OPTOELECTRONICS LETTERS Vol.4 No.2, 1 Mar. 2008

Properties of ITO:Zr films deposited by co-sputtering*

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(Received 26 September 2007)

ITO:Zr films were deposited on glass substrate by co-sputtering with an ITO target and a Zirconium target. Substrate temperature and oxygen flow rate have important influences on the properties of ITO:Zr films. ITO:Zr films show better crystalline structure and lower surface roughness. Better optical-electrical properties of the films can be achieved at low substrate temperature. The certain oxygen flow rates worsen the electrical properties but can enhance the optical properties of ITO:Zr films. The variation in optical band gap can be explained on the basis of Burstin-Moss effect.

CLC numbers: O484.1 **Document code:** A **Article ID:** 1673-1905(2008)02-0137-3

DOI 10.1007/s11801-008-7132-5

At present, transparent conductive oxide (TCO) films such as ITO (In_2O_3:Sn), FTO (SnO_2:F) and ZAO (ZnO:Al) exhibit outstanding optical-electrical properties with low resistivity and high transmittance in the visible range [1-3]. Indium Tin oxide (ITO) film is a highly degenerate n-type semiconductor and the semiconducting mechanism is oxygen vacancies and Sn^{4+} doping. ITO films possess the best optical-electrical properties, which make them have wide applications in flat panel displays, solar cells and organic light emitting devices (OLED) [4]. In order to improve the chemical and thermal stability and surface energy as well as to increase the electrical conductivity without sacrificing optical transparency, some studies on multi-component oxide based on ITO films were carried out[5-7]. As a result, some high-valence metal elements (such as Zirconium) can be regarded as the donor, which replaces indium in the In_2O_3 matrix of ITO films and provides some free electrons to contribute the electrical conductivity. The better stability of Zirconium oxide can improve the chemical and thermal stability of ITO films, and the certain amount of Zr-doping can contribute to the activation of Sn dopant. In this paper, Zr-doped ITO films were deposited by magnetron sputtering with two targets, and the influences of substrate temperature and oxygen flow rate on the properties of ITO:Zr films were investigated.

ITO:Zr films were deposited on glass substrate by co-sputtering with an ITO target (In_2O_3 containing 10 wt% SnO_2) and a Zirconium target (99.995 %). DC sputtering power of ITO target was 45 W, and RF sputtering power of Zirconium target was 10 W. The distance between target and substrate was 60 mm. The pressure was stabilized at about 0.5 Pa during the deposition processing by controlling argon gas flow. Oxygen flow rate varied from 0 sccm to 1.5 sccm by a mass flow controller. The substrates were heated from room temperature (20 ℃) to 300 ℃. The film thickness was about 240 nm after 30 minutes of deposition. The averaged metal atomic ratio of ITO:Zr films was In:Sn:Zr=9:1:0.2. In this study, only oxygen flow rate or substrate temperature was varied, while all other parameters were fixed.

The film thickness was measured using an alpha-step profilometer (Dektak 6M). The sheet resistance was determined using a four-point probe system (SDY-5). The carrier concentration and mobility of the films were measured using the Hall effect in van der pau mode. The crystal structures were examined by X-ray diffractometer (D/max 2550 V) using Cu-K_α radiation. The surface morphology of films were evaluated by atomic force microscopy (AJ- Ⅲ). Optical transmittance and reflectance spectra of ITO/glass structure were measured with a UV-VIS-NIR scanning spectrophotometer (Lamda 950).

Fig.1 shows the variations of XRD patterns of ITO:Zr films with preparation condition. All samples are well crystallized and show clear XRD peaks, and they are crystallized in the cubic bixbyite structure of In_2O_3. With the increase in substrate temperature, an increase in intensity of XRD peak is observed. We find that the preferred orientation growth between (222) and (400) planes has a kind of competition. The XRD patterns of ITO:Zr films show the preferred orientation along the (400) direction. Oxygen

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* This work is supported by the Research Fund for Shanghai applied material (0525).

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incorporation leads to films oriented in the (222) direction, and (400) orientation is related to oxygen deficiency [8]. Zr-doping leads to oxygen deficiency in the In_2O_3 matrix, which favors the preferred orientation along the (400) direction. When oxygen flow rates vary from 0.0 to 0.7 sccm, (400) plane is preferred.But the excess oxygen at 1.5 sccm leads to the preferred orientation changing from (400) to (222) plane. Besides, the variation of orientation is also related to the composition of the films and the technologcial conditions.

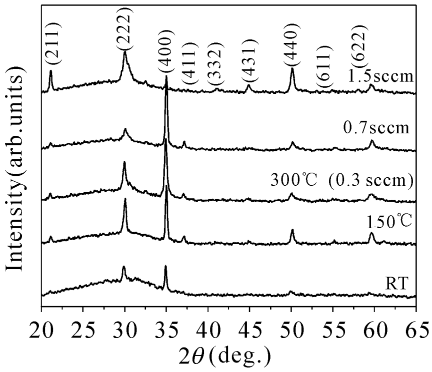

Fig.1 XRD patterns of ITO:Zr films under various preparation conditions.

