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Microstructure and performances of ITO film prepared by ion beam sputtering

Abstract: Ion beam sputtering deposition was firstly introduced to prepare indium tin oxide (ITO) film in this study. The ITO film was annealed at different temperature in a flow of nitrogen or air, respectively. The effect of annealing process on the microstructure, optical and electrical performances of the ITO film was studied. The results showed that the crystallinity and optical properties of the ITO film were improved with the increase of annealing temperature. The transmittance of the ITO film in visible regions increased up to 96% after it was annealed at 500℃ in nitrogen or in air. It was found that the resistivity of ITO film depended on both the annealing temperature and the annealing atmosphere, which showed a close relationship to the atomic percentage's sum of oxygen vacancy and Sn^{4+}, which was quantified by XPS result.
***Keywords**:* ITO film, ion beam sputtering, annealing, performances

1. Introduction

As an oxide semiconductor with a wide band gap, indium tin oxide (ITO) is transparent and electrically conductive due to its high electrical conductivity and good transmittance in the visible wavelength region. It has wide applications in the transparent electrodes such as various optoelectronic devices, antistatic conductive coatings, solar cells, electrochromic devices [1-3]. Recently, ITO film has been used as high-temperature strain sensors, thermocouples, and thermoelectric devices due to their excellent chemical stability, phase stability, and resistivity to oxidation at elevated temperatures [4-7]. In the last few years, various deposition methods such as RF magnetron sputtering, thermal evaporation, pulsed laser deposition, spray pyrolysis and etc. for obtaining ITO films were developed [8-11]. Compared with other deposition methods, the films fabricated by ion beam sputtering deposition (IBSD) had an excellent adhesion to the substrate since a wide atomic intermixed zone could be set up at the film/substrate interface by ion-assisted dynamic mixing, which played a very important role in improving the interface quality [12-14]. Besides, the moderate energy of ion-assisted source could significantly improve the flatness and compact density of the films [15-16]. However, there has few reports about the ITO film deposited by IBSD so far.

In this paper, The ITO film was deposited by IBSD technique and the influence of annealing process on the microstructure, surface morphology, optical and electrical performances of ITO films were investigated by SEM, XRD, XPS, and four probe conductivity measurement.

2. Experimental

The ITO films were deposited on both Al_2O_3 substrate and glass substrate by a IBSD system (Beijing Institute of Advanced Ion Beam Technology), as indicated in our previous study [17]. All the substrates were ultrasonically cleaned to remove organics and other impurities. High purity (99.99%) ITO (In_2O_3:SnO_2 = 90:10 wt %) disk with a diameter of 100 mm was used as the target. The base pressure was about 5×10^{-4}Pa and working pressure was 2.0×10^{-2}Pa. The energy and current for ion source was 900eV and 80mA, respectively. The substrate kept rotating to enhance uniformity of ITO film. Prior to ITO deposition, a pre-bombardment of target with ion source for 3 min was carried out to remove the contamination layer on the surface of ITO target. And the samples were cleaned with assisting ion source for 2 min so as to clean the sample and enhance the samples' affinity for target composition. The deposition time was 2 hours and the thickness of film was 1.2um.

After the deposition, the films deposited on the

Al_2O_3 substrate were annealed in a flow of air or nitrogen for 1.5h at the temperature varying from 200℃ to 800℃. The films deposited on the glass substrate were annealed in a flow of air or in nitrogen for 1.5h at the temperature from 200℃ to 500℃ since the melting point of glass substrate was lower than that of Al_2O_3.

The crystal phase of the ITO film was measured using X-ray diffraction (XRD) with a Cu Ka source. The morphology was observed by Scanning Electron Microscopy (SEM). The chemical composition and chemical state were analyzed using X-ray photoelectron spectroscopy (XPS). The thickness of the film was determined by a-step surface profiler. The sheet resistance was measured by a four-point probe. The optical transmittance spectrum was measured by a PerkinElmer Lambda 950 UV/VIS Spectrometer. The ITO films deposited on alumina substrate were used for XRD, SEM, XPS and sheet resistance characterization, while the ITO films deposited on glass substrate were used for thickness and optical transmittance measurement.

