

## Research Article

# Characterization of Al-Doped ZnO Transparent Conducting Thin Film Prepared by Off-Axis Magnetron Sputtering

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The off-axis sputtering technique was used to deposit Al-doped ZnO (AZO) films on glass substrates at room temperature. For the illustration of the sample position in the sputtering chamber, the value of  $R/r$  is introduced. Here,  $r$  is the radius of AZO target and  $R$  is the distance between the sample and the center of substrate holder. A systematic study for the effect of deposition parameters on structural, optical, and electrical properties of AZO films has been investigated in detail. As the sample position of  $R/r$  is fixed at 1.8, it is found that the as-deposited AZO film has relatively low resistivity of  $2.67 \times 10^{-3} \Omega\text{-cm}$  and high transmittance above 80% in the visible region. Additionally, after rapid thermal annealing (RTA) at  $600^\circ\text{C}$  with  $\text{N}_2$  atmosphere, the resistivity of this AZO film can be further reduced to  $1.19 \times 10^{-3} \Omega\text{-cm}$ . This indicates the AZO films prepared by off-axis magnetron sputtering and treated via the appropriate RTA process have great potential in optoelectronic applications.

## 1. Introduction

Recently, transparent conducting oxides (TCOs) are commonly used for a wide range of applications consisting of solar cells, flat panel displays, touch panels, and light-emitting diodes. Among many TCO materials, ZnO has gained a lot of attention owing to its advantages including nontoxicity, low cost, and highly thermal stability [1, 2]. However, regarding to the above-mentioned applications, the conductivity of ZnO is not good enough and requires improving. To solve this problem, there have been several researches focused on the doping into ZnO, and it confirms that the conductivity of ZnO is indeed enhanced by doping with various elements such as F, Al, and Ga [3–5]. Particularly, among these ZnO-based materials, Al-doped ZnO (AZO) thin films have attracted more interest because of their relatively low electrical resistivity and high optical transmittance [6]. On the other hand, ZnO-based films can be grown by many deposition techniques consisting of sputtering [7], evaporation [8], chemical vapor deposition [9], spin coating [10], sol-gel [11], spray pyrolysis [12], and so on. Among these methods, sputtering is widely employed because the

deposited films usually possess plenty of advantages, such as good adhesion, high uniformity in thickness, and high film density. Nevertheless, the bombardment formed on the film is a serious drawback of sputtering technique. At present, to reduce the effect of bombardment during the film deposition, the off-axis sputtering technique has been proposed [13, 14].

In this study, the off-axis sputtering was used to grow AZO thin films. In the off-axis sputtering system, the value of  $R/r$  was defined to depict the sample position in the chamber. By investigating the effect of  $R/r$  value on the characteristics of AZO films, a more suitable sample position for the AZO deposition was obtained. Moreover, the AZO films were further treated by rapid thermal annealing (RTA). Via the modifications of the sample position and the annealing conditions, the AZO films prepared with the optimal parameters can possess better optoelectronic characteristics.

## 2. Experimental Procedure

In our work, the AZO thin films were deposited by radio frequency magnetron sputtering on Corning 1737 glass substrates at room temperature. During the deposition process,

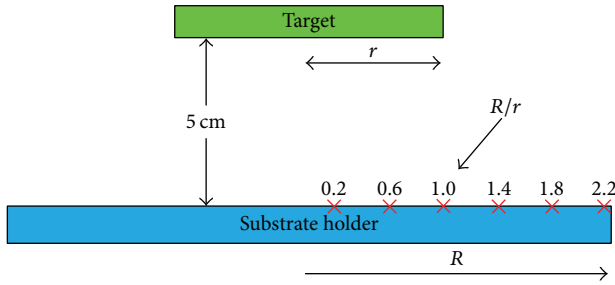


FIGURE 1: Schematic illustration of the sample position in the sputtering chamber.

