EFFECTS OF RF SPUTTERED AL-DOPED ZNO FILMS BY HYDROGEN PROCESS GAS DILUTION

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Abstract --- *The influences of different $H_2/(H_2 + Ar)$ gas flow ratio on Al doped zinc oxide (AZO) thin films deposited by RF magnetron sputter were investigated. The deposition temperature was kept at 200℃ and the working pressure was maintained at 5×10^{-2} Torr. The $H_2/(Ar+H_2)$ gas flow ratio was ranging from 2 % to 11.76 %. Results show that the AZO film with gas flow ratio of 2% exhibits the lowest resistivity. Besides, post-H_2 plasma treatment by PECVD was carried out. The resistivity of the AZO films after post-H_2 plasma treatment does not obviously vary but its electrical stability is improved. The average transmittance in the visible region for all films shows above 90 %.*

Keywords: *RF magnetron sputter, Hydrogen dilution, Resistivity, Al doped ZnO*

1. INTRODUCTION

Recently transparent conductive oxide (TCO) thin films have received much attention due to their wide range of applications. One of the TCO films, indium tin oxide (ITO) film has been widely used with its low resistivity, stable electrical and mechanical properties. However, ITO has disadvantages including toxicity, expensive and instability in hydrogen plasma [1]. In the recent decade, zinc oxide (ZnO) attracts interest as a transparent and conductive coating material for many optical devices such as flat panel display, solar cells and electro-optical devices [2-4]. ZnO is a II-VI n-type semiconductor with a wide band gap of approximately 3.4 eV and a hexagonal wurtzite structure [5], but the poor electrical properties restrict the industrial use. It should be improved by control both the stoichiometry and the donors like impurities. Many deposition techniques such as CVD, spray pyrolysis, sol-gel and sputtering have been employed to prepare the AZO thin films [4-9].

In this paper, AZO thin films are prepared by r.f. sputtering and followed up a post-hydrogen plasma treatment to discuss the characteristics of the films. This study introduced the role of hydrogen in sputtering process and post plasma treatment for the synthesis of highly conducting, transparent and stable AZO films.

2. EXPERIMENT DETAILS

AZO thin films are deposited on glass in a 13.56 MHz r.f. sputtering system with a ceramic target that is made of 98 wt. % high-Purity ZnO (99.999 % purity) and 2 wt. % Al_2O_3 (99.999 % purity) powders. The substrates are sliced into 3 × 3 cm portions and cleaned. The distance between the target and the substrate is fixed at 10 cm. The working pressure is maintained at 5×10^{-2} Torr. The temperature is kept at 200 °C. The chamber is preserved under different $H_2/(Ar+ H_2)$ gas flow ratio. All films have a thickness about 1200 Å. The as-deposited AZO films are subsequently treated by hydrogen plasma for different times ranging from 15 to 120 min at 200 °C by a PECVD system. The working pressure is maintained at 1 Torr and the r.f. power is 10W.

An ellipsometer “Nano-view SE MF-100” is used to measure the films’ thickness. X-Ray diffraction (XRD) of the AZO films’ crystallity is carried out using a “PANalytical” diffractometer with Cu Kα radiation (λ=1.54056Å) operated in the θ-2θ mode over angles in the range of 20-60°. A “JEOL JSM-7401” field emission scanning electron microscope (FE-SEM) is used to observe the surface morphology and grain size. The electrical property is determined with a “Napson RT-70/RG-5” four-point probe instrument. The optical transmittance measurements are performed with a “Hitachi U-3300” UV/Vis spectrophotometer in the 300–800 nm wavelength range.

3. RESULTS AND DISCUSSION

Figure 1 shows the XRD spectra of the AZO thin films deposited at 200 °C for various $H_2/(Ar+H_2)$ gas flow ratio. All films exhibit the (002) peak at diffraction angle 2θ ~ 34.4°, which is close to that (2θ ~ 34.45) of the ZnO crystal. The smaller diffraction angle results from increased lattice parameter. The (002) peak intensity was decreased with the increasing $H_2/(Ar+H_2)$ gas flow ratio, indicating the structure of the film to become amorphous crystalline.

It implies a saturation stage will be arrived as H_2 gas increased. Because the excess H atoms

incorporate the Zn-O bond centers result in the over relaxations of the surrounding atoms to increase the number of grain boundary defects.

