The influence of H_2/Ar flow ratio on the structure and optoelectronic properties of ZnO:Al films deposited on glass and polymer substrates

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Aluminium doped ZnO (ZnO: Al) films were deposited on glass and polymer substrates by RF magnetron sputtering at various mass flow ratio of H_2/Ar. The influence of H_2/Ar ratio on structure and properties of films was investigated by X-ray diffractometery (XRD), X-ray Photoelectron Spectrum(XPS),UV-visible spectrophotometer, as well as Four-point Probes System. The results revealed that low H_2 content in the deposition atmosphere is helpful to improve the crystal quality and optoelectronic properties of ZnO:Al films.H_2 has a notable effect on the stoichiometry of ZnO:Al films.The O 1s and Zn 2p peak of the films with H_2 dilution shifted towards the small binding energy and larger value respectively.The resistivity of $5.32\times10^{-4}\Omega$cm and the average transmittance of 91.3% in the visible region was obtained for the film prepared in the 5% H_2/Ar ambient on glass.

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1. Introduction

ZnO:Al(ZAO) thin films are attracting more and more attention in photovoltaic applications because of their advantageous properties, such as non-toxicity, thermal stability, low cost and especially the high stability in hydrogen plasma during the fabrication process of silicon thin film solar cells by plasma-enhanced chemical vapor deposition[1-2]. Magnetron sputtering is the most widely used technology to prepare ZAO thin films, which has characteristics of high deposition rate, low substrates temperature, good film adhesion, easy preparation for a large area etc[3-5].The structure and properties of ZAO films are influenced significantly by the sputtering processing conditions, such as the substrate temperature, sputtering power, deposition pressure etc.The optimisation of these parameters can result in high quality ZAO films with excellent electrical and optical properties.Many researchers have been studying on the dependence of ZAO performances on these parameters[6-8]. Recently, the role of hydrogen in ZAO films attracted researchers' attention because of some results from theory calculations and experiments indicating that hydrogen should be a shallow donar in ZnO[9-10] . There have been some studies on the role of Hydrogen in ZnO[11-12].But it is still many works to be done to understand fully on the effects of Hydrogen in ZnO.

In this paper, ZAO thin films were deposited on glass and polymer substrates by RF-Magnetron Sputtering method. The polymer is transparent TPT, which can be seen in our paper before[13].The mass flow ratio of H_2/Ar varied from 0 to 12.5%. The influence of H_2/Ar ratio on the structural, optical and electrical properties of the ZAO films on different substrates were investigated.

2. Experimental procedure

The ZAO thin films were deposited on glass and polymer substrates at 400℃ and 25℃ respectively by RF magnetron sputtering system from a ZnO: 2.0 wt % Al_2O_3 target (purity: 99.99%). The target size is Φ60mm×5mm.The substrates were ultrasonically cleaned in acetone and then alcohol for 15 min respectively before they were loading into the deposition chamber. The distance between the target and substrate was about 50 mm. The sputtering power and the working pressure were maintained at 120W and 1Pa respectively. The mass flow of Ar was maintained at 20 sccm and the mass flow of H_2 was varied in 0 , 1sccm,1.5sccm, 2sccm and 2.5sccm.The mass flow ratio of H_2/Ar was expressed as "R", which varied from 0 to 12.5%.The film thickness is measured by cross-section scanning images of ZAO films and calibrated by means of spectrophotometric method.The thickness of the ZAO films were in the range of 800nm~600nm.The structure properties of the ZAO films were analyzed with X-ray diffraction (XRD, X'Pert PRO, λ=0.154 nm) using Cu-Kα radiation and X-ray

Photoelectron Spectrum (XPS , VG Multilab2000). The transmittance of the films was measured by spectrophotometer (UV, Lambda 35) in the range of 300~900 nm and the electrical properties were characterized by Four-point Probes (RTS-8).

