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ARTICLE

Influence of Substrate Temperature on Electrical and Optical Properties of Sputtered Binary SnO_2-Al_2O_3 Thin Films on Slide Glasses

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Abstract: SnO_2-Al_2O_3 (SAO) binary thin films were prepared on slide glasses substrates by RF magnetron sputtering. The influence of the substrate temperature on the surface morphology, crystal structures, electrical and optical properties were analyzed by the scanning electron microscopy (SEM) images, X-ray diffraction (XRD) patterns, four-probe measuring, UV-IR and photoluminescence (PL) spectra. With increasing substrate temperature, the grain sizes of SAO binary films are increased. Uniform patterns and large size grains indicate a better surface morphology and crystallinity of SAO films, which are verified by SEM and XRD investigations. All the films have a high average transmittivity of ~80%~90% in visible light region 400~800 nm. The calculated band gap is in a range of ~4.11~4.14 eV, and the measured sheet resistances of SAO films are in a range of ~7.0×10^4 to ~9.4×10^4 Ω/□. At proper sputtering temperature, the band gap can be widened, and the sheet resistances can be reduced. The PL emissions from the films in UV and red bands were also observed. These polycrystalline SAO films can be used in the application of transparent conductive oxide (TCO) films, solar cell windows, sensors, as well as lighter emitters.

Key words: SAO binary thin films; radio frequency (RF) magnetron sputtering; electrical properties; optical properties

SnO_2 materials can be extensively used as semiconducting materials in electrical and optical devices. However, challenges remain for improving the fabrication processes for various advanced applications. This optimization requires a further investigation of the morphologies, the micro/nanostructures, electrical and optical properties of SnO_2 thin films[1]. In these investigations, thin films with binary compounds such as SnO_2, In_2O_3, ZnO and Al_2O_3 have been reported by several authors[2-6]. SAO films with low cost and good chemical stability can a good candidate in the application of photoelectric industry, since Sn has large orbital which is as large as In, and Al creates stable bond with oxygen[6].

In this work, we prepared SAO binary thin films on slide glasses substrates by RF magnetron sputtering at different substrate temperatures, and investigated the morphology, crystal structures, electrical and optical properties. It was shown that the SAO thin films fabricated in this work have less surface defects, and the parameters of the substrate temperature can be used to control the sheet resistance, transmittance and PL properties of SAO films. These polycrystalline SAO films can be used in the application of TCO films, solar cell windows, sensors, as well as lighter emitters.

1 Experiment

SAO binary thin films were prepared by RF magnetron sputtering on 2 cm×2 cm slide glasses with a thickness of 1 mm. A target with 99 mol% SnO_2+1.0 mol% Al_2O_3, in experiments was used. The slide glass substrates were first cleaned in acetone, rinsed in deionized water and dry blown with N_2 gas before loading into the chamber. The distance between the target and the substrate was ~50 mm. The base pressure was 2×10^{-4} Pa, and the film growth was carried out

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in the growth ambient with the ratio of oxygen to argon gas flow of 14:7. The target was pre-sputtered in pure Ar for 10 min to remove surface contamination and maintain system stability. The sputtering power was maintained at 80 W during sputtering for all the films. Films denoted as a, b, c, d, e and f were deposited on slide glass substrates at room temperature ~25 ℃, and heating at ~100, 150, 200, 250 and 300 ℃, respectively. The sputtering time for the films was 2 h.

The micrographs (SEMs) were studied by JEOL JSM-6930A. To identify the crystalline structure in the SAO films, an X-ray diffractometer (Brucker D2 Phaser) with CuK radiation (0.154 nm) was used at 40 kV, 40 mA. The film thickness was determined by spectroscopic ellipsometry (SE) methods with J. A. Woollam M-2000UI. The electrical resistivity was measured by a four-point probe. The absorption/transmission and PL spectra were carried out by UV-IR spectrometer and Horiba FluoroMax-4, respectively.

