Exploiting Disorder in Novel Semiconductors for Optoelectronic Devices

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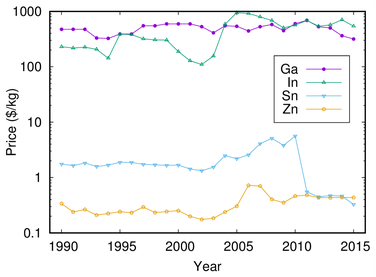
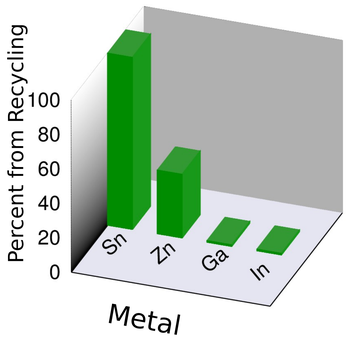
The Problem

- Currently most optoelectronic devices contain materials based on indium or gallium
- In and Ga are relatively expensive metals with currently no recycling infrastructure

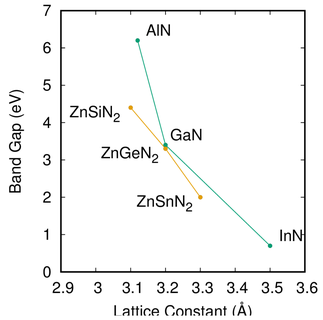


- The family of Zn-IV-N_2 compounds could be viable alternatives for optoelectronic devices
- Very little is known about the synthesis and properties of these compounds, however
- Both Zn and Sn are eco-friendly metals since reclamation sources account for a large portion of their annual production

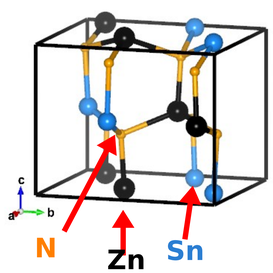
U.S. 2015 Production via Reclamation

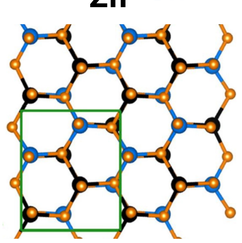


Band Gaps and Cation Disorder



- The band gap is a fundamental property of semiconductors; it arises from the periodic arrangement of atoms
- $ZnSnN_2$ is predicted to have an orthorhombic lattice structure with a band gap of 2.0 eV – suitable for red LEDs
- Randomizing the placement of Zn and Sn (the cations) in the structure causes the lattice to become hexagonal and the band gap to decrease to 1.0 eV
- The optimal band gap for a solar cell is 1.5 eV – halfway between the two extremes
- The goal of this research project is to test this set of order/disorder based band gap predictions for ZnSnN2, and determine to what extent it can be controlled using a commercially important crystal growth technique

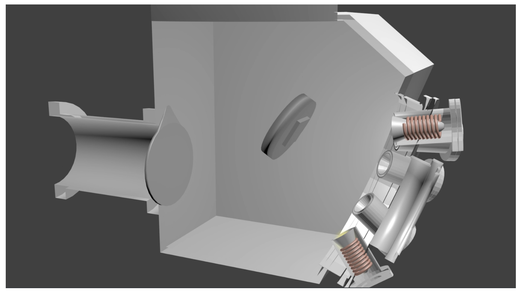




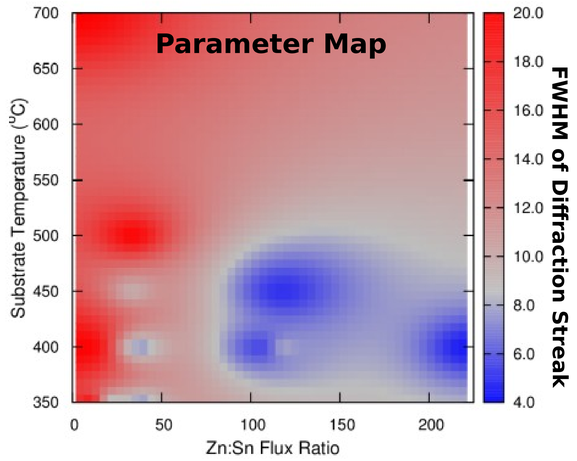
Ordered $ZnSnN_2$ unit cell **(top)** and lattice **(bottom)**

Growing $ZnSnN_2$ via Plasma Assisted Molecular Beam Epitaxy (PAMBE)

- PAMBE is an ultra-high vacuum thermal vapor deposition technique. High purity Zn and Sn are heated to create vapor beams, which then condense and crystallize on the substrate
- Active Nitrogen is supplied using a radio-frequency inductively coupled plasma source
- The $ZnSnN_2$ growth parameter space has been explored with a series of films to optimize crystal quality and to obtain ordered and disordered $ZnSnN_2$

