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Marked Effects of Bias-Sputtering on the Resistivity of ITO Films Prepared by Gas Flow Sputtering

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Tin-doped indium oxide (ITO) films were prepared on glass and polyethylene terephthalate (PET) substrates by gas flow sputtering (GFS), and the effects of bias sputtering on film resistivity were investigated. GFS is a high-pressure (about 100 Pa) sputtering, and energetic particles are completely thermalized to the temperature of sputtering gas. Thus, GFS is suitable for bias sputtering at a low voltage. Although the resistivity of films sputtered without substrate bias was very high (ca. 2×10^{-2} $\Omega\cdot$cm), resistivity was dramatically reduced by the addition of substrate bias. A film with resistivity of 2.6×10^{-4} $\Omega\cdot$cm was obtained at the dc bias of –50 V. X-ray diffraction (XRD) studies revealed that the bias sputtering promoted crystallization of ITO films. The effect of rf bias sputtering for thin (<50 nm) films was also studied, and almost the same results as those in the case of dc bias sputtering were obtained.
Key words: ITO film, sputtering, bias sputtering, gas flow sputtering

1. INTRODUCTION

Since Sn-doped In_2O_3 (ITO) is transparent in the visible light region and conductive at room temperature, ITO films are widely used in various display devices such as liquid crystal displays and input units of touch panels. ITO films are generally prepared by a sputtering process and must be heated during or after deposition in order to have low resistivity. The substrate is usually heated at a temperature above 200 ℃ to obtain a film with a resistivity of about 2×10^{-4} $\Omega\cdot$cm, a condition required for application to display devices. Thus, formation of an ITO film with a low resistivity on plastic substrates such as polyethylene threphthalate (PET) foil is very difficult. Many efforts have been made to establish sputtering conditions for preparing low-resistivity ITO films at low temperatures [1-4].

We have developed a new method, a combination of gas flow sputtering (GFS) [5, 6] and a bias sputtering, for depositing ITO films with low resistivities (< 4×10^{-4} $\Omega\cdot$cm) at a low substrate temperature below 100 ℃. Bias sputtering, which is a technique for deposition by applying a negative voltage to the substrate, results in bombardment of the substrate by ions during the film growth [7]. Such an ion-assistance has been anticipated to promote low-temperature crystallization and/or low-temperature epitaxy in the growth of various thin films [8]. The suitable energies of bombarding ions are thought to be in the range of several eV. GFS is superior to other methods for controlling the energy of bombarding ions in that range.

GFS is a high-pressure (around 100 Pa) sputtering. Its principle is shown in Fig. 1 in comparison with an ordinary diode sputtering. Hollow cathode discharge occurs in a hollow target, a tube or a pair of facing plates, and sputtered atoms in the hollow target are carried from target to the substrate by a forced flow of Ar gas. The mean free path of sputtered atoms in Ar gas at a pressure of about 100 Pa is so short that the dissipation of their initial energy by collision with Ar gas, thermalization, is completed near the target. High-energy particles such as reflected Ar and negative ions are also thermalized under this condition. The energy of ions in plasma at this pressure is also low, probably less than 0.1 eV. Therefore, GFS should be a suitable method for bias sputtering with low applied voltages because the energy of accelerated ions is never higher than that of the bias potential between the substrate and plasma.

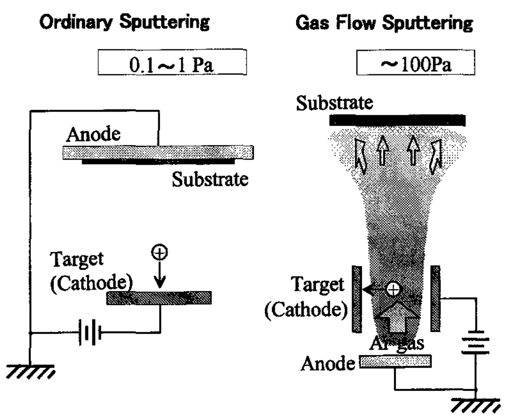

Fig. 1. Principles of ordinary sputtering and gas flow sputtering.

