A new fabrication method for ZnO:Al thin films using modified DC magnetron sputtering

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ZnO:Al thin film was deposited on glass substrates at room temperature. We used a ceramic ZnO:Al target. Since the oxygen vacancies were artificially introduced into the target, thin film could be deposited by DC magnetron sputtering. When ceramic targets are used, fabrication of transparent conductive ZnO:Al thin film in the facing-target is impossible, due to direct resputtering by oxygen anions. The substrate was colored yellow, and the conductivity was also lost. In this state, the thin film was considered to be “ZnO$_{1-x}$:Al”. In order to avoid the damage, we used a shield consisting of an upper plate, side plates, back plate and base plate. The substrate encapsulated in the assembled shield was placed on the anode in the magnetron sputter we used, the target was installed in the upper side of the chamber and the anode was installed in the under side. We also described the method of deciding the size of the shield. “Thermalized” sputter particles entered the channel consisting of upper plate, side plates and base plate, and are deposited on the substrate. The oxygen anions were blocked by the shield plates. The values of the resultant thin films were enumerated. Carrier concentration was $1.25 \times 10^{21} \text{cm}^{-3}$, a rather high value. Resistivity was $1.13 \times 10^{-3} \Omega \text{cm}$ and Hall mobility was $4.43 \text{cm}^2/\text{Vs}$. Also in the area of high temperature superconductive oxides, thin films were damaged by resputtering by oxygen anions. A shield was also tried in this area. In such cases, simple metal plates were installed beneath the substrates in an off-axis position. Side shields were not installed beside the substrates. This confirmed the necessity of side shield plates. We removed the side shield plates and conducted sputtering. The carrier concentration was $6.92 \times 10^{19} \text{cm}^{-3}$; resistivity was $1.15 \times 10^{-2} \Omega \text{cm}$ and Hall mobility was $7.86 \text{cm}^2/\text{Vs}$. Based on these values, the effectiveness of the side plates was confirmed.

Key-words: TCO, ZnO:Al, Oxygen anion, Resputtering, Shield

1. Introduction

Sn doped Indium Oxide (ITO) has long been the main transparent conductive oxide (TCO). Recently, Indium resources have been depleted and the cost of Indium has been rising. In addition to the rise in cost, Indium is a toxic element.\(^1\)

For the above reasons, the alternative TCOs are required. Aluminum doped ZnO (ZnO:Al), Gallium doped ZnO (ZnO:Ga) and Niobium doped TiO$_2$ (TiO$_2$:Nb) are among the next-generation TCOs.

TCOs show carrier concentrations as high as $10^{21} \text{cm}^{-3}$. These high carrier concentrations enable the TCOs to cause plasma vibrations. The frequency of the plasma vibrations of TCOs is favorably in the infrared region. Therefore, TCOs are also attracting much attention recently as the infrared shield films.

Among the materials enumerated above, ZnO:Al is considered to be the most feasible material, because of the abundance of Al and Zn resources and these elements lack of toxicity.

There are several techniques for manufacturing ZnO:Al thin films. Examples include the Sol–Gel method,\(^7\)–\(^9\) chemical vapor deposition,\(^10,11\) pulse laser deposition,\(^12,13\) electroless deposition,\(^9\) and direct current reactive (DCR) magnetron sputtering.\(^1\)

For DC and/or RF magnetron sputtering is the most common technique for forming metals and compound thin films. The sputtering of metal thin films is quite simple. The sputtering gas is Ar and the metal targets are used. Direct voltage (about 200–400 V) is applied between the target (cathode) and the anode.

In the case of compound thin films, the sputtering procedure is much more complicated compared with metal sputtering. As the compounds, oxide and/or nitride films are the main objects.

In the 1980’s–1990’s, high temperature oxide superconductive oxides such as Bi–Sr–Ca–Cu–O oxide and Bi$_2$Sr$_2$Ca$_1$Y$_1$Cu$_2$O$_y$ compounds were studied extensively.\(^\)\(^12,13\)

At present, many TCOs thin films are manufactured using reactive DC magnetron sputtering.\(^1,14\) In the area of oxide thin films, DC reactive magnetron sputtering is now the most common method because of its high deposition rate.\(^15\) However, when the multi-component oxide films are produced, it is difficult to control the stoichiometry precisely.

DC magnetron sputtering is the main technique in the area of metal sputtering. In addition, recent ceramic targets are given conductivity by artificially introducing oxygen defects into the ceramic target. As a result, ceramic targets can be used with DC magnetron sputtering equipment.

