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ITO thin films prepared by electron beam evaporation with End-Hall ion source assisted without heating to the substrat

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Abstract: ITO (indium oxide doped with tin) thin films were deposited on glass substrates by using ITO pellet with a composition of $w(In_2O_3)=90\%$ and $w(SnO_2)=10\%$ by electron beam evaporated with End-Hall ion source assisted without extra heating. The rate of deposition and flow rate of oxygen were measured and changed to obtain the best properties of ITO thin films. Furthermore, the post annealing process was done in vacuum at different annealing temperatures for 2 h and at 400℃ for different keeping time, respectively. The relation between optical, electrical properties and structure was discussed in detail.

Key words: ITO film; End-Hall ion source; optical transmittance; sheet resistance; annealing

1 Introduction

ITO (indium oxide doped with tin) transparent conducting films have unique optical and electrical properties of high transmittance in the visible region and strong reflectance in the infrared region as well as the excellent conductivity. For these characteristics, ITO films play an important role in the field of optoelectronic devices, such as transparent electrode for electromagnetic interference (EMI) shielding, electrochromic window[1], liquid crystal displays (LCD)[2], and architectural applications. A variety of thin film deposition techniques have been employed to make ITO films, including chemical vapor deposition[3], reactive evaporation[4], DC magnetron sputtering[5] and pulsed laser deposition[6], etc. It was reported that the electrical and optical properties of ITO films were found to strongly dependent on the growth conditions and deposition methods. Therefore, it is necessary to choose an appropriate process to make high quality ITO film.

Traditional e-beam evaporation method could hardly make the ITO thin films with high optical and electrical quality and less roughness. To make up the disadvantage of the e-beam evaporation, it was well known that many assisted deposition techniques were employed to modify many of the optical and physical characteristics of thin films and they were different from most ion assisted deposition (IAD) techniques available for depositing ITO thin films by e-beam evaporation, such as broad beam cold cathode ion source[7], Kaufman-type ion source[8], ECR ion source[9], etc. There was few study on the use of End-Hall ion source to assist the deposition of ITO transparent conductive film.

The use of End-Hall ion source assisted

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deposition with the substrate heated at a certain temperature could easily prepare good quality ITO films of 200 nm thick with the mean transmittance in visible light of 90% and the sheet resistance of 13 Ω/□.

In our study, End-Hall ion source was used to assist the e-beam evaporation to deposit ITO films at low temperature. By changing the rate of deposition and flow rate of oxygen, the properties of ITO thin films were studied to find out the effect of deposition condition on the properties of ITO films, including optical and electrical properties. A post vacuum annealing process was done to the ITO films, as well.

2 Experimental detail

The ZZSX-1600 coater with electron beam gun and End-Hall plasma ion source were used for the deposition of ITO films. It has an evacuation system of mechanical vacuum pump, oil diffusion vacuum pump. The schematic of experimental setup for deposition was shown in Fig. 1. The evaporation source material in this study was ITO pellet with a composition of $w(In_2O_3) = 90\%$ and $w(SnO_2) = 10\%$. The substrates were carefully polished K9 glass pretreated with washing acetone. The substrate was unheated.

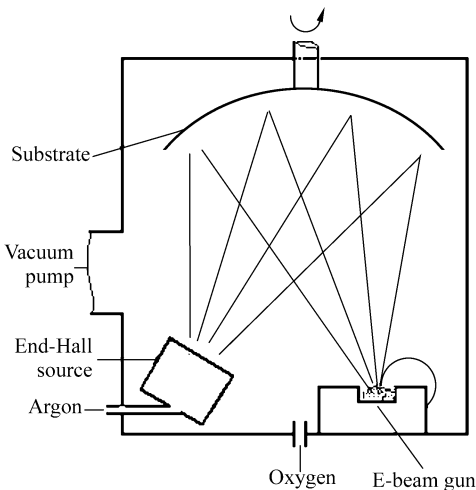

Fig. 1 Schematic diagram of the deposition of ITO by PIAD

Two separate mass flow controllers were used to monitor the gas flow rate of argon and oxygen. Base pressure of the chamber was 1.0×10^{-3} Pa. Argon gas was introduced into the End-Hall source and the oxygen gas was used as the reactive gas coming into the chamber. Adjusting the anode voltage and current, make the argon ionized and produce glow discharge. The deposition was carried out at dynamic pressure below 1.2×10^{-2} Pa. The deposition rate and oxygen flow rate were changed separately to observe the properties of ITO films changing at low substrate temperature.

