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Tuning the structural, electrical and optical properties of tin oxide thin films via cobalt doping and annealing

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ABSTRACT

Pure and cobalt-doped SnO_2 ($Sn_{1-x}Co_xO_2$, $0 \leq x \leq 0.09$) thin films were grown by dissolving $SnCl_2 \cdot 2H_2O$ in ethanol and spin coating on glass substrates. The X-ray diffraction and Raman analysis show that the films are polycrystalline and correspond to the rutile phase with a preferred orientation along (110) direction. The grain size and crystallinity of the films that annealed at 450 °C for 1.0 h are enhanced after annealing at 500 °C for 2.0 h. According to atomic force microscopy (AFM), the films consist of grains influenced by doping and annealing temperature and time. I–V measurements reveal non-Ohmic contacts of the films with the electrodes. Transmittance spectra, optical band gap (E_g), Urbach energy (E_U), refractive index, film thickness, and the optical constants of the films are dependent on the Co content and annealing conditions. The obtained results illustrate the possibility of controlling the film's physical properties for the optoelectronic devices and applications.

1. Introduction

For the past few decades, tin oxide (SnO_2) based transparent conducting oxide (TCO) thin films are gaining considerable attention in the new area of applications like optical and optoelectronic domains. SnO_2 exhibit better electrical conductivity with free carrier density in the order of 10^{18} cm^{-3}, thermal stability, optical transparency in the visible region, the reflectance in the infrared region and have a direct wide band gap of E_g ~3.6 eV at room temperature (RT) [1,2]. These properties enable it to be used as electrode material for rechargeable Li-ion batteries, solar cells, light emitting diodes, displays, heat mirror coatings and electrochromic windows [3–7]. This is due to that the electrical contact needs to be made without obstructing photons from either entering or escaping the optically active area. SnO_2 is a perfect insulator in its bulk form. However, it is *n*-type semiconductor in the thin film form due to the presence of native defects, *i.e.* non-stoichiometry (interstitial of tin (Sn_i) and oxygen vacancy (V_o)) [1]. These lattice defects were also proposed as the origin of the observed RT ferromagnetism in these films [8,9]. Moreover, SnO_2 is the most widely studied material among all the oxides that used for gas sensor applications [10]. The antibacterial activities of SnO_2 against Escherichia coli and Bacillus help to protect underwater optical instruments against biofilms in seawater [6].

To achieve better electrical and optical properties of SnO_2 thin films, continuous work has been done by using various physical and chemical preparation techniques and adding several dopants. In this regard, the influence of annealing

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temperature on the pulse laser deposited (PLD) SnO_2 films [8] and RF magnetron sputtered Ni/In -doped SnO_2 films [11] have been reported. SnO_2: Mo thin films were prepared by thermal evaporation and used for H_2S gas detection and self-cleaning application [12]. SnO_2: F thin films were deposited by atmospheric pressure chemical vapor deposition (APCVD) for enhancing the light trapping [13]. An electrospinning method was applied for the Preparation of Sr- and Ba-doped SnO_2 nanofibers [10,14]. The influences of NaCl salt [3], Pt [15], Nd, Zn [9,16], Mg [17] doping and (Si+F) co-doping [1] on the physical properties of SnO_2 films prepared by spray deposition technique were studied. Among the dopant elements, cobalt (Co; [Ar] $3d^74s^2$) is widely used in lithium-ion battery electrode, as a catalyst in petroleum and chemical industries and the electroplating industry [18].

