Study of AZO Thin Films Under Different Annealing Atmosphere on Structural, Optical and Electrical Properties by rf Magnetron Sputtering

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***Abstract*—In this paper, the transparent conductive aluminum-doped zinc oxide (ZnO: Al, AZO) thin films with different annealing conditions are studied. The AZO thin films were prepared on the Coring glass substrate by RF magnetron sputtering. The AZO thin films were annealed in atmosphere of vacuum and hydrogen at temperatures from 100 to 400℃ in steps of 100℃ for 1 min, respectively, to investigate the effects of annealing on electrical and optical properties of the films. Optimization of the prepared thin films shows low resistivity of 6.04 × 10^{-4} Ω-cm, mobility of 5.213 cm^2/V-s, carrier concentration of 7.147 × 10^{20} cm^{-3} and a average optical transmittance of 84.89 % in the visible range at 200℃ annealing temperature in hydrogen are obtained. These results indicate that AZO thin films are a promising high conductivity transparent electrode scheme for solar cells and various displays applications.**

Keywords:—AZO , rf magnetron sputtering ,transparent conductive oxides, thin film, annealing conditions

I. INTRODUCTION

In recent years, transparent conducting oxides (TCOs) have received much attention as the applications to flat panel displays, electrochromic windows, gas sensors and solar cells, such as Sn-doped indium oxide (ITO) and Al-doped zinc oxide (AZO) have been studied in recent year [1-4]. For these films applications, the average optical transmittance up to 80% in the visible wavelength range and the resistivity of below ~10^{-3} Ω-cm are required.

At present, AZO thin films as TCO films have most attention, due to the advantages of AZO thin films are cheap, non-toxic, abundant elements and wide bandgap semiconductor materials (Eg ≒ 3.4 to 3.9) resulting in the optical transmittance properties in the visible regions [5-6]. Therefore, AZO thin films are usually used as transparent electrodes in many opto-electronics devices. Several studies using different deposition methods have been reported, such as sol–gel processes [7], pulsed laser deposition [8], sputtering [9] and molecular beam epitaxy [10].

The annealing effect is considered as an effective technique to modify intrinsic defects and improve electrical properties [11-13]. Annealing the AZO thin films in vacuum or hydrogen would improve the crystallinity, but also could induce hydrogen to be incorporated into the films, which degraded the electrical properties [14-15].

In this paper, the AZO thin films were prepared by using the rf magnetron sputtering with different annealing conditions are studied. The deposited AZO thin films are annealed in different atmospheres of vacuum and hydrogen at different temperature from 100℃ to 400℃. The lowest resistivity of 6.04 × 10^{-4} Ω-cm (60. 36 Ω/sq) and average transmittance of 84.89 % was obtained at 200℃ annealing temperature in hydrogen. The observed property of the AZO thin films is suitable for transparent conductive electrode applications.

II. EXPERIMENTAL

The AZO single layer films were deposited on the glass substrate (Corning Eagle XG ; 20 × 20 × 0.7 mm^3) by rf magnetron sputtering using an AZO ceramic target (99.9995% purity, 200 mm diameter, 50 mm thickness Al_2O_3 : ZnO = 2 : 98 wt%). The glass substrates were ultrasonically cleaned in an ethanol/acetone solution and then rinsed in deionized water. The deposition of AZO layers was performed in an argon (purity: 99.99%) atmosphere. The Ar flow was maintained at 180 sccm and the RF power was controlled at 200 W. The rotating speed of the substrate was 10 rpm. Substrate temperature kept at 70℃. The working pressure was controlled in the range of 2.2 × 10^{-2} torr. The thickness of the AZO layer was 100 nm for this study. The deposition rate of the AZO is 0.0143 nm/s. Then, the AZO films are annealed by using the rapid thermal annealing (RTA) and processing in the condition of hydrogen and vacuum, respectively. The annealed temperatures of the films are at 100, 200, 300 and 400℃ for 1 min. The heating rate was controlled to 10℃ /min and the gas flow rate was maintained of 1000 sccm in 4 Pa for all cases. The thickness of the deposited films was measured by an surface profilometer (Veeco Dektak 6M). The resistivity (ρ), carrier concentration (n) and Hall mobility (μ) were measured by the four point probe method (Jiehan 5000 Electrochmical workstation, SRS-400) and Hall Effect measurement (Ecopia HMS 3000). Conventional θ–2θ XRD studies on the films were carried out in Rigaku (BRUKER D8 ADVANCE) diffractometer using

