A Combinatorial Material Study on ZnSnN₂ Solar Absorber

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Abstract
ZnSnN₂ is an Earth-abundant analog to the III-Nitrides with potential as a solar absorber due to its direct bandgap, steep absorption onset, and the possibility to tune its bandgap through introducing disorder into the cation sublattice. Here we present a combinatorial study of ZnSnN₂ that has achieved dense crystalline films with photovoltaic-relevant carrier concentration. We report evidence of a Burstein-Moss shift widening the apparent bandgap, and tunable carrier concentration with cation composition. These results reaffirm the potential of ZnSnN₂ for energy-conversion applications.

1 Introduction
ZnSnN₂ is an Earth-abundant III-N analog with a direct bandgap, steep absorption onset, and the possibility to tune its bandgap through introducing disorder into the cation sublattice. Here we present a combinatorial study of ZnSnN₂ that has achieved dense crystalline films with photovoltaic-relevant carrier concentration. We report evidence of a Burstein-Moss shift widening the apparent bandgap, and tunable carrier concentration with cation composition. These results reaffirm the potential of ZnSnN₂ for energy-conversion applications.

Despite the many potential benefits of this material, ZnSnN₂ is one of the least-studied members of the II-IV-V₂ class. Computational research into its properties did not begin until 2008, and the first synthesis of ZnSnN₂ was not reported until 2013. Since then, synthesis of ZnSnN₂ has been reproduced, but questions remain concerning both its structure and its fundamental properties.

One critical challenge frustrating initial ZnSnN₂ development for optoelectronics was the degenerately high n-type carrier density consistently found in stoichiometric samples. Carrier densities were typically greater than 10²⁰ cm⁻³. However, with the publication of Ref. [12] and the results of the present study, it is now known that carrier densities on the order of 10¹⁷–10¹⁸ cm⁻³ are attainable, which certainly reaffirms the potential of ZnSnN₂ for PV. Still, major discrepancies in the value of the fundamental bandgap are prevalent in the ZnSnN₂ literature. Calculated values range from 0.35–2.64 eV depending on the approximation used, and experimental results are also scattered. This discrepancy has been attributed to band-filling due to degenerate carrier density or to disorder on the cation sub-lattice causing a narrowing of the fundamental gap. Thus far, it has been difficult to determine which hypothesis is correct, or if it is a combination of both effects, because the body of work available on ZnSnN₂ remains somewhat limited. Although the existing studies on this material are clearly foundational to this area of research, collectively they still only provide an incomplete picture of the physics of ZnSnN₂ and how
we might manipulate those physics to create the next great functional material.

In this work, we utilize a combinatorial approach to identify a practical range of growth temperatures and cation compositions for growing cation-disordered ZnSnN₂. We find [0001] growth with wurtzite structure, and present the first report of doping control in ZnSnN₂ through varying cation off-stoichiometry. We find that a 10% zinc-rich cation composition yields an n-type carrier density of 3 x 10¹⁸ cm⁻³; the lowest carrier density achieved thus far for as-deposited films. This finding provides tantalizing insight into the fundamental properties of the Zn-Sn-N material system; namely that some version of defect compensation or defect complexing must be taking place. Finally, we report ZnSnN₂ films that luminesce at cryogenic temperatures, and exhibit no free carrier absorption below the absorption edge. These findings not only justify continued research into ZnSnN₂, but also reaffirm its potential as a PV absorber material.

2 Experimental

**Combinatorial RF Sputter Deposition:** Combinatorial thin film libraries of compositionally-graded ZnSnN₂ were grown on glass via reactive RF-sputtering using an RF-plasma atomic nitrogen source. Two angled sputter guns at 45° to the substrate normal created a continuous composition spread of Zn:Sn. A growth temperature gradient was induced perpendicular to the cation composition gradient by contacting the 50x50 mm substrate on one end with a heated metal pad. Each sample prepared in this way yielded a 44-point library of unique deposition conditions, thus making it possible to directly connect observed trends in estimated bandgap, crystal structure, and other properties to changes in film composition or growth temperature. Sample libraries were characterized by X-ray diffraction (XRD), X-ray fluorescence (XRF), four-point probe (4pp), and UV-Vis-NIR spectroscopy using a 4 x 11 mapping grid and custom data analysis software.