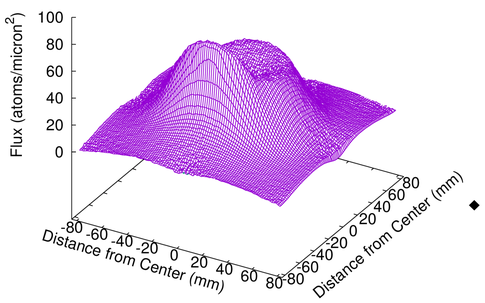


Schematic of PAMBE System

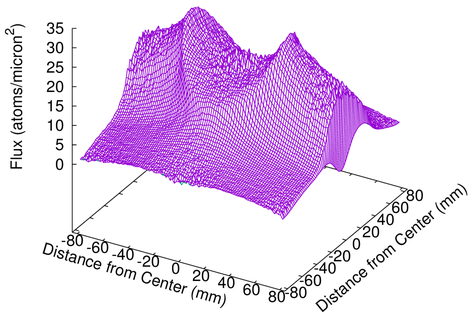


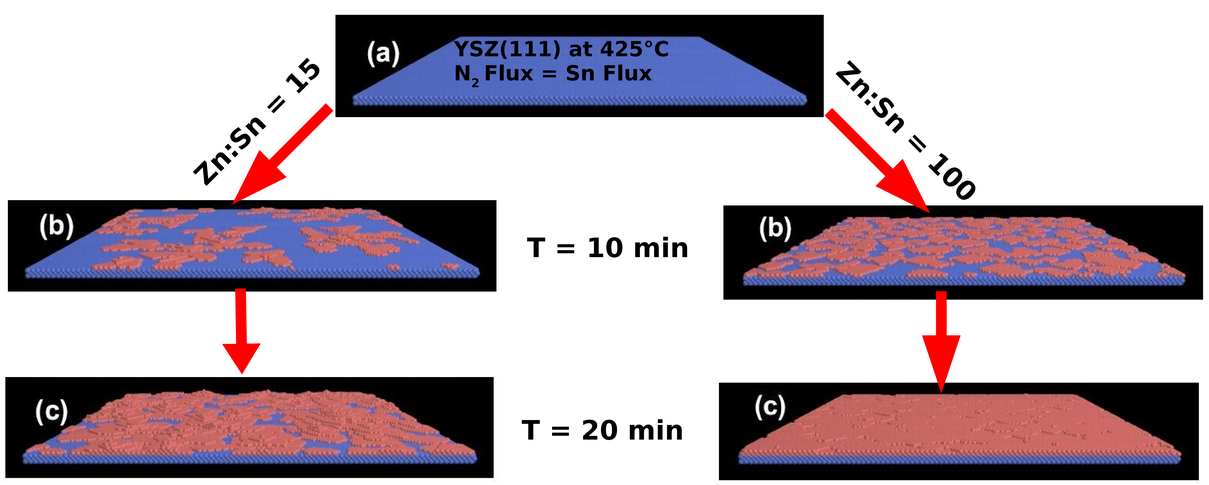
- A smaller full-width-at-half-max (FWHM) represents a higher quality crystal, while a larger FWHM represent a lower quality crystal

Monte Carlo Simulations: Modeling Growth

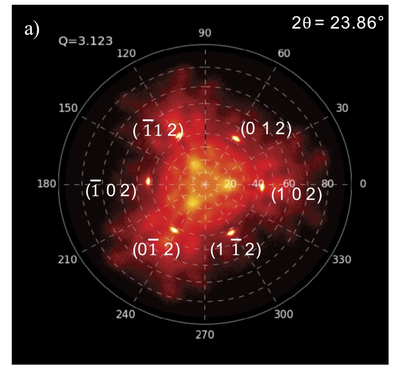


- Discrete Monte Carlo simulations of the evaporation sources were used to calculate the flux distribution for a conic crucible that is nearly depleted **(left)** and mostly full **(right)**
- Kinetic Monte Carlo simulations showed that $ZnSnN_2$ grown under higher Zn:Sn flux produces smoother films than films grown under low Zn:Sn flux

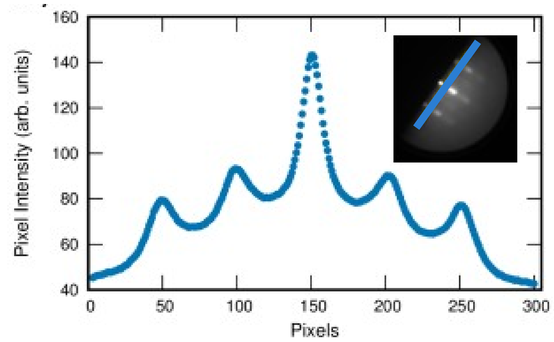




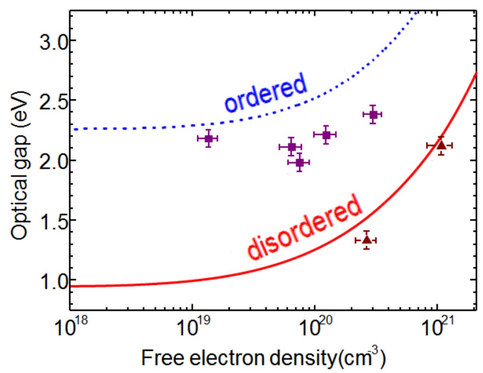
Measuring Success



- Film structure is characterized using synchrotron x-ray diffraction (XRD) at Argonne National Lab. Above is an XRD pole figure from a disordered sample, confirming a hexagonal structure
- Lattice structures are also determined in-situ using electron diffraction, providing real time feedback about the success of the growth
- Inset below is the electron diffraction pattern from an ordered film, with the graph showing a line profile from the pattern



- Band gap and electron concentration are measured via optical absorption and Hall effect, respectively
- The optical gap is a strong function of the electron concentration, which can mask the actual band gap



Conclusions

- We have successfully grown and characterized both disordered and ordered $ZnSnN_2$ crystals
- We are now working to reduce the free electron concentration in the films to obtain more accurate measurements of the fundamental electronic properties of $ZnSnN_2$ as a function of cation order