TECHNICAL REPORT

Near-infrared reflective characteristics of aluminum-doped ZnO thin films fabricated by *off-axis* sputtering

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Aluminum-doped ZnO (AZO) thin films were deposited by sputtering on glass substrates. Normally, the radio frequency method is applied for sputtering of insulators. However, in this study, the AZO target was made conductive, and then, the thin AZO films were deposited on it by direct current sputtering. We found that there is a significant problem involving the creation of oxygen anions at the target surface, which are then driven into the AZO films, thus resulting in a loss of conductivity due to the formation of oxygen vacancies. At first, the AZO films were deposited on silicon wafers to search for the *off-axis* positions. After deposition, we observed a white circle on the wafers. We investigated the distribution of surface sheet resistances on the wafer, and found that these were high within the circle (diameter: 87 mm), whereas outside of it, the sheet resistances were quite low and the incidence of oxygen anions was negligible. A small aluminum fitting was made to hold the substrates in the *off-axis* position, and although the sputtering was carried out at room temperature, crystalline AZO films were obtained. Sputtering at 400 W for 5 min resulted in the best reflectance, with the AZO film reflected in the near-infrared region above 1250 nm. The maximum specular reflectance was 60% at 2500 nm and the film thickness was about 300 nm (although it was somewhat inhomogeneous, probably because of differences in the sputter-particle density). Hall measurements were performed to determine the quality of the resulting AZO films. The carrier concentration was excellent, whereas the resistivity and Hall mobility were average.

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1. Introduction

Indium tin oxide^{1)–5)} is widely used as a transparent conductive oxide (TCO). However, due to its toxicity and limited availability, alternate TCOs are required. Recently, niobium-doped titanium dioxide has appeared as an alternative,^{6)–9)} but at present, aluminum- and/or gallium-doped ZnO (ZnO:Al, ZnO:Ga) are the most recommended TCOs because of their abundance in nature, low cost, and low-toxicity.^{10)–17)} Both ZnO:Al (AZO) and ZnO:Ga (GZO) have high carrier concentrations, and therefore, are highly conductive. Especially, aluminum is abundant and cheap compared to gallium.

TCOs have high carrier concentrations (above 10^{20} cm⁻³), so they are also able to reflect near-infrared light by plasma oscillation. However, most of the studies available to date have focused on the transmittance of TCO films, so herein, we intend to evaluate the near-infrared reflection ability of TCOs. In previous reports on the transmission and reflection of TCOs, the transmittance and reflectance measurements were apparently performed

using the same thin film, but for the exact measurement of the specular reflectance, the backside reflection must be eliminated. Therefore, in this study, the backside of the substrates was made rough using abrasives. As mentioned previously, we will give priority to the specular reflectance of the AZO thin films (their transmission properties will not be treated in this study).

The AZO target is usually an insulator, and therefore, radio frequency magnetron sputtering is usually applied to fabricate thin AZO films. Recently, AZO targets have been invested with conductance by artificially introducing oxygen vacancies into the target crystal structure, and this improvement has enabled the sputtering of AZO thin films by direct current (DC) magnetron sputtering.

Here, a significant problem arises: If the targets are metals, there is no problem, but if they are compounds, such as oxides, oxygen anions are released from them. The released anions are then accelerated by the ion sheath, reaching energies as high as 200 eV. The oxygen anions can thus penetrate the fabricated thin films, producing defects in the form of oxygen vacancies.^{18),19)} This problem occurs when the substrates directly face the targets, so to avoid it, the substrates are installed perpendicular to the target–substrate line. This is the so-called *off-axis* position,

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which depends on the type of sputtering instrument and the researcher's idea.

The *off-axis* position of our sputtering instrument was searched and high-quality, thin AZO films were deposited at the *off-axis* position. The appropriate *off-axis* positions were determined using silicon wafers: A 4-in Si wafer was placed beneath the target and the AZO film was then fabricated on it. The conductivity of the AZO film was not homogenous throughout the wafer. Some parts were conductive, while others were not. The areas exhibiting high conductivity are the so-called *off-axis* spots.

