

Earth-Abundant $\text{ZnSn}_x\text{Ge}_{1-x}\text{N}_2$ Alloys as Potential Photovoltaic Absorber Materials

Naomi C. Coronel¹, Lise Lahourcade¹, Kris T. Delaney², Amanda M. Shing¹, and Harry A. Atwater¹

¹California Institute of Technology, Pasadena, CA, 91125, USA

²University of California, Santa Barbara, CA, 93106, USA

Abstract — Large-scale energy demands will require low-cost, earth-abundant materials for high efficiency solar energy conversion. Here we present $\text{ZnSn}_x\text{Ge}_{1-x}\text{N}_2$ as a tunable band gap photovoltaic absorber layer with a predicted range of 1.4 eV to 2.9 eV. Thin films of $\text{ZnSn}_x\text{Ge}_{1-x}\text{N}_2$ are synthesized by reactive RF co-sputtering with a wide range of compositions. X-ray diffraction shows a linear shift in lattice parameter with changing composition, indicating no phase separation. These results suggest that $\text{ZnSn}_x\text{Ge}_{1-x}\text{N}_2$ can potentially be tuned to span a large portion of the solar spectrum and could therefore be a viable earth-abundant photovoltaic material.

Index Terms — germanium alloys, semiconductor materials, solar energy, sputtering, thin films, tin alloys.

I. INTRODUCTION

In recent years, $\text{Al}_x\text{Ga}_y\text{In}_{1-x-y}\text{N}$ alloys have gained considerable attention because of their favorable properties for use in optoelectronic devices [1]-[2]. In particular, $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloys have become promising materials for use in solar cells because the direct band gap can be tuned over a large portion of the solar spectrum, from 0.7 eV to 3.4 eV. However, $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloys with high indium content have been difficult to grow since InN and GaN have a large difference in lattice parameters leading to indium segregation and phase separation [3]-[4]. In the case that the growth becomes feasible, indium is still an expensive and non-abundant element, which limits its utility for large-scale photovoltaics. Instead, we propose replacing the group III element in the III-nitride system with earth-abundant group II and group IV elements, with the anticipation that this new system of materials will have properties similar to their III-nitride counterparts [5].

We have focused on zinc for the group II element and tin, germanium, or silicon for the group IV element. Based on density functional theory calculations using the hybrid HSE06 functional, we expect these materials to have direct band gaps with energy values of 1.4 eV for ZnSnN_2 , 2.9 eV for ZnGeN_2 , and 4.8 eV for ZnSiN_2 [6]. A plot of energy band gap vs. lattice parameter for these materials and for the III-nitrides is shown in Fig. 1 and suggests that the two systems are comparable, although the Zn-IV-nitride system has a smaller energy range and overall lattice mismatch. Even though the smaller energy range is not advantageous, $\text{ZnSn}_x\text{Ge}_{1-x}\text{N}_2$ alloys alone can potentially be tuned to span an energy range of 1.4 eV to 2.9 eV, which still covers a large portion of the solar spectrum. The smaller lattice mismatch, on the other

hand, does provide an important advantage for this new system in terms of heterostructure device fabrication and alloying by reducing the strain that obstructs epitaxy at interfaces and encourages phase separation.

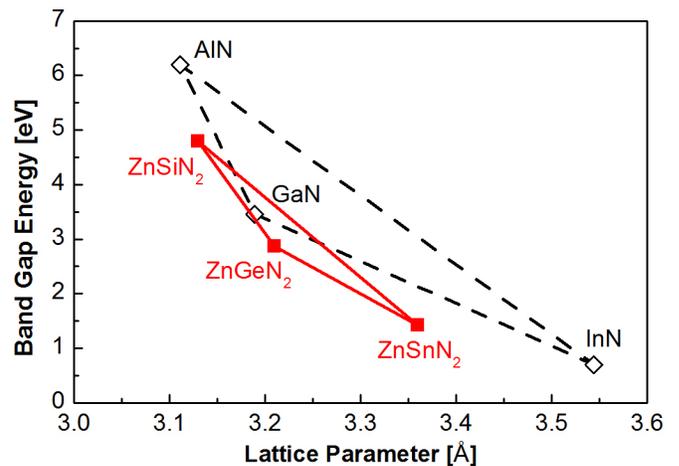


Fig. 1. Comparison of band gap energy versus lattice parameter for the III-nitride and Zn-IV-nitride material systems. The new Zn-IV-nitride system has a smaller overall lattice mismatch and energy range than the well-studied III-nitride system. Still, quaternary alloys of $\text{ZnSn}_x\text{Ge}_{1-x}\text{N}_2$ could potentially be tuned to span a large portion of the solar spectrum.

