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Influence of substrate temperature on mechanical, optical and electrical properties of ZnO:Al films

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ABSTRACT

The Al-doped zinc oxide (ZnO:Al) films were prepared on quartz glass flakes and silicon wafers by radio frequency (RF) magnetron sputtering which uses an aluminum-doped zinc oxide ceramic target. Meanwhile, their properties were characterized by scanning electron microscopy, X-ray diffraction, infrared-UV spectrophotometry, resistance measurement, nano-scratch and indentation test. Evolutions of the structural, optical, electrical and mechanical properties of the ZnO:Al films as a function of substrate temperatures ranging from room temperature to 400 °C were analyzed. The results indicate that the ZnO:Al films with a low resistivity value of $4.97 \times 10^{-4}\,\Omega$ cm, a relatively higher adhesion and a high transparency above 90%, can be prepared at a substrate temperature of 400 °C.

1. Introduction

Considering the potential applications in transparent electrodes, light-emitting diodes, solar energy cells, new sensors and energy-efficient windows [1–4], the transparent conductive oxide (TCO) films have attracted great attention because of their excellent and comprehensive physical properties in these fields. Indium tin oxide (ITO) films have been widely used in the industrial production [5–7]. However, they have some limitations such as poor raw materials, high cost, toxicity and instability to H_2 plasma, which limit their practical applications [2,5,8–10]. Therefore, alternative materials are essentially needed to change this awkward situation. Researchers have made great efforts to develop this kind of potential substitutes, and a lot of solid research results have been conducted [7,8,11–16]. Until now, Al-doped ZnO (ZnO:Al) is thought to be the most promising candidate. Similar with ZnO, ZnO:Al is also a wide-band-gap material with large excitation binding energy at room temperature, and has high transparency and stable physical properties to H_2 plasma. More importantly, ZnO:Al is rich-storage and non-toxic [7,8]. Compared with ZnO, ZnO:Al has a higher electrical conductivity because of the concentration of the carries is increased by doped Al [9]. In order to further improve the properties of the films [8–10], researchers have paid a lot of attention on the preparation methods and the experimental parameters optimization. However, some mechanical properties, such as hardness and adhesion have rarely been reported, although they are very important in industrial applications. Therefore, the mechanical properties of the TCO films need to be further studied.

In this article, RF magnetron sputtering was used to fabricate the ZnO:Al films and the dependence of the structural, electrical and optical properties of the ZnO:Al films at different substrate temperature (T_s) were systematically investigated. Also, the effect of substrate temperature on the hardness and adhesion of the ZnO:Al films was studied.

2. Experimental

The ZnO:Al films were deposited by a RF magnetron sputtering apparatus on quartz glass flakes and (1 1 0) silicon wafers, which were carefully cleaned with acetone and ethanol. In our experiments, a high purity aluminum-doped (2% in weight) zinc oxide ceramic target was used. The thickness of ZnO:Al films was fixed to 400 nm by changing the deposition time. During deposition, the Ar gas flow rate was fixed at 20 sccm which controlled by the mass flow controller, the work pressure was 0.3 Pa, and the substructure temperature ranged from room temperature (RT) to 400 °C.

The crystalline structures of the samples were characterized by an X-ray diffractometer (Panalytical X'Pert-PRO) using Cu Kα radiation (40 kV, 30 mA) at X'celerator_normal mode. The adhesion and hardness were measured by a nano-scratch (CSM-nst) and nano-indentation tester (CSM-nht). A scanning electron microscope (LEO-1530FE) was used to analyze the surface morphology. A Dektak-III Series thickness-measuring instrument was used to record the film thickness and a D41-11A/ZM four-probe resistance tester was used to measure the DC resistance. The optical transmittance (%T) spectra were recorded by a Varian Cary 5000 infrared-UV spectrophotometer in the wavelength (λ) range of 200–800 nm.

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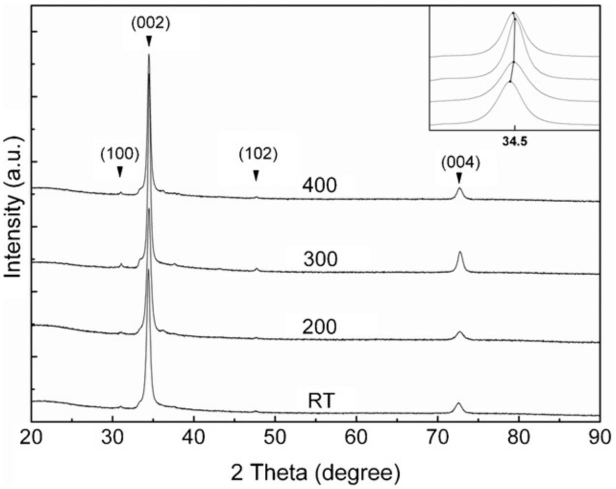

Fig. 1. XRD patterns of ZnO:Al films prepared at different substrate temperatures.

