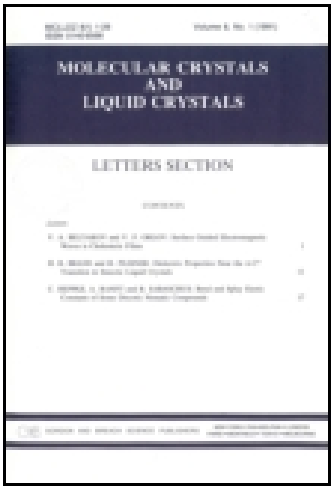

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Preparation of Transparent Metal Films, Gallium-Doped Zinc-Oxide $(Ga_2O_3)_x$ $(ZnO)_{100-x}$ Films by Using Facing Target Sputtering System

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Preparation of Transparent Metal Films, Gallium-Doped Zinc-Oxide $(Ga_2O_3)_x$ $(ZnO)_{100-x}$ Films by Using Facing Target Sputtering System

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$(Ga_2O_3)_x(ZnO)_{100-x}$, x = 3, 5, 7, 9 wt.%, (GZO) films were prepared at room temperature by using a conventional rf-magnetron sputtering method. Their electrical resistivity was investigated as a function of the Ga_2O_3 content. The GZO film with x = 7 wt.%, shows the lowest resistivity of $1.5\times10^{-3}\Omega$. cm. This GZO films were also prepared at various substrate temperatures from room temperature to 400°C, Their electrical resistivity was found to be improved as the substrate temperature was increased, A very low resistivity of $4.5\times10^{-4}\Omega$.cm was obtained in the film prepared at the substrate temperature of 300°C. In addition, we found that the GZO films prepared by using facing target sputtering (FTS) system showed a dramatically improved conductivity as compared with that of the film prepared by the conventional sputtering system. In particular, we also found that the lowest resistivity of $2.8\times10^{-4}\Omega$.cm that is almost comparable with that of ITO film was obtained in the GZO films prepared at the substrate temperature of 300°C by using the facing target sputtering (FTS) system.

Keywords GZO; thin film; rf-sputtering; facing target sputtering; resistivity

Introduction

Transparent and conductive oxide(TCO) films have been widely used as transparent electrodes for optoelectronics devices such as touch panels, flat-panel displays (FPDs) and thin-film solar cells [1–15]. To date, doped oxides such as In_2O_3, SnO_2, and ZnO have mainly been used. However, these materials have often been limited in their application because they are chemically and thermally unstable in various environments [16–20]. In general, TCOs consist of a degeneration wide-band-gap semiconductor with a low electrical resistivity and a high transparency in the visible and the near-infrared wavelength range. At

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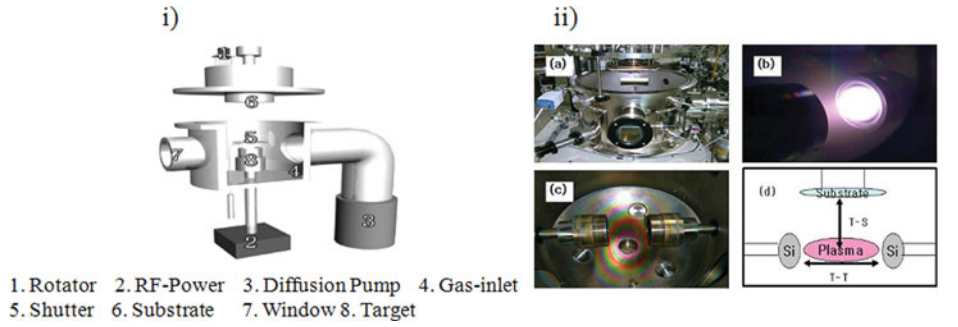

Figure 1. i) A diagram of conventional rf-magnetron sputtering system and ii) photographs of (a) FTS apparatus, (b) the faced two cathodes with a circular type, (c) the plasma formed between the faced two targets and (d) a diagram of the definition for T-T and T-S.

present, In_2O_3-SnO_2 (ITO) films deposited on glass substrates by using a sputtering method are most commonly used as TCO films [5–7]. In particular ITO film has been mainly used as an electrode in a-S solar cell of Supersaturate type, but a few serious problems have been proposed. For example, the high deposition temperature, in stability under hydrogen plasma atmosphere, the rough surface, etc. In addition, since indium(In) is expected to be depleted within a few years, the prices of ITO is also expected to continue to skyrocket. Nevertheless, the demand of ITO has been ever increasing.

