Structural, Electrical and Optical Properties of Aluminum-Doped Zinc Oxide Deposited on Glass and Polyimide by RF Magnetron Sputtering Method

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Abstract　The 2% (mass fraction of Al_2O_3) Al-doped ZnO (ZnO∶Al) thin films were sputtered on glass and polyimide (PI) substrates by radio-frequency (RF) magnetron sputtering technology. The effects of substrate materials on the structural, electrical and optical properties of ZnO∶Al thin films deposited on different substrates are studied. It is found that substrate materials have significant influence on film crystallization and resistivity but little on optical transmittance. Highly c-axis oriented ZnO∶Al films in (002) direction are observed on both glass and PI. Besides, it is manifested that the average optical transmittance in the visible-light range (400～800 nm) is around 85% for both films. Films on glass presents stronger (002) diffraction peaks and lower full-width at half maximum (FWHM). The lower resistivity of 2.352×10^{-4} Ω·cm is obtained in samples deposited on glass. Also, films on glass show larger grain size and denser microstructures than films on PI. Meanwhile, the ZnO∶Al films deposited on PI also own good crystallinity and low resistivity of 6.336×10^{-4} Ω·cm, which make them suitable as window materials in flexible solar cells. Films on glass are available as transparent electrodes in flat panel displays and solar cells.

Key words　thin films; ZnO∶Al film; radio-frequency magnetron sputtering; substrate material; polyimide substrate

OCIS codes　310.6860; 310.7005

玻璃和聚酰亚胺衬底上磁控溅射沉积的 ZnO∶Al 透明导电膜的结构、电学和光学性能

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摘要　利用射频磁控溅射方法在玻璃和聚酰亚胺膜(PI)衬底上沉积了氧化铝质量分数为2%的掺铝氧化锌透明导电薄膜(ZnO∶Al)。系统地研究了不同衬底材料对薄膜的结构、电学以及光学性能的影响。分析表明，衬底材料对薄膜的结晶性和电学性能有较大的影响，对可见光透射率却影响不大。X射线衍射(XRD)分析得出所有的ZnO∶Al具有良好的 *c* 轴择优取向性，在可见光区(400～800 nm)两种衬底上的薄膜都达到了85%的透射率。玻璃衬底上的薄膜呈现出更强的(002)衍射峰及相对更小的半峰全宽(FWHM)，薄膜电阻率达到了 2.352×10^{-4} Ω·cm。电镜分析表明，相对于PI上的ZnO∶Al膜，玻璃上ZnO∶Al膜表面有更致密的微观结构及更大的晶粒尺寸。PI衬底上的ZnO∶Al膜也有相对较好的电、光学性能，其中电阻率达到了 6.336×10^{-4} Ω·cm，而且由于PI衬底柔性可弯曲，使得它适于在柔性太阳电池和柔性液晶显示中做窗口层材料及透明导电电极。玻璃上的ZnO∶Al膜则可应用在平板显示和太阳电池技术中。

关键词　薄膜；ZnO∶Al薄膜；射频磁控溅射；衬底材料；聚酰亚胺衬底

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1 Introduction

ZnO:Al is a potential substitute for indium tin oxide (ITO) in corresponding applications, infrared (IR) windows and other optoelectronic devices. One reason is indium and tin are rare and much expensive than ZnO:Al[1~5]. Moreover, ZnO:Al is an ideal alternative material due to its cost saving as well as viable fabrication techniques[6~10].

A number of studies on ZnO:Al films deposited on various substrates have been conducted[7,8,11~13]. However, most attention is paid to the influences of sputtering parameters on the properties of ZnO:Al films rather than substrate materials. Properties of epitaxial growth ZnO:Al thin films rely on substrate conditions such as the crystal orientation, the surface structure, the stability as well as the inherent property. We have chosen two common materials, glass and polyimide (PI), as substrates in the study. Also we systematically investigate the structural, electrical and optical properties of the ZnO:Al films deposited on different substrates.

