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Transparent Conducting Al-Doped ZnO and Ga-Doped ZnO Thin Films Prepared by Laser Ablation Method

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Thin films of ZnO:Al (AZO) have been deposited on glass substrates by a pulsed laser deposition technique employing ArF laser (λ =193nm). For all experiment, a repetition rate of 10 Hz, an energy density of $1J/cm^2$, and an irradiation time of 20-30 min (12000-18000 shots) were assumed. A resistivity of $1.43\times10^{-4}\ \Omega\cdot cm$, a sheet resistance of 9.3 Ω/sq were obtained in 154-nm-thick film deposited at a substrate temperature of 300℃. An average transmittance in the visible range was 93% and this value increased to 95.7% when oxygen gas was introduced onto the substrate through the plume. For 142-nm-thick film prepared with the substrate temperature of room temperature, a resistivity of $5.62\times10^{-4}\ \Omega\cdot cm$, a sheet resistance of 39.5 Ω/sq and an average transmittance in the visible range of 89% were obtained.

On the other hand, for films of ZnO:Ga (GZO), resistivities of $1.67\times10^{-4}\ \Omega\cdot cm$ and $3.25\times10^{-4}\ \Omega\cdot cm$ were obtained at substrate temperatures of 200℃ and room temperature, respectively. It was found by SEM and AFM observations that the surface of AZO films was flatter than that of AZO films.

1. INTRODUCTION

Aluminum-doped zinc oxide (AZO) films possess remarkable combination of properties: high tranmitance from UV to near IR, nearly metallic electrical conductivity and low cost fabrications, making them indispensable in the solar cell transparent electrodes [1]. Almost all of the major deposition techniques such as sputtering [2-4] and chemical vapor deposition (CVD) [5] etc. have been employed for the growth of AZO films. In the sputtering method, however, the growth of single-crystal films requires a substrate temperature higher than 400℃ [6], and the surface-flatness of films is not enough to use for electronic device electrodes such as liquid crystal display to be fabricated with high precision. In the CVD method, AZO films with resistivities below $3\times10^{-4}\ \Omega\cdot cm$ have not been obtained, even though smooth surfaces being obtained by this method. Thus, it is necessary to grow AZO films at a temperature below 300℃ and to lower their resistivities. Since the pulsed laser deposition (PLD) method has been reported to enable growth of high quality thin films at relatively low substrate temperatures [7], it was employed for the growth of AZO films. We reported in the previous papers [8], a experimental results for the AZO (2 wt%) films grown at substrate temperature below 300℃ by the PLD technique employing an ArF laser: an average transmittance above 90% in the visible range, a resistivity of $1.43\times10^{-4}\ \Omega\cdot cm$ and a sheet resistance of 10 Ω/sq were obtained. The problem of efficient and controlled patterning of the films deposited, however, remained to be resolved as another essential technological issue. It is known that gallium zinc oxide (GZO) films have not only an attractive optical and electrical property but also a property suitable for etching due to surfaces smoother than that of AZO films [9]. Therefore, GZO films are expected to use for highly precise electronic device electrodes such as TFT liquid crystal display. In this paper, we have also focused our attention on the surface flatness of GZO films prepared by the PLD method.

2. EXPERIMENTAL

Figure 1 shows a schematic diagram of the pulsed laser deposition system. AZO and GZO films were deposited on quartz or Corning 7059 glass substrates with a area 26×38 mm by focusing an excimer ArF (193 nm) laser onto a rotating target. The substrate was heated by a sheath-like heater and substrate temperatures were measured through the thermocouple touched onto the substrate. The composition of target, which was 2 inches in diameter, was ZnO doped with 0.75-7 wt% Al_2O_3 and with 4-13 wt% Ga_2O_3 (99.999% purity Furuuchi Co., Ltd.). For all experiments, a repetition rate of 10 Hz, an energy density of 1 J/cm^2, an irradiation time of 20-30min (12000-18000 shots), and a target-to-substrate distance of 5 cm were assumed. The deposition rate under these conditions was about 0.1 Å/pulse. The deposition cell (Shimadzu HRS-522S with a turbo-molecular pump) was initially evacuated to pressures on the order of 7×10^{-6} Pa, and film deposition was performed at a working pressure of 1×10^{-5} Pa. In order to obtain highly transparent films, oxygen gas introduced at a rate of 1 cc/min onto the substrate through the plume, and film deposition in this case was done at a working pressure of 1×10^{-3} Pa. The substrate temperatures T_{SUB} ranged from 25-300℃ and increased only by 2-4℃ after holding for 20-30min. Then, the sample was allowed to cool spontaneously to room temperature. Film thickness was measured by a stylus instrument (Veeco Inst. Inc, DEKTAK 3030). The crystal orientation and the surface morphology of films were evaluated by X-ray diffraction using Cu K α radiation (XRD: RIGAKU, RAD-B system), scanning electron microscopy (SEM: HITACHI, S-4500 & S-5000) and atomic force microscopy (Shimadzu, SPM-9500 & TOPOMETRIX, TMX-2000). The electrical properties of resistivity, carrier concentration and Hall mobility were measured by the van der Pauw method (BIO-RAD, HL5500PC). The transmission through the films, referenced to the Corning 7059 glass, was measured in the wavelength range from 300-3200 nm by a spectrophotometer (HITACHI, U-3500). The plume spectra were measured through a glass-fiber scope (Nikon, G-250).

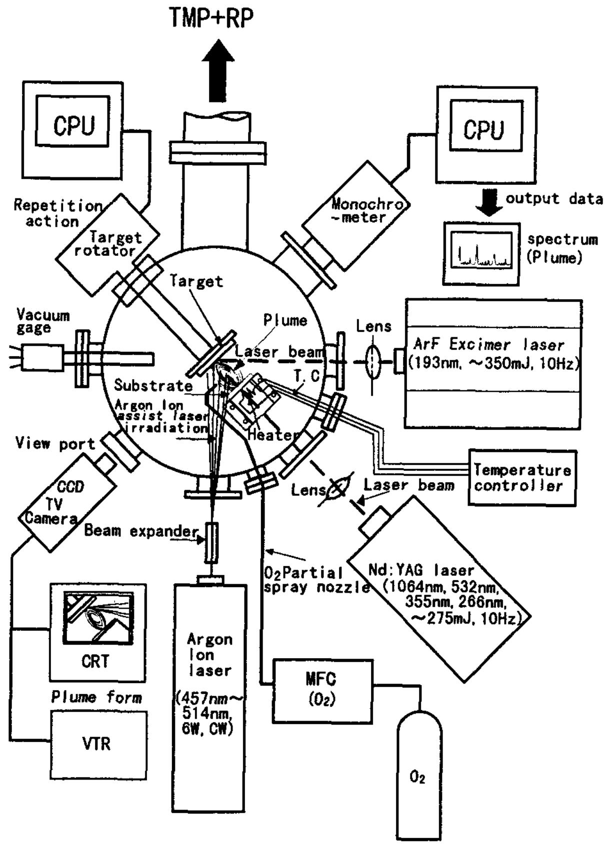


Figure 1. Schematic diagram of pulsed laser deposition system for AZO and GZO films.

3. RESULTS AND DISCUSSION

Figure 2 shows the dependence of the resistivity (ρ), carrier concentration (n) and Hall mobility (μ), on the substrate temperature. The lowest resistivity was obtained for films deposited from the target with 2 wt% Al_2O_3 ; the resistivites of 5.62×10^{-4} Ω·cm and 1.43×10^{-4} Ω·cm were obtained at T_{SUB} =25℃ and T_{SUB}=300℃, respectively. The decrease in the resistivity at 300℃ (solid line) is attributed to the increase in the carrier concentration and the Hall mobility. Moreover, the finding that the resistivity is 10^{-4} Ω·cm at room temperature suggests that film deposition onto the semiconductor devices is possible.

Figure 3 gives the optical transmittance spectra of AZO films deposited on a quartz substrate heated to 300℃ It was found that the film with 2 wt% Al_2O_3 became opaque at wavelength above 1000nm.

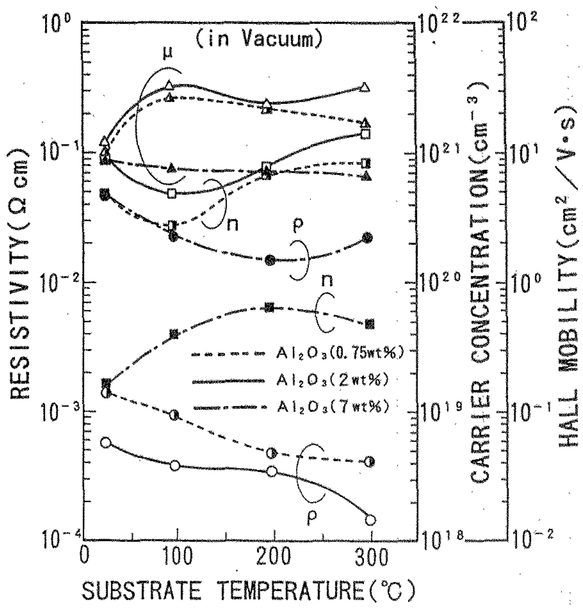


Figure 2. Dependence of the electrical properties of AZO films deposited in vacuum on the substrate temperature.

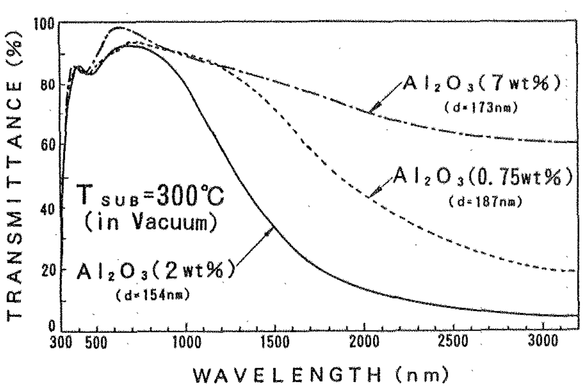


Figure 3. Optical transmittance spectra of ZnO films doped with 0.75, 2 and 7 wt% Al_2O_3

Figure 4 shows the SEM micrographs of (a) the surface of GZO (7 wt%) film grown at T_{SUB}=300℃ in vacuum, and (b) its cross section. It was found that (1), very smooth surfaces with microcrystallites were obtained because droplet formation was suppressed by the use of an ArF excimer laser in the chemical ablation region (~0.1Å/pulse), (2) , small columnar structures were observed in the film.

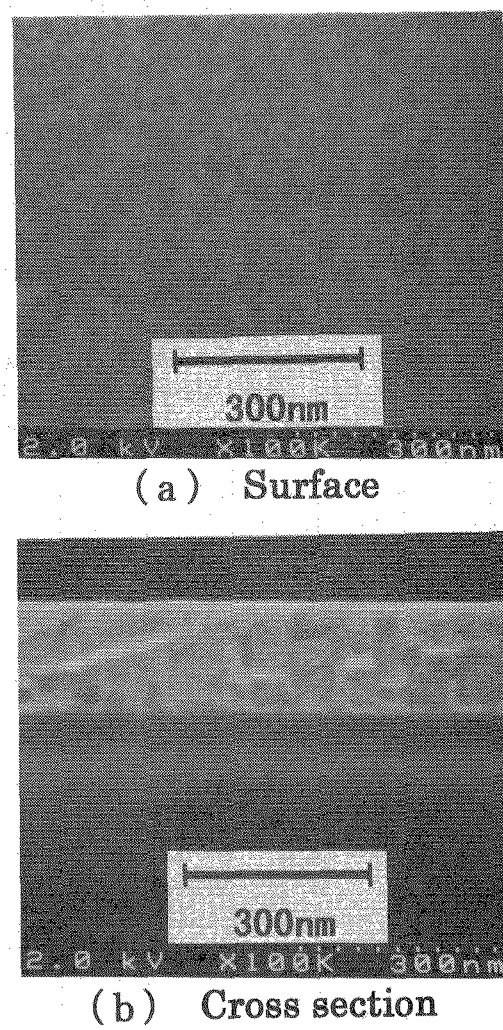
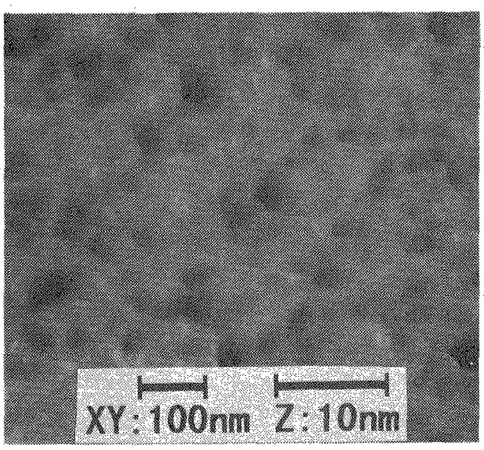
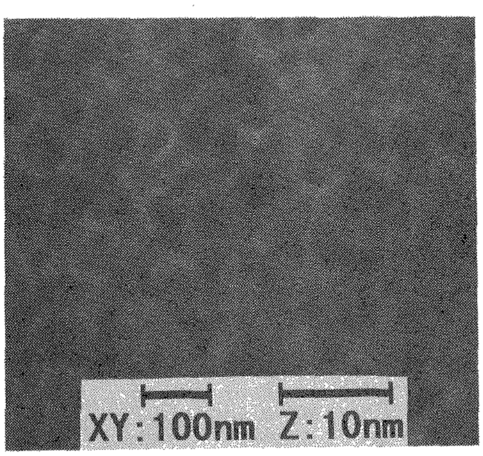


Figure 4 . High-resolution SEM images of GZO (7 wt%) films deposited at substrate temperature of 300℃; (a) surface and (b) cross section

Figure 5 shows compositional and substrate temperature dependence of the AFM images of surface morphology on GZO films, corresponding to the SEM images. For all conditions, the grain size of the 300℃ sample was smaller than that of 25℃ sample. These results suggest that the densification of film is attributed to a rearrangement process of crystalline particles deposited on the substrate heated to 300℃. Moreover, trvial irregularities (50-100 nm in size, 3-5 nm in height) were observed the GZO (7 wt%) films grown at T_{SUB}=300℃ and even at T_{SUB}=25℃.



(a) T_{SUB}=25℃



(b) T_{SUB}=300℃

Figure 5. High-resolution AFM images of GZO (7 wt%) films deposited at substrate temperatures (a) of 25℃ and (b) of 300℃.

4. CONCLUSIONS

A Highly transparent and conductive AZO and GZO thin films were prepared by the PLD method in the chemical ablation region. An average transmittance above 90% in the visible range, a resistivity of 1.43×10^{-4} Ω·cm and a sheet resistance of 10 Ω/sq were obtained for the AZO(2 wt%) film grown at T_{SUB}=300℃. No droplets on the film surfaces were observed by a high-resolution scanning electron microscope. It was found by the AFM images that the GZO (7 wt%) films, when grown at T_{SUB}=300℃ and even at T_{SUB}=25℃, reveal very smooth surfaces with trivial irregularities (50-100 nm in size, 3-5 nm height). The lowest resistivity of 1.67×10^{-4} Ω·cm and the lowest sheet resistance of 10.8 Ω/sq were obtained for the GZO (4 wt%) films grown at T_{SUB}=200℃ in oxygen. It should be stressed that the AZO films prepared by the the PLD method are indispensable in the solar cell transparent electrodes and the GZO films obtained by the same method are useful for precise electronic device electrodes such as TFT liquid crystal display.

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