

Growth of ZnO thin films synthesized by chemical routes for optoelectronic applications

Raúl Sánchez Zeferino¹, M. Enrique Álvarez Ramos¹, Roberto C. Carrillo Torres¹, Sergio Munguía Rodríguez², J. Ángel Gonzalez², and Gerardo Saavedra Rodríguez²

¹ Departamento de Física, Universidad de Sonora, Hermosillo, Sonora, México, C.P. 83000.

² Posgrado en nanotecnología, Universidad de Sonora, Hermosillo, Sonora, México, C.P. 83000.

Over past decade, thin films have been important component in device fabrication of many technological applications such optical transmitters, gas sensors, conducting films, solar cells [1]. In recent years, a new category of thin films technology is based on luminescent materials which are mainly used in applications as white light emitting diodes (LED) and field emission displays (FED). Recently, luminescent thin films have been proposed to efficiency enhancement of solar cells [2]. Zinc oxide (ZnO) is currently one of the key functional materials in advanced optoelectronic and photonic applications, including photovoltaics, due to its high transparency across the solar spectrum, excellent electrical properties, and the possibility to synthesize a rich variety of nanostructures [3].

In this study, the ZnO thin films were synthesized using a typical chemical bath process. Before the chemical bath, a ZnO layer was deposited on glass substrates by sol-gel method using dip-coating technique. The sol solution was prepared by mixing zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$), diethylamine (DEA), and adequate volume of deionized water, the mixture was added to 25 ml ethyl alcohol. The cleaned glass was dipped in the sol-gel by a controlled withdrawal speed of 200 mm/min. The dip-coating process was repeated 1 and 3 times to get seed ZnO layers (ZnO-1C and ZnO-3C, respectively). The seed ZnO layers were then placed in the heated (80 °C) aqueous solution containing 0.025M zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and hexamethylenetetramine (HMT) for 30 min.

The morphological information about the ZnO thin films, prior and after coating with the chemical bath process, was obtained by SEM. Fig. 1a) shows the surface image of ZnO seed layer deposited by sol-gel method. It can be observed the formation of nanoparticles which are spherical in shape with a diameter around 30-50 nm. Figure 1b) and 1c) present the nanorods growth using seed ZnO layers with 1 and 3 cycles of deposit, respectively. Comparing the two figures, it can be seen that nanorods diameter slightly increases from 80 to 120 nm as the seed layer growth cycle is increased. However, for ZnO-3C thin film, it is evident that the nanorods grew disorderly which could be explained due to an inhomogeneous deposit of ZnO seed layer on the surface of glass substrate.

In order to analyze the structural properties of obtained ZnO thin films, they were characterized by Raman spectroscopy. Both Raman spectra shown four fundamental bands located at 98, 380, 436, and 580 cm^{-1} , which correspond to the $E_2(\text{low})$, $A_1(\text{TO})$, $E_2(\text{high})$, and $E_1(\text{LO})$ vibrational modes of ZnO in hexagonal phase (Fig. 2a)). The Raman bands around 200 and 330 cm^{-1} are associated to the second order $2E_2(\text{low})$ and multi-phonon $E_2(\text{high})-E_2(\text{low})$ modes, respectively. As can be observed, there is a decrease in the intensity of all the Raman bands for ZnO-3C film respect to the ZnO-1C film. This indicated that the film had a low degree of crystallinity, possibly due to the formation of structural defects induced by misaligned growth of the nanorods. On the other hand, the optical properties of thin films were determined from the transmission measurement in the range of 350-1000 nm. Figure 2b) clearly shows that numbers of seed ZnO layers affect the transparency in a considerable amount (~20%). Photoluminescence spectra of all films contain a narrow and sharp emission peak in the UV region

(~378 nm) and a broad band in the visible range (Figure 2c)). Commonly, the first peak is attributed to the near band edge emission (NBE) and originates from the free excitons recombination. The visible emission band centered at 565 nm is assigned to defects, as oxygen vacancies or zinc interstitials, forming deep levels in the band gap [4]. The intensity ratio of UV emission to visible emission (I_{UV}/I_{VIS}) is usually employed as an important criterion to indirectly evaluate the quality of ZnO. The values of intensity ratio are 3.5 and 6.2 for ZnO-1C and ZnO-3C films, respectively. This indicates a higher concentration of defects in the ZnO-3C film that is congruent with the results found in Raman spectroscopy.