3. Results and discussion

Fig. 1 shows the typical X-ray diffraction patterns of the films prepared at different substrate temperatures. The strong (0 0 2) and weak (1 0 0), (1 0 2), and (0 0 4) peaks can be indexed to wurtzite hexagonal structure of ZnO (see JCPDS file No. 36-1451). And no peaks of Al and Al_2O_3 phase can be identified, proving that the Al atoms are doped into ZnO lattice. All the samples have a very strong (0 0 2) peak of ZnO, indicating that the as-deposited films have *c*-axis preferred orientation due to self-texturing phenomenon. We also observed that the intensity of (0 0 2) peaks increases with increasing substrate temperature below 300 °C. However, the intensity becomes slightly weaker when prepared at 400 °C. This indicates that increased substrate temperature can promote the crystallization of the samples, but a heating temperature of 400 °C will make the crystallization degenerate. From the inset of Fig. 1, a slightly shift of the (0 0 2) peak position with different substrate temperatures can be observed. According to Bragg's equation [14]:

$$2d_{hkl}\sin\theta = \lambda$$

d_{hkl} is the crystalline plane distance for indices (h,k,l), θ and λ are Bragg angle and X-ray wavelength, respectively, the shift of the peak position implies the changes of the lattice constants. In order to investigate the dependence of structure on substrate temperature more clearly, we calculated the lattice constant *c*, and the average grain size *d* based on the X-ray diffraction data. The lattice constants *c* can be calculated by using the following formula [14]:

$$\frac{1}{d_{hkl}^2} = \frac{4}{3}\left(\frac{h^2+hk^2+l^2}{a^2}\right) + \frac{l^2}{c^2}.$$

where *a* and *c* are the lattice constants. The average grain size *d* of the ZnO:Al films was estimated by Scherrer's equations [17]:

$$d = \frac{0.9\lambda}{B\cos\theta}.$$

where *d* is the average grain size and *B* is the FWHM of ZnO:Al (0 0 2) diffraction peak. The calculated results are listed in Table 1. It can be seen that the lattice constant *c* decreases when $T_s \leq 300\,^\circ$C and then increases as T_s increases. A minimum value of the lattice constant was obtained at T_s of 300 °C, which is smaller than the standard ZnO value of 0.5206 nm (JCPDS file No. 36-1451). This can be ascribed to two reasons: one is that smaller Al atoms (the radii of Zn^{2+} and Al^{3+} are 72 pm and 53 pm, respectively) are substituted into Zn sites in the lattice; the other is that larger grain boundary ratio of the nanocrystal films creates larger compressive stress (discussed below).

Table 1
Lattice parameters *c*, grain size, strain and hardness of ZnO:Al films deposited at different substrate temperatures.

T_s (°C)	Lattice parameters *c* (nm)	Grain size (nm)	Strain ε_{zz} (%)	Hardness (GPa)	Adhesion (mN)
RT	0.5211	24	0.177	5.60	22.90
200	0.5202	27	−0.155	4.08	23.58
300	0.5197	43	−0.339	4.46	26.84
400	0.5202	33	−0.155	4.22	32.00

However, the evolution of the average grain size on substrate temperature follows a contrary path. It increases at first and then decreases as the substrate temperature rises, and has a maximum value of 43 nm at T_s = 300 °C (Table 1). It is well known that the thermal treatment can promote the diffusion of atoms to form large grains. But the preferred orientation structure can be partially destroyed if the substrate temperature is too high (see Fig. 3).

