NAMBE

Room Cummings Ballroom - Session NAMBE1-MoA

Small Bandgap Materials: Bismuthides and SiGeSn

Moderator: Kevin A. Grossklaus, MIT Lincoln Laboratory

1:30pm **NAMBE1-MoA-1 Determination of the Temperature Dependent Complex Refractive Index of GaSbBi Films by Variable Angle Spectroscopic Ellipsometry**, ***John McElearney***, *K. Grossklaus, T. Vandervelde,* Tufts University

III-V-Bi alloys, such as $GaSb_{1-x}Bi_x$, offer a slew of advantages for use in infrared optoelectronics. An anti-crossing interaction between the Bi impurity state and the host valence band dramatically reduces the film's bandgap energy [1], opening up new lattice constant and bandgap combinations. A second interaction in the split-off band [2] has recently been shown [3] to increase the spin-orbit splitting energy (Δ_0), potentially leading to a suppression of Auger recombination [4]. Finally, it has been predicted that increasing Bi fraction should reduce the bandgap energy temperature dependence as the film moves towards the semi-metal GaBi [5]. These effects can be observed by tracking critical points in the complex refractive index as functions of temperature and film composition [6, 7]. As many target applications for GaSbBi-based optoelectronics are operated either cooled, such as IR photodetectors, or at elevated temperature, such as thermophotovoltaic cells, a deeper understanding of this material's temperature dependent optical properties will improve device design and modelling.

In this work, we determine the optical constants of GaSbBi alloys as functions of wavelength, Bi fraction, and temperature using variable angle spectroscopic ellipsometry (VASE). Specifically, we measure the refractive index (*n*), the extinction coefficient (*k*), and the absorption coefficient (α) for GaSbBi films with Bi fraction $x \leq 4.2\%$, over a spectral range of 0.5 to 6.2 eV, at temperatures ranging from 78 to 473.2 K. Samples were grown on unintentionally doped, (100) GaSb substrates in a Veeco GENxplor MBE, with Sb supplied by a valved cracker cell, and Ga and Bi by high temperature effusion cells. Scans were taken using a J.A. Woollam VASE with samples mounted and held under vacuum in a JANIS cryostat. The energies of key interband transitions, such as the bandgap (E_0) and split-off band energy ($E_0 + \Delta_0$), were determined by critical point analysis of the second derivative of *k* with respect to energy. Finally, the temperature dependence of these transitions, including each film's Varshni parameters, were extracted.

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1:45pm **NAMBE1-MoA-2 Interplay of Al and Bi Incorporation in AlInSbBi**, ***Amberly Ricks***, *R. White,* University of Texas at Austin*; H. Hijazi,* Rutgers University*; S. Bank,* University of Texas at Austin

InSb-based alloys are widely explored as an alternative to HgCdTe for mid-wave infrared operation.[1,2] While InSb alone cannot access the long-wave infrared (LWIR), incorporating small amounts of Bi can decrease the bandgap energy, and photoluminescence has recently been demonstrated out to 7.6 µm at 230K from InSbBi.[3] Because narrow-gap materials are required for extended infrared operation, parasitic dark currents often arise to the detriment of device performance.[2] While nBn structures are shown to suppress sources of high dark current, AlInSb barriers in InSb-based nBn detectors introduce a tradeoff between a desirably large conduction band offset and an undesirably large valence band offset.[4] This tradeoff is exacerbated for InSbBi absorbers as experimental evidence suggests that the bandgap energy of InSb is expected to decrease by 29 meV/% Bi incorporated,[3] and most of this bandgap change is expected to manifest in the valence band.[5] To break this tradeoff in InSb-based nBn detectors, small amounts of Bi can be incorporated into the AlInSb barrier to independently decrease the valence band offset while maintaining a sufficiently high conduction band offset. In this work, we explore the interplay of Al and Bi incorporation in AlInSbBi.

AlInSbBi films were grown on InSb substrates under similar growth parameters to those used for high quality InSbBi:[3] a 300^{0}Csubstrate temperature, 0.975x V/III flux ratio, and ~1 µm/hr growth rate. At low Al concentrations, Bi incorporation was limited to ~0.4% and the excess Bi precipitated out into droplets on the surface. However, we found that higher concentrations of Bi could be incorporated as the Al concentration was increased; this may be due to the shorter AlBi bond being more energetically favorable than that of InBi.[6] Rutherford backscattering spectrometry measurements demonstrated that AlInSbBi films containing 25 and 32% Al enabled incorporation of 3.2 and 4.2% Bi, respectively. Atomic force microscopy scans revealed the presence of Bi droplets, indicating Bi saturation was reached under these growth conditions. Future work on optimizing the AlInSbBi growth regime and experimentally measuring the band offsets in these materials is underway to better understand the efficacy of Bi in an AlInSb barrier layer for LWIR devices. This work was supported by the NSF (Award Nos. ECCS-1933836).

