

Exploring Physical And Optical Behavior Of Co:Zno Nanostructures

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Abstract- Zinc oxide (ZnO), one of the very important and versatile semiconductors with direct band gap of ~ 3.37 eV and a large exciton binding energy of ~ 60 meV at room temperature (RT) is a promising candidate for functional components of devices. Selective doping with transition metal ions into ZnO lattice host is capable of tailoring its physical properties. In this paper, the structural and optical properties of pristine ZnO and Co doped ZnO is highlighted. We have fabricated Co doped ZnO and pristine ZnO by adopting solid state chemical reaction route. At the end of synthesis, all samples were obtained in the form of powder. Structural and optical investigations of the as fabricated samples were carried out by utilizing XRD, HRTEM, PL spectroscopy

Keywords – Diluted magnetic semiconductor, nanostructures

I. INTRODUCTION

The study of nanostructures with controlled morphology, shapes and size is essential for developing materials with novel properties and tailorable functions. Different types of semiconducting nanomaterials have attracted a large group of scientific community because of their exceptional properties, which are different from bulk materials [1, 2]. Zinc oxide (ZnO), one of the very important and versatile semiconductors with direct band gap of gap of ~ 3.37 eV and a large exciton binding energy of ~ 60 meV at room temperature (RT) is a promising candidate for functional components of devices. Selective doping with transition metal ions into ZnO lattice host is capable of tailoring its physical properties. In this paper, the structural as well as optical properties of pristine ZnO and Co doped ZnO is highlighted. We have fabricated Co:ZnO and pristine ZnO by adopting solid state chemical reaction route. The concentration of TM were varied 1%, 3% and 5%, accordingly they were indexed as Co-1, Co-3 and Co-5. At the end of synthesis, all samples were obtained in the form of powder. Structural and optical investigations of the as fabricated samples were carried out by utilizing XRD, EDS, HRTEM, FTIR, PL and UV-Vis spectroscopy. The change of structural and optical properties due to Co-doping is one of the major directions of this investigation.

II. EXPERIMENTAL DETAILS

Nanostructured bare ZnO and Co doped ZnO were fabricated [3] by adopting low cost solid state chemical reaction route. To fabricate pristine ZnO nanostructures, zinc acetate dehydrate (ZAcD), Cetyltrimethyl ammonium bromide (CTAB) and Sodium hydroxide flakes (NaOH) were utilized. To get Co doped ZnO system, in the precursor, acetates of Zn and Co were taken in the appropriate molar ratio to obtain 1at.%Co, 3at.%Co and 5at.%Co. The sample so fabricated was marked as Mn-1, Co-3 and Co-5 respectively.

The as-synthesized powder samples thus obtained were characterized by powder x-ray diffraction (XRD) by using Philips 1730, Cu-K α radiation, $\lambda = 1.54 \text{ \AA}$. The X-ray diffraction pattern of pristine ZnO and Co-1, Co-3 and Co-5 samples is presented in figure: 1. All the diffraction peaks can be indexed to a hexagonal wurtzite structured ZnO (space group P63mc), without any additional impurity phases, thereby indicating that the wurtzite structure might have not affected due to the substitution of Cobalt. Further, as no excess peaks were detected, it has been concluded that all the starting organic precursors might have been completely decomposed and the Co ions successfully occupy the lattice site rather than interstitial ones. Previous report revealed that XRD study of Co powder alone shows one intense peak at around 44° [4]. In our XRD study with Co doped samples no such peak around 44° has been detected, it indicated that Co was doped well in the ZnO sublattice. However we can't deny the existence of Co, CoO clusters or other impurity phases in the samples since the sensitivity of the X-ray diffractometer may not go beyond to measure their existence. Further, the existence of Co phases had been detected by J. Cui et al. [5] in their Co:ZnO samples annealed above 700°C , but in our case, fabrication of all samples were done below 100°C .

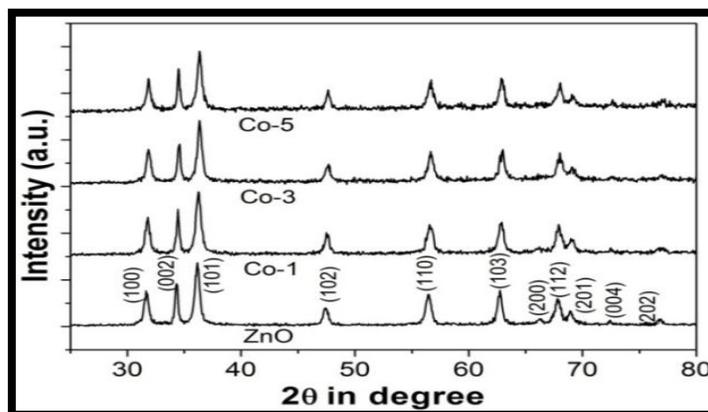


Figure 1: XRD pattern of Co-1, Co-3, Co-5 and bare ZnO samples.