2. Experimental methods

Quartz-glass substrates (USD-300, Daiko Seisakusho Ltd.) with dimensions of 20×20 mm and thickness of 1 mm were used in our studies. The surface of the USD-300 quartz glass was hydrophobic, so to make it hydrophilic, the material was immersed in a supersonic cleaner containing a 1 N sodium hydroxide solution for 30 min. To prevent backside reflection of the glass substrate, which can interfere with the measurements of infrared reflection, the backside of the substrates was made rough using 600 mesh SiC. Before sputtering, the glass substrates were treated in acetone for 10 min using a supersonic cleaner, rinsed with deionized water, and finally dried at 50°C .

An Anelva SPF-210H magnetron instrument equipped with only one target was used for sputtering. An AZO target with a diameter of 4 in and containing 2 wt % Al_2O_3 was purchased from Furuuchi Chemistry Inc. Oxygen voids were artificially introduced into this target to enable the use of a DC power source. The sputtering gas was Ar and the flow rate was 10 SCCM with a base pressure of 1×10^{-5} Pa and a working pressure of 0.7 Pa at room temperature. The specimen stand was the anode and its diameter was 90 mm; the S–T distance was 65 mm.

4-inches, p-type silicon wafers (Sunco Corporation Inc.) with (100) orientation and a resistivity of $1\text{--}10\ \Omega\text{cm}$ were used. The silicon wafers were placed on the specimen stand. The sputtering power was varied between 200 and 400 W at room temperature, fixing it at 400 W for the deposition of the thin AZO films. The pre-sputtering time was 10 min for AZO and the sputtering time was varied between 1 and 20 min.

The glass substrates were fixed on an aluminum board (Fig. 1) using double-sided adhesive polyimide tape. The aluminum board was then fixed onto the specimen stand with a screw.

The thickness of the thin films was determined using an ET200 profiler (Kosaka Laboratory Inc.), and the sheet resistance (Ωsquare^{-1}) was measured by the four-point probe method. The specular reflectance of the AZO films was determined using a spectrophotometer (U4100 Hitachi Inc.) in the wavelength range of 200–2500 nm. The crystalline phases were examined on a thin-film X-ray diffractometer (Rigaku Rad-2X) operated at 40 kV and 25 mA with $\text{Cu K}\alpha$ ($\lambda = 0.154056\text{ nm}$) radiation.

Soda-lime glass substrates with a size of 10×10 mm and thickness of 1.1 mm were used for the Hall measure-

Fig. 1(a). A photograph of the Si wafer after sputtering at 400 W for 20 min.

Fig. 1(b). A photograph of the Si wafer after sputtering at 200 W for 20 min.

ments. These substrates were treated in acetone for 10 min using a supersonic cleaner, rinsed with deionized water, and finally dried at 50°C . Carrier density, mobility, and resistivity were measured on a Hall measurement system (Toyo Technica Resitest 8340 HT).

3. Results and discussion

Figures 1(a) and 1(b) show photographs of the Si wafers after sputtering at 400 and 200 W, respectively. The sheet resistance, measured by the four-point probe method, is shown in Table 1. The position of the measured points is shown as pink solid circles in Figs. 1(a) and 1(b). In the case of the AZO films deposited at 400 W, concentric circles and a white circle are observed. The sheet resistance in the central area is about $20\ \Omega\text{square}^{-1}$, while that in the region where the density of the concentric circles is high is above $100\ \Omega\text{square}^{-1}$. Within the white circle, the resistance drops suddenly to $2.5\ \Omega\text{square}^{-1}$, and in the outer part of the white circle, the density of concentric circles becomes sparse and the sheet resistance decreases to below $1\ \Omega\text{square}^{-1}$.

Figure 1(a) shows that the AZO film is thicker at the center of the wafer and becomes much thinner toward the circumference. In this area, abundant oxygen anions enter

Table 1. Sheet resistances of the surface of silicon wafer

Point Number	1	2	3	4	5	6
400 W	$0.42 \Omega \text{ square}^{-1}$	$2.54 \Omega \text{ square}^{-1}$	$101.3 \Omega \text{ square}^{-1}$	$250.2 \Omega \text{ square}^{-1}$	$23.4 \Omega \text{ square}^{-1}$	$17.4 \Omega \text{ square}^{-1}$
200 W	$0.37 \text{ k}\Omega \text{ square}^{-1}$	$5.16 \text{ k}\Omega \text{ square}^{-1}$	$1.95 \text{ k}\Omega \text{ square}^{-1}$	$19.2 \Omega \text{ square}^{-1}$	$1.5 \Omega \text{ square}^{-1}$	

the AZO film, creating oxygen vacancies. This results in a higher sheet resistivity.

