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Indium tin oxide thin films deposited by RF-magnetron sputtering for organic electro-luminescence devices

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Indium tin oxide (ITO) thin films for organic electro-luminescence (EL) devices were deposited by radio frequency (RF) magnetron sputtering at low temperature. Process parameters such as working pressure, RF power, deposition time, Ar flow rate and target-to-substrate distance are tuned to optimize ITO properties. Transmittance is strongly dependent on the film thickness: Overall transmittance was slightly decreased with the thickness while local fluctuations of a sinusoidal shape occurred. Transmittance of the crystalline films is generally lower than that of amorphous films due to high scattering on the rough surface of the crystalline film. However, sheet resistance was relatively insensitive to crystallinity and orientation of the film. An ITO thin film deposited under the condition of 7 mTorr, 100W and 6minutes had a sheet resistance of ~22 Ω/sq., transmittance of 89% and the rms (root-mean-square) value of 0.46 nm.

Key words: Indium tin oxide(ITO), organic electroluminescence(EL), RF sputtering.

Introduction

Transparent conducting oxides (TCO) such as ZnO, SnO_2 and ITO are widely used as conducting wires in solar cells, flat panel displays and touch screens. Especially, ITO which has low resistivity (as low as 10^{-4} Ωcm) and high transmittance of above 80% in the visible range can be applied as an anode contact for an OELD (organic electro-luminescence display) and a LCD (liquid crystal display). OELD consists of organic emission layers and an ITO electrode on a glass or plastic substrate without a backlight. An OELD is, therefore, an hopeful candidate for the display for handheld devices such as PDAs (personel digital assistant), cellular telephones etc.

ITO is an n-type wide-band gap semiconductor. The low resistivity of ITO thin films are believed to be due to a high carrier density. These carriers are believed to be generated by two processes. Free electrons can be introduced by the creation of oxygen vacancies or by the doping with Sn. Therefore, in order to optimize the electrical properties, the control of the Sn dopant and nonstoichiometry is necessary. In order to apply this film to OELD devices, it should have a transmittance of 85%, a resistivity of $\sim 2 \times 10^{-4}$ Ωcm and a surface roughness of 1 nm in rms.

ITO thin film is commonly fabricated by electron beam (EB) evaporation [1], RF and DC magnetron sputtering [2-4] and so on. However, most of the films are deposited at high temperature above 300°C because crystalline ITO can not be obtained at lower temperature. However, if we want to deposit the ITO on a plastic substrate, we should lower the deposition temperature so as not to damage the substrate. Electrical and optical properties of ITO thin films are also extremely dependent on the deposition conditions. In the case of using RF magnetron sputtering, properties of ITO thin films are affected by the conditions such as deposition temperature [5, 6, 7], working pressure [8], RF power [9] etc.

In this study, ITO thin films that were deposited on glass substrates at room temperature were investigated. We tried to find out the dependency of the properties on the deposition conditions to optimise the deposition conditions for OELD applications.

Experimental Details

ITO thin films were deposited on a nonalkali glass (Samsung SCP, Ltd., 5KS) from a 4" ITO target (99.99%, In_2O_3:SnO_2 = 9:1, High Purity Chemical Co., Ltd., Japan) by RF magnetron sputtering. The chamber was evacuated to $2\text{-}4 \times 10^{-6}$ Torr by using a turbo molecular pump (ALCATEL Co., ACT 1000T), and then pure argon gas were introduced while maintaing 6 to 10 mTorr by a pressure controller (MKS 600). Ar flow rate was controlled from 20 to 100 sccm by a mass flow controller (MKS). The substrate was constantly rotated at 20 rpm to improve film uniformity. In

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order to initiate the plasma, the working pressure was controlled to 40 mTorr, and then adjusted to the desired pressure. The deposition time was controlled by a shutter located near the target. All experiments were done under an RF power density from 0.62 W/cm^2 to 1.85 W/cm^2, which corresponds to an RF power of 50-150 W.

