Structural, electrical transport and optical studies of Li ion doped ZnO nanostructures

Rajendran Ajay Rakkesh, Subramanian Balakumar*

National Centre for Nanoscience and Nanotechnology, University of Madras, Maraimalai Campus, Chennai-600025, India

Received 16 February 2014; Received in revised form 20 March 2014; Accepted 23 March 2014

Abstract

In the present work, we studied the morphological aspects, electrical transport and optical properties of pure and lithium ion doped semiconducting ZnO nanostructures successfully prepared by a co-precipitation method. The effect of lithium doping and various morphologies on the structural, electrical and optical properties of these nanostructures were investigated. The X-ray diffraction (XRD) pattern demonstrated that the Li doped ZnO nanostructures exhibits the hexagonal wurtzite structure. A slight change in the 101 peak position was detected among the samples with various morphologies. The UV-Vis diffused reflectance spectroscopic (DRS) studies showed that the band gap increases with Li doping, due to the Burstein-Moss band filling effect. Photoluminescence (PL) studies confirm that the Li incorporation into ZnO material can induce oxygen enrichment of ZnO surface that leads to increase the cyan emission. This material could be used in light emitting diodes in nanoscale optoelectronic devices.

Keywords: ZnO nanostructures, photoluminescence, cyan emission, Burstein-Moss shift

I. Introduction

Zinc oxide is a direct-band-gap semiconducting material with an energy gap of 3.3 eV at room temperature. It has higher excitation binding energy and good optical property at room temperature. ZnO is a very attractive and promising material for low-voltage and short-wavelength electro-optical devices such as light emitting diodes and laser diodes; its other applications comprise transparent ultraviolet protection films, gas sensors and varistors [1–6]. Recently, considerable attention has been focused on ZnO low-dimensional materials such as nanorods, nanowires and nanobelts [7,8]. There are a number of techniques for preparing nanosized ZnO materials. However, it is still attractive to find a simple method to synthesize ZnO nanomaterials. The electronic band structure and its optimization are of great importance in designing semiconductor devices and it can be simulated by changing the material crystal structure and chemical composition. As the impurity atoms are introduced, the spatial geometries which are providing the lowest energy configuration in the bulk may not provide the same as when the surface atoms and surface bonds are altered. Such modifications are much more important in many electronic and optoelectronic devices, especially illustrated in injection lasers and bipolar transistors [9]. Theoretically and experimentally, the importance of dopants and their influence on optical and transport properties are evaluated. To achieve stable p-type ZnO semiconductor, dopants from I and V group elements are introduced and their property studies including structure, morphology, optical, magnetic and transport properties are updated periodically [10–12]. Few citations refer that the addition of lithium tremendously increases the electrical resistivity and hence is applied to transparent conducting oxides (TCO) electrodes, piezoelectric devices and memory devices [13–15].

The present work was undertaken to access the effect of Li doping influence on the morphological, electrical and optical properties of ZnO nanomaterials. The as-synthesized nanomaterials were characterized by X-ray diffractometer (XRD), field emission scanning electron microscope (FESEM), UV-Vis diffused reflectance spectroscopy (DRS) and photoluminescence
(PL) spectroscopy. Further, the formation mechanism
from nanospheres to nanorods was proposed. The de-
tailed investigation of the cyan light emitting Li doped
ZnO nanostructures is discussed.

II. Experimental details

2.1. Materials

Zinc acetate dehydrate was procured from Merck
chemical companies and lithium hydroxide was bought
from the Sisco chemical laboratory. All chemicals used
in this work are analytical grade and used without fur-
ther purification. All solutions were prepared from dou-
bly distilled water obtained from in-house developed
water purification system.

2.2. Methods

An aqueous solution containing a mixture of zinc ac-
etate and lithium hydroxide in an appropriate amount of
\( \text{Zn}_1-x\text{Li}_x\text{O} \) \((x = 0, 0.05 \text{ and } 0.10 \text{ mol})\) is used to synthe-
size pure and Li doped ZnO nanomaterial without any
expensive surfactants. The aqueous solution was kept in
a magnetic stirrer for 4 h. The white precipitate was ob-
tained by washing and filtered with ethanol and water
solution. Finally, the filtered product was annealed in a
muffle furnace at 350 °C for 2 h.

III. Results and discussion

3.1. Phase analysis

Figure 1 shows the XRD profile of the pure and
lithium-doped ZnO nanomaterials with different dopant
concentrations. All the diffraction peaks are well in-
dexed with pure hexagonal phase of wurtzite structure,
and the phase remains unaltered even with the increase
in dopant content from 0 to 0.10 mol. The assigned peak
is made by comparing with the standard JCPDS data
(Card ID-36-1451). By doping with lithium, the dopant
atoms occupy the Zn sites in the ZnO lattice as their
ionic radii are comparable [16].