Based on the results of lattice constants, the strain ε_{zz} along the *c*-axis can be calculated by using the following equation [15]:

$$\varepsilon_{zz}\quad(\%) = \frac{c - c_0}{c_0} \times 100.$$

where *c* is the lattice parameter of the strained ZnO:Al films calculated from X-ray diffraction data and c_0 is the unstrained lattice parameter of ZnO (0.5206 nm). The results of the calculation above and hardness values measured by nano-indentation were also listed in Table 1. It can be seen from Table 1 that there are relationships between the strain and hardness: both larger positive strain and negative strain lead to higher hardness. At the beginning, samples were deposited on RT substrate where atoms were difficult to diffuse, thus the prepared films were poorly crystallized and caused large positive strain which leads to large hardness. With the increased substrate temperature, the strain was partially released and the crystallization of the films was improved. However, the grain boundary of the films can make atoms diffuse easily and gather along with it the grain boundary has a high activity. As a result, the grain boundary will expand and compress the formed grains, thus negative strain is created in the films. The largest negative strain occurs at T_s = 300 °C. But when T_s increases further to 400 °C, atoms between grains diffuse easily and the lattice

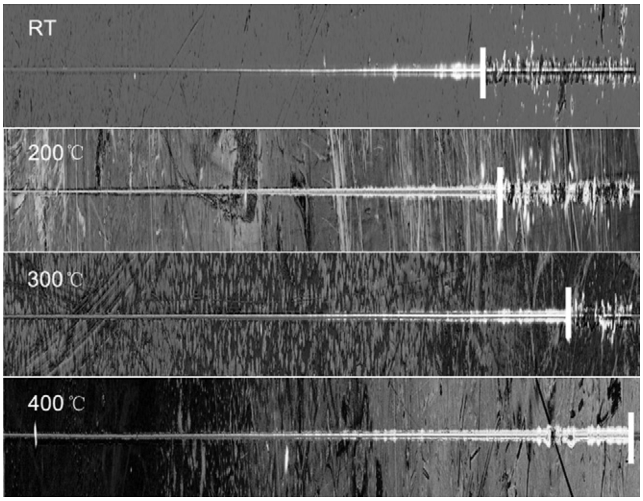

Fig. 2. The adhesion (measured by nano-scratch) of as-prepared films at different substrate temperatures.

