FULL ELECTRONIC BAND STURCTURE ANALYSIS OF Cd DOPED ZnO THIN FILMS DEPOSITED BY SOL-GEL SPIN COATING METHOD

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Abstract

Optimized Empirical Pseudopotential Method (EPM) in conjunction with Virtual Crystal Approximation (VCA) and the compositional disorder effect is exploited for simulation to extract the full band structure of ZnO thin films to ensure excellent agreement with the experiments. The full band structure of undoped and doped thin films, deposited by sol-gel spin coating technique, have been analyzed in detail with FullBand^{TM} Simulator from Tech Next Lab by using lattice parameters obtained through XRD studies. The impact of polycrystalline planes in thin film on the band gap is analyzed in terms of structure factor u. Reasonable agreement is obtained between the simulated and experimental band gap results.

Numerical Technique

Empirical Pseudopotential method (EPM) inbuilt in FullBand^{TM} Simulator is able to provide behavior of electrons on full electronic band structures of the crystals with spin-orbit interactions and also provides flexibility to fit experimental transport data [3-4]. The pseudopotential Hamiltonian is given in Rydberg atomic units by

$$H = -\vec{\nabla}^2 + V^{PS}(\vec{r}) \quad (1)$$

Here V^{PS} is the pseudopotential and ∇ is the energy operator, dependent on effective mass. For wurtzite structures, the matrix elements of the crystal pseudopotential appear as

$$V^{PS}(\vec{r}) = \sum_G V(\vec{G}) e^{i\vec{G}.r} \quad (2)$$

$$V(\vec{R}) = V^S(|\vec{R}|^2)\, S^S(\vec{R}) + iV^A(|\vec{R}|^2)\, S^A(R) \quad (3)$$

Here V^S and V^A are respectively the symmetric part and the asymmetric part of the pseudopotential. The parts of pseudopotentials can be defined in terms of form factors associated with the material, whereas S^S and S^A are respectively the symmetric and antisymmetric structure factors of the wurtzite ZnO and are given as:

$$S^S = \cos\left[2\pi\left(\frac{\Delta l}{6} + \frac{\Delta m}{6} + \frac{\Delta n}{4}\right)\right]\cos(\pi u \Delta n) \quad (4)$$

$$S^A = \cos\left[2\pi\left(\frac{\Delta l}{6} + \frac{\Delta m}{6} + \frac{\Delta n}{4}\right)\right]\sin(\pi u \Delta n) \quad (5)$$

where $\Delta l, \Delta m \; and \; \Delta n$ are the difference in Miller indices. The reciprocal lattice vector $\overrightarrow{R}$ is given by $\vec{R} = \vec{G} - \vec{G}'$. The electronic structure of the binary wurtzite compounds are simulated using lattice constant of thin film obtained from XRD studies. The form factors can be modified for obtaining good fittings with the experimental value of the band gaps [3]-[5].

Results & Discussion

This section concentrates on the results obtained regarding specific aspects of full band structure investigated in this paper using FullBand^{TM} Simulator from Tech Next Lab, which is based on EPM technique. Full band structure of ZnO has been shown here in **Figs. 1a-1d,** with different lattice parameters (a & c) and internal parameters (u) on which the symmetric and the antisymmetric structure factors depends. The accuracy of calculated results from FullBand^{TM} simulator is tested against experimental values of optical band gap. Our extracted band gap results show excellent agreement with the experimental results as reflected from Table I.

The ideal wurtzite structure has a hexagonal unit cell with two lattice parameters a and c in the ratio of $c/a = \sqrt{\frac{8}{3}}$. The unit cell ZnO crystal structure is composed of two interpenetrating hexagonal close packed (hcp) sublattices, each of which consists of one type of atom displaced with respect to each other along the three fold c-axis by the amount of $u = \frac{3}{8} = 0.375$, in an ideal wurtzite structure, in fractional coordinates. The internal parameter u is defined as the length of the bond parallel to the c-axis i.e. anion–cation bond length or the nearest-neighbor distance divided by the c lattice parameter. The basal plane lattice parameter (the edge length of the basal plane hexagon) is universally depicted by a; the axial lattice parameter (unit cell height), perpendicular to the basal plane, is universally described by c. Each sublattice includes four atoms per unit cell, and every atom of one kind (group II atom) is surrounded by four atoms of the other kind (group VI), or vice versa, which are coordinated at the edges of a tetrahedron.