**Thin Film X-Ray Diffraction:** XRD was performed using a θ – 2θ geometry with Cu Kα radiation and a proportional 2D detector on a Bruker D8 Discover equipped with General Area Detector Diffraction System (GADDS) software.

**X-ray Fluorescence:** X-ray fluorescence was performed on a Fischer XDV-SDD instrument to determine both the Zn/Sn ratios and the thickness of the films. Film thickness from XRF was calibrated with scanning electron microscopy (SEM) measurements.

**Electrical Measurements:** Sheet resistance measurements were performed on a 4pp mapping instrument built in-house, and then correlated with thickness measurements from XRF to obtain resistivity and conductivity data. Room temperature Hall effect measurements were performed on a BioRad HL5500 PC instrument to determine carrier density and majority carrier mobility. Hall measurements were performed on small (7 x 7 mm) sections of the original sample libraries, which were considered to be approximately uniform with regards to composition and morphology due to the small size of the film sections.

**UV-Vis-NIR Spectroscopy:** Absorption coefficient spectra were collected using a thin film optical spectroscopy instrument with mapping capabilities built in-house. Two Ocean Optics light sources were used to provide incident photons in the UV-Vis and NIR ranges.

**Electron Microscopy:** SEM and transmission electron microscopy (TEM) were also performed on the 7 x 7 mm sample pieces. High resolution TEM, bright-field TEM, and selected area electron diffraction patterns were collected from thin sections of the 7 x 7 mm film pieces that had been subjected to lift-out by focussed ion beam (FIB). Interplanar spacings were calculated using a pattern taken from single crystal GaAs for calibrating the spacings given by the instrument under the same measurement parameters. Scanning TEM paired with energy dispersive X-ray spectroscopy (EDS) was used to analyze the composition of the grain boundaries.

**Electron Backscatter Diffraction (EBSD):** EBSD was performed in the same instrument used for SEM and on sample pieces of the 7 x 7 mm size. Kikuchi patterns were indexed using hexagonal and cubic lattices to check that the highest coincidence indices came from the hexagonal lattice.

**Photoluminescence Spectroscopy (PL):** PL was performed at 4.25 K with a 514 nm laser operated at 10 mW power on samples of the 7 x 7 mm size.

3 Results and Discussion

3.1 Broad Combinatorial Study

3.1.1 Morphology and Structure

Using a combinatorial approach, we were able to identify optimal conditions for depositing wurtzite ZnSnN₂ on glass with long range phase-purity by XRD. Six combinatorial libraries were prepared spanning growth temperatures from 35–340°C and cation compositions of 0.30–0.75 Zn as determined by XRF.
Throughout this work, the fraction of zinc atomic percent (at%) to total cation at% as measured by XRF gives the degree of off-stoichiometry in reference to zinc content. A value of 0.50 Zn indicates stoichiometric, while a value of 0.60 indicates zinc-rich. A set of samples was also prepared isothermally at 400°C. However, films grown at 400°C showed regions of no net deposition and of metallic zinc and tin. Films with 0.40–0.60 Zn and grown at 160–340°C growth temperature exhibited no secondary phases by XRD and had dense, columnar grains >20 nm in diameter by SEM.

Fig. 1a displays XRD patterns on a log scale for ZnSnN$_2$ films grown within the optimal range described above. At all temperatures explored (except for 400°C), films grown with cation compositions of 0.40–0.60 Zn exhibited crystal structure consistent with the monoclinic or “average wurtzite” structures observed previously (i.e. random cation site-occupancy). Films grown outside the cation composition range of 0.40–0.60 Zn exhibited broad XRD peaks that were not well resolved and were often shifted to higher or lower Bragg angle, indicating the presence of amorphous character or secondary phases.

The top panel of Fig. 1a (turquoise curve) shows the effect on crystal structure of growing stoichiometric films between 280–340°C. Two peaks appear at ~30° 2θ, which are at the expected peak positions of the Pna2$_1$ orthorhombic structure calculated for ZnSnN$_2$ in prior work. Off-stoichiometric films grown between 280–340°C exhibited wurtzite ZnSnN$_2$ structure. Finding evidence of higher order at high growth temperature and wurtzite ZnSnN$_2$ at lower temperature indicates the potential for tuning order parameter, and subsequently bandgap, through varying growth temperature in this material.

