



On the Optical and Structural Properties of ZnO Thin Films Synthesized by a Sol-Gel Technique

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Recibido 22 de Oct. 2007; Aceptado 15 de Oct. 2008; Publicado en línea 5 de Ene. 2009

Resumen

Zinc oxide (ZnO) films were prepared by an alternative route to the sol-gel process and their structural and optic properties carefully investigated. The deposition of the films was carried out on glass substrates by using a dip-coating technique. Zinc acetate dihydrate was used as inorganic precursor. This compound was first dissolved in ethanol and nitric acid. The obtained solution was then mixed with a citric acid and ethylenglycol, which were previously dissolved. XRD pattern confirmed the hexagonal wurtzite structure of the synthesized material. Optical transmittance spectra showed absorption band at 3.3 eV. Scanning Electron Microscope (SEM) analysis showed excellent morphology of the samples with very flat surfaces.

Palabras claves: Zinc Oxide, dip-coating, sol-gel films, optical devices.

Abstract

Películas delgadas de ZnO fueron preparadas por una ruta alternativa a la técnica convencional de sol-gel. Las propiedades estructurales y ópticas de dichas muestras fueron cuidadosamente estudiadas. La deposición de las películas fue llevada a cabo sobre sustratos de vidrio usando la técnica de "dip-coating". Acetato de Zinc dihidratado fue usado como precursor inorgánico. Este compuesto fue primeramente disuelto en etanol y ácido nítrico. La solución obtenida fue entonces mezclada con ácido cítrico y etilenglicol. El análisis por difracción de rayos X confirmó la estructura wurtzita del material sintetizado. De otro lado, los espectros de transmitancia mostraron una banda de absorción a aproximadamente 3.3 eV. Adicionalmente, análisis de superficie de las películas por medio de Microscopía Electrónica de barrido (SEM) mostraron excelente morfología con superficies muy planas.

Keywords: Óxido de Zinc, recubrimiento por inmersión, películas por sol-gel, dispositivos ópticos.

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1. Introducción

Zinc oxide (ZnO) is a member of the II–VI compound semiconductors with a wide band gap (3.31 eV) and a large excitonic binding energy (60 meV) [1]. It possesses an unique position among materials owing to its superior and diverse properties such as piezoelectricity, chemical stability,

optical transparency in the visible region, high voltage-current nonlinearity, etc. [2]. In this way, ZnO seems to be a good candidate for diverse applications as short wavelength optoelectronic devices [3]. ZnO-based thin films are indeed interesting for their applications in semiconducting, photoconductive or piezoelectric and optical waveguide materials [4]. Although physical methods (molecular-beam epitaxy,

sputtering or spray pyrolysis) have been extensively used, sol-gel processes and variants as the polymeric precursor method (Pechini) are particularly adapted to produce ZnO colloid and films, in a simple, low cost and highly controlled way [5].

In this work, the growth of high-quality ZnO films by a chemical method as well as the corresponding structural and optic characterization is reported.

2. Experimental procedure

Zinc acetate dihydrate was used as inorganic precursor. Firstly, the Zinc acetate was dissolved in ethanol and nitric acid. The obtained solution was then mixed with citric acid and ethylenglycol, which were previously dissolved. ZnO films were deposited on glass substrate by dip coating with a velocity of 4 cm/min. After deposition, the films were heat-treated at 200°C for 30 min, 350°C for 30min and 550°C for 30 min with increments of 2 °C/min between each temperature.

The crystalline phase of th ZnO films were determined by x-ray diffraction (XRD) (using the Cu K α = 1.54). The morphology of the sample was investigated by Scanning Electron Microscope (SEM) and EDS. The UV absorption spectra were investigated by using a spectroscopic D₂-Lamp. An optical fiber was used to transmit the UV-light continuum to the sample. The detection system is sensitive in the spectral range between 200 nm and 900 nm.

3. Results and discussion

Fig.1 displays the XRD pattern of the as grown ZnO thin film. Analysis of this pattern reveals that the film is monophasic with a very good crystallinity, showing the hexagonal wurzite structure. No additional peaks were observed suggesting that there is not inclusion of additional phases. The right compositional content of the film is evident from the EDS analysis, plotted in the inset of Fig. 2.

