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투명 전도막 응용을 위한 Ga 도핑된 ZnO 박막의 열적 안정성에 관한 연구

오상훈, 안병두, 이충희, 이상렬
연세대학교 전기전자공학과

Thermally stability of transparent Ga-doped ZnO thin films for TCO applications

Sang Hoon Oh, Byung Du Ahn, Choong Hee Lee and Sang Yeol Lee
Department of Electrical and Electronic Engineering, Yonsei University

Abstract - Highly conductive and transparent films of Ga-doped ZnO have been prepared by pulsed laser deposition using a ZnO target with 3 wt% Ga_2O_3 dopant. Films with the resistivity as low as 3.3×10^{-4} Ωcm and the transmittance above 80 % at the wavelength of 400 to 800 nm can be fabricated on glass substrate at room temperature. It is shown that a stable resistivity for the use in oxidation ambient at high temperature can be obtained for the films. Heat treatments were performed to examine the thermal stability of ZnO and GZO films at ptemperature range from 100℃ to 400℃ in O_2 ambient for 30 minutes. The resistivity of ZnO film annealed at 400℃ increased by two orders of magnitude, in case of GZO film was relatively stable up to at 400℃. For practical applications at high temperatures the thermal stability of resistivity of GZO thin films might become an advantage for transparent electrodes.

1. Introduction

Recently, the demand for indium-tin-oxide (ITO) thin-film transparent electrodes has dramatically increased in the field of optoelectronic devices. The increase in usage of ITO films for flat panel displays and solar cells causes not only to raise the price of ITO but also to be jeopardized the availability of indium in the near future. Therefore, the development of alternative transparent conducting oxide (TCO) materials is necessary to resolve this serious problem [1]. In recent years, III group elements doped zinc oxides have been attracting much attention as an alternative candidate to ITO due to their inexpensive, abundant, and non-toxic features [2]. It is well known that group III elements such as Al, In and Ga act as donors in ZnO.

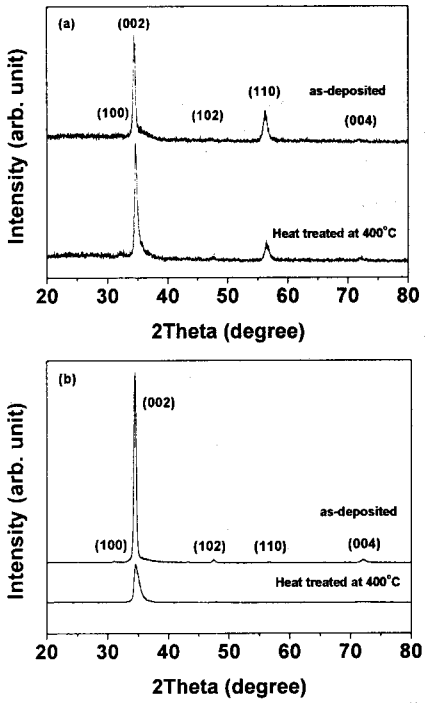
In this paper, the influence of the gallium impurity on structural, optical and electrical properties in ZnO film deposited by pulsed laser deposition is reported. Comparisons of the stability of the electrical of ZnO and Ga doped ZnO films after heat treatment are analyzed and discussed.

2. Experimental

GZO thin films were grown on glass substrates by pulsed laser deposition (PLD). Ga-doped ZnO targets were prepared by a conventional ceramic powder process. Ga-doped ZnO target was composed of 3 wt% Ga_2O_3 and 97 wt% ZnO. ZnO and GZO thin films were deposited at room temperature under the oxygen pressure of 3.0×10^{-2} Torr. The film thickness was about 1000 nm confirmed by scanning electron microscopy (SEM). Heat treatments were performed to examine the thermal stability of ZnO and GZO films at temperature range from 100℃ to 400℃ in O_2 ambient for 30 minutes. The structural property of the samples has been investigated by using X-ray diffraction (XRD) where a Ni-filtered Cu $K\alpha$ (λ= 1.54056Å) source was used. The electrical property of Ag-doped ZnO films has been investigated by Hall measurements in the van der Pauw configuration at a room temperature.

