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A Study of Annealing Time Effects on the Properties of Al:ZnO

Xue Shu-wen*

Department of Physics, Zhanjiang Normal College,Guangdong 524048, P.R. China

Abstract

ZnO:Al films with Al/Zn atomic ratio of 1% were prepared on quartz glass by a sol-gel process. The films were annealed in argon at 500 ^{o}C. The annealing time varied between 1h and 5h. The effects of annealing time on the properties of ZnO:Al films were investigated by X-ray diffraction (XRD), optical transmittance and four-point probe method. The results showed that the films exhibited *c*-axis preferred orientation after annealing for 1h. The transmittance in the visual region was ~ 80%, and the conductivity was 4×10^{-2} Ω·cm. As the annealing time increased, the crystal preferred orientation was absent, and the conductivity increased.

Keywords: Sol-gel; ZnO:Al films; Annealing time; Transmittance

1. Introduction

As a good semiconductor material, transparent conductive films (TCO) have wide application in solar cells and liquid crystal displays, etc. [1-3] ZnO:Al (AZO) transparent conductive films not only have good optoelectronic properties as ITO (In_2O_3:Sn), but also have the advantages of low cost, non-toxic, high thermal stability and chemical stability in hydrogen plasma environment. It has been the best substitute for ITO. In recent years, Zinc oxide has received increasing attention in the research community due to its potential applications in optoelectronic devices. Many techniques have been employed to synthesize high-quality ZnO films, such as atomic layer deposition, radio frequency (RF) magnetron sputtering, chemical vapor deposition, pulsed laser deposition, plasma-assisted molecular beam epitaxy (MBE) and sol-gel process [4-9]. Among them, the sol–gel chemical deposition technique is very attractive as it can be

* Corresponding author. Tel.: +86-759-3167343.
E-mail address: xueshuwen@263.net.

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implemented easily in a laboratory for the deposition of semiconducting thin films. This technique offers the possibility of preparing a small- as well as large-area coating of ZnO thin films at low cost for technological applications.

The properties of ZnO films are determined not only by the growth processes, but also by the post-growth treatment, for example thermal annealing. The effects of annealing on the properties of ZnO thin films have been reported by many groups [10-13]. However, the annealing conditions, such as ambient gas species, annealing temperature and time, are different for the different groups, and results are still under debate, especially for the effects of annealing time on the structural and opt-electrical properties of ZnO:Al films.

In this work, we prepared ZnO:Al thin films by the sol-gel technique. The films were annealed at 500 ^{o}C for 1~5 h. The effects of annealing time on the structural and electrical properties of the films were investigated.

2. Experimental

ZnO:Al thin films were prepared by the sol–gel method. As a starting material, zinc acetate dehydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$) was used. 2-methoxyethanol and monoethanolamine (MEA) were used as a solvent and stabilizer, respectively. The dopant source aluminum is ($Al(NO_3)_3{\cdot}9H_2O$). Zinc acetate dihydrate and dopant were first dissolved in a mixture of 2-methoxyethanol and MEA solution at room temperature. The molar ratio of MEA to zinc acetate ($Zn(CH_3COO)_2$) was maintained at 1.0 and the concentration of zinc acetate was 0.35 M. The solution was stirred at 60 ^{o}C for 2 h to yield a clear and homogeneous solution, which served as the coating solution after cooling to room temperature. The coating was usually made 24 h after the solution was prepared. The solution was dropped onto sapphire substrates, which were rotated at 4000 rpm for 30 s. After depositing by spin coating, the films were dried at 300 ^{o}C for 10 min on a hot plate to evaporate the solvent and remove organic residuals. The procedures from coating to drying were repeated twelve times. The films were then inserted into a furnace and annealed in air at 550 ^{o}C for 1 h.

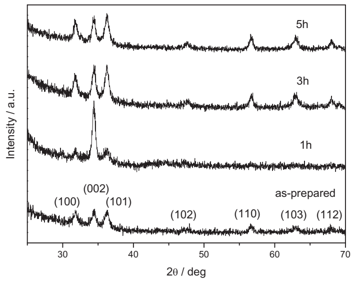
To investigate the effects of annealing time on the structural and opt-electrical optical properties of ZnO:Al thin films, the as-prepared samples were annealed in a quartz tube furnace in argon at 500 ^{o}C with the annealing time varying between 1 and 5 h. A BEDE-D1 X-ray diffractometer (XRD) was used to investigate the crystal orientation of ZnO:Al films. The radiation source of is CuKα. Optical transmittance and absorbance were measured using a UV-Vis spectrophotometer (SHIMADZU UV2550). The resistivity of the films was measured by the four-point probe method.

3. Results and discussions

3.1. Structural properties

To investigate the effects of the annealing time on the structural properties of ZnO:Al films, we annealed the samples in argon at 500 ^{o}C for different time. Figure 1 shows the XRD patterns of ZnO:Al films annealed for different time. The as-prepared samples exhibit hexagonal wurtzite structure. The peaks were identified to originate from (100), (002), (101), (102), (110), (103) and (112) reflections of hexagonal ZnO crystal structure (PDF 74-0534). The samples have three relatively higher diffraction peaks, i.e. (100), (002) and (101), indicating a random orientation of crystallites. After annealed at 500 ^{o}C for 1h, (002) peak enhances greatly, and ZnO:Al films appear c-axis preferred orientation. In addition, the FWHM of (002) decreases, suggesting a evident improvement of the crystallinity of ZnO:Al films. However, with the extension of the annealing time, c-axis preferred orientation in ZnO:Al films is absent.

