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Optical properties of ITO/AlO_x thin films prepared by reactive d.c. magnetron sputtering

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Abstract

ITO/AlO_x films were deposited on PMMA by reactive d.c. magnetron sputtering. A transparent AlO_x film was selected as a antireflective coating material in this investigation. The feasibility of using AlO_x as an antireflective coating material for ITO films, and the influence of oxygen flow rate and bias voltage on the optical properties of AlO_x films were studied. A dramatic increase in absorption was observed near a wavelength of 380 nm. The absorption of ITO/AlO_x films increased initially with the bias voltage. However when the bias voltage exceed a critical value, the absorption decreased again. There was a close relationship between the content of Al and the IR absorption of ITO/AlO_x films. The absorption in the infrared region of ITO/AlO_x films increased with the oxygen flow rate and film thickness.

Keywords: C. Optical properties; ITO/AlO_x; Transmission; Absorption

1. Introduction

Indium tin oxide (ITO) is a n-type degenerated semiconductor with a wide band gap (E_g ~3.3 eV) [1]. It has good electrical conductivity and high transparence in the range of visible spectrum [2]. Similar to a metallic material, ITO has high reflectance in the infrared (IR) range due to its high density of free electrons in the conduction band [3]. The free carriers in ITO are generated by two mechanisms: (1) oxygen vacancies acting as electron donors [4], and (2) Sn atom substitution for the In atom giving out one extra electron [5]. ITO films are used in opto-electronic devices [6], solar cells [7], transparent heat mirrors [8], and anti-reflective coatings [9].

A substantial mismatch in refractive index between the ITO films (n~2.0) [3] and ambient air (n=1) can result in substantial reflection and therefore reduce the transmission, particularly in the visible range. This problem has became an impediment for further utilization of ITO films. To resolve this long-term problem, an innovative layer material of AlO_x antireflective (AR) coating on the ITO films is proposed in this study.

A transparent AlO_x film was selected as a new antireflective coating material for ITO in this investigation. The substrate employed in this investigation was polymethyl methacrylate (PMMA). In order to avoid the deformation of PMMA during deposition, the ITO/AlO_x films were deposited on PMMA by a low temperature reactive d.c. magnetron sputtering technique. The major goal of this study is to investigate the feasibility of using AlO_x as an antireflective coating material for ITO films. The influence of oxygen flow rate and bias voltage on the optical properties of ITO/AlO_x films are also discussed.

2. Theory

The reflectivity of a thin film combination (R) is given by [10]

$$R = \left|a/b\right|^2 \quad (1)$$

where a and b are obtained from

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$$\begin{pmatrix} a \\ b \end{pmatrix} = \begin{pmatrix} n_o & -1 \\ n_o & +1 \end{pmatrix} \begin{pmatrix} \cos\delta_A & i\sin\delta_A/n_A \\ in_A\sin\delta_A & \cos\delta_A \end{pmatrix} \times \begin{pmatrix} \cos\delta_{ITO} & i\sin\delta_{ITO}/n_{ITO} \\ in_{ITO}\sin\delta_{ITO} & \cos\delta_{ITO} \end{pmatrix} \begin{pmatrix} 1 \\ n_s \end{pmatrix} \quad (2)$$

where n is refractive index, δ is phase difference, and the subscripts O,A,ITO and S stand for the air, AR film, ITO film and substrate respectively.

The substrate employed in this study is PMMA ($n=1.49$) [11]. In order to obtain a minimum reflectivity, the selected AR layer material must have a refractive index of 1.67 based on the calculations from Eqs. (1) and (2). The refractive index of transparent AlO_x films was reported to be in a range from 1.54 to 1.70 [12], and it was therefore selected as an anti-reflective coating material in this investigation.

3. Experimental procedures

The ITO films were deposited on PMMA by reactive d.c. magnetron sputtering. The substrates were machined into blocks of 15 mm×15 mm×7 mm, degreased and ultrasonically cleaned in acetone and ethyl alcohol, rinsed in deionized water, and subsequently dried in flowing nitrogen gas before deposition.

