

New Transparent Conducting Al-doped ZnO Film Preparation Techniques for Improving Resistivity Distribution in Magnetron Sputtering Deposition

Tadatsugu MINAMI, Toshihiro MIYATA, Yuusuke OHTANI and Yuu MOCHIZUKI

Optoelectronic Device System R&D Center, Kanazawa Institute of Technology, 7-1 Ohgigaoka, Nonoichi, Ishikawa 921-8501, Japan

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For the purpose of substituting transparent conducting Al-doped ZnO (AZO) thin films for indium–tin-oxide (ITO) transparent electrodes, investigations have been conducted to improve resistivity distribution using magnetron sputtering techniques. New techniques, such as adding an rf (13.56 MHz) component to dc magnetron sputtering depositions with or without the introduction of hydrogen gas into the deposition chamber, resulted in a considerable improvement of resistivity distribution. A resistivity as low as $5 \times 10^{-4} \Omega \text{ cm}$ and a more uniform resistivity distribution on the substrate surface were obtained in AZO films prepared with a thickness of 200 nm on glass substrates at a temperature of 200 °C. [DOI: 10.1143/JJAP.45.L409]

KEYWORDS: zinc oxide, ZnO, AZO, Al-doped ZnO, magnetron sputtering, transparent conducting oxide, thin film, transparent electrode

Recently, Al- or Ga-doped ZnO (AZO or GZO) thin films have attracted much attention as promising materials to substitute for indium–tin-oxide (ITO) thin films used as transparent electrodes in most flat panel displays because of the cost and scarcity of indium, the principal component of ITO.^{1,2)} In most ITO transparent electrode applications such as liquid crystal displays, thin films with a thickness of 100–200 nm are prepared at a temperature below 200 °C by magnetron sputtering (MSP).^{3,4)} However, it is well known that a spatial distribution of resistivity corresponding to the target erosion area pattern is formed on the substrate surface when transparent conducting oxide (TCO) thin films such as ITO and AZO are deposited on a low-temperature substrate by MSP using an oxide target.^{5–10)} Consequently, the resistivity distribution causes an increase in the resulting resistivity of TCO thin films deposited on large-area substrates with moving the substrates, as used practically. It has been reported by Ishibashi *et al.* that a considerable improvement of the resistivity distribution of ITO thin films deposited by direct current MSP (dcMSP) could be obtained by decreasing sputtering voltage.¹¹⁾ In contrast, in AZO thin films deposited by dcMSP, it was difficult to obtain sufficient improvement even when using a low sputter voltage combined with a stronger magnetic field cathode.¹²⁾ It is well known that the resistivity distribution of deposited AZO and GZO thin films is larger than that of ITO thin films. Therefore, improving resistivity distribution is necessary to obtain lower-resistivity AZO and GZO thin films suitable for use as alternatives to ITO transparent electrodes.

In this paper, we describe new AZO film preparation techniques for lowering resistivity as well as improving resistivity distribution. A resistivity as low as $5 \times 10^{-4} \Omega \text{ cm}$ and a uniform resistivity distribution in AZO thin films with a thickness of approximately 200 nm could be obtained on substrates at a temperature of 200 °C by introducing hydrogen gas into the deposition chamber during depositions with dcMSP incorporating rf power.

AZO films were deposited using a planar magnetron sputtering apparatus with an oxide target and dc or rf (13.56 MHz) supply power applied separately or in combination. The target (ZAO, TOSOH Corp.) was a commercially available high-density-sintered disk (diameter, 150 mm) made from a mixture of powdered ZnO and Al₂O₃; the

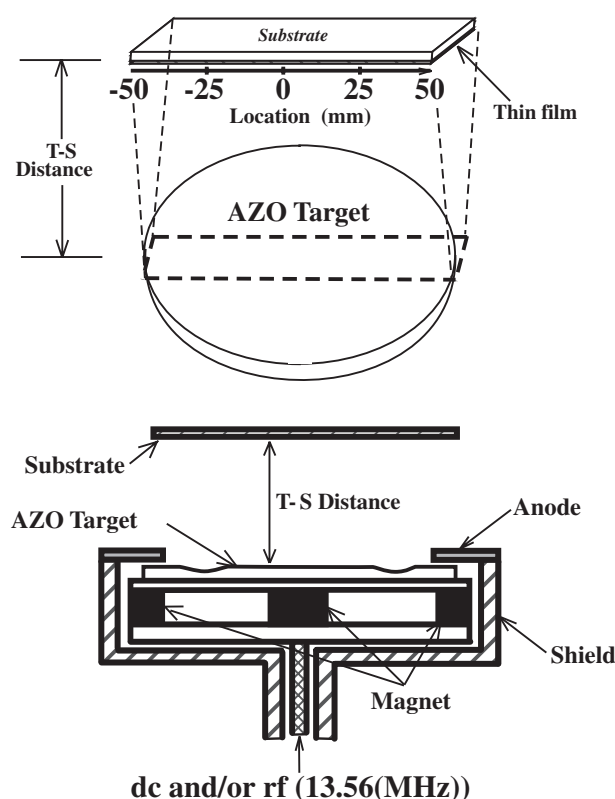


Fig. 1. Schematic diagram of magnetron sputtering target and substrate configuration.