After the deposition, the samples were separately annealed in vacuum with the pressure lower than 1×10^{-3} Pa at different annealing temperatures for 2 h and for different annealing time at 400℃.

The film deposition rate was monitored by INFICON IC/5 Thin Film Deposition Controller. The optical transmittance spectra of the films were recorded by Perklin-Elmer Lambda 900 UV/VIS/NIR spectrometer. Sheet resistance of the films was measured by Model BD-86 Semiconductor Resistivity Meter. Film structure was investigated by SHIMADZU XRD-6000 performed between the values of 20～70° with a step of 0.05°.

3 Results and discussion

When taken out from the vacuum coater, all the samples of ITO films were brown visual appearance without extra heating to the substrate by e-beam evaporation with End-Hall ion source assisted. The calculated thickness data was 280～290 nm by characteristic matrix[10].

Fig. 2 shows the influence of the oxygen flow rate on sheet resistance and maximum transmittance in visible spectral region of ITO thin films. The argon flow rate, deposition rate and the anode current and voltage of the End-Hall ion source were kept as constant for 10.0

cm^3/min, 0.6 nm/s, 5 A, 180 V, respectively. The sheet resistance increased much with the oxygen flow rate increasing till to 1.53 kΩ at 25 cm^3/min of oxygen flow rate. The transmittance in visible spectral region of the ITO films deposited with little oxygen was lower than those with high oxygen content in the chamber.

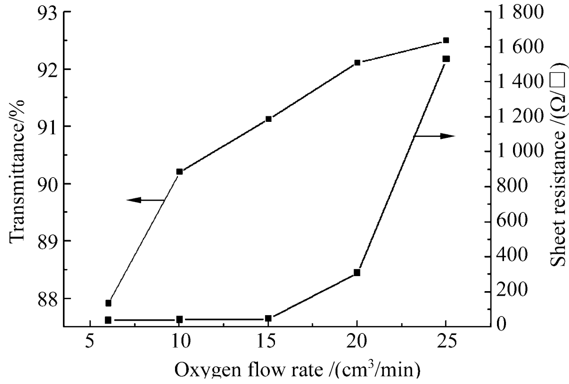

Fig. 2 Influence of oxygen flow rate on sheet resistance and maximum transmittance in visible spectral region of ITO thin films

The adequate oxygen content in the ITO films suggested that insufficient oxygen vacancies and sufficient oxidization of the indium. The decreasing carrier concentration resulted in a low conductivity. A lot of opaque low valence state compound of In and Sn changed to transparent In_2O_3 and SnO_2. Therefore, the transmittance in visible light region was raised.

Fig. 3 shows the effect of the deposition rate on sheet resistance and maximum transmittance in visible spectral region of ITO thin films. The argon flow rate, oxygen flow rate and the anode current and voltage of the End-Hall ion source were kept as constant for 10.0 cm^3/min, 15.0 cm^3/min, 5 A, 180 V, respectively. With the oxygen flow rate increasing, the sheet resistance decreased slightly first and then increased greatly. The transmittance in visible spectral region of the ITO films fell down gradually as the deposition rate increased.

Fig. 4 shows the XRD diffraction spectral of different deposition rates of 0.3, 0.4, 0.6, 0.8

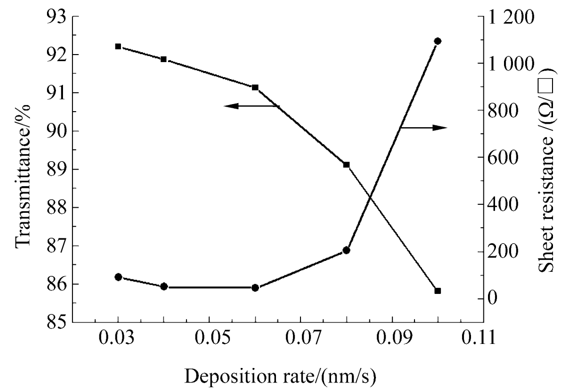

Fig. 3 Influence of deposition rate on sheet resistance and maximum transmittance in visible spectral region of ITO thin films

and 1.0 from the top to the bottom, respectively. With the deposition rate increased, the crystalline of the ITO films became worse till the deposition rate reached 0.8 A/s, the crystalline of the ITO films disappeared.