Due to the promise of using $\text{In}_x\text{Ga}_{1-x}\text{N}$ as an absorber layer for solar cells, we have focused on its analogue in this new material system, $\text{ZnSn}_x\text{Ge}_{1-x}\text{N}_2$. The predicted band gap range is wide enough for efficient solar energy conversion and the small lattice mismatch between ZnSnN_2 and ZnGeN_2 suggests a lower probability of phase separation. Therefore, we believe that $\text{ZnSn}_x\text{Ge}_{1-x}\text{N}_2$ will be an important earth-abundant alternative to $\text{In}_x\text{Ga}_{1-x}\text{N}$ for use in photovoltaic devices.

II. THIN FILM DEPOSITION

$\text{ZnSn}_x\text{Ge}_{1-x}\text{N}_2$ thin films were deposited on *c*-sapphire substrates, from MTI Corporation, by reactive RF co-sputtering from metal targets in an argon/nitrogen plasma. The chamber pressure was kept at 3 mTorr during deposition with 75% nitrogen in the plasma, and the substrate temperature was held at around 270°C. For $x = 0$ or 1, films were deposited by

co-sputtering from zinc (99.99%) and germanium (99.999%) or zinc and tin (99.999%) elemental targets, all obtained from the Kurt J. Lesker Company. An RF power of 44 W was applied to the zinc target, while the tin and germanium targets required 74 W and 104 W, respectively, to obtain stoichiometric films as determined by energy dispersive X-ray spectroscopy. For films with $0 < x < 1$, we sputtered from a $Zn_{0.75}Sn_{0.25}$ pressed powder target (99.99%, ACI Alloys) and a germanium elemental target because our system is limited to two RF power supplies. The combined target is zinc-rich because the high vapor pressure of zinc limits its incorporation during deposition at substrate temperatures above $\sim 200^\circ\text{C}$. For the data presented here, the RF power on the $Zn_{0.75}Sn_{0.25}$ target was kept at 134 W and the power applied to the germanium target was varied from 44 W to 134 W to create a set of samples with ranging compositions. From previous studies, we determined that the combined target requires a higher power than the elemental targets to get a comparable deposition rate that limits oxygen incorporation in the film [7].