a homemade AZO ceramic target (98 wt.% ZnO and 2 wt.%  $\text{Al}_2\text{O}_3$ ) of 2-inch diameter was used. The vertical distance between the target and the substrate holder was fixed at 5 cm. In order to illustrate the sample position, we defined the value of  $R/r$  in the sputtering chamber, where  $r$  is the radius of AZO target and  $R$  is the distance between the sample and the center of substrate holder, as shown in Figure 1. When the off-axis sputtering technique was used to grow the AZO films, the substrates were placed at six positions with various  $R/r$  values of 0.2, 0.6, 1.0, 1.4, 1.8, and 2.2, respectively. By varying the value of  $R/r$ , the influence of the geometry inside the chamber on the AZO properties can be realized. As the base pressure was less than  $7.5 \times 10^{-5}$  Pa, the 60 sccm pure Ar gas was introduced into the sputtering chamber, and the working pressure for the AZO growth was kept at  $7 \times 10^{-1}$  Pa. The sputtering power of AZO target and the deposition time were maintained at 100 W and 60 min, respectively. Except for the sample position in the chamber, the annealing conditions including the temperature and the ambient atmosphere also can be changed to reach better characteristics of AZO films. In the annealing process, the RTA equipment with a heating rate of  $5^\circ\text{C/s}$  was used. The as-deposited AZO films were annealed at various temperatures ranging from 200 to  $600^\circ\text{C}$  for 1 min. In addition, three ambient atmospheres consisting of air,  $\text{N}_2$ , and vacuum were adopted in the annealing process.

Structural, optical, electrical, and morphological properties of the AZO films prepared with various parameters were characterized. The growth orientation of the AZO film was analyzed by X-ray diffraction (XRD, Philips X'PertMRD). Scanning electron microscopy (SEM, JEOL JSM-7001F) was employed to investigate the film's morphology and thickness. The electrical properties such as resistivity, mobility, and carrier concentration of AZO samples were characterized in Van Der Pauw configuration by a Hall analyzer (Accent HL5500/5580). The transmittance spectra of AZO films were measured by an UV-Vis-NIR spectrometer (V-570, JASCO).

### 3. Results and Discussion

The crystal structures of AZO films deposited on glass substrates were examined by XRD. Figure 2 shows the results of XRD  $\theta$ - $2\theta$  scan for AZO films placed at various positions with  $R/r$  values of 0.2–2.2, where  $2\theta$  is increased from  $20^\circ$  to  $60^\circ$ . It can be observed that there is no diffraction peak appearing in the XRD pattern for the sample at the position

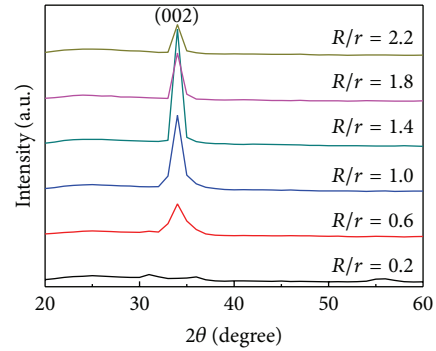


FIGURE 2: XRD patterns of AZO thin films prepared at various sample positions of  $R/r = 0.2$ – $2.2$ .

of  $R/r = 0.2$ , indicating this AZO film possesses amorphous phase. Moreover, by changing the sample position of  $R/r$  from 0.6 to 2.2, only the ZnO(002) diffraction peak can appear in the patterns of these AZO films, which reveals the  $c$ -axis preferred orientation growth is dominated due to the self-texturing phenomenon [15]. Besides, when the sample positions of  $R/r$  were set at 1.0–1.8, the intensity of ZnO(002) diffraction peak of these AZO films is obviously higher than that of the others.

