OPTOELECTRONICS AND ADVANCED MATERIALS – RAPID COMMUNICATIONS Vol. 4, No. 11, November 2010, p. 1651 - 1654

Preparation of transparent conducting Al-doped ZnO thin films by single source chemical vapor deposition

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Transparent conducting Al-doped zinc oxide (AZO) thin films have been fabricated on quartz substrates by single source CVD system. Effects of annealing temperature and Al-doping concentration on the optical and electrical properties of AZO films were investigated. AZO film with Al/Zn ratio of 1 % annealed at 700 ℃ has high optical transmittance of 88.2 % and low electrical resistivity of 1.85×10^{-2} Ωcm. Hall measurements and absorption edge analysis demonstrate that resistivity of AZO films is determined by carrier concentration rather than carrier mobility.

(Received September 28, 2010; accepted November 10, 2010)

Keywords: Chemical vapor deposition, AZO, Thin film

1. Introduction

Transparent conducting oxide (TCO) films have been studied extensively because they exhibit low resistivity and high optical transmittance, and they are widely used in optoelectronic devices such as solar cells and flat panel displays. Among the various TCO materials, Al-doped ZnO (AZO) has been considered as potential candidates to replace indium tin oxide due to the low cost, non-toxicity, and chemical stability [1-4]. Previously, many researchers had fabricated AZO films using various growth methods, such as RF-magnetron sputtering, pulse laser deposition (PLD), electron beam evaporation and chemical vapor deposition (CVD) [5-9]. Among these, the popular technologies to prepare AZO films are sputtering and PLD, which have the complicated control system and also the high cost. Because cost effectiveness is an important factor in the practical application of AZO films, it is attractive to develop a simple and effective technology to lower the preparation cost. Single source chemical vapor deposition (SSCVD) is a simple and useful method for fabricating high quality films and has been extensively used in the fabrication of epitaxial films of many semiconductor films [10-12]. However, there was little report about the preparation of AZO films by SSCVD method [9]. In this work, Al-doped ZnO thin films with high optical transmittance and low electrical resistivity were fabricated by SSCVD using zinc acetate as precursor. Effects of annealing temperature and Al-doping concentration on the optical and electrical properties were also investigated.

2. Experimental

The AZO thin films were prepared on quartz substrates by single source CVD. A schematic diagram of the experimental system is shown in Fig. 1. The precursor was zinc acetate dehydrated ($Zn(CH_3COO)_2)$) mixed with different content of aluminum acetate dehydrated ($Al(CH_3COO)_3$). The nominally Al/Zn ratios were 0 %, 0.3 %, 1 %, and 3 %, respectively. The carrier gas is pure nitrogen (N_2) with the flow rate of 0.2 L/min. A vacuum pump was used to keep the pressure of reactor chamber less than 0.1 atm. After cleaning process, the quartz substrate was put on a quartz boat and then placed in the reactor chamber. The temperatures of the precursor and the substrate were about 190 and 380 ^oC, respectively. During the growth, the sublimated precursor was carried by N_2 to the quartz substrate, and decomposed to form AZO film on the substrate surface. The thickness of the deposited AZO thin films was about 100 nm confirmed by Spectrometric Ellipsometer. After deposition, the films were annealed at 500-800 ^oC in pure N_2 ambient for 1 h (hour).

In order to characterize the films structure, X-ray diffraction (XRD) patterns were measured using a D/MAX-RA XRD spectrometer with a Cu Kα line of 1.5406 Å. The films resistivity was measured by Four-probe method and carrier concentration and mobility were measured by Hall measurement in Van der Pauw configuration at room temperature. The transmittance of the AZO film was measured by spectrophotometer in the wavelength range of 300-800 nm.

3. Results and discussion

The X-ray diffraction patterns for pure ZnO and 1 % Al-doped AZO thin films deposited on quartz substrates are shown in Fig. 2. As it shows, pure ZnO film showed strong (002) and a weak (101) peak, indicating that it has a hexagonal structure and a preferred orientation with the *c*-axis perpendicular to the substrate. After 1 % Al was doped into the film, the diffraction peaks of (100), (002), (101) and (110) of ZnO film were displayed, still corresponding to the hexagnal wurtzite structure. However, the intensity of (002) diffraction peak weakened and a (100) peak dominated the pattern. Generally, ZnO crystal grows along [001] direction, i.e. *c*-axis, the abnormal oriented growth may attribute to the change of chemical conditions resulting from importing Al atom. After the AZO film was annealed in N_2 ambient at 700 ^{o}C, the (100) peak intensity increased about 15-fold. Furthermore, for all the films, neither Al_2O_3 nor Al phase was detected from the X-ray patterns. This may be due to Al atoms substituting Zn in the crystal lattice or redundant Al segregating to the non-crystalline region in the grain boundary.

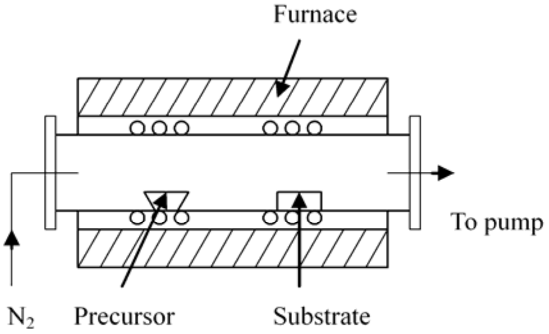

Fig. 1. A schematic diagram of the CVD system for growth of AZO thin films.

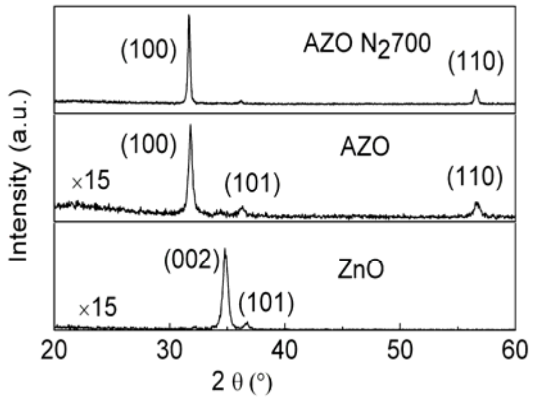

Fig. 2. XRD patterns of ZnO and AZO thin films with Al/Zn ratio of 1%.

Table 1. Hall data of AZO thin films with Al/Zn ratio of 1 at % at different annealing temperatures.

Annealing temperature (℃)	Electrical resistivity (Ωcm)	Carrier concentration (cm^{-3})	Hall mobility (cm^2/vs)
500	6.75×10^{-1}	7.29×10^{18}	12.70
700	1.85×10^{-2}	2.50×10^{19}	13.51
800	2.33×10^{0}	—	—

Table 2. Hall data of AZO thin films with different Al/Zn ratios annealed at 700 ℃.

Al/Zn Ratio (%)	Electrical resistivity (Ωcm)	Carrier concentration (cm^{-3})	Hall mobility (cm^2/vs)
0.3	5.50×10^{-1}	1.19×10^{18}	9.53
1	1.85×10^{-2}	2.50×10^{19}	13.51
3	3.75×10^{-1}	3.50×10^{17}	47.63

The electrical resistivity ρ of all AZO films was measured by four probes method as shown in Table 1 and 2. Table 1 shows ρ for 1 % AZO thin films annealed at different temperature in N_2 ambient. It can be seen that the electrical resistivity ρ decreases with increasing of annealing temperature from 500 to 700 ^{o}C. While annealing temperature increases further to 800 ^{o}C, an opposite variation tendency occurs. The sample with 1 % Al doped under 700 ^{o}C annealing has the lowest resistivity. The dependence of ρ for AZO films annealed at 700 ^{o}C on the Al/Zn ratios was shown in Table 2. As the Al/Zn ratios changed from 0.3 % to 3 %, the resistivity becomes higher when the Al/Zn ratio deviates from 1 %. Thus, the optimal condition for the lowest resistivity (1.85×10^{-2} Ωcm) AZO film was that the Al-doping concentration is around 1 % and the annealing temperature is about 700 ^{o}C.

Carrier concentration N and mobility μ were obtained by Hall measurements in Van der Pauw configuration at room temperature. AZO films annealed at 800 ℃ with high resistivity had not been measured with the instrument resolution limitation. Table 1 summarizes the Hall data of 1 % AZO thin films annealed at 500 and 700 ^{o}C. The carrier concentration N has a large increase as the temperature changed from 500 to 700 ^{o}C. This indicates that the higher N of AZO films may be related to the better activation of Al dopants, which need appropriate temperature. However, the film became high resistivity as temperature reached 800 °C, which may be due to the congregating of Al atoms at high temperature. The carrier mobility does not show a significant change in AZO films annealed at 500 and 700 °C.

Under the optimal annealing temperature of 700 °C, the carrier concentration N and mobility μ for AZO thin films with different Al/Zn ratios were listed in Table 2. The N of AZO film with 0.3 and 1% Al concentration were 1.19×10^{18} and 2.50×10^{19} cm^{-3}, respectively. While increasing Al content to 3 %, the carrier concentration N decreased to 3.50×10^{17} cm^{-3}. It means that Al alloys may formed at high Al concentration resulting the low carrier concentration.

