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Low Temperature Deposition of the In_2O_3-SnO_2, SnO_2, and SiO_2 on the Plastic Substrate by DC Magnetron Sputtering

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Abstract

Thin films of In_2O_3-SnO_2 (ITO), SnO_2, and SiO_2 were prepared on the PET substrate by DC magnetron roll sputtering. 135 nm thick ITO film on SiO_2/PET substrate has sheet resistance as low as 55 Ω/square and transmittance as high as 85%. H_2O gas permeation through the film was 0.35 g/㎡ in a day. These properties are enough on optical film for the plastic LCD substrate or touch panel. Both refractive index and sheet resistance of ITO was found to be very sensitive to O_2 flow rate. Oxygen flow conditions have been optimized from 4 to 5 SCCM at 10^{-3}torr. It is also shown that both thickness of SnO_2 and refractive index of SiO_2 decrease as O_2 flow rate increases.

Keywords : Indium tin oxide (In_2O_3-SnO_2 ; ITO), SnO_2, SiO_2, thin film; roll sputtering, conductive layer

1. Introduction

Recently, indium tin oxide (In_2O_3-SnO_2 ; ITO) and tin oxide (SnO_2) have been widely used as transparent conductive and semi-conductive materials for display and photo-voltaic devices. At present, ITO films which have a low resistivity of the order of 10^{-4} Ωcm, stable electrical, optical, and mechanical properties are generally used for practical applications. ITO is an n-type semiconductor, which has a band-gap under 3.0 eV. The functional characteristics of ITO layer are high refractive index and high transparency. Because of this unique combination of wide band-gap and high electrical conductivity at room temperature, ITO has also been used as the electrode for solar cells and flat panel display (FPDs).

Sputtering has recently been noted as a method of depositing high quality film of uniform thickness on a large screen substrate. The normal sputtering process uses a dielectric or metal target with a radio frequency (RF) power source. However, this process has some drawbacks such as low deposition rate and thermal damage of substrate. In general, RF powered magnetrons can be operated with dielectric compound targets, but for economic mass production on large size their use is prohibited because of low deposition rate, high equipment costs, and scaling difficulty. DC powered magnetrons enhances high deposition speeds, although they require conductive targets. The poor conductive or insulating compound has to be deposited in a reactive gas environment. Since the reactions take place not only on the substrate surface, but also on the target and all other surfaces in the vicinity of the magnetron, the deposition process is not sufficiently stable and the maximum deposition rates are limited by the occurrence of arc discharges. In particular, SiO_2, which can only be deposited by sputtering, is the most important low refractive and insulating material which is used as a gas barrier and an adhesive between ITO and plastic substrate.

Since their development in the late 1970s, thin film depositions of ITO on continuous rolls of polymeric films have been studied as one of the product successes for the sputter roll coating process. In the late 1980s, and early 1990s, a handful of basically new magnetron

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systems have been developed, which brought about a quantum leap in deposition rate and process stability [1-3]. J.S. Matteucci [2] described 65 Ω/square ITO coating on PET film that had thickness of 120 nm and had a visible light transmission of 80 %. They also had developed an anti-reflected version of this film which had 90 % transmission. In 1990, Leybold introduced the concept of medium frequency (MF) AC magnetron to be used in reactive sputter deposition of oxides and nitrides. This approach proved to be very useful because it solved the "vanishing anode problem"[3].

This report covers our work on fast and low temperature deposition of thin films of ITO, SnO_2, and SiO_2. We applied DC power for reactive sputtering [4] to deposit the highly conductive, semi-conducting and transparent thin films on plastic substrates with roll to roll process. Silicon oxide (SiO_2) is not only the adhesion enhancement material between ITO and plastic substrate, but also a gas barrier and transparency improving material. The optical and electrical properties of these materials are studied.

2. Experimental

The experiments were carried out using a ULVAC Coating Technology's DC magnetron Sputter. Figure 1 shows the outline of the equipment used for thin film deposition. It is an illustration of an experimental system for rolling up a web substrate of 100 mm in effective width. Target size is used with the 5×8 inches (12.7 cm × 20.3 cm) M size. The vacuum vessel is subdivided into two separate chambers, which are pumped by separate cryo pump sets for high vacuum: the winding chamber and the coating chamber. The winding chamber contains the strongly degassing roll of web. It is connected with the coating chamber only through very small slits around the coating drum. Inside the winding chamber the following elements are located: unwinder, AC bombard for glow discharge plasma pretreatment, coating drums, rewinder, several tension rolls, and targets (ITO, Sb_2O_3 10 wt% doped SnO_2, and Silicon). Sputter deposition was carried out at a pressure of 10^{-3}-10^{-5} torr with a DC power of 2.0 kW for SiO_2 and 0.35 kW for ITO and SnO_2, respectively. Sputtering gas was a mixture of Ar, N_2, and O_2. In the preparation of highly conductive films, substrates without intentional heating were suspended perpendicular to the target surface [5-6]. Feed rates of gas were controlled by a mass flow controller. This system was used to determine the optimum conditions for magnetron sputtering in this experiment. It is equipped with a 40 kHz positive-pulse applicator unit (A^2K unit by ULVAC Co.) to prevent abnormal discharges (arcing) in the case of a silicon cathode for SiO_2 deposition. As a basic material for our film, PET of optical grade was selected. Optical characteristics of the PET film used in this experiment are excellent, with the haze value smaller than 1 % but larger than 86 % in respect to transparency. The thickness of the PET film was fixed at 100 μm, to meet stiffness requirements.

