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Ab initio study of N-doped β-Ga_2O_3 with intrinsic defects: the structural, electronic and optical properties

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ABSTRACT

We investigated the compensation mechanism between N acceptors and native defects in β-Ga_2O_3 by employing the approach of pseudopotential plane-wave under the density functional theory framework. Four types of defect complexes: $N_{Ga2O3}V_O$ (N-doped β-Ga_2O_3 with O vacancy), $N_{Ga2O3}V_{Ga}$ (N-doped β-Ga_2O_3 with Ga vacancy), $N_{Ga2O3}Ga_i$ (N-doped β-Ga_2O_3 with Ga interstitial), and $N_{Ga2O3}O_i$ (N-doped β-Ga_2O_3 with O interstitial) are take into consideration. The electronic structures, formation energies, structural, and optical properties of the defect complexes are calculated. The calculated results indicate that N dopant acts as a deep acceptor with an acceptor level at 1.33 eV above the valence band maximum, which cannot be an effective P-type dopant. The formation energies of defect complexes $N_{Ga2O3}V_O$ and $N_{Ga2O3}Ga_i$ under Ga-rich atmosphere condition are 2.06 eV and 2.07 eV, respectively, which are close to the value of N_{Ga2O3} (1.90 eV) and indicate these two defect complexes are stable under Ga-rich atmosphere. Compensated by these two native defects, N-doped β-Ga_2O_3 converts into weak n-type conductivity. After N-doped, a slight red-shift appears in the intrinsic absorption edge. When the intrinsic defects introduced, all the other defect complexes models induce a red-shift of the optical absorption edge compared with the pure β-Ga_2O_3 except for $N_{Ga2O3}Ga_i$.

1. Introduction

Among the five crystal structures of Ga_2O_3 (α, β, γ, δ and ε), the most stable phase monoclinic β-Ga_2O_3 with a wide band-gap of 4.9 eV, excellent chemical and thermal stability has gained widely interest in recent years [1,2]. It has been used as spintronic devices, gas sensors, photocatalyst, solar-blind UV photodetectors, and resistance random access memory devices [3–7]. Besides, it is also as a promising candidate for next-generation power devices since its property of high Baliga's figures of merit (over 3000), high breakdown field (8 MV/cm), and suitability for mass production [8,9]. It has been successively applied for the power devices with superior performance, such as MESFET, MOSFET and SBD [10–12].

As is well-known, nominally un-doped β-Ga_2O_3 usually presents intrinsic n-type conductivity because of the existence of oxygen vacancies [13]. Intentional doping is necessary in order to meet the demand for practical devices applications and performance enhancements of devices. The n-type doping is widely reported in the past few years, Sn and Si dopants can be selected as effective donors to adjust the electron densities in wide range of 10^{15}-10^{19} cm^{-3} in β-Ga_2O_3 [14–16]. The development of p-type doping in β-Ga_2O_3 is relative hard compared with other wide band-gap semiconductors, such as ZnSe and GaN, which hampers the further application of this promising material. Thus, it is an urgent need to address the issue to make p-type β-Ga_2O_3 available. Nitrogen (N) element is considered to be an effective p-type dopant among group IV acceptors [17]. Besides, the ionic radius and electronic structure of N^{3-} are close to O^{2-}, which make it a promising p-type dopant in β-Ga_2O_3. However, up to now, only N-doped β-Ga_2O_3 nanowires with a p-type electric conductivity has been reported [18]. Like β-Ga_2O_3, p-type doping ZnO is hard to acquired, and previous study revealed that N acceptors are strongly compensated by the intrinsic defects in ZnO, and N atoms cannot be an effective acceptors due to the deep acceptor levels in the bandgap of ZnO [17,19,20]. Except for the dopant atoms, the intrinsic defects (vacancies and interstitials) play important roles on the properties of the material. However, the N-doped β-Ga_2O_3 with native defects has not be discuss systematically, moreover, the reason that N dopant cannot be an effective acceptor in β-Ga_2O_3 is not clear.

Recently, first-principles calculations based on density functional theory (DFT) have been used for many studies of the material properties such as optics, magnetisms and electronic structures [21–23]. The theoretical calculation can give a deep insight of the

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material, which help us get further acquainted with the material itself. In this paper, first-principles based on all-electron DFT is used to study the atomic structures, formation energies, electronic structures and optical properties of the N-doped β-Ga_2O_3 with native defects. In order to avoid the error caused by the underestimation of the bandgap, the Generalized Gradient Approximation (GGA) with a Hubbard U approach is used, which is computational frugally compared with other hybrid density functionals and also can give an accurate description by controlling the Hubbard U parameter [24,25]. The rest of the paper is organized as follows: in section 2, we make a detailed description of the computational method. The calculation results including the atomic structures, band structures, densities of states, distribution of charge density difference and optical properties of N-doped β-Ga_2O_3 with intrinsic defects, along with the discussion of the compensation mechanism are presented in section 3. Section 4 provides a final brief conclusion.

2. Calculation methods

All calculations are performed with Cambridge Serial Total Energy Package (CASTEP) code, which is a plane-wave, pseudopotential based on the density functional theory (DFT) [26]. The exchange-correlation potential is described with the Perdew-Burke-Ernzerhof (PBE) scheme under the GGA functional [27]. The ultrasoft pseudopotential method is used for the interactions between electrons and ions. The valence electrons configurations for gallium, oxygen as well as nitrogen are [Ar] $3d^{10}4s^24p^1$, [He] $2s^22p^4$ and [He] $2s^22p^3$, respectively. To reproduce the experimental band-gap of the intrinsic β-Ga_2O_3, the DFT + U method is adopted. The value of Hubbard U parameters for Ga and O ions are referenced in our previous study [28].