Fig. 2 (a) to (e) shows the SEM images of the AZO films deposited with the $H_2/(H_2+Ar)$ ratios of 0, 2, 3, 4 and 11.76 %, respectively. It was found that the films with H_2 gas flow ratio of 2 % had the largest surface grain size. The surface morphology started to change slightly as the increasing of hydrogen dilution ratio. The surface grain size becomes smaller after the dilution ratio is over 4 %. It is possible that high hydrogen dilution ratio reduces the effect of argon ion bombardment during sputtering process and causes limited diffusion of ions on surface and slow nucleation rate, so that's why we see small grains in the samples [10]. In addition, the combination of hydrogen and oxygen atoms will restrain the growth of zinc oxide priority orientation. Hydrogen is a strong reductant and it will reduce the transformation of zinc ions into zinc atoms in the thin film. The zinc atoms will evaporate in the vacant system because of the melting point reduction effect under nano-structure [11]. The oxygen atoms may leave on the thin film surface and cause the forming of the nanoscale holes as shown in Figs. 2(d) and 2(e).

Figure 3 exhibits the dependence of the resistivity on H_2 gas flow ratio. The minimum resistivity is 1.372×10^{-3} Ω-cm at 2 % H_2 gas flow ratio ($H_2/(H_2+Ar)$ = 2 %), while the as-deposit films under pure Ar ambient is 2.516×10^{-3} Ω-cm. The resistivity increases with increasing the $H_2/(H_2+Ar)$ ratio. Because H_2 creates more defects and generates more free carriers, both of the neutral and ionized impurity scattering centers should decrease [9]. Besides, a small quantity of hydrogen atoms situates in the Zn-O bond center to relax the surrounding atoms. A degenerated structure occurs to increase the grain boundary scattering ability as shown in the diffraction patterns in Fig. 1.

Figure 4 gives the resistivity of the AZO films treated by H_2-plasma for 0 (as-deposited) and 1 hr and exposed to air ambient for 2 weeks as a function of H_2 gas flow ratio. The resistivity of the films with/without plasma treatment increased after 14 days. The increase ratios of the resistivity of the as-deposited films after 2 weeks were between 32.53 and 125.93 %, while the plasma treated films exhibited smaller variation in resistivity (11.52~ 76.25 %). It is because the as-deposited films have a lot of grain boundaries covered by oxygen species such as –OH, $–CO_3$ and absorbed O_2, and the oxygen vacancies are filled with such oxygen species as increasing the air exposure times. The oxygen vacancies act like a negatively charged species and electron trapping to form the depletion regions near the grain boundary to deteriorate the resistivity [12], however, the atomic hydrogen in plasma can permeate into the grain boundary to fill up the dangling bound among the oxygen vacancies near the grain boundary and passivate the surface to protect from the moisture and oxidation [13].

After 2 weeks, the AZO films without treatment by H_2 plasma present an obvious increase in resistivity compared to those with H_2 plasma treatment. It is expected that the density of absorbed oxygen species on the surface of the grain boundaries increases and the part of the oxygen vacancies are full of oxygen species after air exposure for 2 weeks. The characteristic of all films is sparse morphologies with small clusters and conical grains distribute uniformly. This means a lot of splits and interstices between these microstructures even if the island structures are joined by many channels compared with the densely compact and faceted morphologies prepared at optimal condition as shown in Fig. 2.

Varieties of structural defects exist in AZO films prepared by pre-sputtering process. These mainly defects such as vacancies, interstitials, and impurities exist in the bulk structure. All the defects are associated with dangling bonds, which act as traps of charge carriers to reduce the drift mobility and lifetime of the carriers. As a result, the energetic hydrogen ions from plasma can readily diffuse into the bulk and terminate the dangling bonds associated with the structural defects, hence decreasing the resistivity of the film. Furthermore, the improvement of the electrical characteristics of the AZO films exposed to hydrogen plasma is due to the defect passivation of grain boundaries and the generation of oxygen vacancies. The passivation will prevent the films from the oxidation and moisture to make the films stable [14].

