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Structural, optical and electrical characterization of Ga-Mg co-doped ZnO transparent conductive films

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ABSTRACT

The transparent conducting Ga-Mg co-doped ZnO films were prepared on glass substrates by radio-frequency (rf) magnetron sputtering. The effect of growth temperature on structural, morphological and optoelectronic properties of the films was investigated by XRD, XPS, SEM, UV-visible spectrophotometer and four-point probe. The results show that all the films are polycrystalline and (0 0 2) oriented. The growth temperature significantly affects the structure and optoelectronic properties of the films. The film deposited at the growth temperature of 270 °C has the largest grain size of 52.38 nm, the minimum tensile stress of 0.037 GPa, the highest average visible transmittance of 89.39%, the lowest resistivity of 1.52×10^{-3} Ω·cm and the maximum figure of merit of 5.87×10^{3} $\Omega^{-1}\cdot cm^{-1}$. Furthermore, the optical band-gaps were determined by extrapolation method and observed to be in the range of 3.36–3.59 eV.

1. Introduction

Tin-doped indium oxide (ITO) thin film has been most widely used as a transparent conducting oxide (TCO) electrode in light-emitting diodes, solar cells, flat panel displays, thin film transistors and gas sensors [1–5], since it has high visible transmittance, low electrical resistivity and relatively high work function [6]. Since indium (In) is a rare and an expensive element, however, the cost of ITO thin film is very expensive. As a result, a stable supply of ITO may be difficult to achieve for the recently expanding market demands. Presently, zinc oxide (ZnO) has been actively investigated as an alternate material to replace ITO due to its inherent characteristics such as wide direct bandgap, large excitation binding energy, abundant raw materials, environmental friendliness and high radiation resistance [7]. It is used in various technological domains such as solar cells, photodetectors, light-emitting diodes and laser diodes [8–12]. Aluminum (Al), gallium (Ga), boron (B), titanium (Ti), zirconium (Zr), magnesium (Mg), and rare earth-doped ZnO TCO films have been studied [11–16]. Recently, much attention has been paid to the co-doping process in which the two elements are doped into ZnO simultaneously, because the co-doped ZnO films are expected to show some improvements in electrical and optical properties. In singly-doped ZnO, Mg doping has several advantages in terms of transmission and optical band-gap, while Ga-doped ZnO has superb properties for the conductivity and humidity durability. Thus, it appears that co-doping with Mg and Ga is attractive because an improvement in performance can be expected in various properties. To our knowledge, although many experimental studies have been conducted on the synthesis and electrical properties of Ga-Mg co-doped ZnO [ZnO:(Ga, Mg)] thin films, there are few quantitative studies on their optoelectronic characteristics. In this work, the transparent conducting ZnO:(Ga, Mg) thin films were prepared by radio-frequency (rf) magnetron sputtering at different growth temperatures, and the structural, morphological and optoelectronic properties of the films were studied in detail.

2. Experimental

The ZnO:(Ga, Mg) TCO samples were deposited on glass substrates by rf magnetron sputtering system (MS-560C). A sintered Ga and Mg co-doped ZnO ceramic sputter target (2 wt% Ga_2O_3:2 wt% MgO:96 wt% ZnO, 99.99% purity) was employed as source material. The sputtering chamber was evacuated to a base pressure below 3.1×10^{-4} Pa before argon gas. After vacuum pumping, the sputtering argon gas with a purity of 99.999% was introduced into the chamber and controlled by the standard mass flow controller (MFC). The MFC has accuracy of 1% of the maximum value (50 sccm). Before the ZnO:(Ga, Mg) samples deposition, the

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pre-sputtering was conducted for about 10 min to attain stability and to remove impurities. The deposition parameters for preparing the samples were as follows: target-substrate distance, 75 mm; argon flow rate, 30 sccm; argon pressure, 3.5 Pa; rf power, 140 W; sputtering time, 40 min; and growth temperature, 90–360 °C. X-ray diffractometer (XRD, D8-Advance) with Cu source, X-ray photoelectron spectroscopy (XPS, VG Multilab 2000) with Al source, scanning electron microscopy (SEM, JSM-6700F), four-point probe (RH-2035) and ultraviolet-visible spectrophotometer (TU-1901) were used to characterize the samples.

3. Results and discussion

Fig. 1(a) displays XRD patterns of the films prepared at different growth temperatures. All the samples exhibit a dominant (0 0 2) peak with slight (0 0 4) peak, indicating the deposited films have hexagonal wurtzite structure with highly *c*-axis orientation. With increasing growth temperature from 90 to 270 °C, the intensity ratio of (0 0 4) to (0 0 2) ($I_{(0\,0\,4)}/I_{(0\,0\,2)}$) decreases and the intensity of (0 0 2) peak ($I_{(0\,0\,2)}$) increases obviously, suggesting that the crystalline quality of the films becomes better. However, with further increase from 270 to 360 °C, the $I_{(0\,0\,4)}/I_{(0\,0\,2)}$ increases and the $I_{(002}$ decreases slightly, the crystalline quality deteriorates. This result implies that the sample deposited at 270 °C exhibits the best multicrystal structure. Note also that no other phases are detected from the XRD patterns, which indicates that the dopants have not destroyed the ZnO structure and act as typical dopants. Similar results have been reported elsewhere in the literatures [11,12].