Fast deposition rates of up to 300 nm/hr were achieved at all deposition conditions up to 340°C. Films were dense by SEM and exhibited grains with diameter 20–100 nm (Fig. 1b) if grown between 160–340°C and 0.40–0.60 Zn/(Zn+Sn). Films with <0.40 Zn on the cation site had voided grain boundaries and did not exhibit columnar grains. Columnar growth was also disrupted for films with >0.60 Zn on the cation site. Zn-rich or stoichiometric films grown at temperatures lower than 160°C had small grains <20 nm and sometimes even <5 nm. Grain size was consistently <100 nm for all films grown in this work, but this can be attributed to sputtering onto glass without subsequent post-growth annealing.

We observe surprisingly good phase stability and a lack of significant crystallographic defects for films grown over a wide range of deposition conditions. This is in contrast to the very narrow window of equilibrium phase stability predicted by Ref. [1], in which Zn$_3$N$_2$ and metallic Zn and Sn secondary phases were predicted to be difficult to avoid. We see no evidence of these secondary phases by XRD within the range of
0.40–0.60 Zn on the cation site and 160–340°C growth temperature. The absence of secondary phases in our films suggests that our growth conditions are not in line with the assumptions used to construct the phase stability diagram from prior work. For example, the use of activated nitrogen in the present study provides non-equilibrium growth conditions that have been previously shown to widen the range for stable phase formation in other nitride materials. Indeed, prior work on the metastable material Cu$_3$N using an atomic nitrogen source showed a distinct broadening of the window where this material could be grown. For ZnSnN$_2$, the defect formation enthalpies reported in Ref. [1] predict that O$_N$ and V$_N$ donor defects are two of the four most favorable defects. This indicates that nitrogen-rich growth should lead to better material in terms of point defect density. The ability in this work to grow wurtzite ZnSnN$_2$ at a wide range of conditions highlights the advantage provided by non-equilibrium growth and the use of an activated nitrogen source.

### 3.1.2 Electrical Properties

To determine the effect of growth temperature and composition on the electronic properties of ZnSnN$_2$, electrical resistivity and Hall effect measurements were collected (Fig. 2). Resistivity plotted as a function of Zn fraction on the cation site is shown in Fig. 2a, with the data sets color-coded by growth temperature. In terms of composition variation, a peak in overall resistivity is observed for films with 0.65 Zn on the cation site, as determined by XRF. In terms of temperature effects, the resistivity values are minimally affected by growth temperature in the Sn-rich and stoichiometric regions, but increase and then decrease with growth temperature in the Zn-rich regions.

To understand these observations, we now consider the Hall effect data presented in Figs. 2b-c. Mobility values (Fig. 2c) were above 1 cm$^2$V$^{-1}$s$^{-1}$ across all composition and temperature regions measured, with the exception of the Sn-rich sample grown at 35°C. Within the practical range of deposition conditions we identified, the highest mobility measured was 8.3 cm$^2$V$^{-1}$s$^{-1}$ and the lowest was 1.1 cm$^2$V$^{-1}$s$^{-1}$. In Fig. 3b, a clear downward trend in carrier density is observed over the same composition range for which the conductivity reaches its minimum. The minimum conductivity coincides with an overall minimum n-type carrier density of 2.1 x 10$^{18}$ cm$^{-3}$, and we therefore conclude that the observed changes in conductivity are mostly driven by changes in carrier density and not driven by changes in mobility.

![Figure 2](image-url)
ing growth, we assume that V_N and O_N concentrations are consistently low at all cation compositions explored and likely do not contribute to changes in carrier density. Sn_{Zn} antisites are predicted to be more favorable to form than Zn_i (or any of the other defects), so it may be that Zn-rich growth somehow compensates the density of Sn_{Zn} antisite defects to lower the ultimate n-type carrier density observed. Whether this compensation takes the form of defect complexes or competing Zn_{Sn} antisites, or some other possible mechanism is, for now, unclear. The defect formation enthalpies referenced here\(^1\) were calculated for the Pna2\(_1\) orthorhombic crystal structure for stoichiometric ZnSnN\(_2\), and may not apply to the off-stoichiometric, wurtzite version observed in this work. This discrepancy highlights the need for future computational efforts on understanding the defect physics of disordered wurtzite ZnSnN\(_2\).

