Role of cation disorder in carrier localization and density of states in ZnGeN₂

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Abstract

Cation site disorder provides a degree of freedom in the growth of ternary nitrides for tuning the technologically relevant properties of a material system. For example, the band gap of ZnGeN₂ changes when the ordering of the structure deviates from that of its ground state. By combining the perspectives of carrier localization and defect states, we analyze the impact of different degrees of disordering on electronic properties in ZnGeN₂, addressing a gap in current studies which focus on dilute or fully disordered systems. The present study demonstrates changes in the density of states and localization of carriers in ZnGeN₂ calculated using band gap-corrected density functional theory and hybrid calculations on partially disordered supercells generated using the Monte Carlo method. We use localization and density of states to discuss the ill-defined nature of a band gap in a disordered material, comparing multiple definitions of the energy gap in the context of theory and experiment. Decreasing the order parameter results in a large reduction of the band gap in disordered cases. The reduction in band gap is due in part to isolated, localized states that form above the valence band continuum and are associated with nitrogen coordinated by more zinc than germanium. The prevalence of defect states in all but the perfectly ordered structure creates challenges for incorporating disordered ZnGeN₂ into optical devices, but the localization associated with these defects provides insight into mechanisms of electron/hole recombination in the material.

Keywords

site disorder, II–IV–V₂, nitrides, localization

1 Introduction

Site disorder, the replacement of chemical species on a fixed crystallographic lattice, has recently grown in interest across semiconductor research areas as a means to control optoelectronic properties. While site disorder—referred to from here on simply as disorder or degree of order—has notably been studied as a mechanism for managing properties in chalcogenide transistor and solar cell materials for some time [1–5], its application to such a vast array of ternary and multinary nitrides and phosphides is a more recent development [6,7]. Specifically, site disorder has been investigated as a means of lowering band gaps to ideal ranges for targeted applications. For instance, in ZnGeN₂, cation disorder may be able to reduce the band gap from the calculated [8–10] and measured [11–14] 3.0–3.6 eV to the 2.1–2.5 eV range desired for amber to green wavelengths in a light emitting diode (LED), often referred to as the green gap [15]. Disordered ZnGeN₂, which is lattice matched to GaN, may be desirable as a replacement for high In content InₓGa_{1−x}N, which suffers from a miscibility gap and large lattice mismatch with GaN in...
heterostructure devices.\textsuperscript{11,16–18} To investigate the impact of disorder on the band gap of ZnGeN\textsubscript{2}, we utilize disordered structures generated from Monte Carlo simulation in large supercells of 1,024 atoms.\textsuperscript{19} These structure models incorporate site disorder consisting of cation antisite pairs, which numerous defect studies have highlighted as the dominant native defects in ZnGeN\textsubscript{2}.\textsuperscript{8,10,20–25} In contrast to a dilute defect model, site disorder accounts for the interaction of Zn\textsubscript{Ge} and Ge\textsubscript{Zn} present in high concentrations representative of materials grown under non-equilibrium conditions. This study separates the impact of site disorder explicitly from stoichiometry, non-native defects and crystalline quality, all known to further influence optical and electronic properties of interest. To illustrate the ordered system, Figure 1 provides the crystal structure, reciprocal space map and band structure.

Figure 1: a) Ordered ground state crystal structure of ZnGeN\textsubscript{2} b) reciprocal space map of ZnGeN\textsubscript{2} \((b_3 > b_2 > b_1)\) c) band structure and DOS of ordered ZnGeN\textsubscript{2}.

