FULL ELECTRONIC BAND STRUCTURE CHARACTERIZATION of ZnO NANOROD

Praveen Saxena, Anshika Srivastava
Tech Next Lab Pvt Ltd,
Lucknow - 226003, India,
Email: a.saxena@technextlab.com,
Tel: (011) 522 404 1565, (011) 983 915 1284

Abstract

In the present work the full electronic band structure of ZnO nanorod is characterized using TNL-Full Band™ simulator from Tech Next Lab. The calibrated band gaps against the experiments are found to increase with increasing Al content from 0 to 5 at% into ZnO. It also justify the Burstein–Moss shift effect. The computation reported here is independent of the topology of the film surface i.e. the shape of the nanostructure (nanorod in present case). The effect of structure topology is taken care through the lattice disorder. The band structure analysis of ZnO and AZO samples predict that the band gap value is strongly dependent on the internal structure parameter, u. The value of u is significantly affected by lattice disorder generated due to bond angle or length alteration dependent on topology of structure and impurity addition. Reasonable agreement is obtained between the reported and experimental optical band gap results.

Numerical Technique

The empirical pseudopotential method (EPM) coupled with virtual crystal approximation (VCA) method inbuilt in TNL-FullBand™ simulator is used to predict the various physical properties associated with the behavior of electrons transport on the full band structures of ZnO and AZO nanorod structure. The technique also takes into account the spin-orbit interactions to resolve degeneracy effect [1]. The proposed technique is tested, verified and proven its capabilities for accurate prediction of band structure of Si, Ge, GaAs, ZnO thin/thick film, group III-V nitrides binary & ternary alloys and other semiconductors [2-3]. The outcomes of TNL-FullBand™ simulator have proven its superiority against density functional theory (DFT) based methods [2-3]. All the results reported in present manuscript are reproducible.

The details of numerical method used here is given in our previous publications refer to reference [2-3]. The input parameters require to simulate the full electronic band structure are the thickness of thin film, the lattice constants and the crystal orientation of the sample. The structure factor u is computed with the lattice parameters i.e. a and c values. The XRD studies

obtained lattice constant are taken to calibrate the experimental band gap values [4]. The full electronic band structure obtained for ZnO and AZO structures are shown in Fig. 1.

Results & Discussion

This section concentrates on the results obtained regarding specific aspects of full band structure investigated in this paper exploiting TNL-FullBand^{TM} simulator. Full band structure of ZnO has been shown here in **Figs. 1a-1d,** with different inputted XRD obtained lattice parameters (a & c) [4] and computed internal parameters (u) values. The accuracy and reliability of in-house developed method is again tested against experimental optical band gap. The band gap results show excellent agreement with the experimental results at Γ-valley, **Table I**. The full band structure shown in Fig.1 depicts bands 1 and 2 show strong s-like character and rest of the bands i.e. 3 to 6 exhibit p-like character. Especially bands 6 and 8 illustrate pure p_{xy}-like and p_z-like characters respectively, whereas band 9 to continuum show d-like character and treated as conduction band in the Brillion zone. The primary valley for all materials lies at Γ_c^1. The secondary valleys included in the simulation are located at U and Γ_c^3. The U-valley minima are taken at the midpoint between the M and L symmetry points, with six equivalent valleys.

The Full band structure of undoped ZnO is shown in Fig. 1a, whereas AZO bandstructures are depicted in Fig 1b, 1c, 1d respectively. At normal pressure in wurtzite structure four atoms exist in the unit cell which produces eight valence bands. The projected density of states (per unit energy) and carrier effective masses at different valleys are extracted from full band structure using energy-wave vector (E–k) data. It should be noted that their relative energy ordering varies among the materials studied here—undoped ZnO, AZO(2%at), AZO(3%at), and AZO(5%at) doped ZnO nanorod films.

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. 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. The real ZnO wurtzite structure deviates from the ideal arrangement, changing the c/a ratio, the u value changes [2-3]. 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. Refer to reference [2], the alloy disorder coefficient (P) is the measure of lattice deformation due to intrinsic atomic arrangements or the addition of extrinsic doping. The theoretical knowledge is the basic requirement to demonstrate the experimental results with the inclusion of the effects of the presence of intrinsic defects (e.g., oxygen vacancies) and lattice disorder effects due to the extrinsic doping. The value of disorder coefficient, *P* is listed in Table I, used to predicts the disorder behavior. The comparison of undoped ZnO and AZO band gap values, the impact of Al addition in ZnO prompts more lattice disorder and thus increase in bandgap values. The relation between lattice disorder and bandgap is explained on the basis of atomic radii of Zn, O and Al atoms (R_{Zn}=1.22 A, R_O=0.66 A and R_{Al}=1.21A respectively) and their arrangement into lattice. There are two probabilities of incorporation of Al atoms into ZnO lattice;

i) Al atom replaces Zn atom and occupy its position onto the lattice

ii) Al atom replaces O atom and occupy its position onto the lattice

In first case, as the atomic radii of Zn and Al atoms are almost comparable i.e. probability of less lattice mismatch generation, the alloy disorder effect will be low in this case. However, in case of O atom replacement by Al atom, due to large atomic radius of Al atom as compared to O atom, it will occupy more space onto the lattice. In turn it will alter the bond length of Al-Zn-O atoms i.e. the ratio of a/c will be changed drastically. The effect can be concluded from the XRD obtained lattice parameters i.e. a and c [4], Table I. Increasing the content of Al doping the values of lattice parameters a and c increases as compared to undoped ZnO sample. The change in bond length is responsible for the generation of the lattice disorder and justifies the alloy disorder effect, in turn bandgap value increases. On the basis of values of disorder coefficient (P), it is also concluded that addition of Al content in ZnO make them p- or n- type conductive.

