Low temperature growth of ITO transparent conductive oxide layers in oxygen-free environment by RF magnetron sputtering

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Abstract. Indium Tin Oxide (ITO) thin films were grown at room temperature (RT) in oxygen-free environment by rf-magnetron sputtering on glass and Si(100)-substrates. The effects of argon pressure, sputtering power and film thickness on the electrical and optical properties of ITO films were investigated. For a 100 nm thick ITO films grown at RT in argon pressure 1.95·10^-3 mbar and sputtering power of 50 W, the transmittance was near 90% at 480 nm and resistance was 5.4·10^-4 Ohm·cm. It has been shown that the sputtering power plays an important role in electric properties of ITO films. SEM images of these samples show smooth surface with sharp substrate/ITO interface.

1. Introduction
Indium Tin Oxide is used in a wide range of important applications: LCD panels, solar cells, touch panels and electronic inks due to its high transparency in the visible part of the spectrum and low electrical resistivity ~10^-4 Ohm·cm. It is a degenerate n-type semiconductor with a large bandgap of around 4 eV [1]. Among various sputtering techniques ITO films can be obtained by rf-magnetron sputtering resulting in thin films with good homogeneity and thickness uniformity.

Electro-optical properties of sputtered ITO films are sensitive to the growth conditions, such as substrate temperature, sputtering power or pressure [2]. Usually ITO films are grown under argon-oxygen environment and elevated temperatures (>350° C). This causes various restrictions on substrate material choice – only high thermal and oxygen resistance materials can be used. A few publications have reported high quality ITO films grown at low temperatures [3,4]. This work presents the optical and electrical properties of ITO films grown at room temperature by rf-magnetron sputtering in oxygen-free environment.

2. Experimental
ITO films were deposited at room temperature on Si(100)-wafers and microscopic glass slides by rf-magnetron sputtering techniques (BOC Edwards Auto 500 RF) using (90% In₂O₃-10%SnO₂) 3” ITO-targets supplied by LTS Chemicals. Substrates were mounted on 300 mm stainless steel rotating disk. Distance between target and substrate was 100 mm. The sputtering chamber was evacuated to less than 5·10^-6 mbar prior to deposition. High purity argon gas (99.999%) was introduced at rate of 2-10 sccm. Before deposition, the target was always presputtered in argon plasma for 10 min to remove contaminants. No oxygen was added during deposition. The working pressure was varied from 1·10^-3
to $4 \cdot 10^{-3}$ mbar and rf power was varied from 20 to 65W. All the ITO samples were with film thickness about 100 nm.

Film thickness was measured with a stylus profiler AMBiOS XP-1. The resistivity of ITO films was measured with a conventional four-probe technique. The Hall mobility and carrier density of the films were determined by Ecopia HMS-5000. The microstructure of the samples was analyzed using a scanning electron microscope SUPRA 25-30-63. The optical transmittance of the films was measured using spectrophotometer based on Solar Laser Systems M266 monochromator. Refractive and absorption indexes of ITO film were measured using HORIBA JOBIN YVON and Horiba UVISEL2 Spectroscopic ellipsometers.

3. Results and Discussion

Figure 1 shows the ITO growth rate as a function of argon pressure at rf-power of 50 W. The curve has a maximum at gas pressure of $1.95 \cdot 10^{-3}$ mbar. At higher pressures, there is an increase of the collisions number between sputtered and argon atoms, resulting in decreasing deposition rate. Low argon pressure reduces the sputtering efficiency due to low carrier’s concentration near magnetron area [5]. All subsequent experiments were performed at argon pressure of $1.95 \cdot 10^{-3}$ mbar.

![Figure 1. ITO growth rate at rf-power of 50W as a function of the argon pressure](image)

SEM image of ITO film sputtered at rf-power of 50 W is shown in figure 2. A smooth surface without visible defects is observed. Similar morphology was observed for thin ITO films grown at rf-power of 20-65 W.

The deposition rate is found to be linearly dependent on the rf-sputtering power. Experimentally determined proportional coefficient was 2.98 nm/(hour·W). Similar dependences were observed in [3,4]. At sputtering power above 100 W periodic arc flashes over the magnetron area were observed. Therefore the subsequent experiments were performed at rf-power of 20-65 W.

The resistivity (Rho) of an ITO films sputtered on Si-substrate as well as on glass slices decreases with increasing of sputtering power (figure 3) and reaches a minimal value of $5.4 \cdot 10^{-4}$ Ohm·cm at 50 W. Further increase of sputtering power results in increasing Rho. The measured Hall mobility of the majority carrier for the ITO film grown at 50 W was $17.4 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and the carrier concentration was $6.8 \cdot 10^{20} \text{ cm}^{-3}$ (regardless of the substrate). Similar relations were obtained in [3] where authors shown changes in ITO structure (from a mixed amorphous/crystalline phase to polycrystalline) with increasing of rf-power. The results of the XPS analysis performed in [3] indicate that thin ITO films with minimal resistivity achieve the Sn/In ratio value of 0.099 as in sputtering target.
Sputtering power as well as argon pressure did not have a distinct influence on the refractive index (n) of ITO films. It was equal to 1.97 ± 0.01 (at 632.8 nm) under rf-power of 20-65 W and working pressure of 1-4·10^{-3} mbar. A measured plot of the refractive index as a function of the wavelength for the sputtered at 50 W ITO thin film can be seen in figure 4. It can be seen that in the main spectral transmission region the refractive index increases towards shorter wavelength. Additionally the squared line in figure 4 shows the extinction coefficient (k) as a function of the wavelength. The absorption coefficient, α, is related to the extinction coefficient, k, by the following formula:

$$\alpha = 4 \pi k \lambda^{-1}. \quad (1)$$
Figure 4. Measured optical constants of 100-nm ITO film sputtered at power of 50 W.

The transmittance spectra of the deposited ITO films at different rf-power are shown in figure 5. The transmittance of the glass slices was also measured for comparison (thick line).

Figure 5. Optical transmittance spectra of ITO films vs rf-power. Inset shows a transmittance value of ITO films at $\lambda=480$ nm vs rf-power.

It can be seen that the 100 nm ITO films deposited on 1.0-mm microscopic glass slides were 80-90 % transparent in the visible region. Below 400 nm ITO films show strong absorption because of sub-band and band-to-band absorption. Also it was shown (figure 5 inset) that ITO transmittance $\lambda=480$ nm increases with decreasing of rf-power (at constant ITO thickness). It can be explained by
changes in crystalline structure of ITO films with rf-power [3]. ITO films deposited at rf-power of 25 W and argon pressure of $1.95 \cdot 10^{-3}$ mbar had the best transmission with the resistivity of $6.7 \cdot 10^{-4}$ Ohm·cm. Lower rf-power values result in low deposition rate (< 74 nm/hour) and unstable plasma behavior.

ITO films grown under rf-power of 50 W had the best conductance with transmittance of 85-90% in visible region. Also it was found no significant effect of argon pressure on the electrical and optical properties of the ITO films.

**Conclusion**

High quality 100 nm ITO films were grown on Si-substrate and glass slices by rf-magnetron sputtering at room temperature in oxygen-free environment. The sputtering power was shown to play a major role in ITO film resistivity and transmittance. For a 100 nm thick ITO films grown at RT in argon pressure of $1.95 \cdot 10^{-3}$ mbar and sputtering power of 50 W, the transmittance was near 90% at 500 nm and resistivity was $5.4 \cdot 10^{-4}$ Ohm·cm.

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