Study on the growth and properties of highly conductive and high transmittance AZO films

LEI QINGSONG*, XU JINPING, WEN XIXING
Department of Electronics Science and Technology, Huazhong University of Science and Technology,
Wuhan 430074, P. R. China

Al doped ZnO films (AZO) were prepared by mid-frequency magnetron sputtering on glass substrates. The electrical and optical properties of the films were measured. The influence of deposition parameters such as substrate temperature (T_S), working pressure (P), and plasma power (P_W) on the growth and properties of the films were studied. Results suggest that the deposition parameters have great influence on the growth and properties of the films. Highly conductive and high transmittance of AZO thin films with a minimum resistivity of 2.45×10^{-4} Ωcm and optical transmission greater than 85% in visible spectrum region were achieved for the film deposited at a substrate temperature of 225 °C and a low plasma power of 160 W.

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1. Introduction

Transparent conductive oxide (TCO) thin films are widely used in thin film solar cells and flat panel display devices[1-3]. As intermediate or back reflectors in silicon based thin film solar cells, TCO films with low resistance and high transparency are required to obtain low series resistance and to avoid absorption losses. Comparing with other TCO films such as tin-doped In_2O_3 (ITO) and tin oxide (SnO_2), ZnO films doped with Al (ZnO:Al) are more stable in hydrogen plasma environments. Furthermore, ZnO:Al films exhibit high optical transmission and electrical conduction and have a low material cost[4]. These advantages are beneficial for the applications in solar cells and other opto-electronic devices [5-7].

In order to obtain ZnO:Al films, technologies such as sputtering [8,9], pulsed laser deposition [10], chemical vapor deposition [11], spray pyrolysis [12], and metal-organic chemical vapor deposition (MOCVD) [13] are usually applied. For the above technologies, there are two ways to apply TCO coatings to glass. One is on-line process and the other is off-line process. During the pyrolitic (on-line) process, the coating is applied during float glass production. The off-line process occurs after the glass has been produced. Magnetron sputter vacuum deposition is the off-line process. Magnetron sputtering techniques such as radio frequency (RF), direct current (DC), and mid-frequency magnetron sputtering are widely used because of the advantage in obtaining good adhesion, good orientation and uniform films [14-16]. In order to obtain AZO thin films with the desired properties, deposition parameters such as sputtering power, deposition pressure, gas flux, substrate temperature, and the distance between the target and the substrate should be well determined and controlled. Although the influence of the pressure and sputtering power on the structural properties and postetching surface topography was studied [17], the performance and reliability of this technique require further investigation in order to meet the needs of industrial production. In this study, highly conductive and transparent ZnO:Al films were deposited by mid-frequency magnetron sputtering. The influence of the substrate temperature, working pressure, and plasma power on the growth, electrical and optical properties was studied.

2. Experimental details

AZO films were prepared on glass substrates by magnetron sputtering technology in an in-line high vacuum deposition chamber. A ceramic target composed of ZnO:Al_2O_3 (98:2wt%) was mounted on magnetron cathode in dynamic mode as the target can moved forth and back in front of the substrate. The Distance between substrate and target surface was approximately 60 mm. For all ZnO:Al films, the system was operated in mid-frequency mode with an excitation frequency of 20 KHZ. The base pressure of the process chamber is less than 4×10^{-4} Pa. High purity argon was used as sputtering gas at a flow rate of 40 sccm. The sputtering power was varied from 80 to 180 W, and the argon gas pressure was controlled from 3 to 7 mTorr (mT) by throttle valves. The substrate temperature was varied from 150 °C to 280 °C.

To study the optical properties, a 7-SCSpec solar spectroscopy system was used to measure the transmittance. The optical band gap (E_g) was determined by applying the Tauc model[18], in which E_g were deduced from the optical absorption spectra using the relation $(\alpha h\nu)^2=(h\nu-E_g)$ by plotting $(\alpha h\nu)^2$ versus hν and extrapolating the linear portion of the plot to $(\alpha h\nu)^2=0$, where α is the absorption coefficient, hν is the photon energy. Electrical properties of the ZnO:Al films were characterized by Hall-effect measurement using van der Pauw geometry (Keithley 926 Hall set-up). The film resistivity was measured using a four point probe measurement system. The thicknesses were measured with a surface profiler (Dektak 3030 supplied by Veeco Instruments Inc.). The deposition rate is calculated by thickness divided by deposition time.

