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Synthesis and characterization of In-doped ZnO nano-powders produced by combustion synthesis

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Indium-doped ZnO powder was performed by a solution combustion technique using metal nitrates as oxidizer agents and carbohydrazide as fuel. The powders synthesized by this method are spongy clusters consisting of platelet-shaped nanocrystals with a wurtzite structure and narrow particle size distribution. Photoluminescence studies reveal that the powders emit high intensity luminescence. Defect-related green-yellow luminescence was found to be dependent upon the level of indium doping.

Keywords: Combustion synthesis; luminescence; ZnO; semiconducting II-VI materials.

1. Introduction

ZnO has attracted much attention towards applications in electronic and optoelectronic devices, such as UV photodetectors, solar cells, light emitting diodes and diode lasers [1,2]. Normally n-type dopants for ZnO are the III group elements such as indium [3,4], aluminum [5] and gallium [6]; while silver [7] and lithium [8] have been used for p-type doping. Indium doping is known to cause a red-shift in the band gap [3], while aluminum doping causes a blue shift, which increases with doping concentration [9,10]. In this work, a one-step synthesis method by combustion has been used to produce In-doped ZnO powder, using the nitrates of the metals as oxidizer agents and carbohydrazide as fuel. The effect of doping concentration on the structure and luminescence of ZnO has been investigated by x-ray diffraction and photoluminescence.

2. Experimental Procedure

Undoped and indium-doped ZnO powders were prepared by combustion synthesis, using zinc nitrate hexahydrate (Zn(NO$_3$)$_2$·6H$_2$O), de-ionized (DI) water as the solvent and carbohydrazide (CH$_6$N$_4$O) as fuel. Indium nitrate pentahydrate (In(NO$_3$)$_3$·5H$_2$O) was added into the solution as a doping source with the molar concentration of 0.1%, 0.5%, 1%, and 5%, respectively. The solution was thoroughly stirred and homogenized in a beaker, and then it was transferred to a preheated furnace at 500°C. Combustion occurred after few minutes in the furnace and ZnO powder are formed in the beaker. The powders showed white and yellow color depending on indium concentration.

3. Results and discussion

Figure 1 shows SEM images of ZnO samples. The powders present a sponge-like appearance within homogeneous sized grains. Doping with indium has no significant effect on the powder morphology.

XRD spectra of undoped and In-doped ZnO are shown in Fig. 2. The effect of indium doping on the ZnO lattice structure is studied by monitoring the diffraction peak position and its FWHM. The main diffraction peaks can be related to the hexagonal wurtzite structure.

The Bragg equation and Scherrer’s formula were used to determine the lattice parameter and the grain diameter $d$, shown in Fig. 3.

A slight shift to lower diffraction angles, lower peak intensity, and peak broadening are observed with increasing In-doping concentration. The slight shift in peak position can be related to the substitution of Zn$^{2+}$ ions with In$^{3+}$ ions as the difference between the ionic radii of In$^{3+}$ and Zn$^{2+}$ is very small (0.076 nm and 0.074 nm respectively) [11]. The expansion of the lattice can be observed only at higher doping concentration (> 5 at.%). The crystalline quality diminishes with the introduction of indium, as seen in the broadening of diffraction peaks related to the presence of smaller grains. The optical properties of undoped and In-doped ZnO were...
characterized by PL spectroscopy at room temperature; the results are shown in Fig. 4. For the undoped ZnO powder there are two dominant emission bands: one is in the ultraviolet (UV) region with the emission peak at 388 nm corresponding to near-band-edge emission; and the other is a broad peak in the green-yellow region centered at \( \sim 520 \) nm.
With indium doping in various concentrations, the near-band-edge emission has the same energy, but its intensity is significantly reduced in the 5 at. % doped sample.

The other emission peak in the green-yellow region undergoes a red shift to \( \sim 580 \text{ nm} \) and quenches gradually with indium concentration. It has been previously reported that indium doping leads to blue shift and broadening of the UV emission peak [4,12]. In our study, the introduction of indium into the ZnO lattice with concentrations less than 1% does not affect the luminescence intensity, and does not produce a noticeable blue shift in the UV emission line. This indicates that the indium as dopant is not involved in the near band edge transition. The broad green emission centered at 520 nm in undoped ZnO has been attributed to oxygen vacancies \( (V_0^+) \) [10,13,14]. The 0.1% indium introduced into the ZnO shifts the green luminescence towards \( \sim 580 \text{ nm} \) in the yellow region with a considerable reduction in the intensity. This is due to In-doping introduces negatively-charged oxygen interstitials \( (O^-_i) \), which help to maintain charge equilibrium and contribute to the yellow luminescence [10,14,15]. When indium concentration increases, the yellow luminescence decreases instead of the expected increase. This suggests that at higher concentration levels, more indium atoms take up the lattice or interstitial sites in the ZnO lattice, which has no contribution to radiative recombination and only expands the lattice parameter and deteriorates the material quality. This also explains the suppression of both UV and green-yellow band emission at higher doping concentrations. The red shift of the green emission from 540 nm in undoped to 550 nm in In-doped ZnO is due to the formation of \( \text{In}^{3+} - V_0^+ \) complexes [14]. Furthermore, it can be found that the intensity of the green emission at 550 nm is reduced with increasing indium doping concentration, as illu. Janotti and Van de Walle [16] have presented in a model for the formation energy of oxygen vacancies in ZnO, which establishes a relationship between green emission intensity and the indium doping concentration.

4. Conclusions

Homogeneous undoped and indium-doped ZnO nano-sized powders with a hexagonal wurtzite structure have been produced by combustion synthesis. It is observed that indium doping has no significant effect on the UV emission from ZnO and only influences the green-yellow luminescence. This may be due to \( \text{In}^{3+} \) ions inducing the generation of oxygen interstitials to retain the charge neutrality, an event that causes a deep level emission shift from green to yellow. Also, it was found that the formation of \( \text{In}^{3+} - V_0^+ \) complexes induces a red shift of green emission in In-doped ZnO.

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