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Influence of the RF magnetron sputtering power on the optical and electrical properties of AZO films

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Thin AZO films were synthesized using radio frequency magnetron sputtering method on the surface of polished silicon samples and glass slides. The sputtering power was varied in the range of 150–300 W with the step of 25W; deposition time was adjusted so that the film thickness remained equal to 70 nm. The rest of the deposition parameters: working pressure, temperature, and the substrate rotation rate, remained unchanged. The thickness and deposition rate of thin films were measured using X-ray reflectometry. The electrical properties (resistivity, Hall mobility and charge concentration) of thin films were measured by the Van Der Pauw method using the Hall effect. The transmission spectra of the films were measured in the wavelength range from 300 to 1100 nm. The average crystallite size was determined using X-ray diffraction spectra and the Scherrer equation. As a result, it was shown that AZO films synthesized at a power of 300 W have the best electrical and optical properties. At this power, the lowest resistivity value of 2.83×10^{-3} Ω·cm and the maximum charge mobility of 9.6 $cm^2V^{-1}sec^{-1}$ were achieved for films of the same thickness 70 nm. The decrease in the electrical resistivity of the films with increasing power is explained by more intense heating of the substrate during deposition, which leads to an improvement in the crystallinity of the film, and, as a consequence, to an increase in the mobility of charge carriers.

Key words: transparent conductive oxide, RF magnetron sputtering, zinc oxide.
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1 Introduction

Transparent conductive oxides (TCO), consisting of one or two metal elements, have important physical properties for many industries. High transparency in the visible light region (~80-90%) and low resistivity allow to use TCO thin films in many applications, such as touch displays, thin-film and heterojunction solar cells, optical coatings, etc [1–6]. Among various TCO materials, indium tin oxide (ITO) has become the most widely used due to its chemical resistance, high transparency (more than 85%) and low resistivity (~10^{-4} Ohm·cm). However, the high content of indium in these films (In_2O_3>90%) significantly increases the cost of the final product. Therefore, inexpensive alternatives with suitable optical and electrical properties are required.

Zinc oxide (ZnO) thin films were considered the most promising candidates to replace ITO [7]. However, pure ZnO films have a relatively high resistivity, which is unacceptable for wide application in the industry. Doping of zinc oxide films with aluminum ZnO:Al (AZO) makes it possible to significantly increase the charge concentration, which has a positive effect on the conductivity of the films. AZO films are produced by various deposition methods, such as chemical vapor deposition, thermal evaporation, sol-gel method, magnetron sputtering, etc. However, magnetron sputtering has become the most widespread due to the high quality of the obtained films, low deposition cost, and ease of increasing the deposition area [8].

Due to the high conductivity, AZO films can be synthesized in the direct current (DC) [9–11] and radio frequency magnetron sputtering (RF) regimes [12–14]. Nevertheless, RF sputtering makes it possible to obtain films based on ZnO with a much lower electrical resistivity. For example, Gao et al. [15] attributed this to a more uniform grain distribution with good crystalline quality, which in turn leads to higher carrier mobility and hence higher conductivity. There are already works [16,17], where the optical and electrical properties of AZO films synthesized at various RF sputtering powers have been studied. However, the influence of the thickness of AZO thin films has been put on the background, although it is known [18] thickness has a key effect on electrical resistivity. The point is that the AZO layers at the film–substrate interface have a strongly disordered structure, which adversely affects the electrical characteristics. For a comparison and optimization of the deposition parameters, it is necessary to consider films of equal thickness. In this work, we study the dependence of the optical and electrical properties on the RF power of magnetron sputtering for AZO films of equal thickness.

2 Materials and Methods

Thin AZO films were synthesized on the surface of polished n-type silicon samples (100) and cover microscopic glass slides. Electrical resistivity of Si samples were calculated to be 20–30 Ω·cm, thickness ~400 μm and an area of 20 × 30 mm, while thickness of glass slides was ~170 μm and an area of 18 × 18 mm. Prior to film deposition, the surface of silicon samples was cleaned from residual impurities by a standard three-stage cleaning procedure [19], the surface of glass slides was cleaned in an HNO_3:H_2O_2:H_2O solution. AZO films were deposited in a MAGNA-TM200-1 setup [20]. Before the sputtering, a base pressure of $5 \cdot 10^{-4}$ Pa was achieved using oil-free rotary and turbomolecular pumps. The deposition was carried out in an argon ambient (99.999%) at a pressure of 0.7 Pa. A cylindrical AZO target 100 mm in diameter, supplied by Girmet, was used as a sputtering source. RF power varied from 150 to 300 W with the step of 25 W. The deposition time varied depending on the power to obtain films of the same thickness ~70 nm. For uniform film deposition, the substrate holder was rotated. The substrates were not subjected to external heating, but the temperature increased during deposition. The thickness of the resulting films was measured by X-ray reflectometry (XRR) using a ComplexRay C6 setup [21]. The transmission spectra of the films were measured in the wavelength range from 300 to 1100 nm on an Evolution UV-Vis 300 spectrophotometer (Thermo Scientific™). The electrical properties of the films were measured by the van der Pauw method using a Keithley 2400 source-meter. The X-ray diffraction spectra of the resulting films were measured on a ComplexRay C6 setup in the grazing incidence mode (GIXRD).

