

Effects of Ar flow rate and substrate temperature on the properties of AZO thin films by RF magnetron sputtering

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Transparent conductive Al doped ZnO (AZO) thin films were deposited by radio frequency magnetron sputtering method. Using XRD rocking curves measurement, it is found that at a substrate temperature of 300 °C, the AZO has the best crystal quality. The influence of argon flow rate on growth rate, the electrical and optical properties of the AZO films prepared at 300 °C was investigated by surface profilometer, Hall measurement and UV-vis spectrometer. With increasing the argon flow rate, the growth rate decreases while the carrier concentration of the AZO films increases. Resistivity of the films presents a minimum value of $4.35 \times 10^{-4} \Omega \cdot \text{cm}$ at the argon flow rate of 20 sccm. AZO thin film grown at this optimal Ar flow rate shows the highest Hall mobility of $31.2 \text{ cm}^2/\text{V} \cdot \text{s}$ and the highest average optical transmittance of 81.6% in the 400-800 nm range.

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1. Introduction

Inexpensive and nontoxic Al-doped ZnO (AZO) film is a good transparent and conductive thin film for applications in silicon-based thin film solar cells [1-3], organic solar cells [4], and other optoelectronic devices [5]. Compared with $\text{In}_2\text{O}_3:\text{SnO}_2$ and $\text{SnO}_2:\text{F}$, AZO has higher stability in a reductive environment of the hydrogen plasma or atomic hydrogen, which are commonly used during the process of Si-based thin film solar cells [6, 7].

There are a lot of methods to prepare AZO thin films, such as chemical vapor deposition (CVD) [8], pulsed laser deposition (PLD) [9], and magnetron sputtering. Among these methods, magnetron sputtering is a major technique which has merits of low cost, low toxicity and good reproducibility. So it is often used to produce various transparent and conductive thin films in commercial production. For magnetron sputtering of ceramic $\text{ZnO}:\text{Al}_2\text{O}_3$ (Al_2O_3 doped ZnO) target, parameters such as substrate temperature [10], sputter pressure [11], Al atoms concentrations in the target [12], sputter power [13] would influence the properties of AZO film. Additionally, the Ar gas flow rate, which is less noticed, can also influence the properties of AZO films [2, 14]. In Zhu's study [2], the Hall mobility of the AZO films increased as the argon flow rate increased from 50 sccm to 250 sccm. But according to the Yang's results [14], the AZO film has the largest Hall mobility at 30 sccm in the range from 15 sccm to 75 sccm.

Considering the difference among the results from different author, it is necessary to study effects of Ar flow rate on the properties of AZO further.

In our study, the substrate temperature for obtaining a good crystal quality of AZO films was determined at first. At the optimal substrate temperature, we prepared AZO films on glass substrates and investigated the influence of working gas flow rate in the range of 10 sccm to 100 sccm on the electrical, optical properties and wet etching properties of AZO thin films.

2. Experimental details

AZO thin films were deposited on sapphire and glass substrates by a magnetron sputtering system. The system has three targets and the target-substrate distance is 140 mm. The substrate holder rotated at 20 rpm (rounds per minute) during the deposition for making uniform films. The ceramic $\text{ZnO}:\text{Al}_2\text{O}_3$ (2 wt%) target with 99.99% purity and 60 mm in diameter. All substrates were cut into 20 mm×20 mm×1 mm. Substrates were ultrasonic cleaned by an organic solution and deionized water successively, then dried with nitrogen gas. After these procedures, the substrates were moved to the magnetron sputtering system immediately. The experiment parameters for depositing AZO on glass substrate and sapphire substrate were shown in Table 1.

Table 1. Experimental parameters for depositing the AZO thin films on glass and sapphire substrates.

Substrate	Ar flow rate (sccm)	Sputter pressure (Pa)	Substrate temperature (°C)	Sputtering power (W)
Sapphire	20	0.05	RT*, 100, 200, 300, 400	150
Glass	10, 20, 40, 80, 100	0.15	300	150

RT: Room temperature

Structural properties of AZO were investigated by a double-crystal X-ray diffractometer (QC200, BEDE Instruments, UK). Cu K α 1 line was used as the source and Ge (004) was used as the reference crystal. The electrical properties were measured by Hall-effect measurement using Van der Pauw method at room temperature. Film thickness was measured by an Ambios XP-1 Series Stylus-Type Surface Profilometers after etching away part of the films with diluted 0.5% HCl solution, which was also used to obtain light-scattering structure in the AZO surface. The morphology of etched AZO film was evaluated by scanning electron microscopy (SEM). The optical transmission spectra were obtained from a UV-vis spectrophotometer (Shimadzu UV-2550) in the wavelength range from 200 to 900 nm.

3. Results and discussion

A series of AZO films were deposited on sapphire substrates at different substrate temperature. Fig. 1 presents the (002) XRD rocking curves of AZO films on sapphire substrate at different substrate temperature from RT to 400 °C. The peak positions of these curves are shifted to 0 arcsec for the comparison of the result. As seen in the Fig.1, the intensity of the (002) peaks increased at first then decreased, from RT to 400 °C. At 300 °C, the (002) peak has the highest intensity. For the samples at RT and 100 °C, the intensities are not high and the full width at half maximum (FWHM) of the curves are 10.31 and 7.16 arcsec, respectively. When the temperature is increased to 200 °C, the intensity increases but the FWHM becomes to a larger value of 11.41 arcsec. And a small broad component turns up in the tail of the curve. As the temperature is increased to 300 °C, the peak becomes narrow with the lowest FWHM of 6.91 arcsec and the small tail is eliminated. It suggests that when the temperature is increased from 200 °C to 300 °C, the crystal quality is improved. This improvement should be related to the increase of atomic mobility and reduction of structural defects. But when temperature is increased further to 400 °C, the intensity of the peak decreases and the peak becomes broad. This may be related to the thermal stress and lattice mismatch [15]. The present results show that the film deposited at 300 °C has the best crystal quality in terms of the (002) c-axis orientation. So we chose 300 °C as the substrate temperature for

depositing AZO film on glass substrate. Samples with different argon flow rates from 10 sccm to 100sccm were deposited on the glass substrate while other deposition conditions were kept constant (experiment parameters are listed in Table 1).

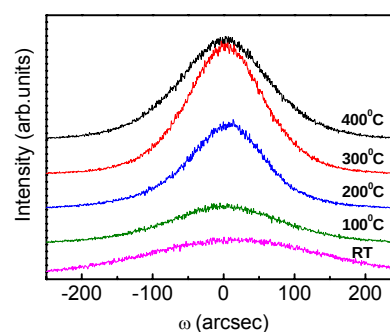


Fig. 1. XRD rocking curves for AZO thin films deposited on sapphire substrate at different substrate temperature from RT to 400 °C.

Fig. 2 shows that the trend of the film growth rate decreases when the flow rate increases. This phenomenon is seldom reported. It is reasonable to say that the argon atoms velocity increases with the increasing of flow rate. The higher speed argon atoms could take the sputtered target atoms away more easily so that some low energy atoms could not reach the substrate, especially at long target-substrate distance in our sputtering system, causing the growth rate dropped with the increasing flow rate.

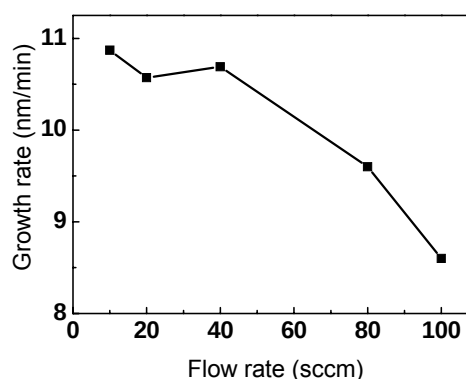


Fig. 2. The relationship between the growth rate of AZO and different argon flow rate.

Electrical properties of the AZO films with different argon flow rates are shown in Fig. 3 (a), (b) and (c). The carrier concentration increases with the increase of argon flow rate. This is different from the results of Zhu [2] and Yang [14], in which the carrier concentration is kept almost constant. It is noticed that the target-substrate distance described by Zhang and Yang are much smaller than ours. According to the results of the relationship of growth rate with argon flow rate, at larger target-substrate distance, increase of argon flow rate could reduce the kinetic energy of the particles sputtered from the target. These particles, at higher argon flow rate, have lower energy that results in much more defects such as oxygen vacancies in the AZO films. The oxygen vacancies can offer electrons to increase the carrier concentration. So the carrier concentration increases with increasing the argon flow rate.

