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Effects of H_2 ambient annealing in fully 0 0 2-textured ZnO:Ga thin films grown on glass substrates using RF magnetron co-sputter deposition

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ABSTRACT

Gallium doped zinc oxide (ZnO:Ga) thin films were grown on glass substrates using RF magnetron co-sputtering, followed by H_2 ambient annealing at 623 K to explore a possibility of steady and low-cost process for fabricating transparent electrodes. While it was observed that the ZnO:Ga thin films were densely packed *c*-axis oriented self-textured structures, in the as-deposited state, the films contained Ga_2O_3 and $ZnGa_2O_4$ which had adverse effect on the electrical properties. On the other hand, post-annealing in H_2 ambient improved the electrical properties significantly via reduction of Ga_2O_3 and $ZnGa_2O_4$ to release elemental Ga which subsequently acted as substitutional dopant increasing the carrier concentration by two orders of magnitude. Transmittance of the ZnO:Ga thin films were all over 90% that of glass while the optical band gap varied in accordance with the carrier concentrations due to changes in Fermi level. Experimental observation in this study suggests that transparent conductive oxide (TCO) films based on Ga doped ZnO with good electrical and optical properties can be realized via simple low-cost process.

1. Introduction

Transparent conductive oxide (TCO) thin films, of which the representative material is the indium tin oxide (ITO), have been widely used in transparent electrodes for flat panel displays, solar cells, and organic light-emitting diodes due to the high luminous transmittance, good electrical conductivity, superior adhesion to substrate, and chemical inertness [1–5]. Due to the high cost in raw materials of indium, however, zinc oxide (ZnO) thin films with n-type dopants including Al, Ga, In, and B have been extensively studied to be an alternative to ITO. As previously reported, Al doped ZnO (ZnO:Al) thin films show good transparent and conducting properties whose resistivity has achieved the order of $1 \times 10^{-4}\ \Omega$ cm with average transparency of more than 85% in visible regions [6–8]. Despite of the superior properties of ZnO:Al as a replacement for TCO, it shows relatively low thermal stability and degeneration problem in long time exposure to air ambient originated from high reactivity of aluminum [9,10].

Recently, gallium as a dopant in ZnO has drawn great attentions due to low reactivity and more resistant characteristics to oxidation compared to aluminum. In addition, slightly smaller bond length of Ga–O (1.92 Å) than that of Zn–O (1.97 Å) allows higher solubility of Ga in ZnO matrix leading to the high flexibility in doping concentration [11]. Thus, it is considered that

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ZnO:Ga-based TCOs are relatively inexpensive while they have desirable properties besides electrical and optical properties such as non-toxicity, long-term environmental stability and excellent infrared (IR) shielding which are not easily obtained in ZnO:Al [12–14].

Published electrical resistivity, carrier concentration, mobility, and optical transmittance of polycrystalline ZnO:Ga thin films range from 2.58×10^{-2} to $1.4 \times 10^{-4}\,\Omega$ cm, 5.28×10^{19} to 5.51×10^{21} cm^{-3}, 0.669 to 54.2 cm^2/V s, and approximately 70 to well above 90%, respectively [15–17]. Excellent electrical and transparent properties of high crystalline ZnO:Ga thin films grown on single crystal substrates had been reported [16,18,19]. Bhosle achieved the lowest resistivity of $1.4 \times 10^{-4}\,\Omega$ cm with (0 0 2) epitaxial ZnO:Ga thin films grown on sapphire by pulsed laser deposition (PLD) [16]. Park et al. reported that high quality ZnO:Ga thin film deposited by PLD on quartz substrate at 573 K shows a low electrical resistivity of $8.12 \times 10^{-5}\,\Omega$ cm, a carrier concentration of 1.46×10^{22} cm^{-3}, and a carrier mobility of 30.96 cm^2/V s with a visible transmittance of above 90% [18]. These large differences on electrical property are presumably due to corresponding variations in film composition, microstructure, deposition technique, and post-deposition process.

In this article, we studied the growth characteristics and properties of ZnO:Ga thin films on glass substrate by varying growth temperature ranging from room temperature (RT) to 623 K, focusing on the effect of subsequent H_2 ambient annealing on the electrical, structural, and optical properties. Among various deposition techniques, RF magnetron sputtering system was chosen due to its advantageous features such as simple apparatus, high deposition rates, and low deposition temperature. Particularly, with the potential controllability of the dopant concentrations in mind, dual target co-deposition system was used. It was demonstrated that in despite of initially poor electrical properties due to the formation of undesirable oxides phases, once post-annealed in hydrogen at relatively low temperature, the ZnO:Ga thin films showed significant improvement in electrical properties ensuring that it is a promising potential ITO substitute that can be produced with relatively simple process.