3. Results and discussion

3.1 Crystal structure

Figure 1 showed the XRD patterns of the as-deposited ITO film on Al_2O_3 substrates and the annealed ones at different temperatures in a flow of air or nitrogen. The XRD patterns revealed a clear polycrystalline structure of ITO films. The peak at 2θ = 30.7°, 35.6° and 21.7° was attributed to (222), (400) and (211) of polycrystalline cubic bixbyite In_2O_3, respectively. The peak at 2θ = 25.7°, 35.3° and 43.5° was due to (012), (104) and (113) of Al_2O_3 substrate, respectively. None of the spectra indicated any characteristic peaks of Sn, SnO or SnO_2, which meant that the tin atoms were doped substitutionally or interstitially into the In_2O_3 crystal lattice. The as-deposited ITO film in this study showed good crystallization than that prepared using RF sputtering, DC sputtering and electron beam evaporation [18-20], all of which showed an amorphous nature. The most prevalent peak related to the (222) plane indicated a preferential orientation of the ITO film. It can be seen that the intensity of (222) plane became more significantly high with the increase of annealing temperature, both in air and in nitrogen. All diffraction peaks were shifted to larger 2θ angles by 0.1°-0.5° after annealed, as depicted in Table 1. This implied that post annealing process shrank the lattice constant or caused a change in the residual strain between the lattice planes resulting in a decrease of the lattice parameter [21]. Furthermore, the grain size was calculated according to Sherrer's equation, as listed in Table 1. For both the ITO films annealed in nitrogen and in air, the grain size increased with increasing temperature. However, for the same annealing temperature, the grain size of ITO in nitrogen was bigger than that in air, indicating the annealing gas also influenced the grain size of ITO film.

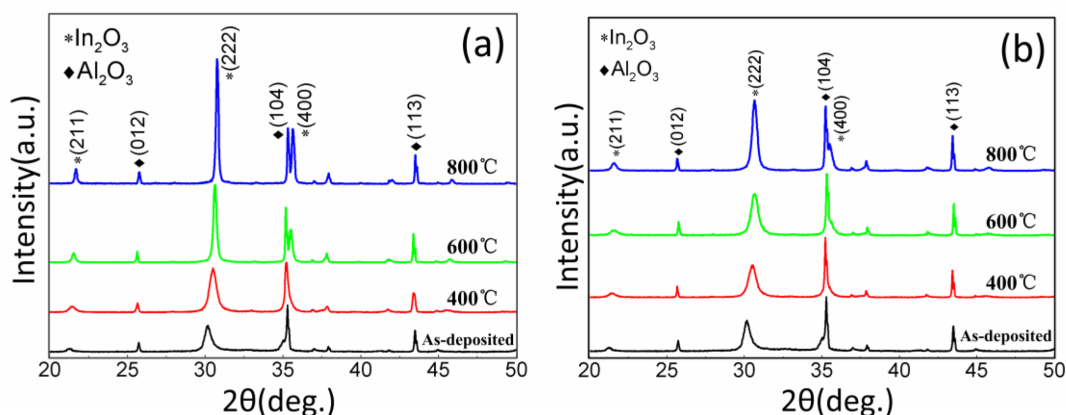

Figure 1. XRD patterns of ITO thin films deposited on Al_2O_3 substrate annealed at different temperature in N_2 (a) or in air (b).

Table 1 XRD parameters and grain size of ITO film annealed at different temperature

Annealing environments	2-Theta$_{(222)}$(°)	FWHM$_{(222)}$(°)	Grain size(nm)
As-deposited	30.066±0.004	0.475±0.010	17.7±0.5
400°C in Nitrogen	30.438±0.004	0.536±0.006	20.6±0.3
600°C in Nitrogen	30.593±0.001	0.224±0.002	41.1±0.4
800°C in Nitrogen	30.745±0.001	0.153±0.001	71.1±0.6
400°C in air	30.451±0.006	0.594±0.009	19.1±0.3
600°C in air	30.611±0.005	0.547±0.008	32.3±0.3
800°C in air	30.630±0.002	0.373±0.003	43.0±0.3

