Electronic Structure and Band Gap Engineering of

ZnO-based Semiconductor Alloy Films

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ABSTRACT

We conduct first-principles total-energy density functional calculations to study the atomic structures, band structures, and electronic structures of $Zn_{1-x}M_xO$ (M = Be, Mg, Cd, Ag, Cu) semiconductor alloys. The Heyd-Scuseria-Ernzerhof (HSE) hybrid functional has been performed to yield lattice constants and bandgaps of $Zn_{1-x}M_xO$ semiconductor in much better agreement with experimental data than the standard local exchange correlation functional. We find that the strong coupling between O 2p and Cu 3dor Ag 4d bands plays a key role in narrowing of band gaps and leading to the half-metallic behavior interpreted with the unique spatial distribution pattern between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO).

Keywords: ZnO; bandgap; first-principles calculations; light emitting diodes

1 INTRODUCTION

The quickly emerging light emitting diodes (LEDs) market is expected to grow from USD 6.9 billion in terms of sales in 2010, to about USD 17.4 billion by 2015 [1]. As this market continues to develop and grow, the demand for higher quality epilayers driven by new materials and processes will surely increase. To provide immediate solutions to those industry demands, the wide band-gap ZnO-based semiconductor has gained great attentions and its applications have become a hot and active field in the world range wide. This is considering as the next generation materials applied in the field of photo-electronic devices for several reasons. First, wurtizite ZnO, a II-VI compound semiconductor, is wide band gap of 3.37 eV compared to 3.39 eV for wurtizite GaN and large exciton binding energy (60 meV) for leading to the lasing action even upon room temperature [2,3]. Second, the novel photonic device based on Group II-VI materials makes it possible to de-couple strain of emitters and modulators grown on $Zn_{I-x}M_xO$ (M = Be, Mg, Cd, Ag, Cu, etc.) buffered sapphire or virtual substrates [4]. Third, the fabrication of $Zn_{I-x}M_xO$ offers great flexibility in designing novel photonic devices based on Group II-VI materials via band gap engineering [3,5,6].

The new family of ZnO-based semiconductor systems covers a wide range of operating wavelengths from green

through blue to ultraviolet (UV) lighting in $Zn_{l-x}Be_xO$ and $Zn_{1-x}Mg_xO$ alloy films [7,8]. The ternary $Zn_{1-x}Cd_xO$ alloy films are possible to turn the wavelengths from green through red to infrared (IR) lighting [9]. In addition, wurtizite ZnO films by alloying with group-IB elements such as $Zn_{I-x}Ag_xO$ and $Zn_{I-x}Cu_xO$ alloy films are not only important optical material in the visible region and the nearinfrared region but also good candidates for producing the stable p-type ZnO [10]. Our calculations are based on the theory densitv functional (DFT) and emplov pseudopotentials derived from the planewave projector augmented-wave (PAW) method [11] with the Heyd-Scuseria-Ernzerhof (HSE) hybrid functional [12]. The HSE exchange-correlation (XC) energy can be written as [13]: $E_{xc}^{HSE} = 1/4 E_x^{HF,SR}(\mu) + 3/4 (E_x^{PBE,SR}(\mu) + E_x^{PBE,LR}) + E_c^{PBE}$

where the screening parameter (or splitting parameter) μ is the range separation, $E_x^{HF,SR}$ is the short-range (SR) components of the Hartree-Fock (HF) exchange, $E_x^{PBE,SR}$



Figure 1: Structural simulations of $Zn_{I-x}M_xO$ alloys. The atoms are represented by spheres: O (red), Zn (gray), Be (green, large), Mg (green, medium), Cd (brown), Ag (light purple), and Cu (light blue).

	Lattice constants (Å)						
Composition	HSE06		LDA		GGA		
	a (axis)	c (axis)	а	С	а	с	
ZnO	3.24(3.25) ^a	5.18(5.25) ^a	3.18(3.20) ^b	5.10(5.17) ^b	3.26(3.28) ^c	5.21(5.29) ^c	
Zn _{0.5} Be _{0.5} O	2.90	4.90	2.90	4.90(4.26) ^d	2.96(2.95) ^e	4.99(4.86) ^e	
Zn _{0.5} Mg _{0.5} O	3.24	5.13	3.20	5.06(4.50) ^d	3.26(3.28) ^c	5.17(5.24) ^c	
$Zn_{0.5}Cd_{0.5}O$	3.38	5.58	3.29	5.48	3.36(3.48) ^c	5.55(5.58) ^c	
Zn _{0.5} Ag _{0.5} O	3.29	5.69	3.22	5.54	3.30	5.63	
Zn _{0.5} Cu _{0.5} O	3.19	5.23	3.14	5.13	3.21	5.24	

TABLE 1. Lattice constants of Zn_{1-x}M_xO alloys calculated within DFT-HSE06, DFT-LDA, and DFT-GGA.