Sheet resistance (Ω/sq.) which was the resistivity times the film thickness was measured with a 4-point probe (NHY Co., SD-510). Film thickness (Å) and transmittance (%) at 550 nm wavelength were measured with an α-step (KLS-Temcor Co., α-step 500) and a spectrophotometer (Minolta Co., CM-3500B), respectively. Resistivities (ρ) of the films were determined using the simple relation, $\rho = R_s \times t$, where R_s is sheet resistance and t is thickness. For phase identification, the ITO thin films were analyzed with an X-ray diffractometer (MAC Science Co., Ltd., Japan) over the scan range from 20° to 70°. The surface roughness and morphology of the ITO thin films were examined with an atomic force microscope (TopoMetrix Inc., ACCUREX) and a scanning electron microscope (JEOL, JSM-6700F).

Results and Discussion

We compared the film properties at various working pressures from 6 mTorr to 10 mTorr at 1mTorr intervals to find out the optimum working pressure while other parameters such as RF power, target-to-substrate distance, deposition time and Ar flow rate were fixed at 125W, 60 mm, 5 min and 40 sccm, respectively. Sheet resistance and transmittance are shown in Fig. 1. At the working pressure of 7 mTorr, ITO thin film had the maximum transmittance of 83% and the minimum sheet resistance of 40 Ω/sq.

We then tried to find out the effect of Ar flow rate on the film properties. ITO thin films were deposited with a variation of Ar flow rate from 20 to 100 sccm at 20 sccm intervals. To reduce the substrate damage by the plasma, RF power was decreased to 100W. Transmittance and sheet resistance of the films are shown in

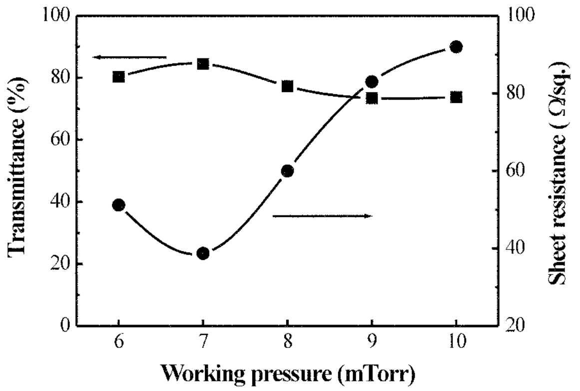

Fig. 1. Sheet resistance and transmittance dependence on working pressure at 125W RF power.

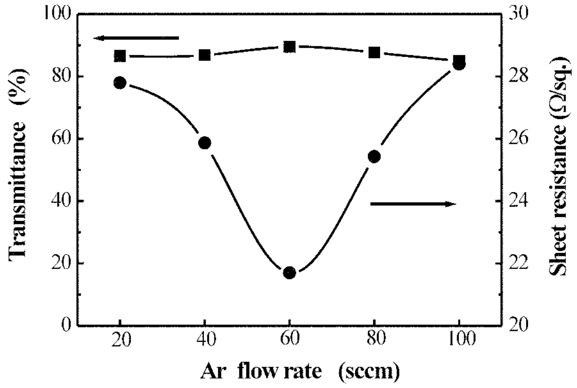

Fig. 2. Sheet resistance and transmittance as a function of Ar flow rate at the deposition conditions of 100W RF power for 6 minutes.

Fig. 2. ITO films deposited at 60 sccm showed the highest transmittance of 89% and the lowest sheet resistance of 22 Ω/sq..

As another variable, we chose the RF power and altered it from 50W to 150W at 25W intervals. By the change of RF power, the electrical and optical properties were greatly affected as shown in Fig. 3(a). Sheet resistance showed a minimum at an RF power of 100W. Optical transmittance showed a complex type of dependence on the RF power. This will be discussed in the later part of this section. As to the thickness and