2.3. Materials characterization

The morphology and structure of the as-prepared
pure and Li doped ZnO nanomaterial samples were
characterized using the field emission scanning elec-
tron microscopy (FESEM) (Hitachi SU 6600) and X-
diffraction (XRD) (PANalytical with CuKα1 of
1.5406 Å). The band gap of the materials was anal-
yzed by UV-Vis DRS spectroscopy (Perkin Elmer Lambda 650). The photoluminescence (PL) spectrum
was recorded by a Perkin Elmer MPF-44B equipped
with 150 W xenon lamp under (325.0 nm) excitation.

The average crystallite sizes of the entire as-
synthesized lithium-doped sample are calculated using
Scherrer equation. For this, the characteristic 101 peak
of ZnO at \(2\theta = 36.28°\) and their full width at half max-
imum (FWHM) are considered by using the Cauchy
Lorentzian fit. The average crystallite size of the pure
ZnO is calculated to be 56 nm. As the dopant con-
tent has increased from 0, 0.05 to 0.10 mol of lithium, there is a regular decrease in crystallite size from 56, 32 and 28 nm, respectively; explaining the incorporation of dopant atom inhibits the growth of the ZnO nanomaterials. The lattice distortion and decrease in crystallite size are denoted in terms of peak shift and peak width. At a low carrier concentration, the peak position at 101 has a 2θ value is 36.28, while at higher concentration, the peak position of 101 plane has decreased to 36.26 degrees. The broadening of the 101 peak can be highly confined and localized in the ZnO lattice fluctuation. This random potential fluctuation due to redistribution, rearrangement of surface atoms and alteration of surface bonding, shift the 101 peak position accordingly. The shift in peak position, doping concentration dependent crystallite size variation and the calculated value of δθ were represented in Fig. 2 with respect to the pure ZnO.

3.2. Morphological analysis

Particle size distribution and direct images of the pure and Li doped ZnO nanomaterials were imaged from FESEM micrographs. Figure 3 shows the high magnified (90,000× and 100,000×) FESEM micrographs of the pure, 0.05 and 0.10 mol Li-doped ZnO nanomaterials. It can be observed that the morphology and particle size are different with respect to doping. The image of the pure ZnO nanomaterials sample indicates the formation of nanosphere bundles. In the case of 0.05 mol lithium-doped ZnO, the nanoparticles are spherical in nature with a high degree of agglomeration and aggregation. It can be concluded that the morphology of 0.10 mol lithium-doped ZnO is a rod like structure with non-uniform size distribution. The individual nanorods have a length of about 500 nm and diameter of about 175 nm. The nanorods are long with blunt end resembling a hexagonal surface. Thus, when the ZnO nanomaterials are doped with lithium atoms there is a morphology evolution from spherical to rod like nature. The incorporation of lithium inhibits the rate of particle growth, but promotes the rate of nucleation, thus producing large number of particles in the given co-precipitation reaction period.

3.3. Band gap widening

The UV-Vis diffuse reflectance spectra of the pure and Li doped ZnO nanostructures as a function of wavelength are shown in Fig. 4 and the inset picture shows the method adopted to mark the onset of reflectance for the sample with 0.10 mol Li. It is shown experimentally that an increase in hole concentration, the onset of reflectance and the spectrum maximum are shifted towards the lower wavelength region. There is a significant change in the amount of reflectance due to the introduction of lithium atom into ZnO lattice. In the lithium-doped ZnO nanoparticles, the UV-Vis spectroscopy is blue-shifted by 10 nm (392–382 nm), due to widening of the band gap (Fig. 5). For the direct transition, the optical band gap energy of the lithium-doped
ZnO nanoparticles is determined using the Tauc plot relation \( a h \nu = C (h \nu - E_g)^{1/2} \) where \( h \nu \) is the photon energy in eV, \( E_g \) is the optical band gap in eV and \( C \) is the constant [17]. The direct band gap is determined by extrapolating and intersecting the linear portion of \((a h \nu)^2\) to the energy axis \( h \nu = 0 \) (shows in inset of Fig. 4). From the graph, the calculated band gap energy of the undoped and doped ZnO comes out to be 3.19, 3.23, 3.24 eV for the pure ZnO, 0.05 mol Li doped ZnO and 0.10 mol Li doped ZnO, respectively. The observed blue shift in the wavelength is the reflection of the band gap widening, owing to the quantum size effect (QSE) [18,19]. However, the QSE is highly evident only when the crystallite size of the nanocrystalline ZnO semiconductor is comparable to its Bohr exciton radius. But, the crystallite sizes of the Li doped ZnO obtained from XRD is far beyond the quantum confinement regime. Accordingly, the shift in reflectance edge and widening of the band gap can be determined on the basis of Burstein-Moss shift and it is well pronounced in highly doped semiconductor [20]. Since, the Li doped ZnO samples are degenerate p-type semiconductors, the Fermi level lies in the valence band, and their position depends on the hole concentrations. Thus, the optical band gap of the materials calculated from UV diffused reflectance is related to the excitation of the electrons from the Fermi level in the valence band to the conduction band. The increase in the optical band gap energy to the increase of dopant concentration is attributed to the Burstein-Moss effect [20]. In the lithium-doped ZnO nanomaterials, when maximum numbers of free carrier holes are added, the topmost electronic states in valence band become vacant and, hence, shift the reflectance edge towards higher photon energy. The shift in Fermi energy level prohibits the interband transition through Pauli’s exclusion principle [21].