^a Ref. [13] ^b Ref. [23] ^c Ref. [24] ^d Ref. [25] ^e Ref. [26]

is the SR components of the exchange functional of Perdew, Burke, and Ernzerhof (PBE) [14,15], $E_x^{PBE,LR}$ is the longrange (LR) components of the PBE exchange functional, and E_c^{PBE} is the PBE correlation energy. For $\mu = 0$, HSE reduces to the hybrid functional PBE0 [16], and for $\mu \to \infty$, HSE is identical with PBE. In this study we employ $\mu =$ 0.207 Å⁻¹ indicated by HSE06, yielding the optimal exchange functional to describe systems with strongly localized *d* or *f* electrons [13].

The HSE06 is the suitable exchange functional for the ZnO and related II-VI semiconductor alloy systems to solve the conventional problems of underestimated band gap due to shortcomings of the strong hybridization of delocalized d (f) status with p status from the standard approximations to The XC energy, i.e., the local density approximation (LDA) and generalized gradient approximation (GGA) functional [17,18]. For comparison, we also employ the LDA and the PW91 form of the GGA functional in this study[17-19].

2 COMPUTATIONAL METHODS

We conduct first-principles DFT calculations to study the band structures in ZnO and related II-VI semiconductor alloys using the Vienna ab initio simulation package (VASP) [20-22]. A series of four-atom wurtizite lattice unit cells of ZnO, Zn_{0.5}Be_{0.5}O, Zn_{0.5}Mg_{0.5}O, Zn_{0.5}Cd_{0.5}O, Zn_{0.5}Ag_{0.5}O, and Zn_{0.5}Cu_{0.5}O (where discrete Zn compositions of 50% or x = 0.5) were first constructed using bulk crystalline configurations as shown in Fig. 1. A plane wave cutoff energy of 400 eV was used in conjunction with a 10×10×8 Monkhorst-Pack grid (corresponding to 227 irreducible k points) to achieve a force accuracy of 0.0001 eV/Å. Using these computational parameters, the atomic coordinates were fully relaxed to their zero force positions, yielding optimized atomic structures.

3 RESULTS AND DISCUSSION

The results of the structural optimizations are presented in Table 1. The table lists the in-plane (a) and perpendicular (c) lattice constants of optimized atomic structures for the HSE06 hybrid, LDA, and GGA functional. The calculated lattice constants of the present work are remarkably similar to that predicted by other theoretical calculations quoted in

TABLE 2 Bandgaps of $Zn_{I-x}M_xO$ alloys calculated within DFT-HSE06, DFT-LDA, and DFT-GGA

	Band-gap energy (eV)					
Composition	HSE06	LDA	GGA			
ZnO ^a	2.54(2.46) ^c	0.83(0.70) ^d	0.81(0.73) ^e			
$Zn_{0.5}Be_{0.5}O^{a}$	4.10	2.36	2.21			
$Zn_{0.5}Mg_{0.5}O^{a}$	3.58	1.87	1.83(2.05) ^e			
$Zn_{0.5}Cd_{0.5}O^{a}$	1.52	0	0.09(0.05) ^e			
$Zn_{0.5}Ag_{0.5}O^{b}$	0.95	0.11	0.13			
$Zn_{0.5}Cu_{0.5}O^{b}$	1.18	0.15	0.20			

^a Direct bandgap ^b Semimetal ^c Ref. [13] ^d Ref. [25] ^e Ref. [24]



Figure 2: Band structures of $Zn_{1-x}M_xO$ semiconductor alloys at DFT-HSE06 level.