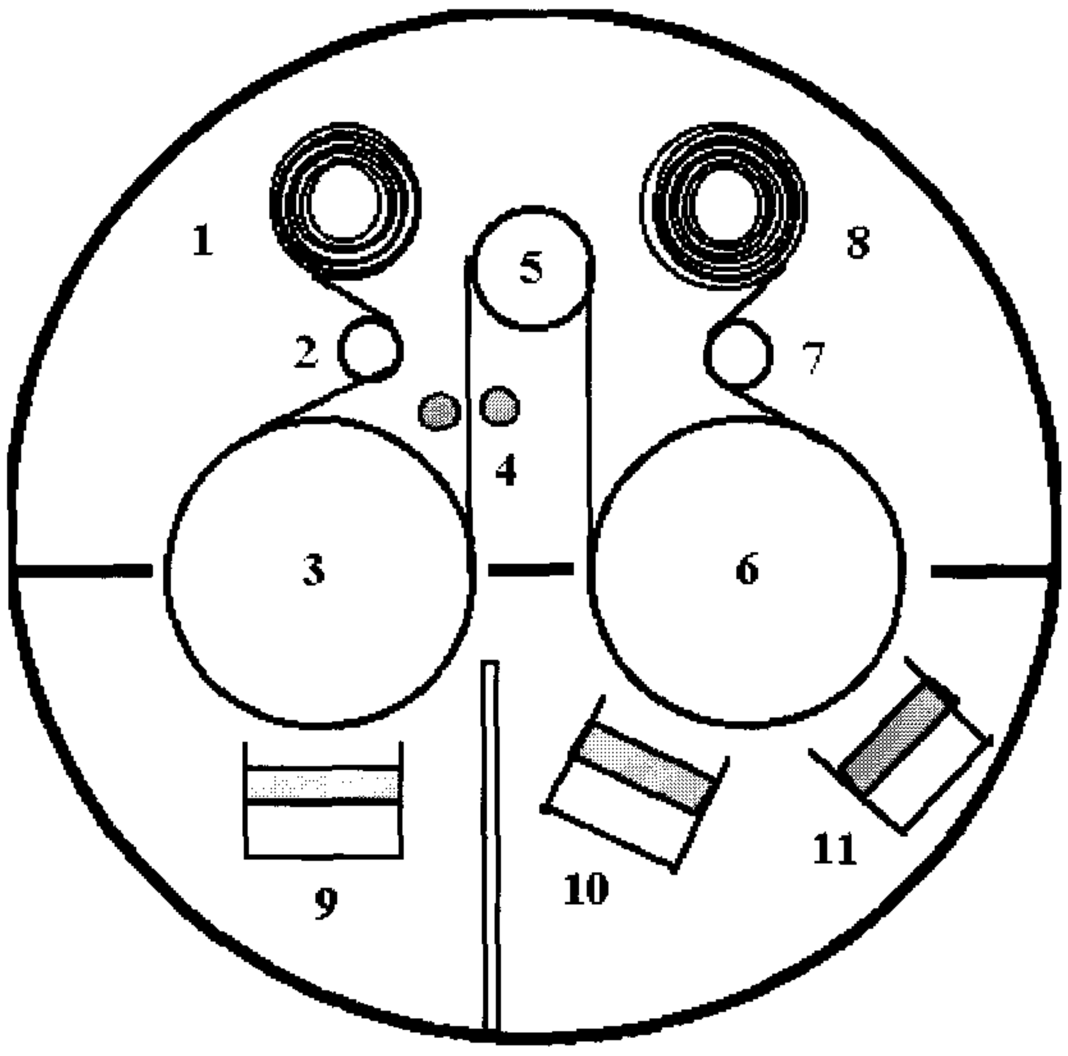

Fig. 1. Roll to roll DC magnetron sputtering system for a web substrate; (1) winder, (2) tension roll, (3) coating drum, (4) AC bombard rod, (5) spreader roll, (6) coating drum, (7) tension roll, (8) winder, (9) silicone target, (10) ITO target, and (11) SnO_2 target.

Film thickness was measured with DEKTAK α-step (SEIKO Co.). An ESM-1A ellipsometer (ULVAC Co.) was used to measure refractive indices for films coated on silicon wafers. The optical transmittance of the film was measured with a U-3500 (HITACHI Co.) spectrophotometer. Sheet resistance was measured with the 4-point probe Loresta MP MCP-T350 (DINS Co.).

