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Properties of cobalt-doped zinc oxide thin films grown by pulsed laser deposition on glass substrates

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ABSTRACT

Undoped and cobalt-doped zinc oxide (CZO) polycrystalline piezoelectric thin films (Co: 3, 5 at.%) using a series of high quality ceramic targets have been deposited at 450 °C onto glass substrates using a pulsed laser deposition method. The used source was a KrF excimer laser (248 nm, 25 ns, 2 J/cm^2). X-ray diffraction patterns showed that the Co-doped ZnO films crystallize in a hexagonal wurtzite type structure with a strong (0 orientation, and the grain sizes calculated from these patterns decrease from 37 to 31 nm by increasing Co doping. The optical waveguiding properties of the films were characterized by using a prism-coupling method. The distinct M-lines of the guided transverse magnetic (TM) and transverse electric (TE) modes of the ZnO films waveguide have been observed. With the aim of study the optical properties of the ZnO films, an accurate refractive index and thickness measurement apparatus was set up, which is called M-lines device. An evaluation of experimental uncertainty and calculation of the precision of the refractive index and thickness were developed on ZnO films. The optical transmittance spectra showed a good transparency in the visible region. Calculated optical band gap varying from 3.23 to 3.37 eV when the content of Co doping increases from 0 to 5 at.%.

1. Introduction

The zinc oxide (ZnO), which is a new type of semiconductor material with a wide direct band gap of 3.37 eV and high exciton binding energy of 60 meV [1–4], has numerous industrial applications in the fields of ultraviolet light emitting devices, ultraviolet laser diodes, transparent conducting films, and solar cells [5–7]. Recently, ZnO thin films and different metal-doped ZnO thin films have been widely investigated [8–11]. In order to develop ZnO thin films with high quality for devices with good performance, it is necessary to clarify the roles and the effects of the different conditions of growth and the doping. Zinc oxide (ZnO), an important multifunctional material, looks like having potential in the future in various fields, such as optical waveguides, solar cell windows, nonlinear properties, piezoelectric and bulk acoustic waves devices [12,13]. We show the advantages of the magneto-optical effect of dilute magnetic semiconductors (DMSs) as regards fabricating magneto-optical waveguide devices that can be integrated with other semiconductor optical devices. In integrated optics, various applications are based on the use of thin film planar waveguides. The approach to use ZnO transparent metal oxide semiconductors films for the realization of such waveguide structures will be reported in the present paper. ZnO can be grown as a thin film by many deposition techniques including chemical

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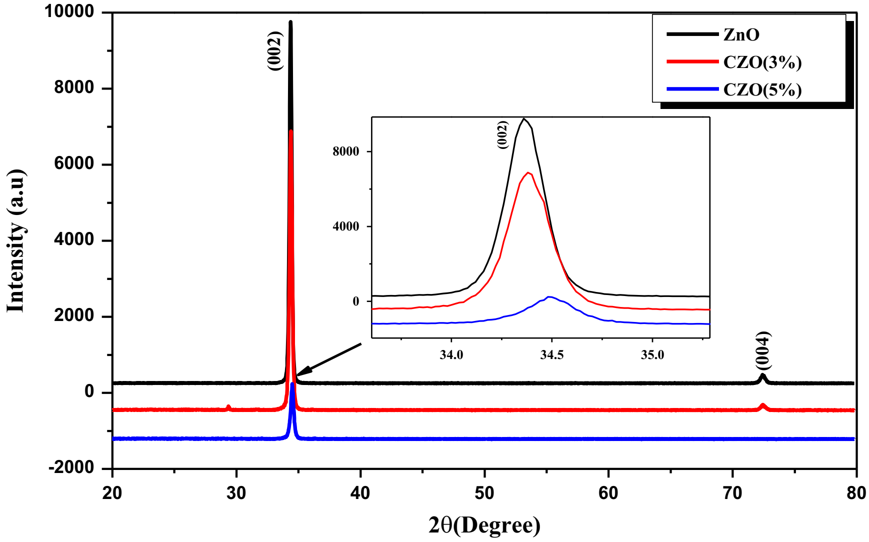

Fig. 1. XRD patterns of ZnO and CZO thin films deposited onto glass substrate at 450 °C.

vapor deposition, radio frequency sputtering, magnetron sputtering, sol–gel method, ion-beam-assisted deposition, molecular-beam epitaxy and pulsed laser deposition [14–18]. In comparison with other techniques, the composition of the films grown by PLD is quite close to that of the target, even for multicomponent targets [19]. The main advantage of PLD technique is the control of the stoichiometry of the material.