Because disorder adds nuance to how a band gap is measured and calculated, when the term ‘band gap’ is used in this work, we refer to the energy difference between the highest occupied and lowest unoccupied states unless specified otherwise. However, this energy difference is not the only viable definition as will be discussed throughout this Letter. In a dilute defect picture, defects do not interact and additional occupied or unoccupied states are viewed as defect states within an otherwise unchanged band gap. Historically, the theoretical discussion of differentiating band gaps and defect states has been held in this context of dilute point defects\textsuperscript{26–28} or in fully random systems,\textsuperscript{29–31} but misses systems with intermediate degrees of order with a few notable exceptions.\textsuperscript{32,33} In materials with both dilute and non-dilute defects, Urbach energy\textsuperscript{34} describes how the optical absorption of a semiconductor tails off exponentially\textsuperscript{35–37} at energies below the band gap due to transitions from within bands to defect states in the energy gap and at even lower energies directly between defect states in the gap.\textsuperscript{38–40} Urbach tails are evident in Tauc\textsuperscript{41} analyses of thin films as well as in bulk systems, where variations of the Kubelka-Munk method\textsuperscript{42,43} are often used to interpret band gaps. These bulk and film methods frequently vary in interpretation of an optical band gap based on differences in their assumptions.\textsuperscript{44–46}

The difficulty in properly defining a band gap stems to a large extent from the fact that the band gap is used as a scalar metric to address a multitude of related but distinct phenomena and questions, either in experimental measurements or theoretical computation, and in various fields of research. Fundamentally, the band gap is the difference between ionization potential (electron removal energy) and electron affinity (electron addition energy). As such, it is not an optical or even excited-state property. However, most experimental approaches for band gap measurements are based on optical spectroscopy, as mentioned above. In such approaches, it is difficult to account for nontrivial physical mechanisms that modify the shape of the spectra from which the band gap value is deduced. For example, calculations using the Bethe-Salpeter equation (e.g.,\textsuperscript{47}) show that excitonic effects (electron-hole interaction) tend to redshift the dielectric response above the ab-
sorption threshold compared to the independent particle approximation, and enable sub-band gap excitations (exciton binding energy). Similarly, the variation of oscillator strength resulting from wavefunction symmetries (direct vs indirect, allowed vs forbidden transitions) is often not precisely known, but can affect the spectra in ways that are not fully captured by model parameters used, e.g. in Tauc analysis. Furthermore, there is a fundamental difference between optical transition energies in absorption and emission, i.e., the Stokes shift, which is non-radiatively converted to heat. These effects add significant uncertainties to band gap determination in all but the most thoroughly characterized systems (e.g., GaAs, Cu$_2$O, ZnO, GaN). These uncertainties are further exacerbated in disordered materials, where one must make additional assumptions or define models to discriminate between defect and continuum states. This work addresses these challenges from the perspective of large-scale supercell electronic structure calculations in disordered ZnGeN$_2$.

This Letter builds on results from previous work in which disordered ZnGeN$_2$ structures in 1,024 atom supercells were generated using Monte Carlo (MC) simulations, providing atomic structure models with systematic variation of the order parameters across the order-disorder transition. The degree of disorder is controlled by an effective temperature describing the site ordering of a cation configuration within a crystalline system. This model includes the configurational entropy contribution to the free energy of the system, but excludes factors such as decomposition reactions which dominate at higher actual synthesis or process temperatures. Thus, the effective temperature provides a link to map site disorder between MC simulations and non-equilibrium synthesis. We focus in this letter on four effective temperatures representing four separate regimes of ordering: 2,000 K and 2,500 K structures include the ground state, ordered configuration as well as mostly ordered structures with few antisites per cell. 3,000 K structures are disordered, but not random and 5,000 K structures are highly disordered but still not random. The level of disorder between 3,000 K and 5,000 K is best understood through differences in electronic properties as discussed later in this Letter. Truly random configurations are not realized below effective temperatures of approximately 400,000 K.

Both long- (LRO) and short- (SRO) range order parameters—measures of Wyckoff site occupancy and nitrogen coordination, respectively—indicate full ordering at low effective temperatures. Both parameters slightly decrease from their ordered values of one when individual defect pairs (site exchange of Zn and Ge) are introduced in the supercells with increasing effective temperature. LRO and SRO parameters then drop abruptly at the transition of 2,525 K. Above the transition temperature, the order parameters taper from small values to their fully disordered extremes at an infinite effective temperature, 0 for LRO and 0.375 for SRO. The transition in order parameters covers a wider range of accessible SRO than LRO parameters, but the transition occurs in both length scales simultaneously (LRO and SRO are strongly coupled). This behavior contrasts with the ZnSnN$_2$ system, where SRO can exist without LRO.

