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First-principles calculation of electronic structures and optical properties of wurtzite $In_xAl_{1-x}N$ alloys

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Abstract

The electronic structures and optical properties of wurtzite $In_xAl_{1-x}N$ have been calculated using a first-principles self-consistent method. The calculated lattice constants and band gap bowing parameter are in good agreement with the experimental results and/or values given by other calculation methods. It is interestingly found that the peaks of total density of states (TDOS) in the conduction band have a tendency of shifting to the lower energy as In concentration increases in $In_xAl_{1-x}N$; while in the deep valence band, the peak splits into three peaks. The optical properties such as the dielectric function, reflectivity, absorption coefficient, refractive index, and electron energy-loss function are also presented. The main peak in imaginary part of dielectric function spectrum, the absorption edge and the peak in $L(\omega)$ spectrum are found to have a remarkable red-shift as In mole fraction increases. Furthermore, the optical properties of wurtzite $In_xAl_{1-x}N$ are discussed based on the band structures and density of states (DOS) analysis.

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Keywords: Density functional theory (DFT); Electronic structures; Optical property; Wurtzite; $In_xAl_{1-x}N$ alloy

1. Introduction

In recent years, group III nitrides and their alloys have gained wide recognition [1–5] as the most promising opto-electronic materials due to their excellent mechanical properties and outstanding optical properties. Much intensive research work has been focused on $In_xAl_{1-x}N$ and $Ga_xAl_{1-x}N$ alloys [6,7], but less effort has been devoted to InN and $In_xAl_{1-x}N$ alloys. The wurtzite ternary $In_xAl_{1-x}N$ is less investigated because the epitaxial growth has suffered from phase separation. Recently, $In_xAl_{1-x}N$ has attracted considerable attention due to the repeated observations of an effective band gap of about 0.7–1.0 eV of InN by optical techniques [8–10] in contrast to the prevailing value of 1.9 eV [11] established 20 years ago. The discovery of the smaller band gap value extends the possible emission range of opto-electronic devices based on group III nitrides from 6.28 eV (AlN) down to 0.7 eV (InN).

Theoretically, *ab initio* calculations were successfully used to investigate the phase diagram, chemical bonds, lattice constants, bowing parameter and gap bowing of cubic $In_xAl_{1-x}N$ alloys [12–14], but the detailed optical properties have not been reported yet. In experiment, the $In_xAl_{1-x}N$ thin films with a wide composition range were prepared by magnetron reactive sputter [15,16], metal organic vapor phase epitaxy [17], and molecular-beam epitaxy [18] etc. Very recently, it was suggested that the $In_xAl_{1-x}N$ nanostructures were possibly fabricated by plasma technology [19,20]. However, there are no results of the optical properties of wurtzite $In_xAl_{1-x}N$ despite its significant importance for fundamental physics and potential applications of materials. In this work, we studied the crystal structure and optical properties of wurtzite $In_xAl_{1-x}N$ by using first-principles calculations based on

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density functional theory (DFT) in CASTEP code. The calculated electron structures are found to be in good agreement with the experimental results. On the other hand, the interesting optical properties are calculated and discussed.

2. Method of calculation

The calculations are performed using the plane-wave pseudo-potential (PWPP), approach within the framework of the DFT. The exchange-correlation energy of the electrons is described in the generalized gradient approximation (GGA). The GGA functional form PBE [21] is used. Coulomb potential energy caused by electron–ion interaction is described by using ultra-soft scheme [22], in which the orbits of Al ($3s^2 3p^1$), In ($4d^{10} 5s^2 5p^1$), N ($2s^2 2p^3$) are treated as valence electrons. In reciprocal vector k space, the plane wave energy cut off 340 eV is set at.

To model the InAlN random wurtzite alloys, we apply a 32-atom $In_nAl_{16-n}N_{16}$ super-cell, which corresponds to a $2 \times 2 \times 2$ super-cell with twice the size of the primitive wurtzite unit cell in both directions of the basal plane and along c-axis. For a given number x of In atom, the CASTEP program randomly determines the geometrical arrangement of Al–In atoms.

