Journal of Luminescence 186 (2017) 135–143

Contents lists available at ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

Study of morphological and luminescent properties (TL and OSL) of ZnO nanocrystals synthetized by coprecipitation method

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ARTICLE INFO

Article history:
Received 29 October 2016
Received in revised form
11 February 2017
Accepted 11 February 2017
Available online 13 February 2017

Keywords:
ZnO
TL
OSL
Dosimetry
Nanocrystal

ABSTRACT

In this work, ZnO nanocrystalline phosphorus were synthesized using the method of coprecipitation, subsequently different heat treatments at 900 and 1000 °C for 2 h and 1000 °C for 4 h were performed. Afterward, Thermoluminescence (TL) and Optically Stimulated Luminescence (OSL) emissions were verified after exposure to β-radiation. Photoluminescence results showed UV and VIS emissions. Morphological studies with X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM) confirmed the crystallinity of the samples, with their well-shaped wurtzite hexagonal structures in nanoscale.

ZnO calcinated at 900 °C – 2 h emitted a broad TL peak located between the 362–372 °C; for ZnO calcinated at 1000 °C – 2 h, two intense peaks were observed at 144 and 308 °C, this TL emission curve was investigated with more details using Computerized Glow Curve Deconvolution and six individual TL peaks were obtained, for sample irradiated with 40.6 Gy, corroborating with the T_m-T_{stop} results. A study of Minimum Detectable Dose (MDD) was made and a dose of (492 ± 40) μGy was determined.

CW-OSL and LM-OSL analysis were made for ZnO calcinated at 1000 °C – 2 h, allowed to verify the behaviour, and the curve existing components (fast and medium, depending on dose). As well as the calculation of the Minimum Detectable Dose for CW-OSL.

1. Introduction

In recent years, more significantly, the use of zinc oxide (ZnO) is increasing, due to its semiconductor characteristics which has direct wide band gap (E_g 3.3 eV at 300 K) and a large exciton binding energy (~60 meV) [1–3], is used for various purposes such as biosensors [4], solar cells [5,6], gas sensors [3,7], antibacterial properties and magnetic [8], among others. Furthermore, there is a range of precursors and methods of synthesis can result in different morphologies and structural arrangements, including nanoscale [7,9,10], which may contribute according to the order given product.

However, the nature of the intrinsic defects of ZnO remains undefined, but as the Zn atom is interstitial, it is known that he is responsible for their n-type properties. As the system moves the micro to nanoscale, crystalline to amorphous phase, increased surface area plays an important role in the properties and intrinsic defects or interstitial zinc. Now from the point of view of being a nanocrystal, it is also well-known that the decrease in crystallite size leads to changes in optical and electrical properties. In a small nanoparticle, large number of atoms will be situated either at or near to free surface. When the size of the particle is of the 5 nm order, 30–50% of the atoms are influenced at the surface, compared to particle with about 100 nm, where only few percent remains. Such structural differences in nano regime are expected to give rise to exciting optical, structural and thermal properties, which are different from bulk. Studies on semiconducting oxides like ZnO, TiO_2 and In_2O_3 have been reported with PL measurements, however in the case of TL and OSL is scarcely yet Panda et al. [11].

Regarding the ZnO luminescent emission, studies show that oxygen vacancies are responsible for luminescence in green region for this oxide, for example, as well as impurities, usually a broad peak at around 500–530 nm [1,12]. In general, the studies show that the emission intensity of green is impacted by the particles on the surface, the density of single ionized oxygen vacancies, and also the photo-sensitivity defect responsible for this state [13].

For example, during the process of sonication (synthesis) studied by Sahu et al. [12] where the gamma radiation was used, it was estimated that two types of defect centres are formed. Irradiation creates F and F^+ centres are formed when an electron is trapped in interstitial surface sites of oxygen vacancy. In addition, vacancy and superficial interstitial sites can form holes trap type during irradiation.

Further, according to Xu et al. [14], who studied films of ZnO,

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http://dx.doi.org/10.1016/j.jlumin.2017.02.028
0022-2313/

also wurtzite crystal structure shows that the green emission is associated with the vacancies of oxygen simple ionized type (V_o^+) that are sensitive to heat treatment; red emission is rarely studied and have two different origins, one attributed to interstitial oxygens (O_i) in the range of 620–690 nm, and 650–750 nm, probably associated with double ionized oxygen vacancies (V_o^{++}). The second state of art quoted by these authors, studies reporting UV and violet emission, where UV emission was related to the recombination of free excitons, for the violet emission, there is still much debate, but there are two hypotheses for their explanation, some studies indicate that occurs because of the interface traps located on the borders of the grain boundaries, and a second, which relates to the interstitial defects ZnO.

Currently, studies of ZnO luminescent properties, such as photoluminescence, TL, OSL have been performed for different ways of synthesis and treatment, either pure ZnO synthesized [15–17] or doped (terbium, manganese, cerium) for example [18–21], demonstrating the importance of these. In addition, studies of TL and OSL of pure ZnO for high doses can be found in literature, as Borbón-Nuñez et al. [22] which uses a range of 25–800 Gy, concerned with dosimetry for high doses, as well as Reddy et al. [23] above 10 Gy, among others.

