Film properties of indium-zinc-oxide films using RF magnetron sputtering evaluated by optical diagnostics in gas phase

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Amorphous Indium Zinc Oxide (IZO) films were synthesized by radio frequency magnetron sputtering. In order to investigate the behavior of the species in the IZO sputtering plasma and the relation between the species in gas phase and film properties of IZO film, the absolute densities of In and Zn atoms were measured simultaneously by absorption spectroscopy employing the multi-micro hollow cathode lamp. The density ratio of In to Zn in the gas phase corresponded to that of film composition and the relative amount of Zn atoms increased with decreasing pressure. The carrier density increased with decreasing the density ratio of In to Zn due to the increase in the oxygen vacancy, which was clarified from O1s spectra of x-ray photoelectron spectroscopy.

1. Introduction

Transparent Conductive Oxide (TCO) films have been used as a transparent conducting electrode of optoelectronic devices such as flat panel displays, thin-film solar cells, touch panels, and so on. Indium Zinc Oxide (IZO) films have been investigated as a promising alternative material to Indium Tin Oxide (ITO) films as increasing the demand of high quality in several aspects such as high transmittance, high uniformity, high chemical stability, and low resistivity.

In the sputtering process of the IZO films used a composite target, multi-metallic atoms are induced on a substrate simultaneously. It is indispensable to measure the densities of electron, ion and neutral radical for understanding and controlling the behavior of species in the gas phase and on the surface.

In this study, IZO films were synthesized by a radio frequency magnetron sputtering. The absolute densities of In and Zn atoms in gas phase were simultaneously measured by absorption spectroscopy employing a multi-micro hollow cathode lamp (multi-MHCL). The multi-MHCL has been developed for monitoring the densities of multi-metallic atoms simultaneously by absorption spectroscopy.[1] The electric properties and the bonding states of the IZO films were analyzed by a four-point-probe method and an X-ray photoelectron spectroscopy (XPS), respectively. The behavior of species in the gas phase was compared with the composition of the IZO films and the properties of the film were discussed as a function of the atomic-density ratio of In to Zn.

2. Experimental

Figure 1 shows the experimental set-up of magnetron sputtering reactor and the optical system of absorption spectroscopy employing the multi-MHCL. The IZO films were deposited by a conventional RF magnetron sputtering using a IZO target (89.3 wt. % In_2O_3 and 10.7 wt. % ZnO) with a diameter of 2 inches. The distance between the substrate and the target was set at 50 mm. The RF power of 13.56 MHz was applied to the lower electrode. Argon gas was used as a working gas and the flow rate was 60 sccm. The borosilicate glass substrate with thickness of 150 μm was set to upper substrate holder and was unheated.

In order to measure absolute densities of In and Zn simultaneously, the multi-MHCL was used as a light source for absorption spectroscopy. In and Zn materials were arranged in one hollow cathode. The discharge was generated by using helium as a working gas at a pressure of 10 kPa. The current and discharge voltage were 20 mA and 370 V, respectively. The light of the multi-MHCL passed through the sputtering plasma and was detected by a fiber-coupled spectrometer. The emission lines of Zn (213.86 nm) and In (303.94 nm) were simultaneously obtained from one hollow cathode, so the absolute densities of In and Zn were simultaneously measured by using the multi-MHCL.

The carrier density was analyzed using a four-point-probe method and a Hall-effect measurement method in the Van der Pauw geometry at a constant magnetic field of 0.5 T. In order to identify the chemical binding states in the samples, XPS measurements were performed.

3. Results and discussion

Figure 2 shows absolute densities of Zn and In atoms as a function of pressure from 1 to 10 Pa at a RF power of 50 W. Simultaneous monitoring of the absolute densities of Zn and In atoms was performed using the multi-MHCL. The Zn and In densities were measured to be 10^{9}-10^{11} cm^{-3} and increased with increasing the pressure. As increasing the pressure, the incident Ar ions to the target increased due to an increase in the ion density, so the sputtered metal atoms increased. The Zn density was higher than In density though the composition of In atom in the target was higher than that of Zn atom. This is because maximum sputtering yield of Zn atom is 16 atoms per incident Ar ion with the energy of 43.5 eV while that of In atom is 7.4 atoms per incident Ar ion with the energy of 66 eV.[2]

The concentration ratio of In to the Zn (C_{In}/C_{Zn}) in the IZO films was estimated from the XPS spectra and shown in Fig. 3. The C_{In}/C_{Zn} increased with the pressure and corresponded to the behavior of the In/Zn in gas phase which was shown in Fig. 2. However, the C_{In}/C_{Zn} was from 8.5 to 11 while the In/Zn was from 0.32 to 0.57. InO radicals in the plasma were observed by optical emission spectroscopy. Therefore, InO radical was speculated to be a main precursor of IZO film from these results. The In/Zn ratio in gas phase can be an index for controlling the quality of IZO film.

Figure 4 shows carrier density as a function of the In/Zn. N-type conductivity of IZO film was revealed in this study and has been reported due to free electrons originating from oxygen vacancies.[3]-[5] With decreasing In/Zn, the carrier density increased in this study. Under our experimental conditions, Hall mobility increased with decreasing In/Zn. When Zn atoms are doped to In_2O_3, the oxygen vacancies are produced because Zn ion is bivalent and In ion is trivalent. Accordingly, carrier electrons are produced to keep electric neutrality. Thus, the carrier density increased with decreasing the In/Zn.

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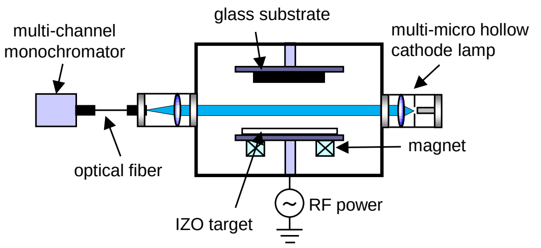

Fig. 1 Experimental set-up of magnetron sputtering reactor and the optical system of absorption spectroscopy employing the multi-MHCL.

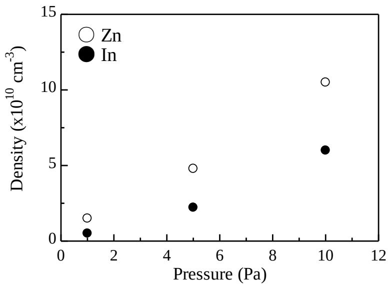

Fig. 2 Absolute densities of Zn and In atoms as a function of pressure.

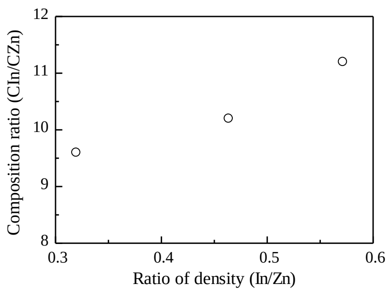

Fig. 3 Concentration ratio of In to Zn content in the IZO films (C_{In}/C_{Zn}) as a function of In/Zn density ratio.

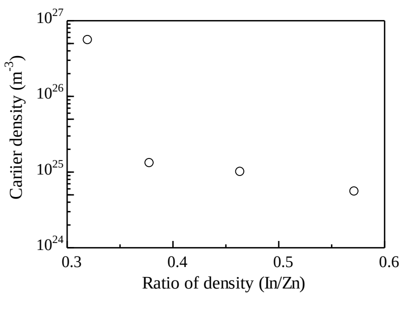

Fig. 4 Carrier density as a function of In/Zn density ratio.

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