For the geometric equilibrium determination of the wurtzite phase we proceeded as follows: we first determined the internal parameter u by fixing basis size for a specific volume V and c/a ratio, then by using it we optimized the c/a ratio to obtain $(c/a)_{eq}$ at $(V,(c/a)_{eq}, u_{eq})$. Finally, the band gap energy, band structures and the optical properties are calculated.

The iteration is repeated until the energy is less than 2.0×10^{-6} meV/atom and the RMS stress is less than 0.1 GPa. The calculations of total energy and charge density by using DFT require several integrals over the Brillouin zone. The integrals are approximated by numerical summation over a finite number of k points. The Monkhorst–Pack scheme [23] with uniform mesh points $(4 \times 4 \times 2)$ is applied. The calculated results are in good agreement with other calculations and experiments.

3. Result and discussion

3.1. Structural property analyses

The equilibrium lattice constants, band gap energies of wurtzite AlN and InN obtained by our simulation and other researchers are displayed in Table 1. The lattice constants obtained in this work are in good agreement with those reported experimentally [24,30]. The calculated band gap of AlN and InN is still smaller than the experimental value, but bigger than those calculated by PWPP [26]. Assuming that the Vegard's law is valid, the lattice constants of $In_xAl_{1-x}N$ are generally expressed as a linear relation to the In composition x. The curves shown in the inset of Fig. 1 can be approximated using the following formula:

$$a(x) = x \cdot a_{AlN} + (1-x) \cdot a_{InN} - \delta_a \cdot x \cdot (1-x), \quad (1)$$

$$c(x) = x \cdot c_{AlN} + (1-x) \cdot c_{InN} - \delta_c \cdot x \cdot (1-x), \quad (2)$$

where $a(x)$ and $c(x)$ are the a and c lattice constants of the $In_xAl_{1-x}N$, a_{AlN} and c_{AlN} are the a and c lattice constants of AlN, a_{InN} and c_{InN} are the a and c lattice constants of

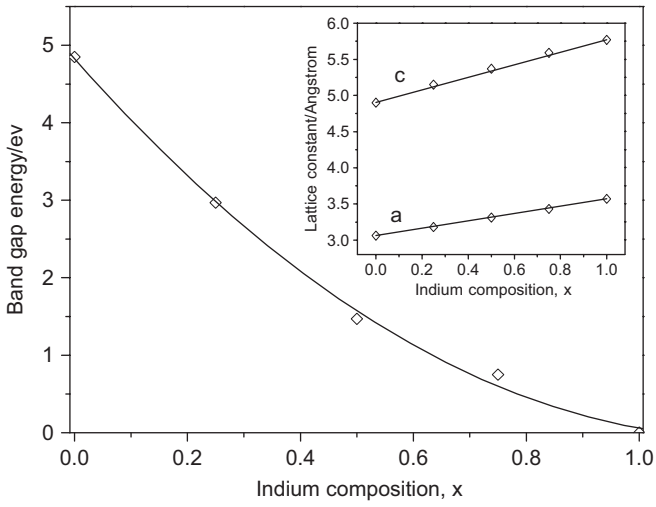

Fig. 1. Band gap with different In concentration in $In_xAl_{1-x}N$.

Table 1
Equilibrium lattice constants, band gap energies of wurtzite AlN and InN

		a (Å)	c (Å)	c/a	E_g (eV)
AlN	This work	3.06	4.90	1.601	4.85
	Expt.	3.110 [24]	4.980 [24]	1.601	6.28 [25]
	PWPP	3.084 [26]	4.948 [26]	1.604 [26]	4.41 [26]
	NLCC	3.10 [27]	5.01 [27]	1.616	
	FP-LMTO	3.073 [28]	4.904 [28]	1.595	
	MBPP	3.144 [29]	5.046 [29]	1.605	
InN	This work	3.572	5.775	1.616	0
	Expt.	3.544 [30]	5.718 [30]	1.613	0.8 [9], 0.9 [8], 1.89 [11]
	PWPP	3.501 [26]	5.669 [26]	1.619 [26]	−0.04 [26]
	FP-LAPW	3.520 [31]	5.675 [31]	1.612 [31]	0.17 [31]
	NLCC	3.55 [27]	5.79 [27]	1.630	