TL response of ZnO has high dependence on the sintered method used and subsequent calcination treatment. We can mention some example as the Sahu et al. [12], 2010 work, they showed TL results of nanoparticles (20–24 nm) of ZnO produced by continuous and pulsed mode sonification. They obtained TL glow curve of sample irradiated with dose from 10–200 Gy, with peaks at 118, 164, 210, 266 and 326 °C for pulsed mode and peaks at 126, 166, 230 and 288 °C for continuous mode preparations. Cruz-Vázquez et al. [16] 2005 used thermal annealing for synthesized ZnO and showed a broad TL glow curve starting from 50 to 350 approximately, the irradiation interval was from 150–10500 Gy. However, the application of undoped ZnO for low doses intervals is still unknown.

The objective of this study is the analyses of the TL and OSL emissions (CW and LM) for ZnO synthesized by the method of coprecipitation. Effects of calcination at different temperatures on morphology, TL and OSL responses of the samples were studied. Additionally, a photoluminescence measurement was made to discover the emission spectrum of Zn. Minimum Detectable Dose (MDD) for TL and CW-OSL were evaluated since, at present, there is no similar study in the literature.

2. Experimental

2.1. Synthesis

For the synthesis of ZnO powders the coprecipitation method was grown in aqueous solutions at room temperature. Zinc nitrate [$Zn(NO_3)2.6H_2O$, Aldrich, $>99\%$] in a molar concentration of 0.3 mol L^{-1} was dissolved in 50 ml deionized water with stirring. Subsequently were added 50 ml of potassium hydroxide [KOH, Aldrich, $>99\%$] in a molar concentration of 2.0 mol L^{-1}. The solids obtained were washed with deionized water and alcohol isopropyl, and dried at 80 °C for 12 h in an air atmosphere.

The heat treatment, that is, calcination was performed from a Novus N480 furnace to a temperature of 900 °C for 2 h and 1000 °C for 2 and 4 h with a heating rate of 15 °C/min. A sample without heat treatment was also considered for morphological and study thermoluminescent.

2.2. Equipments

The morphological characteristics of the crystal structure after different calcinations were investigated by X-ray diffraction (XRD) from a Rigaku D'Max-2500PC with Cu Ka radiation in the range of 20–80°. The scanning electron microscopy (SEM) was obtained from a FEG-SEM Supra 35 VP- equipment, Carl Zeiss, Germany.

TL measurements were carried out with a RISØ TL /OSL DA-20 reader, in the visible spectrum using optical filter BG-39, with a heating rate of 5 °C/s, 0 °C at 500 °C, for different beta doses from 0 to 20.3 Gy and within a nitrogen atmosphere. Further, a experimental methodology was developed in order to enhance the TL and OSL response. T_m-T_{stop} analysis [24,25] were performed in aliquots irradiated with 10 Gy, followed by TL measurements, preheating temperature is raised from 50 to 490 °C in step of 10 °C.

The OSL emission was observed in the same equipment using blue excitation and detected in the UV region, optical filter U340, irradiation was performed in the range 0–100 Gy; for the CW-OSL with 60 sec measurement time, temperature 120 °C and rate 5 °C/s; to LM-OSL, 60 sec measurement time, temperature rate 30 °C and 5 °C/s.

The Computerized Glow Curve Deconvolution (CGCD) it was made from the described in literature [26,27] for TL, CW and LM-OSL emissions.

The photoluminescence emission measurements were carried out, at room temperature, excited at 360 nm, in the Fluorolog 3 Fluorometer, that uses an optical bundle to excite and collecting the luminescence signals.

3. Results and discussions

3.1. Morphological analysis

All samples synthesized with different calcination showed monophasic ZnO with wurtzite hexagonal structure, space group P63mc (JCPDS file # 36–1451) and showing that they have structural long distance organization. The XRD pattern of the obtained results are shown in Fig. 1.

Fig. 2 shows the detail with the zoom of the peak at about 36.3° with respect to the 101 crystallographic plane, where it is possible to observe that the increase in heat treatment temperature and/or time rises the intensity and decreases the peak width, this is due to crystallinity improvement.

The reduction of the peak width is also related to increasing particle size, from 26.9 to 40.6 nm. This result corroborates to those findings by SEM images (Fig. 3) and by calculating the size of the grain given by the Scherrer Equation (Table 1).

The Scherrer Equation is given by [6]:

$$D = 0.94\lambda/(\beta cos\theta) \quad (1)$$

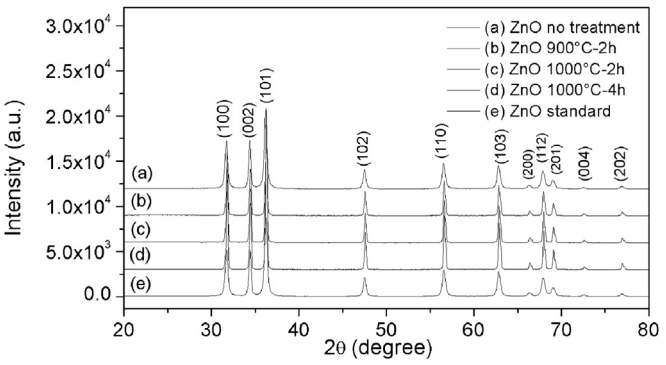

Fig. 1. XRD patterns for (a) ZnO without calcination, (b) ZnO calcined at 900 °C for 2 h, (c) ZnO calcined at 1000 °C for 2 h, (d) ZnO calcined at 1000 °C for 4 h, and (e) standard ZnO.