3. Results and Discussion

Figures 2, 3, and 4 show the dependence of the refractive index and dynamic thickness rate on O_2 gas flow rate for depositing the SnO_2, SiO_2, and ITO, respectively.

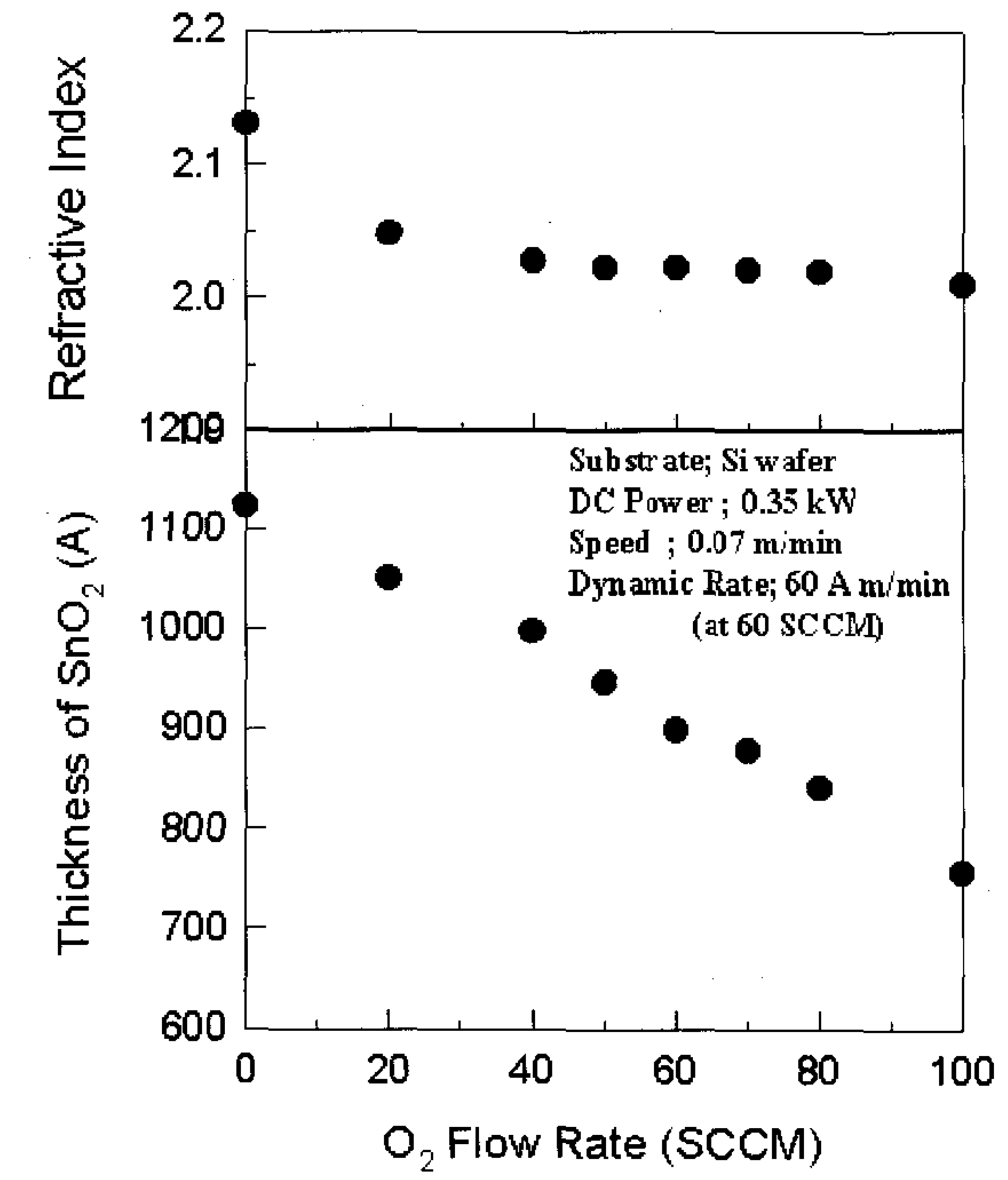

Fig. 2. The change in the refractive index and dynamic rate with respect to the oxygen flow rate for SnO_2 films.