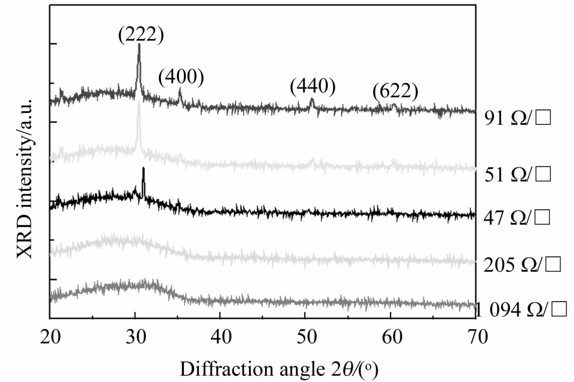

Fig. 4 XRD diffraction spectral of different deposition rates of 0.3, 0.4, 0.6, 0.8 and 1.0 from the top to the bottom, respectively

Compared to the Fig. 3, it can be concluded that the microstructure of the ITO films were closely related to the sheet resistance. The film with crystalline all had low sheet resistance below 100 Ω/□. The low deposition rate was good to the nucleation and grain formation of the ITO layer. When the rate of deposition exceeded 0.06 nm/s, it noticed that the diffraction peak disappeared and the sheet resistance changed greatly with amorphous structure. The factor

influenced the transmittance in the visible light region was gradually decreased due to insufficient oxidation of In and Sn.

Therefore, it was the optimum deposition rate that could produce the better ITO films with high transmittance in visible spectral region and good conductivity.

Fig. 5 presented the X-ray diffraction intensity as a function of 2θ with different annealing temperatures from 100℃ to 400℃ at interval of 100 for 2 h in vacuum from the bottom to the top of the figure, respectively. At 100 ℃, no perceptible change in the microstructure could be observed compared to the sample without annealing process. And then, the crystal initiated with weak [222] diffraction peak at 200 ℃, the intensity of [222] peak increased to the maximum at 400 ℃ and [400] peak not obvious to make out. As the annealing process, the sample became polycrystalline with a cubic In_2O_3. The crystalline film deposited of PIAD using End-Hall ion source was highly [222]-oriented, the same with the films e-beam evaporated with ion beam assisted.

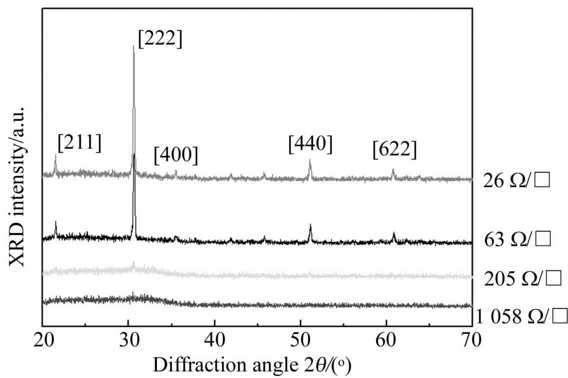

Fig. 5 X-ray spectra of samples with different annealing temperatures in vacuum

Fig. 6 shows the optical transmission curves as a function of annealing temperature for 2 h. The bandgap of ITO films was moved to the high-energy side as the temperature increased, especially after 300 ℃. MB (Moss-Burstein) shift had given detail explanation of the absorption edge shift to the shorter wavelength with increasing carrier concentration[11]. So, it could be believed that the absorbing oxygen atoms on the surface of the films escaped gradually with the perfect crystalline forming and a lot of oxygen vacancies were produced, such as the crystalline samples annealed at 300 ℃ and 400 ℃. Therefore, the carrier concentration increased much, which made the absorption edge shorter.