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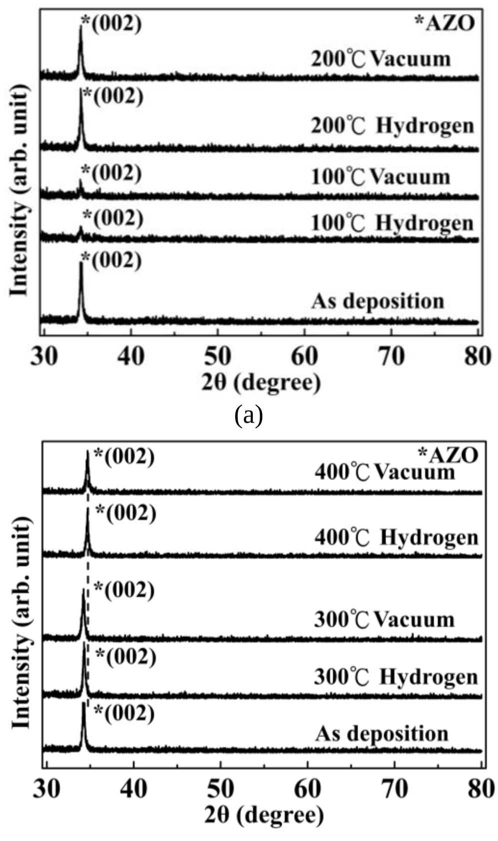


Fig. 1. XRD plots of the AZO films at different annealing conditions of (a) 100 - 200℃ and (b) 300 - 400℃. (The sputtering power is fixed at 200W)

Cu Kα radiation to investigate the crystallinity and crystal orientation of the films. The variations of surface roughness and root mean square (RMS) roughness as a function of working pressure were evaluated using an atomic force microscope (AFM, NT-MDT Solver P47 system). Optical transmittance was measured using a UV-VIS-IR spectrophotometer (JASCO V-670) in the range of 300 - 800 nm.

III. RESULTS AND DISCUSSIONS

Fig. 1 XRD plots of the AZO films at different annealing conditions of (a) 100 - 200℃ and (b) 300 - 400℃. The AZO thin films show strong <002> peaks at 34.45° was observed for AZO thin films and indicated the preferred orientation of c-axis perpendicular to the substrate surface. From fig (a), the <002> peaks have better crystallinity at the annealing temperature of 200℃. Due to the annealing effect can be enhancing the crystallinity in the films. From fig (b), it can be found the <002> peaks shift to higher 2θ values at the temperature of 400℃, which may imply that more Al ions occupy the lattice position of Zn ions by annealing the AZO thin films in hydrogen atmosphere [16]. Another reason is the residual stress of the AZO thin films, which can be reduced by annealing and result in a peak-shift of XRD patterns toward high angles [17]. Increasing the crystallinity of the AZO thin films can decrease grain boundary scattering and increase the carrier lifetime for achieving lower resistivity of the AZO thin films [18]. In general TCO electrodes, optical transmittance and electrical resistivity is depended strongly on the grain structure of the films because the grain boundary may absorb the visible light and reduce the carrier's mobility [19].

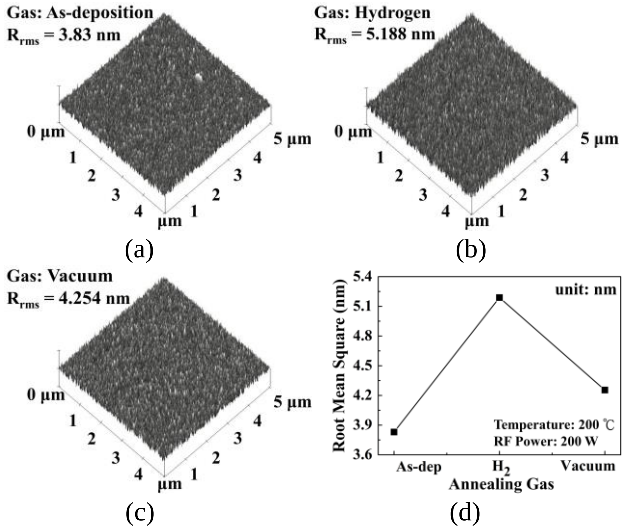
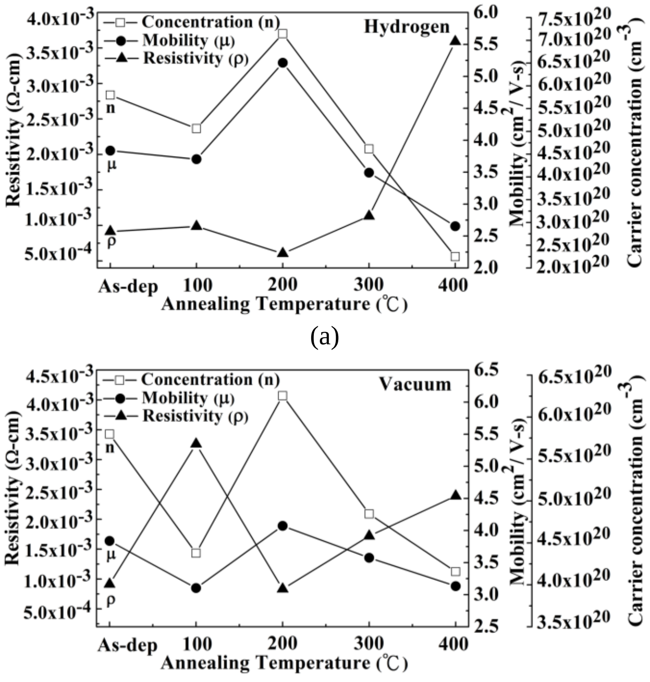