The targets used in this study are In–Sn alloy (99.99% purity) with a composition of 90:10 wt.%, and Al (99.999% purity). The sputtering was performed in a mixed $Ar–O_2$ atmosphere with a target-to-substrate distance of 4 cm. A diffusion pump coupled with rotary pump was used to achieve base pressure of 1.3×10^{-3} Pa before introducing gas mixtures of argon (99.9995%) and oxygen (99.999%). The pressure was measured using an ion gauge and convection vacuum gauge. Two separate mass flow controllers (Hastings HFC-202) were used to monitor the gas flow rates of argon and oxygen.

The target was first sputtered for 10 min at 1.3 Pa in Ar for cleaning purpose. The cathode current and substrate temperature were maintained at 50 mA and 70 °C respectively for depositing ITO films with thickness of 100 nm. An r.f. power supply was used for establishing negative substrate bias of 60 V. The ITO-deposited samples were cooled in Ar atmosphere for 6 h before depositing the AlO_x films.

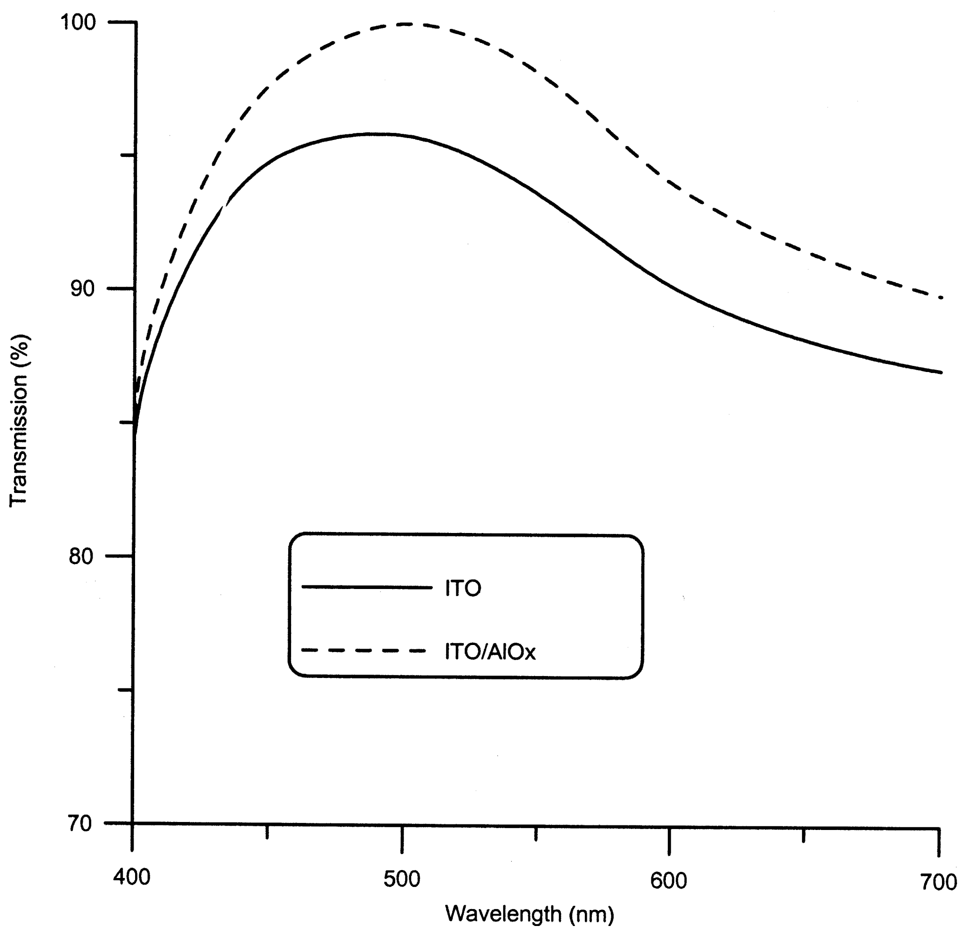

Fig. 1. Transmission spectra in the visible region of ITO films and ITO/AlO_x films. The AlO_x film was prepared at oxygen flow rate of 2 sccm, current of 10 mA, thickness of 60 nm, and bias voltage of −20 V.