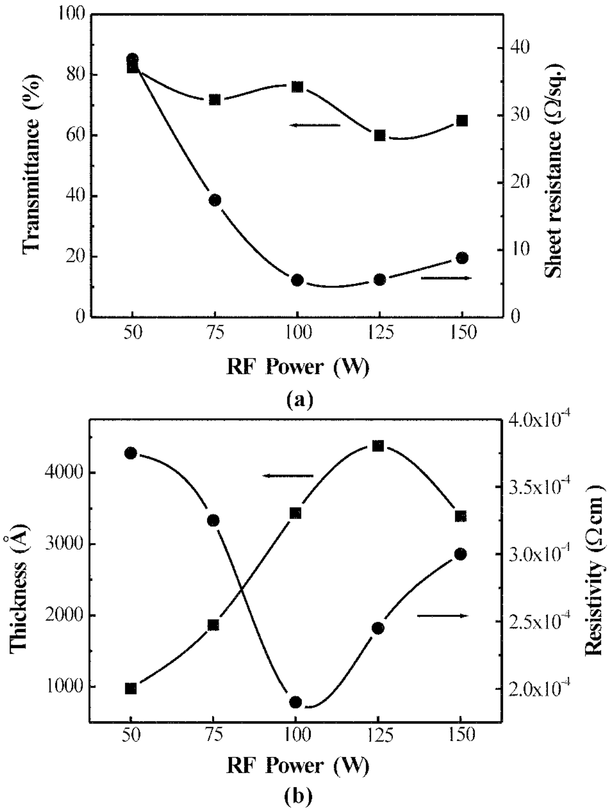

Fig. 3. Plots of (a) transmittance and sheet resistance and (b) thickness and resistivity with variation of RF power of ITO films deposited for 15 minutes.

resistivity, we can see an interesting result that the thickness went to the highest value at 125W and then it started to decrease. On the other hand, the resistivity showed a minimum at 100W RF power.

In order to find out the relationship between the resistivity and the microstructure, the surface morphologies of ITO thin films were observed. We could see a smooth surface of the sample deposited at 50W RF power in Fig. 4(a). It did not contain any type of boundary and could be regarded as an amorphous film, which was confirmed in the XRD patterns in Fig. 5. As the RF power increased, the film was changed to a crystalline structure in nature. The film deposited at 100W RF power had a polycrystalline microstructure with ~150 nm average grain size as is shown in Fig. 4(b). As the RF power went higher than 100W, the ITO film became less conductive. This change could be attributed to two facts; that crystallinity decreased at 150W RF power and the grain size was also decreased at 150W as shown in Fig. 4(c). In the case of the 125W specimen, the grain size effect might dominate the crystallinity effect because the average grain size was reduced from ~150 nm to ~50 nm.

The effect of grain size can be explained by the grain boundary scattering. If the grain boundary scattering is assumed to be the predominant scattering mechanism, then the sheet resistance can be expressed as [10]

$$R_S = \frac{1}{nq\mu t}$$

where n is the free electron concentration, q is the electron charge, μ is the electron mobility and t is the thickness. Here, electron mobility (μ) is directly proportional to grain size. Therefore, if the grain size is reduced to one third, the sheet resistance will become three times of the original.

On the other hand, the thickness of ITO thin film increased up to 125W. However, a further increase of the RF power to 150W resulted in a decrease of thickness. This decrease of thickness is thought to be the result of the following reasons: The incoming ions of high kinetic energy give rise to re-sputtering at the ITO surface. The rate of re-sputtering is known to increase exponentially with the ion energy. Kim and Kim [11] have reported that excess kinetic energy could lead to removal of atoms from the substrate when intense ions hit the growing thin film.

Transmittance of ITO thin films as a function of RF power is shown in Fig. 6(a). All of the films deposited at the RF power of 100W had high transmittance of