Figures 5(a) and 5(b) show the optical transmittance and band gap, respectively, for the AZO films prepared at 200 °C and then treated by various post-hydrogen plasma exposure times. The average transmittance in the visible region of all films shows above 90 %. The optical band gap of the AZO films could be evaluated from the plot of photon energy. The AZO film is a direct n-type semiconductor; therefore, the optical bad gap (E_g) of the films could be determined by the extrapolation methods from absorption edge. The absorption edge for direct interband transition is given by Eq. (1)

$$\alpha^2 = h\nu - Eg, \quad (1)$$

where h is Plank's constant, and ν is the frequency of the incident photon. The coefficient of absorption α is defined as Eq. (2)

$$I = I_0 e^{-\alpha t}, \quad (2)$$

where I is the intensity of transmitted light, I_0 is the intensity of incident light, and t is the thickness of AZO film. The transmittance is defined as I/I_0, therefore α could be obtained from Eq. (2) [15]. The plot of α^2 against the photon energy, $h\nu$, was made in order to obtain band gap of the films, the sharp

absorption edge can be accurately determined by the linear fit [15,16]. The optical band gap of the AZO films monotonically increased from 3.35 to 3.41 eV as the post treatment time increases from 0 to 60 min. and then keeps a saturation value after 60-min. plasma treatment as shown in Fig. 5 (b).

4. CONCLUSION

The effects of H_2/ (H_2+Ar) gas flow ratio on the structural, electrical, and optical properties of the AZO thin films were investigated. All of the AZO films deposited on glass substrates exhibit a *c*-axis preferred orientation. The more H_2 gas flow ratio will lead to the smaller grain size. The films with H_2/(H_2+Ar) gas flow ratio of 2 % have the best electrical properties. The optimized resistivity is 1.372×10^{-3} Ω-cm. After H_2 plasma treatment, the AZO films exhibits better electrical stability as exposing at air atmosphere. The average transmittance in the visible region of all films shows above 90 %.

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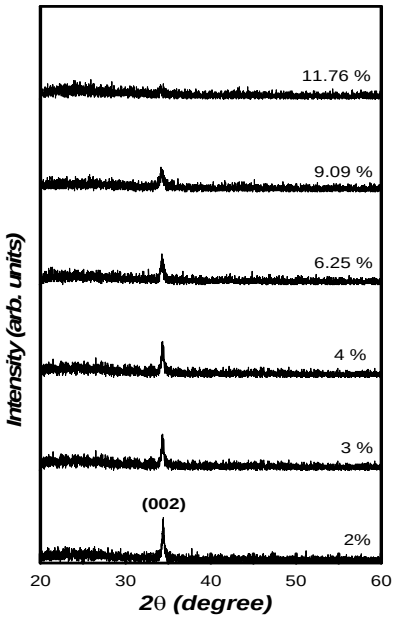


Fig. 1 XRD patterns of the AZO films deposited at 200 °C for various H_2/(Ar+H_2) gas flow ratio.