Al₂O₃ dopant content was 2.0 wt. %. A substrate of OA-10 glass (Nippon Electric Glass Co., Ltd.) with an area of $25 \times 100 \text{ mm}^2$ was placed parallel to the target surface at a substrate–target distance of 50 mm, as shown in Fig. 1.¹³⁾ The glass substrate was mounted on a SiC plate holder (diameter, 120 mm); the substrate temperature was controlled with a SiC heater during sputtering deposition. Sputtering deposition was carried out in a pure Ar or Ar + H₂ gas atmosphere at a pressure of 0.4 Pa. The partial pressure of H₂ gas was varied in the range from 0 to 1.2%. dcMSP and radio frequency MSP (rfMSP) depositions, carried out at a dc power of 80 W and an rf power of 200 W, respectively, both produced the same deposition rate of approximately 35 nm/min. dcMSP deposition that incorpo-

rated rf power (dc + rfMSP) was carried out by adding an rf component in the power range of 0–150 W to a constant dc power of 80 W. The electrical, optical and crystallographical property distributions were evaluated using AZO thin films deposited, as described above, on glass substrates that were subsequently cut into $5 \times 5 \text{ mm}^2$ pieces. Film thickness was measured using a conventional stylus surface roughness detector, and electrical properties were measured at room temperature by the van der Pauw method. The thickness of all AZO thin films prepared in the following depositions was approximately 200 nm.

It was found that when deposited on glass substrates at a temperature below 200°C by MSP, all prepared AZO films exhibited a resistivity on the order of 10^{-3} – $10^{-4} \Omega \text{ cm}$ and a spatial distribution of electrical properties. The resulting distributions were considerably affected by the deposition condition and the magnetron sputtering apparatus as well as the target used. Typical electrical property spatial distributions are shown in Fig. 2 as functions of location on the substrate for an AZO film prepared on a glass substrate by dcMSP at a deposition rate of approximately 35 nm/min: resistivity (ρ), carrier concentration (n), and Hall mobility (μ). The film was deposited in a pure Ar atmosphere at a pressure of 0.4 Pa and a substrate temperature of 200°C . Distances of 0 and about $\pm 37.5 \text{ mm}$ in Fig. 2 indicate substrate locations that correspond to the center and the erosion area of the disk target, respectively, as shown in Fig. 1. It was found that the resistivity at a location of about $\pm 37.5 \text{ mm}$ was always higher than that at a location of about 0 mm. The increased resistivity of the AZO film deposited at the substrate location that corresponds to the target erosion area is related to decreases in both carrier concentration and the Hall mobility. These decreases, attributed to the degradation of crystallinity of the AZO film, may be mainly explained by grain boundary scattering in during carrier transport resulting from the trapping of free electrons caused by oxygen adsorption on the grain boundary surface.^{12–14} Therefore, improving the crystallinity of the AZO film as

well as sputtering depositions in a weakly reducing atmosphere may be effective for suppressing oxygen adsorption on the grain boundary.^{1,2)}

It has been reported that crystallinity is successfully improved in AZO and ITO films deposited by the rf-superimposed dcMSP technique with changes in the rf portion of the constant sputtering power.^{15,16)} For the purpose of improving the spatial distribution of AZO films, we attempted dcMSP deposition that incorporated rf power (dc + rfMSP). When dc + rfMSP deposition was performed under a constant dc power of 80 W, the necessary sputter voltage (applied dc voltage) drastically decreased as the rf power supplied was increased up to about 60 W, reached the minimum at an rf power of about 100 W, and then was relatively constant with any further increase in rf power. For example, the sputter voltage in dcMSP deposition with a dc power of 80 W was approximately 365 V, whereas the sputter voltage in a dc + rfMSP deposition incorporating an rf power of 100 W decreased to approximately 170 V. A typical rf power dependence of spatial resistivity distribution is shown in Fig. 3 for AZO films prepared on glass substrates by dc + rfMSP deposition at various levels of rf power. The resistivity of AZO films deposited at the substrate location that corresponds to the target erosion area decreased markedly as rf power was increased up to about 60 W; further increases in rf power only produced significantly smaller decreases. This result demonstrates that a considerable improvement of resistivity distribution could be obtained by adding rf power. In addition, the deposition rate of AZO films prepared by dc + rfMSP deposition increased proportionally as rf power was increased. For example, deposition rate increased to approximately 57 nm/min in dc + rfMSP deposition incorporating an rf power of 100 W from approximately 35 nm/min in dcMSP deposition incorporating a dc power of 80 W, as described above. This deposition rate increase suggests that the plasma density generated by a hybrid plasma discharge during dc + rfMSP deposition is considerably higher than that generated during dcMSP deposition incorporating a dc power of 80 W.^{15,16)} Therefore, the increased deposition rate, lower sputter