While ITO films fabricated by GFS without the addition of substrate bias have amorphous-like structures and considerably high resistivities of about 2×10^{-2} $\Omega\cdot$cm, it was found that bias sputtering applied at about -40 V resulted in crystallization of the film and a decrease in resistivity by a factor of 100.

In this paper, we describe the dependence of film resistivity on substrate bias voltage, dc bias and rf bias, and we discuss the effects of bias addition.

2. EXPERIMENT

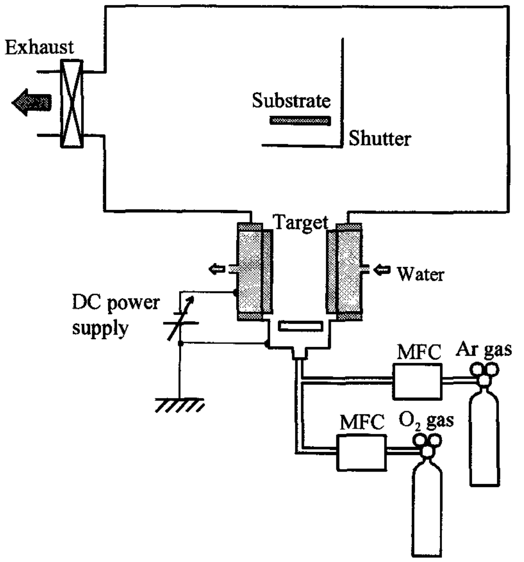

Fig. 2. Schematic diagram of GFS system for the deposition of ITO films.

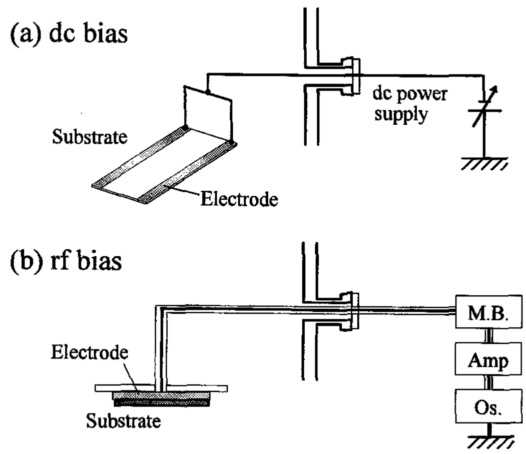

Fig. 3. Schematic illustrations of substrate biasing systems for (a) dc biasing for slideglass substrates, and (b) rf (10MHz) biasing for PET substrates with the thickness of 125 μ m.

Figure 2 shows a schematic illustration of the GFS apparatus used in this experiment. The target was composed of two parallel ceramic plates of 5wt.% SnO_2-doped In_2O_3 with widths of 6 cm and lengths of 30 cm. The flow rates of Ar gas and O_2 gas were 2000 sccm and 1.2 sccm, respectively. Total pressure was maintained at 15 Pa, and the chamber was evacuated to 2×10^{-3} Pa prior to film deposition. The discharge power was set to 500 W, resulting in the deposition rate of 15 nm/min. Slideglass was used as the substrate for dc bias sputtering, and polyethylene telephthalate (PET) foils with the thickness of 120 μ m were used for rf bias sputtering.

Two kinds of bias voltage to be added to the substrate were investigated: dc bias and rf (10 MHz) bias. Figure 3 shows the electrodes for both cases. In the case of dc bias, negative voltages were applied through Al films

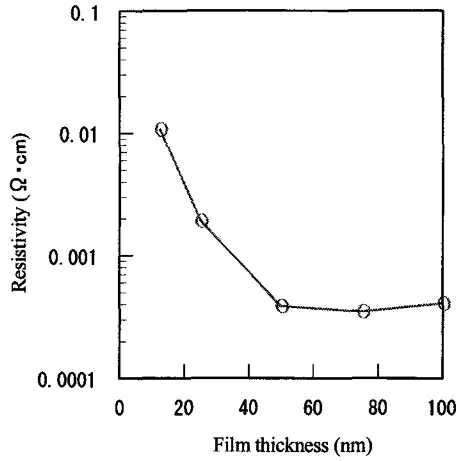

Fig. 4. Resistivity as a function of film thickness for ITO films dc-bias-sputtered at bias voltage of -50V.

evaporated on the edge of slideglass. On the other hand, rf bias was applied through a coaxial line when PET foil was used as the substrate. Since the rf voltage induced on the substrate surface could not be observed during film preparation, the relationship between the voltages of the electrode and the substrate surface had been measured prior to film deposition.