Figures 3(a)–3(f) display the plan-view SEM images of the sputtered AZO samples placed at the positions of  $R/r = 0.2$ , 0.6, 1.0, 1.4, 1.8, and 2.2, respectively. When the position of  $R/r$  was fixed at 1.4, it can be seen that the AZO film had the largest grain size. Based on Scherrer's formula, the full width at half maximum (FWHM) of XRD peak is corresponding to the crystalline grain size [16]. This indicates the thin film with the most intense XRD peak possesses the largest grain size. The results observed in the plan-view SEM images agree well with those of the XRD patterns, as shown in Figure 2. Figure 4 shows the cross-sectional SEM images of AZO films prepared by putting the samples at various positions ( $R/r = 0.2$ – $2.2$ ). According to our observation, as the sample positions of  $R/r$  are kept at 0.2, 0.6, 1.0, 1.4, 1.8, and 2.2, the thicknesses of AZO films are determined to be 631, 607, 506, 461, 336, and 263 nm, respectively. This reveals that the AZO film's thickness decreases with increasing the  $R/r$  value. When the  $R/r$  value is smaller, the moving distance of the ions generated from a target is relatively shorter, and more atoms can arrive at the substrate surface. Thus, this AZO film (at the smaller  $R/r$  value) is relatively thicker. On the contrary, at the larger  $R/r$  value, the AZO film becomes thinner, resulting from the arrival of less atoms at the substrate surface.

The transmittance of the AZO thin film was analyzed by UV-Vis-NIR spectrometer with a wavelength range from 200 to 2500 nm. Figure 5 shows the transmittance spectra of these AZO films prepared by putting the samples at various positions ( $R/r = 0.2$ – $2.2$ ). It is apparent that all AZO films exhibit high transmittance in the wavelength range of 400–1200 nm. As the measured wavelength is higher than 1200 nm, the transmittance spectra of these films all present a decreasing tendency. Even so, the high transmittance above 80% in the visible region still confirms that all AZO films are potentially useful in plenty of optoelectronic applications.