For depositing the AlO_x films on ITO, the substrate temperature was held at 30 °C and the cathode current was maintained at 10 mA. An r.f. power supply was used for establishing various negative substrate bias voltages. Deposited samples were cooled in Ar atmosphere for 3 h before venting the system.

The optical transmission and absorption spectra of films in the visible light and IR regions were determined by an UV-visible, near-IR spectrophotometer (HP 8452A Diode Array Spectrophotometer) and a Fourier Transform Infrared Reflectance spectrophotometer (Magna-IR 550 Spectrophotometer). The chemical composition of films was carried out by X-ray photoemission spectroscopy (XPS) (VG Scientific 210) using Mg Kα radiation.

4. Results and discussion

Fig. 1 shows transmission spectra in the visible region of ITO films and ITO/AlO_x films. The ITO films were prepared at oxygen flow rate of 6 sccm, current of 50 mA, bias voltage of −60 V, with 100 nm in thickness. The AlO_x film was prepared at oxygen flow rate of 2 sccm, current of 10 mA, bias voltage of −20 V, with 60 nm in thickness. The transmission of ITO/AlO_x films in the visible region was substantially higher than that of ITO films. The results indicated that AlO_x film coating is a good candidate material for anti-reflective purpose.

Fig. 2 shows the absorption spectra in the UV-Visible-near-IR region of ITO/AlO_x films. The AlO_x films were prepared at oxygen flow rate of 2 sccm, current of 10 mA, at different bias voltages with 60 nm in thickness. The absorption of ITO/AlO_x films increased with the increase of bias voltage, for wavelengths between 400 and 500 nm. In addition, the absorption edge had a tendency of shifting to visible spectrum range as the bias voltage increased. It suggested that the ITO/AlO_x films had higher absorption in the visible light region as the bias voltage increased, so it was sensitive to the visible light [13].