Recently, ZnO has attractive interest as a conductive coating material because the material consist of cheap and abundant elements, is readily produced for large scale coatings, allows tailoring of the ultra violet absorption, has a high stability in a hydrogen plasma and has a low growth temperature. In addition, the electrical resistivity of a ZnO thin film is readily modified by addition of impurities or by using reactive deposition[22–27].

In this work, Gallium(Ga)) doped zinc oxide(GZO) films were fabricated on the glass substrates by the conventional rf-magnetron sputtering system, as shown in Figure 1(i)[13–15]. Transparent metal films with lower resistivity were achieved by using $(ZnO)_{1-x}(Ga_2O_3)_x$, targets and the films with lower resistivities could be deposited at higher substrate temperatures. The electrical and optical properties of the deposited GZO films were investigated as functions of the composition ratio, the substrate temperature, and film' thickness. These results are compared to those of the films prepare by using facing target sputtering(FTS) system. It is found that the FTS system improves density and crystallinity of the deposited films as compared with films prepared by the conventional sputtering system, which result in much enhanced electrical conductivity of the films.

Experimental Details

The composite powders of $(ZnO)_{100-x(Ga_2O_3)x}$ x = 2∼9 wt.% were mixed by using ball mill for 24 hours with additional hand milling and were calcined at 500°C for three hours to remove the moisture The 2-inch targets were made under a pressure of 12 tons by using a Caver press and were solidified for each one hour at 250°C and 500°C in Ar atmosphere. These sintered pellets were used as the sputter targets for GZO films. The substrates (soda lime glasses) with a size of 50 × 50 mm^2 were cleaned sequentially by distilled water and alcohol, they were placed parallel to target surface at distance of 60 mm. Sputtering depositions were carried out at a sputter gas pressure of 2 mTorr under a pure Ar gas. The rf-power was fixed by 100 W for all films and the substrate temperature was varied from room temperature to 400°C.

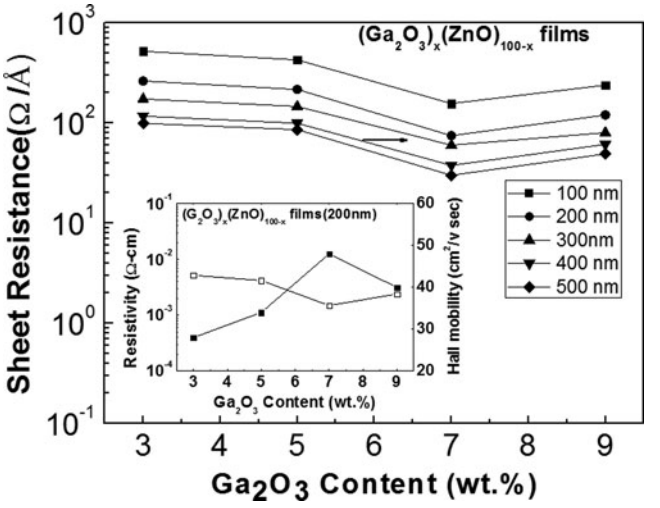

Figure 2. Sheet resistance changes as a function of film's thickness for GZO films with different Ga2O3 content deposited at room temperature.

On the other hand, the GZO films with x = 7 wt.% were also prepared on the glass substrates by using facing target sputtering (FTS) system. The FTS apparatus fabricated for the experiment is shown in Fig. 1 (ii). Two circular targets with a size of 3 inch are located horizontally facing with each other, as shown in Fig. 1.(ii-c), Nd alloy permanent magnets of 4700 Gauss for plasma confining magnetic field was mounted to the back of the target, which was adjusted by variation of the distance between both targets (T-T). In order to control the heat of the system caused by the ion bombardment of the cathode, cooling water was supplied. The GZO films were deposited by using two targets of $(ZnO)_{100-x}(Ga2O3)_x$ with x = 7 wt.% (99.99%). Here, the substrate temperature was room temperature and 300°C and the applied power is 100 W. It was confirmed that the optimum conditions of T-T and T-S for the best quality GZO films in our FTS system were 120 mm and 90 mm, respectively. All films were prepared by above the best conditions. The electrical and optical properties of the deposited films were compared to those of the films prepared by the conventional sputtering system.

