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Effect of post sputter annealing treatment on nano-structured cadmium zinc oxide thin films

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ABSTRACT

Thin films of cadmium zinc oxide (CdZnO) were deposited on glass substrates by reactive dc magnetron sputtering and post sputter annealed at different temperatures: 350 °C, 400 °C, 450 °C, 500 °C and 550 °C. These films were characterized by glancing angle x-ray diffraction, field emission scanning electron microscopy, photoluminescence, UV–vis–NIR spectroscopy and Hall measurements. The structural results revealed that all these films exhibit hexagonal wurtzite structure with complete c-axis orientation in (002) plane. The transmittance of these films increased with the post sputter annealing treatment and minimum band gap observed for the film that was annealed at 500 °C. The carrier concentration and Hall mobility increased with post sputter annealing, while electrical resistivity decreased with the narrowing optical band gap and increase in the crystallite sizes.

1. Introduction

Transparent conducting oxide (TCO) thin films possess unique characteristics such as low electrical resistivity and high optical transmittance in the visible region which has many applications and is used as contacts in flat panel displays and solar cells, light emitting diodes and laser diodes [1–6]. These applications use electrode materials that have greater than 80% transmittance of incident light as well as resistivity less than 10^{-3} Ω cm for efficient carrier transport. The transmittance of these films, just as in any transparent material, is limited by light scattering at defects and grain boundary scattering effects. In general, TCOs for use as thin-film electrodes in solar cells should have a minimum carrier concentration on the order of 10^{20} cm^{-3} for low resistivity [7]. Thus, many efforts have been made to develop the alternative TCO materials. ZnO and Cd doped ZnO are important in technological applications in catalytic, electrical, optoelectronic [8] and quantum devices [9]. ZnO is a potential candidate for the future high quantum efficiency devices because of its large exciton binding energy of 60 meV (25 meV for GaN) and wide direct band gap ($E_g = 3.37$ eV) semiconductor [10]. CdO is an n-type degenerate semiconductor possesses rock-salt structure and narrow direct band gap of 2.3 eV. Hence, it is possible to tune the band gap of ZnO by doping Cd and the luminescence of cadmium zinc oxide (CdZnO) films can cover the visible spectral range. Moreover, the substitution of controlled amount of Zn by Cd is not expected to induce the significant changes in crystal structure and lattice constants because of their similar ionic radii of Cd and Zn ions. 'Post deposition annealing treatment at various atmospheres, such as air, oxygen, hydrogen, nitrogen, or in vacuum for as-deposited TCO films is usually considered as an effective technique to improve the structural, optical and electrical properties [11]. Annealing treatment in vacuum was also usually introduced to improve the physical properties of TCO by desorption of the absorbed oxygen vacancies at the grain boundaries.

There have been several experimental studies in this system [12,13]. A decrease in band gap in Cd doped ZnO has been reported by several authors [14,15]. S. Gowrishankar et al. [16] have studied doping Cd in ZnO using rf sputtering method and found a decrease in the band gap. The effect of post-annealing temperature on ternary CdZnO alloy thin films was investigated by D.W. Ma et al.

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[17] and they also found a decrease in the band gap with the post-annealing temperature and duration. Thin films of CdZnO were synthesized by employing various deposition techniques [18–23], but the crystal quality of the above was not satisfactory due to the coexistence of a multiphase or polycrystalline state without preferred orientation. The dc magnetron sputtering received much attention for the preparation of transparent conducting oxide films using metal targets with high deposition rate onto a large area substrates and good control over the composition of the deposited film. Using reactive dc magnetron sputtering technique, we have successfully deposited completely (002) c-axis oriented ternary CdZnO films.

In this work, the CdZnO thin films have been deposited by dc magnetron sputtering and annealed at different temperatures from 350 °C to 550 °C in vacuum. These thin films were investigated for their structural, optical and electrical properties.

2. Experimental details

Thin films of CdZnO were grown on crown glass substrates by reactive dc magnetron sputtering using Zn–Cd metals of 99.999% purity as sputtering targets. The deposition chamber was evacuated to a base pressure of 8×10^{-6} mbar by a combination of a rotary pump and diffusion pump. High purities of oxygen and argon were introduced through separate mass flow controllers as reactive and sputtering gases respectively. The total pressure during sputtering was maintained at 4×10^{-3} mbar. The target-to-substrate distance was fixed at 60 mm. The deposition time was 30 min for each sample. Before deposition of each film, the Zn–Cd target was pre-sputtered in an argon atmosphere for 15 min to remove the contaminants from the target surface. The sputtering current and voltage were 250 mA and 300 V respectively. The synthesized films were post annealed at 350 °C, 400 °C, 450 °C, 500 °C and 550 °C respectively for 1 h each.