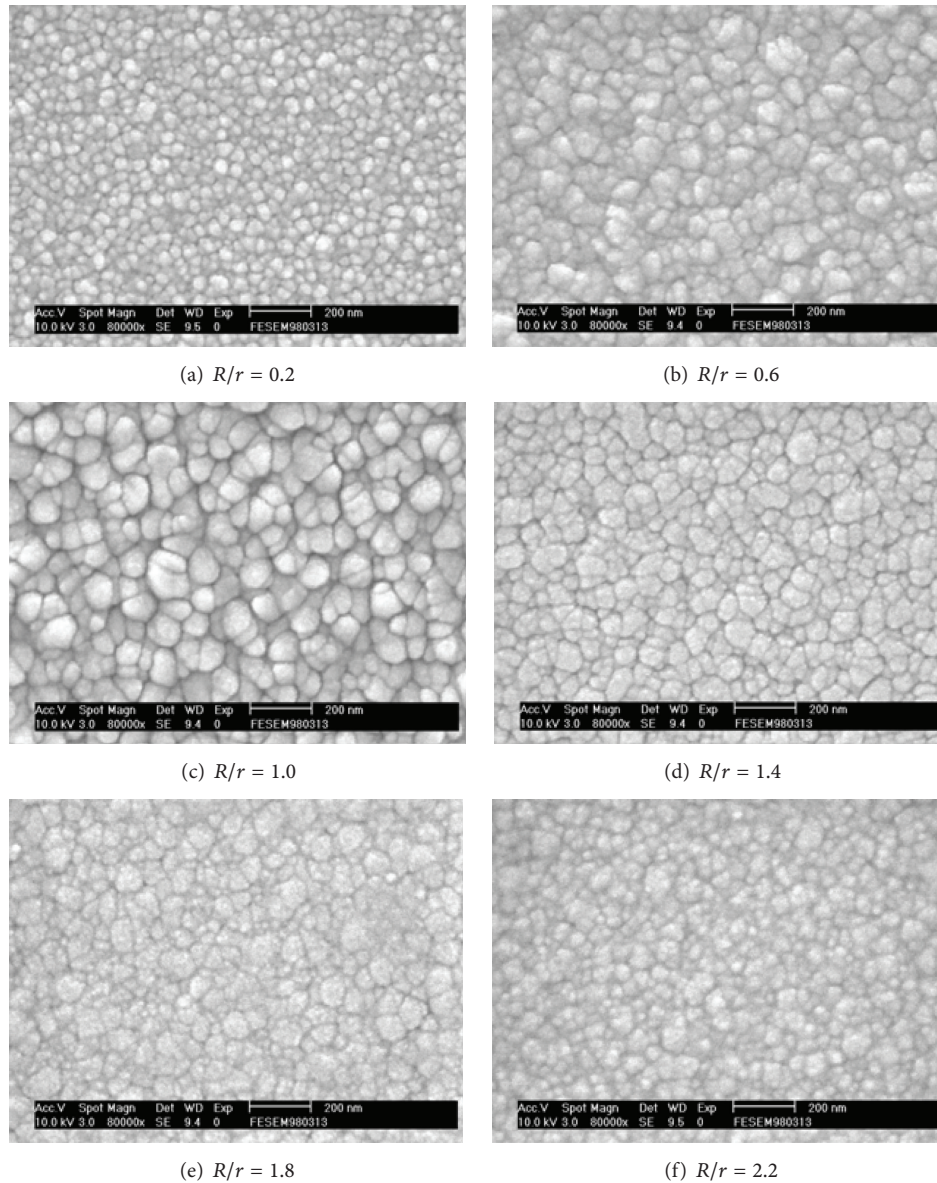


FIGURE 3: Plan-view SEM images of AZO thin films prepared at various sample positions ( $R/r$ ) of (a) 0.2, (b) 0.6, (c) 1.0, (d) 1.4, (e) 1.8, and (f) 2.2.

Figure 6 shows the variations in the resistivity, mobility, and carrier concentration of AZO thin films as a function of sample position ( $R/r$ ). When the  $R/r$  value was set to 0.6, a relatively higher resistivity ( $3.97 \Omega\text{-cm}$ ) of this AZO film was measured. By changing the sample position of  $R/r$  from 0.6 to 1.8, the resistivity of the AZO film gradually reduced. The lowest resistivity of  $2.67 \times 10^{-3} \Omega\text{-cm}$  can be achieved in the AZO film as the sample position of  $R/r$  was set to 1.8. From our observation, the decrease in the resistivity of AZO films can be mainly attributed to the increment in the carrier concentration. The other reason for the decreased resistivity is probably owing to the contribution of Al interstitial atoms in the AZO film. On the other hand, as mentioned above, the unwanted bombardment on the deposited films is a serious disadvantage of the sputtering

technique. The bombardment on ZnO-based films is mainly owing to the generations of energetic O atoms and  $O^-$  ions [17–20]. Tominaga et al. proposed that the bombardment from energetic O atoms or  $O^-$  ions was responsible for the high electrical resistivity of ZnO films [18]. Besides, Nguyen et al. reported that the formation of negative ions from the AZO target was attributed to the surface ionization, resulting from the surface absorption of Al atoms on the AZO target surface [20]. Fortunately, the use of off-axis sputtering technique can reduce the damage caused by negative-ion bombardment to the film growth, leading to an improvement in the electrical conductivity of AZO film. In our research, for the sample at the position of  $R/r = 1.8$ , a better electrical conductivity of AZO film can be achieved, which could also be due to the most efficient reduction in the negative-ion bombardment



