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Transparent conductive ZnO:Ga films prepared by DC reactive magnetron sputtering at low temperature

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ABSTRACT

Ga-doped ZnO (ZnO:Ga) transparent conductive films were deposited on glass substrates by DC reactive magnetron sputtering. The structural, electrical, and optical properties of ZnO:Ga films were investigated in a wide temperature range from room temperature up to 400 °C. The crystallinity and surface morphology of the films are strongly dependent on the growth temperatures, which in turn exert an influence on the electrical and optical properties of the ZnO:Ga films. The film deposited at 350 °C exhibited the relatively well crystallinity and the lowest resistivity of $3.4 \times 10^{-4}\,\Omega$ cm. More importantly, the low-resistance and high-transmittance ZnO:Ga films were also obtained at a low temperature of 150 °C by changing the sputtering powers, having acceptable properties for application as transparent conductive electrodes in LCDs and solar cells.

1. Introduction

Zinc oxide (ZnO) has emerged as one of the most important transparent conducting oxides (TCOs) for a variety of promising applications such as flat panel displays (FPDs), solar cells, and gas sensors in recent years [1,2]. Among the available techniques for deposition of ZnO thin films, magnetron sputtering is a more preferred method in industry for its low cost, high deposition rate, good adhesion on substrate, good controllability, and long-term stability. Furthermore, by reactive sputtering in gas mixtures the compound ZnO films can be deposited from elemental (metallic) targets [3]. Undoped ZnO films are highly resistive. However, doping ZnO with appropriate impurities, usually the Group-III elements, can increase the conductivity by one or two orders of magnitude [4–6]. Based on many reported investigations of the effect of doping ZnO with impurities, Ga doping seems to be the successful and promising element due to its advantages. Ga ions have a similar ionic radius compared to Zn, which should result in only small ZnO lattice deformations even for high Ga concentrations [7]. Furthermore, Ga is less reactive and more resistant to oxidation than Al [8].

The application of a TCO film is strictly dependent on its deposition temperature [9,10]. In the case of liquid-crystal-display (LCD) applications the film deposition temperature should be lower than 150 or 250 °C depending on whether the substrate material is plastic or glass. Also for solar cell applications it should be lower than 200 or 500 °C depending on whether the TCO film is deposited on other films such as semiconductor film or deposited directly on glass. The effects of substrate temperature on the electrical and optical properties of TCO films have investigated in the temperature range above 200 °C [11]. However, for the applications of solar cells and LCDs it is necessary to investigate the effect of substrate temperature in a wider range, especially in low temperatures. In this work we report the effect of the substrate temperature on the structural and electrical properties of ZnO:Ga films prepared by DC reactive magnetron sputtering in a temperature range from room temperature up to 400 °C and try to get low-resistance and high-transmittance ZnO:Ga films at low temperature by changing sputtering power.

2. Experimental

Transparent conducting ZnO:Ga thin films were deposited on glass substrates by DC reactive magnetron sputtering. The sputtering target was a disc of Zn metal (99.999% purity) alloyed 4 at.% Ga (99.999% purity). The vacuum chamber was evacuated to a base pressure of 3×10^{-3} Pa. High purity (99.999%) Ar and O_2 were introduced as the sputtering gases with a ratio of 11:1. The total deposited pressure in the experimental was 1.0 Pa and the substrate-to-target distance was fixed at 60 mm. The film

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thicknesses were in the range from 394 to 654 nm under different growth condition, and the details were indicated in the following XRD patterns. Before deposition, the alloy target was pre-sputtered for about 5 min to remove contaminants from the surface. The ZnO:Ga films were deposited at room temperature, 100, 150, 200, 250, 300, 350, and 400 °C, respectively. The sputtering powers varied from 120 to 200 W. The deposition time was 10 min for all the films.

The crystal structure of the films was analysed by X-ray diffraction (XRD) using a Bede D1 system with a Cu Kα (λ = 0.1541 nm). The film thickness and surface morphology were assessed using scanning electron microscopy (FE-SEM SIRION). Hall measurements were performed using the Van der Pauw technique at room temperature. The optical transmission spectra were measured with a Lamda20 spectrometer.

3. Results and discussion

Fig. 1 shows the electrical resistivity (ρ), carrier concentration (n), and mobility (μ) as a function of substrate temperature in a temperature range from room temperature up to 400 °C. The deposition power and sputtering time were fixed at 140 W and 10 min, respectively. The electrical resistivity of the ZnO:Ga film deposited at room temperature was measured to be $3.6 \times 10^{-3}\ \Omega$ cm. It decreased first as the substrate temperature increased from room temperature to 350 °C. A minimum resistivity of $3.4 \times 10^{-4}\ \Omega$ cm was obtained at 350 °C and then the resistivity increased with a further increase of the substrate temperature to 400 °C. The changes of carrier concentration and Hall mobility were consistent with the change of resistivity with the substrate temperature. The increases of both the carrier concentration and Hall mobility with the temperature from room temperature to 350 °C were attributed to the enhancement in the crystallinity of the ZnO:Ga films, as can be seen in Fig. 2. Fig. 2 shows the XRD patterns of ZnO:Ga films deposited at various substrate temperatures, only the peaks indexed to hexagonal (0 0 2) ZnO can be observed in these patterns. No peak from other compounds such as Ga_2O_3 appeared within the detection of XRD, indicating that the ZnO:Ga films possess a single phase hexagonal wurtzite structure with a preferential *c*-axis orientation. The (0 0 2) ZnO peak intensity increase from room temperature to 350 °C, which indicated the enhancement in the crystallinity of the ZnO:Ga films as the deposited