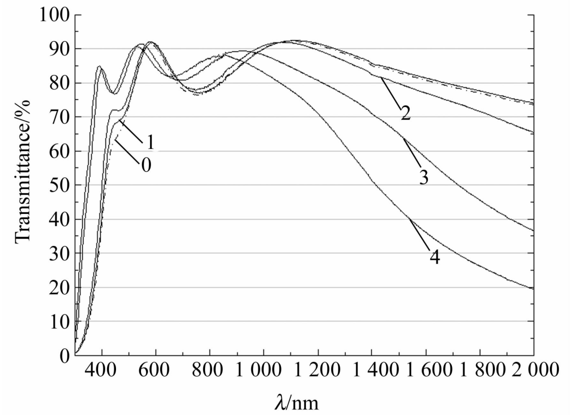

Fig. 6 Optical transmission curves as a function of annealing temperature for 2 h. 0. as-deposited films without annealing treatment; 1. 100 ℃; 2. 200℃; 3. 300 ℃; 4. 400 ℃.

The spectral cut-off region between NIR (near infrared) reflection and the visible light transmission was fairly close to a better filter when heat treatment was at 400 ℃. During this region, the free electron carrier absorption became critical for the optical properties of ITO films[10]. Therefore, the continuous decreases in the transmittance at the NIR region with the raising annealing temperature implied the sequential increases in the carrier concentrations. It was consistent with the bandgap moved to the high-energy side because of carrier concentration increased.

Fig. 7 shows X-ray diffraction intensity as a function of 3θ with different annealing keeping time at 400℃ for 0. 5, 1, 1. 5, 2 h in vacuum from the bottom to the top of the figure, respectively. There was no evident difference between

the four curves peak distribution. The only dissimilarity was peak intensity with little change. The structure of ITO thin films would influence the optical and electrical properties[12]. The annealing keeping time in vacuum could not make remarkable transformation of the ITO films so that the properties of ITO films were little influenced by the time change.

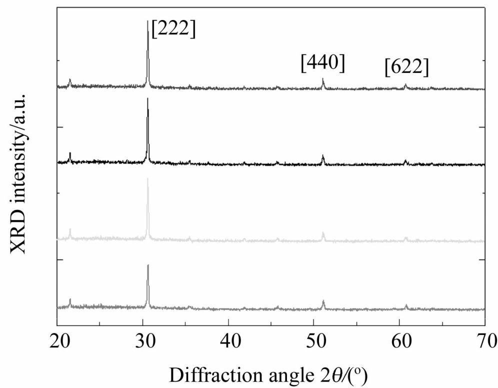

Fig. 7 XRD diffraction spectral of different annealing keepking time of 0. 5, 1, 1. 5, 2. 0 h at 400 ℃

From the Fig. 7 and Fig. 5, it can be concluded that the temperature was a crucial factor for the structure of ITO films. The properties of the films would be improved as long as the temperature was appropriate.

4 Conclusions

The ITO films had been well deposited by e-beam evaporation with End-Hall ion source assisted at low temperature. By changing the deposition rate and the oxygen flow rate, the optical and electrical properties of the ITO films changed much. By vacuum annealing, the ITO films with high transmittance and high sheet resistance were well improved with better conductivity. Compared with the sheet resistance, transmittance and microstructure, it can be concluded that the structure of ITO films changing from amorphous to crystalline can bring about a great change in sheet resistance. The proper deficient oxygen was good to the conductivity of the ITO films at less expense of losing transmittance. Furthermore, End-Hall plasma ion source was a better source to assist deposition ITO thin films. It should be a promising method to deposit ITO films.

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Professor GAO Jing-song received his bachelor degree on July 1993 at Zhejiang University of China, and started to work at Changchun Institute of Optics, fine Mechanics and Physics, Chinese Academy of Sciences (CIOMP). After working 2 years, he continued to study, and got master degree, major in optics on July 1993 in CIOMP. Till now he has 15 years experince in optical coating design and manufacture. He has published several papers about coating science in referee journals and conference proceedings, he has really tough background about coating technology and is quite familiar with the research field of optical thin films.