### 3.1.3 Light Absorption

Fig. 3 shows the absorption coefficient plotted on a log scale as a function of Zn fraction on the cation site at two different growth temperatures: 160°C in panels (a)–(c), and 230°C in panels (d)–(f). The data and absorption trends shown in Fig. 3 are representative of the broader range of libraries studied in this work. Absorption coefficient color maps are shown in Figs. 4b and 3e, in which absorption coefficient values above 3 x 10^4 \(\text{cm}^{-1}\) are displayed in yellow and below 8 x 10^3 \(\text{cm}^{-1}\) are displayed in black. The panels that bookend Figs. 3b and 3e are traditional representations of absorption coefficient versus photon energy, also plotted on a log scale. Panels (a) and (c) correspond to the fully zinc-rich (0.61) and fully tin-rich (0.40) regions on the color map in panel (b), respectively. The same description is true of panels (d) and (f).

For both fully tin-rich panels (Figs. 3c and f), free carrier absorption below the absorption onset can be seen. This phenomenon is visualized as a rise in absorption coefficient at low photon energy preceding the initial absorption edge at ~1.4 eV. The same effect is visualized in the color maps in panels (b) and (e) as low-energy regions of orange-red coloring preceding the mostly black regions that surround the absorption edge. As the film composition moves from tin-rich to zinc-rich in each set of panels, the free carrier absorption decreases, which is visualized in the color maps as orange-red fading to black in the low energy range. Finally, a shifting absorption onset is observed in both sets of panels, which is identified by comparing the lowest absorption coefficient values between panels (a) and (c) and between panels (d) and (f).

We observed a precipitous drop in free carrier absorption below the absorption onset in Fig. 3 as cation composition became increasingly zinc-rich at both temperatures. No detectable free carrier absorption was observed for films grown at 230°C with 0.60 Zn on the cation site (Fig. 3d). Because the limit of our NIR detector is approximately 10^3 \(\text{cm}^{-1}\), any absorption below this threshold could not be observed. For films with 0.60 Zn grown above 230°C up to 340°C, there was a slight increase in free carrier absorption (data not shown), but the absorption edge remained at 1.0 eV. Lowering the growth temperature to the 100–200°C range for 0.60 Zn films caused an increase in free carrier absorption (Fig. 3a). Free carrier absorption could be minimized again at these lower growth temperatures, but the composition had to be pushed far Zn-rich (0.65 to 0.75 Zn on the cation site), which was detrimental to morphology.
The optical absorption edge for films with 0.60 Zn was consistently found to be 1.0 eV for films grown within the temperature window of 160–340°C. This value is in good agreement with the predicted bandgap for cation-disordered ZnSnN\textsubscript{2} reported in literature.\textsuperscript{4,5} For both temperatures shown in Fig. 3, the absorption edge varied from about 1.4 eV to 1.0 eV as cation composition moved from 0.40 Zn to 0.60 Zn, and this variation coincided with decreasing free carrier absorption. This correlation suggests a Burstein-Moss shift\textsuperscript{15} causing an increase in the apparent bandgap for stoichiometric and Sn-rich films. This effect is a result of conduction band filling\textsuperscript{5} and is consistent with the stoichiometric and Sn-rich films having higher carrier density than their Zn-rich counterparts. The Burstein-Moss effect has been cited previously\textsuperscript{4} as possibly leading to a larger than predicted experimental bandgap (1.8 eV as opposed to their predicted 1.42 eV), and this claim is further supported by our results in Fig. 3.

### 3.1.4 Summary of Combinatorial Work

The schematic shown in Fig. 4 summarizes the results of our combinatorial work on ZnSnN\textsubscript{2}. Each black dot displayed in the figure represents a particular set of growth conditions examined in this work. The shaded overlaid shapes indicate boundaries in growth temperature-composition space where particular material properties were observed. Samples grown at conditions beyond these boundaries exhibited one or a combination of the following: (1) under-dense morphology or non-columnar grain growth by SEM, (2) amorphous character or secondary phases by XRD, and/or (3) \textit{n}-type carrier densities upwards of \(10^{20}\) cm\textsuperscript{-3}. Particularly, films grown at 400°C showed regions of no net deposition or regions of metallic zinc and tin mixed with the binary Zn\textsubscript{3}N\textsubscript{2} and Sn\textsubscript{3}N\textsubscript{4} parent phases. This schematic is not intended to present hard rules for preparing ZnSnN\textsubscript{2} thin films. Rather, these ranges are specific to reactive sputtering on glass without post-growth annealing. However, the guidelines presented in Fig. 4 can serve as a useful starting point for any future ZnSnN\textsubscript{2} experiment.