3. Results and discussion

3.1. Deposition rate

Fig. 1 shows the deposition rate as a function of working pressure. As shown in the figure, the deposition rate increases first and then decreases with the working pressure. At the working pressure of 3 mTorr, the deposition rate is about 0.227 nm/s. As working pressure increases to 7 mTorr, the deposition rate decreases to about 0.207 nm/s In magnetron sputtering technology, the sputtering ions increase with the pressure at low pressure, the deposition rate is thus increased. However, when the pressure increases to a certain value, the back reflection and scattering of the sputtering ions increase, which results in the decrease of the deposition rate.

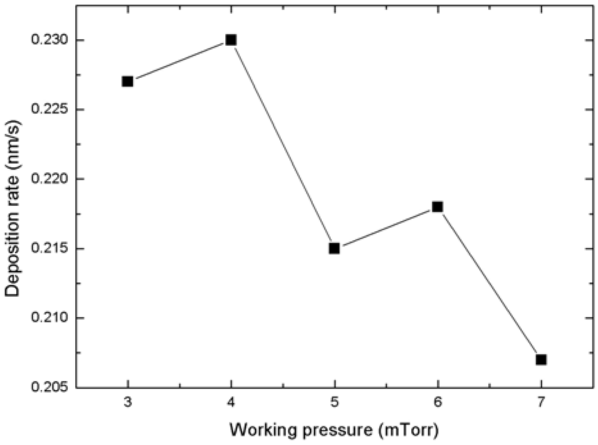

Fig.1. The influence of working pressure on the deposition rate of AZO thin films

Fig. 2 shows the influence of substrate temperature on the deposition rate of AZO thin films. As shown in the figure, the deposition rate increases with the substrate temperature at low T_S. At T_S of 150 °C, the deposition rate is about 0.22 nm/s. At 200 °C, the deposition rate gets to the maximum of 0.23 nm/s. With substrate temperature increasing further, the deposition rate decreases. At T_S of 280 °C, the deposition rate is about 0.195 nm/s. We consider that at a low substrate temperature of 150 °C, the mobility of the growth radicals is low, which leads to the low deposition rate. With substrate temperature increasing, the growth radicals' mobility increases, resulting in the increase of the deposition rate. However, as the substrate temperature increases further, desorption of the growth radicals from surface increases. The deposition rate is thus decreased.

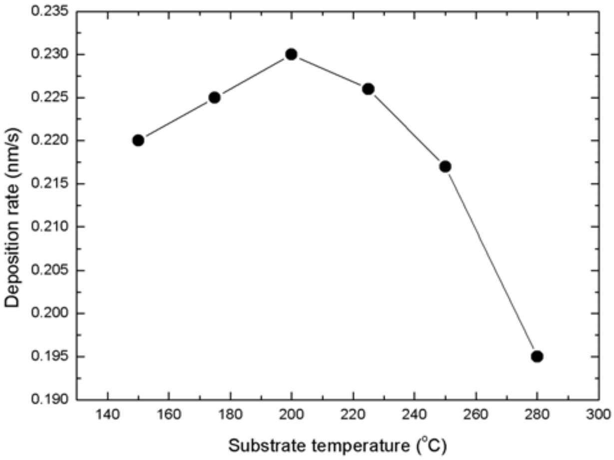

Fig.2. The influence of substrate temperature on deposition rate of AZO thin films

Fig. 3 shows the deposition rate with the sputtering plasma power. As shown in the figure, the deposition rate increases linearly with P_W. As P_W increases from 80 W to 180 W the deposition rate increases form 0.08 nm/s to 0.25 nm/s. With plasma power increasing, the particles sputtered from the target increase. The growth radicals are thus increased, which leads to the increase of the deposition rate.