Here, we investigate the electronic structure consequences from disorder in ZnGeN$_2$ due to non-equilibrium synthesis. We use non-selfconsistent hybrid functional calculations to enable analysis of the density of states (DOS) and carrier localization as a function of LRO and SRO. The band gap of 3.5 eV of ordered ZnGeN$_2$ decreases with increasing degree of disorder and eventually closes for strongly disordered configurations. Calculated inverse participation ratios (IPR) allow us to assess the localization of states in this range of disordered ZnGeN$_2$ and discuss how localization impacts our interpretation of a band gap as well as device characteristics. By comparing the DOS of ZnGeN$_2$ structures from band gap corrected calculations in 1,024 atom cells, we analyze the effect of disorder on the band gap of the system.
2 Disorder and Density of States

Paying special attention to the role of localized states in determining the value of the band gap, we assess what a band gap means in the context of disordered solids. We use the IPR here as a measure of the localization of a state at a given energy as shown in Equation [1] where the IPR indicates that a given state at a given energy is localized on average on one out of IPR atoms. An IPR of 1 indicates perfect delocalization and a value of 1,024 indicates exclusive localization on a single atom within the supercell.

\[ IPR(E) = \frac{N_A \sum_i p_i(E)^2}{\left[ \sum_i p_i(E) \right]^2} \]  

(1)

\(N_A\) is the number of atoms in a supercell and \(p_i(E)\), the local density of states (LDOS) projected on each atom \(i\) as a function of energy \(E\).

To relate DOS, IPR and ordering, we employ the fraction of nitrogen coordinated by exactly two Ge and two Zn \((\text{Zn}_2\text{Ge}_2\text{ motif fraction})\) as a measure of SRO, as well as the Bragg-Williams LRO parameter, \(\eta\):

\[ \eta = r_{\text{Zn}} + r_{\text{Ge}} - 1 \]  

(2)

where \(r_{\text{Zn}}\) (\(r_{\text{Ge}}\)) is the fraction of Zn (Ge) on Zn (Ge) ground state sites.

Figure 2a) shows the total DOS of \(\text{ZnGeN}_2\) configurations grouped by their effective temperature and corresponding range of the LRO parameter. To access the effect of disorder on valence (occupied) and conduction (unoccupied) band states individually, we determined the potential alignment of the disordered structures relative to the ground state (see Supplemental Information). Using a 10 meV increment in data points, defect states appear in the DOS of disordered structures represented by allowed (non-gray) bands separated from the band edges by forbidden (gray) states. Up to \(T_{\text{eff}} = 2,000\) K, the MC simulation largely retains the ordered ground state structure, but is starting to develop some \(\text{ZnGe}\) and \(\text{GeZn}\) antisite configurations. Between 2,000 K and 2,500 K, the concentration of antisite defects increases with a concomitant decrease in the band gap by about 0.7 eV. Just above 2,500 K, the system undergoes an order-disorder phase transition, assuming a state with both long- and short-range disorder. It is important to note, however, that the system retains a significant degree of non-random LRO and SRO up to much higher effective temperatures. As seen in Figure 2 comparing \(T_{\text{eff}} = 2,500\) K and 3,000 K, the phase transition is accompanied by a large reduction of the order parameter \(\eta\) and an additional band gap reduction of about 1.1 eV. The average band gap then decreases by 1.0 eV from 3,000 K to 5,000 K as the system tends toward metallic for mostly disordered structures.