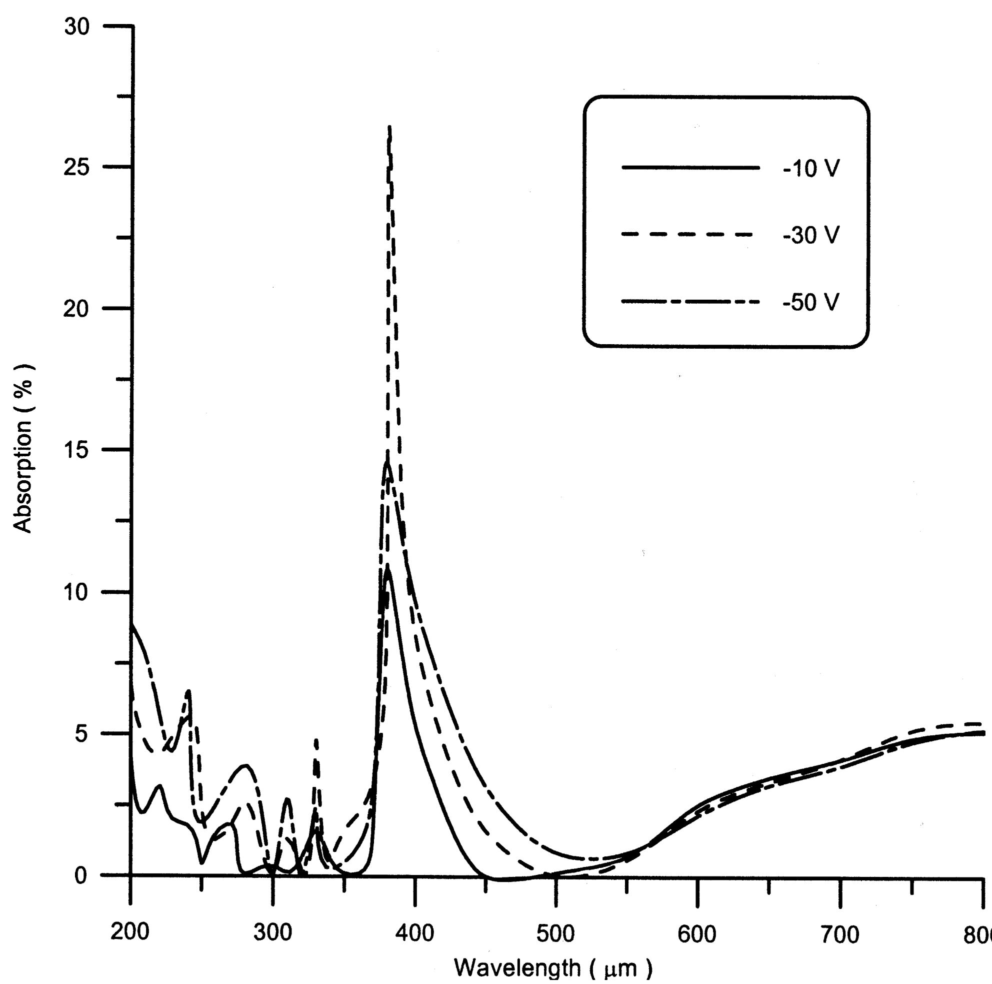

Fig. 2. Optical absorption spectra of ITO/AlO_x films. The AlO_x films were prepared at oxygen flow rate of 2 sccm, current of 10 mA, thickness of 60 nm, and different bias voltages of −10 V, −30 V, and −50 V.

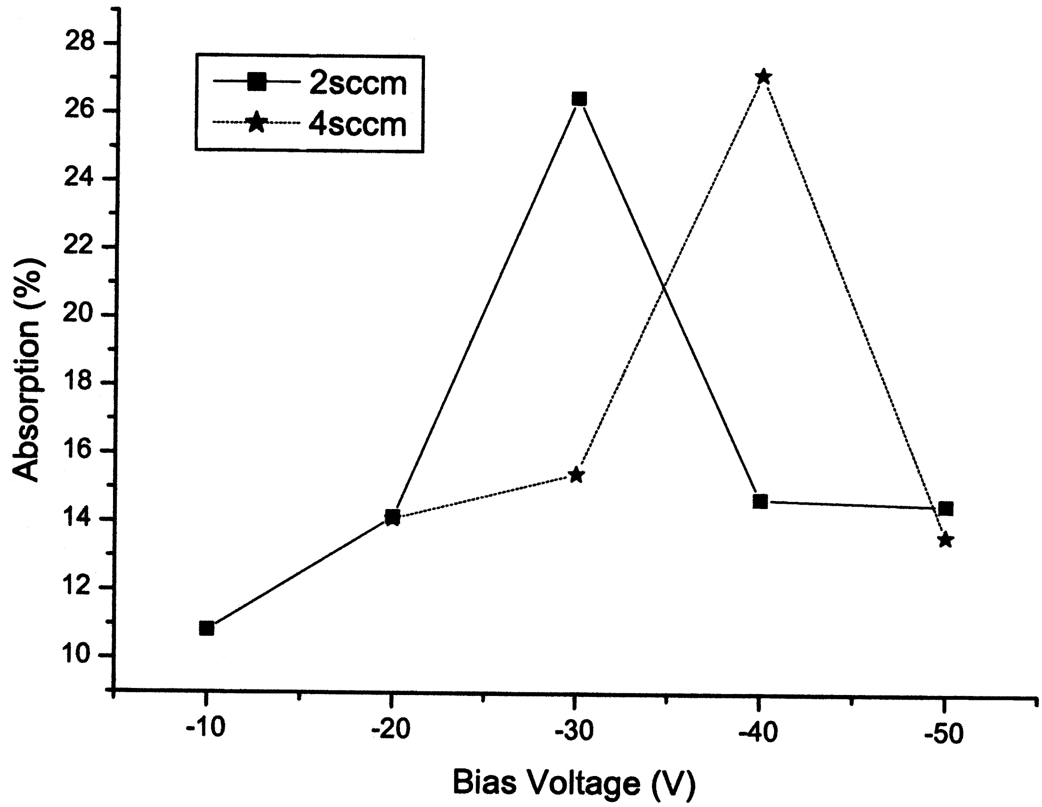

Fig. 3. Optical absorption spectra of ITO/AlO_x films at light wavelength of 380 nm versus bias voltage. The AlO_x films were prepared at current of 10 mA, thickness of 60 nm, and different oxygen flow rates.

