Electronic Supplementary Material (ESI) for Materials Horizons.

Supplemental Information

Exciton Photoluminescence and Benign Defect Complex Formation in Zinc Tin Nitride

A. N. Fioretti,[1,2] J. Pan,[1] B. R. Ortiz,[2] C. L. Melamed,[1,2] P. C. Dippo,[1]
L. T. Schelhas,[3] J. D. Perkins,[1] D. Kuciauskas,[1] S. Lany,[1] A. Zakutayev,[1] E. S. Toberer,[1,2] and A. C. Tamboli[1,2]
[1]National Renewable Energy Laboratory, Golden, CO USA
[2]Colorado School of Mines, Golden CO USA
[3]SLAC National Accelerator Laboratory, Menlo Park, CA USA

1. Methods

To determine oxygen concentration, Rutherford backscatter spectrometry (RBS) was performed on an annealed zinc tin nitride (ZTN) film grown with added hydrogen, with Zn/(Zn+Sn)=0.67 determined by XRF. This sample was taken from the same library as two of the annealed samples used for photoluminescence spectroscopy. RBS was performed on a model 3S-MR10 RBS system from National Electrostatics Corporation. The beam consisted of 2.25 MeV alpha particles at a current of 50 nA. The total accumulated charge was 500 mC. The RBS detector was mounted in a 168° backscatter configuration. Analysis of the RBS spectra was performed as described in a previous work. [1]

Absorption coefficient curves plotted in Figure S1 were obtained by measuring transmission (T) and reflection (R) spectra in the UV-Vis- NIR spectral ranges (300–2000 nm). Measurements were performed using a home-built thin film optical spectroscopy system equipped with deuterium and tungsten/halogen light sources and Si and InGaAs detector arrays. The collected spectra were then used to calculate absorption coefficient (α) using the relation $\alpha = \ln[T/(1-R)]/d$, where d is the measured film thickness [2].

2. Results

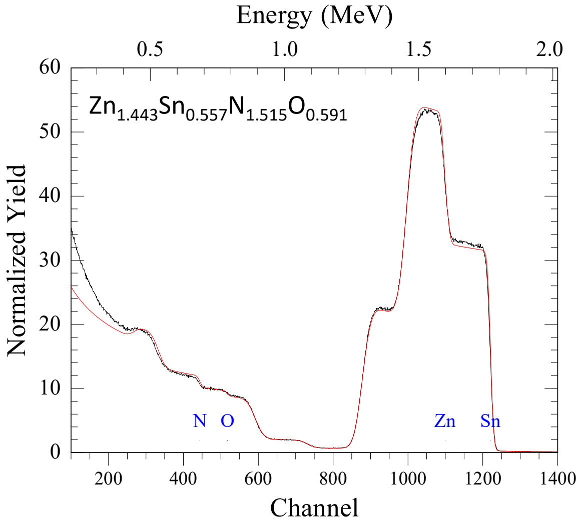

Figure S1: RBS yield vs. backscattered particle energy for an annealed, zinc-rich film grown on glass with added hydrogen. The data is shown in black, and the modeled fit is shown in red.

Figure S1, shows representative RBS data for a zinc-rich ZTN film grown with added hydrogen, then annealed under activated nitrogen. This sample corresponds to the annealed samples used in the photoluminescence section of the main manuscript. Using the Rutherford Universal Manipulation Program, fitting was performed to extract the O/(O+N) ratio (red line in Figure S1 shows the fit). It was found that films of this composition and preparation contain approximately 14 at.% oxygen, or O/(O+N) = 0.28.

