Al:ZnO films deposited on flexible transparent polyimide substrate by magnetron sputtering at different substrate temperatures

WEIMIN LI, HUIYING HAO*
School of Science, China University of Geosciences, Beijing, China

Al:ZnO films were deposited on flexible transparent polyimide(PI) substrate by magnetron sputtering at different temperatures(from room temperature to 250℃) using ceramic ZnO:Al (3 wt.% Al_2O_3) target without any optimized process. The PI has a high glass transition temperature more than 250℃ and high transmittance in the visible spectrum better than 92%.The structural, optical and electrical properties of the film were investigated. The largest grain size was about 26.2 nm with a perfect preferential orientation of (002) planes. The lowest resistivity of AZO films deposited at 150℃ was $2.51\times10^{-3}\Omega\cdot cm$ and average transmittance in the visible spectrum was 74.3%.

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1. Introduction

Wide gap Al doped ZnO(AZO) film has been recognized as a potential material to substitute of indium tin oxide (ITO) film used as transparent conducting oxide film in solar energy cells, transparent electrodes, light-emitting diodes, new sensors and flat panel displays.[1-5]Compared with ITO, AZO has a lot of advantages such as good thermal stability against hydrogen plasma, non toxicity, an easy fabrication, enormous amounts of raw materials and low expense and so on [6-8].

AZO films deposited on flexible transparent plastic substrate are superior to that deposited on glass currently in many aspects. Compared with glass substrate, plastic substrate is lighter, more inexpensive, flexible and more suitable for use in small device, which is even significant important for loading sensing field such as civil aviation and space industries [9-11]. However, AZO films deposited on flexible transparent plastic substrate have common disadvantages: poor temperature resistance or low transmittance in the visible spectrum [12-18].

In this paper, we report a new polyimide(PI) invented by Zhenghua Yang from Changchun Institute of Applied Chemistry, Chinese Academy of Sciences is applied as substrate for producing AZO films. The use of 2,2′-bis(trifluromethyl) benzidine (TFDB) as an essential diamine monomer leads to excellent properties such as significant improvement in solution, light color with high thermostability and good mechanical strength, cut-off wavelength of light transmission about 380 nm, high transmittance in the visible spectrum better than 90%. The most important of all, the high glass transition temperature is more than 250℃ with flattening and no pinhole surface, which can satisfy temperature at which amorphous silicon (a-Si) and nanocrystalline silicon (nc-Si) materials of thin film silicon based solar cells are generally made [19]. AZO films were prepared by magnetron sputtering. The effects of substrate temperature on the properties of AZO films were investigated by X-ray diffractometry (XRD), scanning electron microscopy (SEM), grating spectrometry, as well as Hall Effect Measurement System.

2. Experimental

AZO films were deposited on transparent PI substrates by radio magnetron sputtering at different substrate temperature from room temperature (RT) to as 250℃. The diameter and the purity of ZnO:Al (3wt.% Al_2O_3) target used in the paper were 6cm and 99.97%, respectively. The working gas was argon atmosphere with purity of 99.999%. The sputtering chamber was excavated to lower than 2.0×10^{-3}Pa. The PI substrates were cleaned by ultrasound successively in isopropyl alcohol, alcohol and deionized water for 10 minutes. Then the substrates were dried in vacuum drier to remove water. The target was pre-sputtered for 5 minutes to remove pollutants on the surface by argon atmosphere. The AZO films were obtained at a working pressure of 1.0Pa and a sputtering power of 60W with deposition time of 40 minutes.

The thicknesses of the films were measured by F20 film thickness test system. Keithley system was used to measure the hall effect of the films to get the resistivity, carrier concentration and mobility data. Optical transmittance measurements were carried out in the wavelength range of 330–800 nm by using grating spectrometer. The surface morphology was analyzed by scanning electron microscopy (SEM). XD-3 X-ray diffraction (XRD) produced by PERSEE was used for structure determination.

3. Results and discussions

All the films deposited on PI substrate had a smooth and uniform surface. The thicknesses of all the films were about 700 nm. The PI didn't show little apparent deformation even after being deposited at 250°C. What's more, the AZO films weren't obviously stripped from the substrates after a series of tests.

XRD diffraction patterns of the AZO films deposited at 60W and 1.0 Pa on the polyimide substrate at different temperatures are shown in Fig. 1. All the films deposited on PI substrate had a strong diffraction peak associated with the (002) plane of hexagonal phase ZnO and a very weak (004) peak. The presence of a strong diffraction peak of (002) indicates that films had a (002) preferred orientation. Neither metallic zinc or aluminum characteristic peaks nor aluminum oxide peak was observed from the XRD patterns, which implies that aluminum atoms replace zinc in the hexagonal lattice or aluminum segregate to the nanocrystalline spectrum in grain boundary. The intensity of diffraction peak in the direction (002) becomes stronger with increasing substrate temperature. This means that the higher substrate temperature leads to a more crystalline film. However, when the substrate temperature increases to 250°C, the intensity of (002) peak decreases, which is probably caused by the very small deformation of the substrate.

