Conference, 38, 002524 (2012)

2:40pm **EM2-ThA3 The Role of Native Defects in the Electrical Conductivity of Metal-Oxide Semiconductors**, ***A. Janotti***, University of California, Santa Barbara **INVITED**

Oxide semiconductors exist in a variety of crystal structures, exhibiting a wide range of bonding environments and electronic behavior. For instance, ZnO (wurtzite), In_2O_3 (bixbyite), and SnO_2 (rutile) all support high levels of *n*-type conductivity and are highly transparent to visible light, making them excellent transparent conductors. TiO_2 (rutile and anatase) and $SrTiO_3$ (STO, perovskite) are prototype wide-band-gap transition-metal oxides, widely studied for catalysis and, in the case of STO, often used as a substrate for high-T_c superconductors and other oxides. STO is also at the core of recently fabricated complex-oxide-based heterostructures that display two-dimensional electron gases (2DEGs) with high carrier densities. As in any semiconductor, native defects are expected to greatly influence the electronic properties of these oxides. In particular, oxygen vacancies have been invariably invoked as a source of unintentional *n*-type conductivity, based on annealing experiments. In this talk, the role of native defects in oxide semiconductors will be revisited from the perspective of first-principles calculations. The donor or acceptor character, the likelihood of defects to form as a function of Fermi-level position and chemical potential, and defect-related optical transitions will be discussed. The possibility of *p*-type doping will also be addressed.

This work was performed in collaboration with C. G. Van de Walle, J. L. Lyons, M. Choi, L. Bjaalie, and J. B. Varley, and supported by ARO and NSF.

3:40pm **EM2-ThA6 Electronic and Lattice Dynamical Properties of II-IV-N_2 Semiconductors**, ***W.R. Lambrecht***, *A. Punya*, Case Western Reserve University **INVITED**

An overview will be presented of our recent results on the electronic band structures and lattice dynamical properties of the II-IV-N_2 semiconductors. The electronic band structure of $ZnSiN_2$, $ZnGeN_2$, $ZnSnN_2$ and $CdGeN_2$ were obtained using the quasiparticle self-consistent GW approximation using the full-potential linearized muffin-tin orbital method for the orthorombic wurtzite based structure. They are found to span band gaps from the red to the UV with $CdGeN_2$ having a gap in the green region of the spectrum. Zero point motion corrections of the band gap were estimated as well as exciton binding energies. Comparisons with experimental data are discussed. We also studied the band structure of $ZnSnN_2$ in a few alternative structures and find that the gap can be strongly reduced if besides tetrahedrons of two Zn and two Sn, also tetrahedrons with 1 Zn and 3 Sn or vice versa occur. The splittings of the valence band maximum and the effective masses and generalized Kohn-Luttinger parameters were determined. Spin-orbit splittings are found to be very small. The band offsets between $ZnGeN_2$, $ZnSnN_2$, GaN and ZnO were calculated from interface calculations for different interfaces and indicate an interesting type-II alignment between $ZnGeN_2$, GaN and ZnO. The vibrational spectra were obtained using density functional perturbation theory in a previous series of papers. Infrared and Raman spectra were predicted and compared with the available experimental data. In $ZnGeN_2$ besides the expected peaks for first-order allowed Raman, some additional features are seen in the experimental spectra. We show that these can either be due to disorder induced Raman scattering or to forbidden LO modes and further experimental work using resonant Raman spectroscopy would be useful to distinguish between the two cases. Preliminary results on native point defect calculations will be presented. The difference in energy of formation of the Ge_3N_4 and Sn_3N_4 changes the allowed window for chemical potentials of Zn and Ge or Sn. These in turn may have an important effect on the dominant point defects. The prospects for p-type doping are given particular attention. Zn_{Ge} antisites, V_{Zn} and V_{Ge} are all three found to behave as acceptors while Ge_{Zn} and V_N are donors. The relative stability of Ge_3N_4 together with the requirement to stay on the N-rich line, implies that one cannot make the samples very Ge-rich. This is however favorable for doping Ga on Ge sites which is a potential route to effective p-type doping.

4:20pm **EM2-ThA8 Novel Nitrides and Bismides: Growth and Optical Properties**, ***T.D. Veal***, University of Liverpool, UK **INVITED**

Recent research on the growth by MBE and optical properties of two classes of novel highly mismatched semiconductor will be presented, namely, dilute nitride antimonides and dilute bismide antimonides. These have potential applications ranging from thermophotovoltaics within the 2-4 micron range to night vision in the 8-14 micron IR transmission window. The incorporation of N in GaSb, GaInSb and InSb as a function of temperature and growth rate is investigated using x-ray diffraction, secondary ion mass spectrometry and kinetic modelling. For GaNSb, the optical properties are studied by absorption spectroscopy. In addition to providing evidence of the well-known band anticrossing interaction between the N localized states and the host GaSb conduction band, a strong influence of both lifetime broadening and N pair states is apparent. Meanwhile, incorporation of Bi is a little-explored approach to band gap and lattice constant tuning for GaSb and related materials, in spite of intensive recent studies of GaAsBi and sporadic study of InSbBi over the last thirty or so years. Alloying with Bi offers the potential to reduce the band gap more effectively than with indium (and may even be used in conjunction with N alloying), enabling greater valence band offsets for enhanced hole confinement and also increased spin orbit splitting. Here, MBE growth is reported of GaSbBi with Bi occupying in excess of 3% of the group V sublattice, as estimated from the increase in lattice constant determined by x-ray diffraction. This contrasts markedly with previous reports of GaSbBi MBE growth where lattice contraction was observed upon Bi incorporation and the maximum Bi content, from Rutherford backscattering, was only 0.7%. Our MBE growth study explores the Bi incorporation dependence upon the Bi flux, substrate temperature and growth rate and is compared to our Ga(In)NSb results. The influence of the Bi alloying on the band gap is also reported from Fourier transform infrared optical absorption measurements. The results are compared with predictions of both the lattice parameters and band gaps from our density functional theory calculations employing hybrid functionals. This research is performed principally in collaboration with the University of Warwick, UK, and University College London and is supported by EPSRC grant EP/G004447/2.