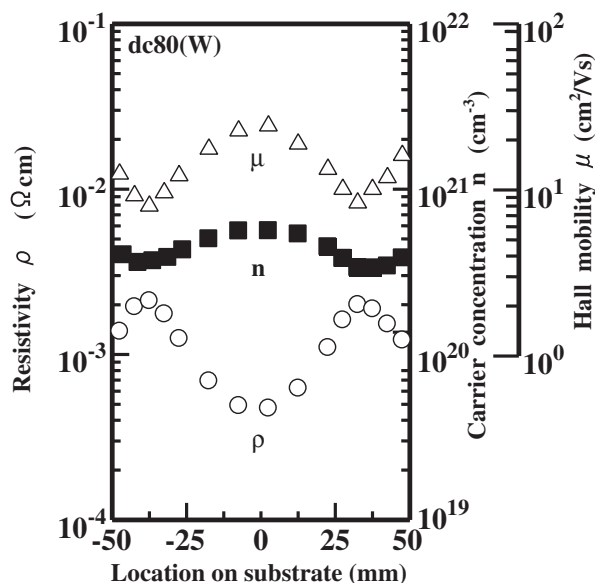


Fig. 2. Electrical properties as functions of substrate location for an AZO film prepared by dcMSP.

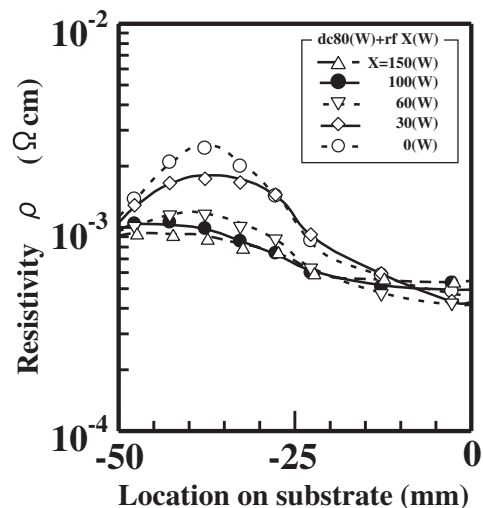


Fig. 3. Resistivity spatial distributions for AZO films prepared by dc + rfMSP deposition at various levels of rf power.

voltage and improved resistivity distribution in dc + rfMSP deposition may be attributed to the increase in plasma density generated by incorporating rf power.

It has been reported, as mentioned above, that decreasing sputter voltage markedly improves the carrier concentration distribution in ITO films prepared by dc + rfMSP deposition, and, as a result, resistivity distribution is improved and the obtained minimum resistivity is decreased.¹¹⁾ Although the resistivity distribution in AZO films prepared by dc + rfMSP deposition improved as rf power was increased, the obtained minimum resistivity was relatively independent of rf power. It was found that the spatial distribution of carrier concentration in AZO films prepared by dc + rfMSP deposition improved markedly as rf power was increased up to approximately 60 W; however, the spatial distribution of Hall mobility only improved a small amount. As shown by the X-ray diffraction (XRD) analysis of the AZO films prepared by dc + rfMSP deposition, the crystallinity at the substrate location that corresponded to the target erosion area was relatively independent of rf power up to approximately 100 W, even with the decrease in sputter voltage that accompanied the increase in rf power described above. From the above, it is difficult to understand the previously reported explanation of how the resistivity increase in AZO films deposited on the substrate location corresponding to the erosion area of the target can be attributed to the degraded crystallinity of deposited films that results from the bombardment of high-energy oxygen, accelerated in the electric field of sputter voltage, over the erosion area.^{7,10)} Therefore, the resistivity increase may be attributed to both the activity and amount of oxygen reaching the substrate surface as well as their spatial distributions; as a result, both oxygen adsorption on grain boundary surfaces and the incorporation of oxygen into the deposited AZO films may be enhanced at the substrate location corresponding to the erosion area.^{9,12,17)} In contrast, the decrease in resistivity resulting from increases in both carrier concentration and Hall mobility at this substrate location, as shown in Fig. 3, is mainly interpreted as a consequence of changes in the spatial distributions of both the amount and the activity of oxygen reaching the substrate surface resulting from the rf discharge induced by the application of rf power. The results also suggest that a sputtering deposition in a weakly reducing (controllable oxidizing) atmosphere is useful for resolving this problem.^{1,2,12)} To enhance reduction, hydrogen gas was introduced into dc + rfMSP deposition.