2 Results and Discussion

2.1 SEM and XRD characterization

SEM images of the films a, b, c, d, e and f are shown in Fig.1. It is evident that the substrate temperature can dramatically modify the films' surface morphologies. The grain sizes increase with increasing substrate temperature. The film a, deposited at room temperature, has a relatively smooth and uniformity surface; however, the grains are very small and the film is in an amorphous state. At low heated substrate temperature (lower than 250 ℃), relatively rough morphology and some cracks emerge in samples b, c and d. As the substrate temperature increases to 250 and 300 ℃, the roughness is apparently lessened due to larger particle coalescence induced grain growth. Thus, the substrate temperature for deposition process has the large effects on the physical properties of SAO binary films.

To verify the microstructures evolution, XRD patterns of the films are shown in Fig.2. In all these patterns, the broad hump between 20 ° and 40 ° is the background intensity due to the glass substrates. There is no apparent diffraction peaks for the film a sputtered at room temperature, which is in an amorphous state. While in films b~f deposited with substrate temperature at 100~300 ℃, the rutile phases SnO_2 crystallites with tetragonal structure can be observed and the peak positions of the films are found to be corresponding to the rutile structure of polycrystalline SnO_2 films (JCPDS no. 41-1445). Peaks corresponding to (110) and (101) planes have relatively larger values for the samples b~f, comparing with those corresponding to (211), (200) and (112) planes with relatively weak intensities. The solid circles indicate the diffraction peaks induced by Al_2O_3 components in SAO binary films; however, the characters of these peaks are not distinguished through due to low level doping of aluminium oxide and broadened diffraction peaks from tin oxide.

It is also observed that the full width of half maximum (FWHM) of the diffraction peaks decreases with increasing substrate temperature (Fig.1b~1f). FWHMs of peaks (110), (101) and (211) for the film b deposited at 100 ℃ are broadened maximumly to ~3.08 °, 1.8 ° and 2.3 °, respectively, while as the substrate temperature increases, these values decrease and reach to minimum values of ~1.94 °, 1.52 ° and 1.96 °, for the film f deposited at 300 ℃. This indicates that the films deposited at higher substrate temperatures have a better crystallinity.

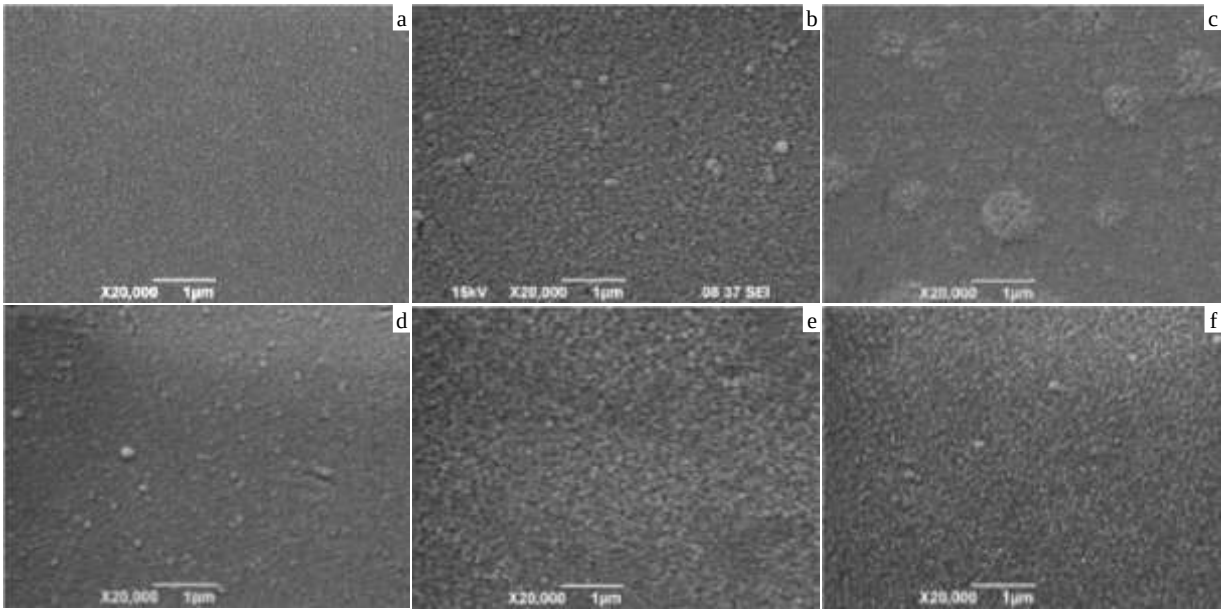

Fig.1 SEM images of SAO binary thin films deposited on slide glasses: (a~f) a, b, c, d, e and f were sputtered by a target (1.0 mol% Al_2O_3) with substrates at room temperature ~25, 100, 150, 200, 250 and 300 ℃, respectively (the sputtering time was 2 h)

