Growth of Epitaxial ZnSn\textsubscript{x}Ge\textsubscript{1−x}N\textsubscript{2} Alloys by MBE

Amanda M. Shing\textsuperscript{1}, Yulia Tolstova\textsuperscript{1}, Nathan S. Lewis\textsuperscript{2} & Harry A. Atwater\textsuperscript{3}

ZnSn\textsubscript{x}Ge\textsubscript{1−x}N\textsubscript{2} alloys are chemically miscible semiconductor compounds with potential application as earth-abundant alternatives to In\textsubscript{1−x}Ga\textsubscript{x}N. Preparation of ZnSn\textsubscript{x}Ge\textsubscript{1−x}N\textsubscript{2} thin-films by reactive RF sputter deposition yield low-mobility, nanocrystalline films. In contrast, the growth of ZnSn\textsubscript{x}Ge\textsubscript{1−x}N\textsubscript{2} films by molecular-beam epitaxy (MBE) on c-plane sapphire and GaN templates is described herein. Epitaxial films exhibited 3D growth on sapphire and 2D single-crystal quality on GaN, exhibiting films by molecular-beam epitaxy (MBE) on c-plane sapphire and GaN templates is described herein. Mobility differences potentially arise from strain or surface effects originating from growth techniques, or from differences in film thicknesses. In general, MBE growth has provided desired improvements in electronic mobility, epitaxy, and crystal quality that provide encouragement for the continued study of ZnSn\textsubscript{x}Ge\textsubscript{1−x}N\textsubscript{2} alloys.

In\textsubscript{1−x}Ga\textsubscript{x}N alloys are widely used in light-emitting diodes (LEDs) and sensors, because alloying enables tuning of the band-gap energy, \( E_g \), within the range set by the two binary compounds, InN (\( E_g = 0.69 \) eV) and GaN (\( E_g = 3.51 \) eV). The large (~10%) lattice mismatch between InN and GaN results in phase separation for In-rich alloys, limiting the ability of In\textsubscript{1−x}Ga\textsubscript{x}N alloys to cover the full visible spectrum, especially the green wavelength range that is important for efficient solar energy conversion. ZnSn\textsubscript{x}Ge\textsubscript{1−x}N\textsubscript{2} alloys are emerging nitride compounds with electronic structures similar to those of the well-characterized In\textsubscript{1−x}Ga\textsubscript{x}N alloys. ZnSn\textsubscript{x}Ge\textsubscript{1−x}N\textsubscript{2} alloys made by reactive RF sputtering have band gaps between 1.8–3.1 eV, which encompasses the visible spectrum, thereby suggesting potential applications as photovoltaic absorber materials, LEDs, or optical sensors. Sputtered ZnSn\textsubscript{x}Ge\textsubscript{1−x}N\textsubscript{2} alloys have also demonstrated stability against phase segregation throughout the alloy series, which constitutes a significant advantage relative to In\textsubscript{1−x}Ga\textsubscript{x}N alloys. Tunability of the structural and optoelectronic properties of the ZnSn\textsubscript{x}Ge\textsubscript{1−x}N\textsubscript{2} alloy series from 0 ≤ x ≤ 1 is a prerequisite for multi-color LEDs and high-efficiency multijunction solar cells. In addition, ZnSn\textsubscript{x}Ge\textsubscript{1−x}N\textsubscript{2} alloys are composed of relatively earth-abundant elements; specifically, the least abundant element in ZnSn\textsubscript{x}Ge\textsubscript{1−x}N\textsubscript{2} alloys is Ge (1.5 mg kg\(^{-1}\)), which is about six times more abundant in the Earth’s crust than In (0.25 mg kg\(^{-1}\)).

Sputtered ZnSn\textsubscript{x}Ge\textsubscript{1−x}N\textsubscript{2} films have exhibited low electronic mobilities\textsuperscript{6} and trap states from defects\textsuperscript{7}, hindering the development of high-performance ZnSn\textsubscript{x}Ge\textsubscript{1−x}N\textsubscript{2} devices based on this alloy series. Inferior electron transport, and the absence of room-temperature luminescence, may be due to the <200 nm crystallite sizes of the sputtered films, estimated by the Debye-Scherrer framework.\textsuperscript{[6]}

The lack of photoluminescence observed in the films, which were predicted to have direct band gaps by various calculation methods and experimentally generated Tauc plots, is also consistent with the presence of defects that prevent radiative recombination from the conduction band to the valence band in these materials. Annealing and sputtering at higher temperatures (>350 °C) have been explored as routes to larger grain sizes, but crystallites remained <200 nm.\textsuperscript{[6]}

To overcome the limitations of sputtered films, specifically to generate higher mobilities and radiative recombination yields, and to reduce defects and impurities, we have explored film growth by molecular beam epitaxy (MBE).