Fig. 2. AFM images of the AZO thin films at (a) as-deposited and the annealing temperature at 200℃ in (b) hydrogen and (c) vacuum atmosphere.

Fig. 2 shows AFM images of the AZO thin films at as-deposited and the annealing temperature at 200℃ in vacuum and hydrogen atmosphere. The maximum roughness in hydrogen atmosphere, that due to the hydrogen has the etching effect [20]. The changes of surface roughness and morphologies of the AZO films can more affect the magnitude of carrier mobility [21]. The AZO thin film with a surface roughness of ~ 2 nm is sufficient to meet the requirement for optical device application [22]. Condition of the surface roughness is the important properties of the TCO thin films for many optoelectronic devices.

Fig. 3 shows the electrical resistively (ρ), Hall mobility (μ) and carrier concentration (n) of the AZO thin films (thickness is fixed as 100 nm) at (a) hydrogen and (b) vacuum atmosphere. The electrical properties of AZO thin films by different annealing conditions are summarized in Table 1. Lower resistivity at 200℃ annealing temperature in hydrogen atmosphere 6.04×10^{-4} Ω-cm (60.36 Ω/sq), that due to the hydrogen can be incorporated in to the ZnO lattice with H_2 annealing and H-plasma treatment, which exists to be a shallow donor state [23] and passivates the V_o defects to form V_o–H complex [24]. When the annealing temperature increases further to 200℃, the resistivity shows an increasing trend and the carrier concentration and mobility show a decreasing trend. The decrease in carrier concentration can be related to segregation of metal atoms into grain boundaries, where they become inactive as donors and modify the potential barrier for charge transport across the grains, resulting also in a mobility decrease [25]. The decrease in resistivity can be known by inspection of the changes in carrier concentration and mobility. Thus, increase in both carrier concentration and Hall mobility would consequently lead to an increase of conductivity.

Fig. 4 shows the optical transmittance spectra of the AZO thin films at 300 - 800 nm wavelengths under different annealing conditions. All AZO thin films have high transmittances in the visible region (400 - 700 nm) and a strong absorption in the UV region. The absorption edge was



(a)

(b)

Fig. 3. Electrical resistively (ρ), Hall mobility (μ) and carrier concentration (n) of the AZO thin films (thickness is fixed as 100 nm) at (a) hydrogen and (b) vacuum atmosphere.

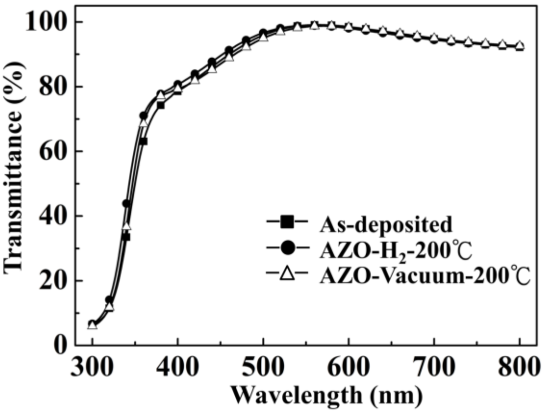


Fig. 4. The optical transmittance spectra of the AZO thin films at 300 - 800 nm wavelengths under different annealing conditions.

about 360 nm and optical transmittance was about 68.5 - 70.4 % in the visible range. The property can be understood from the fact that the AZO thin films is a wide band gap semiconductor with energy gap of ~3.4 eV [18]. The maximum transmittance of around 98.99 % was observed for the prepared AZO films at 200℃ annealing temperature in vacuum atmosphere. However, we can found the average transmittance of the hydrogen annealing is higher than other annealing conditions that due to the AZO thin films had better crystallinity in hydrogen atmosphere. The better crystallinity can be decreasing the defects in grain boundary, which can be increase the transmittance. Comparison of properties between the reported works is summarized in Table 2.