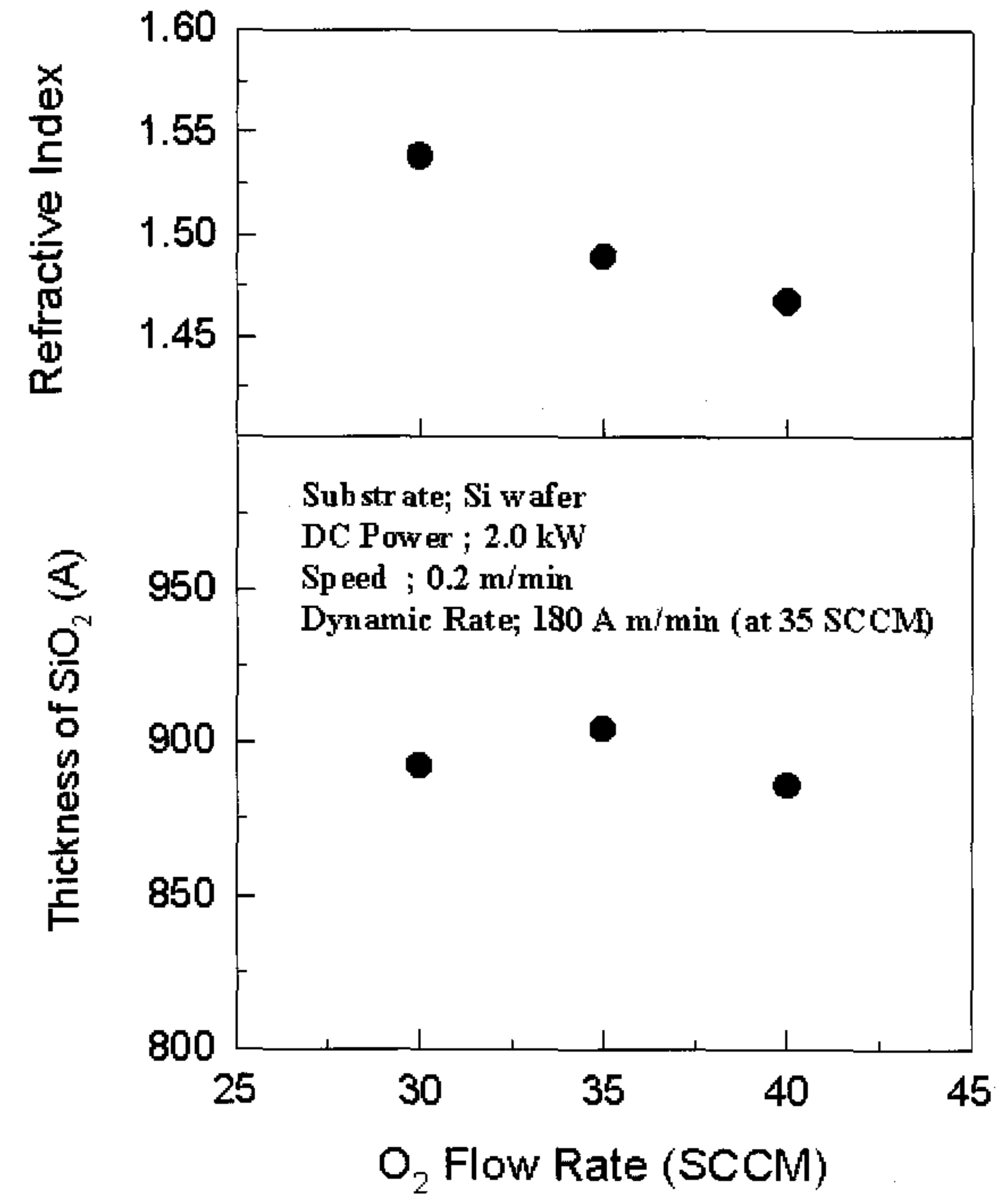

Fig. 3. The change in the refractive index and dynamic rate with respect to the oxygen flow rate for SiO_2 films.

Figure 2 shows the deposition results of SnO_2 film by our process. Deposition was carried out at 0.35 kW and 1.0×10^{-3} torr. O_2 gas flow rate was varied from 0 to 100 SCCM, and dynamic deposition rate was 60 Å m/min at 60 SCCM. Silicon wafer was used as substrate for deposition. This DC sputtering process was carried out using a Sb_2O_3 10 wt% doped SnO_2 target. Figure 2 also shows that the thickness of SnO_2 is rapidly decreased with the increase of O_2 gas flow rate and the refractive index of about 2.0 remains almost constant above 40 SCCM. The sheet resistance of a 100 nm thick SnO_2 was about 10^7-10^8 Ω/square which was prepared at above 12 SCCM.

Figure 3 shows the dependencies of the refractive index and thickness on the flow rate of O_2 gas for depositing a SiO_2 film. Deposition was carried out at the power of 2.0 kW, 1.2×10^{-3} torr. O_2 gas flow rate was changed from 30 to 40 SCCM, and dynamic rate was 180 Å m/min at 35 SCCM. This process was operated at a steady dynamic rate, with little change in the refractive index over a wide range of O_2 gas flow rates. The thickness of deposition film did not show a large change from 30 to 40 SCCM (O_2 gas). Refractive index is decreased with the increase of O_2 gas flow rate of below 40 SCCM, but was almost constant to 1.45 above 40 SCCM. The transmittance of deposited SiO_2 on PET substrate was above 90 % in comparison to 86 % through bare PET film only. This shows an increasing trend in accordance with the increase of O_2 flow rate, which is due to anti-reflection effect because the refractive index of SiO_2 is lowered with increasing O_2 flow rate and the refractive index of SiO_2 (about 1.45) actually is lower than that of PET film. The SiO_2 film on PET has not only been known as the transparent enhancing material due to low-refractive index but also as a material that deters oxygen and water permeation. In this experiments, H_2O gas permeation through the film was 0.35 g/㎡ in a day. However, the deposition of SiO_2 film by the present method is about ten times as fast as deposition of a transparent SiO_2 film by conventional RF sputtering (20 Å m/min), and it is about three times faster than that of SnO_2. This process is carried out from a silicon target in the reactive DC sputtering with an A^2K unit as discharge voltage. Positive potential is periodically applied to compensate for the electric charge to the non-eroded area of the target, thereby preventing abnormal discharge.