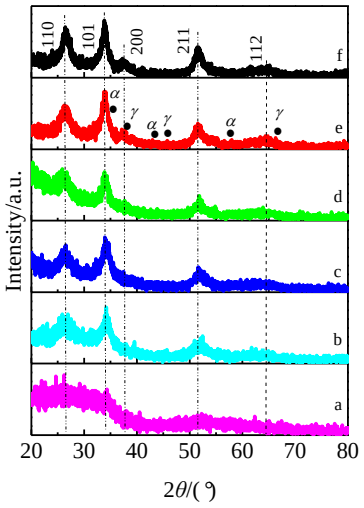

Fig.2 XRD patterns of films a~f

The average grain size of the samples can be calculated by the Scherrer's equation:

$$D=0.9\lambda/B\cos\theta \quad (1)$$

Where, λ is the X-ray wavelength of 0.154 nm, θ is Bragg diffraction angle, and B is the FWHM of the diffraction peak. The average grain sizes shown in Fig.3 were calculated by (110), (101) and (211) peak values. The average grain sizes of films b, c, d, e and f are ~3.95, 4.41, 4.79, 4.80 and 5.13 nm, respectively. The increasing grain sizes are probably due to the contribution of smaller crystallites with sharper convexity surfaces induced by relatively higher substrate temperature. In these cases, larger area adjacent crystallite contact and enhanced coalescence process are provided, and larger crystallites are produced.

2.2 Optical and electrical properties

The optical transmittance in the range of 250~800 nm and $(h\nu\alpha)^2 \sim h\nu$ plots of SAO binary thin films are shown in Fig.4. In general, the transmission of tin oxide thin films is very high in the visible region, due to the low reflectivity and less absorption induced by excitation of electrons from the valence band to the conduction band[7,8]. The transmission strongly depends on the film structure, which is determined

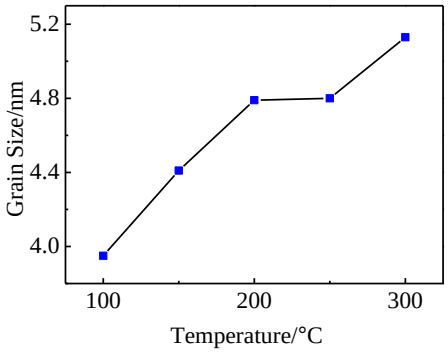

Fig.3 Grain sizes of films b~f

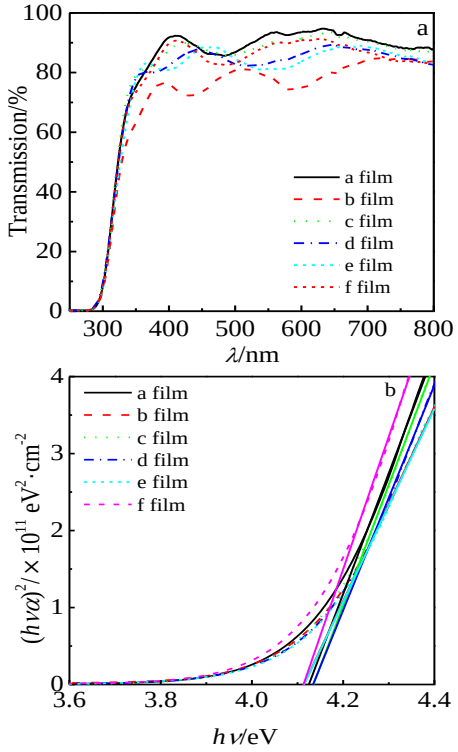

Fig.4 Transmission (up panel) and $(h\nu\alpha)^2 \sim h\nu$ plots (down panel) of films a~f: (a) transmission vs wavelength and (b) $(h\nu\alpha)^2$ vs $h\nu$

by the substrate temperatures. As seen from the figure, the average transmission is found around 80%~90% in the visible range, which is good for opto-electronic devices. The higher transmittance can be attributed to less scattering effects, structural homogeneity and better crystallinity. Furthermore, sharp fall at the band edge is an indication of good crystallinity of the films, which is verified by the XRD analysis in Fig.2.