For the above reasons, we determined to fabricate ZnO:Al films by DC magnetron sputtering using conductive ZnO:Al targets.

2. Experimental procedure

2.1 Substrate

The glass substrate was the high purity quartz glass with dimensions of 20 mm × 20 mm and a thickness of 1 mm. (USD-300, Daiko Seiskusho Ltd.). Before sputtering, the quartz substrates were treated with supersonic cleaner in an 1N NaOH solution for 30 min, rinsed with the deionized water and dried at 120°C. Soda-lime-glass was used for the Hall measurements. The size was 10 mm × 10 mm and the thickness 1 mm. The soda-lime-glass was cleaned by supersonic cleaner in water with
neutral detergent for 30 min and then washed by rinsing with deionized water and dried at 120°C.

2.2 Basic sputtering conditions
Anelva SPF-210H magnetron sputter was used for sputtering. A 4-inch diameter ZnO:Al target was purchased from Furuuchi Chemistry. This target contained 2 wt% of Al2O3 and oxygen voids were artificially introduced to enable use of DC power sources. The ZnO:Al films were prepared by the DC sputtering. First, the sputtering chamber was evacuated to 1 × 10−3 Pa. Then ZnO:Al thin films were deposited under a sputtering power of 200 W. The sputtering gas was Ar and the flow rate was 10 sccm, sputtering pressure was 0.8 Pa. Pre-sputtering was 10 min. Targets are usually installed in the lower side and conducted for the glass substrates in the upper side of the targets. The sputter sources. The ZnO:Al voids were artificially introduced to enable use of DC power sources.

2.3 Sputtering using an authentic DC sputtering procedure
A substrate was put on the specimen stand (anode) and power of 200 W was applied for 25 min.

2.4 DC sputtering with an aluminum plate shield
The sizes of the aluminum plates (thickness 0.5 mm) are shown in Fig. 3(a). The length of the upper plate was 30 mm. The substrates were fixed on the back plate with double-sided adhesive carbon tape.

2.5 Thin film X-ray diffraction measurement
Thin film X-ray diffraction patterns of ZnO:Al thin films were measured with a RAD-2X thin film diffract meter (Rigaku Denki Ltd.) operated at 40 kV and 25 mA with Cu Kα radiation.

2.6 Measurement of the thickness of ZnO:Al thin films
The thickness of the thin films was measured with a Surface Profiler ET200, Kosaka Laboratory Ltd.

2.7 Hall measurement
Carrier density, Hall mobility and electrical resistivity were measured on a Hall measurement system (Toyo Technica Resi Test 8340 HT). The glass substrate for the Hall measurement was soda lime glass. The dimensions of the glass substrate for Hall measurement were 10 mm × 10 mm and the thickness 1 mm. Two substrates were placed side by side on the back plate of the shield. One substrate is used for the thickness measurement.

We first wound Kapton tape (polyimide film, width 5 mm) around the substrate. After sputtering, the Kapton polyimide tape was removed, and the thicknesses of the thin films were then measured with the profiler. Another substrate was used for Hall measurement. The two substrates were sputtered in the same manner as described in 2.1.2.

3. Results and discussion
3.1 Facing-target DC sputtering of ZnO:Al thin films
The sputtering procedure for metals is quit simple. Sputtering of compounds such as oxides is much more complicated. When metal targets are used, reactive sputtering is required. For example, in oxide sputtering, the transition point must be found by changing the flow rate of oxygen. In this case, the two components Zn and Al were sputtered, and the sputtering procedure was all the more complicated;1 however, it had the advantage that the deposition rate was high.15)

It is considered appropriate to use the ceramic targets. Radio Frequency (RF) sputtering is required for ceramic targets with no electrical conductivity. Recently efforts to provide ceramic targets with conductivity have been made. The sputtering conducted in this study was DC sputtering.

First, we deposited ZnO:Al thin film through the facing-target sputtering. The ceramic targets contain oxygen ions. The oxygen anions are created at the surface of the ceramic targets, and exert a negative influence on the formation of the oxide thin films. A photograph of a thin film is shown in Fig. 1. The results of X-ray diffraction are shown in Fig. 2.

The color of the thin film was yellow and it also lacked conductivity. The yellow coloration of ZnO:Al thin films was the result of oxygen vacancies created by the resputtering of the oxygen anions. The oxygen vacancies resulted in color centers and the thin film was colored yellow. The oxygen vacancies also trapped carrier electrons, causing the loss of conductivity.

Fig. 1. Photograph of ZnO:Al thin film fabricated using a facing-target arrangement.