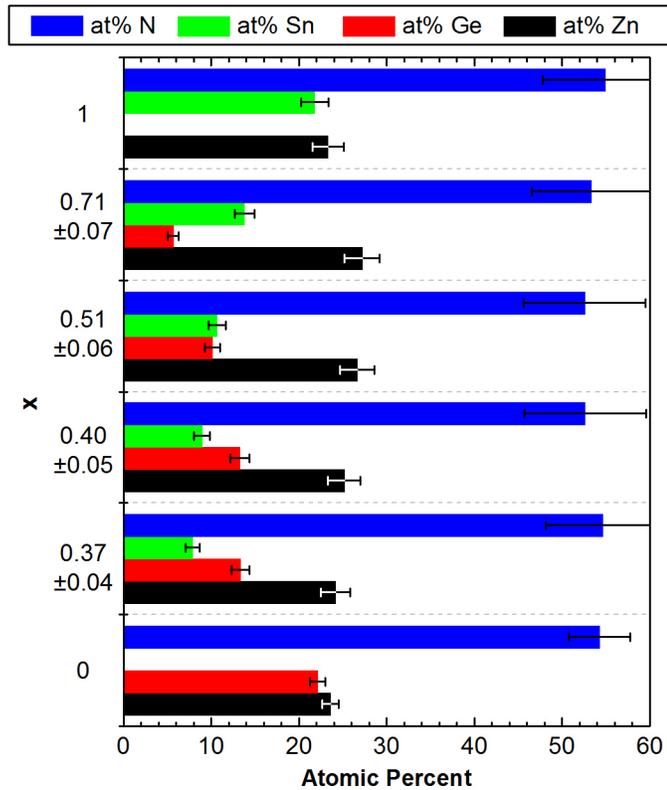


Fig. 2. Energy dispersive X-ray spectroscopy measurements for $ZnSn_xGe_{1-x}N_2$ samples with various compositions. The x values were calculated by taking the ratio of the tin atomic percent to the combined atomic percent of tin and germanium. All samples have about 50 at% nitrogen and 25 at% zinc within error, so only the concentrations of group IV elements are significantly changing. The error bars represent instrument error and the variation in composition measured over different areas of the same sample.

III. RESULTS

A. Film Composition

Fig. 2 presents the composition measurements made using energy dispersive X-ray spectroscopy and shows that all samples have close to 25 at% zinc and 50 at% nitrogen within error. An accelerating voltage of less than 10 kV was used to confine the size of the activation volume to the thickness of the thin film. The quaternary samples presented here have x values of 0.71 ± 0.07 , 0.51 ± 0.06 , 0.40 ± 0.05 , and 0.37 ± 0.04 , corresponding to germanium RF powers of 44 W, 74 W, 104 W, and 134 W, respectively. The value of x was calculated by taking the ratio of atomic percent tin to the total atomic percent of group IV elements.

B. Structural Characterization

X-ray diffraction measurements were performed using copper $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) over a 2θ range of 29° to 42° to determine the crystallinity and orientation of the $ZnSn_xGe_{1-x}N_2$ films. The $ZnSnN_2$ ($x = 1$) and $ZnGeN_2$ ($x = 0$) films each present one prominent peak at $2\theta = 32.4^\circ$ and 34.2° , respectively (Fig. 3a), attributed to a (002) reflection based on calculated lattice parameters [6]. The corresponding experimental c lattice parameters are equal to 5.52 \AA for $ZnSnN_2$ and 5.24 \AA for $ZnGeN_2$. For the quaternary films with $0 < x < 1$, we observed two peaks corresponding to the (002) and (211) orientations, displayed in Fig. 3a. For all of the samples, the 2θ position of each (002) peak was compared with the film composition yielding a linear relationship in which the 2θ position increases with increasing germanium content (Fig. 3b). Consequently, the c lattice parameter decreases linearly with increasing germanium content.

IV. DISCUSSION

Overcoming the difficulties associated with $In_xGa_{1-x}N$ growth would be an important achievement for optoelectronic devices, especially photovoltaics. To date, the major difficulty has been in growing high indium content films because the indium tends to segregate instead of uniformly incorporating into the alloy. For this reason we studied the structural evolution of our materials with a widely varying composition to ascertain if the same problem occurs. The continuously shifting 2θ position of the (002) peak with changing composition, exhibited in our $ZnSn_xGe_{1-x}N_2$ thin films, essentially points to alloying of the material, with no observable phase separation according to this X-ray diffraction analysis. The reason the growth of these materials does not suffer from the same difficulties as $In_xGa_{1-x}N$ growth is likely because the difference in lattice parameter between $ZnSnN_2$ and $ZnGeN_2$ is about half as large as the difference between InN and GaN . Therefore, our material is able to accommodate a larger range of compositions without straining the lattice to a point where phase separation is favorable. This

result is valuable because it suggests that we should be able to easily access the entire range of predicted band gaps for $\text{ZnSn}_x\text{Ge}_{1-x}\text{N}_2$ by tuning the ratio of the group IV elements.