Plasma-assisted MBE growth of ZnSnN\textsubscript{2}, on cubic yttrium-doped zirconia substrates at 400 °C results in monoclinic ZnSnN\textsubscript{2}. Reflection high-energy electron diffraction (RHEED) and x-ray diffraction (XRD) patterns of
such ZnSnN₂ films indicated crystalline film growth; however, microscopic images of the film structure revealed
the presence of metal islands on the surface of the films.

We report herein the synthesis of ternary ZnSnN₂ and quaternary ZnSnₓGe₁−ₓN₂ films grown by MBE on

c-plane sapphire as well as on wurtzite-GaN templates on sapphire. The films have been characterized structur-
ally and optoelectronically using RHEED, XRD, transmission-electron microscopy (TEM), Raman spectroscopy,
ellipsometry, and Hall measurements. Fabrication details for MBE ZnSnₓGe₁−ₓN₂ films for 0 < x ≤ 1 are provided

in the Supplemental Information.

Figure 1 shows the XRD patterns obtained for ZnSnN₂ and for several compositions of ZnSnₓGe₁−ₓN₂ grown
via MBE on c-plane sapphire or GaN substrates. The exclusive observation of (002) ZnSnₓGe₁−ₓN₂ peaks and
their corresponding higher order reflections for all of the stoichiometries investigated indicated that the films
with wurtzite-derived structures were oriented to the substrate. The periodic Pendellösung oscillations on the
(002) peak resulted from films with uniform strain and sharp interfaces between the films and substrates⁹, and are
consistent with pseudomorphic growth and heteroepitaxy. Growth of ZnSnN₂ (ZnSnₓGe₁−ₓN₂) on sapphire gave
rise to weaker Pendellösung oscillations compared to ZnSnN₂ (ZnSnₓGe₁−ₓN₂) films grown on GaN, implying
rougher interfaces, arising from the ~20% lattice mismatch between sapphire and ZnSnN₂ and consistent with the
relatively small mismatch, <5%, between the GaN and ZnSnN₂ lattices¹⁰,¹¹.

RHEED patterns (Fig. 2a,d) for ZnSnN₂ and ZnSnₓGe₁−ₓN₂ films grown on GaN substrates via MBE pro-
vided further evidence of epitaxy, smooth interfaces, and lattice mismatch. The streaks apparent in the RHEED
images of films on GaN indicated that the films were macroscopically smooth, whereas RHEED patterns for films
grown on sapphire substrates (Figure S1) were characterized by intense spots indicative of three-dimensional
island growth¹²,¹³. This difference in growth mechanism is attributable to the corresponding lattice mismatch with
the substrate in each case. The relative mismatch between the substrate lattices and nitride alloys of varying Ge
content can be seen by a comparison of the RHEED patterns. The interplanar spacing of ZnSnN₂ at the [11–20]
azimuth is less matched to the GaN substrate spacing than to the ZnSnₓGe₁−ₓN₂ interplanar spacing (Fig. 2a,d).

Selected area diffraction (SAD) images (Fig. 2b,e) also illustrated the lattice mismatch between the nitride
films and GaN substrates. For ZnSnN₂, the SAD image showed a clear separation between the ZnSnN₂ reflec-
tions and the relatively brighter reflections from the GaN substrate, whereas the ZnSnₓGe₁−ₓN₂ reflections were
effectively coincident with the substrate peaks, implying lattice-matched films. The positions of the reflections
also indicated that the films were hexagon-on-hexagon aligned with the substrate¹⁴. The amorphous rings in the
ZnSnN₂ SAD background can be attributed to the epoxy applied to the sample. Diffraction spots are labeled for
the orthorhombic ZnSnₓGe₁−ₓN₂.