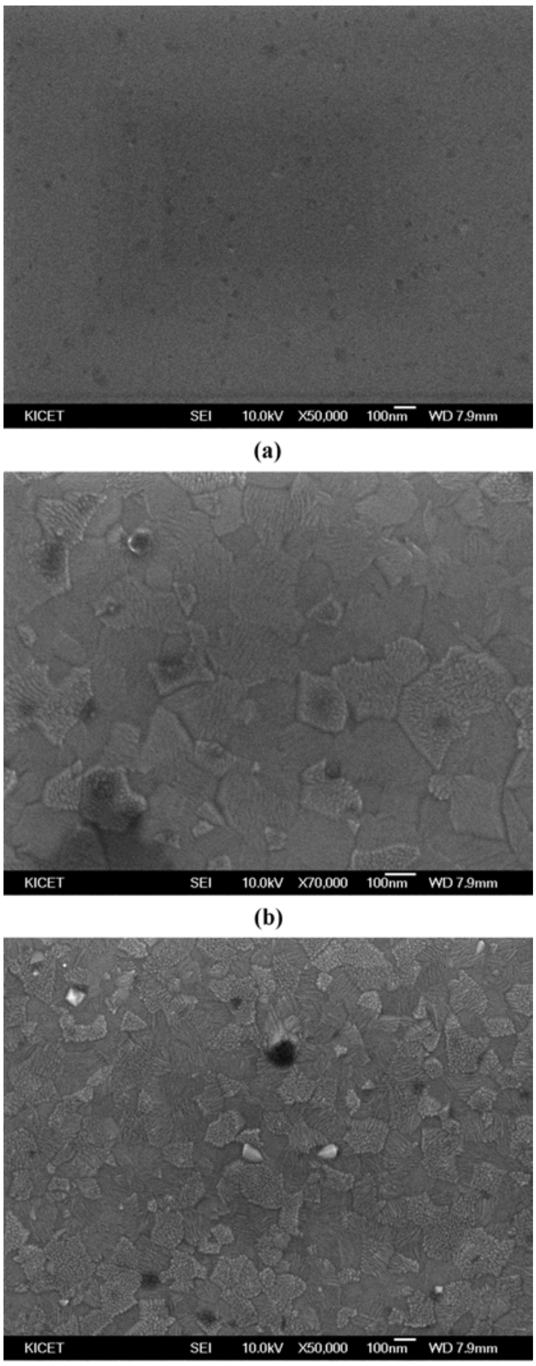

Fig. 4. SEM micrographs of the samples deposited at RF-powers of (a) 50W, (b) 100W and (c) 150W for 15 minutes.

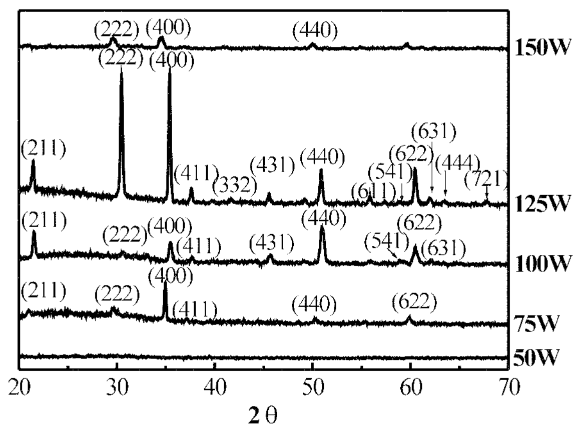

Fig. 5. XRD patterns of ITO films deposited at the given RF power for 15 minutes.

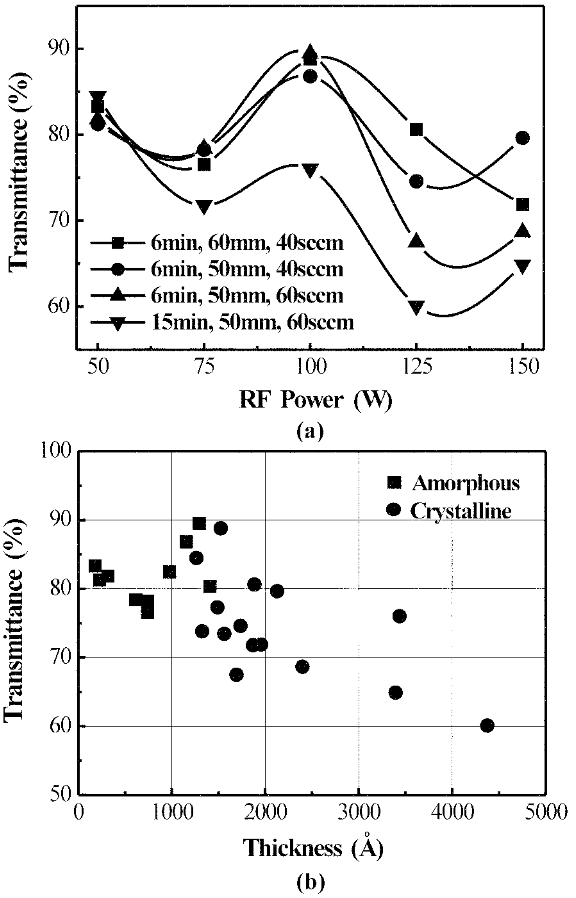

Fig. 6. Optical transmittance at 550 nm wavelength with a variation of (a) RF-power and (b) thickness.

