The effect of Zn vacancies and Ga dopants on the electronic structure of ZnO: *Ab initio* simulations

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Abstract. Zinc oxide modified by metal dopants can be used as a low-cost material for production of transparent conducting films. Its optical and electronic properties vary with the type and the concentration of dopants. In this study we have performed first-principle calculations on ZnO with Zn vacancies and that with Ga dopants in wurtzite type hexagonal morphology using density functional theory approach. Dependence of the electronic properties on the concentration of dopants has been studied using supercells of different sizes.

1. Introduction

ZnO continues to attract enhanced technological interest as a suitable material for manufacturing of transparent conducting films for electrodes and other microelectronic applications. The wide accessibility of ZnO single crystals [1] make ZnO a promising low-cost material for synthesis of nanostructures with a large variety of morphologies and for substrates. Under normal conditions ZnO exists in the wurzite-type hexagonal polymorph, being a wide-gap semiconductor with a band gap $E_g = 3.4$ eV [2, 3]). When ZnO is doped by Ga, Al or transition metal atoms, its electrical conductivity increases retaining high optical transparency. Doped ZnO can be considered as a good substitute for indium–tin oxide in manufacturing of transparent electrodes [1]. Fabrication of doped and undoped ZnO thin films is accompanied by formation of O and Zn vacancies and interstitials [4] and formation of nitrogen complexes [4], as well as hydrogen adsorption [5], which contributes to n-type conductivity.

In recent years energetics of formation of O and Zn vacancies and interstitials was calculated using hybrid QM/MM approach [3, 6], DFT-PAW approach with semi-local GGA [7] and LDA/GGA parametrization [8]. Acting as deep acceptors or deep donors, no intrinsic defects can cause conductivity [9]. In contrast, adsorbed hydrogen is readily incorporated as an H^+ interstitial, ensuring n-type conductivity [9]. Sokol *et al* [6] have shown that metal atom dopants usually act as deep donors, reluctantly taking part in the formation of conductivity.

In this study we have performed first-principles calculations on the atomic and electronic structure of pure and doped ZnO with different concentrations of defects in order to analyze the effect of Ga dopant and V_{Zn} on different properties.

2. Computational details & preliminary calculations

DFT calculations have been performed using basis sets of linear combination of atomic orbitals (LCAO) combined with hybrid DFT-HF exchange–correlation functional PBE0 as implemented

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Table 1. Lattice constants a and c (Å), bulk modulus B (GPa), cohesive energy E_{coh} (eV) and band gap E_{g} (eV) for ZnO compared to other theoretical and experimental data.

	This study	DFT	Expt
a	3.2581	3.2498 [3]	3.2417 [11]
c	5.2218	5.2029 [3]	5.1876 [11]
B	160.4	160.2 [3]	135–183 [12]
E_{coh}	13.07	10.64 [13]	—
E_{g}	3.61	3.18 [14]	3.44 [2]

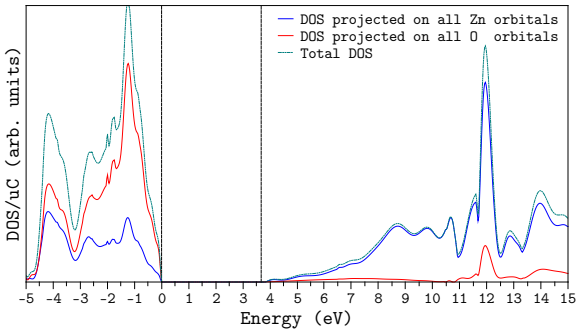

Figure 1. DOS for a pure ZnO, projected on Zn (blue) and O (red) orbitals, as well as total DOS (cyan). Black dashed lines mark band edges. All the energies are wrt TVB. Band gap $E_{\mathrm{g}} = 3.68$ eV

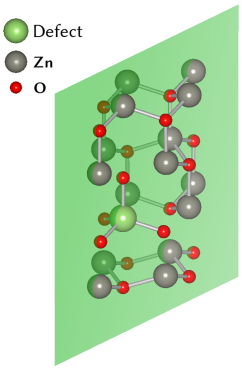

Figure 2. Characteristic vertical cross-section plane (V) (shaded) with the Miller indices (740).

into CRYSTAL09 code [10]. Optimal total energy convergence criterion in all the calculations was 10^{-7} Ha. The effective charges on atoms have been calculated using Mulliken population analysis. The $\boldsymbol{k}$-space integration has been performed by sampling the Brillouin zone with Pack–Monkhorst mesh. The geometry of all the structures was fully relaxed.