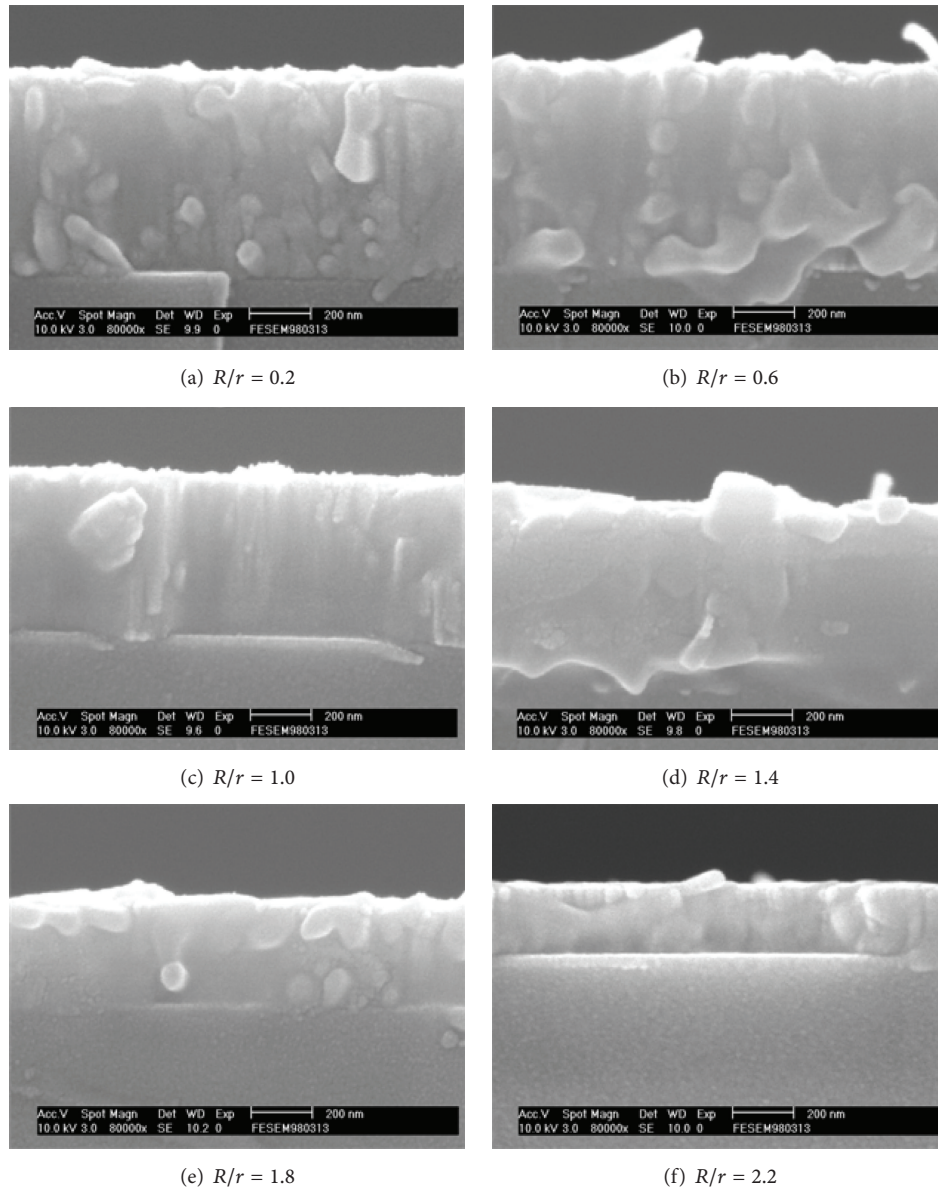


FIGURE 4: Cross-sectional SEM images of AZO thin films prepared at various sample positions ( $R/r$ ) of (a) 0.2, (b) 0.6, (c) 1.0, (d) 1.4, (e) 1.8, and (f) 2.2.

