Research article

Band Structure of Sr Doped into Bulk Wurtzite ZnO: A DFT Study

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Abstract

This work investigates the structural and electronic properties of pure and Sr-doped ZnO using first principles density functional calculations (DFT). The calculations were carried out using GGA-BLYP functional. This functional underestimates the band gap value in semiconductors but does not affect the accuracy of the related properties of the crystals. The Sr-doping caused increase in lattice volume and slight distortions at the unit cell parameters in a wurtzite structure. The doping process presented increase in the band-gap energy E_g at low percentages 25%, 37.5% and 50% with indirect band gap and direct band gap at high percentages 62.5%, 75%, 87.5% and 100%. which we can call it wide indirect band gap. These results can be used as a foundation for more in depth calculations which can be used on optical and Photo-catalytic applications.

Keywords: Doping; DFT; Wurtzite; Wide Semiconductor.

1. Introduction

ZnO can be considered as an 'old' semiconductor which has been compelling research attention for a long time because of its applications in many scientific and industrial areas. ZnO is a wide direct band gap semiconductor with $E_g \approx 3.436$ eV at $T = 0K$ and (3.37 ± 0.01) eV at room temperature (Klingshirn et al. 2010). Wurtzite ZnO crystal structure is the most stable state with lattice parameters $a \sim 3.249 \text{ \AA}$ and $c \sim 5.206 \text{ \AA}$ (Schreyer et al. 2014). The Zn atoms are tetrahedrally coordinated with four O atoms, where the Zn d-electrons hybridize with the O p-electrons.

Often, the first-principles calculation based on density functional theory (DFT) is used

to evaluate the different properties of pure and doped ZnO. Several works have employed DFT with Generalized Gradient Approximation PBE, LDA and other exchange-correlation functions (Mohamad et al. 2017), (Shen et al. 2008), (Kalay et al. 2009), (Mousavi 2017) and the references therein.

Not too much work has been investigated for Sr doped ZnO. Experimental investigation of structural and optical properties of nano thin films of ZnO and Sr-doped ZnO onto glass substrates synthesized by a two-step chemical bath deposition technique revealed that the films are polycrystalline in nature with hexagonal phase having (002)

preferential orientation and The shifts in optical band gap of the SZO films are 2.35 (Vijayan et al. 2008)

First-principles calculations have been performed to determine the effects of Sr doping on the structural, electronic, and optical properties of ZnO nanotubes (Moradian and Shahrokhi 2013); It is found that all doped systems are exothermic and stable, but by increasing Sr-doping concentration the formation energy increased The semiconducting energy gap of Sr-doped single walled ZnO nanotubes is bigger than their pristine ZnO nanotube. This study also showed that the systems have negative formation energy for all impurity concentrations and that all systems have also direct band gap at Γ -point and are nonmagnetic. Mahmood et al employed the PBE exchange–correlation function parameters in GGA to study the electronic structure and optical properties of the pure and Sr-doped ZnO; they find out that The Sr doping significantly affects the electronic band gap, The band gap was observed to increase with increasing Sr content (Mahmood et al. 2017).

In this paper, as the use of ZnO in a wide range of applications would not be possible without the doping process, which can be used to change drastically the material properties, we use density functional theory (DFT) calculations under GGA allied to BLYP exchange correlation functional to study the Sr-doping at 12.5%, 25%, 37.5%, 62.5%, 75% and 87.5% concentration into bulk wurtzite zinc oxide which expected to change the band structure properties in particular direct and indirect band gap of the material.

2. Methods

We used Quantum espresso version 6.3 for our calculations. Density functional theory

estimated to be ~ 3.25 – 3.27 eV with respect to the ZnO film and the refractive index is.

(DFT) was used as implemented in the PWSCF code (“Becke: Density-functional Thermochemistry. III.... - Google Scholar” n.d.). Exchange and correlation were treated with GGA using the Becke–Lee–Yang–Parr (BLYP) functional (Becke 1988). We used the ultra soft pseudopotentials: Zn.blyp-van_ak.UPF, O.blyp-van_ak.UPF and Sr.blyp-sp-hgh.UPF (“Pseudopotentials - QUANTUMESPRESSO” n.d.). It is a well known fact that GGA approximation underestimates the band gap value in semiconductors (“Effect of Phase Transition on the Optoelectronic Properties of Zn_{1-x}MgxS: Journal of Applied Physics: Vol 112, No 7” n.d.) (“Effect of Phase Transition on the Optoelectronic Properties of Zn_{1-x}MgxS: Journal of Applied Physics: Vol 112, No 7” n.d.) (“Structural and Optoelectronic Properties of the Zinc Titanate Perovskite and Spinel by Modified Becke–Johnson Potential” 2013), but does not affect the accuracy of the comparison of the related properties of the crystals.