Band edge absorption of thin films observed on up panel in Fig.4 is due to quantum interaction of light and materials. The modification of the band gap energy E_g of SAO binary films may be due to varied sputtering parameters. To clarify these properties, the optical band gap of the SAO binary films were calculated by the formula:

$$\alpha(h\nu) = C\sqrt{h\nu - E_g} \quad (2)$$

where, C is a constant for a direct transition, α is the optical absorption coefficient, and $h\nu$ is the photon energy. The energy gaps of films were obtained by extrapolating the linear absorption edge parts of the plots $(h\nu\alpha)^2 \sim h\nu$ on the down panel in Fig.4.

The calculated band gap values of a~f are in the range of ~4.11~4.14 eV, As is shown in Fig.4b, the band gap increases from ~4.12 eV at room temperature and 100 ℃, to a maximum value ~4.14 eV at 150 ℃, then decreases to ~4.13 eV at 200 ℃, and 4.11 eV at 300 ℃, respectively. This increasing band gap is related to the decreasing grain sizes, the overlapping of the atomic wave functions and the quantum confinement effect.

Another reason for enhancement in optical band gap is the Moss-Burstein effect determined by $E_g=E_{g0}+\Delta E_{MB}$, with E_{g0} the inherent band gap and ΔE_{MB} the amount of band gap shift induced by increasing carrier concentrations.

The resistivity is the very important parameter in the application of transparent conductor thin films and solid gas sensors. We measured the resistivity by four-probe measuring. For convenience, we plotted the average transmission coefficient in the visible region (400~800 nm), the band gap and the resistivity of SAO binary thin films as a function of the substrate temperature in Fig.5.

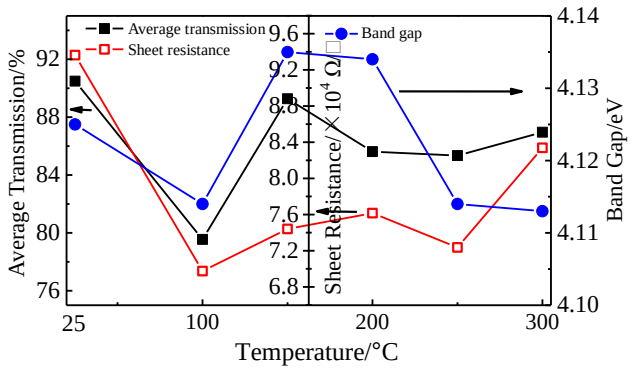

Fig.5 Average transmission, resistivity and band gap evolution of films a~f

Fig.5 shows that, the film sputtered at room temperature has a sheet resistance ~9.4×10^4 Ω/□, and decreases to ~7.0×10^4 Ω/□ at 100 ℃, and then ranges ~$7.2\sim7.6\times10^4$ Ω/□ at 150, 200 and 250 ℃, and finally increases to ~8.3×10^4 Ω/□. This substrate temperature dependence reduction/increasing of resistance are due to decreasing/increasing of grain boundary concentration and increasing of oxygen vacancies, which enhance carrier concentration and mobility of the charge carriers. Thus, the reduction of the resistance is mainly due to the low formation energy of oxygen vacancies, tin and aluminium interstitials, and the enhancement of carrier concentration induced by the addition of Al_2O_3, which can be modified to be an n-type or p-type semiconductors [5].

Finally, we show the PL spectra of the SAO binary films in Fig.6, which were measured by a spectrometer Horiba FluoroMax-4 with 265 nm as excitation wavelength of 150 W Xenon pulse lamp. Two typical emission bands in UV and red bands were observed for all the films, the former being with higher intensity. The peaks position and the shape were modified drastically by the substrate temperature.