Calculations on the perfect ZnO bulk have been performed for reference, and various computed properties are compared with experiment and theory in table 1. The electronic structure was characterized by projected densities of electron states (PDOS; Figure 1).

Mulliken analysis demonstrates a considerable Zn–O bonds' covalency, its population being $0.14e$. Zinc and oxygen charges are $\pm 1.01e$, respectively. Oxygens are coordinated in almost perfect tetrahedrons, and Zn–O bonds have length $d_{\mathrm{Zn-O}} \approx 1.99$ Å.

3. Main Results

A series of calculations has been performed using various supercells to alter concentrations of defects. To match experimental works (*eg* references [15, 16]), we used $3 \times 3 \times 3$ and $2 \times 2 \times 2$ supercells (1.85 % and 6.25 % of defects, respectively).

3.1. ZnO with V_{Zn}

The electronic and structural parameters for ZnO with zinc vacancies are compared in table 2 with pure bulk material. Projected densities of states (Figure 3(a)) have been calculated for a structure with 6.25 % of defects. It shows that this system is a p-type conductor. Similar plot for a more diluted structure not depicted here shows that the latter is an insulator. Electron density redistribution on the plane V (Figure 2) is shown in figure 4(a).

V_{Zn}–O dangling bonds are substantially stretched for $2 \times 2 \times 2$ structure, increasing their

Table 2. Lattice parameters a, c (Å), Zn/Ga/V_{Zn}–O bond lengths d' in [001] direction and d'' in $[\bar{2}2\bar{1}]$ direction (Å), band gaps E_g (eV) and charges on the defect (Zn for perfect ZnO) Q (e) of pure ZnO, V_{Zn}- and Ga-doped structures. Covalent radii for 4-coordinated ions are as follows: $R_{Zn} = 74$ pm, $R_O = 124$ pm, $R_{Ga} = 61$ pm.

	ZnO	ZnO:V_{Zn}	
		$2 \times 2 \times 2$	$3 \times 3 \times 3$
a	3.2581	3.2644	3.2636
c	5.2218	5.2211	5.2042
d'	1.99	2.31	1.99
d''	1.98	2.15	1.98
E_g	3.61	—	3.44
Q	+1.01	−0.05	−0.05

	ZnO	ZnO:Ga	
		$2 \times 2 \times 2$	$3 \times 3 \times 3$
a	3.2581	3.2641	3.2619
c	5.2218	5.2434	5.2302
d'	1.99	1.89	1.87
d''	1.98	1.89	1.88
E_g	3.61	—	—
Q	+1.01	+1.57	+1.63

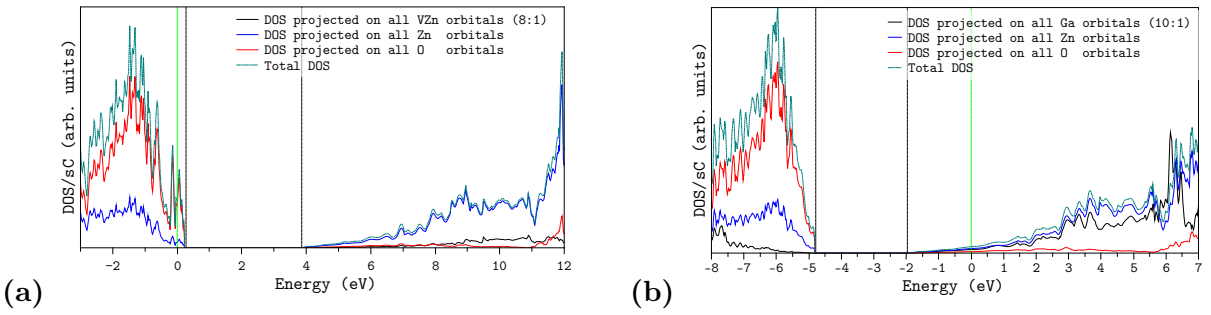

Figure 3. DOS for $2 \times 2 \times 2$ supercells of (a) ZnO:V_{Zn} and (b) ZnO:Ga, projected on Zn (blue), O (red) and Ga/V_{Zn} (black) orbitals, as well as total DOS (cyan). Boundaries of the band gap are shown with black vertical lines. Fermi level (green dashed line) corresponds to zero energy.

