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Theoretical study of $Be_xZn_{1-x}O$ alloys

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Abstract

In this article we have studied $Be_xZn_{1-x}O$ alloys by the method of total energy plane-wave expansions with ultrasoft pseudopotential technology based on density functional theory (DFT). In order to calculate the electronic structures of the $Be_xZn_{1-x}O$ alloys with wurtzite structure, we adopt a 16-atom $Be_nZn_{8-n}O_8$ supercell which allows the simulation of the composition $x = 0.0$, 0.125, 0.25, 0.375, 0.50, 0.625, 0.75, 0.875, and 1.0. We obtained the equilibrium lattice constants, the formation energies, the band gap energy bowing parameter. The calculated results are consistent with experimental results and indicate that $Be_xZn_{1-x}O$ alloys are excellent candidates for achieving band gap modulation to values larger than ZnO. To our knowledge, this is the first time such an *ab initio* study of these semiconductor alloys has been investigated.

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Keywords: BeZnO; Density functional theory; Lattice constants; Bowing parameter

1. Introduction

ZnO is one of the most attractive metal oxides for photonic and electronic applications due to its unique properties such as a direct wide band gap (~3.3 eV), a large exciton binding energy (~60 meV), strong emission, large saturation velocity (3.2×10^7 cm/s), and a high breakdown voltage [1]. Furthermore, its low material cost, high crystalline quality, and high radiation resistance make it a promising material to compete with GaN-based technologies [2–5]. Since reliable and stable p-type ZnO semiconductor material can now be grown using arsenic as dopant [6], a critical step for producing high-efficiency ZnO devices is the fabrication of ZnO-based quantum wells and superlattices. A common approach for the fabrication of such structures would be to develop ZnO-based alloys with band gaps larger or smaller than that of ZnO. Ohtomo et al. reported that the band gap of $Mg_xZn_{1-x}O$ would be increased up to 3.99 eV at RT as the content of Mg is increased up to $x = 0.33$. They fabricated superlattices by employing ZnO and MgZnO as alternate layers [7]. Zhang et al. also reported that the $Mg_xZn_{1-x}O$ band gap would be increased up to 3.90 eV when $x = 0.3$ [8]. However, crystal phase segregation between ZnO and MgO was observed for Mg concentrations $x \geqslant 0.36$, due to the different crystal structures and large lattice mismatch between ZnO (3.25 Å, hexagonal) and MgO (4.22 Å, cubic) [9].

Recently, Ryu et al. have investigated the growth of different alloys for such purposes and proposed that BeZnO alloys are good candidates for achieving band gap modulation to values larger than ZnO [10]. They synthesized BeZnO films on c-Al_2O_3 substrates by the method of hybrid beam deposition (HBD) [11]. Unlike the more limited range for the MgZnO alloy, the Be concentration is varied over the entire range from 0% to 100%, and no phase segregation between ZnO and BeO was detected by XRD measurements. More recently, they reported ZnO-based ultraviolet light emitting diodes that employ a BeZnO/ZnO active layer comprising seven quantum wells [12]. All these experiments confirmed that

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BeZnO alloys can be used for fabricating excellent ZnO-based devices.

In addition to experimental methods, *ab initio* simulations [13] can provide accurate theoretical predictions of bulk geometries, electronic structure, and behavior, and such an approach is the subject of this paper.

BeZnO alloys are important for ZnO-based devices. In this work we have studied the $Be_xZn_{1-x}O$ alloys by the method of ultrasoft pseudopotential technology using total energy plane-wave expansions based upon the density functional theory (DFT).

2. Theoretical model

In this work, all the calculations were carried out using CASTEP code [14], which is based on DFT, using the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE) [15] as the exchange-correlation functional. In order to simulate the ordered $Be_xZn_{1-x}O$ alloys with wurtzite structure, we employed 16-atom $Be_nZn_{8-n}O_8$ supercells, as shown in Fig. 1, which corresponds to a $2 \times 2 \times 1$ supercell that is twice the size of a primitive wurtzite unit cell in base plane direction. The ions were described using an ultrasoft pseudopotential scheme [16], in which the orbitals of $Be(2s^2)$, $Zn(3d^{10}4s^2)$, and $O(2s^22p^4)$ are treated as valence electrons. The wave functions are expanded in a plane-wave basis set up to an energy cutoff of 450 eV where the total energy converged to less than 2×10^{-5} eV/atom. Integrations over the Brillouin zone were performed using a $4 \times 4 \times 4$ grid according to a Monkhorst–Pack set [17] sampling-point scheme.

