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Highly Conducting and Very Thin ZnO:Al Films with ZnO Buffer Layer Fabricated by Solid Phase Crystallization from Amorphous Phase

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We propose a novel method of oxide crystal growth via atomic-additive mediated amorphization. By utilizing this method, solid-phase crystallization (SPC) of ZnO from amorphous phase has been successfully demonstrated via nitrogen atom mediation. The resultant SPC-ZnO films are highly orientated and the crystallinity is higher than that of the films prepared by conventional sputtering. By using the SPC-ZnO as a buffer layer, the resistivity of ZnO:Al (AZO) films is drastically decreased. 20 nm-thick AZO films with a resistivity of $5 \times 10^{-4}\ \Omega\,\mathrm{cm}$ and an optical transmittance higher than 80% in a wide wavelength range of 400-2500 nm have been obtained.

Oxide semiconductors have attracted a great deal of attention not only for their transparency but also for their wide-ranging conductivity, which enable us to make high-performance electronic devices[1,2]. Zinc oxide (ZnO) is one of the most fascinating oxide semiconductors with unique features and a wide application range. The high electrical conductivity, high transparency to visible light, and material abundance make ZnO a very promising alternative to indium-doped tin oxide (ITO) for transparent conductive oxides (TCOs). The conductivity of ZnO films, however, is lower than that of ITO, especially when the film thickness is less than 100 nm, which is mainly due to the deterioration of crystallinity with decreasing film thickness[3,4]. The solid-phase crystallization (SPC) from amorphous phase is a promising way to fabricate films with high crystallinity and fewer defects, and has already been used to fabricate polycrystalline silicon[5], indium oxide[6,7], ITO[8,9], and so on. However, this method has not been applied to the fabrication of ZnO films since the amorphous phase is difficult to obtain, especially when a sputtering method is employed for film deposition, where the high energy of impingement of sputtered species exists. In this paper, we describe a newly developed SPC method of ZnO films, which is realized by sputtering deposition of amorphous zinc oxynitride (ZnON) films and subsequent annealing under adequate conditions. The effects of SPC on the crystallinity of ZnO are described with comparison to those of ZnO fabricated by a conventional method. Furthermore, since controlling the crystallinity in the deposition at an early stage is very important for the sputtering deposition of TCO thin films, we also investigate the effect of SPC-ZnO as buffer layers for ZnO:Al (AZO) TCO thin films.

ZnON films were deposited on quartz glass substrates by radio-frequency (RF) magnetron sputtering without intentional heating of the substrates. The used targets

were ZnO (2 in. in diameter) and the applied RF power was 100 W. The distance between the target and the substrate was 100 mm. Ar and N_2 mixing gasses with a $N_2/(Ar+N_2)$ ratio of 0.78 were used and the total pressure was 0.35 – 1.33 Pa. During the deposition, optical emission spectroscopy was carried out in order to obtain information on the ratio of high energy electrons to low energy electrons in the sputtering plasma. The ratio was deduced from the ratio of optical emission intensities at 750.4 nm (Ar I) to 800.6 nm (Ar I)[10]. After deposition, the ZnON films were annealed at 600 °C for 60 min in air and were converted to ZnO films. In the experiments, the film thickness was in the range of 10 - 300 nm, which was confirmed by spectroscopic ellipsometry analysis. For AZO film deposition, RF magnetron sputtering was employed, where the AZO targets (2wt% Al_2O_3) were used. The substrate temperature was kept at 200 °C. The used gas and pressure were Ar and 0.35 Pa, respectively. No post annealing of AZO was performed. The crystal structures of the films were examined by X-ray diffraction (XRD). The electrical properties of AZO films were measured by 4 point probe measurement, and hall-effect measurement.

Figure 1 shows the XRD patterns of as-deposited ZnON films fabricated at 0.35, 0.80, and 1.33 Pa. The diffracted peak at 2 theta of 44.3°, which is observed for each sample, is attributed to α-Fe from the sample stage. The peak intensities of ZnO (002) and (101) planes decrease with decreasing sputtering gas pressure. At the pressure of 0.35 Pa, no peaks are observed except for α-Fe, indicating that the film is amorphous. Optical emission spectroscopy suggests that the density of high-energy electrons in the sputtering plasma, which dissociate N_2 molecules into N atoms, increases with decreasing the pressure from 1.33 to 0.35 Pa. As a consequence, we have observed an increase in the nitrogen-to-oxygen atomic ratio ([N]/[N+O]) in the film from 5 to 35

at.% with decreasing the pressure from 1.33 to 0.35 Pa. The incorporation of a certain amount of N atoms in the film disorders the ZnO crystal structure and yields an amorphous ZnON film at low gas pressure.

After sputtering deposition, the amorphous ZnON films were annealed in air to be converted to ZnO. Figure 2 shows the XRD pattern of the annealed ZnON films, together with that of ZnO prepared by the conventional sputtering method, which is vapor-phase crystallized and annealed in air at 600 °C for 1 h. The annealed ZnON film shows a strong diffracted peak at 34.4° that corresponds to the (002) plane of the ZnO wurtzite structure, indicating that the SPC of ZnO can be realized by annealing the amorphous ZnON. For the conventional ZnO film, the diffracted peaks from not only the (002) plane but also the (102) and (103) planes are observed, that is, the film is randomly orientated. For the SPC-ZnO film, a strong peak from the (002) plane is obtained and no other peaks are observed. The rocking curves of (002) diffraction indicate that the fluctuation of the crystalline orientation of the SPC ZnO film is much smaller than that of the film prepared by the conventional method. Accordingly, the SPC of amorphous ZnON is very promising to obtain well-orientated ZnO films with high crystallinity.