The crystal quality of the films was analyzed by glancing angle x-ray diffraction (GAXRD) using Brucker-D8 with a Cu-K_α ($\lambda = 0.154$ nm) radiation and the angle 2θ was varied in the range between 20° and 60° with a step of 0.02°. The surface morphology was investigated using field-emission scanning electron microscopy (FESEM). The film thickness was measured using optical interference method. The optical transmittance spectra of CdZnO thin films at as-deposited and different post annealing temperatures (350 °C, 400 °C, 450 °C, 500 °C and 550 °C respectively) were carried out by using UV–vis–NIR spectrophotometer (Hitachi U-3400). The transmittance spectra were measured by taking a similar glass as a reference and hence the spectra were from the films only. The refractive index was also calculated from the optical transmittance data using well known Manifacier's envelope method [24]. Using a He–Cd Laser as source, the photoluminescence (PL) band was observed at room temperature for all the samples. Hall measurements (using Ecopia HMS-3000) in Van der Pauw configuration at room temperature and 0.5 T magnetic field was carried out to determine the electrical properties (resistivity (ρ), carrier concentration (n) and Hall mobility (μ)) of the sputter deposited CdZnO thin films at as deposited and different post annealing temperatures.

3. Results and discussion

The GAXRD patterns of as-deposited and post-annealed (350 °C, 400 °C, 450 °C, 500 °C and 550 °C for 1 h) CdZnO thin films are shown in Fig. 1. It can be seen that the preferential orientation of all these films has been found to be along (002) (JCPDS card number #65–3411) plane. The analysis revealed that all the films are of polycrystalline in nature and having a hexagonal wurtzite crystal structure without any impurity phases within the detection limit of this instrument, keeping the crystalline structure and lattice parameters close to that of the ZnO (Space group: $P6_3mc$) films. This suggests that the films do not have any phase segregation. The shift of the diffraction peak (002) to lower angles corresponds to the variation of c-axis length.

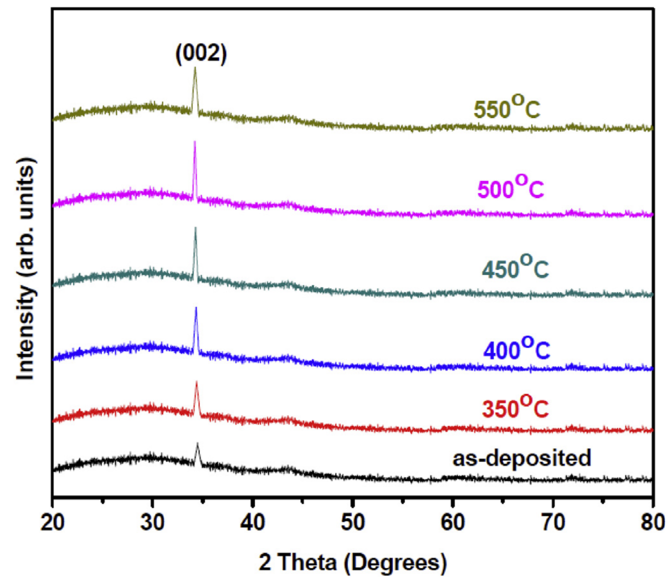

Fig. 1. GAXRD patterns of CdZnO thin films at various annealing temperatures.

It could be seen that the (002) peak was shifted toward smaller angular positions as the post annealing temperature up to 500 °C which indicated an expansion in c-axis length with the increase of post annealing temperature. The expansion of c-axis lattice constant is due to the difference in ionic radii, i.e. the radius of Cd^{2+} is 0.097 nm which is larger than that of Zn^{2+} (0.074 nm). Therefore, the substitution of Zn^{2+} ions by Cd^{2+} ions induces a lattice–volume expansion [25]. The c-axis length above the 500 °C was slightly decreased because of the diffraction peak shifted toward higher angles. The variation of c-axis length is inherently related to the presence of strain in the films. The strain in the films can be calculated along c-axis given by the following relation [26]:

$$\varepsilon = \left[\left(c_{film} - c_{bulk}\right)/c_{bulk}\right] \quad (1)$$

where c_{bulk} is the unstrained lattice parameter ($c_{bulk} = 0.5205$ nm). The strain in the films is likely to be thermal strain. The thermal strain introduced by the different linear thermal expansion coefficients α of the film ($\alpha_{ZnO} = 6.5 \times 10^{-6}\ K^{-1}$ [27]) and the glass substrate ($\alpha_{glass} = 9 \times 10^{-6}\ K^{-1}$ [28]) is significantly smaller than the measured strain. It reveals that the measured film strain is mainly caused by the growth process itself. The strain in the films increased with increase of post annealing temperature is mainly cause of difference in the ionic radii of Cd^{2+} and Zn^{2+}. A negative strain (-2.34×10^{-3}) is observed in the as-deposited film which means that it responds opposite to the applied load. The variation of c-axis length and lattice strain with post annealing temperature are shown in Fig. 2.

The values of full-width at half maximum (FWHM) for (002) crystallographic plane and their crystallite sizes with annealing temperature are shown in Fig. 3. By FWHM and the (002) peak diffraction angle values the crystallite size can be estimated by Scherrer's formula [29]: