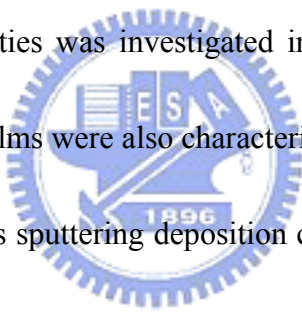# Chapter 4

Results and Discussion

4-1 Introduction

The aim of the thesis on RF sputtered AZO films was to gain a deeper understanding of the relationship between different sputter process conditions and the resulting film properties to improve conductivity and transmittance as much as possible. The influence of target Al concentration, film thickness, working pressure, substrate temperature, and sputter power on the electrical properties was investigated in detail. In addition, the physical and optical properties of the AZO films were also characterized.

In this study, AZO films sputtering deposition consisted of five kinds of target (0wt% ~ 4wt%). Coring (1737F) glass was used as the substrate. The base pressure in the chamber was about 8×10^{-6} Torr and the working pressure were controlled in the range from 2.5mTorr to 40mTorr with a high purity Ar gas. Total gas flow rate is 10sccm. The substrate temperature (Ts) was varied form room temperature (R.T.) to 350℃, and the RF power was varied from 50W to 100W. The significant results will be discussed in detail. Attention is focused on the optimization of the quality of AZO films on the glass substrate.

4-2 Effect of Argon Pressure

Table 4-1 shows the results (Fig.4-1 ~ 4-3) of the 2wt% AZO film at different working

pressure. The growth rate decreases as working increases (Fig. 4-1). This is due to the

decrease of the mean free path of the sputtered atoms with the increase of working pressure.

Therefore, we can improve the growth rate by decreasing working pressure. Figure 4-2 shows

the transmittance at different working pressure. High transmittance can be both observed in

the visible region. Besides, AZO films deposited at higher working pressure have the higher

transmittance. As shown in Figure 4-3, resistivity increases with the increasing of working

pressure. This is due to the decrease of the film thickness (shown in Table 4-1). The mobility

will degrade with decreasing film thickness [18]. Therefore, the resistivity will increase

rapidly.

To separate the effect of thickness, a study of films of controlled thickness but

obtained by different working pressure was undertaken. Figure 4-4-1~3 shows the XRD

patterns of the ~1200Å 2wt% AZO films at different working pressure. AZO films deposited

at higher working pressure have poor crystallinity and small grain size. This is probably due

to the fact that, as working increases, the collision probability between the sputtered atoms

and Ar ions increases so that the energy of the atoms arriving at the substrate surface is

reduced and surface migration is limited [19]. The Ar ions embedded in the film also limit

surface migration. These factors indicate that the excess working pressure is also one of the

impediments to qualified film growth. The optimum working pressure should be reduced

when the ZnO target containing Al_2O_3 is used for RF magnetron sputter deposition. As shown in Table 4-2, the poor crystallinity may lead to low carrier mobility. Therefore, we can find that resistivity increases with the increase of working pressure. Figure 4-4-4 shows their SEM surface morphology. We conclude that lower working pressure can increase growth rate and crystallinity. Therefore, Pw = 2.5mTorr was the optimal parameter for depositing the good quality AZO film.

4-3 Effect of RF Power

In the following, we investigate the influence of deposition power on 2wt% AZO films. Figure 4-5 shows variations of the growth rate with respect to deposition power. The growth rate increases with RF power. This increase indicates that the number of atoms sputtered from the target is proportional to the RF power.

Figure 4-6-1~3 and Figure 4-7-1~3 shows the SEM pictures and XRD patterns of the 2wt% AZO films at different RF power. Table 4-3 listed the result consisted of crystallinity and resistivity. The crystallinity is improved with adding the RF power. In the meanwhile, the resistivity can be reduced. The result indicates high deposition power conduce to increase the conductivity of AZO films. This is due to the fact that, as RF power increase, the frequency of ion bombardment increases so that the number of the sputtered atoms with high kinetic energy will increase. It will lead to improved structural completion and the crystallinity of the thin

films. Because of better crystallinity of thin films having fewer defects in the films, the scattering effect of carrier transport will be reduced. Therefore, the carrier mobility can be Increased, and the conductivity of the films can be improved.

Figure 4-8 shows the transmittance of the 2wt% AZO films at different RF power. Although 2wt% AZO films deposited at 100W have lower resistivity, AZO films deposited at 80W have better transmittance ($>$80%) in the visible region (wavelength from 400nm to 700nm). Therefore, the AZO films deposited at Prf = 80W had both good conductivity and optical property.

4-4 Effect of Substrate Temperature

4-4.1 Growth Rate

First, we discuss the effect of deposition temperature on growth rate. As shown in Figure 4-9, when samples are prepared at Prf = 150W (RF power) and Pw = 2.5mTorr (working pressure), the growth rate decreases and it decrease rapidly at deposition temperature higher than 250℃. This is probably due to the decrease of the number of atoms arriving at the substrate surface at higher deposition temperature. When the working pressure only had 2.5mTorr, it was not have Ar ions sufficient, especially in higher deposition temperature. Therefore, the number of the sputtered atoms will be reduced.

4-4.2 Physical Properties

In the following, we investigate the influence of deposition temperature on AZO films deposited by different targets (0.5wt% ~ 4wt% Al_2O_3 targets). Figure 4-10 ~ 4-13 show the SEM surface morphology of the AZO films prepared using 0.5wt%, 1wt%, 2wt%, and 4wt% Al_2O_3 targets at Pw = 2.5mTorr and Prf = 80W at different deposition temperature. As substrate temperature increases, the grain size of AZO films (all of different wt%) increases. This result, in agreement with the XRD analysis (Table 4-4 and 4-5), implies that the grain size and crystallinity were been improved by increasing deposition temperature. Table 4-4 shows the ZnO(002) peak position of above experiment. It is shown that the (002) peak shifts toward the high angle side. These results indicate that the stress will be reduced in higher deposition temperature. Furthermore, the FWHM of the XRD analysis became narrower when increasing the deposition temperature as shown in Table 4-5. By increasing the grown temperature the diffraction pattern of the AZO films shows a strong increase of the (002) peak. Compared with the ZnO films grown at lower temperature, these results indicate the AZO films of high quality crystallinity and larger grain size at higher deposition temperature. It is well known that if the (002) peak is very strong the grains are strongly oriented in the c-axis of the hexagonal ZnO (normal to the substrate surface). Figure 4-14-1~3 shows the XRD patterns of 2wt% AZO films at Prf = 80W and Pw = 2.5mTorr using different deposition temperature. This implies that the crystallinity can be improved at higher deposition

temperature.

4-4.3 Electrical Properties

Compared with the electrical properties of the above experiment (shown in Table 4-6), we can come to the conclusion that higher deposition temperature will enhance the conductivity of AZO films. It is due to the decrease of defects by increasing crystallinity at higher deposition temperature. As defects of AZO films decrease, the mean free path of electron is increased so that the electron mobility is increased [20]. The decrease in resistivity can be interpreted in terms of crystallite structure enhancement. In short, Resistivity of the AZO films can be improved by increasing deposition temperature.

Furthermore, it is noted that even the R.T. grown AZO films itself is of good crystallinity and conductivity. Because good conductivity AZO films can be made at room temperature and, thus, there is good compatibility with low-temperature process. Low-temperature process makes AZO thin films attractive for flexible electronics on plastic or flexible substrate.

4-5 Effect of Al Content on AZO Films

4-5.1 Physical Properties

At first, we characterize the growth rate of the AZO films prepared by different

amounts of Al_2O_3 in the target. Table 4-7 shows the relationship between growth rate and different Al_2O_3 content in the target (films deposited at Pw = 2.5mTorr, Prf = 80W, and Ts = R.T. (substrate temperature)). We can find that the growth rate decrease with increasing the Al_2O_3 content of the target. Such an effect has been obtained by other researchers [18].

