Synthesis and Characterisation of Al-Doped ZnO Nanostructures in Glucose Matrix

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Abstract—Al doped ZnO nanoparticles of 1.5at.%, 3at.%, 6at.% were synthesized by chemical bath deposition (CBD) method using glucose as capping agent. The structural, optical and electrical properties of the as-prepared samples were investigated employing XRD, HRTEM, UV-Visible and PL spectroscopy characterisation techniques. Polycrystalline nature of the samples was ascertained from XRD traces and SAED patterns. Observed changes in lattice parameters may be attributed to some native defects. In the present work on AZO, particle size around 5nm was obtained in HRTEM image. Enhancement of band gap was well reflected in Tauc plot. Linear I-V graphs of samples satisfy ohmic behaviour. The resistivity measurement of the sample yields a value of $6.745M\Omega$ cm. The PL spectra of AZO sample exhibit two prominent peaks at 522.42nm and at 786.17nm which correspond to the band energies of 2.4eV and 1.6eV respectively.

Keywords: Band gap; conductivity; doping.

1. INTRODUCTION

Doping of zinc oxide (ZnO) with different materials is drawing increasing research interest worldwide. Doping of ZnO with metal such as aluminium (Al) has been studied by many researchers. Literature survey shows the effect observed on various parameters such as lattice constant, crystallite size, band gap, blue shift, etc. of ZnO: Al by introducing variations of the doping concentration. In case of aluminium doping of ZnO, Zn^{2+} ions are substituted by Al³⁺ ions. This substitution of Al in ZnO lattice is found to enhance electrical conductivity due to the increase of charge carriers which also introduce changes in optical, thermal and magnetic properties as well [1].

In this paper we report on synthesis of aluminium (Al) doped ZnO nanoparticles at different concentrations using wet chemical method with glucose being the matrix medium. The structural, optical and electrical properties of the samples are investigated through XRD, HRTEM, PL, UV-Visible and I-V measurement techniques. The Al doped samples with doping percentage of 1.5%, 3% and 6% respectively are represented in the text as AZOA, AZOB and AZOC.

2. EXPERIMENTAL

2.1 Synthesis

Chemical bath deposition method was employed in synthesising ZnO nanoparticle in glucose matrix. 3% aqueous solution of glucose was added to ZnCl₂ solution and another solution of NaOH was mixed with the former solution. The weight of ZnCl₂ was 2.7256gm. Accordingly AlCl₃ of 0.0409gm, 0.0818gm and 0.1635gm were added for the preparation of each of the Al doped samples with doping percentage of 1.5%, 3% and 6% respectively. The prepared solution was of 0.1M.Temperature maintained during the stirring process. was 353^{0} K. While preparing the mixture the duration of the magnetic stirring performed was of 3 hours.

2.2 Characterisation

For structural investigation, X-ray powder diffractometer (Model: Seifert XRD 3003 TT) with CuK α radiation ($\lambda = 0.15406$ nm) the scanning of 2θ was performed in the range 20^{0} - 80^{0} . To study the morphology of the nanoparticle HRTEM (Model: JEM 2100, 200kV, Jeol) was employed. For recording UV-Visible absorption of the sample automated spectrophotometer in the wavelength range 200nm-800nm was used. In order to study the photoluminescence (PL) spectra of the AZO samples, we used Xenon flash lamp as a source for excitation [F-2500 FL Spectrophotometer)]. The excitation wavelength used for this purpose was 260nm. The electrical conductivity measurement was done using a digital picoammeter (DPM-111; SES Instruments).

3. RESULTS AND DISCUSSION 3.1 XRD Study

The fingerprint characterisation of the sample was obtained by employing CuK α radiation of wavelength = 0.15406nm from copper target. XRD peaks shown in Fig. 1 agree with JCPDS data confirming crystallinity and supporting wurtzite structure of ZnO crystal [2]. The most preferred growth direction [002] is observed in the XRD spectra and polycrystallinity is also affirmed.



Fig. 1: XRD spectra of the three as-prepared samples

3.2 HRTEM Study

The HRTEM images of the as-prepared samples are shown in Fig. 2. Fig. 2(a), (b), (c) are the images of AZOA sample. Fig. 2(a) reveals 0.5µm ranged image of AZOA. Here few rods like structures are observed amidst agglomeration of ZnO nanoparticles. Formation of nanocrystal of nearly 5nm in diameter is observed in Fig. 2(b). Fig. 2(c) exhibits polycrystalline nature of AZOA from the selected area diffraction (SAED) pattern. The HRTEM images of Fig. 2(d), (e), (f) are of AZOB and that of AZOC are seen in Fig. 2(g), (h), (i). In Fig. 2(g) nanocrystal of AZOC is found with clear lattice spacing with size around 5nm range. In Fig. 2(h) also nanoparticle of nearly 5nm range is observed clearly for AZOC sample's image at 50nm range. SAED pattern of all the samples exhibit polycrystalline nature.



Fig. 2: HRTEM images of Al doped ZnO nano particle.

3.3 UV-VIS Study



Fig. 3: UV-Visible absorption spectra of Al-doped ZnO samples

ZnO is a wide band gap semiconductor having direct band gap. The optical band gap is given by Tauc

$$\alpha h \nu = \mathbf{A} (h \nu - E_g)^n$$

relationship where α is the absorption coefficient, A is constant, h is Planck's constant, v is the photon frequency, E_g is the optical band gap and n is the ¹/₂ for direct band gap semiconductors. The linear portion of $(\alpha hv)^2$ is extrapolated on the energy axis in the $(\alpha hv)^2$ vs. hv graph and correspondingly band gap is determined. The functional relationship between $(\alpha hv)^2$ and photon energy hv for the as-prepared samples are shown in Fig. 4. [3, 4]. The bandgap values obtained for the samples AZOA, AZOB, AZOC are respectively 5.91eV, 5.55eV and 5.18eV.



Fig. 4: Tauc plot for band gap evaluation of ZnO: Al samples

3.4 PL Study

Strong green emission bands and weak red emission bands are observed in the visible region of the PL spectra. Thus the PL spectra of AZO sample doped at 1.5at.%, 3at.%, 6at.% .as shown in Fig. 5 exhibit two prominent peaks one at 522.42 nm which is attributed to green emission and the other at 786.17nm which is due to red emission. These two distinct peaks correspond to the band energies of 2.4eV and 1.6eV respectively. It is observed that the photogenerated holes recombine with singly ionised oxygen vacancy correspondingly green emission peaks are obtained [5]. Green emission is also attributed to oxygen vacancy and zinc interstitials [6].



Fig. 5: PL spectra of AZO sample doped at 1.5at. %, 3at. %, 6at. % .

3.5 Conductivity Study

Conductivity measurement was performed by inserting the AZO sample between two copper strips in 1mm gap. Digital picammeter measures the necessary current. AZO samples exhibit ohmic behaviour as shown in Fig. 6. The resistivity measurement from the slope in the voltage range (0.04 - 0.05) V obtained from the I-V graph shows a value of 6.745MΩcm.It is being reported that on Al doping in ZnO electron concentration increases from 10^{16} to 10^{21} /cm⁻³[7].



4. CONCLUSION

XRD studies show preferred orientation of the ZnO nanocrystal along [002] direction. SAED pattern of HRTEM image confirms polycrystallinity. Some rod like structures was found in the AZO sample. Nanocrystal of 5nm sizes were obtained having clear lattice spacing. Band gap enhancement and increase in electrical conductivity were observed from UV-Visible and I-V measurements. PL study shows distinct peak in the visible region.

5. ACKNOWLEDGEMENT

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