SEM images of the as-deposited and annealed ITO films at different temperatures were shown in Fig. 2. It could be seen that the grain size increased as the annealing temperature increased, both in nitrogen and in air. The average grain size of the as-deposited ITO film was about 17nm. When the annealing temperature was 400℃, the grain size was about 20nm both in nitrogen and in air. However, when the temperature rose to 600℃, the grain size increased obviously, with 40nm in N_2 and 30nm in air. The grain size further increased when the temperature was up to 800℃, with 70nm in N_2 and 50nm in air, respectively. It was found that the films annealed below 600℃ had uniform grains, while the films annealed at 800℃ had both big and small grains. Meanwhile, the grain size of the ITO film annealed in N_2 was bigger than that in air at the same temperature, which was in good agreement with the X-ray diffraction analysis mentioned above.

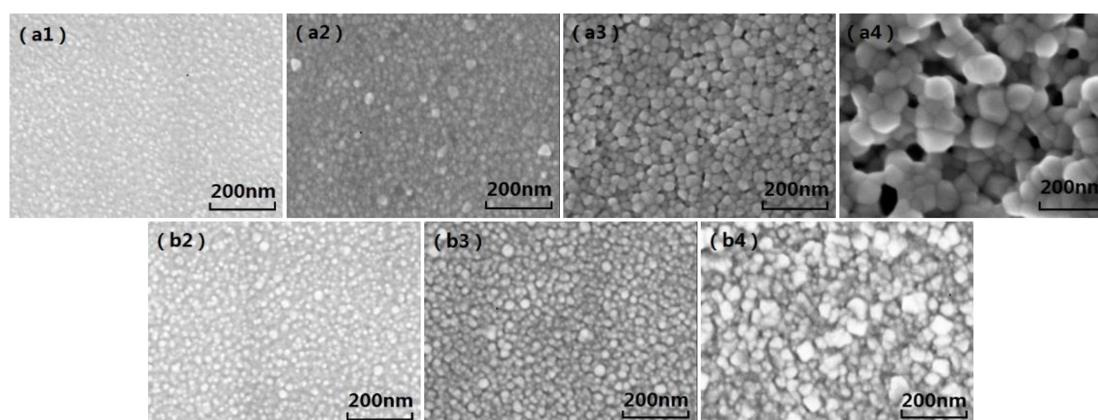

Figure 2. SEM images of ITO films annealed at different temperatures in N_2(a) or in air(b)
(a1) as-deposited； (a2) 400℃ N_2 ；(b2) 400℃ air；(a3) 600℃ N_2；(b3) 600℃ air；(a4) 800℃ N_2 ；(b4) 800℃ air

3.2 Optical transmittance

Fig. 3 showed the transmittance spectra in visible regions for the ITO films as deposited and annealed at different temperatures in air or in nitrogen, respectively. It clearly showed that the as-deposited film nearly couldn't transmit light. With the annealing temperature increased from 200°C to 500°C, the transmittance of the ITO films within the visible light range improved. Meanwhile, the steepness of the band edge absorption also increased.For the ITO film annealed both in nitrogen and in air, the maximum transmittance of 96% was achieved, which was higher than 79%-85% of the ITO film deposited by rf sputtering and other deposition technique [22-24]. The increased transmittance of the ITO film in visible light range was closely related with the improvement in its crystal structure and stoichiometry [25]. In this study, the improved transmittance was attributed to the good

crystallization of as-deposited ITO film, as indicated in XRD patterns of Fig.1. With increasing annealing temperature, the grains of the ITO film grew, as verified by XRD and SEM results. The decreased number of grain-boundaries resulted in few light scattering, which contributed to the improved transmittance of the ITO film. For the ITO film annealed in air, improved O/In stoichiometry or compensation of some oxygen vacancies in the crystals probably contributed to the increase of the transmittance although it had smaller grains than the ITO film annealed in nitrogen [26].