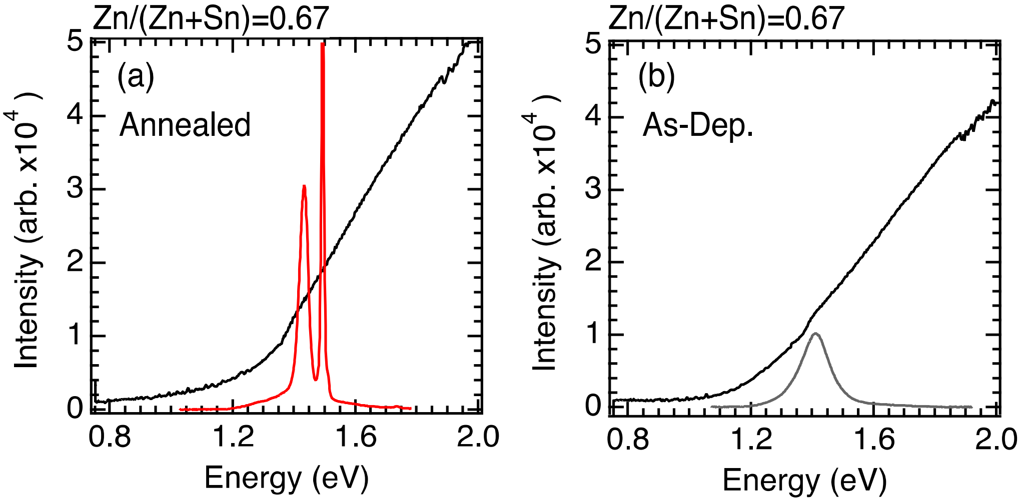

Figure S2: Comparison between the low temperature PL signal and the room temperature absorption coefficient for (a) annealed and (b) as-deposited ZTN films grown in hydrogen.

As shown in Figure S2, the room temperature absorption coefficient curves for both annealed and as-deposited Zn-Sn-N thin films in this work are in good agreement with the low temperature photoluminescence signal. However, sub-gap absorption can be seen in both panels (a) and (b). Such sub-gap absorption likely results in non-radiative recombination during the PL process, since emission below 1.4 eV is weak or not observed.

Figure S3 shows the results of a power law fit to the intensity as a function of incident laser power for the peak at 1.5 eV (red circles) and the shifting transition between 1.42-1.47 eV (black squares) observed in Figure 3a. The slope of each line is *k*, extracted using the functional form $I(P) \propto P^k$, indicates the type of recombination giving rise to the peak in question. Values greater than unity indicate transitions with only a radiative component (i.e. excitons). Values of *k* less than unity indicate transitions in which both radiative and non-radiative recombination pathways were involved (defect-assisted).

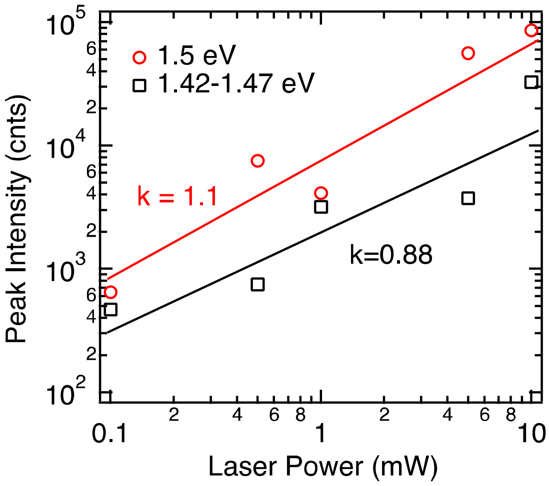

Figure S3: Power law fit of the 1.50 eV and 1.42 eV peak intensities as a function of incident laser power. The slope of each line is denoted *k*, and is found to be greater than unity for the 1.50 eV peak and less than unity for the 1.42 eV peak.

References

[1] A. N. Fioretti, A. Zakutayev, H. Moutinho, C. Melamed, J. D. Perkins, A. G. Norman, M. Al-Jassim, E. S. Toberer, and A. C. Tamboli, *J. Mater. Chem. C*, 2015, **3**, 11017.

[2] A. Zakutayev, T. R. Paudel, P. F. Ndione, J. D. Perkins, S. Lany, A. Zunger and D. S. Ginley, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2012, **85**, 085204.