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ORIGINAL RESEARCH

Structural and optical properties of Cr doped ZnO crystalline thin films deposited by reactive electron beam evaporation technique

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Abstract ZnO and Cr-doped ZnO thin films are grown on to glass substrates using reactive electron beam (e-beam) evaporation technique. Variation of structural, morphological, and optical properties with Cr doping is investigated. X-ray diffraction (XRD) studies show that the films are polycrystalline in nature with single phase. Energy dispersive spectroscopy (EDS) results demonstrate that Cr ions are substitutionally incorporated into ZnO. Atomic force microscopy (AFM) reveals that the films present a compact surface and root mean squared (RMS) roughness increased with Cr contents. The optical band gap energy E_g of the films has been determined using Transmission data by spectrophotometer and ellipsometry. The band gap energy found to be decreased with increasing Cr doping concentration. The optical constants (refractive index, extinction coefficient) are calculated using ellipsometry and found to increase with Cr doping concentration.

1. Introduction

Zinc oxide which is group II–IV semiconductor material with a wide direct band gap of 3.37 eV and large exciton binding energy of 60 meV has numerous applications in the fields of ultraviolet light emitting devices, ultraviolet laser diodes, transparent conducting films and solar cell [1,2]. ZnO nano crystalline structures are attractive due to its fantastic electronic, optical and magnetic properties [3]. It is highly desired to prepare ZnO nano materials to finely tune its electrical, optical

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and magnetic properties for its potential applications in spin-optoelectronics devices. Doping with proper elements is an effective method to tune surface state, energy levels and transport performance of carriers in semiconductors, enhancing their electrical, optical and magnetic properties [4–7]. The doping of transition metal elements in ZnO offers a feasible means of fine tuning the band gap to make use as UV detector and light emitters [8]. Cr is a typical transition metal element with special abundant electron shell structure and close ionic radius of Cr^{3+} (0.063 nm) to that of Zn^{2+} (0.074 nm), which means that Cr^{3+} can easily substitute into ZnO lattice [9]. However, Cr doped ZnO thin films has received little experimental attention, in spite of, favorable for doping, chemical stability against etching and existence of ferromagnetism at room temperature [9–11]. Another important feature of this material is that it has magnetic, semiconducting and optical properties. The samples can be synthesized in the bulk and thin film forms and a wide range of magnetic properties including room temperature ferromagnetism have been reported and can be applied to short-wave magneto-optical devices. Cr-doped ZnO is a promising material for spintronics applications and can be made a room temperature transparent ferromagnetic semiconductor. The control tuning of the optical band-gap with Cr doping in ZnO can be applied in the fabrication of devices such as detector and light emitters.

Much effort has been placed on the fabrication of ZnO based dilute magnetic semiconductor materials, their structural and magnetic characterization. There are no so many reports about the influences of Cr doped ZnO thin films on the lattice structure and optical properties. Nevertheless, the optical properties like optical constants (n, k) and transmittance in UV regions for this material is less reported, despite of its essential importance for applications in spin-optoelectronic devices. Cr doped ZnO thin films have been prepared by a variety of techniques such as, RF magnetron sputtering, co sputtering [12,13], and pulse laser deposition [14]. To our knowledge, none of the report has mentioned the growth of Cr doped ZnO by electron beam (e-beam) technique.

In this work we have reported the influence of Cr doping on structural, optical and morphological properties of Cr doped ZnO thin films using reactive (e-beam) evaporation technique. In addition to this, we achieved tunebility in physical properties with Cr doping using (e-beam) technique.

2. Experimental detail

The targets of ZnO and Cr doped ZnO were prepared by the conventional solid state reaction route method. The desired amount of highly pure ZnO and Cr_2O_3 (0, 3, 6 mol%) powder was taken and mixed for 3 h by pestle and mortar and made its pellets using pellet presser. Then, the pellets were sintered at the temperature of 950 °C for 6 h. The sintered pellets were used as targets for the deposition of the films. The rotary and diffusion pumps were used to evacuate the vacuum chamber of e-beam system up to 2×10^{-5} mbar. The substrate to target distance was 35 cm and to gain homogeneous films, the substrates were rotating continuously with speed 15 cycles/min. Deposition process was carried out for 6 min at 300 °C substrate temperature in oxygen environment. Structural and phase identification of the thin films were carried out by grazing angle X-ray diffraction technique using Bruker D-8 Discover X-ray diffractometer with a CuKα-radiation ($\lambda = 1.54186$ Å) as an X-ray source and 2θ range from 25° to 70°. Concentrations of Cr, Zn and O were determined by EDS installed with leo440i SEM. Surface morphology of thin films was investigated by atomic force microscope (AFM) (Quesant Universal SPM, Ambios Technology, USA) (QScope^{TM} 350) in non contact mode. The optical transmittance measurements were carried out using UV-NIR Spectrophotometer (Hitachi U-4001) in the spectral range from 300 to 900 nm. Film thickness and optical constants (e.g. refractive index, extinction coefficient) were carried out using Jawoolam 200VI Ellipsometer. Ψ and Δ spectra were measured at the incidence angle 70° in the spectral wavelength range from 370 to 900 nm.

3. Results and discussion

3.1. XRD study

The deposited polycrystalline thin films were subjected to XRD analysis for phase and structural identification as shown in Fig. 1. The characteristic peaks with high intensities corresponding to the planes (1 0 0), (0 0 2), (1 0 1) and lower intensities at (1 0 2), (1 1 0), (1 0 3) and (1 1 2) indicate the films is of high quality of hexogonal ZnO wurtzite structure. It is evident from the XRD data that there are no extra peaks due to chromium, other oxides or any zinc chromium phase, indicating that as synthesized samples are single phase. The peaks of diffraction patterns of doped samples are shifted to right as compared to the undoped ZnO. This shows that small variation in lattice parameters occur as Cr concentration in sample increase. The lattice constant C was calculated using the following equation for thin films [15]:

$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2}\right) + \frac{l^2}{c^2} \tag{1}$$

C values are presented in Table 1. As can be seen, with increase of Cr doping lattice constant C decrease from 0.526 nm to 0.521 nm. A decrease in the lattice parameters can be expected when Zn^{2+} ions are replaced by Cr^{3+} ions because of the smaller radius of Cr^{3+} ions (0.063 nm) than Zn^{2+} ions (0.074 nm) [9], so the substitutional incorporation

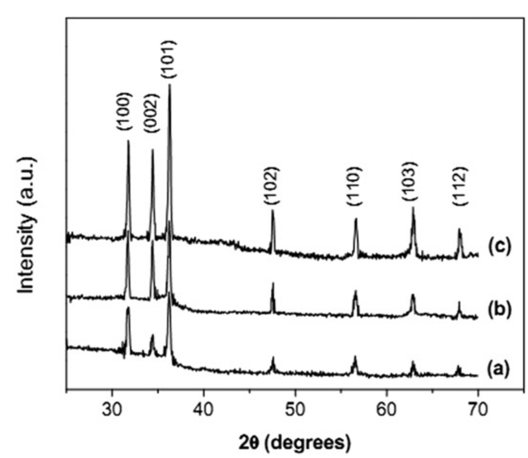

Fig. 1 XRD pattern of (a) pure ZnO, (b) 3.3 at% Cr and (c) 7.7 at% Cr doped ZnO thin films.