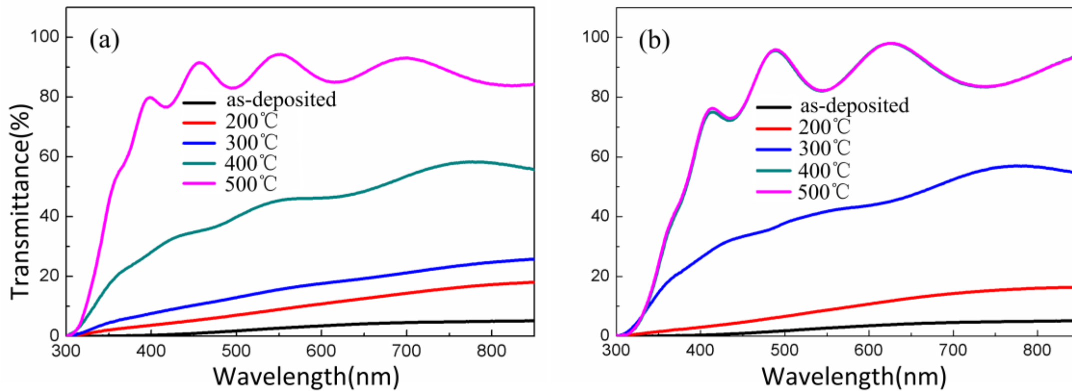

Figure 3. Transmittance spectra of the ITO films as deposited and annealed at different temperatures in different atmospheres (a) in N_2, (b) in air.

3.3 XPS measurement

Fig.4 showed the core level of $In3d_{5/2}$, $In3d_{3/2}$,$Sn3d_{5/2}$, $Sn3d_{3/2}$,and O1s for the as-deposited ITO and the one annealed at 800℃ in N_2 and in air. Compared to that of the as-deposited ITO film, the core levels of both the annealed ITO films shifted to high binding energy, both in N_2 and in air. films. For $In3d_{5/2}$, the shift to high binding energy was about 0.12eV. The shift for $Sn3d_{5/2}$ was 0.22eV and 0.27eV for O1s, respectively. The shift to high binding energy was probably related to the increase of carrier concentration or the good crystallization of the ITO films [27,28].

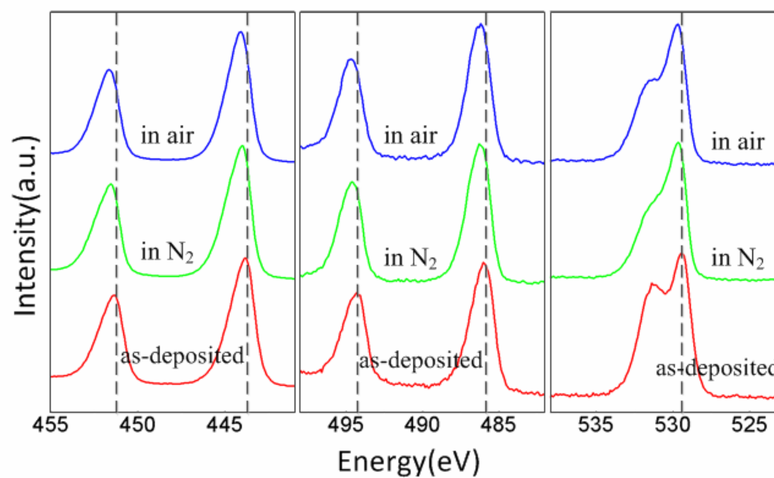

Figure 4. X-ray photoelectron spectra corresponding to In 3d, Sn 3d, and O 1s for the as-deposited and annealed ITO films at 800℃ in N_2 and in air.