In the following, we report on the physical and electrical properties of AZO films prepared by RF sputter deposition system using the targets that was made from high purity ZnO powder containing different amounts of Al_2O_3 powder as the Al doping source. Figure 4-15-1~5 shows the SEM surface morphology obtained from ~ 4000Å thickness AZO films prepared by different sputtering targets. As shown in Fig. 4-15-1~5, grain size (obtained from SEM) of the AZO films became larger at higher Al_2O_3 weight percent of the target. This result, in agreement with the XRD analysis (Fig. 4-16 and 4-17), shows the crystallinity of AZO films will be improved by increasing the Al_2O_3 content in target from 0 to 2wt%. Such an effect also has been observed by other researcher [18]. When the weight percent is up to 4wt%, the crystallinity began to weaken. This is probably due to the degradation of mobility. As shown in Figure 4-16, only ZnO(002) peak was observed. Besides, the Al-doping procedure caused no additional X-ray diffraction peaks or at least Al_2O_3 content was below the detection limit. Table 4-8 shows the grain size of above experiment. In conclusion, the 2wt% grown AZO films have the best crystallinity and largest grain size.

4-5.2 Electrical Properties

4-5.2.1 Influence of Dopant Content

The conduction characteristics of ZnO are primarily dominated by electrons generated by the oxygen vacancy and zinc interstitial atoms. The electrical conductivity in AZO film is higher than that in pure ZnO films due to the contribution from Al^{3+} ions on substitutional sites of Zn^{2+} ions and Al interstitial atoms as well as from oxygen vacancies and Zn interstitial atoms. Figure 4-18 shows how the resistivity is related to the Al_2O_3 content in the sputtering target. All the samples were prepared at the same deposition conditions with Ts = R.T., Pw = 2.5mTorr, and Prf = 80W. And their thicknesses are about 4000Å. As Al_2O_3 in the target increases, resistivity decreases and reaches a minimum value of about 5×10^{-4} Ω-cm for the 2wt% grown AZO films. On the other hand, resistivity increases to about 3.50×10^{-3} Ω-cm for the 4wt% grown AZO films.

For highly degenerated transparent semiconducting ZAO films, ionized impurity scattering dominated the Hall mobility of the films in the low-temperature range. However, lattice vibration scattering became a major scattering mechanism in the high-temperature range. Grain-boundary scattering played a major role when the grain size was smaller than the mean-free path of carriers [21]. According to above experiment, we had found that resistivity increase at 4wt%. The comparison with literature data implies that ionized impurity scattering is the major scattering mechanism, which limits the mobility in these AZO films. In detail,

this drop in mobility of the 4wt% grown AZO film in our experiment can be explained by an increasing amount of scattering center present in the AZO films at higher wt%. These scattering centers can consist of ionized Al or Al_2O_3 and its suboxides [18]. Both will cause additional scattering of the charge carriers, which adversely affects the carrier transport. It leads to the decrease of carrier mobility. Besides, for higher wt% up to 4wt%, the effectiveness of doping began to decrease [18] thereby indicating that an increasing extent of the built-in Al was electrically nonactive.

In conclusion, a higher resistivity obtained for 4wt% is due to the low mobility, which is probably caused by an increased incorporation of suboxides of Al-O, either in Al_2O_3 form or some intermediate. This result, in agreement with the XRD analysis, implies that the poor crystallinity of 4 wt% grown AZO films was due to the decrease of carrier mobility. In order to get the optimal conductivity, we should increase carrier concentration while maintaining a acceptable carrier mobility or improve the carrier mobility under high carrier concentration condition. The 2wt% grown AZO films have both high carrier concentration and mobility so that it had the lowest resistivity of the above experiment.