The sheet resistance drops steeply on the white circle and decreases to below $1 \Omega \text{ square}^{-1}$ outside of it (the outer diameter of the white circle was 87 mm). The AZO film should be thinner here than in the high-resistance area, while the resistance is quite low, which means that the oxygen anions does not enter the AZO film at the wafer edges.

Figure 1(b) shows a silicon wafer after sputtering at 200 W. Concentric circles are also observed in this case, although at a lower density compared to 400 W. In general, the AZO film is thinner in this case as compared to the film obtained at 400 W. At the center, the sheet resistance is $0.366 \text{ k}\Omega \text{ square}^{-1}$ (this value is higher than that observed at 400 W), and similarly, the sheet resistance is high in the area containing the concentric circles. In this part, the sheet resistances are 5.159 and $1.935 \text{ k}\Omega \text{ square}^{-1}$. These values are about one order of magnitude higher than those obtained at 400 W, because the AZO films fabricated at 200 W are thinner. The thickness of the AZO film is proportional to the sputtering power, and the outer diameter of the white circle is 87 mm at 200 W. The sheet resistance outside the white circle is $1.486 \Omega \text{ square}^{-1}$, and as described above, this value means that oxygen anions do not enter the AZO film.

The AZO target used here is 4-in (i.e., 101.6 mm) thick. The reason why the white circle is created is unclear, but apparently, the oxygen anions do not enter the AZO film formed outside of the white circle. The outside diameter of the white circle is within the diameters of the AZO target and the specimen stand. Simultaneously to the deposition of the AZO film, the oxygen anions move directly toward the target.

Thus, to deposit thin AZO films without defects, it is appropriate to place the substrate outside of the white circle where the sputter particles are “thermalized”. If the sputter pressure is assumed to be 1 Pa, the mean free path for Ar is calculated to be about 10 mm. In this case, the sputter particles collide with Ar, and since each sputter particle loses its kinetic energy after several collisions, by the time it reaches the anode, the kinetic energy has decreased to 1/10 of the initial value, so the energy of the sputter particles becomes almost the same as that of ambient gas. Also, the moving direction of the sputtered particles becomes random, a phenomenon that is called “thermalization”.

A rectangular aluminum plate was used to place the quartz-glass substrate outside of the white circle, as shown in Figs. 2(a) and 2(b). Since the oxygen anions should not migrate to the region outside of the specimen stand, the substrate is placed there. This arrangement of the substrate is the so-called *off-axis* position.

Fig. 2(a). Rectangular aluminum plate to place the quartz-glass substrate outside of the white circles observed in Figs. 1(a) and 1(b).

Fig. 2(b). A photograph of rectangular aluminum plate to place the quartz-glass substrate

When the substrates are placed at the *off-axis* position, they are always exposed to sputter particles, because the standard shutter equipment used herein is designed to shield the substrate only on the specimen stand. Consequently, it is impossible to perform pre-sputtering experiments at the *off-axis* position. Replacing the standard equipment by a shutter that can cover the substrate in the *off-axis* region too can be considered as a way to solve this problem. Nevertheless, thermalized sputter particles can detour the shutter and reach the substrates at the *off-axis* place.

An alternative shutter using an aluminum plate was made as shown in Figs. 3(a) and 3(b) (the square part is put on the substrate). Here, the aluminum plate has to be placed on the substrate without leaving any free space in order to prevent the thermalized sputter particles from depositing on the substrate. The projected part, which has a length of 35 mm and width of 5 mm, is located on the specimen stand. The incidence of sputter particles can be prevented by placing the square part directly on the

Fig. 3(a). A drawing of the alternative shutter.

Fig. 3(b). A photograph of the alternative shutter.

substrate. The 5-mm-wide plate is put on the specimen stand and then bent vertically; the height is 30 mm. At the beginning of the sputtering, the aluminum plate is removed by swinging the shutter equipped with the sputtering instrument and touching the perpendicular aluminum plate.