3. Results and discussions

3.1. Structure properties

Fig.1 (a) and (b) show XRD patterns of the ZAO films deposited on glass and polymer substrates at various "R". It could be seen that "R" had different effects on the crystalline structure of ZAO films deposited on different substrates.All ZAO films deposited on the glass had a diffraction peak at 2θ about 34.3°~34.4°, which is associated with the (002) plane of hexagonal phase ZnO and implies that the prepared films had a c-axis preferred orientation.But the ZAO films deposited on polymer existed (101),(110) plane except for (002) when "R" was 0 and 5%, then had no diffraction peak of (002) plane and only had weak peak of (101),(110) plane when "R" was 7.5~12.5%. For both substrates, the position of (002) peaks of the ZAO films with hydrogen shifted to smaller diffraction angle compared with the position of (002) peaks of the films without hydrogen.It was perhaps because that hydrogen atoms existed in the form of Zn–H–O, which made the lattice parameter of ZnO films increase, thus diffraction angle becoming smaller[14]. The (002) peak intensity of ZAO films on glass substrates increased and then decreased with increasing "R", which indicated that "R" had a optimal value,which is about 5% in our experiments. When H_2 /Ar ratio in the deposition atmosphere exceeded the value, the grain boundary defects would raised resulting from Superfluous Hydrogen atoms, and then caused the crystal quality of ZAO films worsening[15].However, the (002) peak intensity of ZAO on the polymer substrate increased with increasing "R". This maybe have two reasons:low atom mobility due to poor thermal conductivity of the polymer and low temperature, and chemical reactions between the polymer substrate and the hydrogen plasma[16].

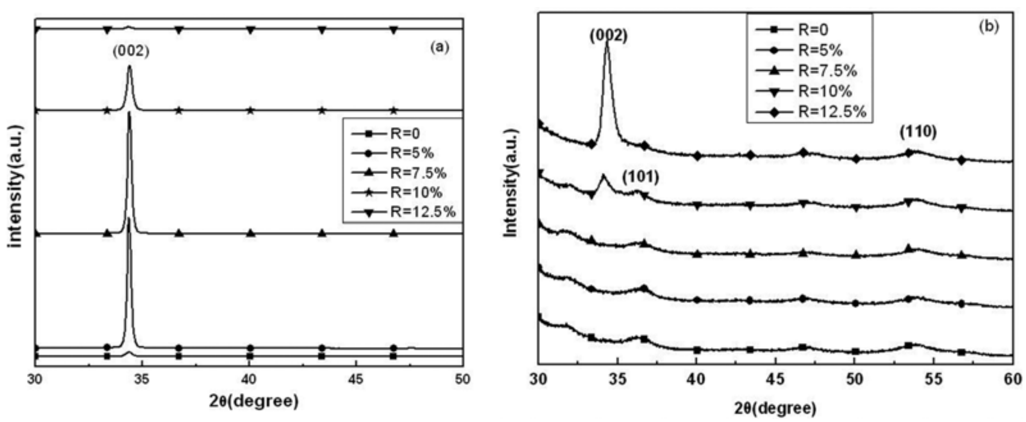

Fig.1.XRD patterns of the ZAO films deposited on glass(a) and polymer (b) substrates at various H2/Ar ratio(R)

3.2. Chemical state in the surface of ZAO films

XPS spectra for Al, Zn and O of the ZAO films prepared with 5% H_2/Ar ratio and without H_2 were investigated. It was difficult to detect the element Al due to its low concentration in the films and its low ionization cross-section value[17].Fig.2(a) and (b) are the XPS spectra of O 1s and Zn 2p of ZAO films on glass and polymer substrates. From figure2(a), it could be found that O 1s peak of the films with H_2 dilution and without H_2 was 530.2eV and 530.6eV, respectively. The O 1s peak of the films with H_2 dilution shifted towards the small binding energy, which indicated that the ZAO films were oxygen-deficient with the introduction of hydrogen. This was because that hydrogen combined with oxygen of ZAO films.The resistivity of ZAO films decreased with oxygen vacancy increasing, which was confirmed by the results of four-point probe test. Moreover, oxygen deficiency was found to be of benefit to the stability of ZAO films against plasma[18].As shown in Fig.2(b), the binding energy of Zn 2p moved to larger value with the introduction of hydrogen, indicating that more zinc atoms remained in the ZAO films.From the results of the XPS mesurements, it was revealed that H_2 had an remarkable influence on stoichiometry of ZAO films.