The hydrogen (H_2) gas content [ratio of H_2 to total (Ar + H_2) gas] dependence of spatial resistivity distribution is shown in Fig. 4 for AZO films prepared on glass substrates at 200 °C by (dc power of 80 W and rf power of 100 W) along with the introduction of H_2 gas at various contents. It should be noted that a resistivity as low as $5 \times 10^{-4} \Omega \text{ cm}$ and a uniform resistivity distribution were obtained by introducing H_2 gas into the deposition chamber during dc + rfMSP deposition at an appropriate rf power. As can be observed in Fig. 4, the resistivity distribution considerably improved as H_2 gas content was increased up to approximately 0.4%, reached a uniform distribution at a H_2 gas content of 0.4–0.6%, and worsened with further increases in H_2 gas content. This introduction of H_2 gas at a content up to approximately 0.6% markedly improved the spatial distribution of Hall mobility in AZO films by increasing Hall

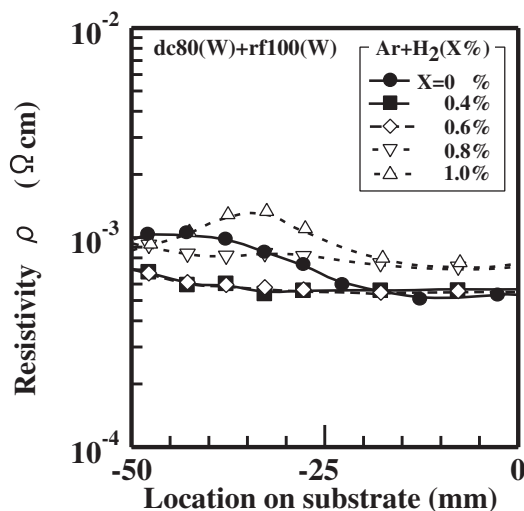


Fig. 4. Resistivity spatial distributions as a function of H_2 gas contents for AZO films prepared by dc + rfMSP.

mobility at the substrate location that corresponds to the target erosion area; however, the spatial distribution of carrier concentration was only slightly improved by this introduction. In addition, crystallinity at the substrate location that corresponds to the target erosion area improved as H_2 gas content was increased up to approximately 0.8%, as shown by the XRD analysis of the deposited AZO films. It should be noted that sputter voltage in this dc + rfMSP deposition was relatively independent of the introduction of H_2 gas up to a content of 1.2%. In contrast to the introduction of H_2 gas during dc + rfMSP deposition, it was also found that its introduction during either the dcMSP or rfMSP deposition of AZO films on glass substrates at 200 °C resulted in no significant improvement in resistivity distribution. Thus, the above suggests that the increase in Hall mobility resulting from the improvement of crystallinity was caused by the hybrid plasma discharge during dc + rfMSP enhancing the reduction effect of the introduced hydrogen that, in turn, leads to the suppression of both oxygen adsorption on grain boundary surfaces and the incorporation of oxygen into the deposited AZO films. The above results may also support the implication that the increased resistivity observed in AZO films at a substrate location corresponding to the erosion area of the target can be attributed to both the activity and the amount of oxygen reaching the substrate surface rather than to the degraded crystallinity of deposited films that results from the bombardment of high-energy oxygen. In addition, it was found that all the AZO thin films, including those prepared by a dc + rfMSP deposition that introduced hydrogen gas, exhibited an average transmittance above 85% in the visible range.

New transparent conducting AZO film preparation techniques for improving resistivity distribution in MSP depositions were developed with dc + rfMSP (dcMSP incorporating rf power) deposition as well as by introducing hydrogen gas into the deposition chamber during the deposition. The improvement in distribution can be attributed to the incorporation of rf power, which resulted in both

an increase in plasma density and the reduction effect of the introduced hydrogen being enhanced by the hybrid plasma discharge. A resistivity as low as $5 \times 10^{-4} \Omega \text{ cm}$ and a uniform resistivity distribution on the substrate surface could be obtained on glass substrates at a temperature of 200°C by dc + rfMSP deposition using a commercially available high-density-sintered AZO target. The newly developed dc + rfMSP deposition techniques for AZO film preparation on low-temperature substrates were found to be useful for developing AZO transparent electrodes to substitute for ITO transparent electrodes used in liquid crystal display applications.

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