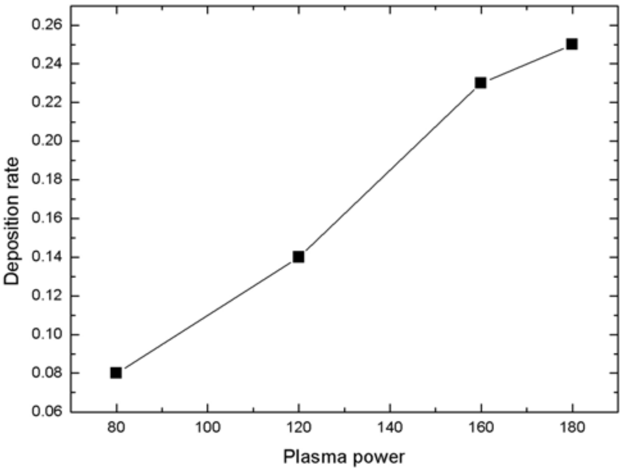

Fig.3. The influence of sputtering power on deposition rate of AZO thin films

3.2 Electrical properties

3.2.1 Influence of working pressure on the electrical properties

The change of resistivity as a function of working pressure is shown in figure 4. From the figures, it is observed that the resistivity is relatively high (2.77×10^{-4} Ωcm) at a low pressure (3 mTorr). As the working pressure increases to 4 mTorr, the resistivity decreases to 2.45×10^{-4} Ωcm. However, as the working pressure increases further, the resistivity increases to 2.92×10^{-4} Ωcm at a working pressure of 7 mTorr. It is known that the resistivity is determined by the carrier concentration (N_h) and Hall mobility (μ_τ). The influence of working pressure on the electrical properties is further investigated by the study of the carrier concentration and Hall mobility of the films. Figure 5 shows N_h and μ_τ for the samples deposited at various working pressure. From the figure, it is observed that the film deposited at the pressure of 4 mTorr has the largest carrier concentration and Hall mobility. At working pressure of 3 mTorr, the N_h is 1.27×10^{20} cm^{-3} and μ_τ is 62.4 cm^{2}V^{-1}s^{-1}. With working pressure increasing to 4 mTorr, the N_h increases to 3.2×10^{20} cm^{-3} and μ_τ increases to 69.3 cm^{2}V^{-1}s^{-1}. However, as the working pressure increases further, the carrier concentration and Hall mobility decrease to 1.04×10^{20} cm^{-3} and 57.4 cm^{2}V^{-1}s^{-1} at 7 mTorr.

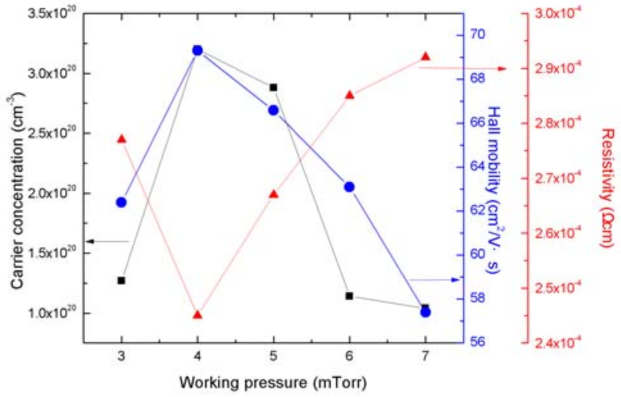

Fig.4. The influence of work pressure on resistivity, carrier concentration and Hall mobility of AZO thin films

In Magnetron sputtering, the working pressure has the great influence on the density and energy of the sputtering particles[19]. With pressure increasing, the mobility of the growth radicals on the surface increases because of the increase of the energy of the sputtering particles. The growth radicals thus have the enough time to find suitable sites, resulting in the reducing of defect and the increasing of the grain size in the film. So, the carrier concentration in the film increases and the resistivity of the film decrease[19]. However, as the increase of working pressure exceeds a certain value, the sputtering particles colliding with argon atoms or ions becomes more frequent, which increases the scattering degree of the sputtering particles. The crystallinity of the films is thus deteriorated, leading to the reduction of the carrier concentration and the Hall mobility.

3.2.2 Influence of substrate temperature on the electrical properties

Fig. 5 shows the resistivity, carrier concentration and Hall mobility of the films as a function of substrate temperature. As shown in the figure, the Hall mobility, carrier concentration is low and the resistivity is high at low substrate temperature of 150 °C. At T_S of 150 °C, the carrier concentration, Hall mobility and resistivity are 1.88×10^{20} cm^{-3}, 22.6 cm^{2}V^{-1}s^{-1} and 1.51×10^{-3} Ωcm respectively. As substrate temperature increases to 225 °C, a low resistivity of 2.45×10^{-4} Ωcm was obtained. However, as substrate temperature increases further, the resistivity increases. At T_S of 280 °C, the resistivity is 6.08×10^{-4} Ωcm with carrier concentration of 2.3×10^{20} cm^{-3}and Hall mobility of 50.9 cm^{2}V^{-1}s^{-1}. At a low substrate temperature, the mobility of the growth radicals is too low to move to the lowest energy location. The film with poor crystallization quality and a large amount of defect in the film is thus formed. The mobility of the carriers is thus low and the resistivity of the film is high. As substrate temperature increases, the grain size is increased and the quality of the film is improved, which is beneficial for the reduction of the defect scattering in the grain boundary. Meanwhile, higher substrate temperature is conducive to the desorption of adsorbtive oxygen at grain boundary and the substation doping of Al, which is helpful for the increase of the carrier concentration. The resistivity of the film is thus decreased. However, as the substrate temperature increases further, the oxygen vacancy in the films is reduced.

