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Effect of ion beam assistance on Cu- doped ZnO thin films deposited by simultaneous RF and DC magnetron sputtering

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Abstract

Ion-beam-assisted Cu-doped ZnO (CZO) thin films were deposited on unheated glass substrates by simultaneous RF and DC magnetron sputtering of zinc oxide (ZnO) and copper (Cu) respectively. The as-deposited films were subjected to thermal annealing at 200 °C for one hour. The effects of ion-beam-assistance and thermal annealing on the structural, morphological and optical properties of CZO films have been systematically studied. From XRD studies, it was found that the deposited films were polycrystalline in nature with (002) as a predominant characteristic orientation of ZnO crystallized in hexagonal wurtzite structure along the *c*-axis perpendicular to the substrate surface. Ion-beam-assistance on CZO films significantly influenced the predominant (002) reflection. Additional diffusion energy gained by the adatoms during film growth enhances the Cu concentration in ZnO host lattice, leads to disruption of (002) reflection. In addition, the surface morphology of deposited films displayed the presence of hexagonal granular-shaped grains vertical to the substrate. Furthermore, we observed that optical transmittance of the as-deposited and annealed films decreased with effect of ion-beam-assistance. Consequently, the optical absorption edge gradually shifted towards longer wavelength side, it resulted to decrease of band gap energy.

Keywords: A. Films; A. Grain growth; C. Optical properties; D. ZnO

1. Introduction

Zinc oxide (ZnO), a unique metal oxide semiconductor material crystallized in hexagonal wurtzite structure with a relatively wide direct band gap of 3.37 eV has been extensively used as a prime material for optical and photovoltaic applications. Over the past few years, pure and doped ZnO in thin film and nanostructure form have attracted considerable attention for device applications due to their outstanding optical and electrical properties. Several thin film deposition techniques have been carried out to deposit doped ZnO thin films using various dopants at desired concentrations for practical applications [1–6]. Among many dopants, copper (Cu) behaves like a peculiar dopant element in ZnO host lattice, which leads to diverse best known applications, such as gas sensors [7,8], magnetic materials [9], luminescence material [4,10] and solar cells [11]. Owing to similar ionic radii of Cu^{2+} (0.072 nm) and Zn^{2+} (0.074 nm), Cu can be easily soluble in hexagonal ZnO host lattice. Simultaneous RF and DC magnetron sputtering is one of the promising deposition technique has significant attention towards tailoring of dopant material in the host lattice. Indeed, few research groups have managed to study on Ti [12,13], Al [14], In [15], Ag and Cu [16,17] doped ZnO thin films by simultaneous RF and DC magnetron sputtering technique. External ion-beam-assistance plays a vital role during film deposition at room temperature. It greatly enhances the film quality, such as adhesion to the substrate, film density and minimization of film porosity. To date, Mo [18,19] and Ga [20] doped ZnO thin films have been deposited under ion-beam-assistance at various discharge current and voltages.

In this present work, we reported the results of Cu-doped ZnO (CZO) thin films deposited under ion-beam-assistance by simultaneous RF and DC magnetron sputtering of ZnO and Cu respectively. During film deposition, external ion-beam-assistance has been varied as a function of discharge current

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and voltage. Applied discharge current and voltage enhances the bombardment of argon ion flux on the substrate surface. With this phenomenon, the Cu concentration in hexagonal ZnO host lattice can be improved by the substitution of Zn^{2+} ions with Cu^{2+} ions. The crystalline structure, surface morphology and optical properties of the ion beam assisted CZO films were investigated in detail using X-ray diffraction (XRD), Field emission scanning electron microscopy (FESEM), Atomic force microscopy (AFM), and UV–vis spectrophotometer respectively.