3 Results and Discussion

By X-ray reflectometry method using Kissig oscillations [22] the thickness of the deposited films was determined, which varied from 18.4 to 61.4 nm. To estimate the deposition rate at each RF power, the resulting film thickness is divided by the deposition time. As a result, dependence of the deposition rate on the power was obtained, shown in Figure 1. A linear dependence of the deposition rate on the RF power of magnetron sputtering on the MAGNA-TM200-1 setup was revealed, which varied from 0.077 to 0.210 nm/s. The obtained values will be used for the synthesis of films with the same thickness. As expected, the maximum deposition rate is achieved at the highest value of the sputtering power. This is due to more intense sputtering of the target at a higher power of the magnetron.

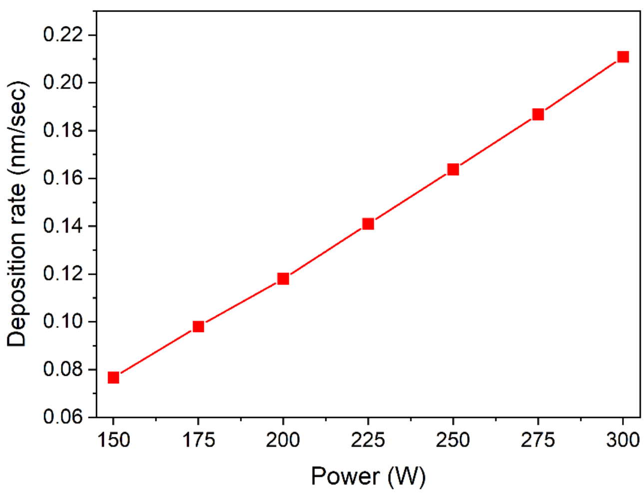

Figure 1 – Dependence of the deposition rate of AZO films on the RF power of magnetron sputtering

Figure 2 shows the dependence of electrical characteristics, namely, resistivity, charge carriers concentration and Hall mobility, on the value of RF power. Resistivity of all deposited films does not exceed 9×10^{-3} Ω·cm and decreases with increasing RF power. A sharp decrease in resistivity occurs with an increase in power from 150 to 175 W. This is due to the simultaneous increase in the mobility and concentration of charge carriers. An increase in RF power from 175 to 300 W leads to a smooth decrease in resistivity, except for a more noticeable drop at 250 W. The minimum resistivity of 2.83×10^{-3} Ω·cm is achieved at 300W RF power. Such low resistance is due to high values of mobility and concentration of charge carriers 9.6 $cm^2V^{-1}s^{-1}$ and 2.3×10^{20} cm^{-3}, respectively. From the data obtained, it follows that a further increase in power should lead to the deposition of AZO films with even higher conductivity. However, such an increase in magnetron power is not recommended for this type of targets. The decrease in the electrical resistivity of the films with increasing power can be associated with a more intense heating of the substrate during deposition. A dense flow of energetic atoms and ions heats up the substrate, and at a higher temperature, the film crystallinity improves and, as a result, the grain size grows, which leads to an increase in charge mobility. Thus, additional heating of the substrate can lead to a further increase in the conductivity of the films.

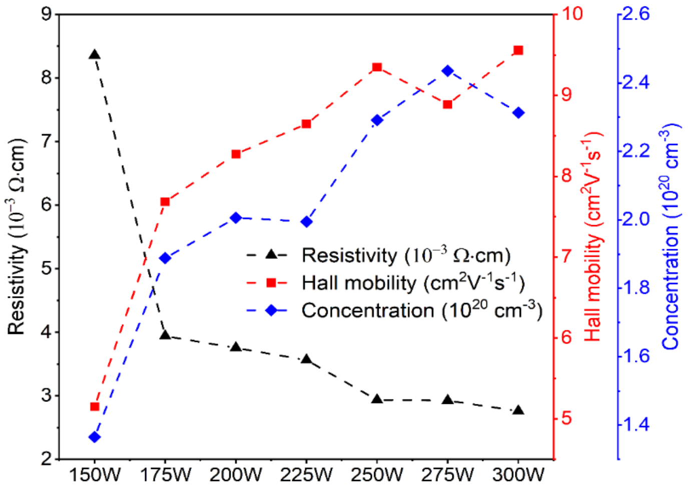

Figure 2 – Dependence of the resistivity, concentration and Hall mobility of charge carriers of thin AZO films on the RF power of magnetron sputtering

As is known, transparency is an important parameter for TCO films. Figure 3 shows the transparency spectra of films deposited on the surface of microscopic glass slides. For all films, transparency exceeds 75% in the visible and near infrared ranges, and for wavelengths above 600 nm, transparency exceeds 80%. The obtained spectra testify to the high transparency of the AZO films. Moreover, it can be concluded that the sputtering power has little effect on the optical properties of the films.