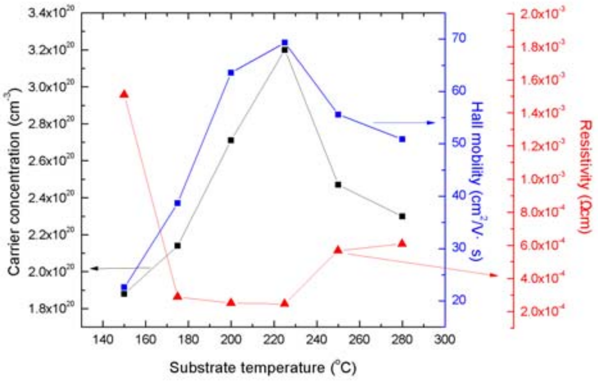

Fig.5. The influence of substrate temperature on resistivity, mobility and Hall concentration of AZO thin films

3.2.3 Influence of plasma power on the electrical properties

Fig. 6 shows the resistivity, Hall mobility, and carrier concentration of the AZO thin films as a function of plasma power. From the figure, it is observed that the resistivity of the film showed a tendency to decrease with power. The resistivity decreased from 3.15×10^{-4} Ωcm to 2.45×10^{-4} Ωcmwhen the plasma power increase from 80W to 160 W. In addition, the carrier concentration decreases with power increasing. At power of 80 W, the carrier concentration is about 6.7×10^{20} cm^{-3}. As power increases to 180 W, the carrier concentration decreases to 3.6×10^{20} cm^{-3}. The Hall mobility increases first and then tends to decrease when the power exceeds 160 W. At the power of 80 W, the Hall mobility is about 5.2 $cm^2V^{-1}s^{-1}$. With power increasing to 160 W, the Hall mobility increases to 69.3 $cm^2V^{-1}s^{-1}$. With power increasing further to 180 W, the Hall mobility increases to 47.6 $cm^2V^{-1}s^{-1}$. The improved electrical properties are due to the desorption of negatively charged oxygen species from grain boundary surfaces[20]. In addition, the passivation of surface and defects at grain boundaries, which diminishes scattering and trapping of free carriers and enhances the doping effect of Al, also contributes to the conductivity of the film [21].

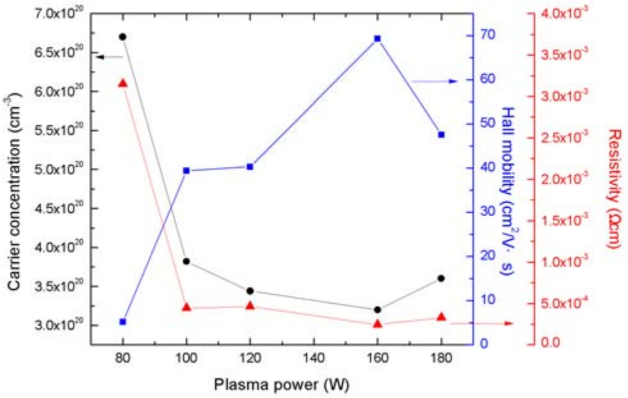

Fig.6. The influence of sputtering power on resistivity, carrier concentration and Hall mobility of AZO thin films

3.3. Optical properties

3.3.1. Influence of working pressure on the optical properties

Fig. 7 shows the optical transmission and optical band gap for the films deposited at various working pressures. As shown in the figure, the films deposited at lower pressure have the higher transmission and optical band gap. Also, it is observed that the transmission for all films decreases at long wavelength band. This phenomenon indicates that the films have the strong absorption at red band. It is reported that the doped AZO film has a phenomenon of band gap narrowing, in which the value of the shrinking of the band gap is proportional to 1/3 power of the carrier concentration[22]. In figure 7, the curve corresponding to 0.5 Pa decreases rapidly in the long-wavelength, indicating that the carrier concentration is high and the absorption on the red end of the spectrum is strong for the film deposited at this pressure.

