Ab-initio valence band spectra of Al, In doped ZnO

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ABSTRACT

We present the structural and electronic characterization of n-doped (Aluminium or Indium) ZnO and the effect of the doping on the calculated photoelectron spectroscopy (PES) spectra. The fully-relaxed calculations have been made using the density functional theory, including a Hubbard correlation term that increases the Zn-3d states binding energy, and which matches the experimental values. The effect of Oxygen vacancies is also included in our study. Our results show that the new Al or In-donor levels appearing in the conduction band hybridize with the Oxygen-2p states and help decrease the resistivity of these doped systems as was found experimentally. The calculated PES spectra show a small enhancement in the intensity close to the chemical potential as a result of these new Al or In levels.

1. Introduction

Zinc Oxide (ZnO) is a wide band-gap (3.4 eV) semiconductor material at room temperature. Like other II–VI semiconductors, it is used in optoelectronic devices because of its band-gap. When it is pure it is an n-type semiconductor which has been experimentally observed to contain excess metal (or Oxygen deficiency) [1] and that this excess can be accommodated in part by the presence of Zinc interstitials or Oxygen vacancy donor defects. Its optical and electric properties are not very stable at high temperatures [2] which is why in some cases it is preferred in n-type doping. A way to obtain low-resistivity n-type ZnO is doping it with group IIIA atoms, like Indium or Aluminium.

ZnO, either doped or not, is frequently used in thin-film CuInGaSe₂ (CIGS) solar cells. When undoped, it is used as a buffer layer because of its high resistivity. When doped however, it is used as a transparent and conducting window layer; n-doped ZnO can be grown by different methods such as spray pyrolysis [3–6], laser ablation [7,8], electrochemical deposition [9,10] and sol–gel [11].

This work focuses on an ab-initio study of the electronic properties and PES spectra of Indium and Aluminium doped ZnO with Oxygen vacancies and the effect on its resistivity.

2. Theoretical approach

Calculations have been carried out using density functional (DFT) methodology, at the generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) functional [12] using the plane-wave Vienna Ab-initio Simulation Package (VASP) [13] with Projector Augmented Wave (PAW) potentials [14]. The Zinc d-states in the

potential were explicitly treated as valence states having in this case 12 electrons ($3d^{10}4s^2$). For Oxygen we used 6 electrons ($2s^22p^4$), 3 for Aluminium ($3s^23p^1$) and 13 for Indium ($5s^24d^{10}5p^1$).

To describe the pure semiconductor we have used a plane-wave basis set with a 400 eV energy cutoff, and the Brillouin Zone (BZ) was sampled using different Monkhorst–Pack (MP) grids including the Γ point in the calculations. Full atomic relaxations were made using convergence parameters up to 0.01 eV/Å for atomic forces and less than 1 meV for the total energy.

Standard DFT underestimates the binding energy of the Zn-d semi-core states so the hybridization between them and the p-Oxygen states is not taken into account correctly, pushing up the valence band (VB) and reducing the band-gap [15]. This effect adds an additional error to the standard DFT band-gap underestimation. In order to correct that, we have included the effects of an on-site Coulomb correlation (DFT+ U) in the calculations. This method is based on two empirical parameters: U and J , which represent the average screened Coulomb and the exchange interaction respectively in a given localized shell. Here these interactions were taken into account using the simplified approach introduced by Dudarev et al. [16] which uses only an effective U parameter ($U_{\text{eff}}=U-J$). The meaningful parameter U_{eff} used was evaluated by adjusting the Zinc d-orbitals position to experimental results (7.5 eV below Fermi energy) [17].