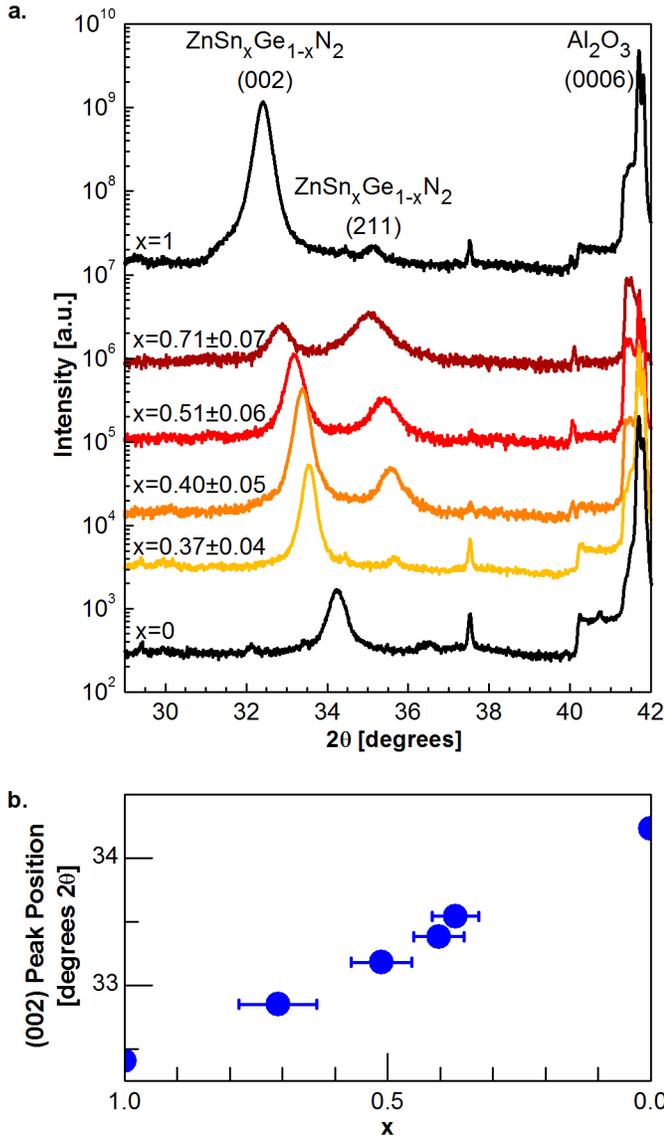


Fig. 3. a. X-ray diffractograms for $\text{ZnSn}_x\text{Ge}_{1-x}\text{N}_2$ samples with different compositions. The most prominent peak for the samples with $x = 0$ or 1 is from the (002) reflection, and the samples with $0 < x < 1$ exhibit (002) and (211) reflections. b. Plot showing the linear relationship between the 2θ position of the (002) peak and the composition, represented by the x value.

We previously measured an optical absorption edge of about 2.2 eV for ZnSnN_2 , using absorption values derived from spectroscopic ellipsometry measurements [7]. The large deviation from the calculated value of 1.4 eV is attributed to band filling from a high electron carrier concentration (up to 10^{21} cm^{-3}) that contributes to the Burstein-Moss effect [8]-[9]. The strength of the effect is likely due to the small conduction

band effective mass of ZnSnN_2 that allows the absorption edge to increase rapidly with increasing carrier concentration. On the other hand, the literature reported band gap value for reactively sputtered ZnGeN_2 of 3.1 eV is only slightly larger than the expected value of 2.9 eV [10]. If this difference is also due to a high electron carrier concentration, the reduced effect could be explained by the larger conduction band effective mass of ZnGeN_2 compared to ZnSnN_2 . Unfortunately, the sputtered ZnGeN_2 films are fairly resistive, causing difficulty in determining a carrier concentration using Hall measurements. Based on these experimental band gap estimations, the tunable energy range of our $\text{ZnSn}_x\text{Ge}_{1-x}\text{N}_2$ films may not be as wide as we predicted, primarily because of the Burstein-Moss effect in ZnSnN_2 .

Nevertheless, the X-ray diffraction results are promising because they show that the band gap of $\text{ZnSn}_x\text{Ge}_{1-x}\text{N}_2$ alloys can potentially be varied over a wide range as a function of the composition. Reducing the carrier concentration in our sputtered ZnSnN_2 films will be important for demonstrating the full tunability of $\text{ZnSn}_x\text{Ge}_{1-x}\text{N}_2$. Additionally, the range of accessible band gaps could be extended into the ultraviolet regime by using $\text{ZnGe}_x\text{Si}_{1-x}\text{N}_2$ alloys [11]. If the device properties of $\text{ZnSn}_x\text{Ge}_{1-x}\text{N}_2$ are comparable to those of $\text{In}_x\text{Ga}_{1-x}\text{N}$, it may be possible to achieve large-scale, inexpensive, and efficient solar energy conversion in the near future.

