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Characterization and control of $ZnGeN_2$ cation lattice ordering

Eric W. Blanton*, Keliang He, Jie Shan, Kathleen Kash

Department of Physics, Case Western Reserve University, Cleveland, OH 44106, United States

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ABSTRACT

$ZnGeN_2$ and other heterovalent ternary semiconductors have important potential applications in optoelectronics, but ordering of the cation sublattice, which can affect the band gap, lattice parameters, and phonons, is not yet well understood. Here the effects of growth and processing conditions on the ordering of the $ZnGeN_2$ cation sublattice were investigated using x-ray diffraction and Raman spectroscopy. Polycrystalline $ZnGeN_2$ was grown by exposing solid Ge to Zn and NH_3 vapors at temperatures between 758 °C and 914 °C. Crystallites tended to be rod-shaped, with growth rates higher along the *c*-axis. The degree of ordering, from disordered, wurtzite-like x-ray diffraction spectra to orthorhombic, with space group $Pna2_1$, increased with increasing growth temperature, as evidenced by the appearance of superstructure peaks and peak splittings in the diffraction patterns. Annealing disordered, low-temperature-grown $ZnGeN_2$ at 850 °C resulted in increased cation ordering. Growth of $ZnGeN_2$ on a liquid Sn–Ge–Zn alloy at 758 °C showed an increase in the tendency for cation ordering at a lower growth temperature, and resulted in hexagonal platelet-shaped crystals. The trends shown here may help to guide understanding of the synthesis and characterization of other heterovalent ternary nitride semiconductors as well as $ZnGeN_2$.

1. Introduction

For heterovalent ternary semiconductors the cation or anion sublattice of a wurtzite or zincblende binary semiconductor is replaced by an ordered sublattice of two different atom types such that the average number of valence electrons stays the same. These semiconductors often have properties similar to those of their parent binary compounds. For example, in $ZnGeN_2$ the Ga sublattice of GaN is replaced with equal numbers of Zn and Ge atoms, arranged so that in the lowest enthalpy state each N atom is bound to two Zn and two Ge atoms, and hence the average number of valence electrons remains the same; $ZnGeN_2$ is predicted to have a band gap within 100–200 meV, and lattice spacings within approximately 1–2%, of those of GaN [1]. However, the heterovalent ternaries also have interesting and potentially useful differences in comparison to the binaries. Because of the reduced symmetry, heterovalent ternary semiconductors can have high nonlinear optical coefficients [2]. Their more complicated lattices offer more opportunities for doping strategies, and defect and band structure engineering [2]. Furthermore, the degree of ordering on the cation sublattice can be used as a tuning parameter since it can change the optical properties, vibrational properties, and lattice parameters. For example, one experimental report found that the band gap of $ZnSnP_2$ changed by 0.3 eV when the ordering parameter was changed [3]. In that study chalcopyrite ordering was confirmed by the appearance of sphalerite-disallowed superstructure reflections. The greater flexibility of choice in materials provides additional opportunities. For example, $ZnSnN_2$, composed entirely of abundant elements, might replace InN or $Ga_{1-x}In_xN_2$ in some applications.

1.1. Cation sublattice ordering

The nature of disorder in the heterovalent ternary semiconductors is of both fundamental and practical interest. However, it is not yet well understood. One model for disorder assumes the random placement of atoms on the mixed cation sublattice. In this model there are many instances where local charge neutrality is disrupted; the so-called octet rule is thus violated [4]. These defects disrupt the electronic structure of the material, sometimes substantially reducing the band gap. Recent theoretical work on $ZnSnN_2$ predicts that for random placement of Zn and Sn atoms on the cation sublattice, the band gap can be lower than that for the ordered $Pna2_1$ by more than 1 eV [5]. The band gap disappears altogether for the space group $Pm31$, for which the cation sublattice consists entirely of octet rule violations—each nitrogen atom is bound to either three Zn atoms and one Sn atom, or vice versa [1].