Fig. 1(b) shows the peak position (2θ) and full-width at half-maximum (B) of (0 0 2) plane for all the films. It is found that the 2θ and B decrease obviously with the growth temperature up to 270 °C, and then increase significantly above 270 °C. When the growth temperature is 270 °C, the 2θ value is 34.427°, approaching the value (34.421°) of the pure ZnO (JCPDS No. 36-1451). From the values of 2θ and B of the (0 0 2) peak, the grain size (D) can be estimated by Scherrer's formula [17]: $D = 0.89\lambda/(B\cos\theta)$, where λ and θ are the X-ray wavelength (0.15406 nm) and diffraction angle, respectively. The stress (σ) in the plane can be calculated using the biaxial strain model [18]: $\sigma = -2.32812 \times 10^{11}(c\text{-}c_0)/c_0$, where c is the lattice constant of the strained samples calculated from XRD result, and c_0 (0.5207 nm) is the lattice constant of the pure ZnO (JCPDS No. 36-1451) [19]. The D and σ values of all the films are plotted in Fig. 1(c). It can be seen that all the samples have a positive stress which indicates a tensile stress in the deposited films. As the growth temperature increases from 90 to 360 °C, the σ drops initially and subsequently rises, while the D exhibits the reverse variation trend. The samples deposited at 270 °C possess the best crystallinity and microstructural properties, with the narrowest B (0.157°), the largest D (52.38 nm) and the minimum σ (0.037 GPa). The results suggest that the crystalline quality of the ZnO:(Ga, Mg) films is strongly dependent upon the growth temperature.

Fig. 2 presents SEM images of the samples prepared at different growth temperatures. As can be seen, the surfaces of films are smooth, and the grains are homogeneously distributed. The morphology of the sample deposited at the lower growth temperature of 90 °C is observed to be continuous and dense. With the growth temperature increasing to 270 °C, the crystallinity quality of films is improved and the grain size evidently becomes larger than that of the sample of 90 °C, which is in agreement with the XRD results.

Fig. 3(a) gives XPS survey spectrum for the sample deposited at the growth temperature of 270 °C. From the figure, no photoelectron peaks of other elements except Ga, Mg, Zn, O and C are observed in the spectrum. High-resolution XPS spectra of Ga 2p, Mg 2p and Zn 2p for the sample are shown in Fig. 2(b–d), respectively. The Ga 2p spectrum only consists of one peak at 1117.75 eV (Ga $2p_{3/2}$), indicating Ga is in the form of Ga^{3+} [20]. The Mg 2p peak at 50.17 eV, which is closer to the reported value of 50.50 eV [21], is attributed to Mg^{2+} in MgO. The line of Zn 2p exhibit high symmetry and no metallic Zn with a binding energy of about 1021.46 eV [22] is observed, which confirms that Zn exists only in the oxidized state. The XPS studies demonstrate the presence of Ga-O and Mg-O chemical bonds and the absence of any Ga Mg, and Zn metallic bonds, indicating that the Ga^{3+} and Mg^{2+} ions

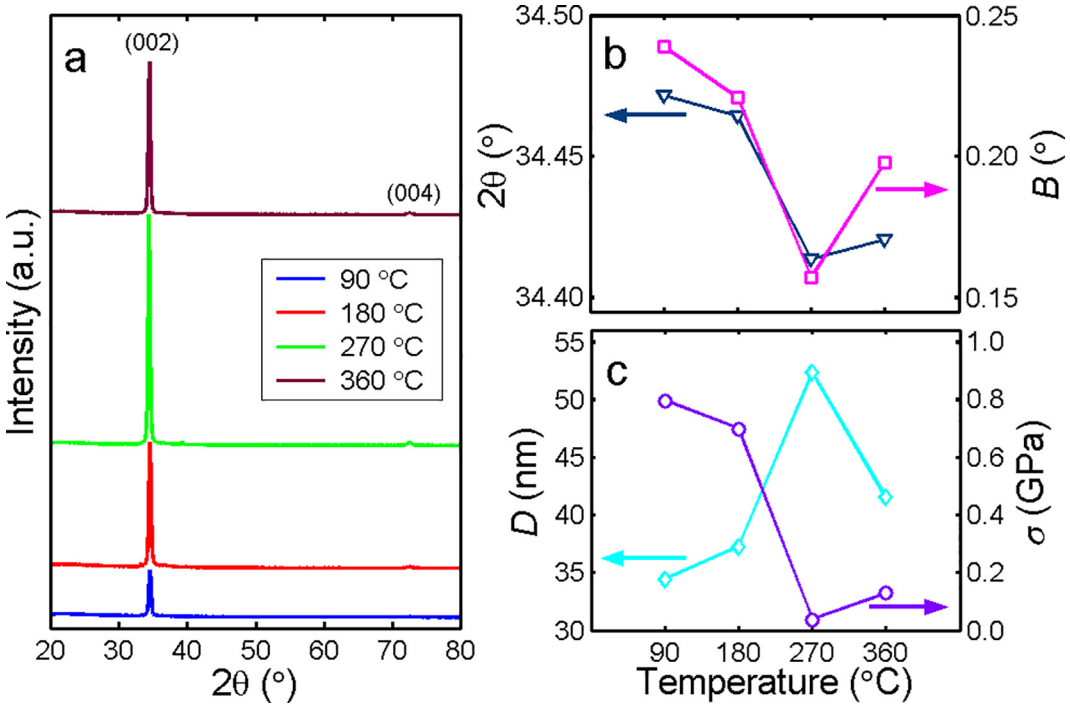

Fig. 1. (a) XRD patterns, (b) peak position and full-width at half-maximum, (c) stress and grain size of all the films.