Figure 2c and f show high-resolution TEM (HRTEM) images of interfaces of ZnSnN₂ and ZnSnₓGe₁−ₓN₂ with GaN. Cross-sections exhibited few notable defects at the interface or throughout the films, and film surfaces
were specular, indicating continuous, smooth films, heteroepitaxy, and single-crystalline morphology. The vari-
ations in contrast apparent in the ZnSnN₂ and ZnSnₓGe₁−ₓN₂ reflections were effectively coincident with the substrate peaks, implying lattice-matched films. The positions of the reflections also indicated that the films were hexagon-on-hexagon aligned with the substrate¹⁴. The amorphous rings in the
ZnSnN₂ SAD background can be attributed to the epoxy applied to the sample. Diffraction spots are labeled for

SCIENTIFIC REPORTS | 7: 11990 | DOI:10.1038/s41598-017-12357-9
Although the positions of the (002) XRD peaks differed between MBE-grown and sputtered films, Raman spectroscopy revealed similar bonding within MBE films and sputtered films, respectively (Fig. 3b). The Raman spectra showed broad peaks at 270 cm\(^{-1}\), 650 cm\(^{-1}\), and 760 cm\(^{-1}\) for both sputtered and MBE-grown ZnSn\(_x\)Ge\(_{1-x}\)N\(_2\) films, reflecting the material congruence. Raman spectroscopy probes bond vibrations, with sharp peaks expected for defined, periodic bond vibrations, unlike amorphous solids that instead exhibit broad features. The broad ZnSn\(_x\)Ge\(_{1-x}\)N\(_2\) peaks indicate that the bond vibrations probed are not well ordered, representing non-periodicity in the lattice\(^{16}\) that may result from random cation positioning\(^{17-19}\). Studies of plasma-assisted vapor-liquid-solid
growth of ZnSnN$_2$ at 485 °C resulted in similarly broad Raman peaks, with the broad peaks attributed to imperfect lattice ordering$^{16}$ such as cation anti-site defects$^{18-20}$. Lattice-site disorder, point anti-site defects, and oxygen or other impurities may generate unwanted dopants or trap states not found in ideal computational predictions$^{17,20-22}$. Additionally, surface states, strain, and grain boundaries, especially of 3D films grown on sapphire, influence electronic properties by bending bands, breaking band degeneracies, and inducing mobility changes$^{22,23}$.

These imperfections may contribute to the difference in electronic properties between the nanocrystalline sputtered films and heteroepitaxial MBE films. Figure 4 shows the carrier concentrations and mobilities of the ZnSn$_x$Ge$_{1-x}$N$_2$ MBE films grown on sapphire compared to the properties of the sputtered alloys. Sputtered alloys display an average mobility of $\sim$2 cm$^2$ V$^{-1}$ s$^{-1}$ (Fig. 4b). Furthermore, their carrier concentrations decrease from degenerate ZnSn$_2$ at 25% atomic Sn to non-degenerate low-tin ZnSn$_x$Ge$_{1-x}$N$_2$. In contrast, epitaxial MBE films grown on sapphire showed degenerate carrier concentrations throughout the various compositions. Although high-tin-concentration MBE ZnSn$_x$Ge$_{1-x}$N$_2$ and ZnSnN$_2$ grown on sapphire exhibited a mobility of $\sim$18 cm$^2$ V$^{-1}$ s$^{-1}$, other compositions of MBE ZnSn$_x$Ge$_{1-x}$N$_2$ samples grown on sapphire still had mobilities of $<10$ cm$^2$ V$^{-1}$ s$^{-1}$.

Heteroepitaxial MBE films grown on GaN were probed for electronic mobility, but contributions ascribable to the GaN substrate did not allow measurement of the film properties. The GaN templates were $>1$ μm thick, whereas ZnSn$_x$Ge$_{1-x}$N$_2$ alloy films did not exceed 50 nm in thickness. Slow growth rate limited the ability to obtain sufficiently thick ZnSn$_x$Ge$_{1-x}$N$_2$ films to probe the bulk electronic properties of the 2D epitaxial films on GaN.

The epitaxial strain or surface contribution of the $<50$ nm thick MBE films on sapphire may be the cause of the ZnSn$_x$Ge$_{1-x}$N$_2$ degeneracy and mobility change. The ZnSn$_x$Ge$_{1-x}$N$_2$ carrier concentrations should decrease with increasing Ge content, in accord with the trend observed in the measured bulk carrier concentrations of sputtered films ($\sim1$ μm thick). The resulting degeneracy of the MBE-grown ZnSn$_x$Ge$_{1-x}$N$_2$ thin films, for which the limited MBE film thickness enables surface effects to dominate measurements relative to bulk properties, potentially arises from excess mobile carriers from surface states or surface oxides. High carrier populations reduce the
mobility, but the increased mobility of MBE films with increasing tin content (toward ZnSnN$_2$) may be attributed to the epitaxial strain, as strain can influence the carrier mobility and the observed ZnSn$_x$Ge$_{1-x}$N$_2$ strain increases with increasing tin content$^{14,24}$. Thus, strain and surface- state effects likely dominate the electronic results.