Figure 4 shows the dependencies of the refractive index and thickness on the flow rate of O_2 gas for depositing ITO film. Deposition was carried out at the 0.35 kW and 1.2×10^{-3} torr. O_2 gas flow rate was from 0

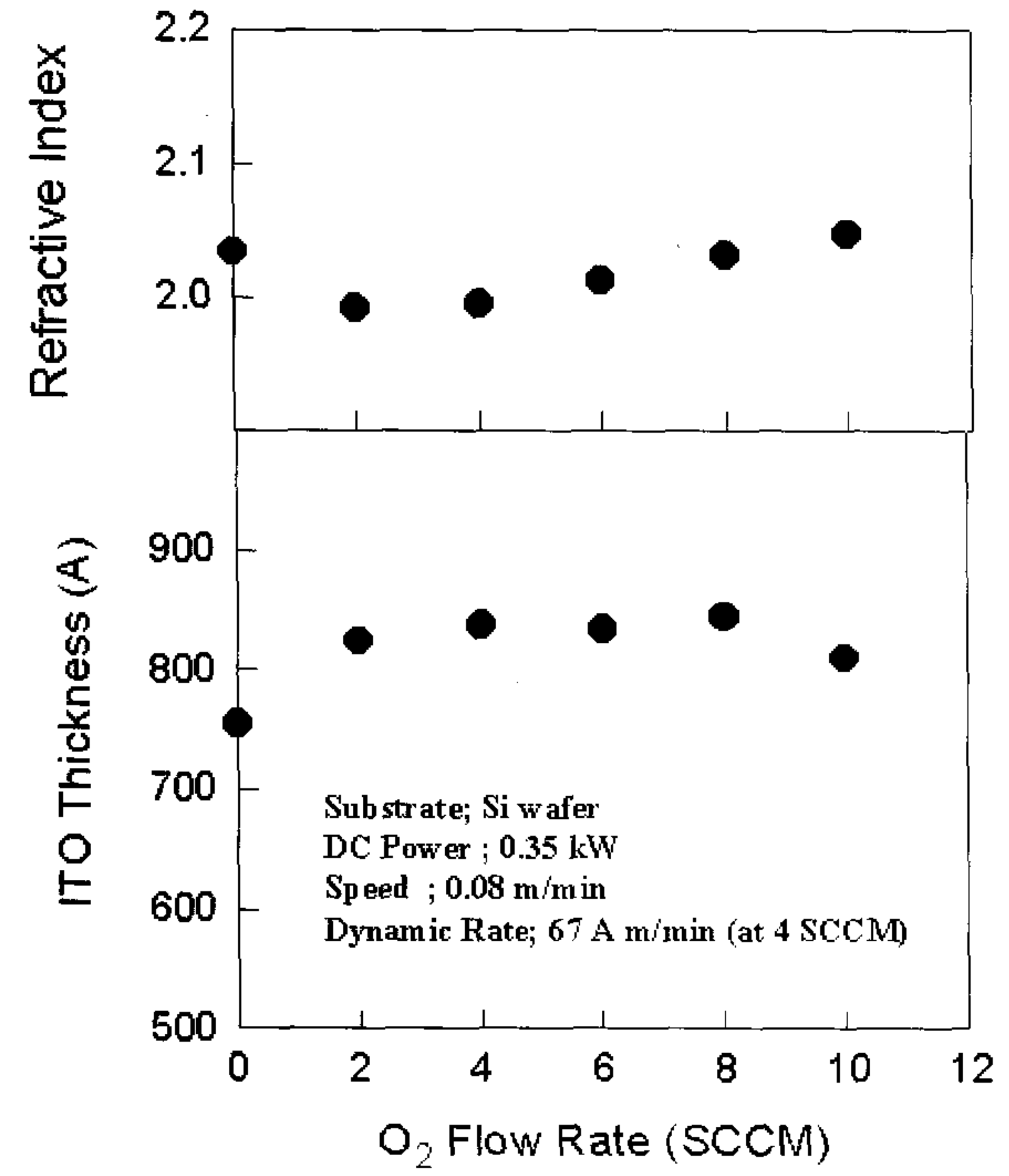

Fig. 4. The change in the refractive index and dynamic rate with respect to the oxygen flow rate for ITO films.