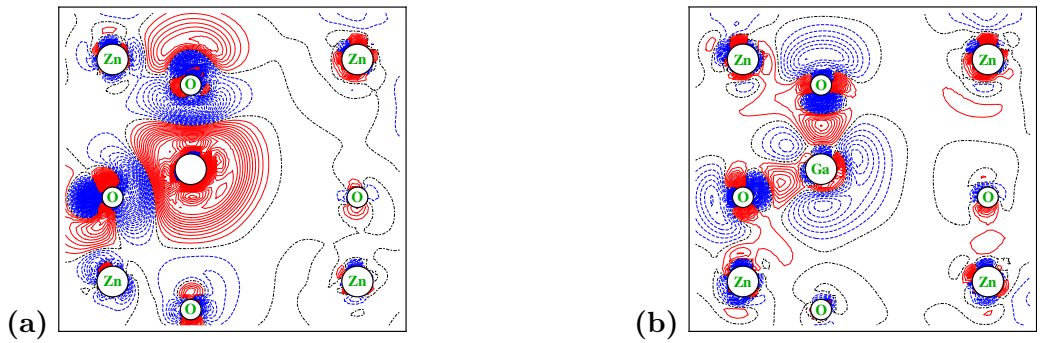

Figure 4. Differential electron charge density in (a) $2 \times 2 \times 2$ ZnO:V_{Zn} and (b) $2 \times 2 \times 2$ ZnO:Ga, projected on plane V of figure 2. Increment for isolines is $0.001e$ within the interval of electronic charge $(-0.1 \div +0.1)e$.

length by 0.2–0.3 Å. Bond lengths in the $3 \times 3 \times 3$ structure coincide with those for the parent material. Effective charge on the vacancy is almost zero ($0.05e$) and does not depend on defect concentration. To estimate vacancy creation costs, its formation energy should be calculated: $E_V^F = E_D + E_{Zn} - E_P$, where E_D, E_P and E_{Zn} are the energies of defective system, perfect system and isolated atom, respectively. $E_V^F = 15.8$ eV for ZnO:V_{Zn} (6.25 %) and $E_V^F = 10.6$ eV for ZnO:V_{Zn} (1.85 %). The structures with lower defect concentrations are found to be insulating, while more concentrated ones are p-type conductors.

3.2. Ga-doped ZnO

Same properties were calculated for ZnO:Ga and are shown in table 2. For ZnO:Ga (6.25 %) a projection of differential charge density on V plane (figure 2) is shown in figure 4(b), and densities of states are shown in figure 3(b).

After structural relaxation in ZnO:Ga (6.25 %) Ga–O bond length decreased by *ca* 0.11 Å. The effectve electronic charge on Ga atom exceeds the charge on the substituted Zn atom by $\sim 0.6e$. The same trends are found for more diluted systems, but trends therein are generally less pronounced. Atomic charge of Ga behaves inversly and grows with the concentration reaching $+1.63e$ at 6.25%. Densities of states for the ZnO:Ga (6.25 %) show that the system is an n-type conductor. Ga impurity levels are delocalized over conducting and valency bands of ZnO. The defect formation energies for ZnO:Ga (6.25 %) and ZnO:Ga (1.85 %) were found to be 4.52 eV and 2.98 eV, respectively. As expected, making less concentrated Ga solutions in ZnO is energeticaly more favourable.

4. Conclusions

Our calculations show that the possible formation of large concentrations of Zn vacancies is limited by high energy costs. Lower concentrations of vacancies are formed more readily. States of zinc vacancy are delocalized mainly over its conduction bands. Large concentration of Zn vacancies can make the material conducting, whereas small one does not give rise to conductivity. The lattice distortions associated with introduction of zinc vacancies in large concentrations are drastic and can make a whole structure unstable. With defect dilution, this problem disappears, and the geometrical properties of a defective material tend to those of the perfect one. Ga-doped ZnO is found to be an n-type conductor. Increase of Ga impurity concentration leads to an increase of the dopant effective charge wheras distances to the nearest neighbour ions decrease.

Acknowledgments

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