The decrease in band gap with disorder comes from movement in both the conduction band minimum (CBM) and valence band maximum (VBM); replacing a single pair of cations in the ground state structure with an antisite pair raises the Fermi level by 200-500 meV depending on the proximity of the pair. The Fermi level in this context is taken as the midpoint between the energy levels of the highest occupied and lowest unoccupied states and lies just below 2 eV on the energy scale of Figure 2. Further decreasing the degree of order does not significantly impact the Fermi level beyond the initial shift until the band gap effectively closes. Without contributions from non-native, non-antisite defects and stoichiometry, site disorder alone drastically changes the band gap of \(\text{ZnGeN}_2\) over a 3.5 eV range.

Figure 2b) provides the corresponding IPR of the DOS from Figure 2a) allowing a look at the localization of states. IPR is undefined where the DOS is zero (in the band gap). Like the DOS, IPR are discretized with a step size of 10 meV. The scaling of the color bar representing IPR in Figure 2b) highlights the most localized states, the movement of which can be tracked across the band gap (gray region). These localized states remain relatively constant in energy relative to the VBM but increase in quantity and density with decreasing degree of order. The localized, mid-gap states indicate a high probability of non-radiative recombination centers in disordered \(\text{ZnGeN}_2\), which would
coincide with lower conversion efficiencies in LEDs.

While configurations with both small and large (disordered) fractions of antisites have states with relatively high IPRs, one identifying factor for interpreting band gaps is the continuity of these localized states as a function of energy. Individual antisite pairs result in defect states that can clearly be associated with either the conduction or valence band edge; however, this clarity is lost as the gap closes and high IPR states spread throughout the gap. The high IPR values in the gap, close to the valence band edge for dilute defect structures are strongly correlated with the \( \text{Zn}_1\text{Ge}_1 \) motif centered on nitrogen whereas the \( \text{Zn}_1\text{Ge}_3 \) and \( \text{Zn}_2\text{Ge}_2 \) motifs contribute significantly less to the IPR. \( \text{Zn}_1\text{Ge}_0 \) and \( \text{Zn}_0\text{Ge}_4 \) motifs only appear in very limited cases below 3,000 K. At and above 2,500 K, some conduction band states separate from the continuum in energy. The highest contributor to the IPR in these bands is mostly Zn with few instances of highest contribution from Ge. The participation of the cations independent of their first and second shell coordination contrasts separated valence bands where nitrogen and its first shell coordination play the largest role. The IPR in these separated conduction band states reaches a maximum of 20, significantly less than the maximum of 200 for elevated valence band states.

Until this point, we have treated the band gap of a system simply as the difference in energy between the highest occupied and lowest unoccupied states as this definition is typically effective in ordered systems. This definition (labeled “IPR unlimited” in Figure 3) often results in the inclusion of defect states as part of the band continuum when in reality, these isolated states hinder electronic transport and can be considered defect states inside the band gap. In this context, “bands” are typically assumed to consist of delocalized states, but Figure 2b) shows this is not necessarily the case. The IPR of a system is large for defect states and shrinks for states in the band continuum thus providing a measure of the extent to which a state acts as a defect. Using this information, we define an alternative band gap where only states below a certain IPR threshold are allowed when taking the highest occupied and lowest unoccupied states. A high IPR cutoff (or no cutoff in the case of unlimited IPR) yields the smallest gaps, whereas a low cutoff considers only continuous conduction and valence band states and results in the largest gaps. In the ground state structure, the IPR at the VBM and CBM are 1.54 and 1.29, respectively. IPR limits of 5 and 10 are used in Figure 3 to give mid- and low- IPR cutoff examples. Providing too low of a cutoff excludes valid continuum states giving unphysical band gaps larger than that of the ground state structure. In Figure 3 these band gaps are plotted over the full range of the LRO (\( 0 < \eta < 1 \)) and SRO (\( 0.375 < \text{Zn}_2\text{Ge}_2 < 1 \)) parameters and amber/green bands are drawn at their relevant energies for comparison of calculated band gaps in this region.

