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Tailoring the structural and optical properties of ZnO by doping with Cd

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Abstract

Cadmium-doped zinc oxide ($Zn_{1-x}Cd_xO$ ($0 \leq x \leq 0.03$)) samples are synthesized by polymeric precursor method. X-ray diffraction, Fourier transform infrared, Raman and Ultraviolet–visible spectroscopy techniques are used for the characterization of the synthesized samples. The X-ray diffraction study shows that $Zn_{1-x}Cd_xO$ nanoparticles have wurtzite structure with a weak secondary phase for higher Cd concentration i.e $x=0.03$. The Raman study demonstrates the red-shift behavior and broadening of the Raman modes with increasing content of Cd in ZnO. It reflects the structural distortion due to the atomic substitution in the samples. Fourier transform infrared analysis has confirmed the presence of Zn–O stretching mode of vibration in the samples. The Ultraviolet–visible spectroscopy shows that the optical band gap exhibit red-shift behavior with the increasing concentration of Cd. The band gap is found to decreases from 3.17 eV for pure ZnO to 3.05 eV for Cd doping concentration of 0.02 at%.

Keywords: Cd-doped ZnO; Sol–gel method; Structural properties; Optical band gap

1. Introduction

In the recent years, engineering the band gap of the semiconductor materials has attracted the attention of researchers because of the improvement in their properties as well as an enhancement in the device performance. Kroemer et al. [1] have proposed the concept of varying the band gap of semiconductor materials by varying its stoichiometry. It leads to change in band structure and resulted in new material with different properties as compared to their intrinsic counterpart. ZnO is one of the widely studied wide band gap semiconductors owing to its various useful applications [2–6]. The properties of the ZnO can be improved by tuning its band gap by doping with variety of dopants like Mg, Cd, Ni, Hf etc. [7–10]. Several techniques such as metal organic chemical vapor deposition (MOCVD) [11], thermal evaporation [12], pulse laser deposition (PLD) [13], molecular beam epitaxy (MBE) [14], electrochemical deposition [15], spray pyrolysis [16] and sol–gel [17] are employed to prepare Cd-doped ZnO samples. The sol–gel method has gained much attention due to its low cost, cheap operation and the controllability of the dopant concentration.

In the present work, we employed the sol–gel derived polymeric precursor method [18] to synthesize Cd doped ZnO. We have investigated the influence of Cd doping on the structural and optical properties of ZnO material by X-ray diffraction (XRD), Raman, Fourier transform infrared (FTIR) and Ultraviolet–visible (UV–vis) spectroscopy. Synthesized Cd doped ZnO samples are explored in numerous applications for developing sensors, solar cells, environmental remediation and optoelectronic devices [2–5].

2. Experimental

2.1. Materials used

Zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$ – Purity 99%), citric acid (CA, $C_6H_8O_7$ – Purity 99%) and ethylene glycol (EG, $C_2H_6O_2$ – Purity 99%) are obtained from Merck (India). Cadmium acetate ($Cd\ (CH_3COO)_2 \cdot 4H_2O$) is purchased from Otto Kemi. All chemicals are used without further purification.

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Deionised water used in preparation has a resistivity of 18.2 MΩ and obtained from Lab Pure Andel BIO-AGE.

2.2. Preparation

A simple and versatile polymeric precursor process has been adopted to prepare nano-crystalline $Zn_{1-x}Cd_xO$ ($0 \leq x \leq 0.03$) powder samples named as Cd_0, $Cd_{0.5}$, Cd_1, Cd_2 and Cd_3 corresponding to Cd doping concentrations of x=0, 0.005, 0.01, 0.02 and 0.03, respectively. Deionised water, EG and CA are used as the solvent, chelating agent and complexation agent, respectively. The molar ratio of EG to CA to metal ions is maintained at 4:1:1. Accordingly, the proportional amount of Zn $(NO_3)_2 \cdot 6H_2O$, Cd $(CH_3COO)_2 \cdot 4H_2O$, and CA is dissolved in 100 ml deionized water and then the solution is stirred at 80 °C. Chelating agent (CA:EG=1:4) is added after 1 h and resulting solution is continuously heated as well as stirred in order to promote the polyesterification reaction between metal ions and CA. Due to elevated temperature the solution medium is evaporated within 4 h and a high viscous homogeneous gel is obtained. This viscous gel is further heated at 100 °C for 12 h and brownish xerogel was obtained. The xerogel was then fully grounded in agate mortar. Finally, it is calcined at 600 °C for 6 h in air.

2.3. Characterization

The crystal structure of the synthesized samples are investigated using XRD (X'Pert Pro, Philips) with Cu-$K\alpha$ radiation (λ=1.5406 Å). Raman spectroscopy is performed with an InVia Raman spectrophotometer (Renishaw) with Ar^+ ion laser beam having a wavelength of 514 nm. The FTIR spectra of the samples are recorded using Perkin Elmer IR Spectrophotometer with KBr pellets over the range 400–4000 cm^{-1}. The optical absorbance spectra are recorded using a UV–vis spectrometer (Perkin Elmer, model LAMBDA 750) in the wavelength range of 200–850 nm.

3. Results and discussion

XRD study has been carried out to estimate the lattice parameters and average crystallite size of pure and Cd doped ZnO samples. The XRD patterns obtained for the pure and Cd-doped ZnO samples are presented in Fig. 1. For all the samples the XRD peaks appearing at $2\theta \sim 31°$, 34°, 36°, 47°, 56°, 62°, 66°, 67° and 69° corresponds to the (100), (002), (101), (102), (110), (103), (200), (112), (201) planes of the hexagonal wurtzite structure. All peaks are in good agreement with standard diffraction data (JCPDS Card no.: 36-1451). However, for the higher-Cd content of $x=0.03$ additional weak peaks at $2\theta \sim 33°$, 38° and 55° are also observed which can be assigned to the (111), (200) and (220) planes of cubic CdO secondary phase and are in agreement with standard diffraction data (JCPDS Card no.:75-0592). It is observed that the intensity of peaks corresponding to wurtzite phase decreases with the increase of Cd concentration. It reflects the deterioration in crystalline nature of the samples. It is also noticed that the position of the peaks in the doped ZnO samples is shifting slightly towards lower 2θ value. This shift arises due to the incorporation of a larger Cd^{2+} ion with ionic radius of 0.074 nm in place of Zn^{2+} ion with smaller ionic radius of 0.060 nm in the $Zn_{1-x}Cd_xO$ samples.

The lattice parameters 'a' and 'c' of wurtzite structure are calculated for all compositions using equation [19]

$$\frac{1}{d_{hkl}^2} = \frac{4}{3}\left(\frac{h^2+hk+k^2}{a^2}\right) + \frac{l^2}{c^2} \tag{1}$$

where (hkl) are the Miller indices and d_{hkl} is inter planar spacing. The volume of the unit cell for a hexagonal system is calculated from the following equation:

$$V = 0.866 \times a^2 \times c \tag{2}$$

Furthermore, the average crystallite size (D) of these samples is estimated from a single diffraction peak using Scherrer's formula:

$$D = \frac{K\lambda}{\beta \cos \theta} \tag{3}$$

where $K=0.89$ is the shape factor, λ is the X- ray wavelength, θ is the Bragg angle, and β is the full width at half-maxima (in radian). The various calculated parameters using Eqs. (1)–(3) for different doping concentrations of Cd are summarized in Table 1.

It is observed that the calculated values of lattice parameters and volume of the unit cell are increasing with doping. It is attributed to the higher ionic radius of Cd^{2+} as compared to Zn^{2+}. The lattice expansion is significant when $0 \leq x \leq 0.02$; whereas, little for $x=0.03$. On the other hand, the average crystallite size is decreasing with the increasing concentration of Cd in ZnO. All the above results also suggest that the solubility of Cd^{2+} ions in the ZnO lattice is limited, and excess doping tends to segregate on the surfaces of the nanocrystals. It also results in decreasing the crystallite size.

To investigate influences of Cd doping in zinc oxide, Raman spectra of the pure and doped-ZnO nanoparticles are measured. Group theory predicts that near the center of the Brillouin zone ($k=0$) for ZnO with the $P6_3mc$ space group, the optical phonons belong to the following irreducible representations: $\Gamma_{opt} = A_1 + E_1 + 2E_2 + 2B_1$, where B_1 modes are silent, the A_1 and E_1 are polar modes and both Raman and infrared active, E_2 modes are non-polar and only Raman active [20]. Additionally, A_1 and E_1 optical phonons are split into transverse (TO) and longitudinal (LO) branches due to the macroscopic electric field associated with the LO phonons, while E_2 mode consists of low-and high-frequency phonons. The E_1(TO) and A_1(TO) first-order Raman modes reflect the strength of the polar lattice bonds, which are of the interest in relation with the c-axial displacement of cations. The A_1(LO) and especially E_1 (LO) modes signify the presence of long range electrostatic order in the system and are strongly affected by defects and impurities [20,21].

The Raman spectra of the pure and doped-ZnO samples are shown in Fig. 2. The peak positions and width of various