Before the properties calculation, structural relaxations are employed. The lattice parameters and internal coordinates are relaxed with Broyden-Fletcher-Goldfarb-Shanno (BFGS) optimization method [29]. The energy tolerance, tolerance of the force, maximum stress, and maximum displacement are 1×10^{-5} eV/atom, 0.03 eV/Å, 0.05 Gpa, and 0.001 Å, respectively. The kinetic-energy cutoff for the plane wave basis set is 450 eV, and a Monkhorst-Pack $2 \times 6 \times 4$ k-points is used for integrations of the Reduced Brillouin zone [30].

A $1 \times 2 \times 2$ β-Ga_2O_3 supercell based on the optimized primitive cell with 80 atoms is constructed to act as the computational model, which is presented in Fig. 1. The N-doped model is created by substituting one O atom with one N atom, which is denoted by N_{Ga2O3}. There are two different lattice sites for gallium and three different locations for oxygen. We confirm the substitution site for nitrogen by the comparison of the formation energies of three N-doped structures, and conclude that the O2 site is the most stable substitution site. Due to the low monoclinic symmetry of β-Ga_2O_3, many different intrinsic defects sites have to be considered in the N_{Ga2O3} structure. Similar with the determination of N substitution position, we confirm the Ga and O vacancies by the comparison of the formation energies of the different defective N_{Ga2O3} structures. For the sites of interstitial Ga and O, we adopt the results from the reference, interstitial Ga and O locate at the same site [31]. The O vacancy ($N_{Ga2O3}V_O$), Ga vacancy ($N_{Ga2O3}V_{Ga}$), Zn interstitial ($N_{Ga2O3}Ga_i$) and O interstitial ($N_{Ga2O3}O_i$) are represented as 1, 2, and 3, respectively.

3. Results and discussion

3.1. Atomic structure

The calculated lattice parameters of β-Ga_2O_3 are a = 12.42 Å, b = 3.07 Å, c = 5.89 Å, and β = 103.85°, respectively. The lattice parameters calculated from the GGA calculations are in good agreement with the experimental values, which means our calculated results are reliable [32]. Based on the calculated structure, the supercells of N-doped β-Ga_2O_3 with different intrinsic defects are optimized. The optimized Ga–N bonds and volume difference ratio are listed in Table 1.

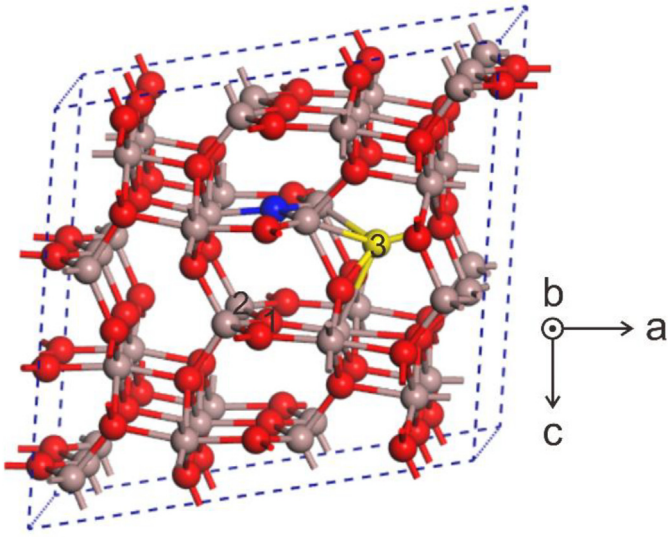

Fig. 1. The N-doped β-Ga_2O_3 supercell with various intrinsic defects. Here, the Ga, O and N atoms are demonstrated by brown, red and blue spheres, respectively. Number 1 and 2 represent the vacancy sites of O and Ga, respectively. The yellow sphere labelled with number 3 denotes the interstitial sites for both O and Ga. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

After the substitution of oxygen atom by nitrogen atom, the Ga–N bond between N atom and the Ga atom in octahedron is shorter than the corresponded Ga–O bond (1.97 Å), while the other two equivalent Ga–O bonds between N and Ga atoms in tetrahedron are slight longer than Ga–O bond (1.86 Å). Compared with the intrinsic structure, the volume of N_{Ga2O3} expands a little. These variations can be attributed to the bigger N^{3-} radius (1.46 Å) than O^{2-} radius (1.32 Å). The presence of interstitial defects leads to a slight expansion of the supercell volume, while the presence of vacancies leads to a shrinkage of the supercell volume. It is noted that when Ga vacancy induced, the variation of the two equivalent Ga–O bonds between N atom and the Ga atoms in tetrahedron are different, the supercell volume increases a little. Compared with the N-doped β-Ga_2O_3, the Ga vacancy decreases the volume of the supercell.

3.2. Formation energy

To confirm the relative stability of N-doped β-Ga_2O_3 with intrinsic defects, the formation energies of supercell structures with different intrinsic defects in neutral states are calculated. The

Table 1
The optimized structures and formation energies of N-doped β-Ga_2O_3 with native defects.

	Optimized structure				Formation energy (eV)	
	Ga–N (Å)	Ga–N (Å)	Ga–N (Å)	ΔV (‰)	Ga-poor	Ga-rich
N_{Ga2O3}	1.95	1.88	1.88	8.3	1.90	2.99
$N_{Ga2O3}Ga_i$	1.86	1.83	1.83	27.9	3.15	2.06
$N_{Ga2O3}O_i$	1.95	1.89	1.89	8.6	4.64	7.83
$N_{Ga2O3}V_{Ga}$	2.09	3.06	2.01	2.2	11.01	12.10
$N_{Ga2O3}V_O$	1.92	1.85	1.85	−1.5	5.26	2.07