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Atomic geometry and electronic structure of defects in Zn_3N_2

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Abstract

Atomic geometry, electronic structure and formation energy of native defects in Zn_3N_2 films have been studied by means of density functional theory to interpret the different behaviors of defective Zn_3N_2. The effects of the vacancy and self-interstitial N on electronic and optical properties of zinc nitride were investigated, from which we conclude that N vacancy is responsible for n-type conduction character. Various defects may cause energy shift or gap change, which explains different optical band gap detected in Zn_3N_2 samples.

Keywords: Zn_3N_2; Electronic and optical properties; Native defect

1. Introduction

Zinc nitride is the least studied of the group-III-nitride materials, which is currently under intense investigation motivated by the potential applications for engineering devices. Zn_3N_2 powder was firstly synthesized in 1940 [1], and had not been refined as a cubic structure with the lattice constant $a=9.7691(1)$ Å until 1997 [2]. Recently, a series of experiments were focused on preparing Zn_3N_2 and related materials for different purposes. For example, Zn_3N_2 nanowires exhibit ultraviolet and blue emission [3], and zinc nitride films can be thermally oxidized to fabricate p-type ZnO materials [4]. However, few theoretical investigations on the properties of Zn_3N_2 materials have been done, and many issues, such as the mechanism of optical transition and the electronic properties of Zn_3N_2, are still under debate [3,5–7]. Therefore, it is important to probe the effects of native defects on the electronic and optical properties of Zn_3N_2. Despite the importance of Zn_3N_2 for potential device applications, little is known about its intrinsic defects. Calculations of total energies and electronic structure of defects make it possible to investigate the characters, position of defect levels, atomic structure, and the formation energy of defective Zn_3N_2.

In this work, we performed calculations for defective Zn_3N_2 by means of density functional theory to study the related properties. The bond lengths of Zn–N in pure and defective system were determined and the formation energies of several native defects, such as vacancy, self-interstitial N and Zn, were calculated. Our results indicate that forming self-interstitial Zn in Zn_3N_2 requires larger energy than the formation of vacancies where N interstitials are relatively smaller even when the concentration is high enough to affect the electronic and optical properties. The electronic band structure suggests that N vacancy defective Zn_3N_2 shows n-type conduction character. The origin of different optical band gaps observed in samples is qualitatively discussed in the text below.

2. Methods

All the spin-polarized density functional theory calculations were performed employing the program package DMol^3 [8–10]. The double-numeric quality basis set with polarization functions was used. Density functional semicore pseudopotential [11] was used for core treatment. The Perdew-Wang 1991 (PW91) version of the gradient-corrected GGA functionals was employed [12,13] and a real-space cutoff of 3.9 Å was used. Increasing the value of real-space cutoff to 4.4 Å did not change the results. For the numerical integration, we used the medium quality mesh size of the program. The tolerance of self-consistent field convergence was 1.0×10^{-5}. Zn3d states were treated as valence electrons. The Monkhorst–Pack [14] grid

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with $2\times2\times2$ k points was used for structural optimization and self-consistent energy computations, and the electronic band structures and density of states calculations $4\times4\times4$ k points by parallelepipeds method with no broadening were used. The tolerances of energy, gradient, and displacement convergence were 5.44×10^{-4} eV, 0.218 eV/Å, and 5.00×10^{-3} Å, respectively. The maximum gradient for the optimized structures was less than 0.109 eV/Å.

In the calculations, a 80-atom supercell ($Zn_{48}N_{32}$) is adopted to simulate the pure Zn_3N_2. Several types of defects including vacancy and self-interstitials in Zn_3N_2 were studied. The pure Zn_3N_2 supercell was fully optimized and defective models were optimized for the atoms around the native defects.

3. Results and discussion

3.1. Optimized structure and formation energy

The $Zn_{48}N_{32}$ supercell was constructed for the pure Zn_3N_2 as a basic model and the optimized structure is shown in Fig. 1(a). The lattice constant is 9.769 Å, and the Zn–N bond lengths are 2.122 Å (Zn–N(1)), 2.002 Å, 2.060 Å and 2.287 Å (Zn–N(2)), respectively, which are in good agreement with experiments [2].

On the basis of Fig. 1(a), we simulated several possible native defects, i.e. N vacancy, Zn vacancy, and self-interstitial N or Zn defect. We introduced two types of N vacancies by removing N atoms at N(1) and N(2) sites respectively [denoted by $V_{N(1)}$ and $V_{N(2)}$ in Fig. 1(a)]. We also constructed the model with the Zn vacancy by removing one Zn atom from the $Zn_{48}N_{32}$ supercell [marked with V_{Zn} in Fig. 1(a)]. In the models of self-interstitial defects, either N or Zn atom is stabilized at an interstitial position, denoted by I_N or I_{Zn}, and their local structures are shown in Fig. 1(b) and (c), respectively. We also performed calculations for vacancy and self-interstitials systems with a small 40-atom primitive cell. As a result, the structure parameter and formation energy for $V_{N(1)}$ in the 40-atom system are within 5% of those obtained in the 80-atom supercell. In addition, the shortest distance between two defects is 7.635 Å in the 80-atom supercell. Therefore the 80-atom supercell is sufficient to model isolated defects. The $V_{N(1)}$ and $V_{N(2)}$ have been surrounded by six Zn atoms and three N atoms that are denoted as first-nearest neighbors (1-nn). The Zn atoms in 1-nn tend to leave the vacancy, because the 1-nn Zn atoms are positively charged and should, therefore, repel each other as the central N atom is removed. The three N atoms in 1-nn also tend to leave the Zn vacancy, since the electrostatic attraction by the Zn atom is missing. The removal of a neutral Zn atom creates two holes in the valance band, then two of the surrounding three N atoms