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2:00pm **NAMBE1-MoA-3 Growth of GaBi Thin Films via Molecular Beam Epitaxy**, ***Molly McDonough***, *S. Law,* Pennsylvania State University

Like the well-known arsenides, antimonides, and phosphides, the bismides are part of III-V semiconductor class. Bismides include the ternaries $GaSb_{1-x}Bi_x$, $GaAs_{1-x}Bi_x$, $InSb_{1-x}Bi_x$, and the binary compounds AlBi, GaBi, and InBi. The ternary bismides are relatively well-studied due to their applications in infrared sensing: their bandgaps can be decreased significantly with the inclusion of a relatively small amount of bismuth. Density functional theory (DFT) calculations indicate that the binary bismides should be topologically non-trivial materials, converting to topological insulators or semimetals upon the application of a small amount of strain. The ternary compounds $GaSb_{0.5}Bi_{0.5}$, $GaAs_{0.5}Bi_{0.5}$, and $InSb_{0.5}Bi_{0.5}$ have also been predicted by DFT to be metastable Dirac semimetals. Despite the long-standing interest in bismides, progress in the synthesis of high-Bi content-containing alloys has been slow due to the surfactant behavior of bismuth, making the growth of defect-free coalesced films with high-Bi content challenging. There have only been two reported attempts of growth of the binary bismides via molecular beam epitaxy (MBE). In 2014, the growth of InBi on GaAs(100) resulted in large droplet formation and uncoalesced films. This attempt was likely unsuccessful due to the large lattice mismatch between the substrate and the bismide films. In 2019, a paper was published on the growth of InBi on Si(111), showing coalesced InBi films in the tetragonal structure with some remaining crystalline bismuth in x-ray diffraction (XRD) measurements.

Here, we present the successful synthesis of coalesced GaBi films using MBE. The GaBi films were grown with a Ga:Bi beam equivalent pressure (BEP) ratio of 1:1 on InSb(100) substrates. The choice of InSb(100) for GaBi growth is due to the near-perfect (-0.34%) lattice matching between the substrate and the predicted lattice constant of GaBi. Using XRD and energy dispersive spectroscopy (EDS) measurements, we demonstrate that we can stabilize the zinc-blende structure of GaBi and grow this material as a thin film. We show that substrate temperatures below 100C, as measured by thermocouple, result in droplet formation. Substrate temperatures exceeding 200C result in phase segregation of the Ga and Bi. However, within the substrate temperature window of 100-200C, crystalline GaBi thin films will form. These results are promising for further study of GaBi and have the potential to inform future work on InBi and AlBi for applications in infrared detectors and topological materials.

2:15pm **NAMBE1-MoA-4 Long-Wave Infrared Sensing via InSb-Based Dilute-Bismide Alloys**, ***Corey White***, *M. Bergthold, A. Ricks, F. Estévez, D. Wasserman, S. Bank,* The University of Texas at Austin

Due to the significant bandgap reductions induced by bismuth incorporation in III-V alloys,[1,2] dilute-bismide alloys present a unique opportunity to access technologically significant operating wavelengths for optoelectronics. Specifically, long-wave infrared (LWIR) detectors are of critical importance for chemical sensing and thermography, but the corresponding narrow bandgap energies have proven challenging to reach with III-V alloys. By incorporating small concentrations of bismuth[3,4] and arsenic[5] into InSb, the quaternary alloy InAsSbBi can be grown lattice-

matched to InSb substrates with tunable narrow bandgap energies, thus highlighting a route to LWIR detectors that do not suffer from the fabrication, growth, and toxicity challenges plaguing the current state-of-the-art material, HgCdTe. Here we report the first InSbBi nBn detector showing a significant bismuth-induced extension in cutoff wavelength. Building on this, we will show how arsenic incorporation can be leveraged to lattice-match to InSb substrates enabling the growth of thick absorbers for strong absorption.

Epitaxial In(As)SbBi alloys were grown on InSb substrates. To impose a kinetically-limit growth regime,[6] low substrate temperatures, Sb/In flux ratios near stoichiometry, and fast growth rates were employed to encourage significant bismuth incorporation. From these alloys, we observed room temperature photoluminescence (PL) with significant wavelength extension into the LWIR indicating high optical quality, which is promising for high-performance detectors. Furthermore, by incorporating arsenic and bismuth in ~1:3 proportions, we grew InAsSbBi lattice-matched to InSb and observed that the arsenic incorporation assisted in reducing the alloy's bandgap as expected due to the band bowing between InAs and InSb.[5]

To demonstrate a prototype InSbBi detector, an nBn detector was grown with an InSbBi absorber and an AlInSb barrier. Comparing this detector to an identical device with no bismuth, we observed a significant extension in cutoff wavelength at 79K from 5.5 µm for InSb to 6.6 µm with 1% bismuth incorporation. Building on this, growth of optimized detectors with thicker InAsSbBi absorbers are underway and results will be presented at the conference.