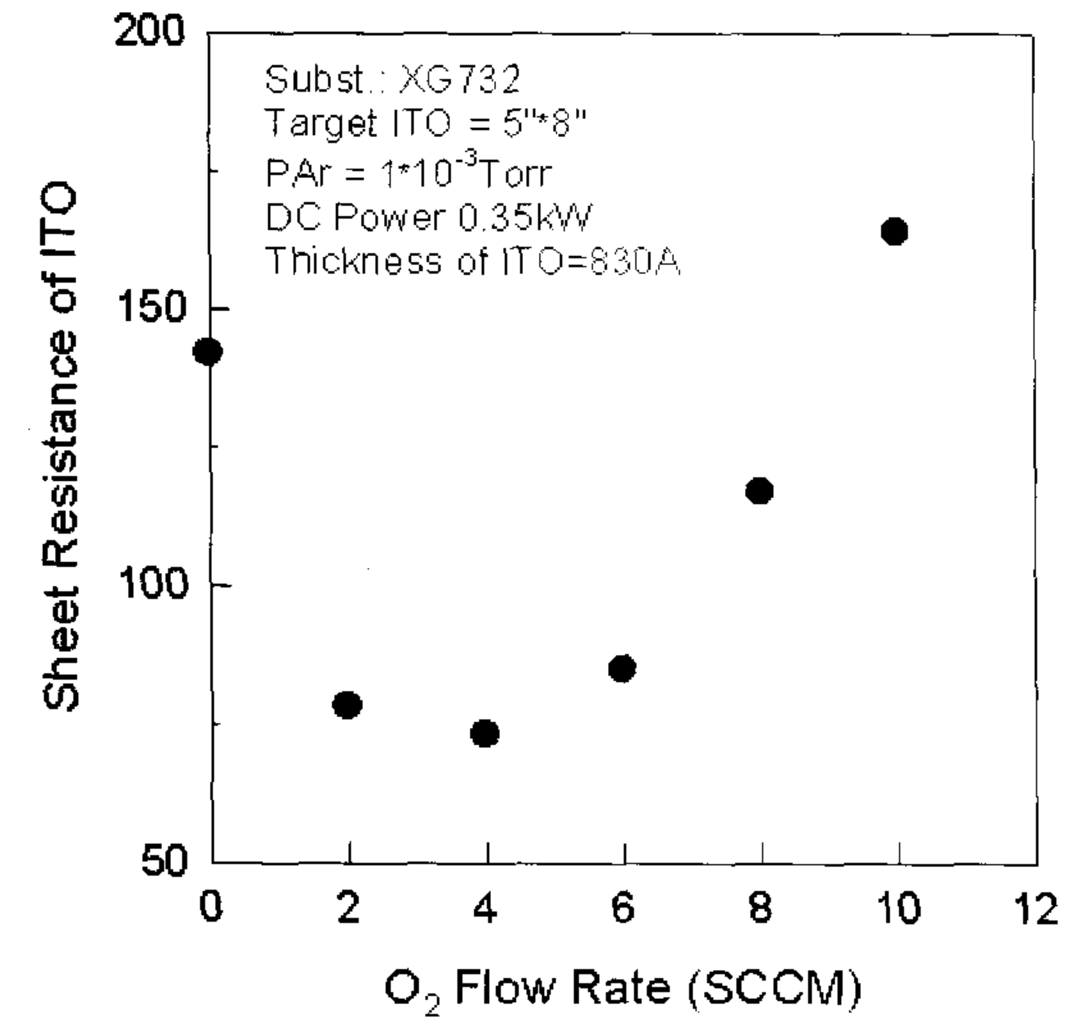

Fig. 5. Sheet resistance (Ω/square) of ITO as a function of oxygen flow rate.

to 10 SCCM, and dynamic rate was 67 Å m/min at 4 SCCM. The thickness of ITO according to the change of O_2 gas flow rate was nearly constant at 4-6 SCCM. The refractive index was generally 2.0 at 800 Å thickness, however it showed minimum (RI: 1.99) from 2 to 4 SCCM. The sheet resistance of ITO was very sensitive to O_2 gas flow rate, as shown in Figure 5, which showed the U-shape curve with the change of O_2 gas flow rate and the minimum resistance (75 Ω/square; at 830 Å thickness) at from 2 to 4 SCCM. In the case of Figure 5, the substrate used for deposition was PET film (XG732 grade of SAEHAN Co.).