At present, much attention has been paid to replace glass substrate with flexible substrate, particularly in flexible solar cell and flat-panel display technologies. Transparent conducting films deposited on flexible substrates have many advantages compared with those on glass substrates; they are light weight and are of small volume. Devices made of these films can be folded and easily carried. They can be used in flexible solar cell, plastic liquid crystal displays and unbreakable heat-reflecting mirrors.

Suitable substrate materials and film preparation process are crucial for fabricating high-quality ZnO:Al transparent conductive thin films. In order to fully understand the properties of the ZnO:Al film deposited on different substrates, we give a further study on the dependence of properties of ZnO:Al films on substrate materials at low temperature by radio frequency (RF) magnetron sputtering.

2 Experiment

ZnO:Al thin films have been grown on glass and PI substrates using RF magnetron sputtering method from a sintered ceramic ZnO target which contains 2% Al_2O_3 (mass fraction). All substrates were carefully cleaned in acetone, rinsed in alcohol and then cleaned in an ultrasonic cleaner within a neutral solution. The substrates were placed parallel to the target surface with a 60 mm distance. The deposition was carried out with 2 h sputtering duration and 120 W sputtering RF power. The base pressure in the chamber was fixed at 10^{-4} Pa. The process was performed in a pure argon ambient and the flow rate was constant 20 sccm (sccm: standard cubic centimeters per minute), which was controlled by the mass flow controller. The depositing pressure was 1 Pa. The substrate temperature was 300 ℃.

The structural properties of the ZnO:Al films were analyzed with X-ray diffraction (XRD, X′Pert PRO). The surface profile were observed using atomic force microscope (AFM) under contact mode as well as field emission scanning electron microscopy (FE-SEM). The electrical resistivity of the film was measured by a four-point probe system. The optical transmittance was measured by ultraviolet (UV) visible spectrophotometer (UV-2550) in the wavelength range of 300~900 nm.

3 Results and discussion

3.1 Structural features and morphological structures

The crystalline structures of ZnO:Al films sputtered on glass and PI were examined by XRD measurement in $\theta-2\theta$ scan mode. In the experiment, the substrate materials varied from glass to PI while the deposition conditions were kept the same. Figure 1 shows the XRD patterns of ZnO:Al thin films deposited on glass and PI substrates. XRD patterns reveal that all the ZnO:Al films own highly (002) preferred orientations with c-axis perpendicular to the surface. The main diffraction peaks for films on glass and PI are around 34°, as shown in Fig. 1. Comparing the XRD pattern of ZnO:Al film deposited on glass with that on PI, the former shows stronger diffraction intensity which indicates an enhancement in crystallization. The full-widths at half-maximum (FWHM) of (002) diffraction are 0.1632 on glass and 0.2007 on PI, which reveals the single phase and good crystalline quality of all the ZnO:Al films on various substrates. Overall, films on glass own relatively better crystallinity.

The ZnO:Al thin film deposited on glass substrate shows a stronger and sharper (002) diffraction peak than the film deposited on PI, which indicates that films on glass have better crystalline quality. Table 1 gives the XRD data and crystal size calculated using the FWHM values according to Scherrer′s equation[14].

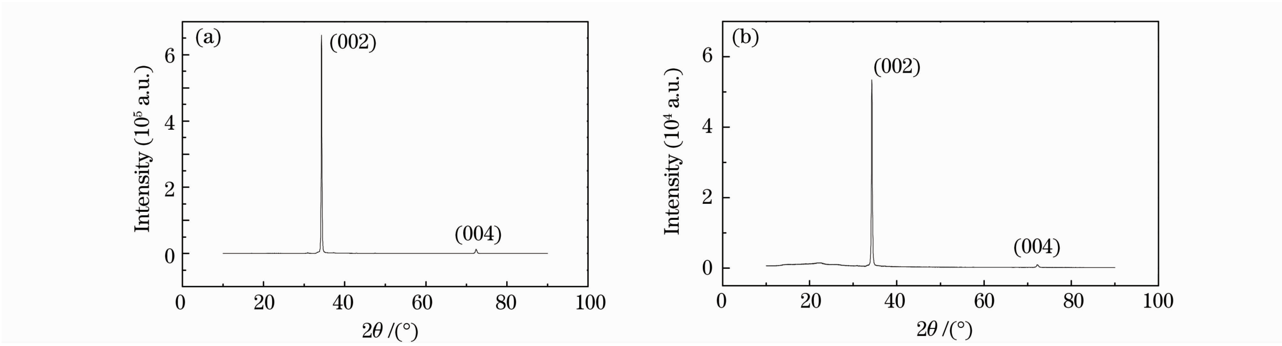

Fig. 1 XRD spectra of (a) ZnO:Al thin film deposited on glass and (b) ZnO:Al thin film deposited on PI substrate