Conclusions

TNL-FullBand^{TM} simulator accurately predicts the full band structures of undoped, 2at.%Al, 3at.%Al and 5at.%Al doped films of ZnO nanorod structure. The bandgap values are calibrated against 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 are achieved. The significant role of Al doping responsible for generation of lattice disorder is extracted along with the alloy disorder coefficient (P). The change in bandgap values are predicted based on crystal quality and in terms of internal structure parameter. The results may provide valuable physical

insights during bandgap tailoring by addition of impurity. The proposed method can provide useful epitaxial growth guideline and extract various physical properties e.g. density of states (DOS), effective mass, energy etc.

Table 1: Undoped and Al doped ZnO optical and simulated energy band gaps

Material	a (°A)	c (°A)	$u = \frac{1}{3}\left(\frac{a}{c}\right)^2 + \frac{1}{4}$	Disorder Coefficient P)	Experimental Band gap	Simulated Band gap
ZnO	3.257	5.203	0.3806	0.0104		3.25844 eV
2at%.Al:ZnO	3.253	5.2112	0.3799	0.0041	3.26 to 3.67	3.3287 eV
3at%.Al:ZnO	3.249	5.2363	0.3783	0.007	eV	3.38824 eV
5at%.Al:ZnO	3.253	5.2392	0.3785	-0.0005		3.39068 eV

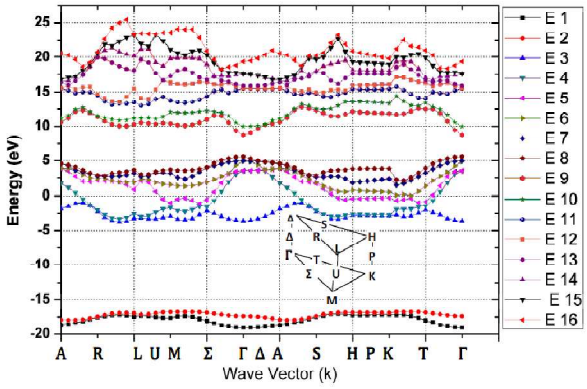

Fig.1a

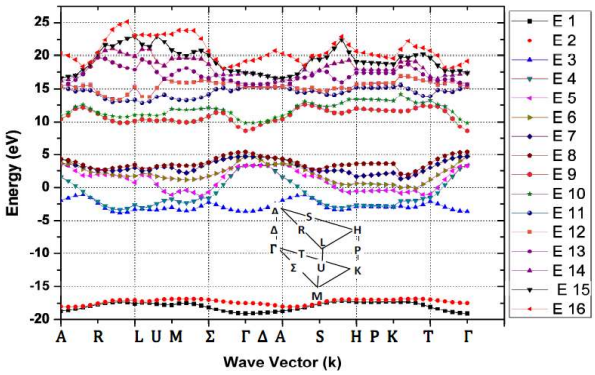

Fig.1b

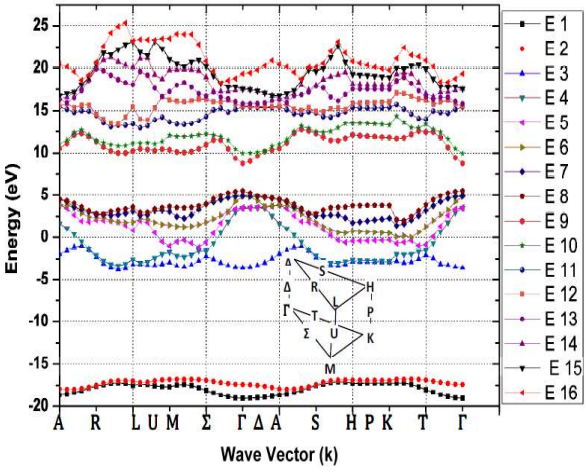

Fig.1c

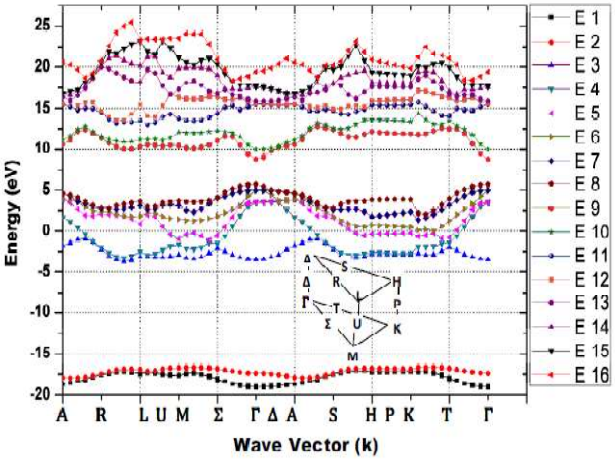

Fig.1d

Fig.1: Full band structure investigated in this paper using FullBand™ Simulator from Tech Next Lab for a) undoped, b) 2at.%Al, c) 3at.%Al and d) 5at.%Al doped ZnO.

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