Fig. 2. Thin film X-ray diffraction patterns of as deposited and after annealing of ZnO:Al thin film fabricated using a facing-target arrangement.
The chemical composition of thin film deposited by target-facing sputtering is zinc oxide with a small amount of aluminum. X-ray diffraction peaks are also observed. This means there is a regular arrangement of constituent atoms. However, stoichiometric ZnO and/or ZnO:Al are not colorized.

The XRD results show two sharp diffraction peaks and one weak peak. The most striking peak appeared at 33.8° and the second highest peak was situated at 62.2°. A weak peak was found at 47.1°. Each peak was at an angle of 0.7° lower than the 2θ ZnO angles of (002), (102) and (103), respectively.

As shown above, it was impossible to form ZnO:Al thin films fabricated by facing-target sputtering. In order to make transparent conductive ZnO:Al thin film, resputtering of the oxygen anions must be avoided.

As a general observation, the cause of yellow coloration of ZnO:Al thin films is oxygen vacancies created by resputtering. This state should be expressed as “ZnO$_{1-x}$:Al”. If this hypothesis is correct, high-temperature annealing will restore the oxygen in the lattice oxygen vacancies.

We annealed the colorized thin film at 400°C for 6 h in air. A photo of the resulting film is shown in Fig. 1. After the annealing, the three X-ray diffraction peaks, (002), (102) and (103), appeared at the angles as described on the ZnO 36-1451 card from Powder diffraction file shown in Fig. 2. It was considered that the oxygen vacancies in the thin film were reduced by annealing. The mechanism of the peak shift to a lower angle due to resputtering of the oxygen anions is obscure at present.

### 3.2 ZnO:Al thin film produced by the DC sputtering with a shield

In the previous section, resputtering of oxygen anions into the ZnO:Al thin films resulted in two significant problems. One was yellowish colorization and the other was a lack of conductivity. In order to prevent resputtering of oxygen anions into thin film on the substrates, we tried a modified sputtering method in which the substrates were enclosed in a shield.

Hereafter, we use the word “shield” to mean the assembled “plates”. “Plate” means an individual aluminum plate (thickness 0.5 mm). A schematic figure of a shield and a photograph of a shield are shown in Figs. 3(a) and 3(b), respectively.

In our sputtering instrument, the substrate-target distance (S-T distance) is 65 mm. Two shutters were installed in the chamber of our sputtering instrument. Accordingly, the size of the glass substrate was limited to 20 × 20 mm and the thickness of 1 mm. If the S-T space were much larger, sputtering on larger substrates would be possible. The size and shape of the shield depend on the S-T distance, the size of the substrate and the target size.

For example, when the S-T distance is 100 mm, the substrate size is 30 × 30 mm with a thickness of 1 mm and the diameter of the target is 4 inches, the size of the shield is estimated to be roughly as shown in Fig. 4.

First, a substrate (30 × 30 mm, thickness 1 mm) is placed on the center axis of the anode. The substrate faces to the right, and this time, the substrate is completely exposed to oxygen anions. Here, we assume that oxygen anions fly from the right edge, glancing off the right edge of the upper plate, and then reach the substrate. Although oxygen anions are created in limited numbers at the edge of the target, we assume that oxygen anions are created there in order to estimate the size of the shield for the sake of convenience.

While the substrate is shifted to the left side and the upper plate is also extended to the left side, the incidence point on the substrate gradually drops. During the course of the movement, oxygen anions are unable to reach the substrate above the upper side of the incidence point.

When the substrate reaches the point of 20 mm from the center axis, it is impossible for oxygen anions to reach the substrate completely, since the upper plate interrupts the oxygen anion incidence. The length of the upper plate is estimated at be roughly 22 mm, as shown in Fig. 4 the above-mentioned 20 mm and the thickness of the substrate (1 mm) and the back plate (0.5 mm), as shown in Fig. 4.

The side plates are essential in order to block the oxygen anions. The size of the side plates is about 30 × 20 mm. The width of the upper plate depends on the size of the substrate. The width of the upper plate right above the substrate is 30 mm. The length of either side of the hanging part of the upper plate is 20 mm. The upper plate must be a single plate in order to prevent oxygen anions from passing through the slits between the upper plate and the side plates. The size of upper plate is 22 × 70 mm, but 25 × 70 mm might be better to give the space some leeway.
The base plate supports the upper plate and the side plates. The dimension of the base plate must be large enough to prevent the shield from turning.