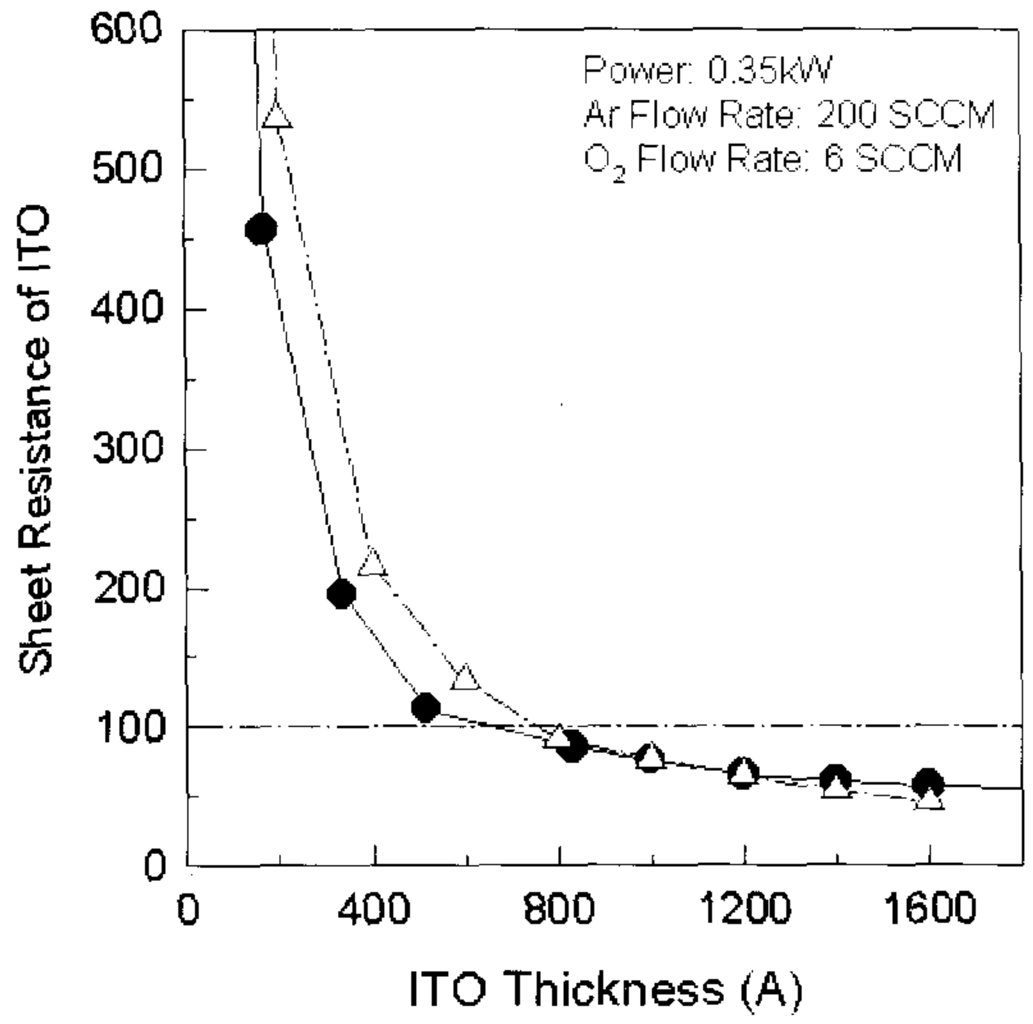

Fig. 6. Sheet resistance (Ω/square). as a function of ITO thickness; Substrates are (1) PET film, (2) hard coated PET film.