Room temperature (RT) transmittance spectroscopy has been conducted measuring the band gaps of the samples. Fig. 3 shows the transmittance spectra of a ZnO thin film. The measured sample is highly transparent in the visible region and has a sharp absorption band in the UV region. Theory of optical absorption gives the relationship between the absorption coefficients α and the photon energy $h\nu$ for direct allowed transition as $(\alpha h\nu)^2 = h\nu - E_g$. The calculated optical direct band gap is presented in Fig. 4. A value of 3.1 eV is obtained for this film, which is very close to the theoretical one (3.37 eV) [3]. Thus, the quality of the grown films is further demonstrated.

A SEM image of the deposited film, shown in Fig. 5, gives a general view of the morphology of ZnO thin films synthesized by the described chemical route on glass substrates. Interesting enough, the surface of these films is extremely flat and the frequently reported granular character of ZnO thin films was not observed for the samples reported in this

work. Such surfaces are desired to the growing of multi-layered system, which find direct application in electronic devices.

In summary, high quality ZnO thin films on glass substrates have been achieved by a variant route to the standard sol-gel technique. The films show good structural, optical and morphological properties. The surface quality of the grown films would make possible that devices based on multilayers involving this material to be currently fabricated.

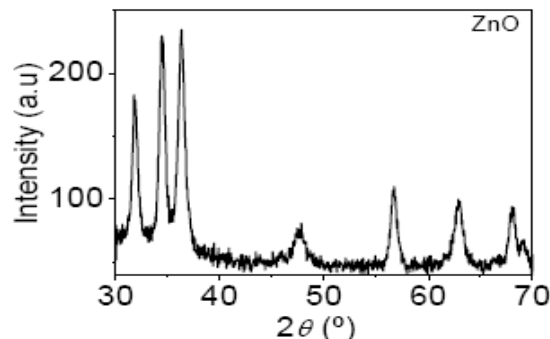


Fig.1 XRD pattern of ZnO film grown by chemical route on a glass substrate.

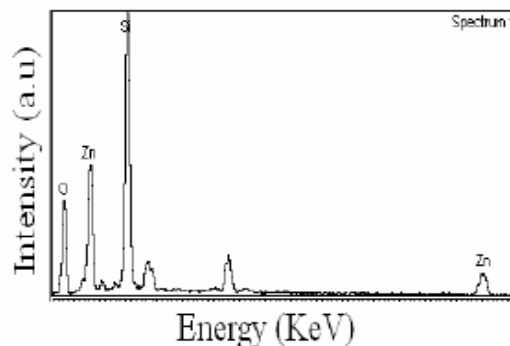


Fig. 2 EDS spectrum of a ZnO film showing its chemical composition. The Si peak corresponds to that of the substrate

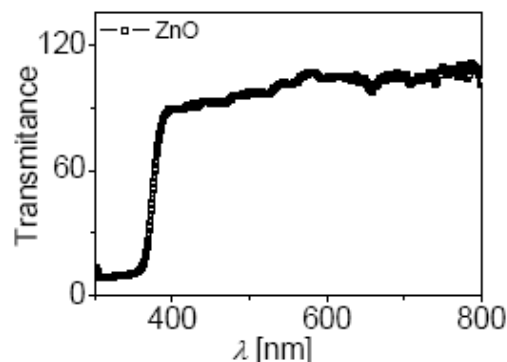


Fig. 3 Transmittance spectrum of a ZnO film.

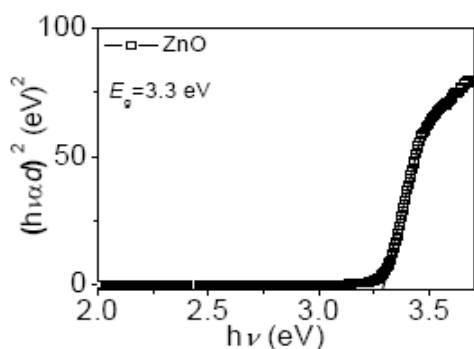


Fig. 4 Optical direct band of the same film. A band gap of 3.3 eV is calculated extrapolating the straight part of the curve to the energy axis.

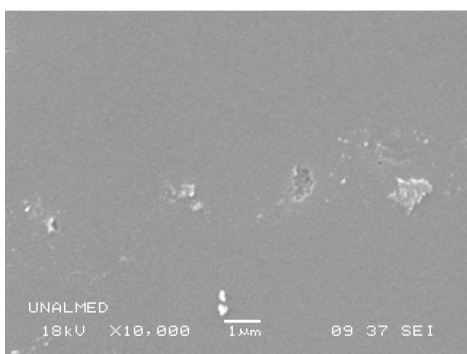


Fig. 5 SEM morphology of a ZnO film. No evidence of granular character of the surface of the film is appreciated from this picture.

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