The teal shaded region shown in Fig. 4 indicates the growth temperature and cation composition range we identified for growing dense ZnSnN\textsubscript{2} films with grains larger than 20 nm in diameter by SEM. The overlapping yellow region gives the boundaries for obtaining films with \textit{n}-type carrier density below \(10^{19}\) cm\textsuperscript{-3}. Finally, the orange triangle gives the boundary conditions for growing films that exhibit no free carrier absorption below the absorption edge, and should be considered a subset of the yellow region. As shown in the enlarged inset in Fig. 4, these regions of desirable properties were only found to overlap at 230°C growth temperature and \(\sim0.60\) Zn/(Zn+Sn); a very narrow region that would be difficult to find without a combinatorial approach. Future work on ZnSnN\textsubscript{2} will likely be able to expand on our “property diagram” by including the effects of annealing on these ranges, in addition to creating similar schemas for growth on different substrates. Given the considerable difficulty so far experienced in determining the fundamental properties of ZnSnN\textsubscript{2}, it is our hope that these guidelines can now provide a platform for accelerated development of this promising material in the future.

![Figure 4: Summary of combinatorial experiments. Each point on the figure represents one of 44 data points collected from each of six combinatorial libraries. The shaded colored regions indicate regions where particular properties were observed.](image-url)
ties. To balance this, advanced characterization techniques are necessary to provide a more focused view of the regions of interest identified by our initial combinatorial work. In the following section, we delve deeper into the properties of a small selection of samples in order to better understand (1) the challenges that remain to be addressed in future work, and (2) possible routes toward optimization of ZnSnN$_2$ moving forward.

### 3.2 Advanced Characterization

#### 3.2.1 Crystal Structure

To gain deeper insight into the properties and challenges of our most interesting ZnSnN$_2$ films, more advanced characterization techniques were applied in a non-combinatorial way. We selected a handful of samples grown at temperatures in the range of 230–300°C that were all either stoichiometric or zinc-rich in composition. These samples represent regions in which the lowest carrier density, best crystallinity, and/or best absorption coefficient curves were observed by combinatorial characterization. The advanced characterization techniques we utilized allowed us to highlight challenges still to be addressed in this material, as well as to identify unique property relationships not yet reported in the existing ZnSnN$_2$ literature.

Columnar grain structure was observed by bright-field TEM, as shown in Fig. 5a, in which a representative image taken from a stoichiometric film grown at 280°C is shown. Figs. 5b-d, showing SAED, HRTEM, and STEM, respectively, were also taken from the same sample. The SAED pattern shown in Fig. 5b was used to calculate interplanar spacings corresponding to the six smallest-diameter diffraction rings. These were found to be consistent with those calculated previously$^4$ for wurtzite ZnSnN$_2$ with Zn and Sn distributed randomly on the cation sublattice. The pattern in Fig. 5b is consistent with polycrystalline film morphology, which is consistent with XRD analysis, and exhibits evidence of some preferential orientation along the [0001] direction (c-axis).

HRTEM of a representative grain boundary is shown in Fig. 5c. Grain boundaries were free of precipitates, such as metallic Zn or Sn, and were crystalline at their interfaces. Small regions of high dislocation density were also observed within grain interiors and away from the grain boundaries. These regions were no more than 5 nm across and sometimes less than 1 nm across, and were only found in about half the grains imaged. Here again, these dislocations are more likely artifacts of a fast deposition rate and growth on non-oriented substrates, and may be avoided under more stringent deposition conditions or through post-growth annealing.