emitted from the AZO target surface. With further changing the sample position of  $R/r$  to 2.2, the resistivity of the AZO film was slightly increased to  $4.54 \times 10^{-3} \Omega\text{-cm}$ . In addition, when the samples were placed at the positions of  $R/r = 0.6, 1.0, 1.4, 1.8,$  and  $2.2$ , the mobility of these AZO films was measured to be 16.0, 0.1, 3.2, 3.5, and 2.3  $\text{cm}^2/\text{Vs}$ , respectively. Except for the higher mobility of the AZO sample placed at the position of  $R/r = 0.6$  (16.0  $\text{cm}^2/\text{Vs}$ ), the other AZO films all exhibit the relatively lower mobility of 0.1–3.5  $\text{cm}^2/\text{Vs}$ . The low mobility of these as-deposited AZO films (sample positions of  $R/r = 1.0\text{--}2.2$ ) can be attributed to the excess scattering center.

According to the above-mentioned results, the as-deposited AZO film prepared at the sample position of  $R/r =$

1.8 has a lower electrical resistivity in comparison to the other films. As a result, this AZO film was selected for the RTA annealing treatment. Figure 7 shows the resistivities of AZO films (sample position of  $R/r = 1.8$ ) annealed with various atmospheres consisting of air,  $\text{N}_2$ , and vacuum as a function of annealing temperature. Additionally, the annealing temperatures of 200, 300, 400, 500, and 600  $^\circ\text{C}$  were chosen. For the AZO films annealed in the air atmosphere, a relatively lower resistivity of  $5.87 \times 10^{-3} \Omega\text{-cm}$  was obtained at the annealing temperature of 200  $^\circ\text{C}$ . However, in comparison to the resistivity of as-deposited AZO film (as shown in Figure 6), it indicates that the resistivity cannot be reduced through the annealing process in the air atmosphere, which is similar to the result proposed in previous research [21].

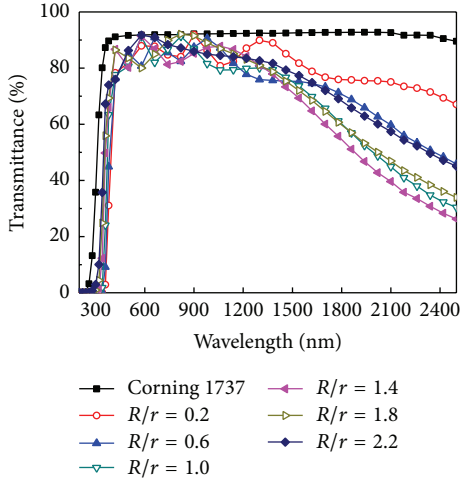


FIGURE 5: Transmittance spectra of AZO thin films prepared by putting the samples at various positions ( $R/r = 0.2$ – $2.2$ ).

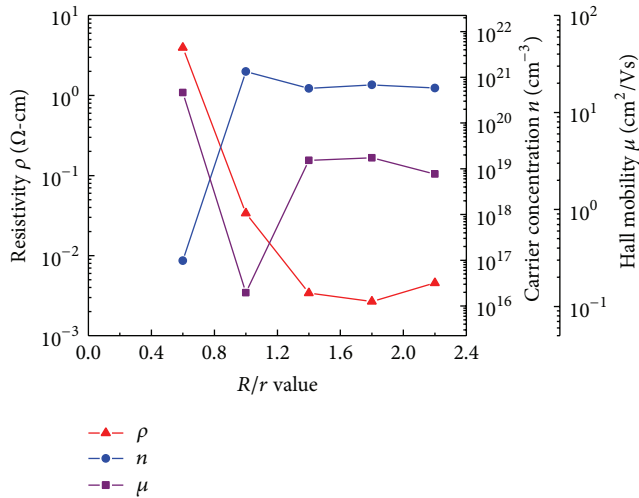


FIGURE 6: Variations in the resistivity, mobility, and carrier concentration of AZO thin films as a function of sample position ( $R/r$ ).