4-5.2.2 Influence of Film Thickness

In the following, we discuss the effect of thickness on the AZO films. Table 4-9 shows the relationship between resistivity and film thickness of variable wt% grown AZO films at Ts

= R.T., Prf = 80W, and Pw = 2.5mTorr. We can find that the resistivity decreases with the increase of AZO films in any wt% of target. In previous section, the 2wt% grown AZO films had the lowest resistivity at the same film thickness (about 4000Å). To further improve the electrical properties for 2wt% film, the effect of film thickness should be investigated. Table 4-10 shows the XRD patterns data of 2wt% grown AZO films with different film thickness. The AZO films with thicker film thickness have better crystallinity and larger grain size. This result indicates that the grain size along the direction of growth has increased for thicker films. Such increase will favorably contribute to the increase in mobility with thickness. Because thicker films had lower FWHM and higher angle of ZnO(002) peak, the stress in the films could be reduced. Therefore, the conductivity of 2wt% grown AZO film can be further increased with improving the crystallinity by increasing film thickness. (shown in Figure 4-19).

A higher resistivity obtained for the 4wt% grown AZO films is due to the lower mobility, and for 0.5wt% is due to the lower carrier concentration. But the conductivity of 0.5wt% grown AZO films can be further improved with increasing the film thickness, which can be mainly attributed to the increase in carrier mobility. However, the overall lowest resistivity was obtained by using 2wt% Al_2O_3 content of target, which had both high carrier concentration and mobility. In this thesis, using 2wt% target is the optimal solution for high conductivity.

4-5.3 Optical Properties

4-5.3.1 Influence of Dopant Content

In this study, the AZO films were deposited on the Corning 1737F glass substrate. Figure 4-20 shows the optical transmittance of Corning 1737F glass substrate. Corning 1737F glass substrate has about 90% transmittance in the visible region (wavelength from 400nm to 700nm). Figure 4-21 shows the optical transmittance of ~ 4000Å thick AZO films prepared with targets having different Al_2O_3 content at Ts = R.T., Pw = 2.5mTorr, and Prf = 80W. The optical transmittances of these AZO films in the visible region are about 85%. The optical absorption edge shifted monotonically toward the shorter wavelength region with the increasing of Al doping in the films. The movement of the absorption edge to the shorter wavelength region is the Burstein-Moss shift, which is due to the increase of carrier concentration in the films. Controlling Al doping concentration can control the spectrum edge in the UV region.

The optical absorption coefficient of a direct band gap semiconductor near the band edge, for photon energy hν greater than the band gap energy Eg of the semiconductor, is given by equation (3-4). Then optical band gap (Eg) can be determined by using that equation. Figure 4-22 shows the optical band gap of the above experiment. From Fig. 4-22, the optical bandgaps of for the samples prepared by 0.5wt%, 1wt%, 2wt%, and 4wt% Al_2O_3 target are about 3.33eV, 3.5eV, 3.68eV, and 3.69eV, respectively. This is the well known Burstein-Moss

effect. Burstein pointed out that the increase of the Fermi level in the conduction band of the degenerate semiconductor leads to the energy band widening (blue shift) effect. The energy band gap widening (ΔEg^{BM}) is related to carrier concentration n_e through the equation (2-3). We can increase the optical bandgap by increasing the doping content. Although the blue shift in the AZO films is proportional to a one-third power of carrier concentration n_e, it began to saturate when the carrier concentration increases above $\sim 10^{20}$ cm^{-3}. Therefore, the optical band gap is no longer increased rapidly when the Al$_2$O$_3$ content of the target is up to 4wt% (Fig. 4-22). This phenomenon is due to the bandgap shrinkage at high carrier concentration (bandgap narrowing effect). It will adversely affect the BM shift. The electronic state of the materials can be calibrated by electron-electron or electron-impurity scattering. That is, the many-body effect such as exchange interaction or Coulomb interaction makes the energy bandgap decrease.