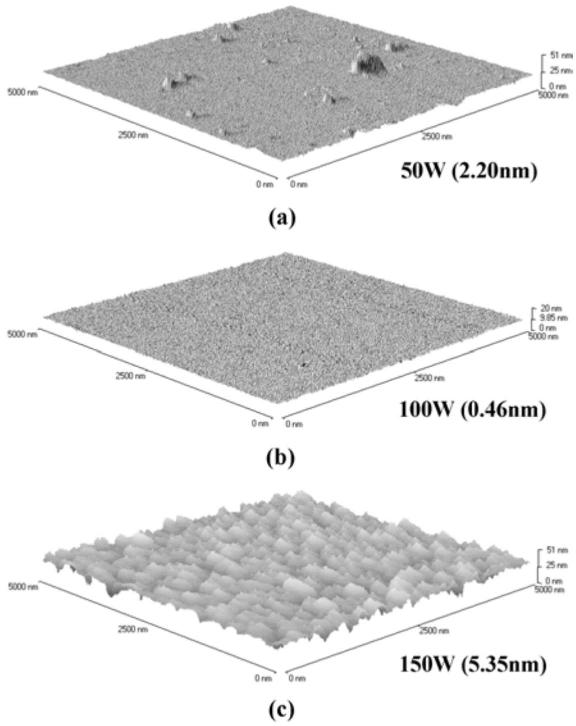

Fig. 7. Surface morphologies and rms roughnesses of ITO films deposited at RF power of (a) 50W, (b) 100W and (c) 150W for 6 minutes.

Table 1. Figure of merit for ITO thin films deposited at 7 mTorr, 50 mm and 60 sccm [unit: $\times 10^{-3}\ \Omega^{-1}$]

Deposition time	50W	75W	100W	125W	150W
6 min	1.24	2.08	15.18	0.85	1.14
15 min	3.80	2.10	11.67	1.10	1.50

85% or more except the film deposited for 15 minutes. Also the transmittance monotonously decreased with the film thickness due to the absorption in the film. On the other hand, the fluctuation of the transmittance is thought to be the result of the interference between the light reflected on the ITO surface and that at the interface. The ITO thin films show a sinusoidal shape of transmittance as experimentally given by Kim *et al.* [12]. Transmittance of all the ITO films deposited in this study is shown in Fig. 6(b) as a function of thickness. The amorphous films showed high transmittance above 75%. Eisgruber *et al*. [4] have reported that transmittance was relatively insensitive to the crystallinity of ITO thin films. The low transmittance of the crystalline ITO films in this study was regarded as due to their high surface scattering on their rough surfaces. The amorphous films have rather smoother surfaces than the crystalline films.

Surface morphologies examined with AFM are shown in Fig. 7. In case of the sample at 50W RF power, some clusters of irregular shape were found on the rather smooth surface. Also as a result, the roughness rms value of 2.2 nm was not so small. The sample at 100W RF power showed the lowest rms value of 0.46 nm in a 5 μm $\times$ 5 μm scan. As shown in Fig. 7(b), there were no islands or clusters on the surface of this sample. It is considered that the surface was very smooth because sputtered ions had sufficient energy to move on the substrate by the high RF power. Under the still higher RF power of 150W, the surface morphology was changed to a rough and highly crystalline structure due to the fact that the sputtered ions had sufficient energy to make large crystals.

The values of the figure of merit which is defined as $\varnothing_{TC} = T^{10}/R_s$ [13] are shown in Table 1 where T and R_s are transmittance and sheet resistance, respectively. The maximum value was $15.18 \times 10^{-3}\ \Omega^{-1}$ for the sample at RF power of 100W and a deposition time of 6 minutes. These values are high enough to use this ITO film in EL devices [14].

Conclusions

By control of the deposition variables, we could get a surface roughness in rms of 0.46 nm and a figure of merit of $15.2 \times 10^{-3}\ \Omega^{-1}$. This film can be used for the cathode of organic EL devices. However, we need to check more practical characteristics such as the permeability of moisture in order to make the devices.

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