

The influence of external magnetic field on the structural and optical properties of nanocrystalline ZnO thin films prepared by dip coating method



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ABSTRACT

ZnO thin films were prepared by the sol gel dip coating method. Some samples were prepared under a DC magnetic field DC-MF (B); others were done without it. The sol gel was also continuously stirred. The field orientation in each case of deposition was chosen perpendicular as well as parallel to the growing ZnO-film substrate and the film depositions were carried out at a fixed B intensity value. The influences of magnetic field on the structural, morphological, and optical properties of ZnO thin films were investigated. In the perpendicular case, a cubic structure phase was observed at ambient conditions. It is noteworthy that this phase growth is only possible at high pressure deposition. In the parallel case, the films improved the crystal structure without creating a new phase. The structural properties of the ZnO films such as surface morphology and crystallinity were determined using scanning electron microscopy (SEM) and X-ray diffractometry (XRD), respectively. The optical properties of the ZnO films were characterized by the ultraviolet–visible (UV–Vis) spectroscopy.

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1. Introduction

Zinc oxide (ZnO) is a very important II–VI semiconductor material with a direct bandgap of 3.37 eV at room temperature and a large exciton binding energy of 60 meV [1]. ZnO has received a lot of attention due to its unique physical properties and wide range of applications. These applications include: optoelectronic devices [2], antireflection coatings transparent electrodes in solar cells [3], thin films, gas sensors [4], varistors [5], spintronic devices [6], surface acoustic wave devices [7], light emitting diodes, and lasers [8]. Because of its high aspect ratio of atoms, ZnO nanostructures also have vast applications such as dye sensitized solar cells, field effect transistors, targeted drug delivery, anticancer agents, and antibacterial activity [9–13].

ZnO thin films are prepared by a variety of techniques such as chemical vapor deposition [14], sputtering [15], pulsed-laser deposition [16], sol–gel [17–18] thermal evaporation, oxidation, and anodizing [19–21]. Among these, the sol–gel process is a versatile and low-cost technique to prepare thin films. It also allows excellent control of the stoichiometry, possibilities to modify the composition, dopant incorporation, and large area substrate coating.

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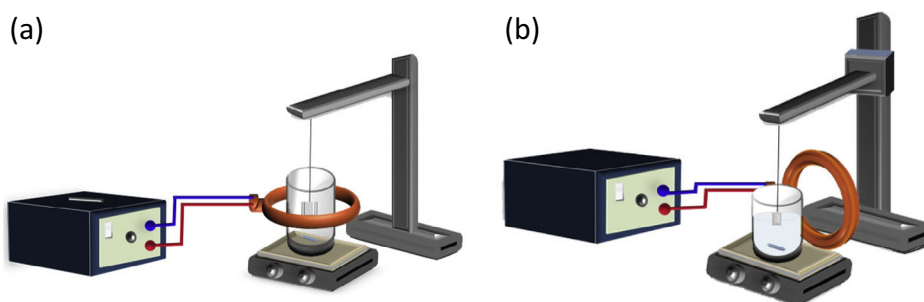


Fig. 1. Dip coating with: (a) parallel magnetic field; (b) perpendicular magnetic field.

Advances in nanotechnology led to the quest for more ways of control over size, morphology, and nanostructure. An alternative way for obtaining thin films with the capacity to control some of their properties is to grow the layers under the influence of external agents such as electromagnetic radiation [22], photo-assistance, ion enhancement, electrical field or DC magnetic field (MF) [23,24].

Magnetic field proved to influence growth of thin films in many diverse cases. In some cases, magnetic field is essential and part of the mechanism, e.g. magnetron sputtering [25–31]. In other cases, magnetic field played a role of external factor that influenced the growth of thin films such as depositions from ionic solutions [32–34], different types of electro deposition [35–39], redox deposition [40–42], electrophoresis [43], as well as influencing particles in the plumes produced in pulsed-laser depositions [44–47], and alterations of the plasma in plasma enhanced chemical vapor deposition processes [48–51].

In the formation of thin films by the sol gel method, electrically charged elements (ions, colloids, clusters) take part in the process; therefore, the application of an external magnetic field with specific strength and orientation with respect to the growing substrate might have an effect on the properties of the resulting thin films. The effect of the MF on the growth mechanisms is that of the acceleration of colloids in the sol produced by the Lorentz force, which seems small due to the low velocities and large masses of the colloids. Therefore, in order to enhance the influence of the magnetic field, we used a magnetic stirrer to increase the speed of the colloids. Growing the layers under the influence of external magnetic field forms an alternative and important possibility for obtaining thin films with the capacity to control some of their properties.

2. Experimental

All the reagents were analytically pure and they were used without further purification. ZnO thin films were deposited on soda lime glass slide substrates by the sol–gel dip coating method. Commercial glass (16 mm × 76 mm) was thoroughly cleaned by detergent solution, acetone, ethanol washed, and deionized water. The sol gel was prepared by dissolving the required amount of zinc acetate dehydrate $[\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}]$ into 10 mL of isopropanol containing monoethanolamine (MEA) that acted as a stabilizer. The homogenous solution was then stirred at 70 °C for 1 h to accelerate the hydrolysis reaction and obtain a transparent sol that was used as the coating sol after being cooled to room temperature and aged for 24 h. The slides were then dipped into the sol gel and withdrawn at a rate of 4 cm/min. The experimental arrangement for the ZnO deposition under the action of an external magnetic field is shown schematically in Fig. 1. The magnetic field ($B = 0.077$ T) source was Helmholtz's coils which were applied either perpendicular or parallel to the substrate. After each coating, the samples were heat-treated using an infra-red lamp for 10 min before applying a new coating. This preheat treatment is necessary for the evaporation of the organic group content present in the thin film. The dip-coating and the drying were repeated for depositing of seven layers. Then the 7-layer films were annealed in a furnace at a temperature of 450 °C for 3 h. Thin films of zinc oxide were subjected to phase analysis by employing an X-ray diffractometer (Rigaku, Model: Ultima IV), which was equipped with a graphite monochromator, and Cu $K\alpha$ as a radiation source ($\lambda = 1.542$ Å). The glancing incidence configuration was used to obtain higher sensitivity to the film structure. Glancing Incidence X-ray diffraction (GIXRD) measurements were collected at an incidence angle of 1°. The diffraction patterns were obtained at constant incidence angle. The absorbance was measured using Labomed Inc., Spectro UV–Vis Double Beam model UVD-2950. The morphology of the ZnO thin films was determined by a field emission scanning electron microscope (FESEM, JSM-7600F, JEOL) using a 20 kV operating voltage.

3. Results and discussions

3.1. Structural and morphological properties

The crystal structures shared by ZnO are: (i) hexagonal wurtzite (B4), (ii) cubic zinblende (B3), and the (iii) cubic rock salt (B1), which is rarely observed [9], as schematically shown in Fig. 2. XRD patterns of ZnO films consisting of 7 layers deposited by dip coating on the glass substrates are presented in Fig. 3.

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