Next, in order to investigate the thickness dependence of the crystallinity, XRD measurements were performed for ZnO films with different thicknesses. For a SPC-ZnO film, the diffracted intensity of the (002) plane gradually decreases with decreasing thickness, as shown in Fig. 3. On the other hand, for a conventional ZnO film, the XRD intensity decreases exponentially with decreasing thickness, indicating that the (002) orientation and the crystallinity deteriorate with decreasing thickness in the case of vapor-phase crystallization, where the excessive nucleations with various orientations

occur at the initial stage of the deposition. The SPC from amorphous phase can also lower the film thickness dependence of the crystallinity. Here, it should be noted that no difference in the transparency has been observed between the SPC-ZnO films and the conventional ZnO films.

As described above, controlling the crystallinity in the deposition at an early stage is very important for the sputtering deposition of TCO films, particularly those with small thickness. Hence, we investigate the effects of SPC-ZnO as a buffer layer for ZnO:Al (AZO) TCO films. Figure 4 shows the resistivity, hall mobility, and carrier density of AZO films prepared on SPC-ZnO films with a thickness of 10 and 20 nm, which are plotted against the total film thickness of the SPC-ZnO layer and the AZO layer. For comparison, the resistivities of AZO films without a buffer layer and with a buffer layer of conventional ZnO (C-ZnO) that is vapor-phase crystallized and annealed at 600 °C are also shown. For all film thicknesses, the resistivity of AZO films with a SPC-ZnO buffer layer is lower than that of the films without the buffer layer and with a C-ZnO buffer layer. For the films thicker than 200 nm, a low resistivity of around 2×10^{-4} Ω **cm** is achieved by preparation on an SPC-ZnO buffer layer, which is attributed to the high mobility. The most remarkable effect of the SPC-ZnO buffer layer is a significant reduction in the resistivity for the films thinner than 100 nm. As shown in Fig. 4, the resistivity of AZO films without an SPC-ZnO buffer layer increases substantially with decreasing film thickness, which is associated with the decrease in carrier density. On the other hand, the resistivity of AZO films with SPC-ZnO does not change much, where the carrier density is almost constant irrelevant of the film thickness. Recently, it has been reported that the dopant activation efficiency in ZnO films depends on the degree of c-axis orientation[11]. The report is consistent with our results that the significant

improvement of resistivity, particularly for thicknesses of less than 100 nm, is accompanied by an enhancement in the orientation degree of the AZO films by using the SPC-ZnO buffer layers. As a result, highly conducting ZnO films with a very small thickness, that is, high transparency, have been obtained. Figure 5 shows the optical transmittance of 20 nm-thick AZO films with a resistivity of 5×10^{-4} Ω cm. We observed that the film has high transmittance (> 80%) in a wide wavelength range of 400-2500 nm.

We report here a novel method of oxide crystal growth via atomic-additive mediated amorphization. By utilizing this method, SPC of ZnO from amorphous phase has been successfully demonstrated via nitrogen atom mediation. The resultant SPC-ZnO films are highly orientated and the crystallinity is higher than that of the films prepared by conventional sputtering. By using the SPC-ZnO as a buffer layer, the resistivity of AZO films is drastically decreased. 20 nm-thick AZO films with a resistivity of 5×10^{-4} Ω cm and an optical transmittance higher than 80% in a wide wavelength range of 400-2500 nm have been obtained. The fabrication method proposed here is very promising for oxide films, especially for oxides whose amorphous phase is difficult to obtain.

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Figure Captions

Fig. 1 XRD patterns of as-deposited ZnON films fabricated at 0.35, 0.80, and 1.33 Pa. The diffracted peak at 2 theta of 44.3° is attributed to α-Fe from the sample stage.

Fig. 2 Log plot of XRD patterns of ZnO films prepared by (a) solid phase crystallization and (b) conventional sputtering method. Both films were annealed in air at 600 °C. The thickness of both resultant films was 150 nm. The inset shows the rocking curves of ZnO (002) planes.

Fig. 3 XRD patterns of ZnO (002) for the different film thicknesses. Here, the ZnO films were prepared by (a) solid phase crystallization and (b) conventional sputtering method. Both films were annealed in air at 600 °C.

Fig. 4 Resistivity, Hall mobility, and carrier density of AZO films prepared on SPC-ZnO films with the thickness of 10 and 20 nm as a function of total film thickness of SPC-ZnO layer and AZO layer. For comparison, the resistivities of AZO films without a buffer layer and with a buffer layer of conventional ZnO (C-ZnO) that is vapor-phase crystallized and annealed at 600 °C are also shown.

Fig. 5 Optical transmittance of 20 nm-thick AZO film with a resistivity of 5×10^{-4} Ω cm.