There is another model for disorder on the cation sublattice that does not produce octet rule violations. In $ZnGeN_2$ and other wurtzite-based heterovalent ternary semiconductors, there are two ways of ordering the cation lattice that preserve the octet rule. One configura-

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* Corresponding author.
E-mail address: ewb7@case.edu (E.W. Blanton).

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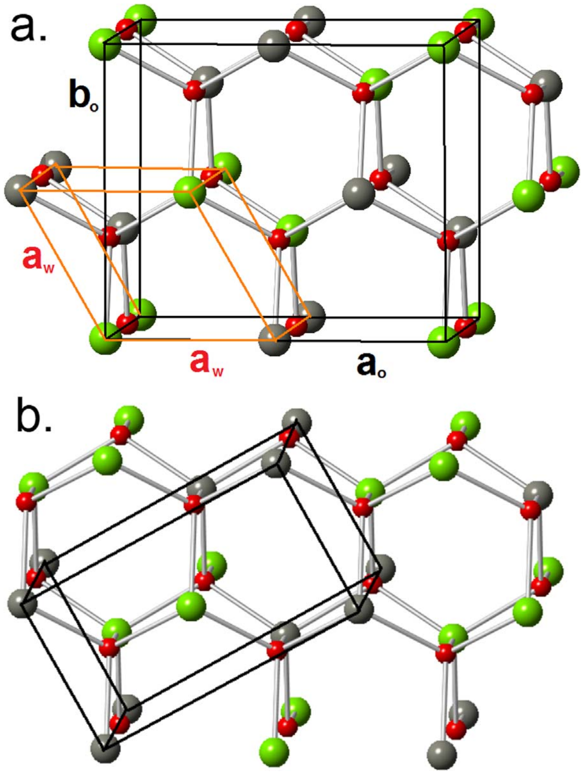

Fig. 1. (a) The unit cell of the orthorhombic $Pna2_1$ structure and its relation to the wurtzite unit cell. Red spheres are nitrogen, green spheres are germanium, and grey spheres are zinc. (b) The alternate ordering arrangement structure with space group $Pmc2_1$. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this paper.)

tion has the space group $Pna2_1$, shown Fig. 1a. The unit cell has sixteen atoms instead of four as for wurtzite, and the symmetry is orthorhombic [6]. The other way of ordering has the space group $Pmc2_1$ and an eight-atom unit cell [7] depicted in Fig. 1b. It has been shown that by randomly stacking $Pna2_1$- and $Pmc2_1$-like layers in the crystal's y direction, an effectively disordered structure is formed without producing any octet-rule violations [1]. This alternative model of cation disorder could explain why $ZnSnN_2$ grown by Quayle et al. is observed to be disordered, as evidenced by XRD, but also has a band gap, measured by photoluminescence excitation spectroscopy and by photoluminescence spectroscopy, that is consistent with that predicted for perfectly ordered $ZnSnN_2$ [1,8]. Similarly, there are two ways of ordering zincblende-based heterovalent ternary compounds, and a similar model of disorder has been presented for these materials [9,10].

1.2. Detection of ordering

The x-ray diffraction (XRD) and Raman spectroscopy measurements used in the present study can differentiate between ordered and disordered material, but not whether the disorder obeys or violates the octet rule.

Ordering of heterovalent ternary semiconductors is usually detected through XRD. For ternary semiconductors derived from both zincblende and wurtzite lattices, there is often a lattice distortion associated with the cation lattice ordering. In chalcopyrite structures $\frac{c}{a}$ can deviate from the zincblende value of 2 [11]. In wurtzite-derived orthorhombic structures with space group $Pna2_1$, the a parameter increases and the b parameter decreases, causing $\frac{a}{b}$ to become greater than the ideal wurtzite value of $\frac{2\sqrt{3}}{3}$. These distortions, if large enough, can be detected using XRD through the splitting of many of the peaks.