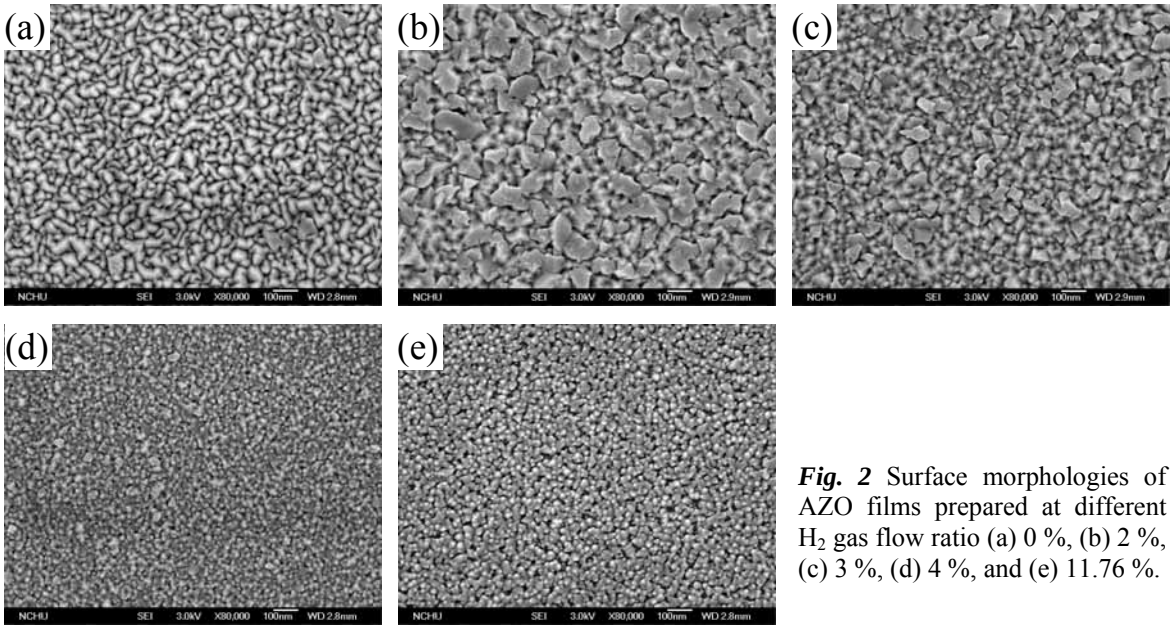


Fig. 2 Surface morphologies of AZO films prepared at different H_2 gas flow ratio (a) 0 %, (b) 2 %, (c) 3 %, (d) 4 %, and (e) 11.76 %.

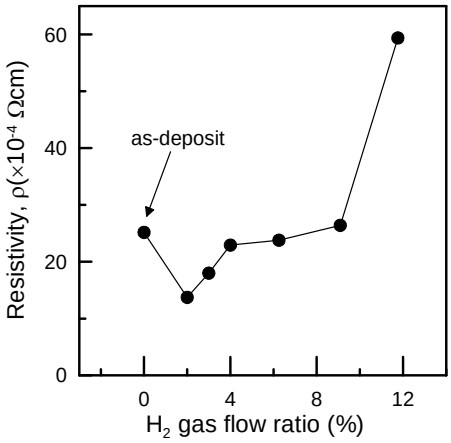


Fig. 3 Resistivity (ρ) of the AZO films as a function of the H_2 gas flow ratio.

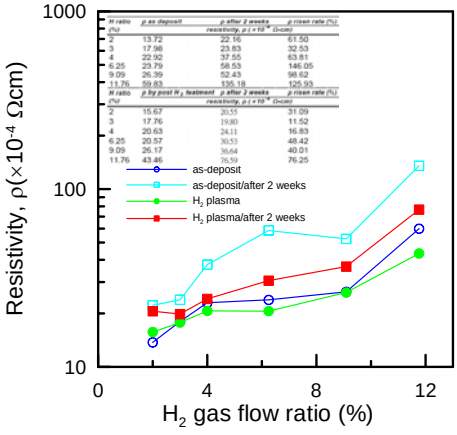
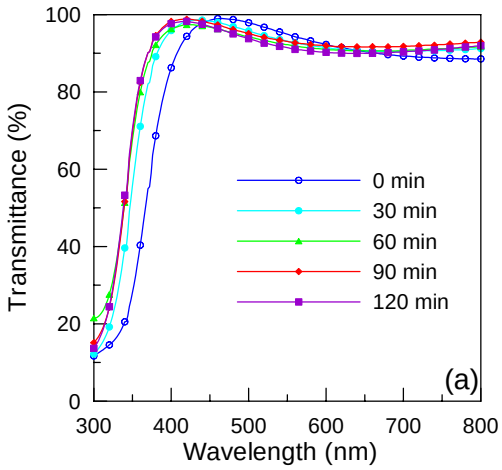


Fig. 4 Resistivity of the AZO films exposed to air ambient for 2 weeks as a function of H_2 gas flow ratio.



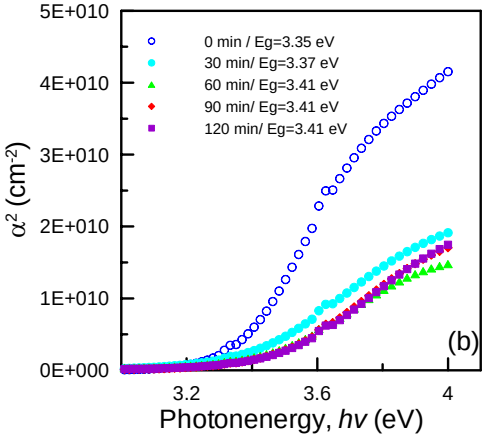


Fig. 5 (a) Optical transmittance and (b) optical band gap of the AZO films prepared by pre-sputtering at 200 °C for various post-hydrogen plasma treatment times.