Annealing time shows evident influences on the crystal orientation of ZnO:Al films. The degrees of orientation in the films can be calculated from the XRD patterns by using a formula proposed by Lotgering [14]. The calculated degrees of orientation of the (100), (002) and (101) peaks for ZnO:Al films annealed for different time are given in figure 2. It can be seen that (002) orientation degree increases, however, (100) and (101) orientation degrees decrease after the films annealed at 500 ^{o}C for 1h. With further extension of annealing time, (002) orientation degree decreases, and (100) and (101) orientation degrees increase.



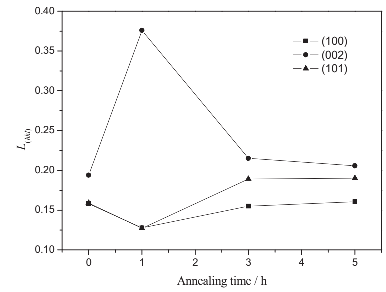


Fig. 1. XRD patterns of ZnO:Al films annealed for different time

Fig. 2. Dependence of the orientation degrees of (100), (002)and (101) on the annealing time

3.2. Optical Properties

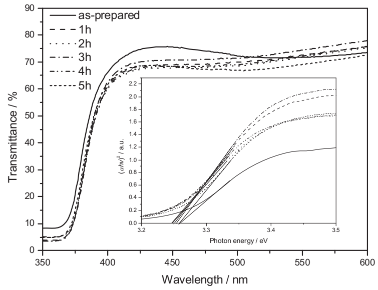


Fig. 3. Transmittance spectra of ZnO:Al films annealed for different time

Figure 3 shows the transmittance spectra of ZnO:Al films annealed at 500 ^{o}C for different time. It can be seen that the transmittance of the as-prepared sample in the visible region is about 70%. The transmittance increases to ~ 80% after the samples annealed at 500 ^{o}C for 1h. However, with the extension of annealing time the transmittance decreases. It is believed that the transmittance of ZnO:Al films relates to the carriers' concentration and the defect concentrations in the films[8,15]. The changes of carriers' concentration can affect optical transmittance. In this study, the resistivity of ZnO:Al films increases with the extension of the annealing time when the annealing time exceeds 1h as shown in the section 3.3. This implies that the carriers' concentration decreases with the extension of the annealing time. So, the decrease of the transmittance does not relate to the carriers' concentration. We presumably attribute the decrease of the transmittance of ZnO:Al annealed for longer time to the increase of the thermally induced defect concentration in the films at high temperature.

In addition, annealing time also has evident influences on the optical bandgaps of ZnO:Al films as shown in the inset in figure 3. The optical bandgaps are analyzed by a conventional method as shown in the inlet of figure 3 [16,17]. It can be seen from the figure that the optical bandgap blueshifts after the samples annealed at 500 ^{o}C for 1h. Subsequent annealing for longer time makes the bandgap blueshift. We attribute the observed behaviors of the optical bandgaps mainly to the changes of defect concentrations in ZnO:Al films. It is believed that many defects are produced during growth process. Annealing at 500 ^{o}C for 1h is helpful to anneal out the defects produced in the growth process, which improves the crystallinity of the films. This results in the blueshift of bandgap due to the decrease of defect concentration in ZnO:Al films. However, during the following annealing stage for longer time, thermally induced defects at high temperatures increase dramatically, which leads to the redshift of the optical band edge due to the increase of defect concentration.

3.3. Electrical properties

Aluminum is a good candidate to dope n-type ZnO. In this study, n-type ZnO:Al with Al/Zn atomic ratio of 1% was prepared by the sol-gel process. The conductivity of ZnO:Al films is higher than that of pure ZnO due to the contribution of extra free carriers of Al^{3+} ions substituting Zn^{2+} ions. To investigate the annealing time effects on the resistivity of ZnO:Al films, we measured the resistivity of ZnO:Al films annealed at 500 ^{o}C for different time with the four-point probe method. Table 1 shows the dependence of the resistivity of ZnO:Al films on the annealing time. The as-prepared films have a higher conductivity than pure ZnO. After annealing at 500 ^{o}C for 1h, the conductivity of ZnO:Al films increases. However, the conductivity of ZnO:Al films decreases with the extension of the annealing time. When the annealing time extends to 4h, the conductivity of the films is too low to be measured by our four-point probe (<$10^{5}\Omega\cdot$cm). The decrease of the conductivity of ZnO:Al films with the extension of annealing time can be attributed to the increase of thermally induced defects in the samples at high temperature. These defects may serve as trapped electron centers and can effectively affect the conductivity of ZnO:Al films.

Table 1. Resistivity of ZnO:Al films annealed for different time

Annealing time (*h*)	As-prepared	1	2	3	4	5
Resistivity (Ω.cm)	0.144	0.04	0.169	0.6	-	-

4. Conclusions

ZnO:Al films doped with Al/Zn atomic ration of 1% have been prepared by the sol-gel process. Annealing time has evident influences on the structural and opt-electrical properties of the films. After annealing at 500 ^{o}C for 1h., the films show *c*-axis preferred orientation with narrow FWHM. The transmittance of the films is ~ 80%, and the band gap redshifts. The resistivity decreases to $4\times10^{-2}\Omega\cdot$cm. With increasing the annealing time, the crystal preferred orientation is absent, and the conductivity increases.

Acknowledgements

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