In a real ZnO crystal, the wurtzite structure deviates from the ideal arrangement, by changing the c/a ratio or the u value. The symmetric and the antisymmetric structure factors of the wurtzite ZnO are strongly dependent on the internal parameter u, the dependency can be shown by Eqs.4 & 5. The experimentally observed c/a ratios are smaller or larger than ideal. It should be pointed out here that a strong correlation exists between the c/a ratio and the u parameter in that when the c/a ratio decreases, the u parameter increases in such a way that those four tetrahedral distances remain nearly constant through a distortion of tetrahedral angles due to long-range polar

interactions. These two slightly different bond lengths will be equal if the following relation holds: $$u = \frac{1}{3}\left(\frac{a}{c}\right)^2 + p \quad (6)$$

The value of p in Eq. 6 is reported as 0.25 by many researchers for single crystalline thin films. In the present article, we have analyzed the various value of p during calibration of experimental optical band gap. It is found that the value of p is dependent on the crystal quality associated with thin films. Here for good matching of experimental and simulated values of the band gaps, the p value is tabulated in Table I. The experimental XRD peaks correspond to the hexagonal wurtzite structure of ZnO showing preferred orientations along (100), (002) and (101) as depicted in reference [1]. However, small peaks along (102), (110) and (103) also appear. No impurity phase of Cd is detected. The peak along c axis i.e. (002) plane is prominent and occurs at $2\theta = 34.21^o, 34.57^o, 34.77^o, \text{and } 34.33^o$ for undoped, 0.45at.% Cd, 0.51at.% Cd and 0.56at.% Cd doped ZnO respectively. At normal pressure the wurtzite ZnO structure consist of four atoms in the unit cell which produces eight valence bands. The projected density of states (per unit energy) has been calculated (not shown here). In ZnO full band structures, on the basis of density of states analysis, bands 1 and 2 show strong s-like character and rest of the bands exhibit p-like character, **Figs.1a-1d.** Especially bands 6 and 8 illustrate pure p_{xy}-like and p_z-like characters respectively. The conduction bands demonstrate almost free-electron-like behavior. The primary valley for all materials lies at Γ_c^1 (k=25). The secondary valleys included in the simulation are located at U (k~12.5) and Γ_c^3(k=25). It should be noted that their relative energy ordering varies among the materials studied here- undoped, 0.45at.% Cd, 0.51at.% Cd and 0.56at.% Cd doped ZnO. The U-valley minima are assumed at the midpoint between the M and L symmetry points, with six equivalent valleys.

Conclusions

Using FullBand™ Simulator from Tech Next Lab, ZnO full band structures of undoped, 0.45at.% Cd, 0.51at.% Cd and 0.56at.% Cd doped ZnO have been obtained and compared with the experimental optical bandgap at Γ valley. There is excellent agreement between the experimental and simulated values of the band gaps of the four samples. The thinfilm quality plays significant role in deciding the band gap values. The crystal quality associated with thin films has been described here in terms of internal parameter in above theoretical studies. The bandgap engineering by introducing impurity can provide useful design guidelines for the

specific device applications and with the help of optimized full band structure design engineers can extract various physical properties e.g. density of states (DOS), effective mass, energy etc.

Table 1: Crystallite size determined by DS formula and WH plot, strain, lattice constants and anion-cation bond length for undoped and Cd doped ZnO thin films along with optical and simulated energy band gaps using EPM method with optimized internal parameter (u) at gamma valley.