Several PL bands have been found in previous reports, e.g., ~564 nm[9], ~488 nm[10], ~417nm[11], ~400nm[12], ~387 nm[13], ~370 nm[14], high resolution peaks around 368~384 nm[10]. However, in this work, the emission of the film a sputtered at room temperature is near ~353 and ~742 nm bands in UV and red region with a much broadened width of FHWMs ~70 and

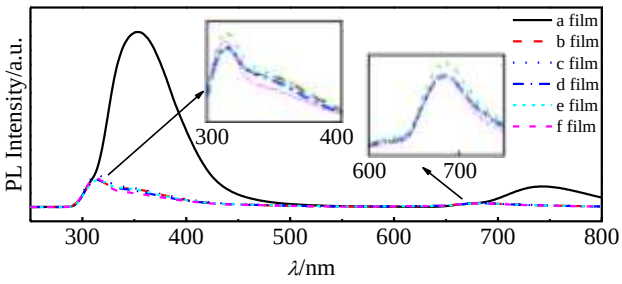

Fig.6 PL lines of the films a~f

90 nm, respectively. The intensity emitted from the film a is five times stronger, and the width two times and ~20 nm broader than those of films sputtered at 100~300 ℃ with two emission peaks shifting to ~313 nm and 686 nm in UV and red bands, respectively. When the substrate temperature increases, the peak around 313nm becomes narrower, a weaker and flatter shoulder around 350nm emerges in the UV band. The UV emission of ~313nm band is very close to the band gap (in the range of ~4.02~4.14 eV) of the SAO binary films, so this UV peak is probably the near band edge emission. In these cases, the modification of band gap, induced by the substrate temperature, contributes to various shapes of UV emissions. However, the UV emission of ~353 nm and red emission peaks are much lower than that of the band gap absorption of SAO films, and the former is probably ascribed to Sn/Al vacancies or interstitials, and the latter is probably due to oxygen vacancies, which form a considerable number of trapped states within the band gap [11]. Thus, these peaks can be attributed to electron transition, mediated by defects levels in the band gap, such as oxygen vacancies and the luminescence centers formed by such tin/aluminium interstitials or dangling in the presence of SnO_2/Al_2O_3 nanocrystals.

3 Conclusions

1) By choosing proper substrate temperature, e.g., the film sputtered at 150 ℃, a high average transmittivity ~89% in visible light region, a relative widened band gap ~4.14 eV, and a sheet resistance ~7.4×10^4 Ω/□ can be achieved. The electrical and optical properties are optimized by proper sputtering parameters.

2) PL emissions in UV and red region of these films are also observed. These polycrystalline SAO films can be used in the application of transparent conductive oxide films, solar cell windows, sensors, as well as lighter emitters.

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玻璃衬底温度对溅射制备 SnO_2-Al_2O_3 双金属元素薄膜电学及光学特性的影响

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摘　要：采用射频(RF)磁控溅射法在玻璃衬底上制备了 SnO_2-Al_2O_3 (SAO) 双金属元素薄膜。通过扫描电子显微镜 SEM，X 射线衍射仪 XRD、四探针测量，UV-IR 及光致发光(PL)谱研究了衬底温度对薄膜表面形貌、晶体微结构、电学及光学特性的影响。当衬底温度升高时，SAO 薄膜的晶粒尺寸增大。SEM 及 XRD 结果显示的均质表面结构及大晶粒尺寸表明薄膜具有良好的表面形貌和结晶度。在 400~800 nm 的可见光范围，薄膜的透射率可达 80%~90%，计算得到薄膜的带隙 4.11~4.14 eV，表面电阻 7.0×10^4~9.4×10^4 Ω/□。通过合理选择溅射温度，薄膜的带隙可得到增宽，表面电阻可被降低。测量还发现，所制备 SAO 薄膜的 PL 谱在 UV 及红光带发光，这种多晶 SAO 薄膜可用于透明导电氧化物(TCO)薄膜，太阳能电池窗、传感器及光发射器。

关键词：SAO 双金属元素薄膜；射频磁控溅射；电学特性；光学特性

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