Even at the current growth temperature settings of 250 °C, the high mobilities of high-tin-concentration MBE ZnSn$_x$Ge$_{1-x}$N$_2$ on sapphire may have resulted from improved crystallinity or strain effects. However, the relatively low temperature of 250°C can limit the potential to obtain a perfectly ordered crystal. Sharp, well-defined Raman peaks have been observed from crystalline ZnGeN$_2$ needles and platelets grown at 750 °C and higher temperatures$^{18,19,25,26}$ suggesting that higher cation ordering might be achieved through the MBE growth of ZnSn$_x$Ge$_{1-x}$N$_2$ samples at higher temperatures than used herein, if thermal expansion coefficients allow for such on suitable substrates. Investigations utilizing higher temperature growth may reduce point defects and strain, with enhancement of optoelectronic properties, and enable the development of material suitable for use in high-performance devices.

In summary, heteroepitaxial MBE growth of ZnSn$_x$Ge$_{1-x}$N$_2$ films on c-plane sapphire and hexagonal GaN templates has yielded improved crystallinity and electronic mobilities of ZnSn$_x$Ge$_{1-x}$N$_2$ relative to sputtered films. The MBE films, while maintaining tunability and phase stability throughout the alloy series (0 ≤ x ≤ 1), form cohesive, 2D films on GaN. TEM showed that low-substrate-temperature (250°C) growth on GaN templates produced smooth, epitaxial, single-crystalline-quality films. Thicker films on GaN may allow electronic measurements of these improved 2D films. Growth at higher temperatures may further reduce point defects and enhance the optoelectronic properties, assisting the development of material for applications in high-performance semiconductor devices.