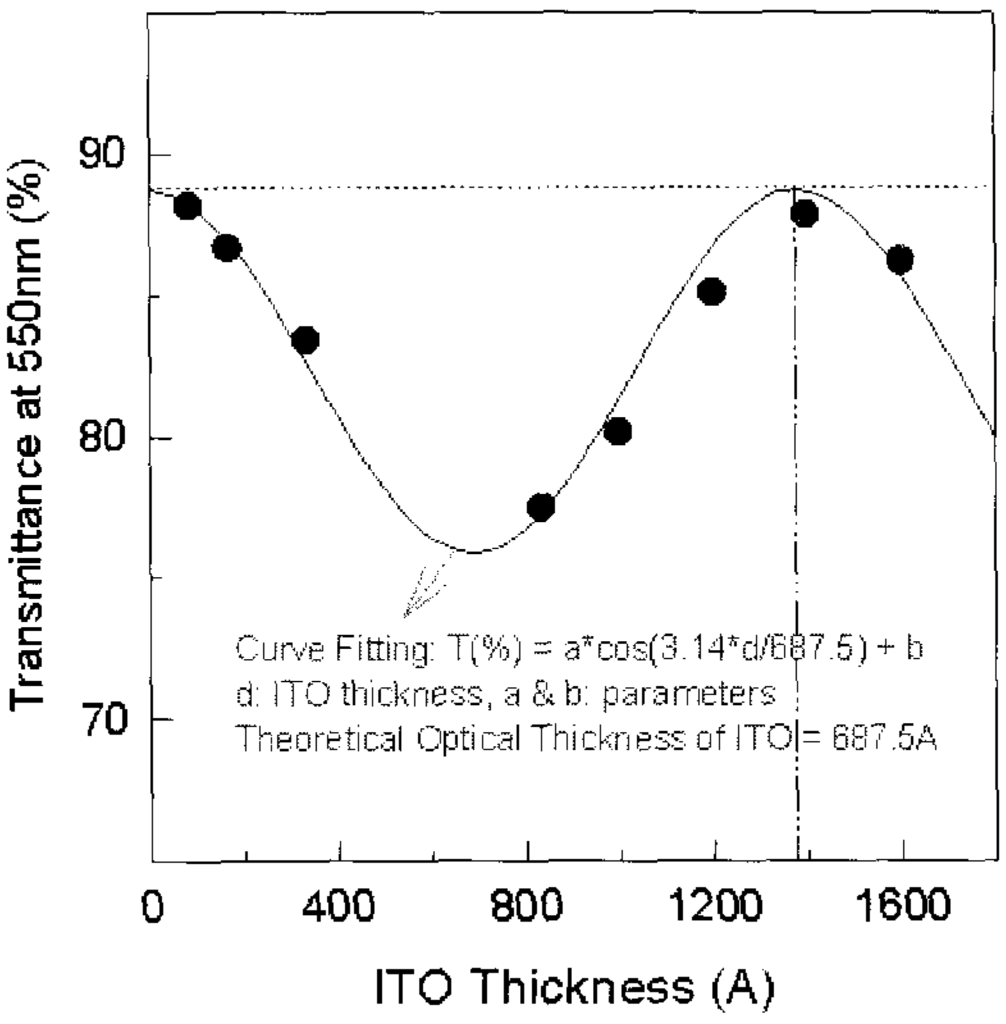

Fig. 7. Transmittance at 550 nm as a function of ITO thickness.

The dependence of sheet resistance on film thickness of ITO is shown in Figure 6. The sheet resistance of ITO films was strongly dependent on film thickness below 600 Å. The film thickness dependence on the sheet resistance was related to the decreased mobility with decrease in thickness up to 1600 Å. There is correlation between the mobility and the crystallinity of the film [7]. The crystallization in polycrystalline ITO films grown on PET substrates may be governed by the deposition conditions or surface condition of substrate film. Consequently, the quality of the crystallinity in the thickness range up to about 400 Å becomes poor, and improvement of the crystallinity is achieved as a result of the enhancement of grain growth with increase of film thickness. As the electrodes of plastic LCD, the sheet resistance below 100 Ω/square is required and photo transmittance should be higher than 85 % at 550 nm of light wavelength. Especially, photo characteristic is a very important factor in LCD.

In Figure 7, it is shown the change of transmittance according to the ITO thickness. Transmittance as a function of thickness follows a sine curve (equation 1) because it can be explained as a destructive interference effect of reflection light at the surface of ITO film and surface of PET.

$$\text{Transmittance } T\,(\%) = a^* \cos(3.14^* d/687.5) + b \quad (1)$$

where "d" is ITO thickness, "a" and "b" are parameters and theoretical optical thickness of ITO is 687.5 Å, respectively.

In general, the reflectance of ITO coated PET film is higher than that of PET film itself; refractive indexes of PET, n_s and ITO after stretching, n_f are 1.65 and 2.0, respectively. The reflection between ITO coated PET film and PET film is internal reflection because $n_f > n_s$, and the condition for constructive reflection is $n_f t = \lambda/4$ whereas the condition for destructive interference is $n_f t = \lambda/2$ (here, t is optical thickness of ITO, λ is wavelength of light). The ITO thickness having the lowest transmittance on PET film is 687.5 Å and ITO thickness having the highest transmittance on PET film is 1375 Å at 550 nm, respectively, as shown in Figure 7. These are also very well matched with the theoretical results.

This highly conductive and transparent PET/SiO_2/ITO films having the sheet resistance as low as 55 Ω/square, transmittance above 85 % at 550 nm and the 1375 Å thickness of ITO layer have been optimized. These properties indicate that it can be also applied as the electrode of plastic LCD or touch panel. Silicon oxide (SiO_2) layer between PET film and ITO layer with high transparency is needed not only for the adhesion improvement between ITO and plastic substrate but also for the gas barrier. The required properties of plastic substrates such as the thermal resistance, gas permeation, and compaction rate are presented briefly as follows. The process temperature have to stay below 180 ℃ which is especially necessary for the deposition of TFT. Gas permeation through the plastic substrates has to be lowered to less than 0.1 cm^3/m^2 with in 24 h at 1 atm for O_2 and to ≤ 0.15 g/m^2 in 24h for water by barrier layers e.g. out of SiO_2, Ta_2O_5 or organic materials. The irreversible shrinkage, and the compaction rate must be lowered to 3 ppm/h by annealing as a rule for 100 h at 150 ℃ for PAR, PET, PEN, PC, and PES [8] which are most common plastics used.

4. Summary

In_2O_3-SnO_2 (ITO), SnO_2, and SiO_2 thin films were prepared on plastic substrate by the reactive DC magnetron roll to roll sputtering process. The detailed study of electrical and optical properties in ITO film was described. A low resistance of 55 Ω/square with transmittance of above 85 % was obtained for PET/SiO_2/ITO film. The refractive index and deposited film thickness according to the O_2 gas flow rate have been investigated, and the sheet resistance of ITO is shown to be very sensitive with O_2 gas flow rate. PET/SiO_2/ITO film can also be applied to the electrodes for plastic LCD or touch panel.

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