AFM images of ITO:Zr films under various preparation conditions are shown in Fig.2. All the films display a very smooth, uniform grain size and void-free surface. The grain size shows an evident increasing tendency with the substrate temperature. It is evident that the substrate temperature changes both the grain size and the grain shape remarkably. Fig.2 also shows the observable variations of the surface morphologies with the oxygen flow rate. As the oxygen flow rate increases from 0.0 to 1.5 sccm, the grain sizes are much reduced with the increase in grain boundaries. These variations would be directly related to the incorporations and the segregations of excess oxygen into the lattices, which prevent the grain growth and favor the formation of grain boundaries. The roughness of ITO:Zr films is shown in Tab. 1. R_a is the average roughness and the surface roughness increases with the substrate temperature.The roughness decreases with the increase in the oxygen flow rate. We find that ITO:Zr films show lower surface roughness than ITO films. The microstructure and surface morphologies can directly affect the optical-electrical properties of the films.

The sheet resistance, carrier concentration and mobility under various preparation conditions for ITO:Zr films are shown in Tab.1.The sheet resistance of the films decreases and the carrier concentration and mobility increase with the increase in the substrate temperature. The increase in carrier concentration with substrate temperature may be due to an increase in the diffusion of Sn and Zr atoms from interstitial locations and grain boundaries into the In location sites in In_2O_3 matrix. The variation of mobility is regarded as the result of better crystallinity of the films, which promotes the increase in grain size, reduces the grain boundary scattering and increases the conductivity. The sheet resistance of the films increases with the increase in the oxygen flow rate. The carrier concentration decreases with the oxygen flow rate, and the mobility increases in the certain oxygen region but decreases in the excess oxygen region. The continuous decreases in carrier concentrations with the oxygen flow rate are due to filling the oxygen vacancies and deactivating the donor. The behaviors of the mobility with the oxygen flow rate are dependent on the dominant grain boundary scattering.

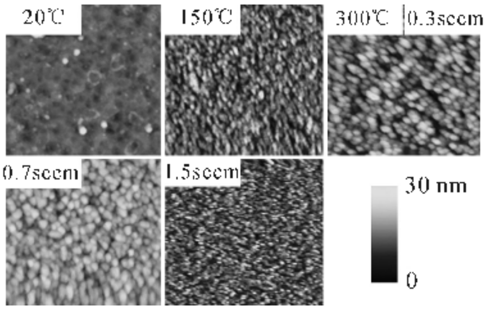

Fig.2 AFM images of ITO:Zr films under various preparation conditions (2000 nm × 2000 nm).

The optical properties of ITO:Zr films under various preparation conditions are presented in Fig.3. The transmission in the visible region increases with the increase in the substrate temperature and the oxygen flow rate, but we find that the excess oxygen flow rate results in the reducing of optical transparency. The reflection in the higher wavelength region is closely related with the carrier concentration of the films[9]. Therefore, the continuous variation in carrier concentrations can further be demonstrated from the change in reflection at the near-IR region. The transmittance spectra also show that the near UV absorption edge shifts toward shorter or longer wavelengths with the substrate temperature and the oxygen flow rate. According to Drude's theory, ITO film is transparent until the fundamental absorption starts at wavelengths close to the corresponding optical band gap energy. The widening of optical band gap energy is due to Burstein-Moss effect [10]. The optical band gap is closely related with the carrier concentration. The direct transition model was established according to the direct allowed transitions equation [11], and the optical band gap energy E_g was obtained. The optical band gap of ITO:Zr films increases with the substrate temperature and decreases with the oxygen flow rate as shown in Tab.1, which may be due to the variation of carrier concentration.

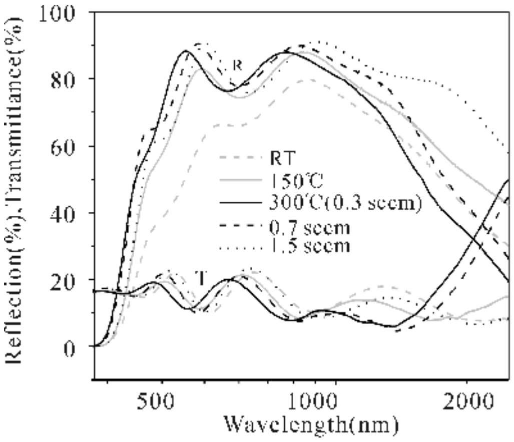

Fig.3 Optical spectra of ITO:Zr films under various preparation conditions.

Tab.1 Summary of some properties for ITO:Zr films under different preparation conditions.

Preparation	conditions	XRD data	AFM data	Electrical data			
Temperature (°C)	Oxygen flow rate (sccm)	I(222)/I(400)	R_a (nm)	sheet resistance (Ω/sg)	Carrier concentration ($10^{20}cm^{-3}$)	Mobility ($cm^2S^{-1}V^{-1}$)	E_g (ev)
20	0.3	0.64	0.7	91.65	1.75	16.22	4.114
150	0.3	0.64	0.92	58.39	2.69	16.58	4.171
300	0.3	0.49	1.55	19.67	8.73	16.80	4.264
300	0.7	0.17	1.52	19.89	7.82	16.76	4.256
300	1.5	4.08	1.47	53.28	3.61	13.54	4.172

In conclusion, the microstructure and optical-electrical properties of ITO:Zr films are strongly dependent on the preparation conditions. ITO:Zr films show better crystalline structure and lower surface roughness. ITO:Zr films deposited at lower substrate temperature show better optical-electrical properties. The carrier concentration has a tremendous influence on the reflection in near-IR range, on the absorption in near-UV range and on the optical band gap. ITO:Zr films have better optical-electrical properties and higher surface energy, as well as better chemical and thermal stability.

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