Table 1
Formation energies (in eV) of defective zinc nitride systems

$V_{N(1)}$	$V_{N(2)}$	V_{Zn}	I_N	I_{Zn}
4.71	2.58	2.99	4.41	14.39

$V_{N(1)}$, $V_{N(2)}$ and V_{Zn} represent removing one N(1), N(2) and Zn atom from $Zn_{48}N_{32}$ supercell respectively, and I_N and I_{Zn} represent one self-interstitial N or Zn atom in zinc nitride supercell.

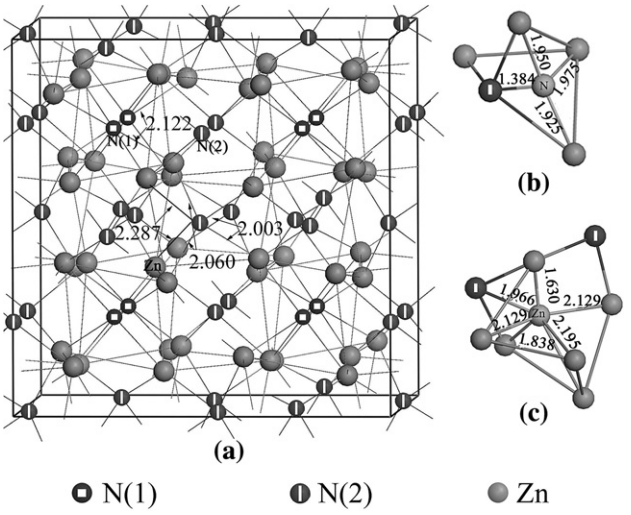

Fig. 1. Models for Zn_3N_2, (a) pure, (b) I_N, and (c) I_{Zn}. The brown balls, green balls and gray balls represent N(1), N(2), and Zn atoms respectively. The selected N and Zn atoms marked with character N(1), N(2) and Zn denote $V_{N(1)}$, $V_{N(2)}$, and V_{Zn} respectively. The interstitial N and Zn atoms are labeled with characters 'N' and 'Zn' in (b) and (c). The unit of bond length is Å.

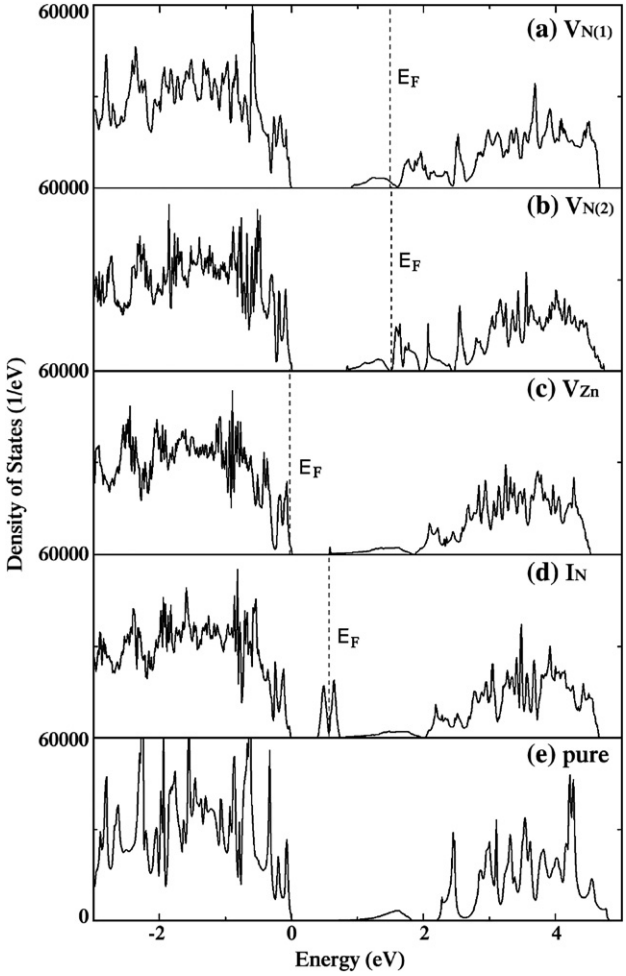

Fig. 2. Total density of states of (a) $V_{N(1)}$, (b) $V_{N(2)}$, (c) V_{Zn}, (d) I_N, and (e) pure. Energy is relative to the top of valence band, which is set as zero-energy point. The dashed line represents E_F. Units in the DOS curves are 1/eV.