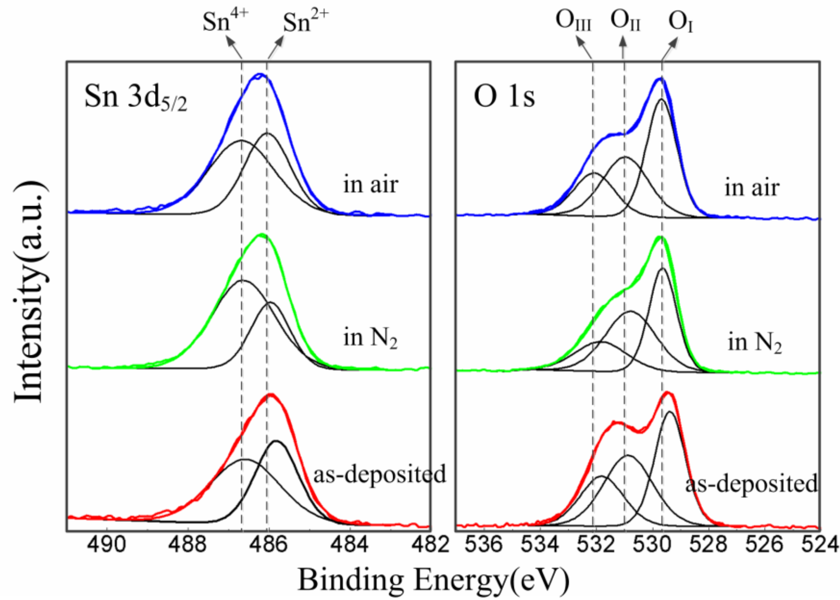

Figure 5. Curve-fitting analysis for Sn3d and O1s of the as-deposited and post-annealed ITO films

In order to analyze chemical state of Sn and O semi-quantitatively, curve-fitting for the core levels of $Sn3d_{5/2}$ and O1s was performed, as shown in Fig.5. It was found that the spectrum of $Sn3d_{5/2}$ composed of two peaks centered at 486.4eV (Sn^{4+}) and 485.8eV(Sn^{2+}), while the O1s composed of three peaks O_I, O_{II} and O_{III}. The atomic percentages of all the peaks were summarized in Table 2. The as-deposited ITO film showed the smallest atomic percentage of Sn^{4+} (SnO_2), while the annealed films showed the increased Sn^{4+} percentage. Comparatively, the ITO film annealed in nitrogen had a more obvious increase in Sn^{4+} percentage than that in air. The increased Sn^{4+} content after post-annealing might be related to the increased carrier concentration since the donor state of ITO originated from the Sn^{4+} ions substituting into the In^{3+} site and oxygen vacancies [29,30].

Table 2. Atomic percentages/ratios of the as-deposited and annealed ITO films.

	Atomic percentages/ratios							
	In-$3d_{5/2}$	Sn-$3d_{5/2}$		O-1s				
ITO film	In	Sn^{2+}	Sn^{4+}	O_I	O_{II}	O_{III}	O_{II}/ O_I	O_{II}+Sn^{4+}
800°C in air	31.2	1.6	2.1	28.8	22.1	14.0	0.77	24.28
800°C in N_2	32.5	1.2	2.6	24.5	23.4	15.5	0.95	26.09
As-deposited	32.3	1.6	1.9	24.7	24.2	15.0	0.98	26.26

The O1s can be divided into three peaks, O_I at 529.5eV ± 0.2eV, O_{II} at 530.8eV ± 0.1eV and O_{III} at 531.9eV ± 0.1eV, respectively. The O_I peak was associated with metal-oxide binding (i.e. the In-O bond in In_2O_3)[30,31]. The O_{II} peak corresponded to the oxygen vacancies [30,31]. The O_{III} peak was

related to the surface oxygen due to the hydrocarbons, surface contamination and so on [32]. From Table 2, it can be seen that two post-annealed films exhibited lower oxygen vacancy content than as-deposited film. Comparing the three ITO films, although the ITO film annealed at 800°C in air had the most metal-oxide bonds, its ratio of O_{II}/ O_I was the smallest indicating the ITO film annealed in air showed the lowest oxygen vacancy content. In addition, the substitution of In^{3+} by Sn^{4+} would generate free electrons and oxygen vacancies, which also contributed to free electron population. So the sum of O_{II} and Sn^{4+} percentage (O_{II}+Sn^{4+}) indicated the number of carrier concentration in the film. The ITO film annealed in nitrogen showed almost the same carrier concentration as the as-deposited ITO film. However, the ITO film annealed in air had the least carrier concentration.