ITO films with thicknesses ranging from 25 nm to 400 nm were bias-sputtered using GFS. The structure of each film was characterized by x-ray diffraction (XRD), and the morphology of each film was observed by using a scanning electron microscope (SEM). The electrical resistivity of the film was determined at room temperature using van der Pauw's method. The film thickness was measured using a surface profiler.

3. RESULTS AND DISCUSSION

3.1 dc bias sputtering

Since the substrate was an insulator, the dc biasing was assumed to be effective after the film had become continuous over the whole substrate plane. Therefore, the thickness dependence of resistivity was investigated by applying a constant bias voltage V_{dc}. Figure 4 shows the relationship between the resistivity and the thickness for the case of V_{dc} = –50 V. Since the resistivity became almost constant with increase in thickness over 50 nm, the dependence of resistivity on bias voltage was investigated for films thicker than 50 nm.

While the resistivity of films deposited without substrate bias (corresponding to V_{dc} = 0 V) was considerably high ($>10^{-2}$ $\Omega\cdot$ cm), resistvity was dramatically reduced by the addition of substrate bias. Figure 5 shows the resistivity of ITO films prepared at various bias voltages. The resistivity decreased with increase in bias voltage, and the minimum value of resistivity was 2.6×10^{-4} $\Omega\cdot$cm at V_{dc} = –50 V. Since bias addition results in bombardment of the substrate by ions, it was thought that bias addition would cause heating of the substrate. However, there was little increase in temperature of the substrate; the temperature of the substrate was 80 ℃ when V_{dc} = –50 V.

In order to clarify the effect of bias addition on resistivity, the crystal structure was investigated. Figure 6 shows typical x-ray diffraction patterns of ITO films

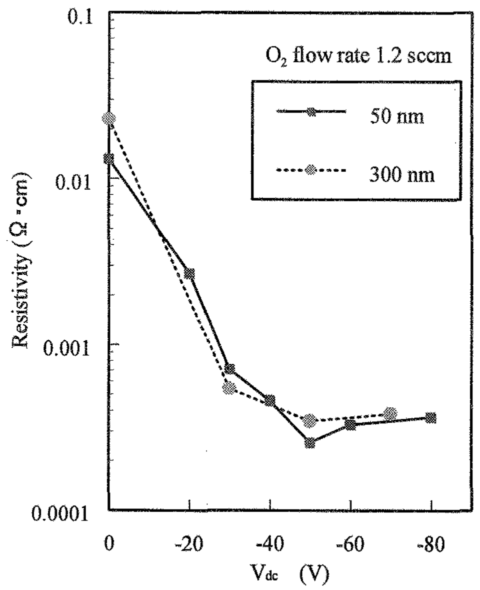

Fig. 5. Resistivity as a function of dc bias voltage Vdc for ITO films deposited on sildeglass substrates. The film thickness was (□) 50 nm and (○) 300 nm.

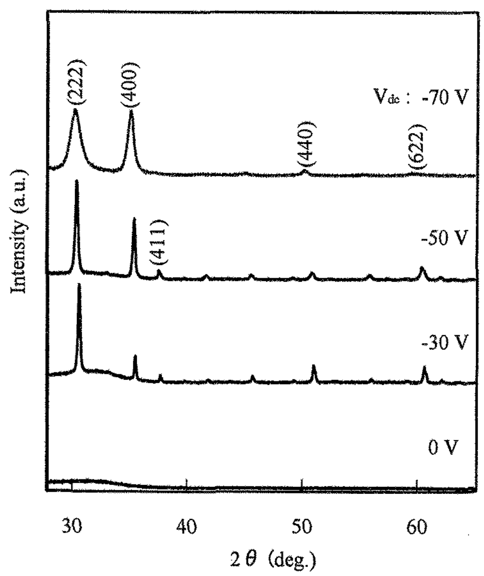

Fig. 6. XRD patterns of ITO films with the thickness of 300 nm, dc-bias-sputtered at various bias voltages Vdc.

deposited at various bias voltages. There is no clear diffraction peak for the film deposited at Vdc = 0 V. On the other hand, the patterns of the films fabricated at Vdc = −30∼−50 V exhibit sharp diffraction peaks. This clearly indicates that crystallization of films is promoted by the addition of substrate bias. When the voltage was higher than 70 V, the diffraction peaks became broad, indicating poor crystallinity and small crystal grains.