ZnO has a wurtzite structure with 4 atoms in the primitive cell. Compounds resulting from the substitution of Zinc atoms by Aluminium and Indium have been modeled using different wurtzite supercells of 48 ($2 \times 2 \times 3$), 64 ($4 \times 4 \times 1$) and 108 ($3 \times 3 \times 3$) atoms. In the latter, the Oxygen vacancies and metal doping have been studied together so we have mainly focused our studies in that. This 108 atom supercell has a IIIA metal concentration (ca. 2%) resulting from substituting one of the Zinc atoms for one impurity atom, and also removing one Oxygen atom to obtain one vacancy. The calculations have been made for both cases at their equilibrium undoped lattice

Table 1

Undoped ZnO geometrical parameters (volume per formula unit, lattice constant, c/a ratio, and distortion parameter) for the GGA and GGA+ U ($U_{\text{eff}}=8.5$ eV) compared with experimental data [18]

	V_o ($\text{\AA}^3$)	a ($\text{\AA}$)	c/a	u
GGA	24.045	3.26	1.609	0.3801
GGA+ U	21.915	3.16	1.6068	0.3801
Expt	23.796	3.249	1.6018	0.3819

constants and then atomic relaxations for metal doped ZnO were made. The MP grids used were a $(6 \times 6 \times 3)$ with 17 irreducible k -points for the $\text{Zn}_{24}\text{O}_{24}$ cell, a $(2 \times 2 \times 6)$ with 8 k -points for the $\text{Zn}_{32}\text{O}_{32}$ cell and a $(2 \times 2 \times 2)$ with 6 k -points for the $\text{Zn}_{54}\text{O}_{54}$ and their doped systems.

3. Results

3.1. Undoped ZnO

After relaxation of undoped ZnO using the GGA approximation, we have found structural parameters very close to the experimental [18] and other theoretical calculations [18 and references therein] (see

Fig. 2. GGA+ U DOS for the undoped (solid line) and with an Oxygen vacancy (dashed line) ZnO.

Table 1). For this optimized cell the observed band-gap was 0.81 eV, smaller than the experimental results but in agreement with similar theoretical results [19–21]. The inclusion of an Oxygen vacancy in the $\text{Zn}_{74}\text{O}_{74}$ supercell causes an occupied state to lie in the gap. After ionic relaxation this donor state appears in the valence band, thus obtaining

Fig. 1. (a) GGA (solid-line) and GGA+ U ($U_{\text{eff}}=8.5$ eV) (dashed line) DOS for the undoped ZnO, (b) GGA+ U ($U_{\text{eff}}=8.5$ eV) PDOS for the different Zinc and Oxygen states for undoped ZnO between -20 eV to 16 eV and (c) an enlarged view between -3 and 12 eV. The Fermi energy is set to zero.

Fig. 3. GGA+ U (a) DOS for the Al-doped ZnO and (b) PDOS for the different Zinc and (c) Oxygen states. (d) PDOS for the total density of Aluminium (solid line) and its projected s and p-states (dashed lines).

a 1.19 eV width band-gap. Therefore the effect of a vacancy causes an increase in the gap. As we have already said, DFT underestimates the binding energy of the Zn-d semi-core states and so we have applied the DFT+ U methodology to correct that spurious fact. We have used different values of an effective U_{eff} parameter in order to match the experimental d-orbital energy value [17]. The optimal value for U_{eff} was 8.5 eV. After atomic relaxation, we obtained d-peaks values narrower than those of GGA-DFT and also valence band states closer to the top of the valence band with a considerable decrease in its d-character (Fig. 1a). Using this DFT+ U methodology, the calculated band-gap was 2.13 eV. As

we show in Fig. 1b and c the valence region is made up of s-Oxygen states of about -18 eV, d-Zinc states between -8.3 and -6.7 eV and mainly p-Oxygen states between -5 eV and the top of the valence band. The conduction band (CB) is mainly made up of s and p-Zn orbitals and Oxygen 2p orbitals. Therefore the DFT+ U method seems to be quite good for describing the hybridization between O-p and Zn-d states. Then we also included an Oxygen vacancy in the 108th atom of the ZnO supercell. After full convergence we found, as in the GGA case, an occupied state close to the top of the valence band which is caused by the interaction between Zn dangling bonds around the vacancy [22]. The composition of the valence and conduction bands remains equal. However an increase in the band-gap compared with undoped ZnO (2.47 eV) is now observed. The comparison between undoped ZnO both with and without an Oxygen vacancy is shown in Fig. 2.