ZnO Samples	t_{DS} (nm)			t_{WH} (nm)	Strain	Lattice Constant		Internal Parameter	Bond Length (Å)	Optical Band gap (eV)	Simulated Band gap (eV)
	(100)	(002)	(101)			a (Å)	c (Å)	u			
Undoped	11	18	10	26	6.5×10^{-3}	3.324	5.243	0.4035	2.013	3.22	3.21785
0.45at.% Cd doped	16	20	17	13	-8.0×10^{-3}	3.328	5.190	0.4023	2.009	3.20	3.19845
0.51at.% Cd doped	19	21	19	26	1.5×10^{-3}	3.332	5.161	0.4025	2.007	3.19	3.19286
0.56at.% Cd doped	11	18	10	31	10.0×10^{-3}	3.313	5.225	0.4040	2.006	3.15	3.15996

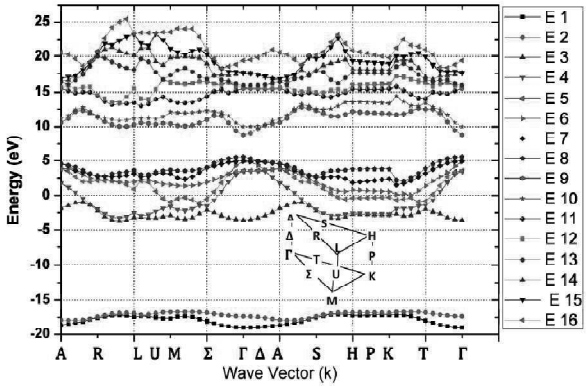

Fig.1a

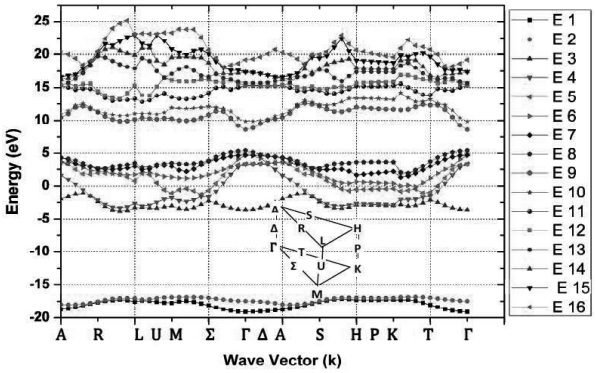

Fig.1b

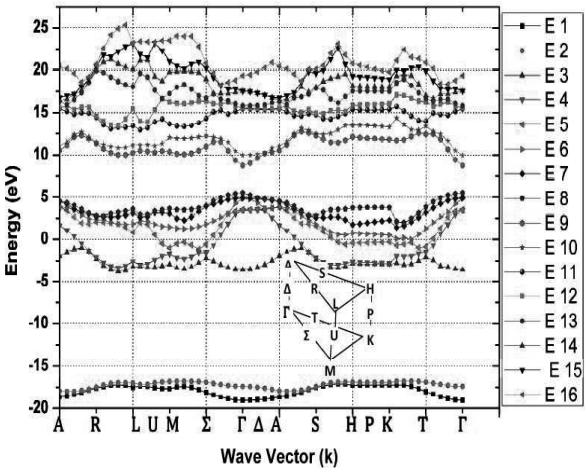

Fig.1c

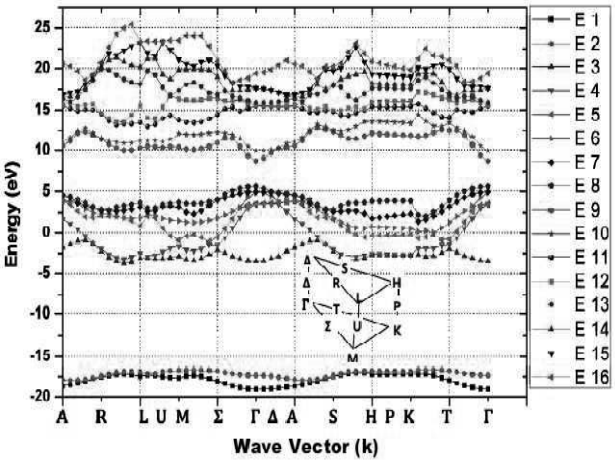

Fig.1d

Fig.1: Full band structure investigated in this paper using FullBand™ Simulator from Tech Next Lab for a) undoped, b) 0.45at.% Cd, c) 0.51at.% Cd and d) 0.56at.% Cd doped ZnO.

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