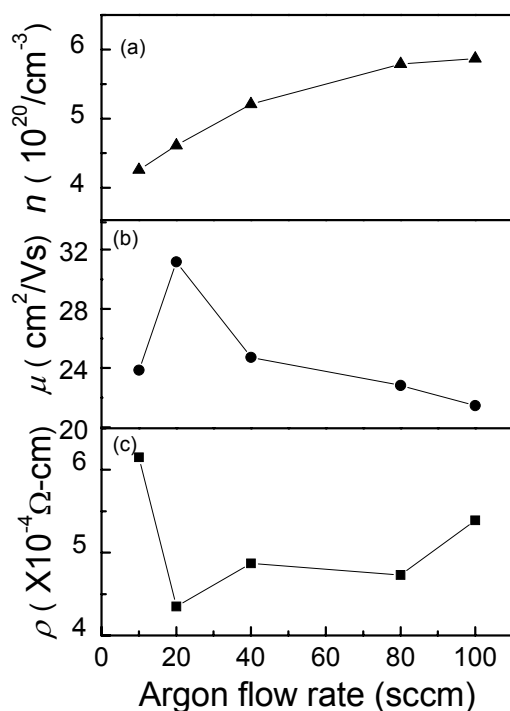


Fig. 3. (a) Carrier concentration n , (b) Hall mobility μ_H , and (c) resistivity ρ as functions of argon gas flow rate.

In Fig. 3 (b), it can be seen that when flow rate increased from 10 sccm to 20 sccm, the mobility increased from $23.8 \text{ cm}^2/\text{V}\cdot\text{s}$ to $31.2 \text{ cm}^2/\text{V}\cdot\text{s}$. According to the explanation from Zhu, lower argon flow rate can lead to a higher oxygen volume in the sputtering gas, which will increase the interstitial oxygen atoms in the deposited thin films. The interstitial oxygen atoms can absorb the moved electrons and disturb the movement of the electrons so that the mobility of sample prepared at 10 sccm is lower than that of sample prepared at 20 sccm. However, in flow rate range from 40 sccm to 100 sccm, the residual oxygen volume decreased while the mobility is also decreased.

Several factors may contribute to the reason why the mobility is not increased as the flow rate increased. Firstly, the higher carrier concentration means stronger ionic scattering which can reduce the mobility. Secondly, higher argon flow rate will make stronger collision between the sputtered target atoms with the argon atoms. This collision can reduce kinetic energy of the sputtered atoms and limit their migrating capability on the substrate, resulting in small grain size of the film. The films then contain lots of grain boundary which also can reduce the mobility of the film. Thirdly, the increased argon flow rate may introduce more argon atoms into the films. These argon atoms can result in structural defects in AZO films. All the factors mentioned above result in the decrease of mobility with increasing of flow rate from 40 sccm to 100 sccm. So the highest mobility was obtained at 20 sccm.

As seen in the Fig (c), the sample prepared at 10 sccm has the highest resistivity due to its low carrier concentration and low mobility. The sample prepared at 20 sccm has the lowest resistivity of $4.35 \times 10^{-4} \Omega\cdot\text{cm}$ for its highest Hall mobility and moderate carrier concentration. As the argon flow rate increase from 40 sccm to 100 sccm, the trend of the resistivity is increased. However, due to the increase of carrier concentration, at the 100 sccm, the sample's resistivity is still lower than that of sample prepared at 10 sccm. According to the comparison of the resistivity, which is inversely proportional to the product of Hall mobility and carrier concentration, the sample prepared at 20 sccm has the best electrical properties.

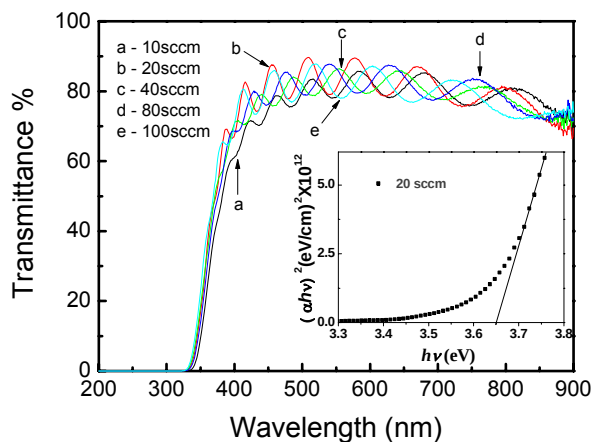


Fig. 4. Transmittance of the AZO thin films deposited at different argon flow rate. The insert graph is the $(\alpha h\nu)^2$ as a function of $h\nu$.