These results allow us to conclude that the ion bombardment induced by substrate-biasing during the film growth promotes the crystallization of ITO films and reduces their resistivities. It should be noted that

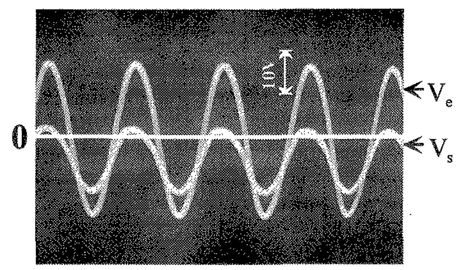

Fig. 7. Wave forms of the voltages observed from the substrate (PET) surface and the electrode; Ve was that from the electrode and Vs was that from the PET surface.

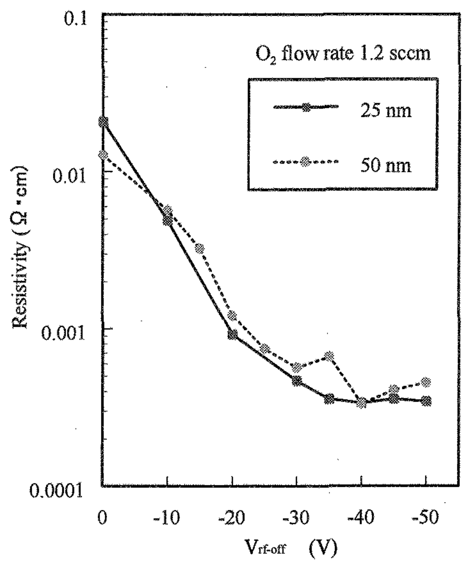

Fig. 8. Resistivity as a function of the off-set voltage Vrf-off for ITO films rf-bias-sputtered on PET substrates. The film thickness was (□) 25 nm and (○) 50 nm.

the substrate temperature is not greatly increased, although the substrate is heated by ion bombardment.

There is much interest about the energy of the ions striking the growing film. Direct measurement of the energies of ions under this condition is very difficult. Thus, we are now measuring some parameters of discharge plasma to estimate their energies. We assume that the ion energies are less than one fifth of the bias potential because the ion sheath, formed by the addition of bias, in front of the substrate has been found to be considerably thicker than the mean free path of ions. The results of our current investigation will be reported later.

3.2 rf bias sputtering

In order to obtain low-resistivity ITO films with thicknesses of less than 50 nm, the effect of the addition of rf bias voltage was investigated, because rf bias would be effective in the initial stage of film growth for insulating substrates. ITO films were formed on PET foils. The bias voltage of rf (10 MHz) was applied through a flat electrode to which the PET substrate was pressed, as shown in Fig. 2. Figure 7 shows the wave forms of the voltage observed from the substrate surface and the electrode. The ratio between their peak-to-peak values was

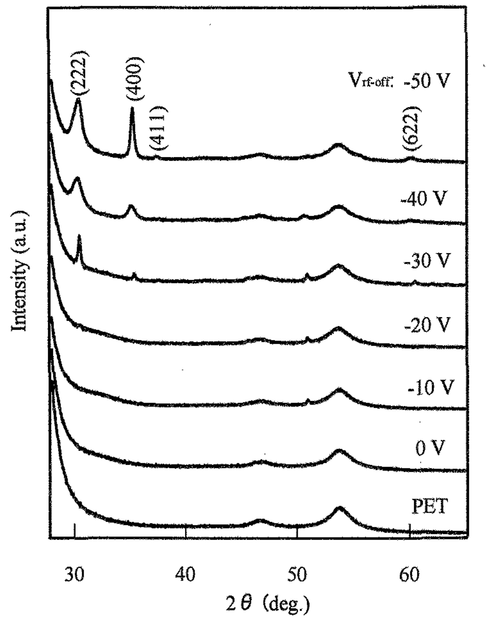

Fig. 9. XRD patterns of ITO films with the thickness of 50 nm, rf-bias-sputtered at various $V_{rf\text{-}off}$.

about 1:2 in these sputtering conditions, and the ratio was found to be dependent on the discharge parameters but not on bias voltage. We confirmed that the voltage of the substrate surface was self-biased negatively against the ground potential, as can be seen in Fig. 7. This negatively off-set voltage $V_{rf\text{-}off}$ is thought to correspond to the mean acceleration voltage for ions in rf biasing [7].