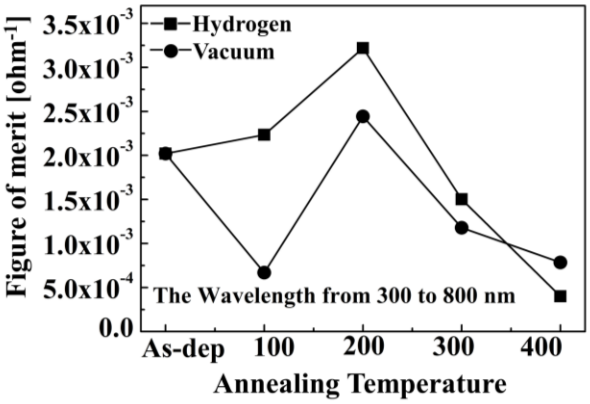


Fig. 5. The figure of merit for AZO thin films under different annealing conditions.

TABLE I
The electrical properties of AZO films under different annealing conditions.

Annealing Atmosphere	**Resistively (Ω-cm)**	**Mobility (cm^2/V-s)**	**Carrier Concentration (cm^{-3})**
(Gas)	200℃	200℃	200℃
As-deposited films	9.13×10^{-4}	3.837	5.798×10^{20}
Hydrogen	6.04×10^{-4}	5.213	7.147×10^{20}
Vacuum	8.32×10^{-4}	4.072	6.255×10^{20}

TABLE I I
Comparison of electrical and optical properties between the literatures and the proposed structures.

Ref.	**Process Method**	**Thickness (nm)**	**Annealing Temperature (℃)**	**Resistivity (Ω-cm)**	**Maximum Transmittance (%)**
[27]	RF sputtering	1420	450℃ (Vacuum)	2.7×10^{-3}	80%
[25]	DC sputtering	300	350℃ (Vacuum)	8×10^{-4}	95%
[28]	RF sputtering	150	500℃ (Oxygen)	2.24×10^{-3}	93.5%
[29]	DC sputtering	280	500℃ (Hydrogen)	2.94×10^{-3}	90%
[30]	Sol-gel	150	700℃ (Vacuum)	4.6×10^{-3}	80%
This Study	RF sputtering	100	200℃ (Hydrogen)	6.04×10^{-4}	99%

Fig. 5 shows the figure of merit for AZO thin films under different annealing conditions. The FOM (φ_{TC}) is calculated for the AZO thin films as defined by Haacke [26]

$$\varphi_{TC} = T_{av}^{10} / R_s \tag{2}$$

where T_{av} is the optica measured transmittance of the AZO film from 300 to 800 nm and Rs is the sheet resistance. It can be seen that the best FOM (= $3.22 \times 10^{-3}\,\Omega^{-1}$) is obtained when the annealing temperature at 200℃ in hydrogen atmosphere, due to the lowest sheet resistance of 60.36 Ω/sq and the average transmittance values of 84.89 % at the wavelength of 300 - 800 nm are well obtained. The method gives a more realistic estimate of the actual merit of the AZO film for transparent electronics. A higher FOM (φ_{TC}) value results in better quality transparent conducting oxide films.

IV. CONCLUSION

In this paper, the AZO thin films were prepared by RF magnetron sputtering. We have investigated the structural, optical and electrical properties of thin films at annealing temperatures from 100 to 400℃ in vacuum and hydrogen atmosphere. The prepared AZO thin films show the optical transmittance greater than 84.89 % in the visible range, the lowest electrical resistivity of $6.04 \times 10^{-4}\ \Omega$-cm (60.36 Ω/sq) and the maximum figure of merit achieved is $3.22 \times 10^{-3}\ \Omega^{-1}$ at 200℃ annealing temperature in hydrogen atmosphere. These results showed the AZO thin films using annealed effect in hydrogen atmosphere are a good candidate for future transparent conductive electrode applications.

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