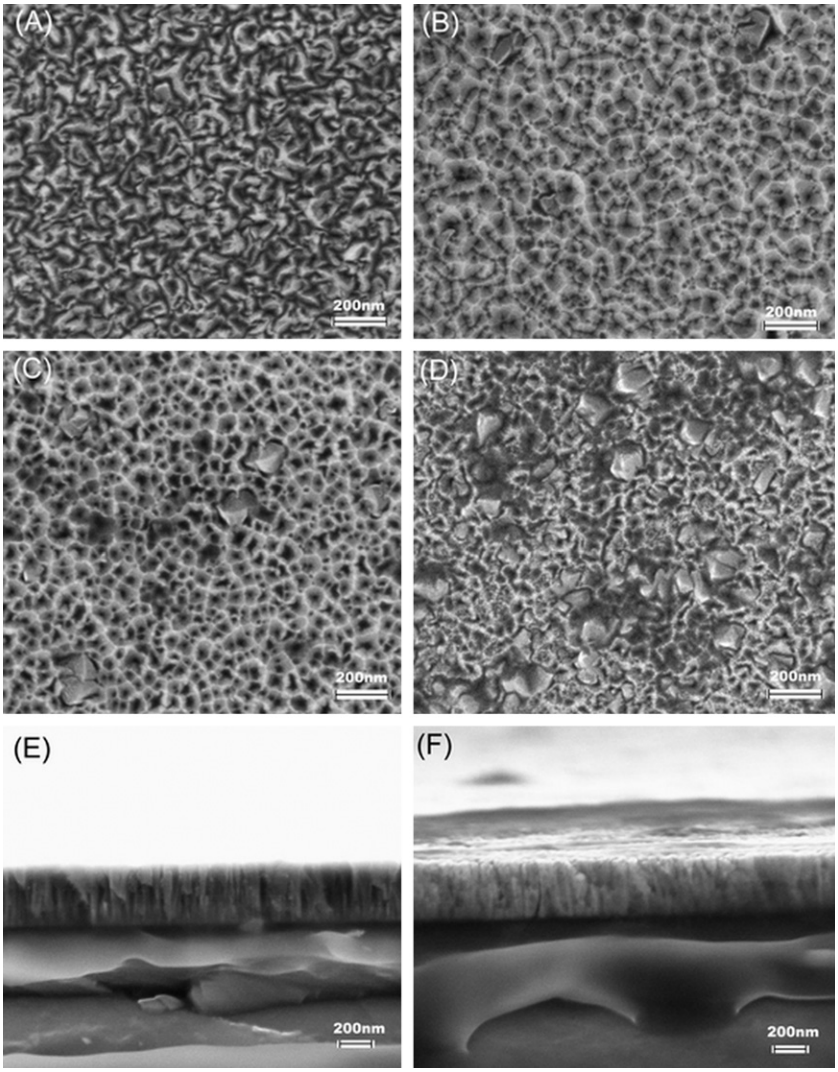

Fig. 3. SEM micrographs of ZnO:Al films prepared at different substrate temperatures: (a)–(d) are ZnO:Al films prepared at RT, 200, 300, and 400 °C, respectively and (e) and (f) correspond to the cross-section of the ZnO:Al films shown in (c) and (d), respectively.

arrangement is improved. This makes the negative strain release and reduces the hardness.

Nano-scratch tester was used to investigate the adhesion of the ZnO:Al films. The begin load was 0.5 mN and loading rate was set to 59 mN/min. The adhesion was defined as the value where the films were completely peeled off. Fig. 2 shows the exact nano-scratch tester photo of the as-prepared films and adhesion value is shown in Table 1. The adhesion increases with increasing the substrate temperature. It is well known that when the substrate temperature increases, the atoms of the substrate surface vibrate fiercely, and the chance of interaction between substrate surface atoms and coming target atoms enhances. Thus, fierce vibration of the atoms results in sufficient diffusion and this process improves the adhesion greatly [18].

To obtain a better understanding on the structural properties and evolution of the ZnO:Al films with the substrate temperature, we have also employed the scanning electron microscopy (SEM) technique to characterize these samples. Fig. 3 shows the SEM images for surface morphology and cross-section of the films deposited at T_S = RT, 200, 300 and 400 °C, respectively. At T_S = RT (Fig. 3a), the film is composed of grains with a uniform distribution and the grain boundary is clear. At T_S = 200 and 300 °C (Fig. 3b and c), the films are more compact and continuous except for some large grains are embedded in the films. However, at T_S = 400 °C (Fig. 3d), the films shows a rough surface morphology. The fractured cross-section images of films prepared at T_S = 300 and 400 °C are shown in Fig. 3e and f, respectively. By comparing Fig. 3e and f, it is easy to conclude that the columnar texture of film prepared at T_S = 300 °C is perpendicular to the substrate clearly while the cross-section structure of film prepared at T_S = 400 °C is disordered. In other words, a substrate temperature at 400 °C can partially destroy the columnar texture and bring strain to the film, which enlarges the lattice constant *c* (see Fig. 2).

Fig. 4 shows the transmittance spectrum of the samples prepared at different substrate temperatures. All the samples have high transparency in visible range and the optical absorption edge of samples is progressively blue shifted with increasing substrate temperature. Such an absorption edge evolution with the substrate temperature has been reported by other researches and is attributed to Burstein–Moss effect [19]. In the present study, the band gap of the films deposited at different temperature was found to follow this rule. According to the results of previous research, the carrier concentration will increase when the substrate temperature increased and the carrier fill in low energy levels of the conduction band. Therefore, the distance of electron vertical transitions from the valence to conduction was increased and the optical band gap

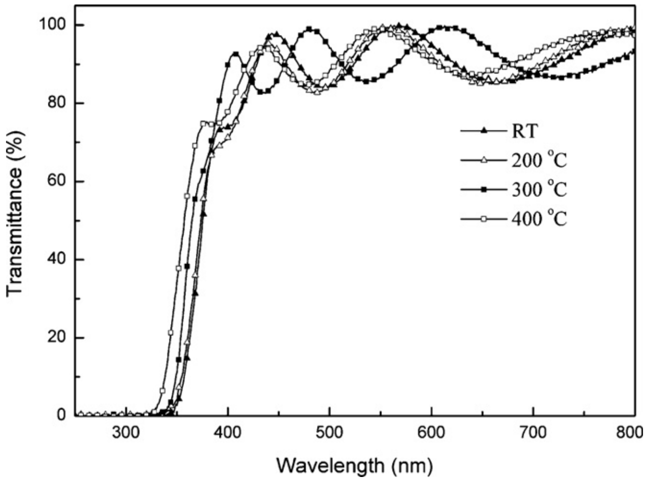

Fig. 4. The transmittance spectra of ZnO:Al films prepared at different substrate temperatures.

was widened with the increase of substrate temperature. In order to determine the exact fundamental absorption edge, we have to calculate the energy gap E_g. The E_g can be determined by [17]:

$$(ah\nu)^n = A(h\nu - E_g)$$

where A is a constant and n characterizes the transition process ($n=2$ and 2/3 for direct allowed and forbidden transitions, respectively, and $n=1/2$ and 1/3 for indirect allowed and forbidden transitions, respectively).