Moreover, as the atmospheres of  $N_2$  and vacuum were used in the annealing processes, the resistivity of the AZO film can be decreased efficiently, especially for  $600^\circ\text{C}$  annealed AZO films. The low resistivities of  $1.19 \times 10^{-3}$  and  $1.22 \times 10^{-3} \Omega\text{-cm}$  are achieved in  $600^\circ\text{C}$  annealed AZO films with the atmospheres of  $N_2$  and vacuum, respectively. The results reveal the atmospheres of  $N_2$  and vacuum are more useful for the improvement in the electrical property of AZO films. The enhancement in the electrical property may be attributed to the fact that the grain boundaries and the crystal lattice deficiencies of the AZO film are reduced with increasing the annealing temperature, leading to an increment in the mobility of the carriers. Additionally, for the ZnO-based materials, it is well known that the oxygen vacancies are mainly responsible for electrons in the conduction band [22]. During the annealing process with the atmosphere of  $N_2$ , it can be expected that the absorption of oxygen atoms on the

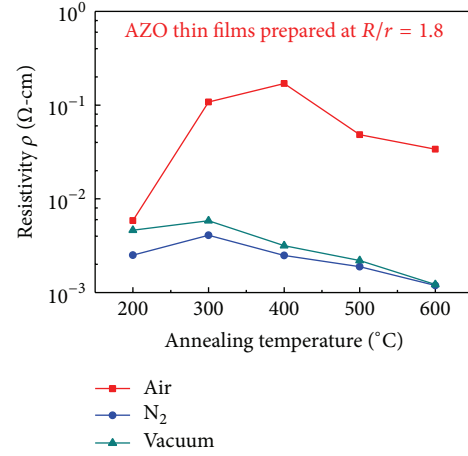


FIGURE 7: Resistivities of AZO thin films (sample position of  $R/r = 1.8$ ) annealed with various atmospheres including air,  $N_2$ , and vacuum as a function of annealing temperature.

film surface would be reduced, leading to an increment of the oxygen vacancy content. This can explain the better electrical conductivity of  $N_2$ -annealed AZO films. Based on the results mentioned above, it indicates the electrical conductivity of AZO films can be improved by placing the sample far away from the target, in particular for the sample position of  $R/r = 1.8$ . Furthermore, after RTA annealing at  $600^\circ\text{C}$  with the atmosphere of  $N_2$ , the optimal electrical property of the AZO film can be obtained. This implies the AZO films deposited by off-axis magnetron sputtering and then treated by RTA annealing in  $N_2$  atmosphere are highly feasible for applications in optoelectronic devices.

Actually, good electrical and optical properties of AZO films deposited by sputtering (this study) also could be obtained by low-cost chemical solution methods, such as sol-gel [11] and spray pyrolysis [12]. However, it should be mentioned that the sputtered AZO films possessed a higher crystal quality and a smoother surface than those grown by sol-gel and spray pyrolysis. Moreover, it is well known that the sputtering technique is highly compatible with the fabrication processes of modern electronic devices.

#### 4. Conclusion

In summary, the AZO thin films were grown by off-axis radio frequency magnetron sputtering. By changing the relative position of sample ( $R/r = 0.2$ – $2.2$ ), better electrical conductivity of the AZO film was achieved when the  $R/r$  value was fixed at 1.8. As the atmospheres of  $N_2$  and vacuum were used in the RTA annealing processes, the electrical conductivity of AZO films can be further enhanced. For the as-deposited AZO film (sample position of  $R/r = 1.8$ ), its resistivity was measured to be  $2.67 \times 10^{-3} \Omega\text{-cm}$  and can be further reduced to  $1.19 \times 10^{-3} \Omega\text{-cm}$  after RTA annealing at  $600^\circ\text{C}$  with the atmosphere of  $N_2$ . Therefore, via the combination of the off-axis sputtering technique and the RTA annealing process in  $N_2$  atmosphere, the AZO films have high potential in the optoelectronic applications.

## Competing Interests

The authors declare that there are no competing interests regarding the publication of this paper.

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