STEM line scans revealed the presence of nanoscale voids in the stoichiometric film shown in Fig. 5. These voids are visible in Fig. 5b as small dark regions between columnar grains (indicated by a red arrow). In addition to finding nanovoids, grain size was found to be no larger than 50 nm in diameter for samples imaged by TEM. Indeed, grains smaller than 100 nm were consistently observed by all imaging techniques used in this study (also see Fig. 1). Nanoscale voids and very small grain size when preparing films by sputtering clearly represent challenges to be addressed as research on ZnSnN$_2$ moves forward. Previous works$^{4,12}$ using sputtering have also reported small grains, while MBE growth$^{5,11}$ on (111) yttria-stabilized zirconia (YSZ) substrates unsurprisingly produced single-crystal ZnSnN$_2$. One report$^{12}$ even showed preliminary evidence that annealing sputtered ZnSnN$_2$ films increases grain size, although the maximum size reported was still only 7.5 nm (based on Scherrer analysis) when the initial grain size was 5.8
nm. Taken together, these examples from literature support the conclusion that the challenges mentioned above are related to the sputtering growth method used in the present study and not fundamental to this material.

When the cation sub-lattice in ZnSnN₂ attains a high degree of ordering (every zinc sits on a zinc site and every tin on a tin site) a larger, orthorhombic unit cell must be drawn to fully capture the translational symmetry of the more ordered crystal structure. For a detailed depiction of how the orthorhombic unit cell relates to the underlying hexagonal lattice in ZnSnN₂, we direct the reader to Ref. [2].

The most prevalent grain orientation observed in Fig. 6 is (0001), shown in red with >95% confidence, and no other orientation was so clearly favored. Regions of black in Fig. 6 represent areas with no or low-quality Kikuchi patterns, which could not be reliably indexed by the EBSD software. Although absence of Kikuchi patterns is often indicative of amorphous material, this explanation is not consistent with the HRTEM and SAED data collected for these films, in which no amorphous character was observed. However, grain size in these films was always smaller than the spot size of the incident electron beam used for the EBSD measurements, and this may have contributed to the difficulty in obtaining Kikuchi patterns in some places. A combination of the small grain size in this sample, which approached the lateral resolution of EBSD, and observed electron-beam damage of the surface probably contributed to the difficulty in obtaining good EBSD data over the whole analyzed area. Moreover, the presence of nanovoids and small regions of high dislocation density found by STEM and HRTEM, respectively, also likely contributed to the dark regions observed in Fig. 6. Such imperfections might partially explain the unexpectedly low mobility found in a previous work in which films were also grown by sputtering and had similarly small grain size.

Finding (0001) preferential growth is interesting since these films were grown on amorphous glass and were expected to exhibit no orientational preference. This finding suggests that growth on lattice-matched (0001)-oriented hexagonal substrates is a promising route forward for optimizing the morphology of these films. This finding also helps explain the success of previous works in growing ZnSnN₂ thin films on (111) yttria-stabilized zirconia, GaN, or c-plane sapphire substrates.

### 3.2.2 Transport

Within the practical range of deposition parameters we identified, an inverse relationship between carrier density and mobility was observed (see Fig.
This relationship suggests ionized defects may be a dominant source of charge carrier scattering in this material. Typically, this sort of relationship would be expected of temperature-dependent Hall effect data, but we observe it as a function of increasing off-stoichiometry (zinc-richness). This is an intriguing parallel to draw, because in the context of temperature-dependent Hall, lowering the temperature decreases the energy available to activate defects and simultaneously decreases the concentration of charged scattering centers. In our case (Fig. 7), we appear to be losing charged scattering centers as zinc-richness increases. This might suggest the formation of defect complexes as the film composition moves away from stoichiometric. However, the defect physics of cation-disordered ZnSnN$_2$ are not well-understood, and neither are the that of off-stoichiometric Zn$_x$Sn$_{1-x}$N$_2$. Therefore, conclusions about mechanism must be regarded as speculative until new theoretical work on the defect physics of the Zn-Sn-N system become available.