4-5.3.2 Influence of Substrate Temperature

From our previous investigation, we had found that the resistivity of the AZO films can be improved by increasing deposition temperature. In the following, we investigate the relationship between optical transmittance and substrate temperature. Figure 4-23-1~3 shows this relationship at different Al$_2$O$_3$ content of target. The transmittances of the AZO films grown at different substrate temperature are still very high in the visible region. Besides, all

the optical absorption edges tended to reach the same location. There is no shift in optical absorption edge when increasing the substrate temperature for deposition. According the BM effect, the position of optical absorption edge depends on the carrier concentration of AZO films. We can indicate that the carrier concentration of the AZO films is probably invariant at the substrate temperature region from room temperature to 250℃. Although the carrier concentration is almost constant (no BM shift) from R.T. to 250℃, the crystallinity of AZO film can be improved in higher substrate temperature (had been discussed in the previous section). It enhanced the increase of carrier mobility. Therefore, the resistivity of AZO films could still be further reduced by increasing the substrate temperature.
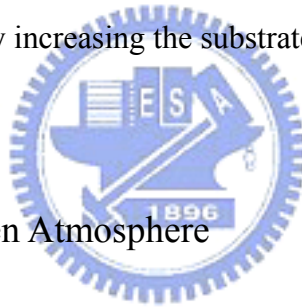
4-5.3.3 Influence of Oxygen Atmosphere

In this section, we investigate the influence of oxygen atmosphere on the resistivity of AZO films. Table 4-1 shows the resistivity of AZO films deposited at Ts = R.T., Pw = 2.5mTorr, Prf = 80W, and O_2/Ar ratio = 10%. And Figure 4-24 is the XRD pattern of 2wt% grown AZO films at Ts = R.T., Pw = 2.5mTorr, Prf = 80W, and O_2/Ar ratio = 10%. Only ZnO(002) peak can be observed as well as the previous experiments. But the resistivity of the AZO films was found to increase drastically when oxygen was introduced together with the sputtering gas. This is due to the decrease of oxygen vacancy (as the carrier in the AZO films). According to the equation (4-1), the oxygen vacancies of the AZO films will decrease in the

oxygen ambience.

$$O_O \leftrightarrow V_O^{\bullet\bullet} + 2e' + \frac{1}{2}O_2(g), \qquad\qquad (4\text{-}1)$$

where O_O, $V_O^{\bullet\bullet}$, and 2e' represent the oxygen ion on its normal site, oxygen vacancy and electron, respectively.

Finally, we discuss the result of optical transmittance of the above experiment. Figure 4-25 shows the transmittances of the different wt% grown AZO films deposited at Ts = R.T., Pw = 2.5mTorr, Prf = 80W, and O_2/Ar ratio = 10%. The transmittances in the visible region are still very high. On the other hand, the optical absorption edges are almost at the same location until the Al_2O_3 content of the target is increased to 4wt%. According BM effect, this result indicates that the carrier concentration had not been further increased with the Al_2O_3 content of target had been up to 4wt%. Compared with the individual optical transmittance of the AZO films (Fig. 4-26-1~4), we found that the carrier concentration of the AZO films grown with oxygen atmosphere is less than that grown in ambience without oxygen atmosphere (according BM effect) even in 4wt% grown AZO films. And the energy gap of these AZO films will become smaller. From above results, we know that the oxygen vacancy plays an important role in the conductivity of AZO films. The conductivity of AZO films would decrease with the decrease of oxygen vacancies. We should deposit the AZO films in

the ambience without oxygen atmosphere for better conductivity of films.

4-6 Optimal Deposition Condition of AZO Flims

Based on the systematic research and these results that followed from this thesis, optimum deposition conditions could be determined for RF sputtered AZO films. The most important parameters and proposed values are summarized in Table 4-12. In general, these optimum deposition conditions resulted in typical growth rates around 20 Å/min. The AZO films exhibited a strong (002) orientation with grain sizes around 23nm. Optimized films demonstrated low resistivity (approach to 10^{-4} Ω-cm), good crystallinity, and good optical transmittance (about 85% in the visible region).