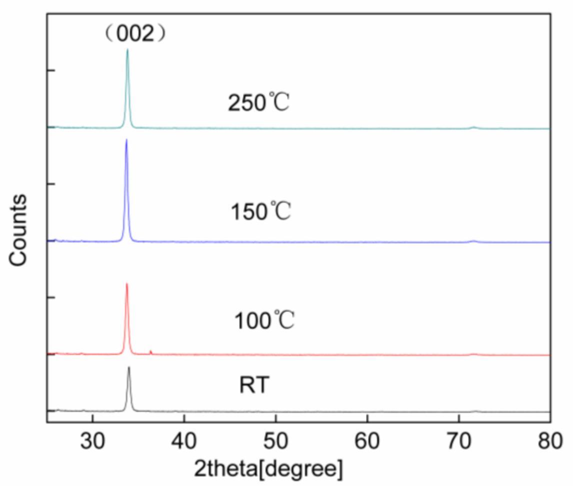

Fig. 1. XRD diffraction patterns of the AZO films deposited at sputtering power of 60W and working pressure of 1.0Pa on the polyimide substrate with different substrate temperatures (from RT to 250 ℃).

The crystal size of ZAO films produced at different substrate temperature can be evaluated by Scherer's formula:

$$D = \frac{0.9\lambda}{\beta\cos\theta}$$

Where λ is the X-ray wavelength (0.15406 nm), β and θ are the FWHM and diffraction angle. As is shown in Fig. 2, the grain size increases with substrate temperature rising. The grain size of film obtained at room temperature is 23.5 nm. When the temperature increases to 150 ^{o}C, the grain size reaches the maximum 26.2 nm. There is a decrease in grain size when the substrate temperature rises to as high as 250°C.

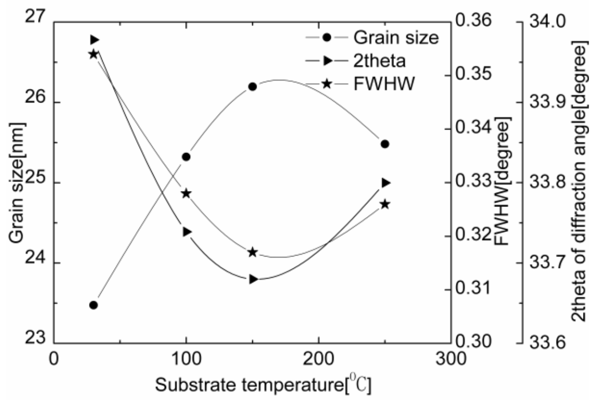

Fig. 2. Grain size, FWHM and 2theta of diffraction angle as a function of substrate temperature.

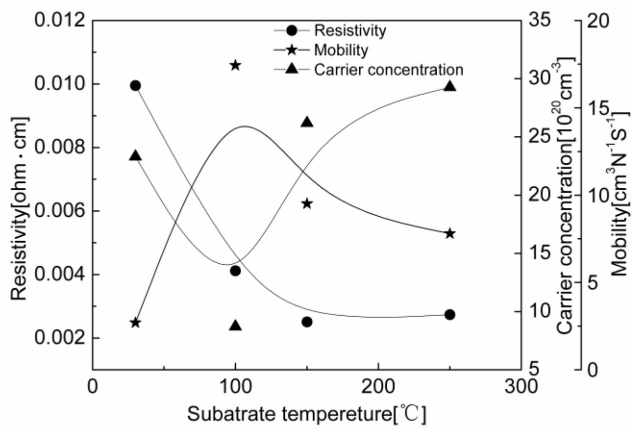

Fig. 3. Resistivity, mobility and carrier concentration as a function of substrate temperature.

Fig. 3 shows the electric properties of AZO films deposited at different substrate temperature. It can be seen that the substrate temperature has a significant effect on the resistivity of AZO films. The resistivity decreased from $9.95\times10^{-3}\Omega\cdot$cm at room temperature to $2.51\times10^{-3}\Omega\cdot$cm as the substrate temperature raised to 150°C. The corresponding mobility and carrier concentration are 9.51cm^{3}N^{-1}S^{-1} and 2.62×10^{21}cm^3, respectively. When the substrate temperature rises to 250°C, the resistivity of AZO film was $2.74\times10^{-3}\Omega\cdot$cm which is a little higher than that deposited at 150°C.