The crystalline phase of the deposited films was examined by wide angle XRD with thin film attachments Cu Ka ($\lambda = 0.154$ nm) and 0.02° angle steps were used. The film thickness were measured by using an α-step profiler (VEECO Co). The surface morphology of the films was observed by using A surface electronic microscope (SEM, Hitachi Co.). Electrical sheet resistance was measured by the 4-point probe method. The optical transmissions through the glass substrate with a GZO layer were measured in the wavelength range from 200 nm to 1100 nm by means of an ultraviolet- near-infrared (UV-VIS) spectrophotometer (Shimadzu Co). It was confirmed by using An electron prove micro-analyzer (EPMA, Shimadzu Co.) that the composition ratios of the deposited films were almost consistent with those of the target.

Results and Discussion

Figure 2 shows the sheet resistance as a function of Ga_2O_3 content for the GZO films with different thicknesses deposited on glass substrates at room temperture by using a

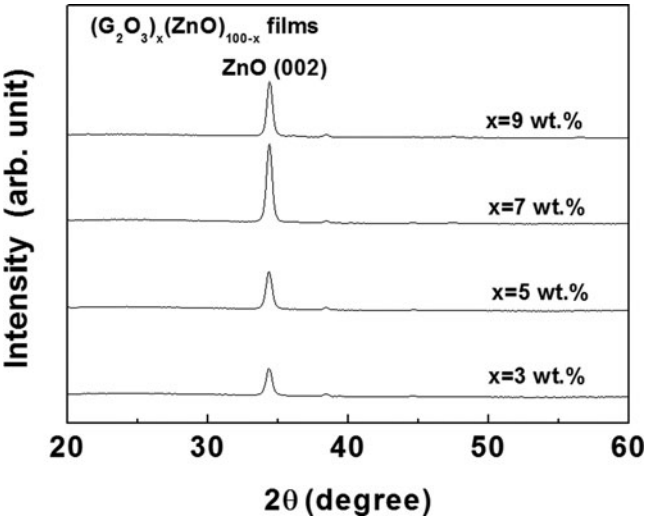

Figure 3. X-ray diffraction patterns of various GZO films.

conventional rf-magnetron sputtering. In general, the sheet resistance inversely proportional to the film's thickness. For instance, $R = \rho/t$, where ρ and t are the electrical resistivity and film's thickness, respectively. Thus, the sheet resistance remarkably decreases with increasing film's thickness for GZO films with the same Ga_2O_3 content while for GZO films with the same thickness, the sheet resistance greatly decreases up to x = 7 wt.% as the Ga_2O_3 content increases. the lowest sheet resistance of 50 Ω/■ was obtained for a GZO film with x = 7 wt.%, but over x = 7 wt.%, the sheet resistance was confirmed to be again increased with increasing x content.

On the other hand, the inset of Figure 1 shows the resistivity and Hall mobility as functions of x the $(Ga_2O_3)_x(ZnO)_{100-x}$ films prepared at room temperature. The resistivity decreased with increasing x up to x = 7 wt.%. In particular, the film with x = 7 wt.% shows the lowest resistivity of 1.5×10^{-3} Ω.cm. However, the Hall mobility showed a behavior opposite that of the resistivity. That is. the Hall mobility increased with increasing x up to x = 7 wt.%. This mobility increase was hypothesized to be caused by microstructural changes in the GZO films. This result was confirmed by X-ray diffraction patterns for the GZO films, shown in Figure 3.

Figure 3 shows X-ray diffraction patterns of 500-nm-thick GZO films with different Ga_2O_3 content. All films were crystalline and showed crystalline peak, (002) related to wurtzite structure of ZnO in the near of $2\Theta = 34^0$, this peak increases with increasing x up to x = 7 wt.%, which means increase of the crystalline phase in GZO film. However, the crystalline phase again decreased at x = 9 wt.%. The mobility is the larger as the crystalline phase increases in the films, as shown in the inset of Figure 2. Therefore, we hypothesized that the resistivity decrease in the GZO films with increasing Ga_2O_3 content was a result of the mobility increase due to the change of the crystalline phase in the films with increasing Ga_2O_3 content while the mobility decrease at x = 9 wt.% can be conversely interpreted.

Figure 4(a) shows the resistivity and the Hall mobility as a function of substrate temperature during the deposition of 200-nm-thick GZO films with x = 7 wt.%. The resistivity decreased with increasing substrate temperature up to 300°C. In particular, the GZO film deposited at 300°C shows the lowest resistivity of 4.7×10^{-4}Ω.cm, which is

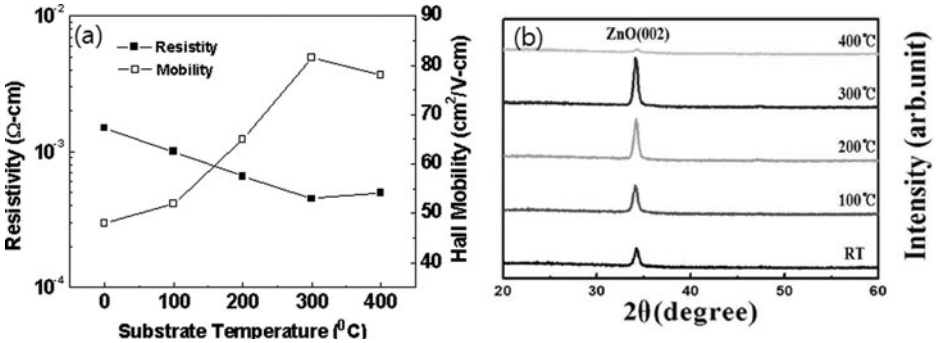

Figure 4. (a) Resistivity and Hall mobility as a functions of substrate temperature during deposition and (b) X-ray diffraction patterns for 200-nm-thick GZO films with x = 7 wt.% deposited at various substrate temperature.

improved by about 70% in comparison with the GZO film deposited at room temperature. However, the Hall mobility increased from 48 to 81 cm^2/V-sec with increasing substrate temperature up to 300°C. This mobility increase was hypothesized to be caused by an increase in the crystalline phase in the GZO films. We could observe microstructural changes in the GZO films due to the substrate temperatures in Figure 4(b), for XRD patterns of GZO films.

Figure 4(b) shows the X-ray diffraction patterns of 200-nm-thick GZO films with x = 7 wt.% prepared at various substrate temperatures. The intensity of (002) peak increased with increasing substrate temperature up to 300°C. This means that the crystalline phase increased in the GZO films with increasing substrate temperature. Therefore, the mobility increase with increasing substrate temperature is caused by the mobility increase due to increase of the crystalline phase in the GZO film.

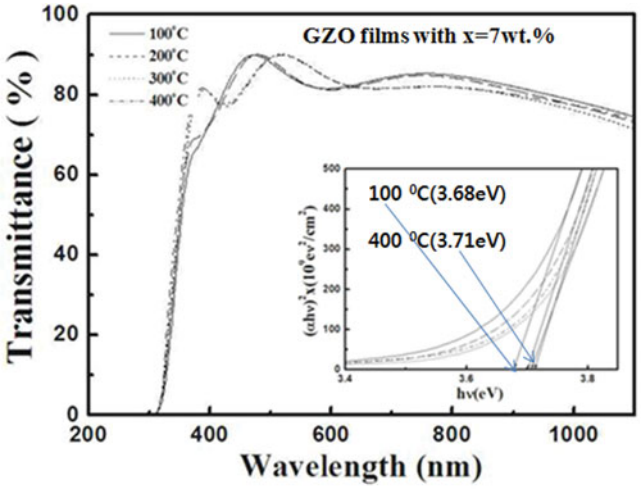

Figure 5. Optical transmission spectra of 200-nm-thick GZO films with x = 7 wt.% deposited at various substrate temperatures.

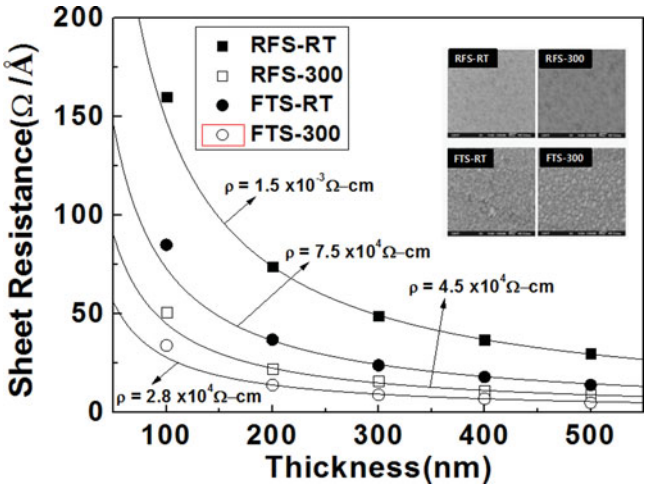

Figure 6. Sheet resistances as a function of film's thickness for GZO films with x = 7 wt.% prepared at room temperature and 300°C by using facing target sputtering (FTS) system. For comparison, those of films prepared by using the conventional rf-magnetron sputtering (RFS) system are also shown. SEM images of the GZO films are also shown on the figure.