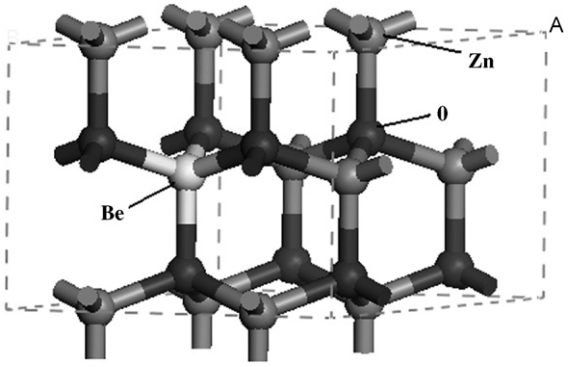

Fig. 1. The 16-atom $Be_{0.125}Zn_{0.875}O$ supercell.

By changing the number of beryllium atoms from 0 to 8, we obtained the compositions $x = 0.0$, 0.125, 0.25, 0.375, 0.5, 0.625, 0.75, 0.825, and 1.0 respectively. We define the formation energies of the alloys as [18]

$$E(x) = E_{\text{tot}}(Be_xZn_{1-x}O) - x \cdot E_{\text{tot}}(BeO) - (1-x) \cdot E_{\text{tot}}(ZnO), \quad (1)$$

where the $E_{\text{tot}}(Be_xZn_{1-x}O)$, $E_{\text{tot}}(BeO)$, $E_{\text{tot}}(ZnO)$ are the total energies of the corresponding supercells. The formation energies defined as the total energy difference between the ternary and binary, and its values reveal the stability of the alloys; negative means that the ternary is more steady than binary, while the positive means inversely, and the larger the positive value the less stable the alloy is.

3. Results and discussion

In order to validate the reliability of the simulated results, both BeO and ZnO binary alloys with wurtzite structure were tested. Bulk ZnO and BeO with 16-atoms supercells were first simulated. The results, summarized in Table 1, indicated that the total energy, lattice constant, width of top valence band, and band gap energy of BeO and ZnO do not approach monotonically to a certain value as the cutoff energy increases, instead, they oscillate. A lower cutoff energy of 300 eV for BeO and ZnO leads to an inadequate representation of the plane-wave function, especially that of BeO, which is reflected in a more non-monotonic behavior. The amplitude of the oscillation is smaller when the cutoff energy increased. From Table 1, it is evident that for BeO and ZnO, the amplitude of fluctuation is negligible when the cutoff energy ranges from 400 to 500 eV. Thus, it seems that for BeZnO alloys with wurtzite structure, a higher cutoff energy is required in order to obtain more accurate result. Therefore, we adopted 450 eV as the cutoff energy by weighing the accuracy and computational ability. The calculated results of the lattice parameters of ZnO and BeO are in good

Table 1
Lattice constants, total energies, band gap energies, width of top valence band at the Γ point for BeO and ZnO with increasing cutoff energies

Cutoff energy (eV)			300	340	400	450	500
Lattice constant (Å)	BeO	*a*	3.249	2.744	2.740	2.738	2.738
		c	5.205	4.457	4.451	4.449	4.449
	ZnO	*a*	3.296	3.274	3.257	3.257	3.258
		c	5.315	5.271	5.258	5.258	5.256
Total energy (eV)	BeO	*a*	−3777.273	−3778.727	−3779.232	−3779.270	−3779.389
	ZnO	*c*	−17 243.783	−17 246.178	−17 246.530	−17 246.584	−17 246.719
Band gap energy (eV)	BeO	*a*	7.073	7.249	7.295	7.320	7.321
	ZnO	*c*	0.926	0.954	0.970	0.971	0.972
Width of top valence band	BeO	*a*	5.800	5.933	5.952	5.959	9.958
	ZnO	*c*	5.638	5.746	5.804	5.804	5.803