V. CONCLUSION

We are studying a new system of Zn-IV- N_2 materials, where the group IV element is tin, germanium, or silicon, that are earth-abundant and have predicted properties similar to those of the III-nitride system for use in photovoltaics. Here we focused on $\text{ZnSn}_x\text{Ge}_{1-x}\text{N}_2$ as a tunable band gap absorber material analogous to $\text{In}_x\text{Ga}_{1-x}\text{N}$. We have demonstrated thin film growth of $\text{ZnSn}_x\text{Ge}_{1-x}\text{N}_2$ alloys by reactive RF co-sputtering from metal targets in a nitrogen-rich plasma, where x is varied by changing the RF power applied to the targets. Our results show that the (002) peak position from X-ray diffraction linearly increases in 2θ with increasing germanium content over a wide range of compositions, signifying that phase separation is not occurring and we should be able to access the entire range of band gaps between ZnSnN_2 and ZnGeN_2 . Therefore, we believe that $\text{ZnSn}_x\text{Ge}_{1-x}\text{N}_2$ has the potential to be an earth-abundant alternative to $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloys for low-cost, tunable band gap, photovoltaic absorber layers.

ACKNOWLEDGEMENT

The authors would like to acknowledge funding from the US Department of Energy under grant DE-FG02-07ER46405 and from the DOW Chemical Company.

REFERENCES

- [1] S. Nakamura, S. J. Pearton, and G. Fasol, *The Blue Laser Diode: The Complete Story*. Berlin: Springer, 2000.
- [2] S. J. Pearton, C. R. Abernathy, and F. Ren, *Gallium Nitride Processing for Electronics, Sensors and Spintronics*. New York: Springer, 2006.
- [3] R. Singh, D. Doppalapudi, T. D. Moustakas, and L. T. Romano, "Phase separation in InGaN thick films and formation of InGaN/GaN double heterostructures in the entire alloy composition," *Applied Physics Letters*, vol. 70, pp. 1089-1091, 1997.
- [4] N. Duxbury, U. Bangert, P. Dawson, E. J. Thrush, W. Van der Stricht, K. Jacobs, and I. Moerman, "Indium segregation in InGaN quantum-well structures," *Applied Physics Letters*, vol. 76, pp. 1600-1602, 2000.
- [5] T. R. Paudel and W. R. Lambrecht, "First-principles calculations of elasticity, polarization-related properties, and nonlinear optical coefficients in Zn-IV-N₂ compounds," *Physical Review B*, vol. 79, 245205, 2009.
- [6] K. T. Delaney, S. K. Shukla, and N. A. Spaldin, "First-principles theoretical assessment of earth-abundant nitrides for photovoltaic and optoelectronic applications using hybrid density functionals," *To be submitted*.
- [7] L. Lahourcade, N. C. Coronel, K. T. Delaney, S. K. Shukla, N. A. Spaldin, and H. A. Atwater, "Structural and optoelectronic characterization of RF sputtered ZnSnN₂," *Submitted*.
- [8] E. Burstein, "Anomalous optical absorption limit in InSb," *Physical Review*, vol. 93, pp. 632-633, 1954.
- [9] T. S. Moss, "The interpretation of the properties of indium antimonide," *Proceedings of the Physical Society Section B*, vol. 67, pp. 775-782, 1954.
- [10] S. Kikkawa and H. Morisaka, "RF-sputter deposition of Zn-Ge nitride thin films," *Solid State Communications*, vol. 112, pp. 513-515, 1999.
- [11] A. Osinsky, V. Fuflyigin, L. D. Zhu, A. B. Goulakov, J. W. Graff, and E. F. Schubert, "New concepts and preliminary results for SiC bipolar transistors: ZnSiN₂ and ZnGeN₂ heterojunction emitters," in *IEEE/Cornell Conference on High Performance Devices*, 2000, pp. 168-172.