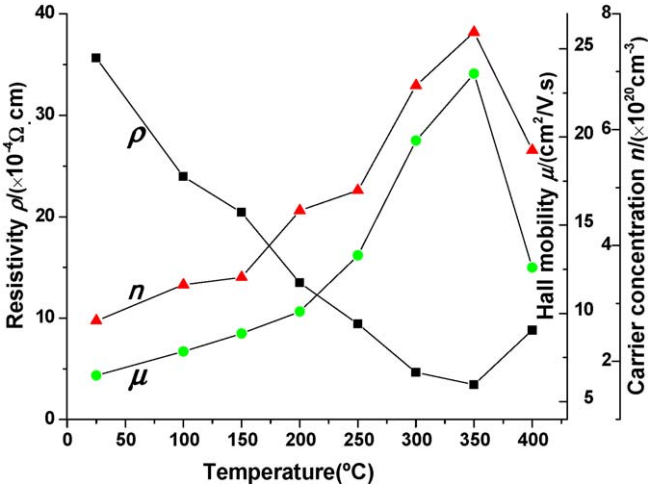

Fig. 1. Electrical resistivity (ρ), carrier concentration (n), and mobility (μ) as a function of substrate temperature.

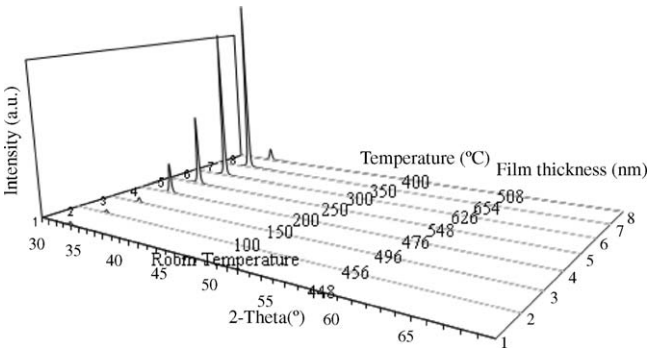

Fig. 2. XRD patterns of ZnO:Ga films deposited at various substrate temperatures.

temperature increase. In general, the film thicknesses increase as the temperature increase. However, when the temperature reaches to 400 °C, the film thickness has a decrease. The decrease in deposition rate at high temperature can be related to the higher vapor pressure of Zn, which gives rise to partial re-evaporation of Zn atom [12].

In the polycrystalline films, gain boundaries and scattering centers are the significantly influencing factors of the mobility [13,14]. The crystallographic defects such as grain boundaries, dislocations, interstitials, vacancies, and Ga substitution induce the scattering of carriers and act as traps making carriers inactive [9]. Fig. 3(a)–(h) shows the surface morphology of ZnO:Ga films deposited at the various substrate temperatures. The films deposited at low temperature are nanocrystalline, whose formation was due to limited mobility of the adatoms at low substrate temperature, as indicated in Fig. 3(a)–(c). When the substrate temperature increases to 200 °C, the sputtered particles had enough energy to diffuse, this results in the formation of a more compact film. With the substrate temperature further increasing, the film exhibited columnar structure and the grain become larger with no grain boundaries can be visible. When the substrate temperature was as high as 400 °C, the grains interacted with each other and agglomerated, as indicated in the inset of Fig. 3(g). The agglomerated grains made the Hall mobility of the film decreased obviously, which can be seen in Fig. 1. This is the main reason why the electrical properties of the film deposited at 400 °C show a slight degradation.

In the process of the preparation of some devices, the films should be low-temperature deposited. So we fixed the deposited temperature at 150 °C and try to improve the performance of the ZnO:Ga films by optimizing the deposition parameters. Fig. 4 shows the XRD patterns of ZnO:Ga films deposited under various sputtering powers. The films also have a *c*-axis orientation perpendicular to the substrate. Variations in the (0 0 2) diffraction angle and the FWHM values of the peak are investigated. As shown in Fig. 5(a), the peak position shows the highest angle at 160 W. Based on the Bragg law:

$$2d \sin\theta = n\lambda \quad (1)$$

where d is the interplanar spacing, θ is the Bragg diffraction angle, λ is the X-ray wavelength. The increase in the diffraction angle corresponds to a reduction in the interplanar spacing ($d_{0\,0\,2}$). Since Ga^{3+} has a smaller ionic radius with respect to Zn^{2+}, the substitution of Ga atoms for Zn atoms at their lattice sites results in the decrease in the lattice constant. Therefore, it can be considered that the decrease in the (0 0 2) spacing with thicknesses is due to the location of more Ga atoms at Zn lattice sites [15]. Fig. 5(b) shows the FWHM values of (0 0 2) peak as a function of sputtering power. As the sputtering power increasing, the FWHM first decreases and then