In a recent work on Co doped ZnO, B. Pal et al. reported that compared to undoped ZnO, the XRD intensities of Co doped samples showed lowering of intensity and increase in full width at half maxima (FWHM) of the XRD pattern. In our case, we have observed slight decrease in the intensity of doped samples but no clear evidence of increase in FWHM for all Co doped samples has been detected. As noted from the table 1, considering the reflection from the plane (101), only Co-1 sample shows maximum FWHM. Further, as observed from the XRD pattern, the sharpness of the peaks reflected from the crystallographic planes (004) and (202) are considerably lowered for Co doped samples.

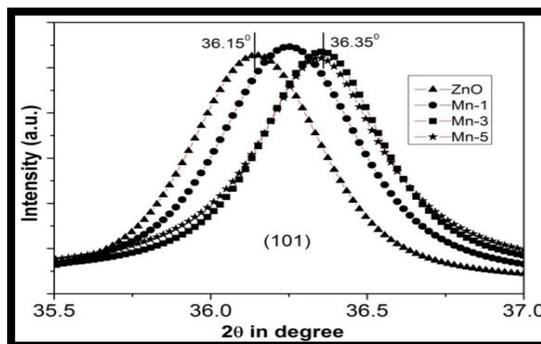


Figure 2: XRD pattern showing shifting of the centres of (101) diffraction peaks.

It has been noticed from a slow scan comparison of the (101) peak of Co-doped and the pristine ZnO NSs that the centers of diffraction peaks of doped ZnOs shift towards high angle compared to pristine ZnO (figure: 2). The diffraction peaks along with their relative intensities are found to be in agreement with those from the other reports [6,7]. The shift of peak position is attributed due to the change of size and strain of the NS for incorporation of Co in the ZnO lattice host induced by mechanical stressing during synthesis. Since the ionic radius of Co and Zn are 0.72 Å and 0.74 Å respectively, which are very close, Co doping induced strain is expected to be less significant. However, as a result of grinding, a compressive strain is introduced in the ZnO NPs [8]. We estimated a reduction in interplanar spacing of ~0.29% from the measured shift in 2θ for (101) plane. This strain in the NPs is expected to influence the electronic, optical, magnetic and other properties including band-structure of ZnCoO.

Table 1. Relative data showing FWHM and 2θ corresponding to the plane (101) for determination of crystallite size and interplanar spacing of bare ZnO, Co-1, Co-3 and Co-5.

Samples	FWHM (in degree)	2θ theta (in degree)	Crystallite size (nm)	d(101) Å
ZnO	0.4985	36.1464	16.5701	2.4823
Co-1	0.5347	36.2499	15.4537	2.4751
Co-3	0.4903	36.3543	16.8575	2.4683
Co-5	0.4923	36.3459	16.7879	2.4689

The high resolution TEM images of Co-3 sample are presented in figure: 3. It could be seen from the micrograph of figure: 3A that the nanoclusters are generally elongated with average length 71 nm and diameter 19 nm. During the study many isolated rods for Co-3 sample were detected. As indicated in figure: 3B, high resolution of TEM image focussed on a single rod with length 44 nm and diameter 16 nm has been observed. It has been noticed that compared to Co-1 sample, elongated shapes are more regular in case of Co-3 sample. The high resolution TEM image of the small crystallite is presented in figure 3C, it indicates uniform lattice structure with clear lattice spacing $\sim 2.4 \text{ \AA}$ corresponding to the plane (101). Thus, we can infer that the growth direction of small crystallite is along (101). Further, from the formation of clear lattice fringes, we can conclude that there is no lattice defect and the nanoclusters are single crystallite state. The estimated lattice spacing 'd's are a little bit higher than those of bulk ZnO, suggesting that the Co atoms are substitutes. Several separated rings in the electron diffraction pattern from the inset are identified as being consistent with wurtzite ZnO structure, implying the unchanged structure of Co-doped ZnO clusters to that of wurtzite ZnO structure [9].

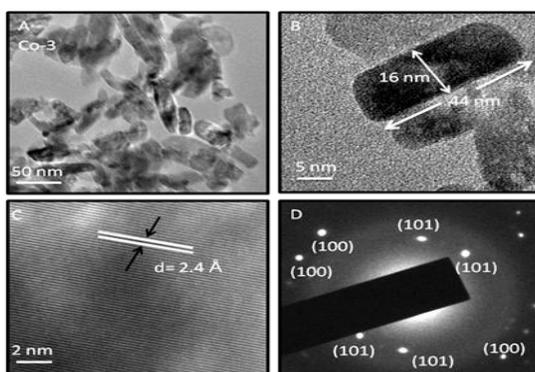


Figure 3. (A) TEM micrograph of Co-3 sample, (B) An isolated nanorod with length $\sim 44 \text{ nm}$ and diameter $\sim 16 \text{ nm}$, (C) HRTEM image of Co3: (D) Electron diffraction pattern obtained from the same section of the Co-3 sample.

Fine structure and clear fringe pattern as observed in this image depicts that the surface of the nanocrystal is free from any defect. Few diffracting points as noticed from the SAED pattern (figure: 3D) of the sample are indexed for (101) and (100) planes.

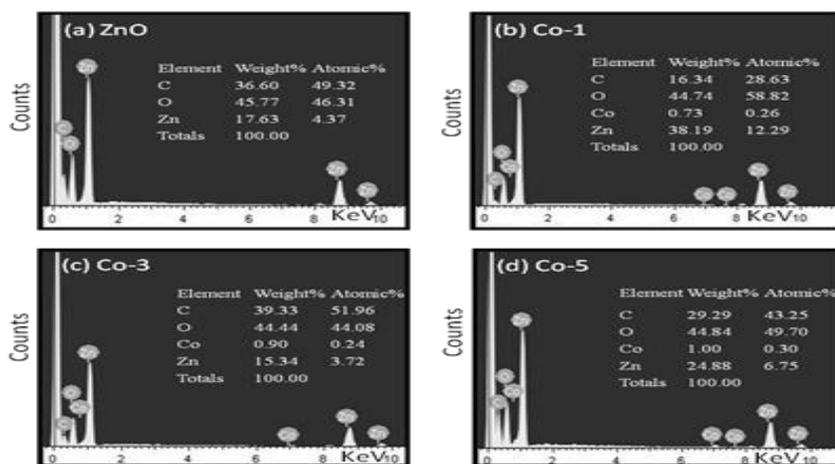


Figure 4. Energy dispersive X-ray study (EDX) of the samples (a) ZnO, (b) Co-1, (c) Co-3 AND (d) Co-5: showing Zn, O and Co related peaks with their relative amount.

Figure: 4(a) represents EDX spectrum for pure ZnO sample, showing Zn and O related peaks and corresponding amount detected in few nanostructures. On the other hand, in the spectrum as presented from Figure: 4(b) to 4(d), it was noticed that the presence of Zn, O and Co related peaks. It is to be noted that EDX investigation was performed with only few particles of each sample, which indicated that cobalt ion was distributed in the entire sample. One can note from the tables cited along with each spectrum that the amount (wt %) of Co is increasing linearly from Co-1 to

Co-5 sample. Moreover, a slight deviation from the fixed amount as given during synthesis is observed during the study. This may be due to the reasons, (a) Only a few particles were exposed to the beam, (b) We cannot neglect the instrumental error, (c) Agglomeration may occur due to the period between synthesis and characterization.

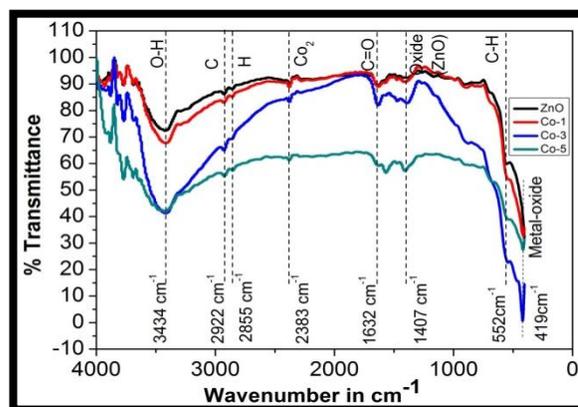


Figure 5. FTIR spectrum for (A) Pristine ZnO (B) Co-1, (c) Co-3 and (D) Co-5.

In the FTIR spectrum, as presented in the figure: 5, for the pristine ZnO and Co doped samples shows similar feature for all samples. Pure ZnO and Co-doped ZnO have wurtzite structure and are further supported by FTIR. For both pristine ZnO and Co doped samples, the corresponding broadening peaks at 3434 cm^{-1} is due to OH Stretching vibrations (from NaOH, used as a precursor), the band at absorption of atmospheric CO_2 on the metallic cations at 2383 cm^{-1} ; the band at 1632 cm^{-1} represents C = O stretching vibrations; the band at 1407 cm^{-1} indicates oxide from ZnO peak and the band observed at 955 cm^{-1} is attributed to C-H band [10, 11]. It is well known that for metal-oxide band stretching the identical absorption peak should present near 500 cm^{-1} . In our case we have observed this identical absorption peak for all samples at 419 cm^{-1} . In figure: 5, a comparative FTIR plot is presented where IR peak positions for all samples (ZnO, Co-1, Co-3, Co-5) corresponding to O-H, C, H, CO_2 , ZnO, C=O, C-H and metal-oxide stretching and bending are shown with respective dash lines. In addition to this, from the FTIR spectrum it has been observed that Co-3 sample exhibit zero% transmittance at 419 cm^{-1} due to Zn-O and Co-O stretching and bending. From this, it can be concluded that Co-3 sample behave differently compared to any other sample. Moreover, the ZnO sample shows slight deviation ($\sim 57\text{ cm}^{-1}$) for the IR peak corresponding to C=O stretching. Except this slight deviation no other peak shift has been observed. No shift of IR peaks indicates that the FTIR result is in good agreement with that of XRD [12].

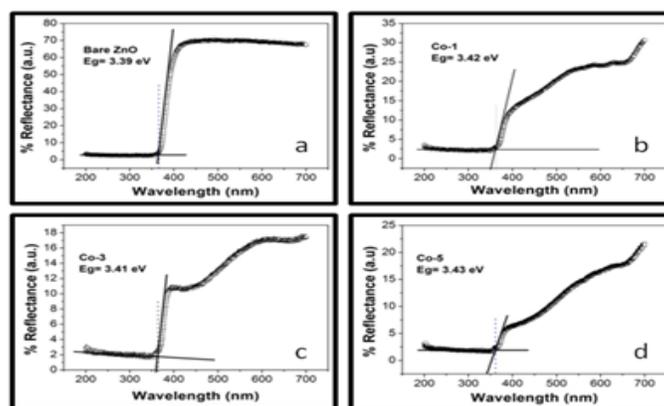


Figure 6. Optical reflectance spectra for the samples (a) ZnO, (b) Co-1, (c) Co-3 and (d) Co-5.

UV- Visible spectroscopy is an important tool to determine band gap of as synthesized samples. The onset of absorption of each spectrum gives the signature of enhancement of individual band gap of the sample due to quantum confinement effect. Comparative reflectance spectra (%) obtained from UV-Vis study for all samples are presented in figure: 4.26. Bare ZnO indicates highest reflectance (%), while reflectance (%) of Co doped samples

decreases with increasing Co concentration. Optical reflectance spectra for all samples reveal strong quantum confinement with increased band gap energies. The increase in the diffuse reflectivity with a definite linear region of the greatest slope is attributed to an exponential drop in the absorption coefficient. The onset of this exponential drop had been suggested as a more universal method of determining absorption edges from which the band gap can be deduced. For calculation of absorption edge a linear fit was given to the linear part of the increase in reflectivity [13]. Band gap of all Co doped and pristine ZnO were calculated from the intersection of two linear portions of each spectrum which showed blue shift. For bare ZnO (figure: 6a) the enhancement is small (~0.02 eV), the enhancement energies estimated for (Co-1 to Co-5) were 0.05 eV, 0.04 eV and 0.06 eV respectively (Figure:6b to 6d). The band gap of all Co doped samples exceeds than pure ZnO, this feature agrees with the values reported earlier [14-17]. Enhancement of energy due to quantum confinement of the nanostructures has been indicated in the UV-Visible study.

III. RESULT AND DISCUSSION

Elongated nanostructures of pristine ZnO and Co:ZnO were obtained through simple inexpensive solid state chemical reaction route at room temperature. HRTEM study reveals formation of isolated nanorods of average size 71 nm length and 19 nm in diameter. Electron diffraction study exhibited that there is no lattice defect and the nanoclusters are single crystallite state. Wurtzite structure as exhibited in the XRD study reveals perfect incorporation of Co ion in ZnO lattice host. The wurtzite structure have not been affected due to the substitution of Cobalt. Further, as no excess peaks were detected, it has been concluded that all the starting organic precursors might have been completely decomposed and the Co ions successfully occupy the lattice site rather than interstitial ones. As from the formation of clear lattice fringes, it is concluded that there is no lattice defect and the nanoclusters so formed are single crystallite state. The estimated lattice spacing 'd's are a little bit higher than those of bulk ZnO, suggesting that the Co atoms are substitutes in the lattice host. The strain as observed in the NPs is expected to influence the electronic, optical, magnetic and other properties including band-structure of ZnCoO. The study of EDX spectra exhibiting Zn and O related peaks gives the evidence of purity of the sample. The wurtzite structure of pristine ZnO and Co doped ZnO are further supported by FTIR study. Enhancement of energy due to quantum confinement of the nanostructures has been indicated in the UV-Visible study.

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