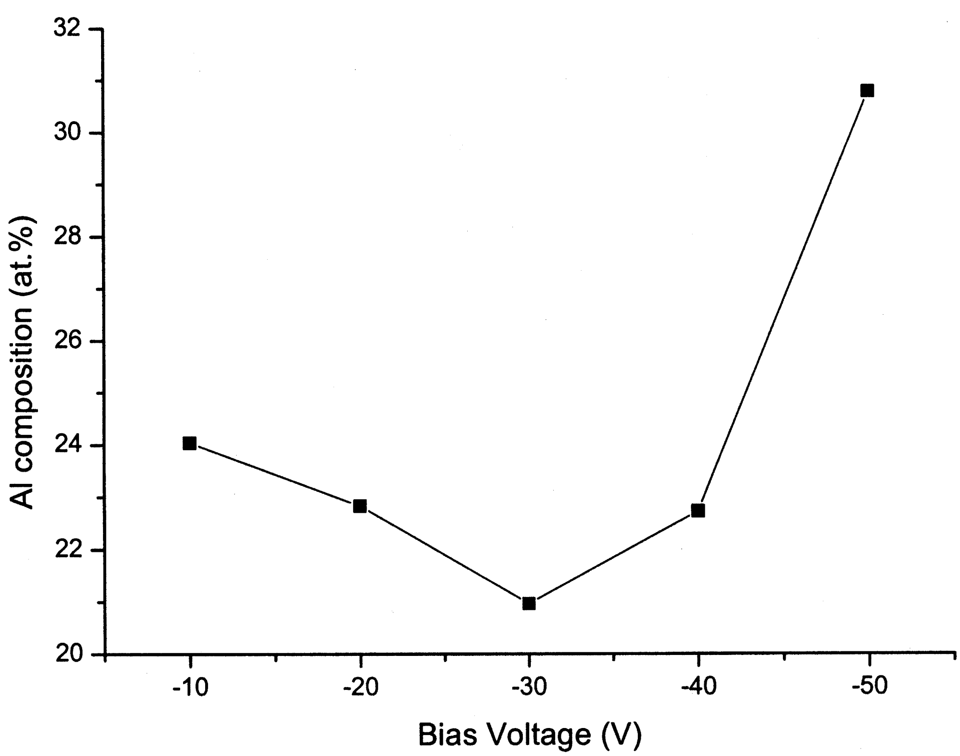

Fig. 4. Al atomic content versus bias voltage of AlO_x films on ITO-deposited PMMA. The AlO_x films were prepared at current of 10 mA, and oxygen flow rate of 2 sccm.