5:00pm **EM2-ThA10 Single Crystal Growth of $ZnSnN_2$ by Molecular Beam Epitaxy**, ***N. Feldberg***, *J.D. Aldous,* University at Buffalo, *W.M. Linhart, T.D. Veal,* University of Liverpool, UK, *P.A. Stampe, R.J. Kennedy,* Florida A&M University, *D.O. Scanlon,* University College London, UK, *L.F.J. Piper,* Binghamton University, *L. Schweidenback, A. Petrou, S. Durbin*, University at Buffalo

Over the past decade indium has experienced significant price fluctuations due to limited supply and increasing demand; these factors have motivated the search for alternative semiconductor materials based on earth-abundant elements. Such materials should still have a direct tunable bandgap similar to existing indium-containing semiconductor compounds. One candidate which may exhibit these desirable properties is $ZnSnN_2$. In addition to the abundance and low price of the constituent elements, Zn and Sn benefit from a well-established recycling infrastructure. Little is known about the properties of this material, however it is predicted to have a band gap near 2.0 eV. This band gap should be tunable through alloying with either wider or narrower band gap members of the Zn-IV-N_2 family, making it attractive for a range of optoelectronic device applications. The crystal structure of $ZnSnN_2$ is derived from that of InN through an ordered substitution of Zn and Sn on the In sublattice. The resulting structure is predicted to be orthorhombic due to the different metal-N bond lengths distorting the wurtzite structure of InN.

A series of $ZnSnN_2$ films have been grown via plasma-assisted molecular beam epitaxy (PAMBE) on (111)-oriented yttria-stabilized zirconia and $LiGaO_2$(001) substrates. Regardless of substrate type and growth conditions, all films exhibit a monoclinic structure based on x-ray diffraction (XRD) and supported by reflection high energy electron diffraction (RHEED). The crystallization in a monoclinic structure can be explained by the existence of a disordered cation sublattice. Similar lattice arrangements have been observed to occur in related compounds $ZnGeN_2$ [1] and $ZnSnP_2$ [2] in the presence of varying degrees of cation ordering. We have found that growth of high quality single crystal epitaxial films is dependent on having a high Zn:Sn flux ratio. Single crystal films were observed for flux ratios in excess of 20:1. The need for such an extremely large overpressure of Zn is expected due to the significant difference in vapor pressures between Zn and Sn. Hall effect and optical absorption suggest a variation in band gap energy as a function of crystal quality beyond expectations for Moss-Burstein and band gap renormalization effects, which is consistent with density functional theory predictions.

This project is supported by NSF grant DMR1244887 (Program Director Charles Ying), and EPSRC grant EP/G004447/2 .

1. 1. W. R.L. Lambrecht, E. Alldredge, and K. Kim, Phys. Rev. B **72** (2005) 155202.

2. D.O. Scanlon and A. Walsh, Appl. Phys. Lett. **100** (2012) 251911.

5:20pm **EM2-ThA11 Growth and Characterization of Zn-IV-Nitride Semiconductors***, **K. Kash**, P. Quayle, E. Blanton*, Case Western Reserve University **INVITED**

The Zn-IV-nitrides, $Zn(Si,Ge,Sn)N_2$, form a family of three ternary semiconductors that, although closely related to the III-nitrides AlN, GaN and InN, have elicited relatively little interest until recently. One reason is surely the great success of the III-nitrides as optoelectronic materials. In addition, while the two higher-bandgap members of the family, $ZnSiN_2$ and $ZnGeN_2$, were first synthesized over four decades ago, it was not until the last couple of years that $ZnSnN_2$, the low-bandgap analogue to InN, was reported. Further investigation of these materials has several motivations, including the promise of strategies for circumventing some of the lingering problems associated with the III-V materials, as well as predictions of interesting properties that are markedly different, in potentially useful ways, from those of the III-V materials. In this talk, we will describe the results of vapor-liquid-solid growth of $ZnGeN_2$ and $ZnSnN_2$, using either ammonia or plasma-activated nitrogen as the nitrogen source. These growth methods have produced high quality polycrystalline material that has made possible the investigation of some of the fundamental properties of these materials, including precise experimental determinations of their band gaps. The investigations have also yielded information relevant to the phase diagrams of the Zn-IV-N systems. In particular, conditions under which Zn_3N_4, Sn_3N_2, or $ZnSnN_2$, separately, are produced, have been defined. Finally, the characteristic Raman spectra of both $ZnSnN_2$ and $ZnGeN_2$ show evidence of varying degrees of phonon localization that correlate with the occurrence of "exchange defects"; that is, the exchange of ions between the group II and group IV sublattices, detected through their influence on the x-ray diffraction spectra. For $ZnGeN_2$, we show that the degree of II-IV sublattice disorder--the density of these exchange defects--can be controlled via the choice of growth conditions.

This work was done in collaboration with Jie Shan, Keliang He, Hongping Zhao and Lu Han.

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