This work was supported by the NSF (Award No. ECCS-1933836) and an NSF Graduate Fellowship (RCW). The work was performed at the UT MRC, a member of NNCI.

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2:30pm **NAMBE1-MoA-5 GePb Alloys Grown using Molecular Beam Epitaxy for Infrared Photodetector Applications***, **Tyler McCarthy**, A. McMinn,* Arizona State University*; X. Liu, R. Hossain, X. Qi,* arizona state University*; Z. Ju,* Arizona State University*; Y. Zhang,* arizona state University

The Group-IV material system, Si, Ge and their alloys, has been one of the most widely used and researched material families in the semiconductor industry for over half a century. The addition of α-Sn, the diamond cubic semiconducting form of Sn, over the last couple of decades has fostered new research into IR materials and novel techniques such as momentum(*k*)-space charge separation (*k*-SCS) for devices. The next evolution of Group-IV alloys is the inclusion of Pb as an exciting new alternative route for IR detectors, quantum materials, and high-speed electronic devices. GePb alloys are an especially promising candidate for *k*-SCS and as an alternative materials for high-speed field effect transistors, due to the indirect to direct bandgap crossover predicted to occur at approximately 1 to 3.4 % Pb and their higher electron mobility, respectively. Short-range order (SRO) effects are also predicted to occur in GePb alloys, altering their optical and electrical properties for a given composition.

DFT modeling has predicted that like the other Group-IV elements, Pb can have the tetrahedral sp3 hybrid bonding required for diamond lattice structure formation, with an estimated lattice constant of 6.83 Å. Similarly to Sn in the Ge-Sn system, there is low solid solubility of Pb in the Ge-Pb system (< 0.5 at.%). Due to this, obtaining single crystal alloys with high Pb concentrations has been challenging and will require non-equilibrium growth conditions, such as MBE.

Single crystal GePb alloys with Pb concentrations between 0.2 % to 7.2 % have previously been grown by pulsed laser-induced epitaxy (PLIE), magneto sputtering, and a layer inversion thermal evaporator method, but there has not yet been work done by MBE. The MBE growth of single crystal GePb alloys on Ge(100) substrates is reported here. Effusion cells of Ge and Pb are used to control the flux ratio independently in a VG-V80 MBE system. The optimal substrate temperature is found to be near the thermocouple temperature of 300 ˚C based on HRXRD and RHEED characterization of the grown films. The RHEED pattern changes from the (2 x 2) of Ge to a (1 x 1) for GePb growths at 400 and 500 ˚C. At 300 ˚C the pattern changes to a streaky pseudo(4 x 2) that remains throughout the epilayer growth and for samples at 200 ˚C and lower, this pattern becomes spotty. SEM images show a large volume of Pb islands on the surface that form into either long trapezoidal rods or uniform droplets that coalesce as growth progresses. Raman spectrometry gives an estimated Pb composition near 1 % with only minimal change in Pb incorporation for a large change in the Ge:Pb BEP ratio.

2:45pm **NAMBE1-MoA-6 Temperature Dependent Optical Constants of Germanium-Tin Alloys***, **Amanda Lemire**,* Tufts University*; K. Grossklaus,* MIT Lincoln Laboratory*; T. Vandervelde,* Tufts University

Mid-infrared materials are desirable for applications in imaging, spectroscopy, telecommunications, and lasing. $Ge_{1-x}Sn_x$ alloys, which have a bandgap tunable by compositional changes and are compatible with existing Si processing techniques, are being developed for photonic devices providing infrared emission and detection. It is necessary for designing such devices to have accurate information on the optical properties of the material, including changes in response to composition and temperature. In this work, we present properties for alloys between 3.6% and 8.4% Sn at temperatures between liquid nitrogen and 200°C.

Three samples were grown on a custom-designed, dual-chamber, VG-90 MBE system. Approximately 100 nm films were deposited on Ge (001) wafers, using an effusion cell for Sn and electron beam gun for Ge. Film compositions were determined by high-resolution x-ray diffraction. The three samples contain 3.6%, 6.5%, and 8.4% Sn respectively. Optical properties were measured by a J.A. Woollam UV-visible spectroscopic ellipsometer fitted with a CRV-725V cryostat. Samples were cleaved and cleaned in dilute hydrofluoric acid to remove surface oxidation before insertion into the cryogenic stage. Data were collected at 50K intervals from 78K to 475K at energies between 0.39 eV and 4.12 eV. Scans were also taken of Ge for modeling purposes. The complex index of refraction was calculated from each data set. Band transition energies are found to decrease in energy as Sn content increases.

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