The AZO film used for the Hall measurements is sputtered at 400 W for 1 min by using metal fitting, as shown in Figs. 4(a) and 4(b). The two substrates are fixed, side-by-side, on the aluminum plate, as shown in Fig. 4. Substrate A is used for the thickness measurements. We first wind a Kapton tape (polyimide film; width: 5 mm) around the substrate, and after sputtering, this tape is removed and the thicknesses of the films are measured using a profiler. Substrate B is used for the Hall measurements. Both substrates are sputtered simultaneously.

Figure 5 shows the specular reflectance of an AZO film fabricated at 400 W for 20 min at the *off-axis* position. At wavelengths below 1500 nm, the specular reflectance is less than 10%. Three specimens were deposited under the same conditions and it was found that the spectra are reproducible. The swell of the reflectance is due to the interference. At wavelengths above 1500 nm, the near-infrared reflectance increases steeply, reaching its maxi-

Fig. 4(a). Glasses for the thickness measurement and the Hall measurement fixed on the rectangle aluminum plate shown in Figs. 2(a) and 2(b).

Fig. 4(b). A photograph of glasses for the thickness measurement and the Hall measurement fixed on the rectangle aluminum plate shown in Figs. 2(a) and 2(b).

Fig. 5. The specular reflectance of an AZO film deposited at 400 W for 20 min.

mum value (60%) at 2500 nm. If the deposition conditions, such as sputtering power and deposition time, are changed, the reflectance spectra are expected to change too. Thus, the deposition times (at 400 W) were varied among 1, 3, 5, and 20 min and measure the specular reflectance of the three resulting AZO films (see Fig. 6). The specular

Fig. 6. The specular reflectance of three AZO films deposited at 400 W for 20 min.

reflectance of quartz glass substrate was also indicated. The reflectance of the AZO film deposited for 20 min is the same as that shown in Fig. 5. The AZO film obtained after 5 min is reflected in the near-infrared region above 1250 nm, reaching the maximum value (60%) at 2500 nm. Minami et al.²⁰⁾ reported similar results, indicating that near-infrared radiation (above 1300 nm) was reflected. The thickness of their AZO films was 425 nm. In this study, the deposition rate is about 60–70 nm/min, so the thickness of our AZO films should be about 300–350 nm. Thus, the thickness of the AZO films is similar in both studies, but there might be other factors affecting their near-infrared reflection. Thick AZO films do not always reflect near-infrared radiation efficiently.

When the sputtering time was shortened less than 5 min, near-infrared reflectance was decreased. The reflectance of the AZO film did not reduce to 0, whereas, the maximum reflectance value was less than 40% at 2500 nm. The reflectance of the AZO film deposited for 1 min was less than 10% in the near-infrared area. The most suitable sputtering time was 5 min.

The Spectra of the AZO film which sputtering time was less than 3 min, did not decrease to 0. The spectra of 3 min and 1 min denoted minima at 1300 nm. The values of the minima were about 4%. In Fig. 6, the specular reflectance of the quartz glass substrate was also indicated. The reflectance was rather low and the value of the reflectance was a little less than 4% through the all wavelength. The AZO films by the sputtering less than 3 min were rather thin. The thickness was less than 200 nm. The value of the minima and the value of the reflectance of the quartz glass substrate was almost the same. There was a possibility that the incident light transmitted these films around 1300 nm. Accordingly, thinner films showed the minima of transmittance at 1300 nm.

Figure 7 shows the thin-film X-ray diffraction patterns of AZO films deposited at 400 W for 20, 5, 3, and 1 min at room temperature. Diffraction peaks corresponding to

Fig. 7. X-ray diffraction patterns of AZO films deposited at 400 W for 20, 5, 3 and 1 min.

Fig. 8. Variation of thickness of AZO film deposited at 400 W for 20 min.

ZnO (002), (102), and (103) are observed (all these peaks were not present before). The intensity of (002) peak was extremely high compared with (102) and (103) peak. The AZO thin film is not completely but highly preferred *c*-axis oriented.¹²⁾

The thickness of the AZO films is not homogeneous. Figure 8 shows the variations in thickness for an AZO film deposited at 400 W for 20 min. This film is thinner (1000 nm) at the outer edges of the substrate and becomes gradually thicker toward the inner part, finally reaching a thickness of about 1700 nm. This result can be interpreted as follows: While sputtering directly under the target is common, in this study, the substrate is placed within the margins of the chamber to avoid the incidence of oxygen anions on the AZO films.

