Synthesis and Characterization of High Quality Indium Doped Zno Nanostructures

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Abstract- Indium doped zinc oxide nanostructures have been synthesized from Zinc acetate dihydrate and indium nitrate dihydrate using sol gel technique. Effect of the dopant (indium) on the structural, morphological, and vibrational modes of zinc oxide nanostructures has been systematically studied using X-ray diffraction, field effect scanning electron microscopy and Raman spectroscopy, respectively. Indium (In^{+3}) being a substitutional dopant in zinc oxide replaces Zn^{+2} ions, thus increasing the carrier concentration and affects vibrational modes. The effect of incorporation of indium and the origin of the observed vibrational modes are discussed. So it can be said that indium doped zinc oxide nano structures of desired characteristics can be synthesized using this low cost sol gel technique for its potential applications in numerous fields.

Keywords: Indium doping; Sol gel method; Raman Spectroscopy

1. INTRODUCTION

Zinc oxide is an abundant, low cost and non toxic n-type material. It is a *II-VI* compound semiconductor and is having a stable wurtzite structure. It has lattice constants of a = 3.25 Å and c = 5.2 Å and their ratio c/a ~ 1.60 is same as a hexagonal cell (c/a = 1.633) [1]. It has a direct and wide band gap of 3.37 eV [2], and a free-exciton binding energy of 60 meV [2]. Owing to the said physical properties zinc oxide has numerous applications, such as semiconductor devices, transparent conductors, solar cell, varistors, gas sensors, etc. [3-5] and hence large effort has been focused on the synthesis, characterization and applications of zinc oxide nanostructures. These nanostructures can be synthesized by a variety of methods which includes sol-gel technique, wet chemical synthesis route, spray pyrolysis, and so on [6-7]. Undoped zinc oxide shows n-type conductivity due to the presence of donor type intrinsic defects such as oxygen vacancies ($V_O^{\cdot\cdot}$) and zinc interstitials ($Zn_i^{\cdot\cdot}$) [1]. Doping with higher valent impurities further enhances the n-type conductivity of zinc oxide. Hence it is important to understand the influence of dopants on the structural and morphological characteristics of zinc oxide. There are several research papers reporting the doping of zinc oxide with n-type impurities such as aluminium (Al), tin (Sn), iron (Fe) and indium (In) [8-9]. Among all n-type impurities being used, indium is found to be one of the best dopant, as it introduces higher conductivity in zinc oxide.

In the present work, we have systematically studied the effect of indium doping on the structural, morphological, and vibrational modes of zinc oxide nanostructures. The possible reasons for the observed characteristics of the synthesized nanostructures are discussed.

2. SYNTHESIS OF NANOSTRUCTURES

Indium doped zinc oxide nanostructures were prepared by sol gel route using Zinc acetate dihydrate (purity 98%) and indium nitrate dihydrate (purity 99.99%). 1 wt.% of indium nitrate was first mixed with zinc acetate and was dissolved in 2-methoxyethanol. Mono-ethanolamine was added drop by drop into the solution through continuous stirring. The solution was heated at 60 °C and cooled to form a gel. The gel was dried in a vacuum oven kept at 80 °C overnight to form powder. The powder was then crushed in a mortar pestle and sintered at 700 °C for 2 h in air. To study the structural properties of the synthesized nanostructures, X-ray diffraction pattern were recorded using Rigaku Ultima III X-ray diffractometer. The micro structural properties were characterized by field emission scanning electron microscopy (FESEM) using CARL ZEISS SUPRA-40. The vibrational properties of the indium doped zinc oxide nanostructures were characterized by Raman spectroscopy. Possible reasons of the observed properties of the nanostructures were discussed.