Interpreting band gaps both as calculated and after excluding states with an IPR above a certain threshold allows us to determine the contribution of those localized states to the electronic structure and where they cluster in en-
Figure 3: Band gap energy as a function of a) long-range order and b) short-range order for three interpretations of the band gap. IPR unlimited: difference in energy between highest occupied and lowest unoccupied molecular orbitals. IPR $< 10$ (5): States with IPR $> 10$ (5) are excluded from the band gap determination.

Energy. In Figure 3, the unlimited IPR definition shows how small fractions of defects drastically reduce the band gap, while ignoring highly localized states shows that this significant change is largely—but not exclusively—due to these isolated defects. In the band gap interpretations that do not consider highly localized states (e.g., IPR $< 10$ and IPR $< 5$), the band gap still reduces by roughly 2 eV, but this reduction occurs through continuous bands in energy in disordered configurations rather than through defect states in structures with near-perfect ordering.

Taking band gaps as the difference between highest occupied and lowest unoccupied states yields a change from 3.5 eV to 2.0 eV with only a drop in LRO parameter from $\eta = 1.00$ to $\eta = 0.94$. For low order parameters, the difference between the unlimited gaps and gaps excluding states with IPR $> 5$ is again significant. The IPR limitation places the gap in the amber/green region of the visible spectrum with some trend toward higher band gap with higher SRO parameter per Figure 3b). For largely disordered structures, this sizable transition creates very small band gaps less than 1.6 eV for $\eta \leq 0.20$, a much larger change in band gap with ordering than predicted for the more researched Cu$_2$ZnSnS (CZTS) system.

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When these structures are fully random (i.e., at infinite effective temperature), the band gaps consistently drop to zero for the unlimited definition and remain undefined for the cases with limited IPR.

Though the supercell size of structures used for the present analysis is large for typical DFT calculations (and especially so for band gap corrected electronic structure calculations), it is still limited in capturing the statistics of configurational disorder, particularly in the dilute defect limit (low effective temperature). The localization of these states in structures with small fractions of defects and the impact of the defects’ spatial proximity were studied by Skachkov et al.

These mid-gap states isolated in energy are generally accepted as detrimental to optoelectronic properties by decreasing the quantity of carriers collected, reducing the lifetimes of those carriers or inhibiting radiation of a photon. However, at higher defect concentrations, where defect bands widen in energy as in largely disordered supercells in Figure 2b), conflicting theories exist as to the impact of defect density on the relative rate of non-radiative recombination.

In one theory, Luque et al. directly connect non-radiative Shockley-Read-Hall recombination to the localization caused by a low density or irregularity of impurities within a lattice, but see a reduction in non-radiative recombination as defect density increases above a certain threshold. In this theory, lower densities of defects correspond to more spatially
isolated and therefore localized defects and spatially connected states exhibit more benign electronic properties. However, gap states in 2(b) show a comparable maximum IPR for every structure other than the ground state, independent of the degree of disorder of those configurations. These comparable degrees of localization independent of defect density align better with prevalent studies in the InGaN$_2$ system. In InGaN$_2$ and similar III-V alloys, higher defect densities and deep gap states cause higher rates of non-radiative recombination. Based on the high degree of localization in disordered configurations, this latter theory of higher defect densities negatively impacting radiative recombination applies to ZnGeN$_2$ as well.

3 Conclusion

In this work we examined the effect of cation disorder on the density and localization of electronic states in ZnGeN$_2$. From non-dilute, disordered, but non-random structures with a significant degree of SRO, we calculated the DOS and the IPR of the material as a function of LRO and SRO, extracting band gaps as a function of both order parameters. We discussed the problem of defining the band gap in disordered materials and the ambiguities associated with the differentiation between defects and band states. While the topic deserves further discussion in the community, we used the IPR as a variable threshold for this separation.