Among the chemical methods employed to prepare nano-sized SnO_2 films, the sol-gel spin coating method is a cost-effective technique. It could be used to better control the film uniformity over a large area substrate. The preparation parameters are easily controlled which leads to high-quality SnO_2 layers [6,19]. Therefore, it has been used by many authors. Uysal et al. [20] developed SnO_2 nanoparticle thin films by dissolving tin chloride in isopropanol and adding water for hydrolysis and polycondensation processes. Henry et al. [6] prepared SnO_2 films using 2-methoxyethanol and monoethanolamine as solvent and stabilizer, respectively. However, Lee et al. [21] synthesized SnO_2:In films by dissolving tin acetate in 2-methoxyethanol and acetylacetone as a chelating agent. Liu et al. [22] used glycerin as a dispersion stabilizer to prevent cracking on the Sb-doped SnO_2 films. Luo et al. [23] deposited SnO_2 films on SAW device substrates using oxalic acid and triethanolamine for H_2S detection. Moreover, Liu et al. [24] and Mazloom et al. [25] prepared (Ce, Sb) co-doped and V- doped SnO_2 nanoparticles (NPs), respectively. Also, Tran et al. [19] prepared F-doped SnO_2 films by green dip coating.

Based on the literature survey, no complete work on the effect of Co doping on the physical properties of SnO_2 spin-coated films. As a new approach, we have prepared SnO_2: Co thin films by spin coating technique without using a chelating agent. Additionally, we studied the influence of Co doping at two different annealing conditions (at 450 °C for 1.0 h and 500 °C for 2.0 h) on the structural, electrical and optical properties of SnO_2 thin films.

2. Experimental procedures

2.1. Films preparation

$Sn_{1-x}Co_xO_2$ thin films with Co content in the range x = 0.0–9.0% were prepared by dissolving 1.128 g tin (II) chloride dihydrate [$SnCl_2 \cdot 2H_2O$, $M_W = 225.63$, Merck] in 10 ml pure ethanol. The required amounts of the dopant source, cobalt (II) nitrate hexahydrate [$Co(NO_3)_2 \cdot 6H_2O$, $M_W = 291.03$, purity > 99%, Aldrich] was added to the solution which then stirred at 60 °C for 3 h to yield a homogeneous and clear solution. Then, the solution was aged for 36 h at RT. Before spin-coating, the glass substrates were pre-cleaned by sonication in acetone, methanol and deionized water for 10 min each. Then, the substrates were dried using an air gun and baked at 100 °C for 20 min to remove any residual moisture. The precursor solutions spin-coated on the substrates at 1500 rpm for 30 s, followed by drying at 150 °C for 10 min on a hot plate. Spin coating and drying were repeated five times to obtain the desired thickness. Finally, the films were divided into two groups; one annealed at 450 °C for 1.0 h and the second group were annealed at 500 °C for 2.0 h in an air furnace.

2.2. Measurements

High-resolution X-ray diffraction (XRD, Philips X'PertPro MRD) was used for crystallographic properties identification of the prepared oxide films using Cu K_α radiation ($\lambda = 1.5418$ Å) with a step 0.02°. The Raman spectra of the films were taken at RT using a Thermo Fisher DXR Raman spectrometer with semiconductor laser beam having the excitation wavelength of 532 nm at a power of 8 mW. Surface morphology and roughness of the fabricated nanostructure films were investigated using an atomic force microscope (AFM, PARK SYSTEM, XE-100E). I-V characteristics were measured by Keithley measurement-source unit (2400) using two point probe method. Optical spectra (reflectance and transmittance) in the spectral range from 200 to 2500 nm were measured using UV/VIS/NIR 3700 double beam Shimadzu spectrophotometer at RT. Barium sulfonate was used as a reference to provide a nominal 100% reflectance measurement.

3. Results and discussions

3.1. XRD analysis

Fig. 1 shows the XRD patterns of the SnO_2: Co thin films annealed at (a) 450 °C for 1.0 h and (b) at 500 °C for 2.0 h. All the films are exhibiting tetragonal, rutile SnO_2 of polycrystalline structure (JCPDS card no: 72-1147) that belongs to the space group $P4_2/mnm$. These patterns reveal that the used annealing temperatures were enough to get fully oxidized SnO_2 films as no peaks for SnO or Sn are detected. The proposed reactions between the involved chemical materials during the fabrication of tin oxide thin films are as follows: