Properties of Amorphous Ga doped ZnO Thin Film Prepared on 10 x 10 cm² Substrate by Pulsed Laser Deposition

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Recently, it has been required to develop large-area deposition techniques for transparent conductive doped ZnO thin films. In this paper, we report position dependencies of film thickness, carrier concentration, carrier mobility, resistivity and transmittance of a Ga doped ZnO thin film deposited on a 10 x 10 cm² silica glass substrate which was set at a distance of 28 cm from the target by Pulsed Laser Deposition method. In addition, mass spectrometry of the ablated species was measured at the substrate position using a quadrupole mass spectrometry system.

Key words: GZO, Large-area Deposition, Transparent Conducting Oxide, Pulsed Laser Deposition

1. INTRODUCTION

Recently, amorphous transparent conducting oxide (TCO) thin films such as Ga doped ZnO (GZO) and Al doped ZnO have attracted much attention because of their potential as transparent electrodes of flexible devices. Development of low temperature and the large-area deposition technique for amorphous TCO thin films is required. There are several techniques for large-area deposition of doped ZnO thin films. The typical technique is a DC or RF magnetron sputtering method [1, 2]. This method needs to suppress generation of arcing between target and substrate and nodule on target. Shirakata *et al.* reported reactive plasma deposition technique using two plasma guns with a traveling substrate system [3]. We have attempted to prepare amorphous GZO thin films on relatively large substrates using pulsed laser deposition (PLD) though it has been recognized that PLD is not suitable method for large area deposition [4-6]. In our previous work, it was revealed that nodule was generated from the target and it deposited as a part of film when the substrate was placed at close position to the target [4, 5].

In this work, we evaluated uniformity of electric, optical and structural properties of an amorphous GZO thin film deposited on a 10 x 10 cm² silica glass substrate set at a distance of 28 cm from the target by PLD method. In addition, a quadrupole mass spectrometry was carried out at the substrate position.

2. EXPERIMENTAL PROCEDURE

A KrF excimer laser (energy density=2 J/cm², repetition rate=10 Hz) was used for the ablation of a GZO target. The target was composed of 5 wt% Ga₂O₃ and 95 wt% ZnO. A chamber was evacuated to base pressure of 10⁻³ Pa by a turbo pump and then the deposition onto a silica glass (10 x 10 cm²) was carried out at the pressure and at the room temperature for 30

min. The distance between the target and the substrate was 28 cm. Masking tapes were put on the substrate to observe the film thickness. After the deposition, the substrate was cut into 7 square pieces along the diagonal line for the evaluation of the film uniformity.

The film thickness was observed by cross-sectional analysis of atomic force microscopy (AFM: SII, SPM3800N). The optical transmittance was measured using aUV-VIS light source (Ocean Optics, DT-MINI) and a multichannel spectrometer (Ocean Optics, HR4000, 200-1100 nm). The carrier concentration (*N*), mobility (*μ*), and resistivity (*ρ*) were determined by Hall measurement using the van der Pauw configuration in the magnetic field of 0.28 T. Structural characterization was confirmed using X-ray Diffractometer (XRD: Rigaku, RINT2000) with CuK α radiation. X-ray photoelectron spectroscopy (XPS: VG Scientific, Sigma Probe) with AlK α (1486.6eV) was used to estimate atomic composition of the film.

A quadrupole mass spectrometry system (ANELVA, AQA-200) was set at the substrate position to measure what kind of ablated species arrive at the substrate.

3. RESULTS AND DISCUSSIONS

Fig.1 shows distribution of the thickness of the GZO thin film observed by AFM. The AFM images at the edges of the film were observed in the range of 20 x 20 μ m² area. The thickness indicates the average value in the area with $\pm$ 5 % uncertainty due to the surface roughness of the thin film. In Fig.1, the abscissa means the measurement position and the position of 0 cm corresponds to the center of the film. As can be seen from Fig.1, the film thickness at the position of 0 cm is 70 nm and that at 5.4 cm shows approximately 72% value compared to that at the center. This thickness distribution is quite larger than those of films deposited at a typical target-substrate distance of several cm in case of PLD.

The deposition rate is 2.3 nm/min. (3.8×10^{-3} nm/pulse) at the center of the film, however it can be increased by increasing the laser repetition rate.

Fig.1 Distribution of thickness of GZO thin film.

Fig.2 shows position dependency of the resistivity (ρ), mobility (μ) and carrier concentration (N) measured by Hall measurement. It is evident from this figure, almost no position dependency of the ρ , μ and N was confirmed. The average values are ρ of $1.4 \times 10^{-3} \Omega\text{cm}$, N of $9.7 \times 10^{20} / \text{cm}^3$ and μ of $5 \text{ cm}^2/\text{Vs}$. The Ga doping rate estimated from XPS measurement was about 4 at%, which generated the electron carrier. The μ value is smaller than that of crystallized GZO thin film because the prepared GZO thin film was amorphous. Therefore, the ρ is a few times higher than typical value of the crystallized GZO film. We confirmed that the substrate heating even less than 150°C is available to increase μ of GZO thin films, which decreases ρ value to the order of $10^{-4} \Omega\text{cm}$.