The band gap of the system decreases significantly with decreasing degree of order from 3.5 eV for an ordered system to effectively 0 eV for strongly disordered systems. This sizable change in the gap raises the question of how we differentiate band gaps and defect levels in disordered solids as the gap-closing states are highly localized. To address this question, we evaluated the band gaps as a function of a localization threshold above which states are classified as defect rather than band states. Localized, occupied states are caused by N with Zn-rich coordination. Isolated conduction band states attributed to cations are much less localized and occur independent of the cations’ second shell coordination environment. Our findings in ZnGeN$_2$ show a strong tendency for localized defect states to form at all order parameters other than the ground state, which could detrimentally impact carrier recombination in a ZnGeN$_2$-based device. This result indicates that SRO is important for inhibiting carrier localization, which corroborates recent findings in ZnSnN$_2$:ZnO with perfect SRO. Whereas in ZnSnN$_2$:ZnO, this perfect SRO phase can exist with long-range disorder, the direct relationship between SRO and LRO in ZnGeN$_2$ means that both SRO and LRO are needed to minimize localization and non-radiative recombination in this system.

4 Electronic structure calculation methods

Data presented in this Letter utilize the atomic configurations of to predict electronic structure properties as a function of the order parameter and effective temperature. In Figure the electronic structure and density of states of ZnGeN$_2$ were calculated in density functional theory (DFT) with band edge corrections to match the band gap from GW calculations (3.63 eV) and plotted using pymatgen. To relax the lattice parameters, volume and ion positions of the 1,024 atom configurations from MC simulations, we used the generalized gradient approximation (GGA), Perdew-Burke-Ernzerhof (PBE) type. Due to the large size of the supercells, a single k-point (1x1x1 mesh) sufficed for the relaxation using the gamma-point-only version of the Vienna Ab-initio Simulation Package (VASP). These calculations rely on Kresse-Joubert projector augmented wave datasets with pseudopotentials from VASP version 4.6 (i.e., Ge_d, N_s and Zn). The soft pseudopotential, N_s, allows for a low energy cutoff of 380 eV that benefits the feasibility of calculations using large supercells. Each supercell achieved convergence when the difference in energy between steps of the ionic relaxation dropped below 10$^{-5}$ eV and forces below 0.02 eV Å$^{-1}$ on each atom. These calculations used a Coulomb potential, $U - J = 6$ eV, applied
to the Zn d orbital following the Dudarev approach.\textsuperscript{[70]}

The large size of the supercells precludes the possibility of applying the GW approach\textsuperscript{[71]} for each structure. In place of GW methods, the DOS and IPR of relaxed structures were calculated using a parameterized single-shot hybrid functional with an additional Coulomb potential \( \text{V}_{\text{SSH+V}} \) of -1.5 eV (comparable to a \( U \) parameter of +3 eV) applied to Zn d orbitals.\textsuperscript{[72]}

The single-shot functional avoids the computationally expensive iteration to self-consistency of the hybrid functional Hamiltonian by holding the initial wavefunctions of the DFT+U calculation fixed.\textsuperscript{[72]} This non-self consistent approach does not reorient band positions from the prior DFT+U step so in cases where DFT+U-which drastically underestimates band gaps-results in no band gap, an additional step was run using VASP’s “none” algorithm to renumber bands. This extra step was needed for most 5,000 K configurations and leads to larger uncertainty in band gaps under 1 eV than other gaps presented in this Letter. The Hartree-Fock exchange mixing parameter of the SSH+V functional was set to 0.19 and screening parameter to 0 for all structures. These parameters were fitted to replicate the total DOS produced by GW calculations for the ground state structure with a band gap of 3.5 eV calculated in SSH+V.

To align potentials for the purpose of comparing the DOS and IPR of various disordered configurations on a common energy axis, a potential alignment was performed for the volume relaxed supercells, as described further in the Supplemental Information. Disordered cells are slightly larger than the ground state structure with a maximum difference in volume of 0.9% for the most disordered supercells described in this study compared to the ground state supercell.

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**Supporting Information Available**

Tabulated band gaps and maximum IPR values used in figures, averaged DOS for each effective temperature simulated and potential alignment used for disordered ZnGeN\(_2\).

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