brackets [13,23-26]. In the case of Zn_{0.5}Be_{0.5}O two lattice constants, a and c, are significantly smaller than others. The ratios of c/a of ZnO (1.60), Zn_{0.5}Cd_{0.5}O (~1.66), and $Zn_{0.5}Cu_{0.5}O$ (~1.63) are closer to the ideal ratio of c/a = $\sqrt{8/3}$ = 1.63. The lowest ratio of c/a found in the $Zn_{0.5}Mg_{0.5}O$ (~1.58) and the highest ratio of c/a found in the $Zn_{0.5}Ag_{0.5}O$ (~1.72) exhibit that the unit cells are compressed and elongated along the c-axis, respectively. The band structures calculated using the HSE06, LDA, and GGA functional are shown in Table 2. The HSE06 result for the band gap of ZnO is direct and 2.54 eV (panel ZnO in Fig. 2), which is much closer to the experimental value 3.4 eV [27,28]. Zn_{0.5}Be_{0.5}O (Zn_{0.5}Mg_{0.5}O) of the SHE06 approach yields a band gap of 4.10 eV (3.58 eV) (panels $Zn_{0.5}Be_{0.5}O$ and $Zn_{0.5}Mg_{0.5}O$ in Fig. 2), which approximately matches the value 4.90 eV (5.10 eV) predicted by the linear dependence of the band gap on the intermediate compositions varying from the ZnO to BeO (MgO) [25]. Zn_{0.5}Cd_{0.5}O at the SHE06 level exhibits a band gap of 1.52 eV (panel $Zn_0 {}_5Cd_0 {}_5O$ in Fig. 2), which is similar to the band gap of 1.94 eV inferred from the



Figure 3: Bandgaps dependence of lattice parameters in $Zn_{I-x}M_xO$ alloys. The novel photonic devices based on Group II-VI materials via band gap engineering denoted by the area illustrated with solid lines. The rainbow shows the visible light spectrum.

experimental observations (where the discrete Cd composition of 50%) [29]. In addition, Zn_{0.5}Ag_{0.5}O and Zn_{0.5}Cu_{0.5}O show a half-metallic behavior (see panels Zn_{0.5}Ag_{0.5}O and Zn_{0.5}Cu_{0.5}O in Fig.2) calculated using HSE06 functional. Note that the half-metallic behavior is the VBM at the Γ -point band gap exceeds the Fermi level. Both results showing semimetallic state are consistent with experimental and theoretical observations [10.30-33]. In contrast, the band gaps of ZnO-based semiconductor systems at the LDA or GGA level are severely underestimated (see Table 2). This is because the LDA or GGA fails to describe systems with strongly localized delectrons which can lead to the bandgap narrowing [24,25]. Furthermore, the strong hybridizations of the O 2p bands with Zn 3d bands, Ag 4d bands, and Cu 3d bands also lead to the band gap shrinkage [10,13,31-33]. Thus the HSE06 gives an excellent description of the crystal structures and wide ranges of the band gaps in ZnO-based semiconductor alloy films as concluded in Fig. 3 derived from Tables 1 and 2.

To elucidate the electronic structures associated with the use of the band structures we carried out a brief comparative study of both highest occupied Kohn-Sham orbitals (HOMO) and lowest unoccupied Kohn-Sham orbitals (LUMO) in the $Zn_{I,x}M_xO$ systems. Unless



Figure 4: HOMO and LUMO isosurfaces of $Zn_{I-x}M_xO$ alloys denoted by the shade of blue. The atoms are represented by spheres: O (red), Zn (gray), Be (green, large), Mg (green, medium), Cd (brown), Ag (light purple), and Cu (light blue).

otherwise specified, all electronic and atomic structure calculations of the $Zn_{1-x}M_xO$ systems were carried out using the HSE06 functional. The HOMO and LUMO density isosurfaces of optimized lattices are reported as shown in Fig. 4. We clearly see that the HOMO and LUMO levels of the isotropic ZnO arrangement are uniformly around O atoms. The cations of Be, Mg, and Cd can distort the lattice (see Table 1) but do not modify the intrinsic nature of the HOMO-LUMO isosurfaces in ZnO-based semiconductors indicating the direct-gap behavior. In the case of the $Zn_{0.5}Ag_{0.5}O$ and $Zn_{0.5}Cu_{0.5}O$ arrangements, the HOMO and LUMO levels are not only around O atoms but also occupied group-IB elements (Ag and Cu) on Zn sites. Our 3D HOMO and LUMO isosurfaces show that the spatial distribution of the localized orbitals exists in the O 2pbands with Ag 4d bands, and Cu 3d bands. The above results suggest a possible explanation in the half-metallic behavior due to large anion p orbitals and cation d orbitals coupling.

4 CONCLUSIONS

Optimized atomic structures, band structures, and electronic structures of $Zn_{1-x}M_xO$ (M = Be, Mg, Cd, Ag, Cu) alloys were studied by first-principles DFT-HSE06 calculations. Our results show that band structures of $Zn_{1-x}M_xO$ models were drastically improved using the HSE06 hybrid functional. By analysing the HOMO-LUMO transition based on the unique spatial distribution behavior, we found that the strong coupling between O 2p and Cu 3d or Ag 4d bands plays a key role in the half-metallic behavior of $Zn_{0.5}Ag_{0.5}O$ and $Zn_{0.5}Cu_{0.5}O$ arrangements.

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