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Physical study on Cobalt–Indium Co-doped ZnO nanofilms as hydrophobic surfaces

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ABSTRACT

The present work reports some physical investigations on (Co,In) codoped zinc oxide nanofilms deposited on glass substrates at 460 °C by the spray pyrolysis technique. The effect of Co and In concentration on the structural, morphological, optical and surface wettability properties have been investigated using X-ray diffraction (XRD) patterns, Raman spectroscopy, SEM, optical measurement, photoluminescence spectroscopy as well as the measurement of hydrophobicity in terms of water contact angle. It is found that all films crystallized in würtzite ZnO phase, with a preferentially orientation towards (002) direction parallel to c-axis. The Raman spectra of the samples exhibit the presence of E_2^{high} characteristic mode of würtzite structure with high crystallinity as well as two dominant bands 1LO and 2LO. Also, no additional modes introduced by codopoing have been found. SEM micrographs show the uniform deposition of fine grains on surface films. Thicknesses of films are less than 100 nm. In addition, optical investigations indicate that the band gap narrowing of (Co,In) codoped ZnO thin films is due to the increase in the band tail width. Indeed, PL study indicates that (Co,In) codoped ZnO nanofilms exhibit a large decrease of the UV luminescence, which is assigned to the trapping of photo-generated electrons by both In^{3+} and Co^{2+} ions as well as an improvement of charge separation in the ZnO thin films. Finally, the (Co,In) codoping influences the surface wettability property and transform the ZnO character from hydrophilic ($\theta < 90°$) for pure ZnO nanofilm to hydrophobic ($\theta > 90°$) for (Co,In) codoped ZnO ones.

1. Introduction

A hydrophobic surface is a surface on which a water droplet achieves a spherical shape with a contact angle greater than 90°. The wetting behavior of a surface presents a great interest on its physical chemical aspects. Hydrophobic materials are highly desirable for broad range of applications such as microfluidic devices, anti-icing and anti-corrosion coatings, self-cleaning, optical devices, textiles … In the last decade, there has been huge interest in studying the wetting behaviors of various transition-metal oxides, such as ZnO [1], V_2O_5 [2], TiO_2 [3], Ag_2O [4] and so on. Among these oxides, zinc oxide has been received much attention due to its fascinating properties and applications. This binary material has a direct wide band gap energy of 3.37 eV, a large exciton binding energy (60 meV), high optical gain (320 cm^{-1}) at room temperature [5,6], high

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optical transparency in the visible region, low electrical resistivity as well as high electrochemical stability, non toxicity and abundance in nature [7]. Besides, it is highly resistant to chemical attack even under plasma of hydrogen. Furthermore, the adding of hydrophobic properties into ZnO surfaces may expand the domain of its classic applications such as electrical and optoelectronic devices. In literature, various methods have been employed to prepare this oxide such as spin coating method [8], RF magnetron sputtering technique [9] and spray [10] which is chosen herein as chemical and humid process to synthesis ZnO nanofilms because of its numerous advantages such as: high homogeneity, uniform distribution, large scale, non-toxic and cost-effective method.

Generally, the doping of semiconductors with appropriate transition metals is one of the most effective ways in research for applications developing. Therefore, good understanding of the interaction will facilitate in principal the fundamental and technical applications. Also, it is well known that the codoping is usually used to obtain and to improve p-type ZnO [11]. However, the codoping inducing n type character ZnO is used to enhance sensitivity applications [12]. Furthermore, the n type conductivity is reinforced with In doping ZnO and it is accentuated with the Co doping.

On the one hand, it is well known that the charge carrier density (n_e (cm^{-3})) is enhancing and the electrical resistivity (ρ) of the ZnO thin films decreases either by the doping with various elements from Group-III. Among these elements, Indium has been the most successful dopant [13]. Moreover, the doping efficiency depends on the difference of ionic radius and electronegativity between the dopant and host element. In^{3+} with ionic radius (0.080 nm) and electronegativity (1.7) possesses a close ionic radius to Zn^{2+} (0.074 nm), and a larger electronegativity (1.65). On the other hand, it was predicted that transition metal doping of ZnO has attract much interest since to improve the electronic and optical properties of the oxide material, and particularly, lead to room-temperature ferromagnetism behavior [14]. In particular, among group BIII, the Cobalt element having close ionic radius Co^{2+} (0.072 nm) to that of Zn^{2+} (0.074 nm), electronic shell structure and large solubility in the ZnO matrix [15] has many physical and chemical properties similar to those of Zn.

This study highlights some physical investigations on hydrophobic (Co,In) codoped ZnO nanofilms prepared by the spray pyrolysis method. Accordingly, the influence of (Co,In) codoping on ZnO nanofilms were investigated through analyzing its structural, morphological, optical and photoluminescence properties. To the best of our knowledge, an investigation on the hydrophilic–hydrophobic transitions of ZnO and (Co,In) codoped ZnO nanofilms has not been yet reported. Thus, the paper is organized as follows. In Section 2, experimental descriptions are presented together with analyses techniques. In Section 3, study and discussion on structural, vibrational, morphological and optical properties have been followed by surface wettability tests. Last section is dedicated to the conclusion.

2. Experimental section

2.1. Preparation of undoped ZnO and ZnO:Co:In nanofilms

Un-doped ZnO and ZnO:In:Cr thin films were deposited on glass substrates at 460 °C, using the chemical spray technique [16] . The aqueous solution was prepared by mixing propanol and distilled water with fraction volumes of 150 cm^3 and 50 cm^3 respectively as well as zinc acetate dehydrate ($Zn(CH_3COO)H_2.2H_2O$).10^{-2} M. The starting solutions were acidified with acetic acid at pH = 5. Indium chloride ($InCl_3$) and Cobalt (II) chloride hexahydrate ($CoCl_26H_2O$) were used as sources of In and Co respectively. The molar ratios (In/Zn) and (Co/Zn) were 0%, 1% and 2%. Nitrogen was used as the gas carrier (pressure at 0.35 bar) by a 0.5 mm-diameter nozzle. Over the deposition process, the flow rate was fixed persistently at 4 ml/min throughout the thin films deposition.

2.2. Characterization

The crystalline structure of the sprayed thin films were investigated via X-ray diffraction analysis by (Analytical X Pert PROMPD) diffractometer using Cukα radiation (λ= 1.54056 Å). Besides, the micro-Raman spectroscopy measurements were performed through Renishaw in Via Raman microscope at room temperature by means of a laser with 532 nm excitation wavelength. In addition, morphological observations of all films were reached by Extreme High Resolution Scanning Electron Microscopy (XHR) SEM. Also, the optical measurements were performed using (Schimadzu UV 3100 double-beam) spectrophotometer, in the UV–Vis-IR range. The transmission data was taken with a glass sample as a reference (i.e., reflection from the substrate was subtracted). Further, PL measurements were carried out at room temperature using HORIBA Jobin-Yvon spectrometer with He–Cd laser with 325 nm excitation wavelength. Finally, the wettability investigations were achieved using Drop Shape Analysis DSA 100 contact angle measuring system at ambient temperature.

3. Results and discussion

3.1. Structural and morphological analysis

Fig. 1.a depicts X-ray diffraction patterns of (Co,In) codoped ZnO sprayed nanofilms. Pure ZnO film shows diffraction peaks at 2θ values of 34.5 and 36.26 attributed to (002) and (101) planes of hexagonal würtzite structure (JCPDS N°. 36-1451), respectively. (002) peak is the most intense and narrow orientation, revealing the highly crystalline character of pure ZnO thin film. By codoping, this peak intensity increases which reflects an improvement in the crystallinity of the nanofilms,