When the sputter pressure is assumed to be 1 Pa, the mean free path of Ar is calculated as about 10 mm. In this case, the sputter particles collide with Ar. A sputter particle loses its kinetic energy after several collisions. By the time, a sputter particle reaches the anode, the kinetic energy decreases to $\frac{1}{10}$ the initial energy and the energy of the sputter particle becomes almost the same as the energy of the ambient gas. Also, the moving direction of the sputtered particles becomes random. This phenomenon is called “Thermalization”.

On the other hand, oxygen anions are created on the target surface and fly linearly with high energy due to acceleration at the ion sheath.

We devised a sputtering method utilizing the difference between the moving behaviors of the thermalized sputter particles and the oxygen anions.

A sputter particle leaves the target with about 10 eV of energy. On the other hand, oxygen anions fly at high rate of about 200 eV of energy, as described above.

If a metal plate is installed above the anode between the target and the anode, the oxygen anions collide and stop. Around the anode, sputter particles are “thermalized” and move in every direction. If an obstacle such as a metal plate is present, “thermalized” sputter particles are able to go around to the opposite side of the obstacle.

Based on the idea presented above, we tried sputtering using a metal shield. A schematic of the shield is shown in Fig. 3(a), and a photograph of the shield is shown in Fig. 3(b). This shield is placed on the anode.

The upper plate blocks direct flow of oxygen anions from the target. The two side shield plates prevent scattered oxygen anions from getting inside the shield. The substrate is fixed to the back plate. “Thermalized” sputter particles enter the channel among the upper plate, two side plates and base plate and are deposited on the substrate. A schematic figure is shown in Fig. 5.

**Figure 6** shows the XRD pattern of the thin film deposited in the shield. In this diffraction pattern, (002), (102) and (103) peaks of ZnO are observed. These three peaks appear precisely in the ZnO position.

In many studies, ZnO:Al thin films fabricated by sputtering show two diffraction peaks, (002) and (004).\cite{1,18} The preferred orientation for (002) is minimum surface free energy, according to Fujimura et al.\cite{16}

In another report, the (103) peak of ZnO was observed.\cite{17} At present, the reason for the appearance of the (103) peak instead of the (004) peak is obscure. In this study, the ZnO:Al thin film was deposited at room temperature. Therefore, the atoms which
constitute the thin film might not move to the minimum energy position. A study by Miao et al.\(^\text{17}\) did not describe the deposition temperature, they might have sputtered at room temperature. Okuhara et al.\(^\text{1}\) showed sputtering at 200°C and X-ray diffraction indicated (002) and (004) peaks. Yamaguchi et al.\(^\text{18}\) also heated the substrate at 400°C and observed clear (002) and (004) peaks.

**Figure 7** shows a photograph of thin film deposited in the shield. This thin film did not show a yellowish color. This shows that these specimens were freed from resputtering of the oxygen anions. The color was gray which suggests that the thin film was rather thin. The thickness obtained by a profiler was 87.5 nm.

In Table 1, the results of Hall measurement are summarized. The data was collected under sputtering with both side plates. These values depend on various factors, such as the sputtering temperature, electric power and crystallinity. The thin films in this study were fabricated at room temperature. The carrier concentration was rather high. The resistivity was less than one order of magnitude larger than with side plates. The decrease in the carrier concentration and resistivity is due to resputtering of the oxygen anion. The sputter particles also enter inside the shield and, as a result, the thickness is increased more than two times that with side plates. The results for Hall mobility are almost the same. The data for Hall measurements show the side shield plates to be effective enough in this study.

From the late 1980s to 1990s, oxide high-temperature superconductive materials such as Y-Ba-Cu-O system and Bi-Sr-Ca-Cu-O system were discovered. Superconductive oxide thin films formed by sputtering had been studied extensively. Sputtering of the Bi-Sr-Ca-Cu-O system had been conducted using oxide targets.\(^\text{12,13,20,21}\) Resputtering by oxygen anions was also inevitable in the case of the superconductive oxides.

In order to avoid resputtering of oxygen anions, *off-axis* arrangement of substrates was widely adopted. In the facing space between the target and the anode, plasma stays and ionized particles such as α-electrons and Ar\(^+$\) fly around.

In an *off-axis* arrangement, the substrate is moved to the outside the facing space and fixed to the wall of the sputter chamber, and the face of the substrate is parallel to the target and anode line. In an *off-axis* arrangement, since substrates are fixed to the chamber wall, there is no means of avoiding oxygen anions from the backside, and damage to the thin film by charged particles in plasma decreases.