2. Experimental

Ion-beam-assisted Cu-doped zinc oxide (CZO) thin films were grown on glass substrates at room temperature by simultaneous RF magnetron sputtering of ZnO and DC magnetron sputtering of Cu. Fig. 1 shows the schematic illustration of ion-beam-assisted simultaneous RF and DC magnetron sputter deposition system of CZO thin films. Ion gun source was positioned vertically to the substrate surface. ZnO and Cu targets in a circular shape with a diameter of 50.8 mm and a thickness of 7 mm were used as source targets. The target to rotating substrate distance was maintained at 15 cm. The glass substrates were ultrasonically cleaned in acetone and pure distilled water successively, then blown with high-pressure nitrogen gas to avoid water spots and finally dried on the hot plate at 100 °C for 5 min. The base pressure of 5×10^{-6} Torr was achieved by an oil sealed rotary and a turbo molecular pump combination. Purified argon as a sputtering gas was introduced into the main chamber (30 sccm) and ion gun chamber (20 sccm) through fine mass flow controllers. All the depositions were carried out under a fixed working pressure of 20 mTorr for the duration of 40 min. During film deposition, the ion-beam-assistance was varied by tuning of discharge current and voltage specifically as 0 A ; 0 V, 0.1 A ; 60 V, 0.2 A ; 100 V and 0.25 A ; 130 V. The output RF sputter power of 150 W for ZnO target and DC sputter power of 4 W for Cu target were kept constant simultaneously. The as-deposited films were thermally annealed at 200 °C for 60 min. Prior to CZO film deposition, targets were pre-sputtered in Ar atmosphere for 10 min in order to remove any surface contaminants present on the target surface. The crystal structures of as-deposited and annealed films were examined by X-ray diffractometer (XRD, X'Pert Pro MPD, PANalytical) using monochromatic CuKα X-ray radiation (λ=0. 15406 nm). Field emission scanning electron microscopy (FESEM, HITACHI, S-4800) and atomic force microscopy (AFM, MOD-1M plus) were employed to study the surface morphology of the deposited films. The UV–vis transmission spectra were measured on a HITACHI U-3900 spectrophotometer over the wavelength range from 300 to 850 nm.

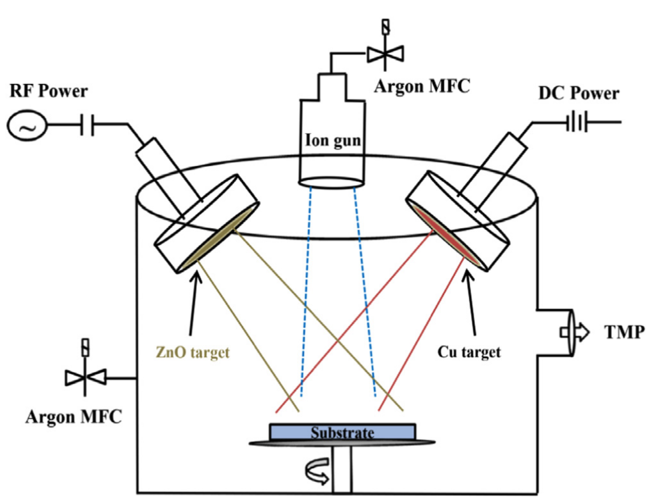

Fig. 1. Schematic diagram of simultaneous RF and DC magnetron sputtering of Cu-doped ZnO films under ion-beam-assistance.

3. Result and discussion

3.1. Effect of ion-beam-assistance on Cu-doped zinc oxide (CZO) thin films

Fig.2 depicts the X-ray diffraction patterns of ion-beam-assisted CZO films grown on glass substrates as a function of discharge current and voltage collected over the 2θ range of 20–70°. It is clear from the XRD results that non-ion beam-assisted CZO films showed a predominant (002) reflection at 34.11° 2θ , assigned to ZnO crystallized in hexagonal wurtzite structure oriented along the *c*-axis normal to the substrate surface. It can be seen that two more weak diffraction peaks at 36.0° and 62.36° 2θ , corresponding to the (101) and (103) reflections of ZnO in addition to the (002) reflection. It is to be noted that, the films formed at lower ion-beam-assisted condition does not show any obvious change in the preferred (002) reflection. But it is clearly seen that, with increase of ion-beam-assistance by varying the discharge current and voltage to 0.2 A and 100 V, the (002) peak intensity decreased and one more weak diffraction peak centered at 31.5° 2θ, attributed to the (100) plane of ZnO grown along the *c*-axis parallel to the substrate. At higher discharge current and voltage of 0.25 A and 130 V, the reflected (002) peak intensity deteriorated further and a concomitant increase in the (100) and (101) peak intensities was noticed. However, CZO films undergoes a structural transition from preferred (002) orientation to (100) and (101) crystal planes with increase of ion-beam-assistance resulted to significant change in the crystal structure. During film growth, external ion-beam-assistance provides additional diffusion energy to adatoms on the substrate surface which improves the Cu concentration in CZO films by effective substitution of Cu^{2+} ions for Zn^{2+} ion sites and at interstitial positions of ZnO host lattice would induce to decrease of (002) peak intensity. Moreover, it was also observed that the Cu content in ZnO host lattice enhanced with increase of ion-beam-assistance at constant DC sputter power of 4 W applied to the Cu target. However, no detectable change in the (103) reflection was observed for the films formed under various ion-beam-assisted conditions. A weak (110) reflection of ZnO suddenly appeared at higher ion-beam-assisted condition of 0.25 A and 130 V. Kuo et al. [18] have been reported the similar structural changes from preferred (002) to (100) and