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Annealing effects on photoluminescence of ZnO nanoparticles

K. Sowri Babu *, A. Ramachandra Reddy, Ch. Sujatha, K.V.G. Reddy, A.N. Mallika

Department of Physics, National Institute of Technology Warangal, Warangal-506004, Andhra Pradesh, India

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ABSTRACT

In this study, the effects of annealing temperature on photoluminescence (PL) of ZnO nanoparticles were studied. ZnO was annealed at various temperatures between 600 and 900 °C. The X-ray diffraction (XRD) results demonstrated that grain size increased with increase of annealing temperature. As the annealing temperature increased from 600 to 800 °C, the intensities of both UV peak and that of green luminescence (GL) enhanced monotonously but reduced at 900 °C. The enhancement in the UV peak intensity is attributed to the decrease of grain boundaries and surface states; whereas, the remarkable improvement in the GL is assigned to the out-diffusion of oxygen from the sample up to 800 °C. It supports that GL is induced by the singly ionized oxygen vacancies. These oxygen vacancies are saturated due to the finiteness of the defects at 800 °C. So, it is speculated that the deterioration of GL intensity at 900 °C is due to the evaporation of Zn which is predominant at temperatures higher than 850 °C.

1. Introduction

ZnO is one of the advanced optoelectronic materials which has been extensively investigated for its use in short wavelength optoelectronic devices such as light emitting diodes (LED) and laser diodes due to its wide band gap of 3.37 eV and large exciton binding energy of 60 meV [1]. The large exciton binding energy facilitates the stable exciton emission even at room temperature. The proper understanding of the photoluminescence (PL) behavior of ZnO is necessary if it is to be used effectively in ultraviolet (UV) LED′s and also in flat panel displays as a low voltage phosphor [2]. Generally, the PL spectrum of ZnO exhibits two emission peaks; a weak and narrow UV emission below 400 nm and a broad deep level emission called green luminescence (GL) at around 530 nm. The feeble UV emission intensity is caused by the crystal imperfections such as point defects, dislocations, grain boundaries and also due to the surface/interface states [2,3]. On the other hand, the exact mechanism of GL is not understood so far. In the very beginning, it was assigned to the divalent copper impurities [4]. Later on, the results of Vanheusden et al. proved that the GL was caused by the singly ionized oxygen vacancies [5]. Van Dijken et al. attributed it to the transition of an electron from the conduction band to a deep trap [6]. Guo et al. ascribed GL to the V_{zn} (zinc vacancy) [7]. Some authors reported that GL is originating due to complex defects involving Zn_i (zinc interstitial) and O_{zn} (oxygen antisite) [1]. Recently, Sharma et al. showed that GL is caused from surface states rather than defects in the bulk [8]. Very recently, GL has been observed again in Cu-doped ZnO nanorods grown on Si substrates by chemical bath deposition [9]. But many authors accepted that GL is originated from singly ionized oxygen vacancies. The lack of consensus on origin of GL is due to the different synthesis procedures used to prepare ZnO and complexity in its microstructure. The PL of ZnO is sensitive to the heating conditions. So the annealing of ZnO at different temperatures would give an insight into the possible defects responsible for the visible luminescence of ZnO.

In this work, ZnO nanoparticles were prepared by using the sol–gel method. The effects of annealing temperature on structural and PL properties of these ZnO nanoparticles were investigated. ZnO was annealed at different temperatures from 600 to 900 °C. The possible reasons for the intensity variations of UV and GL were discussed. These results confirmed that singly ionized oxygen vacancies are the source of GL.

2. Experimental procedure

The preparation of ZnO is same as the method described earlier [10]. $Zn(NO_3)_2 \cdot 6H_2O$, water and PVA in suitable quantities were used to obtain ZnO nanoparticles in powder form. The structure of the samples was studied by Bruker D8 X-ray diffractometer (XRD) equipped with Cu $K\alpha$ radiation. The PL spectra were acquired on a Jobin Yuon spectrofluorometer, Model: FLUOROLOG-FL3-11 equipped with a Xenon lamp of 450 W.

2.1. XRD analysis

Fig. 1 shows XRD patterns of ZnO annealed in air at temperature of 600, 700, 800 and 900 °C, respectively. All the samples showed reflection planes (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0),

* Corresponding author. Tel.: +91 870 2462593; fax: +91 870 2430270.
E-mail addresses: sowribabuk@gmail.com, sowribabu@gmail.com (K. Sowri Babu).

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and (1 0 3) corresponding to the hexagonal crystal structure of ZnO. With increase of annealing temperature, the diffraction peaks became sharper, which suggest that there is an increase of grain sizes. The mean grain size values were calculated from the Scherrer formula [2]. The grain size values are about 51, 57, 65 and 71 nm for the samples annealed at temperatures of 600, 700, 800 and 900 °C, respectively.

2.2. PL analysis

PL analysis is a powerful tool for evaluating the structural defects and optical quality of ZnO. Fig. 2(a) presents the PL spectra of ZnO annealed at different temperatures. These PL spectra consisting of a sharp UV emission peak centered at 396 nm and also a GL peak which is positioned at 530 nm. It can be seen from Fig. 2(a) that the intensities of UV and GL increases with the annealing temperature first, and reaches a maximum at 800 °C; and with a further increase of temperature, intensity starts decrease. It is also discernible that the GL intensity varied significantly compared to the UV emission intensity with change in temperature. But, there is no change in the positions of UV and GL peaks as the annealing temperature increases. The intensity variations of UV and GL as a function of annealing temperatures are represented in Fig. 2(b). The optical quality of the sample is generally estimated by the intensity ratio of UV (I_{uv}) to GL (I_{green}) and is defined as '*R*'. The bigger the ratio *R*, the higher the quality of the ZnO. The '*R*' values calculated for samples annealed at 600, 700, 800 and 900 °C comes out to be 7.085, 5.804, 2.614 and 4.009, respectively. These '*R*' values indicate that the optical quality of the sample deteriorated up to 800 °C and then improved at 900 °C. Similar results were also observed by Kim et al. in ZnO thin films deposited on Si substrate [11]. XRD results discussed in the previous section confirmed that there is an increase in particle size with increase of temperature. As a result of it, grain boundaries and number of particles on the ZnO nanoparticle surface decreased. Consequently, number of non-radiative transitions decreased and hence UV intensity increased.

As far as the GL is concerned, it has been attributed mainly to the oxygen vacancies (V_o) or zinc vacancies (V_{Zn}) [3]. The intensity variations of GL with increase of annealing temperature are shown in Fig. 3. The enhancement in the intensity of GL up to 800 °C and its reduction at 900 °C can be understood in the following way; the formation of V_o and V_{Zn} depend on their formation energies, surrounding environment and temperature. Even though, the formation energies and diffusion behaviors of V_{Zn} and V_o are similar, out-diffusion of oxygen takes place for temperatures at and below 800 °C [12–14]. Therefore, the remarkable enhancement in the GL intensity at 800 °C is attributed to the enhancement of oxygen vacancies (V_o). But, there is a possibility for the oxygen vacancies to saturate at 800 °C due to the finiteness of the defects [15]. However, the sample is deficient of oxygen at 800 °C or in other words, it is rich in zinc at 800 °C. It means, as the V_o increases, more number of isolated Zn atoms will be available in the material, preferably on the surface. These excess Zn atoms evaporate at temperatures greater than 850 °C [9,12] and hence there will be loss of Zn atoms from the sample. As the excess Zn atoms evaporate, the quality of the sample will be enhanced. In other words oxygen vacancies decreased; for that reason intensity of GL decreased. So, the reduction of GL at 900 °C can be assigned to the saturation of oxygen vacancies and evaporation of Zn atoms from ZnO at 900 °C. On the other hand, the small decrease of the

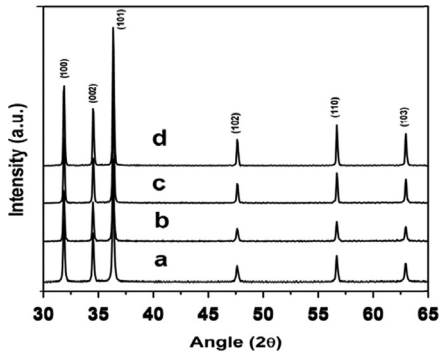

Fig. 1. XRD patterns of ZnO nanoparticles annealed at temperatures of 600 (a), 700 (b), 800 (c) and 900 °C (d) respectively.

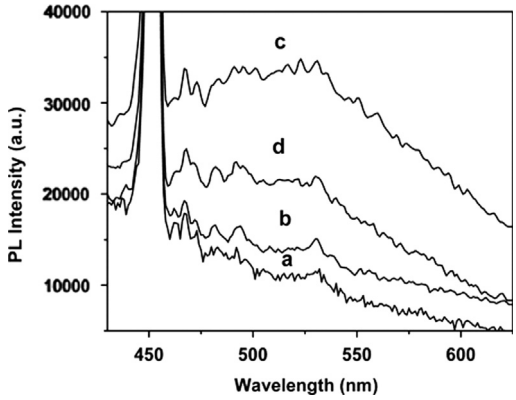

Fig. 3. The GL of ZnO annealed at 600 (a), 700 (b), 800 (c) and 900 °C (d).

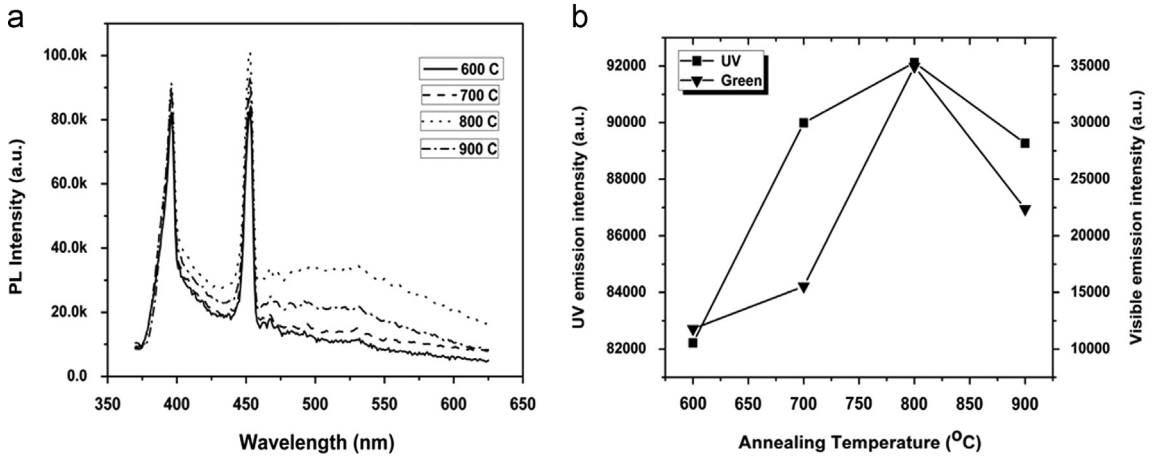

Fig. 2. (a) PL spectra of ZnO nanoparticles annealed at temperatures of 600, 700, 800 and 900 °C, respectively. (b) Intensity variations of UV and GL emissions.

UV intensity at 900 °C is not due to the poor crystal quality of ZnO because '*R*' has the large value at this temperature compared to its value at 800 °C. So, the diminution of UV intensity at 900 °C may be due to the decrease of concentration of Zn atoms in ZnO.

3. Conclusion

The dependence of PL properties of ZnO nanoparticles on annealing temperature was investigated. The UV and GL intensities were enhanced gradually up to 800 °C and then decreased at 900 °C. This kind of variations in UV and GL intensities of ZnO were explained by taking the out diffusion of oxygen and zinc at different temperatures. These results support that GL is originated from the singly ionized oxygen vacancies.

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