3. Results and discussion

Figure 1(a) and 1(b) show the X-ray diffraction (XRD) patterns of ZnO and GZO films deposited at room temperature and after a heat treatment in oxygen ambient. An undoped ZnO thin film shows dominant (002) and (110) peaks as shown in Fig. 1(a). The (100), (102), (110) and a preferentially strong (002) ZnO peaks have been observed in the GZO films. It indicated that GZO thin films were a polycrystalline but with a c-axis oriented perpendicular to the substrate surface, as evidenced from the strong (002) diffraction peak. The crystallinity of GZO films,



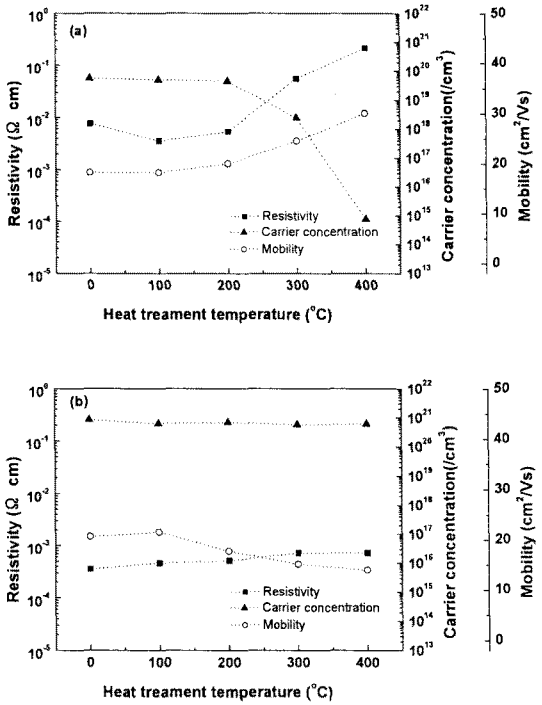
<Fig. 1> X-ray diffraction pattern of (a) ZnO and (b) GZO films before and after heat treatment in oxygen ambient.

evaluated by the intensity and the full-width at half-maximum (FWHM) of the (002) diffraction peak, improved as the Ga_2O_3 content was added. Similar results have been reported on studying Ga-doped ZnO films by Minami et al. [3]. Gallium oxide induced more oxygen during evaporation and Ga^{3+} possessing ionic radius close to that of Zn^{2+} sited in substitution. Thus the stoichiometric ratio between Zn and O became better and the crystallinity improved [4]. The position of the (002) peak shifted to higher 2Θ values for the GZO film as compared with that of ZnO from 34.44° to 34.46°. It indicates the decrease of the c-axis lattice, because the radius of Ga^{3+} ion (0.62 Å) is smaller than that of Zn^{2+} ion (0.72 Å). The decrease of c-axis lattice parameter could be caused by the increase of the number of substitutional Ga^{2-} ions into Zn^{2+} sites [4].

The position of the (002) peak shifted to higher 2Θ angles after heat treatment as shown in Fig. 1. The (002) peak position of ZnO film is varied from 34.44° to 34.84° and that of GZO is changed from 34.46° to 34.48°. It may be due to the O_2 chemisorption on the surface of ZnO and GZO films after annealing in O_2, and resulted in the distortion of crystallites. It can be concluded that the distortion of GZO films is little affected by chemisorption of O_2 than that of ZnO films.

The limitation in a wider field of conducting and transparent coatings applications is known as the temperature instability of the electrical properties in the transparent films. Until now, the

best temperature stability in a vacuum or in a gas ambient, up to 400°C, has been observed in ZnO:Al layers prepared by magnetron sputtering [5]. It has been concluded that for oxygen chemisorption in the films an Al impurity donor, rather than native defect donors such as an oxygen vacancy and interstitial zinc, is stable. We paid particular attention to studying the instability of electrical parameters in GZO films after heat treatment. In order to evaluate the thermal stability of GZO films, heat treatments were carried out in oxygen ambient.