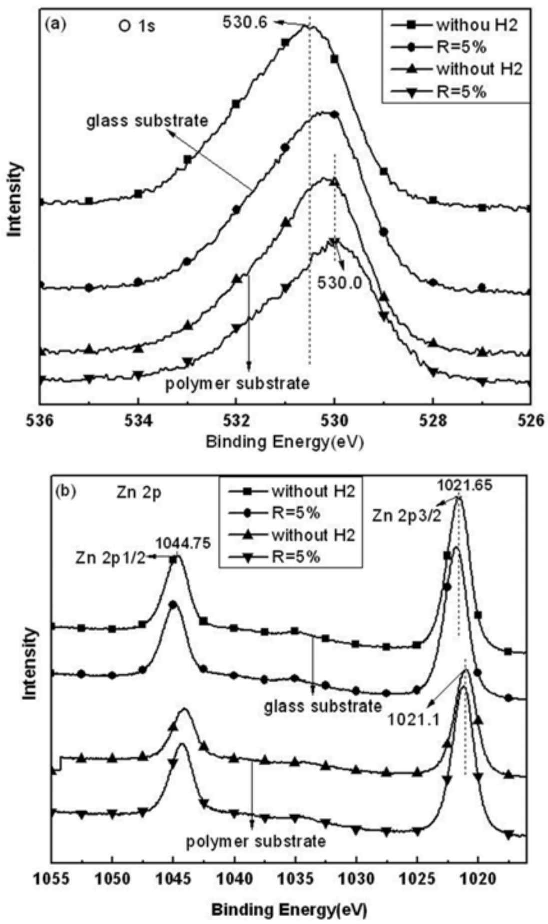

Fig. 2. .XPS spectra of the ZAO films deposited on glass and polymer substrates at various H_2/Ar ratio(R):O 1s(a) and Zn 2p(b)

3.3. Optical properties

Fig.3(a) and (b) show the optical transmittance of the ZAO films deposited on glass and polymer with various "R". It was seen that the average transmittance in the visible region was above 85% for all the films on glass substrates and above 65% for the films on polymer substrates with low "R"(0~7.5%). The transmittance of the films on glass was not affected greatly by the deposition atmosphere. But the transmittance of the films on polymer was influenced obviously by the deposition atmosphere, the samples with high "R" showed bad optical properties, meaning excessive H_2 has negative influence on the transparency of the ZAO films, it could be attributed to intergranular zinc atoms arising from excessive hydrogen. As "R" increasing, the absorption edge of ZAO films was shifted to the shorter wavelength. It is due to the Burstein-Moss effect[19], that is the blue shift of the absorption edge with increasing carrier concentration.It was concluded that the deposition atmosphere with low "R" (0~7.5% in this experiment) can approve optical properties of ZAO films, especially the films prepared on polymer substrates

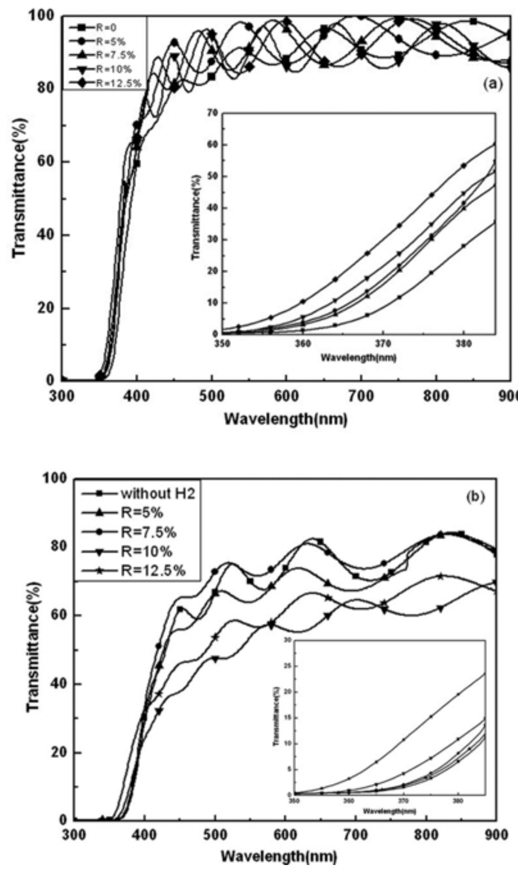

Fig. 3.Optical transmittance of the ZAO films deposited on glass(a) and polymer (b)substrates at various H2/Ar ratio(R)