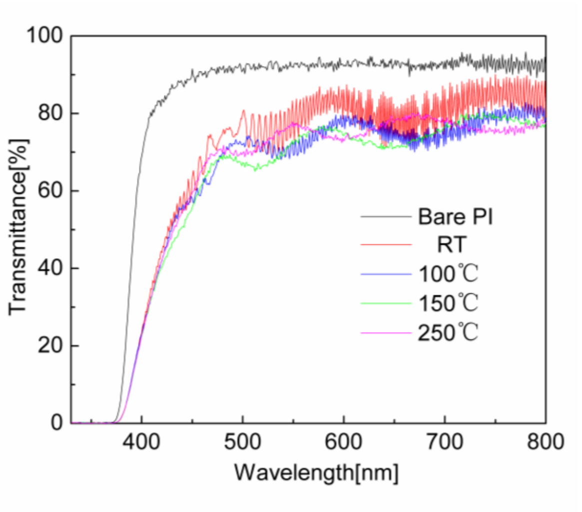

Fig. 4. Optical property of bare PI and AZO films deposited on PI substrate.

Optical transmission of the samples as a function of wavelength is shown in Fig. 4. From Fig. 4 we can see that the bare PI substrate has a relative high average transmittance in the visible spectrum(between 500 nm and 800 nm)which is as high as 92.6% with a cut-off wavelength at about 380 nm.As for the PI substrates coated with AZO films, the transmittance data are 80.1%(room temperature), 75.5%(100℃), 74.3%(150℃) and 75.8%(250 ℃), respectively. The absolute transmittance ($T_{absolute}=T_{average}/T_{substrate}$, where $T_{substrate}$ represents the average transmittance of substrate in visible region) are 87.3% (room temperature), 81.5% (100℃), 80.2% (150℃) and 81.9%(250℃) correspondingly.

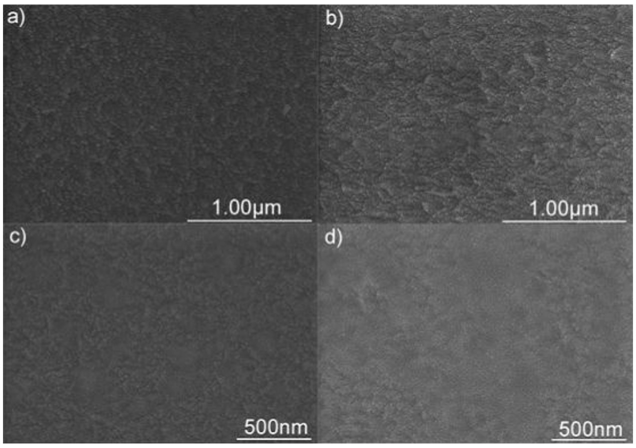

Fig. 5. SEM micrographs of AZO films deposited on PI substrate at different temperature:(a)room temperature, (b)100℃, (c)150℃, (d)250℃

SEM micrographs of AZO films deposited on PI substrate at different temperatures are shown in Fig. 5. All the films have a relative continuous surface, and there are not clear cracks and holes on the surface, which indicates that the AZO films adheres closely to PI substrate and the quality of AZO films is good. As we can see in Fig.5, the surfaces of AZO films become smoother as increasing in substrate temperature.

According to the above discussions, the AZO films can deposit on the heat-resistant transparent PI substrate at temperature higher than 200℃, and the amorphous silicon (a-Si) and nanocrystalline silicon (nc-Si) materials of thin film silicon based solar cells are generally made.[19] So it could be expected that AZO films deposited on the PI substrate by using optimal processing parameters will make significant progress in flexible thin film solar cell.

4. Conclusions

AZO films were successfully produced on a high temperature resistant and transparent PI substrate by magnetron sputtering at various substrate temperatures. The structural, optical, and electrical properties of the film were investigated by X-ray diffractometry (XRD), scanning electron microscopy (SEM), UV–visible spectrophotometry, as well as Hall Effect Measurement System. All the films deposited on PI substrate had a smooth and uniform surface and didn't obviously strip from the substrates after several test. The AZO films showed a perfect preferential orientation of (002) planes at any substrate temperature by X-ray diffractometry investigation. The lowest resistivity of AZO films deposited at 150℃ was 2.51×10^{-3} Ω·cm and average transmittance in the visible spectrum was 74.3%. In conclusion, the achievement of excellent photoelectric properties of AZO thin films on transparent PI substrate at relative high temperature will make contribution to the field of flexible thin film solar cell.

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*Corresponding author: huiyinghaol@cugb.edu.cn