From Table 1, the XRD diffraction intensity of ZnO:Al thin films deposited on glass and PI are 641448.30 and 51474.37 and the FWHM are 0.1632° and 0.2007°, respectively. Based on the above analysis, films deposited on glass present better crystallinity; nevertheless, both ZnO:Al films on glass and PI exhibit highly preferential c-axis orientation with good crystallinity. However, ZnO:Al films deposited on PI film and glass exhibit additional peaks originated from (004) with much weaker intensity. The (002) diffraction peaks of the ZnO:Al thin films deposited on glass and PI film are located at 34.2804° and 34.2506°, respectively. This means that the films deposited on glass and PI substrates almost have the same lattice structure, and both of them are polycrystalline with a hexagonal structure. We ascribe the difference in structures to substrate roughness. Among the substrate materials, glass has smaller roughness, consequentially films on glass have stronger (002) diffraction peak which is close to the single crystal ZnO (002) diffraction peak ($2\theta = 34.43°$). In conclusion, substrate materials have decisive influence on crystal properties of the ZnO:Al films when the deposition conditions keep the same.

Table 1 XRD data and crystal size of the ZnO:Al films deposited on glass and PI

Substrate	2θ /(°)	FWHM /(°)	Crystal size /nm	Intensity (a.u.)
Glass	34.2804	0.1632	50.37341	641448.30
PI film	34.2506	0.2007	40.95806	51474.37

From Table 1, we can see that the crystal size of the ZnO:Al film deposited on PI substrate is 40.9586 nm, much smaller than that of 50.37341 nm on the glass substrate. It can be explained that surface roughness is essential for the film growth. A good crystallinity is attributed to a very flat substrate[15]. Compared with glass, PI films are flexible and not as smooth as glass. This might be the reason that ZnO:Al films on the PI film show weaker XRD diffraction intensity and smaller crystal size. On the other hand, the crystallinity of ZnO:Al thin films is related to the film stoichiometry, the mismatch in the thermal expansion coefficients and lattice imperfections[16,17]. In our experiment, the substrate temperature was fixed at 300℃. For the films deposited on different substrates, the different thermal expansion coefficients of substrates would influence the initial growing process of the films. However, despite the relatively weak diffraction intensity, the films deposited on flexible substrates also exhibit highly preferential c-axis orientation.