The supercell used as the starting point in the calculation was 2x2x1 (16 atoms: Zn=8 atoms and O= 8atoms). Supercell is of the experimental unit cell of wurtzite ZnO. The original lattice parameters are $a=b=3.2493$ Å, $c=5.2057$ Å and space group P6₃mc (186) (“Journal of Applied Crystallography 10.1107/S1600576714003379-Google” n.d.).

The first step in this simulation is applying self-consistent field (scf) calculation to the supercell (16 atoms) of ZnO to determine cutoff energy parameter and obtain the minimum energy. Figure 1 shows the resulting of calculation of cutoff plane-wave energy. The plane-wave expansion

limit to point 40 Ry; accordingly the cutoff density for ultra soft pseudopotentials ($8 \times$ plane-wave cutoff energy) is set at 320 Ry. 8 zinc and 8 Oxygen atoms) was performed. The lattice parameter of the supercell is $a=b= 6.4986\text{\AA}$, $c=5.2057\text{\AA}$ and relaxed volume of the supercell was found to be 1361.6849 a.u.^3 ; is the same as unrelaxed volume. A Sr-doped models (Sr-ZnO) was developed from unit cell expansion of ZnO in the direction of axes a, b as shown in figure2, resulting at 12.5%, 25%, 37.5%, 50%, 62.5%, 75% and 87.5% and 100% concentration. Table 1 shows the amount of percentage in term of atoms replacement. The band structure of the Wurtzite ZnO and its defect Sr-ZnO was calculated along the various symmetry lines [Γ (0.0, 0.0, 0.0), M (0.0, 0.5, 0.0), L (0.0, 0.5, 0.5), A (0.0, 0.0, 0.5), H (0.3, 0.3, 0.5), K (0.3, 0.3, 0.0), M

charge

Optimization of lattice parameters and generation of super cell contains 16 atoms ($(0.0, 0.5, 0.0)$, Γ (0.0, 0.0, 0.0), and A (0.0, 0.0, 0.5)].

3. Results and Discussion

Band structure of pure ZnO

Band structure is an electronic structure in form of energy scheme to describe the conductivity of materials. The calculated band structure of pure ZnO crystal structure is presented along the various symmetry lines (Γ , M, L, A, H, K, M, Γ , and A) of the Brillouin zone in Figure 3. The Fermi level E_F was set to zero; above and below this level were the conduction band CB and

Figure 1: cutoff energy vs. total energy

Figure2: 2x2x1 wurtzite supercell Crystalline structures for Sr:ZnO materials.

Table 1: The amount (in %) of Sr doped on ZnO models used in simulation

No. of Zn atoms replaced by Sr	Doped amount (%)
1	12.5
2	25.0
3	37.5
4	50.0
5	62.5
6	75.0
7	87.5
8	100

valence band VB, respectively. The minimum energy level of the conduction band CBM and the maximum energy level of the valence band VBM were at the same k-point (Γ - Γ), indicating that the ZnO was a direct band gap semiconductor. The calculated band gap of the ZnO was 0.9349 eV. This is a new result. To our knowledge nobody has been work in ZnO used the exchange correlation BLYP functional based on DFT.

Indirect band gap

Substitution of one zinc atom by strontium atom gives 12.5% concentration of Sr in ZnO. The structure formula of this model is $\text{Zn}_7\text{Sr}_1\text{O}_8$. The relaxed volume of the cell is 1455.0 a.u.^3 compare with 1361.6849 a.u.^3 of pure ZnO. This cell volume variation is caused by bond length increase after the doping process. The ionic radius of the dopant Sr^{2+} ($R_{\text{Sr}^{2+}} = 1.18 \text{ \AA}$) is bigger than that of Zn^{2+} ($R_{\text{Zn}^{2+}} = 0.74 \text{ \AA}$). When Sr occupies the Zn site, the repulsion between the Zn and Sr causes further expansion of the cell volume. In addition, the bond length of the Sr-O is lengthier compared to that of