Fig. 5 shows curves of $(\alpha h\nu)^2$ versus $h\nu$ for the ZnO:Al films. The curve has a good straight-line fit over higher energy range above the absorption edge, indicating a direct optical transition near the absorption edge. Also, the results verify the rule that the optical band gap is widened with the increase of substrate temperature.

Fig. 6 shows the resistivity of the films prepared at different substrate temperatures. The resistivity shows a remarkable decrease with increasing substrate temperature and decreases to $4.97 \times 10^{-4}\,\Omega\,\text{cm}$ when prepared at $T_s = 400\,^\circ\text{C}$. This result is consistent with the conclusion as Ref. [20] showed, which indicated that higher substrate temperatures is of advantage to increase the carrier concentration of the ZnO:Al films.

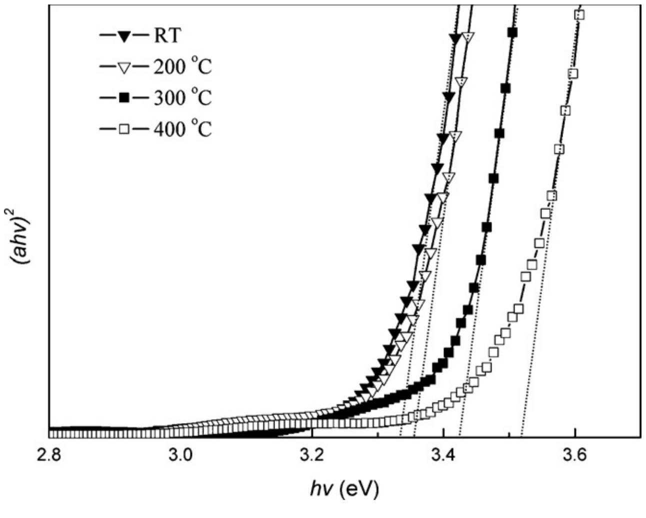

Fig. 5. Band-gaps of the ZnO:Al films prepared at different substrate temperatures.

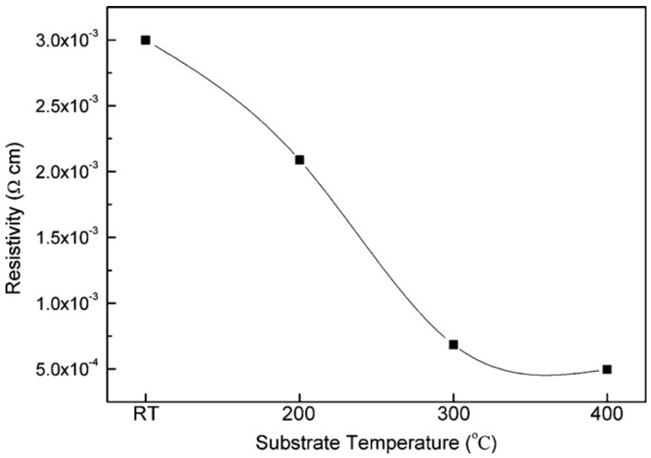

Fig. 6. The resistivity of ZnO:Al films prepared at different substrate temperatures.

4. Conclusions

In conclusion, the effects of substrate temperature on the structural, optical, electrical and mechanical properties of ZnO:Al films were carefully investigated and thus high quality ZnO:Al thin films were obtained. Substrate temperature can strongly affect the crystallization and lattice constants of the ZnO:Al films as well as the adhesion between the film and substrate. At different substrate temperatures (from RT to 400 °C), the strain of the ZnO:Al films is different, and both larger positive strain and negative strain lead to higher hardness. With the increase of substrate temperature, the surface morphology of the as-prepared samples becomes rougher, while the electrical conductivity becomes higher, and a resistivity value of $4.97 \times 10^{-4}\,\Omega\,\text{cm}$ was obtained at 400 °C. Furthermore, a high substrate temperature can improve the adhesion and expand the range of optical absorption when the transmittance is above 90% in most of visible range.

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