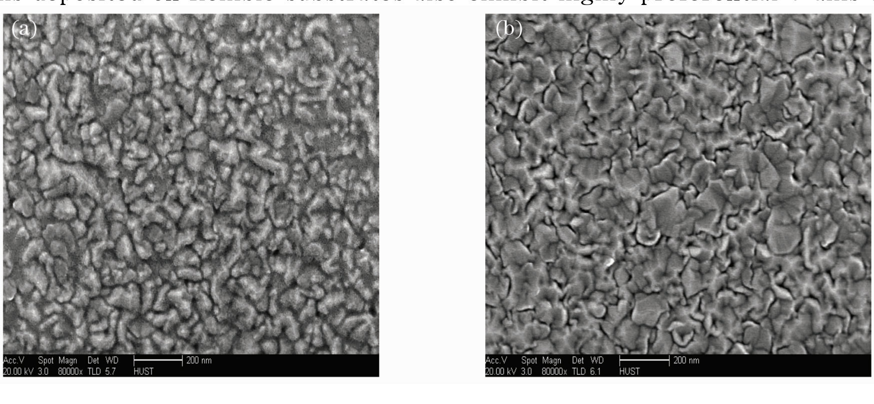

Fig. 2 Planar SEM microstructures for ZnO:Al samples on (a) glass and (b) PI

In addition to the above-described observations in structural behaviors, the more striking difference between the films on glass and PI substrates is on morphological performances. The microstructures for the ZnO:Al samples fabricated on various substrate materials are found to be quite different. As exhibited in Fig.2(a), SEM microstructures of films on glass are dense and hill-shaped with lots of grain boundaries. However, films on PI are schistose structures with some craters, as presented in Fig.2(b). Perhaps the mismatch in lattice and thermal expansion coefficient makes the films grown on different substrates show different microstructures and surface profile. Nevertheless, we can see that both the grain distributions of the ZnO:Al thin films deposited on PI and glass substrates are uniform with dense microstructures.

Fig.3 shows AFM topographies of the ZnO:Al thin films deposited on glass and PI substrates. The root mean square (RMS) average roughness of the substrate materials is calculated from a 2000 nm square scan area, and the results are shown in Table 2. The RMS average roughness of the glass surface is 2.627 nm, smaller than 6.341 nm of the PI surface. The improved crystallinity and larger grain size might be ascribed to the relatively small surface roughness. It is obvious that films on PI are not as good as films on glass. A large number of nanometer-sized peaks have developed, as shown in Fig.3(b). These results, together with the XRD analysis, indicate that the crystallinity is influenced by the substrate materials. The well-crystallized ordered film growth depends on the smooth substrate surface.

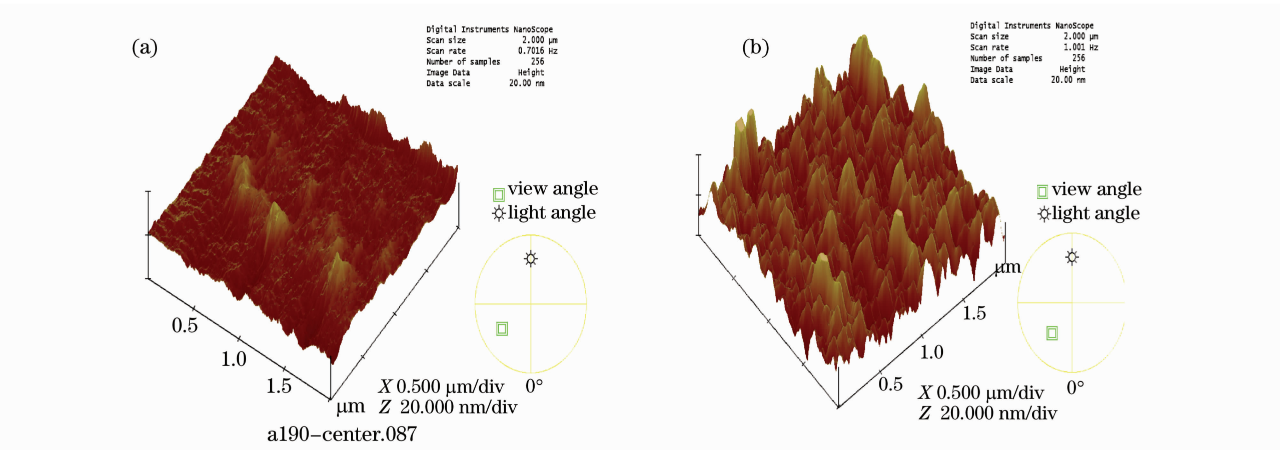

Fig.3 Planar AFM micrographs of ZnO:Al films sputtered on (a) glass and (b) PI

3.2 Electrical properties

Table 2 shows resistivity as a function of substrate surface roughness for films on glass and PI prepared at the same sputtering parameters. We adopted a four-point probe system (RTS-2A) to measure the resistivity, and RMS average roughness was obtained by AFM measurement.