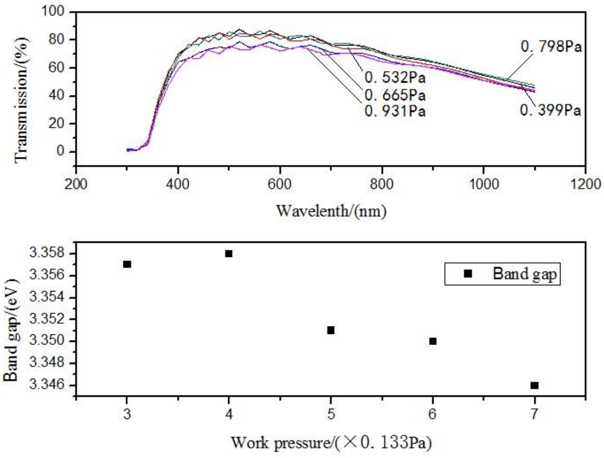

Fig.7. The influence of working pressure on transmission and band gap of AZO thin films

3.3.2. Influence of substrate temperature on the optical properties

The influence of substrate temperature on the transmittance of the deposited film is shown in Fig. 8. From the figure, it is observed that the difference of the transmittance in the visible range is very small. The largest optical band gap is obtained at 225 °C. As the substrate temperature increases to exceed 225 °C, the grain size on the surface and the film roughness increases, which leads to the increases of the diffuse reflection and the light scattering on the surface and the decrease of the transmittance in the long wavelength range.

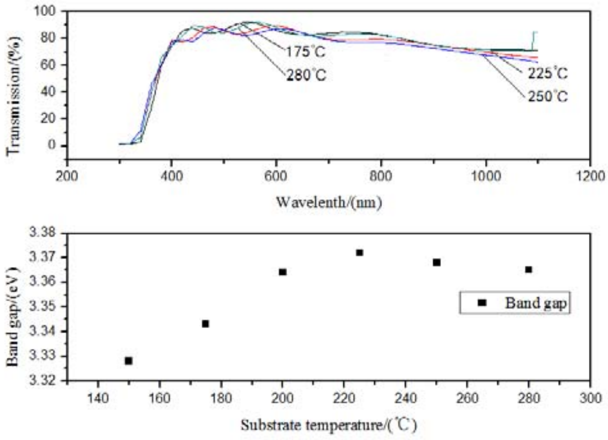

Fig.8. The influence of substrate temperature on transmission and band gap of AZO thin films

3.3.3. Influence of plasma power on the optical properties

Fig. 9 shows the optical transmittance spectra and optical band gap of the AZO thin films deposited at various powers. As shown in the figure, the transmittance decreases with the power. With plasma power increasing, the energy of the sputtering particles increases, resulting in the deterioration of the crystallization quality. The optical scattering in the grain boundary is thus increased. From the figure, it is observed that the average optical transmittance of the films deposited at $P_W < 160$ W is more than 85% in the visible wavelength range. In the ultraviolet range, all the films exhibit a sharp absorption edge because of the onset of fundamental absorption of ZnO:Al. Fig. 9 exhibits E_g of the AZO thin films shifted from 3.35 eV to above 3.75 eV with plasma power. The broadened Eg may result from the increase in carrier concentration[23]. As plasma power increases to exceeds 160 W, the optical band gap decreases, leading to the enhancement of the light absorption and the decrease of the transmittance.

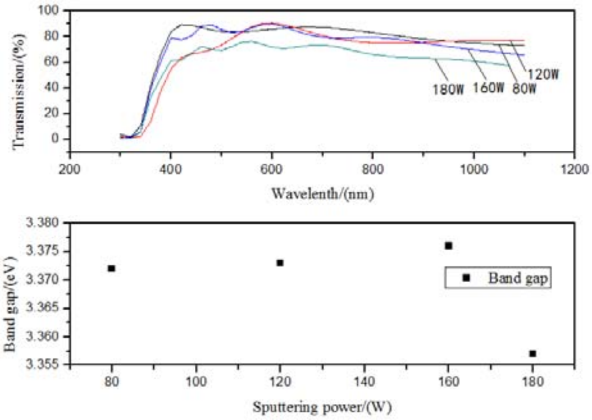

Fig.9. The influence of sputtering power on transmission and band gap of AZO thin films

4. Conclusion

AZO thin films were prepared by mid-frequency magnetron sputtering technique. The growth and properties of the films were studied. Results suggest that the deposition parameters such as substrate temperature, working pressure, and plasma power have the great influence on the growth, electrical and optical properties of the films. AZO films with a resistivity of 2.45×10^{-4} Ωcm and optical transmission greater than 85% in visible spectrum region were obtained at the substrate temperature of 225 ^{o}C and a low plasma power of 160 W.

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[*] Corresponding author: leiqs222@gmail.com