Zn-O, which results in the said expansion. Indirect band gap is predicted at 12.5%, 25%, 37.5% and 50% concentration of Sr on ZnO material. Table2 shows different values of k-points and energy gap of those Sr-ZnO models. Refer to table2, at 12.5% concentration, it can be notice that the conduction band minimum (CBM) is at Γ -point; While the valence band maximum (VBM) is at L-point. This indicates that the band gap in this model is indirect band gap semiconductor with band gap $\approx 1.38 \text{ eV}$. This is because the k-points are different. The picture is described in figure 4. At 25% concentration we found that the conduction band minimum (CBM) is at Γ (Gamma) point while the valence band maximum (VBM) is at A-point indicating indirect band semiconductor with band gap $\approx 1.25 \text{ eV}$. The minimum (CBM) and maximum (VBM) k-points at 37.5% concentration for Sr-ZnO material is at Γ - point and A-point respectively with indirect band gap energy $\approx 1.79 \text{ eV}$. These different K-points of 37.5 concentrations were depicted at 50% concentration but with indirect band gap energy $\approx 2.32 \text{ eV}$.

Figure3: Calculated pseudopotential band structure for pure wurtzite ZnO crystal. Red curve is CBM and the green one is VBM

Table2: conduction band mini, and valence band max., energy gap in (eV) of different k-point for indirect band gap Sr-ZnO models.

Doping amount (%)	K-Points											
	Γ - Γ			M-M			L-L			A-A		
	CBM (eV)	VBM (eV)	E_g (eV)	CBM (eV)	VBM (eV)	E_g (eV)	CBM (eV)	VBM (eV)	E_g (eV)	CBM (eV)	VBM (eV)	E_g (eV)
12.5%	0.6436	-0.9036	1.55	2.6894	-0.7639	3.45	4.0536	-0.7340	4.79	2.7797	-0.9707	3.75
25%	0.6934	-0.8535	1.55	2.8203	-1.1392	3.96	3.8842	-0.8419	4.73	2.4503	-0.5517	3.00
37.5%	0.8850	-1.0844	1.97	2.6537	-1.0825	3.74	3.7277	-1.1645	4.90	2.6355	-0.9048	3.54
50%	1.0940	-1.2356	2.34	3.0663	-1.3480	4.41	4.1933	-1.4986	5.69	2.8823	-1.2266	4.11

Figure4: Indirect band structure for 12.5% Sr doped wurtzite ZnO crystal.

Direct band gap structure

The band structures of the 62.5%, 75%, 87.5% and 100% concentrations of Sr in wurtzite ZnO have a direct band structure. Table3 shows k-point values those concentrations. The minimum conduction band (CBM) and maximum valence band (VBM) are at the same k-points Γ - Γ which

revealed that the band structure for those concentration are a direct band structure. In direct band gap, the electron rising from valence band to conduction band will only change its potential, but in indirect band gap the electron rising from valence band to conduction band will change its potential and momentum.

Table3: conduction band mini, and valence band max., energy gap in (eV) of different k-point for direct band gap Sr-ZnO models

Doping amount (%)	K-Points											
	Γ - Γ			M-M			L-L			A-A		
	CBM (eV)	VBM (eV)	E _g (eV)	CBM (eV)	VBM (eV)	E _g (eV)	CBM (eV)	VBM (eV)	E _g (eV)	CBM (eV)	VBM (eV)	E _g (eV)
62.5%	0.9327	-0.7483	1.68	2.2241	-0.8910	3.12	3.1812	-1.5194	4.70	2.5547	-1.4389	4.00
75%	1.4862	-0.8942	2.38	3.2937	-0.9577	4.25	4.1155	-1.6271	5.74	3.0760	-1.4364	4.51
87.5%	1.3150	-1.0605	2.38	2.7507	-1.2564	4.01	3.5498	-2.1630	5.42	2.7610	-1.8686	4.63
100%	2.2413	-1.1272	3.37	2.8797	1.2268	4.11	4.2318	-2.7048	6.94	4.2285	-2.1091	6.34

Figure4: direct band structure for 87.5% Sr doped wurtzite ZnO crystal.

4. Conclusion

In conclusion, we have investigated the structural and electronic properties of pure

and Sr-doped ZnO using first principles density functional calculations. Band structure calculations were carried out using

GGA-BLYP functional. The doping process presented increase in the band-gap energy E_g at low percentages 25%, 37.5% and 50% with indirect band gap and direct band gap at high percentages 62.5%, 75%, 87.5% and 100%. which we can call it wide indirect band gap. The change in the type of band structure by addition of strange atoms lead to the change in the properties of the original pure material which could be leads to new industrial applications.

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