The number of sputter particles beneath the target is also large. However, the energy of the sputter particles is lower than that of oxygen anions, so the sputter particles are released from the target with a low energy of about 10 eV.

Table 2. Summary of the Hall measurements

	Carrier Concentration cm^{-3}	Resistivity Ωcm	Mobility $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$
0.06 μm	5.11×10^{20}	5.0×10^{-3}	2.40
0.07 μm	4.24×10^{20}	5.94×10^{-3}	2.48
1.3 μm	5.80×10^{20}	5.13×10^{-4}	21.0

After colliding with many Ar-gas atoms, the sputter particles lose their energy and start to move randomly. As a result, they are transferred from the center of the target to the margin of the chamber, where the density of sputter particles is lower than that at the center of the chamber.

In such a situation, the deposition rate of the sputter particles depends on the distance from the target. The AZO-film deposition rate can be calculated from Fig. 6: In the inner part, the film thickness is about 1700 nm, and since the deposition time is 20 min, the deposition rate is 85 nm min^{-1} . On the other hand, at the outer edges, the film thickness is about 1000 nm, so the deposition rate is 50 nm min^{-1} .

This inhomogeneous film thickness is a disadvantage of our method. AZO films are often used to construct AZO/Ag/AZO tri-layers, and in such cases, the thickness of the AZO layer is about 30–50 nm. However, note that up to 10 nm, the thicknesses of our AZO films are less inhomogeneous.

Finally, the quality of the AZO films was examined by performing Hall measurements. The thickness of the studied AZO film is 61 nm at the outer edges and 69 nm in the inner part. Since the differences in film thickness are not small enough. The software for controlling and calculating the Hall parameters requires the thickness of the thin film two places decimal below μm (0.01 μm). Then, we measure Hall parameters with the thickness of 0.06–0.07 μm . The results are shown in **Table 2**. Regarding the carrier concentrations, the value for 0.06 μm is somewhat higher than that for 0.07 μm . The resistivity for 0.06 μm is lower than that for 0.07 μm , and the mobility for 0.07 μm is somewhat higher than that for 0.06 μm . In any case, the differences are small. On the whole, the qualities of the Hall parameters are average. Here, Hall measurements were carried out on an AZO film fabricated at 400 W for 20 min. As shown in Fig. 8, the thickness of the AZO film is inhomogeneous, so these Hall parameters are only reference values. We use 1.3 μm as the AZO-film thickness (this is the value at the center of the substrate, as shown in Fig. 8). The carrier concentration is $5.8 \times 10^{20}\text{ cm}^{-3}$, which is a standard value; the resistivity is $5.13 \times 10^{-4}\text{ }\Omega\text{cm}$, which seems to be quite low; and the mobility is $21.0\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$, which can be considered a high value. Thick AZO films tend to be of high quality, which is necessary for fabricating homogeneous AZO films.

4. Conclusions

When oxide films are fabricated by DC sputtering using an oxide target placed at the target-facing position, it is impossible to obtain thin films on the substrate by the

incidence of oxygen anions. In such a case, it is necessary to search for the off-axis position. A Si wafer was used and it was found that the off-axis position was in the margin of the sputtering chamber. The substrate was therefore shifted 48 mm from the center axis and supported by an aluminum plate.

The thin AZO films were deposited at the off-axis position. In the inner part, the sputter-particle density was high, and therefore, the film was thicker. On the other hand, at the outer edges, the sputter-particle density was low, and consequently, the film was thinner. At a sputtering time of 20 min, the difference in thickness between both parts was as large as about 700 nm.

The AZO film deposited for 5 min reflected near-infrared radiation above 1250 nm, whereas that deposited for 20 min reflected radiation above 1500 nm. The reflection of the near infrared did not necessarily the thin AZO film.

Hall measurements were conducted to evaluate the quality of the AZO films and found that the carrier concentrations were 4.2 to $5.1 \times 10^{20}\text{ cm}^{-3}$, the resistivities were 5 to $5.9\text{ }\Omega\text{cm}$, and the mobilities were 2.40 to $2.48\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$. On the whole, the qualities of the Hall parameters were average.

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