The electrical and optical properties of AZO thin films are closely associated with the film crystallinity. Therefore, X-ray diffraction spectra were measured (Figure 4). Peaks at angles 2θ ~ 34.4° and 62.9°, obtained by reflection from planes with Miller indices (002) and (103) of wurtzite hexagonal ZnO, are present in the spectra of all samples under consideration, and X-ray lines of other aluminum impurities are not observed. The average crystallite size was obtained using the Scherrer equation [23]:

$$D = \frac{K\lambda}{\beta cos\theta} \quad (1)$$

where:

D – the average crystallite size,
λ – the X-ray wavelength,
β – the line width at half maximum (FWHM),
θ – the Bragg angle.
K – dimensionless shape factor.

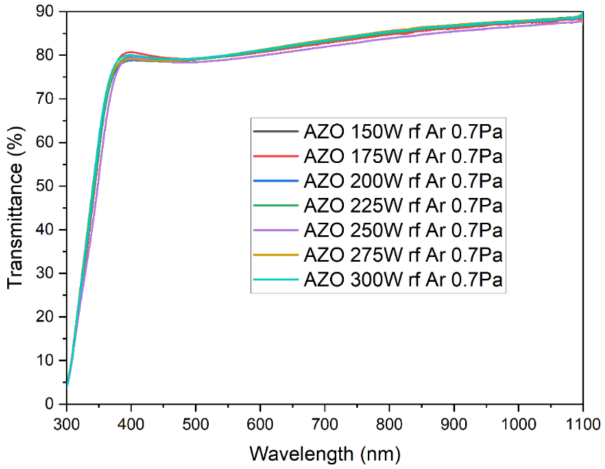

Figure 3 – Transmittance spectra of AZO films synthesized at RF power of magnetron sputtering 150 – 300 W

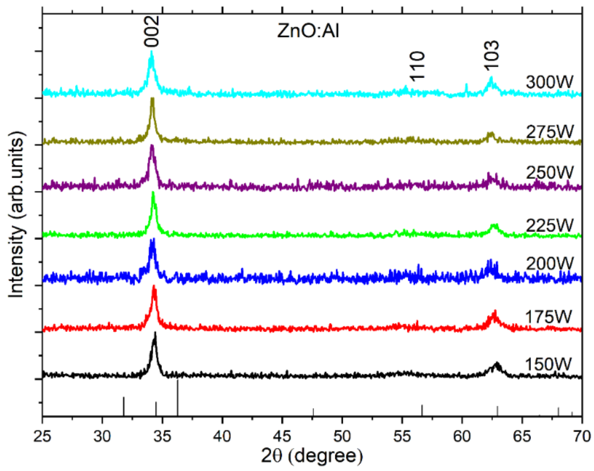

Figure 4 – X-ray patterns of AZO films synthesized at RF power of magnetron sputtering 150 – 300 W

It can be seen that the average crystallite size varies within 6.3 – 9.0 nm. These values are typical for AZO films synthesized by magnetron sputtering [18]. However, we failed to observe the dependence of the average crystallite size on the sputtering power. That is, it can be assumed that the size of crystallites is not the only source of an increase in the conductivity of AZO films.

4 Conclusion

AZO films were deposited on the surface of silicon and glass slides using radio frequency magnetron sputtering. The influence of the power of radio-frequency magnetron sputtering on the film structure, optical and electrical properties has been studied. It was found that with increasing sputtering power, the deposition rate increases linearly, the highest deposition rate was achieved at a power of 300 W (0.21 nm/s). A study of the electrical properties of the films revealed a sharp increase in conductivity with an increase power from 150 W to 175 W. A further increase in power also led to an improvement in electrical properties, but to a lesser extent. The lowest resistivity value of 2.83×10^{-3} Ω·cm and the highest charge mobility of 9.6 $cm^2V^{-1}s^{-1}$ were achieved at a sputtering power of 300 W, while the highest charge carrier concentration of 2.44×10^{20} cm^{-3} was achieved at 275 W. The study of transparency showed that all films have a transparency of 75% in the entire visible and near infrared ranges, and in the wavelength region above 600 nm, the transparency for all films exceeded 80%. X-ray diffraction studies have shown that all X-ray diffraction patterns have reflection peaks, standard for this type of films, at angles 2θ equal to 34.4° and 62.9°, which are characteristic of systems of planes with Miller indices (002) and (103).

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