Fig. 4 shows the transmittance of the AZO thin films deposited at different argon flow rates. At 20 sccm, the highest average transmittance of 81.6% from 400 to 800 nm is obtained, and the highest transmittance of 89.6% turned up at 510 nm. This shows that both the electrical and optical transmittance can achieve an optimal value at 20 sccm flow rate. As a direct band gap semiconductor, the formula [16]

$$\alpha h\nu = A(h\nu - E_g)^{1/2},$$

can be used to describe the relationship between the optical gap and absorption coefficient, where α is the absorption coefficient, A is a constant, $h\nu$ is photon energy, and E_g is optical gap. And the α can be described as [17]

$$\alpha = \ln(100/T)/d,$$

where T is optical transmittance, and d is thickness of the thin film. Using above relationships, the band gap edge of the AZO film prepared at 20 sccm is evaluated by plotting $(\alpha h\nu)^2$ as a function of the energy of the incident photons, and extrapolating the linear part of the curve to intercept the energy axis. The insert graph in Fig. 4 shows the relationship between $(\alpha h\nu)^2$ with the energy of incident light. The optical gap for the sample prepared at 20 sccm is 3.65 eV, which is closed to the Agashe's results [12]. And the optical gap is larger than that of the pure ZnO. This can be attributed to the Burstein-Moss shift [18, 19].

The wet etching behavior of the AZO was also investigated. From the wet etching rate of the AZO thin films shown in Table 2, it can be seen that the etching rate for the sample prepared at 100 sccm is much larger than that for the sample prepared at 20 sccm. Lower etching rate indicates dense structure of the film.

Table 2. Comparison on the different wet etching rate of the samples deposited at argon flow rate of 20 sccm and 100 sccm.

Samples with different argon flow rate (sccm)	Wet etching rate (nm/s)
20	2.03 nm
100	3.3 nm

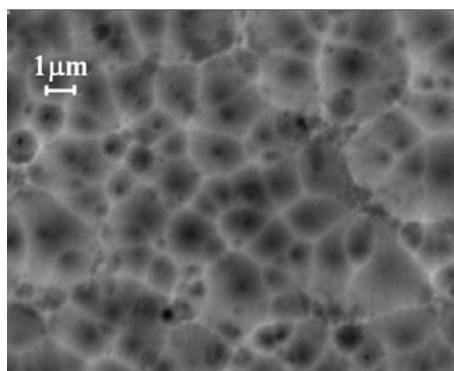


Fig. 5. SEM image of AZO thin film deposited at 20 sccm argon gas flow rate after etching by diluted 0.5% HCl.

For the sample prepared at 20 sccm, we etched it by the diluted 0.5% HCl for 30s to get a light-scattering structure. Fig. 5 shows that a good texture structure after etching is obtained. The sizes of the crater in Fig. 5 are about 1~3 μm, similar with the results of Berginski's [1],

which are effective in light scattering. And this textured structure was used in our silicon based solar cells, where enhanced transition efficiencies were obtained.

4. Conclusions

Using the XRD rocking curves measurement, it is found that the AZO thin film fabricated at 300 °C has highest peak intensity and lowest FWHM of 6.91. At this optimal temperature, we studied the influences of the argon flow rate from 10 nm to 100 sccm on the properties of AZO thin films. It is found that the carrier concentration increased with the increase of argon flow rate. At the argon flow rate of 20 sccm, the AZO film has the best electrical and optical properties. The lowest resistivity of $4.35 \times 10^{-4} \Omega \cdot \text{cm}$ and the highest mobility value of $31.2 \text{ cm}^2/\text{V} \cdot \text{s}$ are obtained. The highest average optical transmittance of 81.6% in the range of 400-800nm and the transmittance of 89.6% at 510nm are also obtained from the same sample. All the results above demonstrate that the argon flow rate is an important experimental parameter to control the electrical and optical properties of the AZO thin film.

Acknowledgements

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