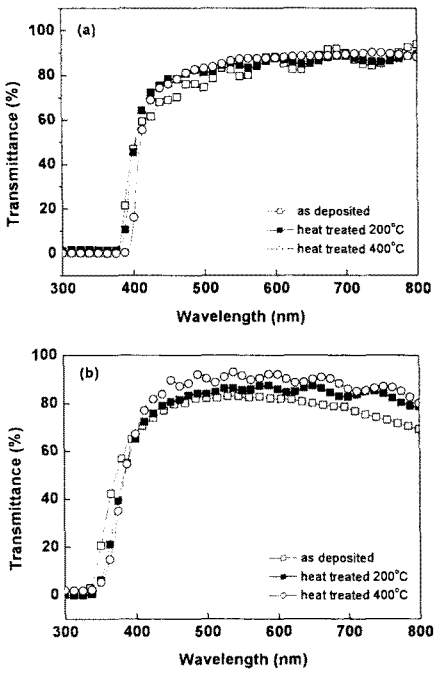
<Fig. 2> Electrical resistivity, carrier concentration and Hall mobility as function of heat treatment temperate for (a) ZnO and (b) GZO films.

Figure 2(a) and 2(b) show the electrical properties of ZnO and GZO thin films grown on glass substrates and anncaled for 30min, as a function of annealing temperature (from 100°C to 400°C), as determined from thermal stability in an oxygen ambient gas. As shown in Fig. 2(a), the resistivity of as-deposited ZnO film was 7.64×10^{-3} Ωcm. However, after heat treatment in O_2, the resistivity of ZnO films increased substantially. Especially, the resistivity of ZnO films was increased by two orders of magnitude after heat-treatment at 400°C. In contrast, As shown in Fig. 2(b), the resistivity of as-deposited GZO film was 3.57×10^{-4} Ωcm. The resistivity of GZO thin films was not nearly changed after heat-treatment of from 100°C to 400°C in an O_2 ambient. It should be noted that the thermal stability of resistivity in GZO films was better than that in ZnO films.

The transmission spectra as a function of the heat treatment temperature for ZnO and GZO thin films are shown in Fig. 3(a) and Fig. 3(b). The blue shift of the absorption edge has been observed in GZO than ZnO films. It is mainly attributed to the Burstein - Moss effect, since the absorption edge of a degenerate semiconductor is shifted to shorter wavelengths with increasing carrier concentration [6]. The transmission in the visible region decreased substantially at short wavelengths near the ultraviolet range for ZnO films as shown in Fig. 3(a). In case of GZO films, decreasing at short wavelengths near the ultraviolet range is a little. This variation of absorption edge is due to the increasing and/or decreasing in free electron concentration in the films evidenced in Fig. 2. The optical transmittance of heat treated films is higher than 80%, the transmittance of GZO films reaches up to 88% in the visible range

4. Conclusion

The transparent conductive GZO thin films were grown on glass substrates using ZnO target containing 3wt% Ga_2O_3. The electrical and optical properties, as well as the thermal stability of resistivity, of GZO films were comparable to those of undoped ZnO films. The GZO film was a polycrystalline but with a preferential orientation along the *c*-axis. After annealing in O_2, (002) peak of ZnO and GZO films shifts towards the higher diffraction angle because of chemisorbed oxygen. The resistivity of ZnO film annealed at 400°C increased by two orders of magnitude, in case of GZO film was relatively stable up to at 400°C. The passivation of surface, more defects annealing out, and the decrease of oxygen vacancies made the resistivity of ZnO films increase substantially. On other hand, GZO films have been less affected chemisorbed oxygen. For practical applications at high temperatures the thermal stability of resistivity of GZO thin films might become an advantage for transparent electrodes.



<Fig. 3> The optical transmittance as function of heat treatment temperature of (a) ZnO and (b) GZO films.

Acknowledgement

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