Fig.2 Position dependency of electric properties of resistivity (ρ), carrier concentration (N) and mobility (μ).

the film (position=0 cm). The average transmittance is 86 % in the visible region. A wavelength where absorption occurs by free electron that can be estimated from Drude's theory using N and μ was about $1.7 \mu\text{m}$. Therefore, the transmittance over 90 % was obtained at the wavelength from 800 to 1000 nm. The transmittance at the position of 5.4 cm was higher than that of the center because the film was thinner.

Fig.3 Transmittance property of GZO thin film measured at center of the film (position=0 cm).

Fig.4 Mass spectrometry results for (a) before and (b) during deposition of GZO thin film.

Fig.3 shows transmittance property in the range of 300 – 1000 nm for the GZO thin film measured at center of

We could confirm the potential for large-area and low temperature deposition of amorphous GZO thin film using PLD method. In previous work, we observed optical emission from plasma plume [4]. However the emission finishes at the substrate position of 28 cm from the target. Then, we measured mass spectrometry of the ablated species at the substrate position of 28 cm using a quadrupole mass spectrometry.

The results of mass spectrometry are shown in Fig.4. The measurement was carried out (a) before and (b) during deposition. There is a small amount of water vapor and air left in the chamber before deposition (Fig.4 (a)). This seems to be a typical remaining gas spectrum. On the contrast, peaks from Ga, Zn and O_2 are observed during deposition at the mass number of 69.72, 65.39 and 32.00 amu, respectively (Fig.4 (b)). It is considered that the oxidation of Zn and Ga may occur at the substrate position because peaks from ZnO or Ga_2O_3 molecules could not be found out.

Fig.5 Selected ion monitor of Zn and O_2 . The mass number was fixed at 65.39 and 32.00, respectively.

Fig.5 shows selected ion monitor for Zn and O_2 after one laser ablation measured by fixing the mass number at 65.39 and 32.00, respectively. In this figure, it is difficult to compare their intensities because multi channel plate voltages for each mass were different. The time of 0 s corresponds to the time laser is irradiated to the target that was detected by PIN photodiode. Even if we take into account the time delay from the ionization process to the detection of ablated species in the equipment, it is obvious that Zn arrives at the substrate position faster than O_2 because Zn is heavier than O_2 . This may be one of the reasons why ZnO molecule can not be generated spatially, nevertheless Zn and O atoms are observed in the plasma plume by optical emission spectroscopy. It is also revealed that it takes relatively long time of about 1 s for O_2 to arrive at the substrate position. We know that the velocity of the head of ablated species (plasma plume) is approximately 10^4 m/s. However, it can be considered from this result that the velocity distribution is rather wide especially for O_2 .

Then, the laser repetition rate becomes very important in case of this deposition condition. Fig. 6 shows selected ion monitor result for O_2 at the laser repetition rate of 5 Hz. Since O_2 arrives at the substrate position for relatively long time of 1 s as mentioned above, O_2 exists continuously at the substrate position in spite of the pulsed ablation when the laser repetition rate is over 1 Hz. Therefore, it can be suggested that O_2 partial pressure is almost maintained and Zn arrives intermittently at the substrate position.

Fig.6 Selected ion monitor of O_2 (Mass number=32.00) at the laser repetition rate of 5 Hz.

4. CONCLUSIONS

We prepared an amorphous GZO thin film on a 10×10 cm² silica glass substrate which was set at a distance of 28 cm from the target by PLD method. The substrate was not heated and the ablation was carried out in vacuum. The position dependency of the thickness, electric properties and transmittance were examined. Moreover, mass spectrometry was measured at the substrate position of 28 cm. The summary is as follows.

The film thickness distribution was rather gentle. The thickness at a position of 5.4 cm shows approximately 72% value compared to that at the center. The deposition rate is 2.3 nm/min. (3.8×10^{-3} nm/pulse) at the center of the film.

There was little position dependency of the ρ , μ and N . The average values are ρ of 1.4×10^{-3} Ω cm, N of 9.7×10^{20} /cm³ and μ of 5 cm²/Vs.

The transmittance depended on the film thickness. The average transmittance was 86 % in the visible region at the center of the film.

Ga, Zn and O₂ were observed by a quadrupole mass spectrometry. In addition, it was revealed that O₂ exists continuously at a substrate position of 28 cm when the laser repetition rate is over 1 Hz because O₂ arrives at the substrate position for relatively long time of 1 s.

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