3.2. Aluminium and Indium doped ZnO

Aluminium doped ZnO, where an Al substitutes a Zinc atom, has been studied for 48, 64 and 108 atom cells using the GGA+ U approach. The total (DOS) and projected (PDOS) density of states results after atomic relaxation for the 108 atom cell, are shown in Fig. 3(a-c). The new density of states spectra and the projections are very similar to the undoped one (see Fig. 1). The main difference appears in the conduction states where the donor band that hybridizes with the ZnO host lattice conduction states is now located. In Fig. 3d the Aluminium projected density of states for the 108 atom cell is presented as example but the results are almost identical for all dilutions. Comparison of Fig. 3a and d shows the aforementioned hybridization very clearly throughout the conduction band. Both graphs have very similar shapes. The calculations have been made for Al-ZnO, with and without Oxygen vacancies and the hybridization appears in both cases. For the Al-ZnO without vacancies, the new VB-CB band gap is smaller than that previously calculated for the undoped system but the chemical potential appears now located 1.22 eV inside the conduction band. Moreover, for Al-doped ZnO with an Oxygen vacancy, the band-gap is again smaller than the calculated undoped system with a vacancy. The chemical potential also appears within the conduction band.

Similar types of GGA+ U calculations have been made for Indium instead of Aluminium doped ZnO, both with and without Oxygen vacancies. The results for the density of states are similar to those of Al-doped system: the Indium donor level appears within the conduction band and hybridizes with it as in the Aluminium case. The main differences appear in band-gap values, where we found

Fig. 4. GGA+ U (a) DOS for the In-doped ZnO and (b) PDOS for the total density of Indium (solid line) and its projected s, p and d-states (dashed lines).

Fig. 5. Calculated PES spectra for ZnO (solid line) and Al-ZnO and In-ZnO (dashed lines). The inset shows the spectra at energies close to the chemical potential.

smaller values than in Al-doped systems. These results are shown in Fig. 4. By taking this DOS into account, it is possible to consider that this hybridization of the donor band will increase the electrical current as was reported for the Gallium system [23] but it is not possible to derive which system should decrease its resistivity more.

4. Comparison with experimental results

Our results for doped and undoped ZnO with and without vacancies are compared with experimental photoelectron spectroscopy (PES) data obtained by [6] with an Aluminium concentration with a ratio $[Al]/[Zn] = 1\%$ and 3% while in the present work the ratio is around 2% . To compare the data calculated on the density of states with the experimental PES spectra, the DOS results must follow a post-process procedure. In the first step DOS were convoluted with a Lorentzian function with a full width at half maximum (FWHM) height proportional to the binding energy of electrons according to $0.1|E - E_F|$ for emulating the finite lifetime of the excited electrons. Then, a Gaussian convolution has been carried out for taking the broadening of the spectrometer into account. In this case the Gaussian function chosen has FWHM = 60 meV which is the usual resolution of the equipment. Finally, a parabolic background has been added to the spectrum. The theoretical results have been shifted by 1.3 eV, which is the difference between the experimental and the GGA+*U* band-gap for the undoped system. The Fermi energy is located at the bottom of the conduction band. For the undoped systems the relative position of the 3d-Zinc levels in respect to the 2p-Oxygen levels agrees very well with the experimental spectra. The main difference with the experimental data appears in the Aluminium or Indium doped system because the chemical potential is inside the conduction band and a small hump appears which has no analogue in the experiment. The comparison of calculated PES spectra data between undoped ZnO, Al-ZnO, and In-ZnO is shown in Fig. 5. Our results compared qualitatively well with other theoretical calculations for the similar system Ga-doped ZnO [23].

5. Conclusions

We have studied theoretical PES spectra of Aluminium and Indium doped ZnO with and without Oxygen vacancy and the effect on the

resistivity of these doped systems. Good structural parameters have been obtained with standard DFT, but VB-CB band-gaps and Zn-3d levels within the VB needed to be corrected. The correction has been made using the GGA+*U* approach matching the 3d levels to experimental results which corrects the most part of the band-gap problem. The study of the Oxygen-vacancy process also allows better band-gaps to be obtained. After including Aluminium or Indium atoms as dopants by substituting the Zinc atoms the donor levels appear within the conduction band. The calculated PES spectra show a new small intensity enhancement as a result of these new Al or In levels. These levels are highly hybridized with the Oxygen-2p states of the conduction band which may explain the increase in electrical current of these doped compounds which are used as transparent conducting top electrodes in thin-film solar cells.

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