Figure 6 easily demonstrates the overall band gap widening mechanism involved in lithium-doped ZnO nanostructures. In a p-type semiconductor, the Fermi energy level lies close to the valence band. As the free carrier concentration (hole) adds up while doping with lithium atom, the position of Fermi level gets disturbed and shifted within the valence band. Due to the incorporation of holes or a vacant energy state, the electrons in the valence band make a transition to occupy the available states. This transition and the gradual addition of holes make the Fermi level to shift further below the valence band and thus widen the band gap [20].

### 3.4. Photoluminescence spectroscopic analysis

The optical properties of the pure and Li doped ZnO nanostructures were investigated by photoluminescence (PL) spectroscopy. To investigate the effects of Li doping and defect-mediated emission by optimize the relative change in the intensity. The PL spectra were obtained for the pure ZnO, 0.05 mol Li doped ZnO and 0.10 mol Li doped ZnO nanostructures. In the emission spectra three different regions can be seen: the ultraviolet (P1: ~350 to 450 nm), blue (P2: ~380 to 500 nm) and green (P3: ~480 to 600 nm) regions, as shown in Fig. 4.

The blue emission and green emission have been reported to arise from Zn ions at interstitial sites (Zn_i) of ZnO nanocrystalline materials [22,23], and oxygen vacancy (V_O) [24,25], respectively. These emissions are confirmed in the spectra of the pure ZnO sample (Fig. 7). On the other hand, the cyan emission at 465 nm is commonly attributed to excess oxygen on the ZnO surface. By increasing the Li doping from 0.05 to 0.10 mol, the relative intensity of the cyan emission increases gradually. It may be due to both Li_{Zn} and Li_i in the ZnO nanocrystalline material. The transitions from donor levels in the crystal (can be both from V_O or Li_i) to Li_{Zn} acceptor levels release cyan emissions. At 0.05 mol doping, the peaks of the native defects (Zn_i and V_O) of ZnO remain relatively unchanged. Thus, the change in the cyan emission intensity confirms the replacement of Zn by the smaller Li atom in the crystal. This is supported by the decrease ZnO crystallite size as observed by XRD analysis (Fig. 2). On the other hand, at 0.10 mol doping, the UV emission of the nanocrystalline material significantly decreased and the cyan emission continued to increase. This indicates the reduction of V_O and a proliferation of Li impurity in the crystal. Li ions cannot substitute for O (Li_{O}) in the crystal lattice due to the high formation energy [26]. The Li ions can diffuse into the spaces in between the lattice (Li interstitial, Li_i). The diffusion of Li_i leads to an increase in both crystallite size and lattice parameter as seen in Fig. 2. Interestingly, the cyan emission band, which relates to excess oxygen at the surface, becomes stronger as the doping content is increased to 0.10 mol Li. We believe that Li incorporation into ZnO can induce oxygen-enrichment of ZnO surfaces that leads to increase the cyan emission [27,28].

### IV. Conclusions

In summary, lithium doped zinc oxide nanostructures have been successfully prepared using co-precipitation method. The nanostructures are crystalline with a wurt-
Figure 6. Schematic illustration of the Burstein-Moss shift in lithium-doped ZnO nanoparticles.

Figure 7. Room temperature photoluminescence spectra for Zn$_{1-x}$Li$_x$O ($x = 0$, 0.05 and 0.10 mol): P1-P3 denotes the ultraviolet emission, blue emission and green emission, respectively.
nite structure. The electronic band gap and photoluminescence intensity of the nanostructure increases, while increasing the lithium concentration. The PL spectra at room temperature showed the cyan emission at 465 nm. The cyan emission bands are attributed to Li incorporation into ZnO that can induce oxygen-enrichment on the surfaces leads to increase the cyan emission. We believe that these nanostructures could be used as light-emitting devices in nanoscale optoelectronic applications.

Acknowledgement: R. Ajay Rakkesh acknowledges the University of Madras for providing NCNSNT fellowship to carry out this research work.

References