![Figure 7: EBSD grain orientation map corresponding to the stoichiometric sample imaged with TEM in Fig. 5. Kikuchi patterns were indexed with high coincidence using a hexagonal lattice. The preferred orientation was found to be along [0001], shown in red. Dark regions indicate regions where no, or low-quality Kikuchi patterns were observed.](image)

The lowest $n$-type carrier density observed in Fig. 7 is $3 \times 10^{18}$ cm$^{-3}$ at 0.60 Zn on the cation site, and this coincides with the highest mobility of 8.3 cm$^2$ V$^{-1}$ s$^{-1}$. This mobility is on par with the highest mobilities reported in some previous works, and twice as high as the most recent report on ZnSnN$_2$. The lowest carrier density reported herein is one to two orders of magnitude lower than reported in all experimental studies on ZnSnN$_2$ leading up to Ref. [12]. Our carrier density is comparable to that of Ref. [12], and their values were achieved through annealing, while ours were achieved through off-stoichiometric growth. This comparison is promising, because it shows that one of the fundamental challenges for ZnSnN$_2$-based photovoltaics, namely degenerate carrier concentration, may in fact be a tractable problem.

Fig. 8a shows the squared absorption coefficient data for three representative cation compositions from a film grown at 230$^\circ$C. The data shown in Figs. 4d-f correspond to the same sample as the curves in Fig. 8a. A clear shift in estimated bandgap can be seen upon comparison of the three curves displayed in Fig. 8a. Moving from turquoise to purple to black curves, the estimated bandgap shifts to a higher value. This shift to higher estimated bandgap coincides with decreasing sub-gap absorption, until no sub-gap absorption is detectable for the turquoise curve. This sub-gap absorption trend also coincides with changes in carrier density; namely, that the most prominent sub-gap absorption is observed for the highest carrier density film (black curve) and none is detectable for the lowest carrier density film (turquoise curve). This demonstrates again the classic Burstein-Moss shift we observe for this material. In the present study, we have teased out the Burstein-Moss shift by varying off-stoichiometry, but it may be the case that sequentially annealing a degenerate stoichiometric film would reveal the same shifting absorption onset coinciding with reductions in carrier density. Either way, what is clear from both Fig. 8a and Figs. 4d-f, is that the Burstein-Moss shift previously proposed to explain unexpectedly high absorption onsets in ZnSnN$_2$ is a real effect.

Fig. 8b displays low temperature PL spectra taken from different cation compositions of a 300$^\circ$C sample. These spectra are also representative of other zinc-rich films grown at lower temperatures. At every composition represented in Fig. 9b, a broad peak is observed somewhere in the range 1.35–1.5 eV. The peak shapes are also similar among the spectra for each composition. Interestingly, the energy range in which our PL peaks occur happens to coincide with the energy at which another broad PL peak was observed in a previous work at room temperature. This previous study attributed their PL peak at 1.4 eV to defect luminescence. However, the corresponding absorption onset at room temperature for the films shown in Fig. 4 was found to be 1.0 eV, which is 0.4 eV below the sharpest peak in Fig. 4 (for the
film with 0.60 Zn on the cation site). Defect luminescence is usually observed at energies below the optical bandgap in PL measurements, so observing luminescence above the optical gap suggests that this signal might not be consistent with a defect state. It is possible that the bandgap of cation-disordered ZnSnN\(_2\) has a large temperature-dependence, but further systematic investigation into this possibility will be the topic of a future study.

4 Summary and Conclusions

In this work, we have presented a comprehensive combinatorial study on the Zn-Sn-N material system. We identified a range of practical deposition parameters for growing cation-disordered ZnSnN\(_2\) thin films on glass. The optimal growth temperature range identified in this work is between 200–300°C. The optimal cation composition was found to be 0.60 Zn/(Zn+Sn). A strong preference for growth in the c-axis direction was found, even though films were grown on amorphous glass. The lowest carrier density observed for as-deposited films showing dense morphology by SEM was 3 x 10\(^{18}\) cm\(^{-3}\), which approaches a useful range for PV devices. Furthermore, we present strong evidence in support of a Burstein-Moss shift increasing the apparent bandgap for this material. Films with the most free carrier absorption below the absorption edge exhibited an absorption onset of ~1.4 eV while films with no detectable free carrier absorption consistently showed an absorption onset of 1.0 eV. Intriguingly, both the lowest carrier density observed and the absence of detectable free carrier absorption occur in films with 0.60 Zn on the cation sublattice as opposed to the 0.50 value, indicating that defect complexes may have a significant effect on the carrier concentration of ZnSnN\(_2\). We conclude that the results presented herein not only reaffirm the potential of this material as a solar absorber, but also help to pave the way for more rapid advancement of research into ZnSnN\(_2\) in the future.

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