2. Experimental procedure

The transparent conductive ZnO:Ga thin films were deposited on glass substrates by RF magnetron co-sputtering using ZnO (99.99%) and Ga_2O_3 (99.9%) targets by varying deposition temperature (T_s) from RT to 623 K. Glass substrates, cleansed via a standard cleaning procedure, was loaded in the central region of the substrate holder located about 50 mm away from the target. The sputtering chamber was initially evacuated to a base pressure of $\sim 5.1 \times 10^{-4}$ Pa and the working pressure was maintained at $\sim 7.3 \times 10^{-1}$ Pa with an Ar ambient gas (99.999%). The RF power of the ZnO and Ga_2O_3 target were fixed at 150 and 75 W, respectively, to deposit in the transparent conductive films for 20 min. As-deposited thin films, after initial characterizations, were annealed in H_2 ambient at 623 K for an hour. The thicknesses of films were determined by cross-sectional scanning electron microscopy (SEM). The surface morphology and the crystalline characteristics of thin films were investigated by atomic force microscopy (AFM, Digital Instruments Nanoscope II) and X-ray diffraction (XRD), respectively. Ga concentration in ZnO film was determined by energy dispersive X-ray spectroscopy (EDS). The chemistry of transparent conductive ZnO:Ga thin films were studied using X-ray photoelectron spectroscopy (XPS). The electrical properties of the ZnO:Ga thin films were measured at room temperature by van der Pauw method. The optical properties of ZnO:Ga thin films were examined using UV–vis spectrophotometer.

3. Results and discussion

Morphology of the ZnO:Ga thin films were evaluated first before the discussion of their electrical and optical properties since the effect of the morphology-related factors on these properties could not be neglected. Fig. 1 shows the SEM images of the as-deposited and post-annealed films for the deposition temperatures of 298, 373, 473, and 623 K, respectively. The films thicknesses estimated from the cross-sectional images (not shown) varied slightly from 420 to 450 nm and these values did not change after the post-annealing treatment in hydrogen. Further, in Fig. 1, it can be seen that all the films have densely packed columnar grain structures, implying the textured growth of the films along a specific crystallographic orientation.

Regarding the surface roughness, Fig. 2 shows that the roughness estimated from the AFM observations (image not shown) increases with higher deposition temperature (from 7.9 to 12.7 nm) in the as-deposited state. It is well known that higher deposition temperature yields increased surface roughness of the ZnO thin films [20] and the ZnO:Ga thin films herein also show the same trend. It is also seen in Fig. 2 that there is no noticeable change in the roughness after the hydrogen annealing treatment (7.5–11.1 nm). As the surface roughness increases, it is more likely that negatively charged oxygen-related species are adsorbed on the surface of the crystallites which in turn act as electron traps [21]. At the same time, the rough surface scatters the incident light beam to reduce the optical efficiencies. However, since the change in the surface roughness is somewhat small with the varying deposition temperature and with the post-annealing treatment, it can be said that the effect of the changes in surface roughness accompanying the processing conditions on electrical and optical properties of ZnO:Ga thin films could be excluded in this study.

Apart from the morphology, crystallinity could also affect the electrical and optical properties of the ZnO:Ga thin films. Therefore, the XRD spectra of the ZnO:Ga thin films shown in Fig. 3 are examined. In the XRD spectra for the as-deposited samples shown in Fig. 3(a), most prominent peaks at the Bragg angle of about 34.3° are assigned to ZnO (0 0 2) while those at 36.3°, 47.7° and 62.8° are to ZnO (1 0 l). Together with this, the intensities of these ZnO (0 0 2) peaks tend to increase with higher deposition temperature whereas those for ZnO (1 0 2) and (1 0 3) decrease. It is therefore deduced that the ZnO:Ga thin films all have the preferred c-axis orientation due to self-texturing regardless of the deposition temperature and that the crystallinity would be improved when the growth temperature is increased from RT. Decrease in the intensity of the ZnO (1 0 l) peaks also suggest that rather random nucleation of ZnO crystallites due to the role of Ga providing nucleation sites [22] is suppressed when higher deposition temperature is employed.

One interesting feature noticed in Fig. 3(a) is the presence of the diffraction peaks due to other oxide phases. While the peak at 43.7° is assigned to $ZnGa_2O_4$ (4 0 0), the 37.5° peak can be assigned to both Ga_2O_3 (4 0 1) and $ZnGa_2O_4$ (2 2 2). Similarly, the 57.5° peak can be assigned to both Ga_2O_3 ($\bar{3}$ 1 3) and $ZnGa_2O_4$ (5 1 1). Peaks related to Ga_2O_3 tend to decrease as the deposition temperature is increased; however, that due to $ZnGa_2O_4$ remain almost similar regardless of the deposition temperature. These changes in the XRD peak intensities suggest that Ga is supplied in the form of Ga_2O_3 from the sputtering target and incorporated into the ZnO phase as clusters without full decomposition at low deposition temperature. Increasing the processing temperature then provide sufficient thermal energy for the dissociation of Ga_2O_3. Presence of the $ZnGa_2O_4$ peaks indicates that some Ga_2O_3 species from one sputtering target can combine with ZnO species from the other target stoichiometrically to form spinel structure. It was reported that when Ga concentration exceeds the solubility limit in ZnO:Ga