3.4. Electrical properties

Fig.4(a) and (b) are the electrical properties of the ZAO films measured by Four-point probes. The resistivities of the films grown on glass were lower than that of films grown on the polymer,the lowest resistivity was $5.32\times10^{-4}\Omega$cm and $6.5\times10^{-3}\Omega$cm separately. The dependence of resistivity on the "R" was strong. From the figures, it could be seen that appropriate H_2 ambient was helpful in improving the electrical properties of ZAO films, but excessive H_2 could be bad to the conductivity of the films. It was perhaps due to low H_2 dilution resulting in the formation of oxygen vacancy, increasing the carrier concentration, thus leading the reduction of the resistivity [20]. Furthermore, low H_2 dilution might improve the Al doping effects, which led to the better electrical properties of ZAO films[21]. However, excessive H_2 might increase significantly electron scattering centers and decreased deeply the carrier mobility, which caused deterioration of conductivity of the ZAO films.The optimal "R" was 5% according to our experiment, which is not too consistence with the results in other literate[22], in which the optimal H_2 flux was 1sccm and then the H_2/Ar ratio was about 1.67%.

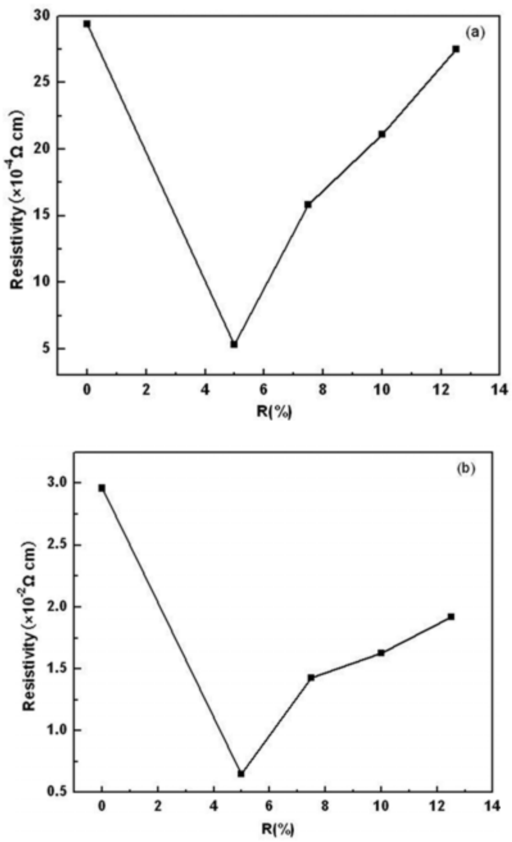

Fig. 4.Resistivity of the ZAO films deposited on glass(a) and polymer(b) substrates at various H2/Ar ratio(R)

4. Conclusion remarks

ZAO thin films with good optoelectronic properties have been prepared on glass and polymer substrates by RF magnetron sputtering with various mass flow ratio of H_2/Ar. The effects of H2 on the conductive properties of ZAO films deposited on both substrates were identical.A moderate H_2 content in the deposition atmosphere was expected to increase the conductivity of ZAO films by increasing carrier concentration. However,the influences of H_2 on the structure of ZAO films deposited on both substrates were distinctly different. For ZAO films on glass, high H_2/Ar ratio(>7.5%) resulted in a poor preferred orientation of crystallites, which was bad to transparency and conductivity of the films,but for ZAO films on TPT polymer,high H_2/Ar ratio(12.5%) was of benefit to preferred orientation of crystallites. A best transparency of more than 90% in the visible region and resistivity of $5.32\times10^{-4}\Omega$cm was obtained for the ZnO: Al films on glass prepared with the 5% H_2/Ar ratio in the deposition atmosphere.

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