Figure 5 shows the optical transmission spectra of 200- nm-thick GZO films with x = 7 wt.% deposited at various substrate temperature. All films are transparent to apply to TCO film The high transmission in the visible range results from the wide band gap of the zinc oxide semiconductor, which is known to about 3.6 eV. The edge of the transmittance shifted to higher energies with increasing substrate temperature. This shift is closely related to a change in the optical band gap energy. The change of the optical band gap is presented in the inset of Figure 5. The optical band gap is shown to be increased from 3.68 eV to 3.71 eV with increasing substrate temperature.

In this work, we also prepared the GZO films with x = 7 wt.% by using facing target sputtering(FTS) system. These films were prepared at room temperature and 300°C, their resistances as a function of thickness are shown in Figure 6. For comparison, those of the films prepared by using the conventional rf magnetron sputtering (RFS) system are also shown. FTS-films shows a very enhanced electrical conductivity. In Figure. 6, the solid lines indicate the theoretical values for the film's resistances that were fitted with measured resistances by a typical resistivity(ρ), using the equation of R = ρ/t. It is shown that the theoretical values are in good accord with the experimental values for the films with thickness of more than 200 nm. In particular, the FTS-films prepared at 300°C shows a very low resistivity of 2.8 $\times 10^{-4}$ Ω.cm that is almost comparable with that of Indium tin oxide (ITO) film. On the other hand, the SEM images for the RFS-films and the FTS-films are also shown in Figure 6. It is found that the distinct grains are formed in FTS films as compared with the RFS-films. Thus, the enhanced resistivity of the FTS-films is also hypothesized to be caused by mobility increase due to improved crystallinity in the FTS-films.

Such a structural difference between the FTS-films and the RFS-films may be attributed to the differences in the ion-flux energy, the adatom mobility and the resulting surface diffusion during the film growth. Since the conventional sputter apparatus has a system of the target and the substrate facing with each other, as shown Figure 1. i), the particles with high energy such as γ-electrons, neutral Ar particles, and negative oxygen ions collide

with the substrate. It is generally considered that the bombardment of the growing surface with energetic particles suppresses the surface migration of sputtered adatoms during the conventional sputtering process, which results in low-density films, like amorphous. In contrast, FTS apparatus is a plasma-free sputter method in which the substrate is located apart from plasma, which enhances the surface migration of the adatoms in the sputtering process, thus inducing a higher packing density, like crystalline. We, therefore, suggest that it is preferable to use the FTS system than the conventional sputtering system for preparation of the GZO films with a higher conductivity, a better surface uniformity and a better crystallinity.

Conclusion

The GZO films with composition ratios of $(Ga_2O_3)_x(ZnO)_{100-x}$, x = 3, 5, 7, 9 wt.% were deposited on slide glass at room temperature by using a conventional rf-magnetron sputtering method. Their electrical resistivity was investigated as a function of the Ga_2O_3 content. The lowest resistivity of 1.5×10^{-3} Ω.cm was obtained in a $(Ga_2O_3)_x(ZnO)_{100-x}$ film with x = 7 wt.%, this film also showed an excellent transmittance with an average of over 85%in the visible range with a wide band gap more than 3.6 eV. This GZO films with x = 7 wt.% were also prepared at various substrate temperatures from 100°C to 400°C, Their electrical resistivity was improved as the temperature was increased, A very low resistivity of 4.5×10^{-4} Ω.cm was obtained in the film prepared at the substrate temperature of 300°C, which was caused by the mobility increase due to an increase of crystalline phase in the GZO films. We found that the GZO films prepared by using facing target sputtering (FTS) process shows a remarkably improved conductivity as compared with that of the film prepared by the conventional sputtering system.

In particular, we also found that the lowest resistivity of 2.8×10^{-4} Ω.cm that is almost comparable with that of ITO film was obtained in the GZO films prepared at the substrate temperature of 300°C by using the facing target sputtering (FTS) system.

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