Data Availability. The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

References

1. Shon, J. W., Oh, J., Ueno, K., Kobayashi, A. & Fujioka, H. Fabrication of full-color InGaN-based light-emitting diodes on amorphous substrates by pulsed sputtering. *Scientific Reports*. 4, 5325 (2014).
2. El-Masyr, N. A., Piner, E. E., Liu, S. X. & Bedair, S. M. Phase separation in InGaN grown by metalorganic chemical vapor deposition. *Appl. Phys. Lett.* 72(1), 40 (1998).
3. Coronel, N. C., Lahourcade, L., Delaney, K. T., Shing, A. M. & Atwater, H. A. Earth-abundant ZnSn$_x$Ge$_{1-x}$N$_2$ alloys as potential photovoltaic absorber materials. *Proceedings of the 58th IEEE Photovoltaics Specialists Conference (PVSC)*. 093204 (2012).
4. Deng, Z. et al. A novel wavelength-adjusting method in InGaN-based light emitting diodes. *Scientific Reports*. 3, 3389 (2013).
5. Haynes, W. M. ed., *CRC Handbook of Chemistry and Physics, 95th Edition*. Internet Version, CRC Press/Taylor and Francis, Florida, p.14–15 (2015).
6. Lahourcade, L. et al. Structural and optoelectronic characterization of RF sputtered ZnSnN$_2$. *Adv. Mater.* 25, 2562 (2013).
7. Shing, A. M., Coronel, N. C., Lewis, N. S. & Atwater, H. A. Semiconductor ZnSn$_x$Ge$_{1-x}$N$_2$ alloys prepared by reactive radio-frequency sputtering. *AIP Mat.* 3, 076104 (2013).
8. Feldberg, N. et al. Growth of ZnSnN$_2$, by Molecular Beam Epitaxy. *J. Elect. Mater.* 43(4), p884 (2014).
9. Hudaie, M. K. et al. BaTiO$_3$ Integration with nanostructured epitaxial (100), (110), and (111) germanium for multifunctional devices. *ACS Appl. Mater. Interf.* 5(21), 11446–11452 (2013).
10. Punya, A., Paudel, T. R. & Lambrecht, W. R. L. Electronic and lattice dynamical properties of IV-N$_2$ semiconductors. *Phys. Stat. Sol. C*. 8, 2492 (2011).
11. Punya, A., Lambrecht, W. R. L. & van Schilfgaarde, M. Quasiparticle band structure of Zn-IV-N$_2$ compounds. *Phys. Rev. B*. 84, 165204 (2011).
12. Tang, E., Parker, T., Wang, G. C. & Lu, T. M. Surface texture evolution of polycrystalline and nanostructured films: RHEED surface pole figure analysis. *J. Phys. D: Appl. Phys.* 40, R427–R439 (2007).
13. Proessdorf, A., Hanke, M., Jenichen, B., Braun, W. & Riechert, H. Volmer-Weber growth of AlSb on Si(111). *App. Phys. Lett.* 102, 041601 (2013).
14. Wang, W. L. et al. Nitridation effect of the α-Al2O3 substrate on the quality of the GaN films grown by pulsed laser deposition. *RSC Adv.* 4, 39651 (2014).
15. Zhou, D. & Uscher, B. F. Deviation of the AlGaAs lattice constant from Vegard’s law. *J. Phys. D: Appl. Phys.* 34, 1461–1465 (2001).
16. Vienoic, R. et al. Prospective investigations of orthorhombic ZnGeN2: synthesis, lattice dynamics and optical properties. *Mat. Sci. and Engineering B*. 82, 45–49 (2001).
17. Quayle, P. C. et al. Charge-neutral disorder and polytypes in heterovalent wurzite-based ternary semiconductors: The importance of the octet rule. *Phys. Rev. B*. 91, 205207 (2015).
18. Blanton, E. W. et al. Raman study of the vibrational modes in ZnGeN$_2$. *J. Appl. Phys.* 121, 055704 (2017).
19. Blanton, E. W., He, K., Shan, J. & Kash, K. Characterization and control of ZnGeN$_2$ cation lattice ordering. *J. Crystal Growth* 461, p38–45 (2017).
20. Feldberg, N. et al. Growth, disorder, and physical properties of ZnSnN$_2$. *Appl. Phys. Lett.* 103, 042109 (2013).
21. Zhang, Z., Hurmi, C. A., Arehart, A. K., Speck, J. S. & Ringel, S. A. Influence of V/III growth flux ratio on trap states in m-plane GaN grown by ammonia-based molecular beam epitaxy. *Appl. Phys. Lett.* 101, 152104 (2012).
22. Schubert, E. F. Doping in III-V Semiconductors. *Rensselaer Polytechnic Institute, Troy, NY USA* (1993).
23. Sun, Y. et al. Fabrication of full-color InGaN-based light-emitting diodes on hexagonal GaN templates. *J. Phys. D: Appl. Phys.* 40, 055704 (2017).
24. Chau, M., Sun, Y., Aghoram, U. & Thompson, S. E. Strain: A solution for higher carrier mobility in nanoscale MOSFETs. *Ann. Rev. Mat. Res.* 39, 203–229 (2009).
25. Peshek, T. J., Paudel, T. R., Kash, K. & Lambrecht, W. R. L. Vibrational modes in ZnGeN$_2$: Raman study and theory. *Phys. Rev. B*. 77, 235213 (2008).
26. Peshek, T. J., Wang, S. L., Angus, J. C. & Kash, K. Growth and Raman spectroscopy of single crystal ZnGeN$_2$ rods grown from a molten Zn/Ge alloy. *Mater. Res. Soc. Symp. Proc.* 1040, Q01–01 (2008).
27. Doppalapudi, D., Ilipoulos, E., Basu, S. N. & Moustakas, T. D. Epitaxial growth of gallium nitride thin films on A-Plane sapphire by molecular beam epitaxy. *J. Appl. Phys.* 85(7), 3582 (2009).
28. Sarney, W. L. Understanding transmission electron microscopy diffraction patterns obtained from infrared semiconductor materials. *ARL-TR-3128* (2007).
Acknowledgements
We gratefully acknowledge support from the Dow Chemical Company under the earth-abundant semiconductor project, the NSF-DOE Quantum Energy and Sustainable Solar Technologies Engineering Research Center, and the Molecular Materials Resource Center of the Beckman Institute at Caltech. We also acknowledge the Joint Center for Artificial Photosynthesis and the Molecular Materials Resource Center of the Beckman Institute at Caltech for instrument access. The authors thank Bruce Brunschwig and Kimberly Papadantonakis for guidance, and Carol Garland for TEM assistance.

Author Contributions
A.S. performed fabrication and measurements. Y.T. provided consultation. N.S.L. and H.A.A. were the PIs. All authors reviewed the manuscript.

Additional Information
Supplementary information accompanies this paper at https://doi.org/10.1038/s41598-017-12357-9.

Competing Interests: The authors declare that they have no competing interests.

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