In the parent binary zincblende and wurtzite structures there are reflections which are extinguished due to the symmetry of the structures. In disordered heterovalent ternary compounds these reflections are similarly extinguished through destructive interference arising from the disordered cation sublattice. Superstructure peaks in the XRD pattern appear when the symmetry is reduced due to cation ordering. The superstructure peaks can be very weak, however, because their presence depends on the difference in scattering cross section between the two cation types. In chalcopyrite, the (101), (217), and (611) peaks are typical superstructure reflections that appear upon ordering [12]. In orthorhombic $Pna2_1$, the (110) and (101) peaks are the strongest superstructure peaks. In $ZnGeN_2$ these superstructure peaks are approximately two orders of magnitude less intense than the strongest peaks, while for $ZnSnN_2$, they are only one order of magnitude less intense [1].

Order–disorder transitions have been observed in many zincblende-based heterovalent ternary semiconductors. At temperatures much lower than the melting temperatures of the compounds, the structure is chalcopyrite. As the temperature is raised, a disorder transition is observed for some compounds, often 50–80 °C below the melting point, as evidenced by XRD. For other compounds, the material melts before the order–disorder transition is observed [11].

There has been much less research reported on ordering in the wurtzite-based heterovalent ternary compounds. $ZnGeN_2$ and $ZnSiN_2$ [13] have been grown with ordered $Pna2_1$ lattices. $ZnSnN_2$ was first synthesized just a few years ago [8,14] and has been receiving more interest lately as a potential earth-abundant solar absorber. Unambiguous observations of $Pna2_1$ ordering in $ZnSnN_2$ have not yet been reported. Identification of ordering through the XRD peak-splitting is more difficult for $ZnSnN_2$ than for $ZnGeN_2$ and $ZnSiN_2$ because the amount of structure distortion due to ordering, for example the deviation of the b/a ratio from that of ideal wurtzite, is predicted to be smaller. For $ZnGeN_2$ the b/a ratio is 2.2% smaller than the wurtzite value, while the b/a ratio of $ZnSnN_2$ is predicted to be within 0.1% of the wurtzite value [1]. On the other hand the (110) and (101) superstructure peaks associated with $Pna2_1$ ordering in $ZnSnN_2$ are predicted to be an order of magnitude larger than in $ZnGeN_2$ [1], but they have not yet been reported to be observed. Kawamura et al. report on a high pressure synthesis method that enabled the growth of polycrystalline $ZnSnN_2$ at a higher temperature (800 °C) than has been possible before [15]. The XRD pattern showed sharp peaks indicating high crystalline quality, but the superstructure peaks were still absent. A recent report of $ZnSnN_2$ grown on $LiGaO_2$ showed some structural distortion that the authors attributed to ordering [16]. Other reports show evidence of control of parameters such as the band gap and carrier concentration [5,17–19] by varying growth conditions and by annealing. While these studies have made progress in the improvement of the quality of the $ZnSnN_2$, definitive XRD evidence of cation ordering is still absent. More research is needed to determine the effects of ordering in $ZnSnN_2$ and how to control it.

A range of ordering has been observed for $ZnGeN_2$, but until recently it has not been understood how to control the cation lattice ordering [13,20–28]. The present study shows that $ZnGeN_2$ grown at lower temperatures tends to have a high degree of disorder on the cation sublattice, while at higher temperatures the cation sublattice becomes ordered. In addition, annealing of disordered material at high temperature causes the cation sublattice to order. Recently, Shang et al. reported temperature-dependent ordering in $ZnGeN_2$ produced by annealing Zn_2GeO_4 under NH_3. Their observations are consistent with the present study [29].

In Section 2 of this paper, the growth methods and the experiments probing the control of $ZnGeN_2$ cation lattice ordering are described. In Section 3, the XRD and Raman results demonstrating the variation and control of ordering are reported and their implications are discussed.

2. Materials and methods

In this fundamental study, $ZnGeN_2$ was grown by a vapor–liquid–