Table 2 Dependence of resistivity on RMS average roughness for ZnO:Al films deposited on glass and PI substrates

Substrate materials	Glass	PI
Resistivity /(Ω·cm)	2.352×10^{-4}	6.336×10^{-4}
Roughness /nm	2.627	6.341

Data in Table 2 manifest that the resistivity of ZnO:Al films varies with substrate material′s surface roughness. The lower resistivity is obtained from the ZnO:Al films deposited on glass substrates with smaller surface roughness. The electrical property is a little worse on flexible substrates with the resistivity of 6.336×10^{-4} Ω·cm on PI. We can see that resistivity presents the similar phenomenon with surface roughness being 6.341 nm on PI and 2.627 nm on glass. As the substrate material′s roughness increases, the resistivity climbs from 2.352×10^{-4} Ω·cm on glass to 6.336×10^{-4} Ω·cm on PI. It can be explained that relatively low surface roughness is beneficial to the growth of initial crystal nucleus, and films grown on glass tend to have better crystallinity, which has been confirmed by the XRD analysis. Consequentially, ZnO:Al films on glass have less neutral impurities and grain-boundary, resulting in better conductivity.

It has been known that various scattering mechanisms might be involved in semiconductor materials, including ionized impurity scattering, neutral impurity scattering and grain-boundary scattering[17]. For the ZnO:Al thin films deposited on different substrates, substrate structure and roughness would influence the initial growth of the ZnO:Al thin films. According to the XRD and AFM results, the crystallinity and the grain sizes of ZnO:Al thin films are significantly different. The mobility of the charge carriers might be affected by grain-boundary scattering. Lattice imperfection and disorder might appear on different substrates during the ZnO:Al thin film growth process, resulting in the variation of resistivity of the different ZnO:Al thin films. However, the mechanism of scattering is not fully understood yet, further investigation is necessary in future work. Combined with the previous analysis, we can see that the smaller surface roughness, the better crystallinity and the lower resistivity.

3.3 Optical transmittance

Fig. 4 shows the transmission spectra of ZnO:Al thin films deposited on glass and PI substrates. An average optical transmittance of 85% in the visible light range is obtained in all of the specimens. As the substrate varies, it seems that substrate materials have little influence on the transmittance. Many researches have confirmed that substrate materials have little effect on the transmittance of transparent conductive oxide (TCO) when the deposition parameters keep the same, especially in the RF magnetron sputtering technologies. However, the absorption edge of films on glass slightly shifts to the shorter wavelength compared with films on PI. This is mainly because of the Burstein-Moss effect[18].

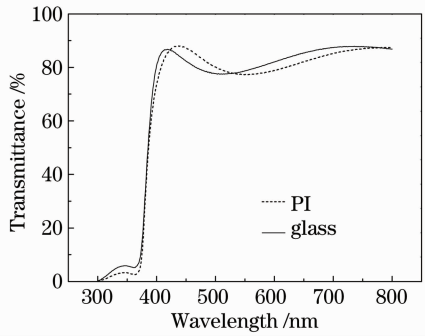

Fig. 4 Transmittance as a function of wavelength for ZnO:Al films deposited on glass and PI substrates

4 Conclusions

The influence of substrate materials on the properties of ZnO:Al thin films by RF magnetron sputtering method is studied. We obtain highly transparent conducting ZnO:Al films on both glass and PI substrates, and all the films present highly (002) preferred orientations. A comparison of the optical, electrical and structural properties for films deposited on different substrates is given. It is found that films on glass show better performance such as enhanced crystallization, stronger (002) diffraction intensity and lower resistivity. However, films on glass and PI have almost the same transmission in the visible light region. We ascribe the differences in crystalline and electrical properties to the varied surface roughness of different substrate materials. Substrate materials have slight influence on optical transmittance, because optical transmittance is mainly affected by film thickness and amounts of Al_2O_3. And film deposited on different substrates under the same conditions own the equal thickness and amount of Al_2O_3. Overall, larger grain size of 50.37341 nm, lower FWHM of 0.1632°and lower resistivity of $2.352\times10^{-4}\ \Omega\cdot$cm are obtained by ZnO:Al films on glass substrates.

Although the quality of films deposited on PI is somewhat worse than films on glass, they also have highly preferential c-axis orientation with good crystallinity and the resistivity is as low as $6.336\times10^{-4}\ \Omega\cdot$cm, which would provide a possibility of achieving excellent TCO films for applications such as plastic liquid crystal displays and flexible solar cells.

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