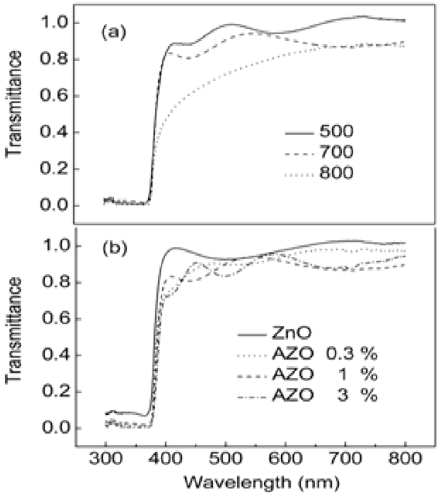

Fig. 3. Transmittance spectra of AZO films with Al/Zn ratio of 1 at % at different annealing temperatures (a) and with different Al/Zn ratio annealed at 700 °C (b).

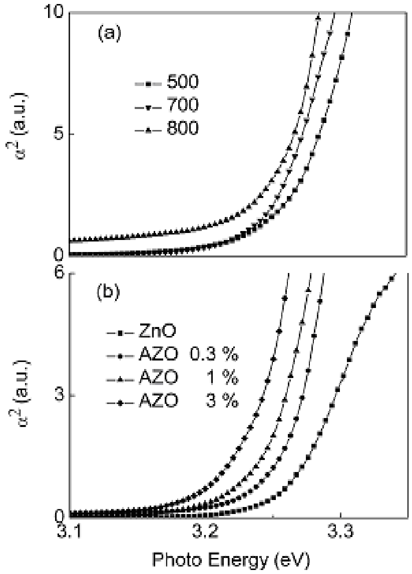

Fig. 4. Plot of α^2 versus photon energy for AZO films with Al/Zn ratio of 1at% at different annealing temperatures (a) and with different Al/Zn ratio annealed at 700 °C (b).

As high transparency is the most important factor in the application of AZO films to TCOs, the optical transmittance was determined by a spectrophotometer within the waveleng –th from 300 to 800 nm. Fig. 3 shows the transmission spectra for the AZO thin films with Al/Zn ratio of 1 at % at different annealing temperatures (a) and with different Al/Zn ratio at same annealing temperature of 700 °C (b). All films exhibit an average optical transmittance of over 85 % in the visible range, and a sharp fundamental absorption edge at about 380 nm. However, the AZO film annealed at 800 °C has a little transmittance of 78 %, which consistenting with the Al congregating as discussed above. The average optical transmittance of the AZO films with the lowest resistivity as shown in Fig. 3 was 88.2 %, which meets the requirement of the TCO application.

Generally, the transmittance T is defined as I/I_0 and optical absorption coefficient α is defined as [13]

$$I = I_0 e^{-\alpha d} \tag{1}$$

where I is the intensity of transmitted light, I_0 is the intensity of incident light, and d is the thickness of the film. In a direct transition semiconductor like ZnO, α is related to the optical band gap E_g for photon energy $h\nu$ as [14]

$$\alpha = A\,(h\nu - E_g)^{1/2} \tag{2}$$

where A is a constant. By plotting α^2 versus $h\nu$, E_g can be determined by extrapolating the linear part of the curve. Fig. 4 shows the plot of α^2 versus photon energy for AZO films with Al/Zn ratio of 1 at % at different annealing temperatures (a) and with different Al/Zn ratio after annealed at 700 (b). From Fig. 4 (a), it can be observed that E_g of AZO films annealed at 500, 700 and 800 ℃ varies little from 3.26 to 3.25 eV, indicating that annealing temperature does not significantly affect the band gap of the AZO films. However, there was obviously change of E_g with the variation of Al/Zn ratios as shown in Fig. 4 (b). The E_g value of pure ZnO is 3.27 eV, according to most literature data [15,16]. For AZO films with Al/Zn ratio of 0.3, 1 and 3 %, the E_g values are 3.26, 3.25 and 3.23 eV, respectively. The red-shift of E_g as the Al-doping in our work is probably due to the Urbach tail effect [17,18]. Further work is necessary to fabricate AZO films with big carrier concentration which is helpful for the lower of the resistivity of AZO film.

4. Conclusions

In conclusion, transparent conducting AZO thin films were fabricated by single source CVD system. Effects of annealing temperature and Al-doping concentration on the optical and electrical properties were also investigated. AZO film with Al/Zn ratio of 1 % annealed at 700 °C has high optical transmittance of 88.2 % and low electrical resistivity of 1.85×10^{-2} Ωcm. Hall measurements and absorption edge analysis indicate that resistivity of AZO films is determined by carrier concentration rather than carrier mobility. With further improvement, the AZO transparent conducting film prepared by single source CVD will be suitable for optoelectronic application.

Acknowledgments

This work was supported by the Knowledge Innovation Program of the Chinese Academy of Sciences (KJCX3.5YW.W01), Science technology development program of henan(102102210452), Natural science program of henan province education department (2010A140011), and Education program of Luoyang normal university (2008-PYJJ-009).

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