In this work, we report results obtained for undoped and Co-doped ZnO (CZO) thin films from a ceramic (Co: 3–5 at.%) target grown by a KrF excimer (λ=248 nm, 25 ns pulse width) pulsed laser deposition (PLD) at 450 °C onto glass substrates. The crystalline and optical waveguiding properties studied by using M-lines spectroscopy of the fabricated films are presented and discussed for the different Co-doping contents. We report guided modes spectra for both transverse electric (TE) and transverse magnetic (TM) polarization in undoped and Co-doped ZnO waveguides. From angular spectra modes, we have measured effective indices which permit to determine ordinary and extraordinary refractive indices of the thin films.

2. Experimental

ZnO targets used for laser ablation were prepared at different doping concentrations of CoO (0, 3 and 5 at.% Cobalt). The stoichiometric amounts of zinc oxide and cobalt oxide were mixed thoroughly, pressed into pellets (diameter 11 mm and thickness 5 mm) and then sintered at 500 °C for 3 h. Co-doped pellets were prepared from ZnO (99.0% purity, Fluka) and CoO (99.9% purity, Aldrich) powders. Glass substrates were chemically cleaned using methanol and deionized water before loading in the deposition chamber. The laser used in this work was a KrF excimer LAMBDA physic (25 ns, 248 nm) with a pulsed repetition rate of 5 Hz, and an energy fluence of 2 J/cm^2. The beam was incident on a rotating target at an angle of 45° with respect to the normal target. The deposition chamber was initially evacuated at 5×10^{-3} Pa using a turbo molecular pump. The oxygen gas was introduced into the chamber, with a pressure maintained at about 1 Pa. The distance between the target and the substrate was 4 cm, and the substrate temperature was maintained at ~450 °C.

The crystalline structure of the films was characterized by conventional X-ray diffraction (XRD) at (θ–2θ) configuration using CuKα radiation (λ=0.1541838 nm) from a Bruker-AXS D8 diffractometer. The waveguide optical properties of Co:ZnO thin films were investigated by M-lines spectroscopy (Ulrich and Torge, 1973) using the Metricon Model 2010/M prism coupler. The profiles of guided modes were obtained by measuring the reflected intensity of a (He–Ne) laser beam with a wavelength λ=633 nm as a function of the incidence angle on a right angle rutile prism (np=2.5822 for TM mode and np=2.8639 for TE mode). The optical transmittance of the ZnO thin films was characterized by an UV–vis spectrophotometer Shimadzu (UV-3101PC) in the wavelength range 300–800 nm.

3. Structural properties

The (θ–2θ) XRD patterns of ZnO and CZO thin films deposited by PLD onto glass substrates at 450 °C are shown in Fig. 1. Only two peaks were recorded in the diffraction range (20–80°) of undoped ZnO films. These two peaks located at 34.36 and 72.30° correspond respectively to (002) and (004) peaks of hexagonal ZnO structure. It is also evident in Fig. 1 that the preferential (002) peak intensity increases with decreasing Co dopant concentration. The degradation in the crystalline quality of thin films was observed with increasing Co content.

However, we note that there are no metallic cobalt or metallic zinc peaks in CZO films. No new phases have been observed in the XRD pattern even at higher doping level. Thereafter, the Co incorporation does not alter the hexagonal structure of ZnO films and does not initiate the formation of CoO phase. This result indicates that the fabricated ZnO films have a c-axis preferred orientation. Highly c-axis preferred orientation, which is critical for