3. RESULTS AND DISCUSSION

3.1. Structural Characterization

Fig. 1 shows the X-ray diffraction pattern of indium doped zinc oxide nanostructures. From the figure

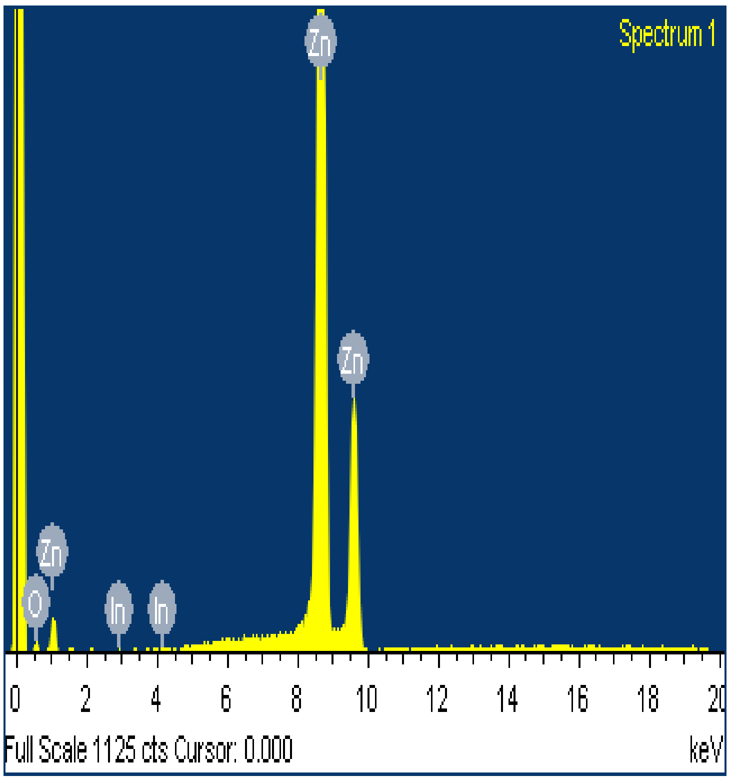

Fig. 1: X-ray diffraction pattern of indium doped zinc oxide nanostructures

polycrystalline hexagonal nano structures with peaks at 31.72^o, 34.28^o, 36.20^o, 47.50^o, 56.46^o, 62.85^o, 67.76^o, 69.04^o, 72.45^o and 76.71^o are observed corresponding to (100), (002), (101), (102), (110), (103), (112), (201), (004) and (202) planes respectively, similar to a standard hexagonal zinc oxide structure [10]. Presence of these peaks shows that there is no additional phase for indium reflecting the uniformity in phase formation behavior and indicating the substitution of indium in zinc oxide lattice.

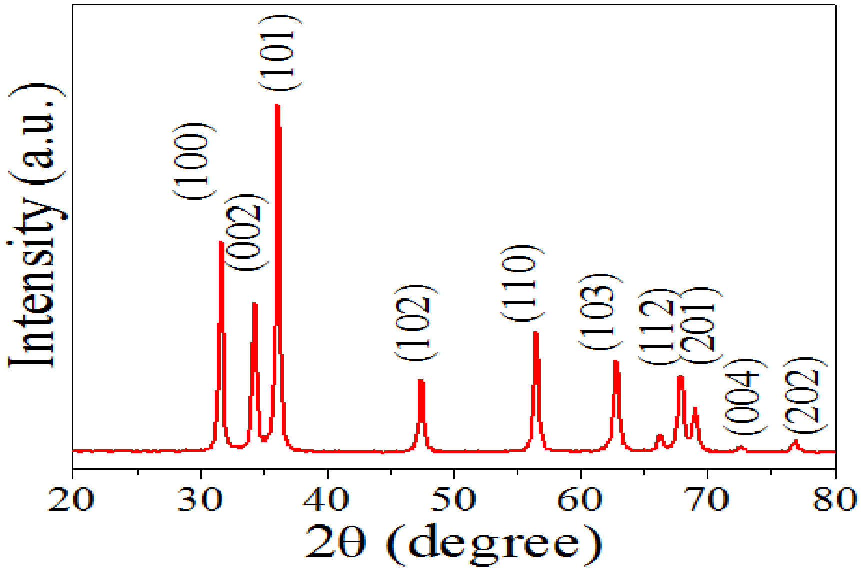

Fig. 2: Energy dispersive X-ray spectroscopy

Fig. 2 shows the energy dispersive X-ray spectroscopy (EDX) of the indium doped zinc oxide nanostructures. It is an analytical technique used to characterize the chemical compositions and purity of the grown samples [11]. As expected the shown spectrum indicates the inclusion of indium in zinc oxide lattice without any impurities.

3.2. Micro Structural Characterization

Fig. 3 shows a typical field emission scanning electron micrograph of indium doped zinc oxide nano structures.

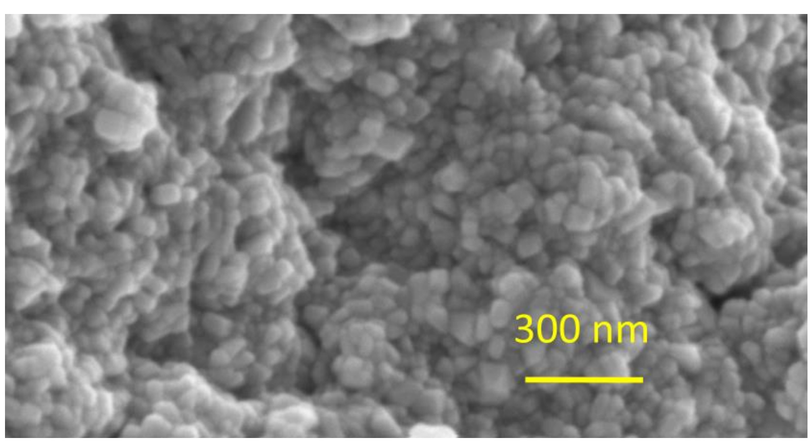

Fig. 3: FESEM image of indium doped zinc oxide nanostructures

As seen from the figure a random orientation of grains with agglomerated nano structures were formed.

This may be attributed to the rapid nucleation and growth of the nanostructures [12]. The random orientation of zinc oxide nano structures is also reflected from the Raman Spectroscopy as outlined below.

3.3: Raman spectroscopy

Raman spectroscopy was performed to study the effect of indium on the vibrational properties of zinc oxide lattice. As reported by E-Morales and Pal, at long and short range orders solids exhibit a correlation between their vibrational properties and the spatial array of the constituent atoms [13]. Fig. 4 shows the Raman spectra of indium doped zinc oxide nanostructures.

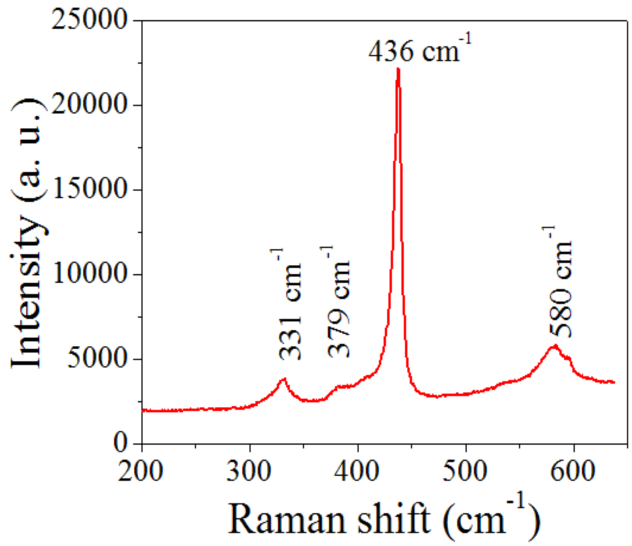

Fig. 4: Raman spectra of indium doped zinc oxide nano structures

The spectrum reflects four peaks, located at about 331, 379, 436, and 580 cm^{-1}. The highly intense peak at 436 cm^{-1} is attributed to the high frequency mode (E_{2H}) and may be due to the involvement of oxygen atoms. The broad LO mode peak at around 580 cm^{-1} is attributed to the overlapping of two polar modes due to the random orientation of nanostructures, which was also observed from the microstructure of the sample.

4. CONCLUSION

In summary, indium doped zinc oxide nanostructures were synthesized by the cost effective sol gel technique using Zinc acetate dihydrate and indium nitrate dihydrate as the precursor materials. Phase formation behavior was studied from XRD technique and it confirmed the formation of hexagonal zinc oxide. EDX indicated the inclusion of indium into zinc oxide lattice without any impurity. FESEM images revealed the effect of indium doping in zinc oxide. Substitution of indium in zinc oxide is also reflected from the study of vibrational modes of Raman spectroscopy. So using sol gel technique indium doped zinc oxide nano structures with required properties can be synthesized for device applications.

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