3.4 Electrical conductivity

Fig. 6 showed the effect of annealing temperature and atmosphere on the resistivity of the ITO film. It can be seen that the resistivity of the ITO films was greatly influenced by the annealing temperature and annealing atmosphere. The resistivity of as-deposited ITO film was 8.9×10^{-4}Ω.cm, which was lower than that of ITO film prepared by thermal evaporation (9.1×10^{-4}Ωcm) [34]. The ITO film showed a slightly decreased resistivity with the increase of annealing temperature. When the annealing temperature increased to 800℃, the resistivity of the ITO film annealed in N_2 decreased slightly to 7.4×10^{-4}Ωcm.

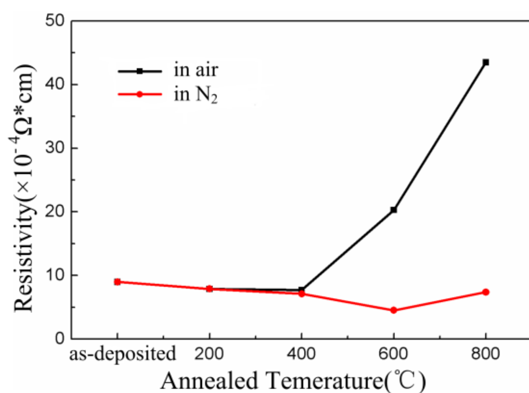

Figure 6. Resistivity of the ITO films deposited and annealed at different anneal temperature in N_2 or in air.

However, for the ITO film annealed in air, the resistivity also decreased a little (7.6×10^{-4}Ωcm at 400℃) when the annealing temperature was below 400℃. But, its resistivity increased obviously (43.5×10^{-4} Ω cm at 800℃) when the annealing temperature further rose to 800℃. Generally, the resistivity of ITO film is related with both the carrier mobility and carrier concentration. The carrier mobility is influenced by crystal micro-structure such as grain boundary or crystal homogeneity. Annealing process made crystal microstructure of ITO film homogenous, and also made grains grow to bigger size, which decreased the number of grain boundaries. In this study, the carrier concentration is related with both tin dopants and oxygen vacancies. When the ITO film was annealed in air, the free oxygen would react with the ITO films, which resulted in the decreased carrier oxygen vacancies, thus decreased carrier concentration. For ITO film annealed at temperature below 400°C, the improved mobility due to crystallization played a more important role than the decreased carrier concentration, therefore, its resistivity slightly decreased. However, for the ITO film annealed at temperature above 400°C, the ITO film would react with air oxygen strongly, as indicated in Table 2, the sum of O_{II} and Sn^{4+} (O_{II}+Sn^{4+}) decreased sharply compared to that of the as-deposited ITO film. In this case, the decreased carrier concentration played a more important role than the improved carrier mobility so that the resistivity improved obviously.

For the ITO film annealed in nitrogen, there was no oxidation reaction occuring, just the improved crystalline. As indicated in Fig.2, with the increase of the annealing temperature, the grains grew and the micro-structure became perfect, so that the mobility of carrier was improved. As shown in Table 2, the O_{II}+Sn^{4+} concentration annealed in nitrogen changed slightly compared to that of the as-deposited ITO so that the carrier concentration changed slightly. Consequently, the resistivity decreased a little as the annealing temperature rose.

4 Conclusion

In this paper, ion beam sputtering was firstly used to deposited ITO film. The structural, electrical, optical, and electronic properties of the as-deposited and post-annealed ITO films were investigated. The post annealing process was carried out from 200℃ to 800℃ in nitrogen or in air. The results indicated that the optical transmittance was improved after the ITO film was annealed both in nitrogen and in air. Post annealing not only made the grains of ITO film grow, but also made the crystal structure more perfect. It was found that the resistivity of ITO film was related to the annealing process, which showed a close dependence on sum of O_{II} and Sn^{4+} (O_{II}+Sn^{4+}).

References