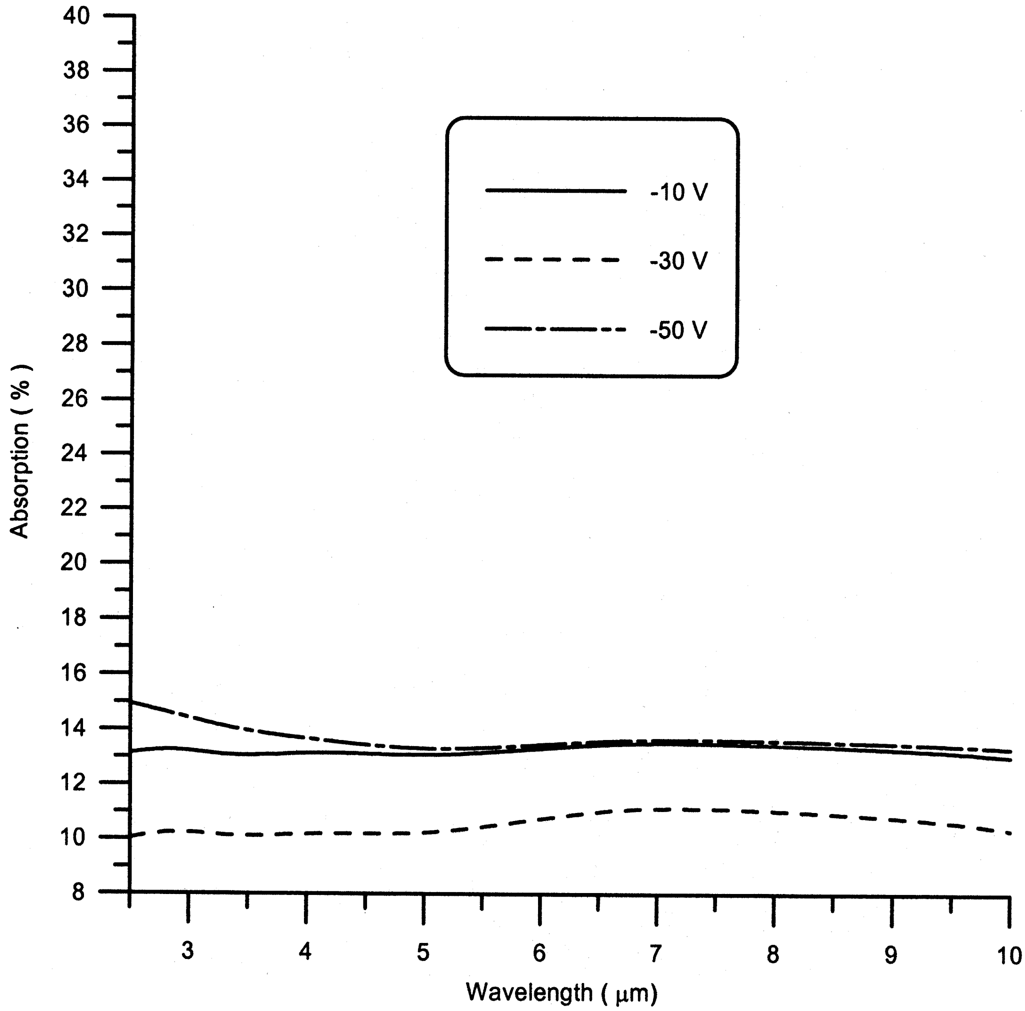

Fig. 5. Optical absorption spectra in the infrared region of ITO/AlO_x films. The AlO_x films were prepared at oxygen flow rate of 2 sccm, current of 10 mA, thickness of 60 nm, and different voltages.

Results in Fig. 2 also indicate a dramatic increase in absorption near a specific wavelength of 380 nm for all samples deposited under various bias voltages. Absorption of ITO/AlO_x films at 380 nm shown in Fig. 2 is also plotted versus bias voltage as expressed by the solid line in Fig. 3. Results indicate that the absorption of ITO/AlO_x films initially increased with the increase of the bias voltage. As the bias voltage exceed a critical value of −30 V, the absorption decreased however. A similar trend was observed in samples deposited under a relatively higher oxygen flow rate of 4 sccm (dotted line in Fig. 3) except that the critical bias voltage increased from −30 V to −40 V.

Fig. 4 shows Al atomic content versus bias voltage of AlO_x films on ITO-deposited PMMA. The AlO_x films were prepared at current of 10 mA, under oxygen flow rate of 2 sccm. Results in Fig. 4 indicate that Al content in AlO_x films initially decreased with the increase of bias voltage, then increased when the bias voltage exceed a critical value of −30 V. The Al content increased as the oxygen flow rate increased from 2 sccm to 4 sccm.

Fig. 5 shows the absorption in the infrared region of ITO/AlO_x films deposited under different bias voltages. The IR absorption decreased as the bias voltages increased from −10 V to −30 V, and then increased as the bias voltages increased to −50 V. Results in Fig. 4 indicated a minimum Al content appeared at the bias voltage of −30 V. The relatively low absorption at −30 V as shown in Fig. 5 was therefore probably due to its low Al content.

Fig. 6 shows the absorption in the infrared region of ITO/AlO_x films with different oxygen flow rates and thickness. The results indicate that the absorption invariably increased with the applied oxygen flow rate and film thickness.