In YBa\(_2\)Cu\(_3\)O\(_{7-x}\) system, an *off-axis* arrangement was successfully fabricated in the superconductive phase.\(^\text{22}\)

![Fig. 7. Photograph of a ZnO:Al thin film fabricated in a shield with side plates.](image)

**Table 1. Summary of the Hall measurements**

<table>
<thead>
<tr>
<th></th>
<th>With side plate</th>
<th>No side plate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carrier concentration cm(^{-3})</td>
<td>1.25 \times 10(^{21})</td>
<td>6.92 \times 10(^{21})</td>
</tr>
<tr>
<td>Resistivity Ωcm</td>
<td>1.13 \times 10(^{-3})</td>
<td>1.15 \times 10(^{-2})</td>
</tr>
<tr>
<td>Hall mobility cm(^3)/V s</td>
<td>4.43</td>
<td>7.86</td>
</tr>
<tr>
<td>Thickness nm</td>
<td>87.5</td>
<td>198.6</td>
</tr>
</tbody>
</table>

However, this *off-axis* arrangement was not effective enough in the Bi-Sr-Ca-Cu-O system.\(^\text{13}\) Shim et al. tried to use a shield.\(^\text{13}\) They used the simple semicircular shields with radii of 20 and 30 mm. They successfully fabricated 2223 high-temperature superconductive phase with the 20 mm shield, although the appearance of the 2223 phase depended on the deposit temperature. Park et al.\(^\text{12}\) used a simple square shield (20 mm × 20 mm) in the sputtering of a Bi-Sr-Ca-Cu-O system. They obtained the 2212 superconductive phase.

### 3.3 ZnO:Al thin film formation using DC sputtering without the side plates

Park et al.\(^\text{12}\) and Shim et al.\(^\text{13}\) used a single metal shield and obtained satisfactory results. They did not consider the effect of the oxygen anions from the side of shield.

In our case, the substrate encapsulated in the shield was placed on the anode. The shield was surrounded by plasma and a large number of oxygen anions flew about.

If the side plates were removed, the oxygen anions would enter into the inside of the shield. In order to confirm the effectiveness of the side plates, the side plates were removed and ZnO:Al thin film was deposited under the same sputtering conditions as with the side plates. **Figure 8** shows the shield with no side plates. Hall measurement was conducted. The results are summarized in Table 1.

The carrier concentration is two orders of magnitude less than that with side shield plates. The resistivity is also one order of magnitude larger than with side plates. The decrease in the carrier concentration and resistivity is due to resputtering of the oxygen anion. The sputter particles also enter inside the shield and, as a result, the thickness is increased more than two times that with side shield plates. The results for Hall mobility are almost the same. The data for Hall measurements show the side shield plates to be effective in this study.

The values of these Hall measurements are somewhat lower than the top data.\(^\text{18}\) The channel to the substrate is only on the front side. Sputter particles enter the channel and reach the substrate where they are deposited. The oxygen anions fly at a high rate, although the probability of scattering of oxygen anions is not negligible. If the oxygen anions were scattered in front of the open channel, some of the scattered oxygen anions could enter the channel and resputter the thin film. In order to improve the performance of our ZnO:Al thin film, it is important to eliminate the influence of the resputtering of the oxygen anions completely.

### 4. Conclusion

In this study, we have considered a new method of fabricating ZnO:Al thin films. In the case of the facing-target sputtering, the thin film was colored yellow and lacked electrical conductivity.
due to the resputtering of the oxygen anions. In order to avoid resputtering of the oxygen anions, the substrate was encapsulated in a shield constructed with an upper plate, two side plates and a base plate. This shield was placed on the anode and the sputtering was conducted. This shield was effective, and transparent, colorless ZnO:Al thin films were fabricated. The upper shield plate and two side shields blocked the oxygen anions. Thermalized sputter particles entered into a channel surrounded by the upper plate, two side plates and base plate and were deposited on the substrate fixed on the back plate. The carrier concentration was $1.25 \times 10^{21} \text{cm}^{-3}$, and resistivity was $1.13 \times 10^{-3} \text{cm}$ and Hall mobility was $4.43 \text{cm}^2/\text{Vs}$.

In order to confirm the effectiveness of side plates, we removed the two side plates and conducted sputtering was carried out. The carrier concentration was $6.92 \times 10^{19} \text{cm}^{-3}$, resistivity was $1.15 \times 10^{-2} \text{cm}$ and Hall mobility was $7.86 \text{cm}^2/\text{Vs}$. The performance of the thin film fabricated with no side shield plates was lower. Thus, the effectiveness of the side shield plates was confirmed.

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References