In summary, the proposed ZnO growth process was a simple and low cost approach for the large scale production of thin films which combine their properties of a high optical transparency and the efficient emission of light in the visible range, properties that are important for the devices of new generation.

[1] F U Hamelmann, Journal of Physics: Conference Series **559** (2014) p. 012016.

[2] E Klampaftis *et al.*, Solar Energy Materials & Solar Cells **93** (2009) p. 1182.

[3] C Battaglia *et al.*, Nature Photonics **5** (2011) p. 535.

[4] A B Djurišić *et al.*, Applied Physics Letters **88** (2006) p. 103107.

[5] The authors acknowledge the financial support from Consejo Nacional de Ciencia y Tecnología (CONACyT) México, through Project 255791-INFR 2015.

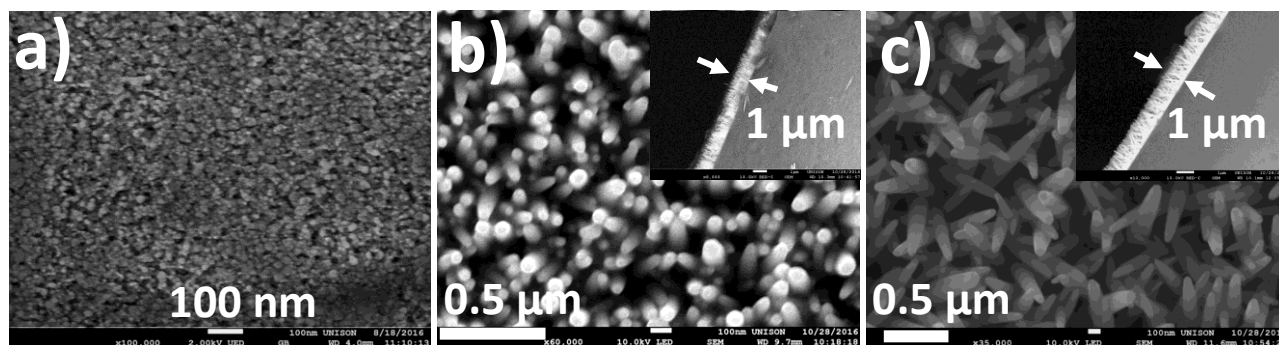


Figure 1. SEM images of a) ZnO seed layer, b) ZnO-1C, and c) ZnO-3C thin films. The inset in each picture shows the cross-section images of the deposited films.

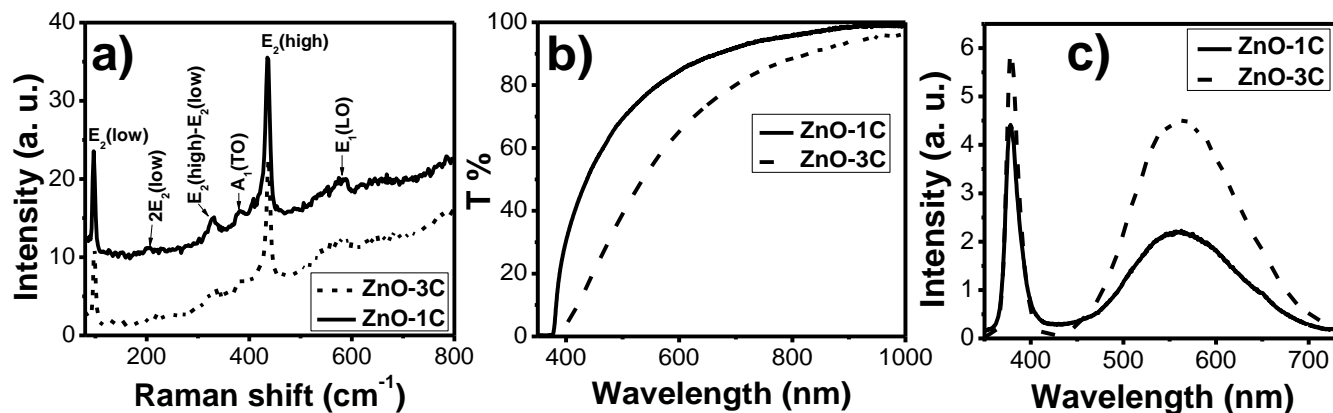


Figure 2. a) Raman spectra, b) transmittance spectra, and c) PL emission spectra of ZnO thin films.