Figure 8 shows the resistivity plotted as a function of $V_{rf\text{-}off}$ for ITO films of 25 nm and 50 nm in thickness that were prepared by applying various rf bias voltages. The resistivity decreases as $V_{rf\text{-}off}$ increases, and it has a minimum value of 3.3×10^{-4} $\Omega\cdot$cm at $V_{rf\text{-}off}$ = –40V～–50V. The substrate temperature was not measured, but it was found that there was no change in the quality of PET after the deposition. It is noteworthy that the effects of dc biasing and rf biasing on resistivity, which are shown in Fig. 5 and Fig. 8, respectively, were found to have the same voltage dependence.

Figure 9 shows the XRD patterns of films prepared at various values of $V_{rf\text{-}off}$. It was found that the bias dependence of the XRD pattern in the case of rf bias sputtering is also very similar to that in the case of dc bias sputtering. That is, bombardment by ions of appropriate energies was confirmed to be very useful for crystallizing ITO films in the initial stage of film growth and for obtaining thin ITO films with low resistivities. The off-set voltage $V_{rf\text{-}off}$ is generally thought to be the mean acceleration voltage of the ions through the ion sheath in an rf biasing process; a good correspondence between the dependences of resistivity and crystallization on the values of V_{dc} and $V_{rf\text{-}off}$ has justified this assumption.

Figure 10 shows SEM images of the surfaces of 50-nm-thick ITO films deposited at $V_{rf\text{-}off}$ = 0V and –30V on a PET substrate. Small grains were formed in both cases, but the grains are larger and have more distinct shapes in the film deposited at $V_{rf\text{-}off}$ = –30V. The enhancement of grain growth is attributed to the growth of crystallites in the film.

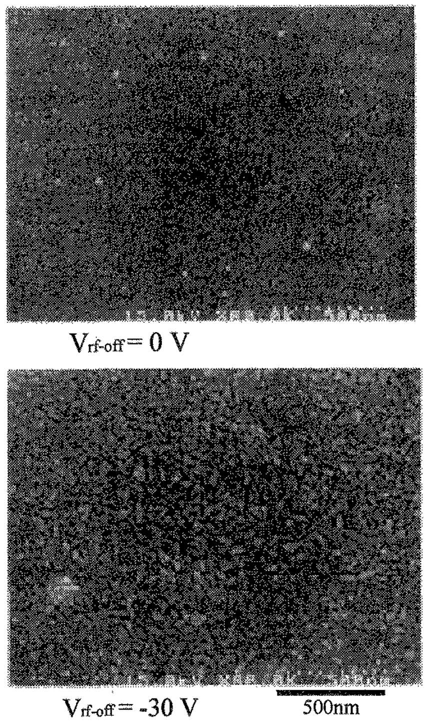

Fig. 10. SEM images of 50-nm-thick ITO films rf-bias-sputtered on PET at $V_{rf\text{-}off}$= 0V and –30V.

4. CONCLUSIONS

We prepared ITO films by using gas flow sputtering (GFS) and found that the application of bias sputtering to the GFS process resulted in reduction in the resistivity of the films. This reduction in resistivity by applying substrate bias is attributed to the crystallization of the film. The effects of two kinds of biases, dc bias and rf (10 MHz) bias, were investigated, and it was found that these two biases had the same effects on resistivity reduction and crystallization for the films. Consequently, ITO films with a low resistivity of 2.6×10^{-4} $\Omega\cdot$cm have been fabricated by adding dc bias of –50V , and 25-nm-thick films with resistivity of 3.3×10^{-4} $\Omega\cdot$cm have been obtained on PET foils (125 μm in thickness) by adding rf bias.

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