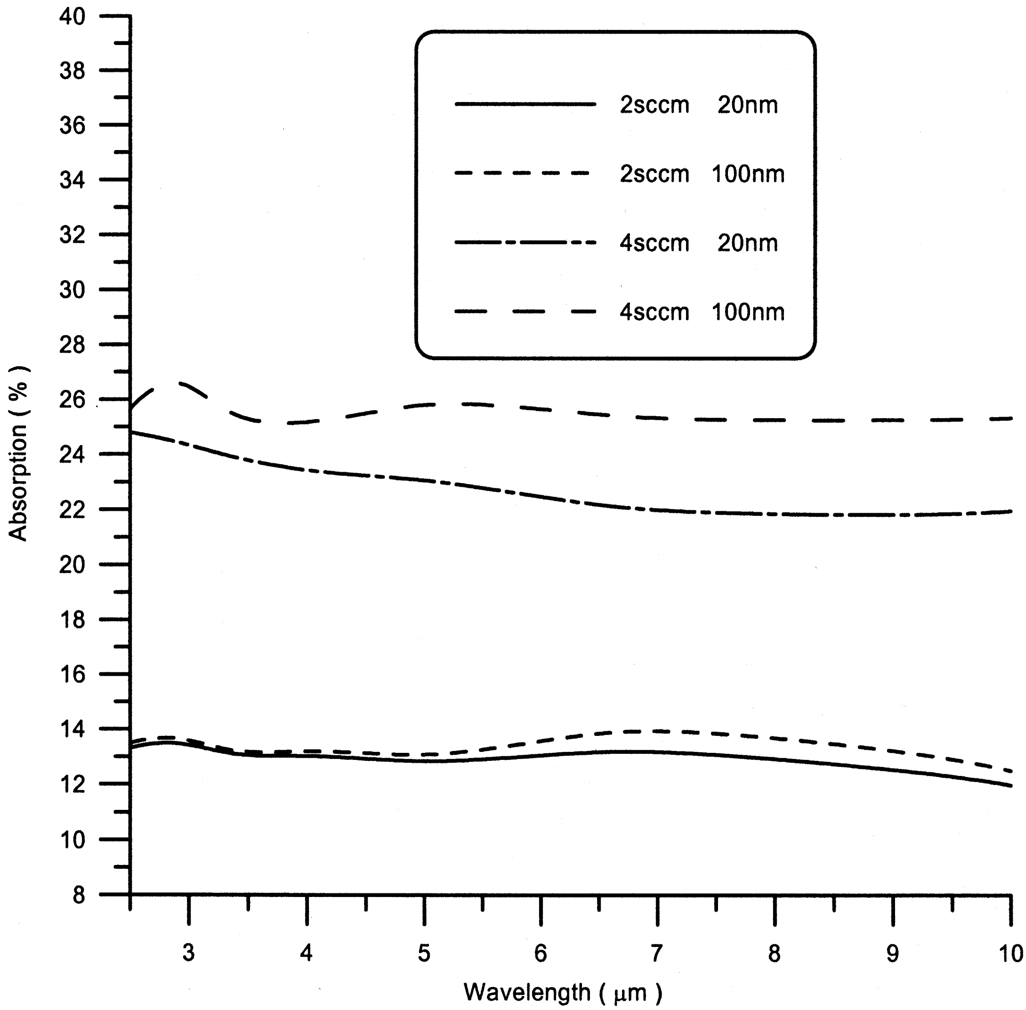

Fig. 6. Optical absorption spectra in the infrared region of ITO/AlO_x films. The AlO_x films were prepared at current of 10 mA, bias voltage of −20 V, at different oxygen flow rates and thickness.

5. Conclusions

1. The transmission of ITO/AlO_x films in the visible region was higher than that of ITO films. It indicated that AlO_x film coating is a good anti-reflective material.

2. A dramatic increase in absorption was observed near a wavelength of 380 nm. The absorption of ITO/AlO_x films increased initially with the increase of bias voltage. However when the bias voltage exceed a critical value, the absorption decreased again.

3. The IR absorption of ITO/AlO_x films are correlated with the Al content. The absorption in the infrared region of ITO/AlO_x films increased with the oxygen flow rate and film thickness.

Acknowledgements

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