The Optical and Electrical Properties of MZO Transparent Conductive Thin Films on Flexible Substrate

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ABSTRACT

In this paper the optical and electrical properties of Mo doped ZnO (MZO) thin films on flexible substrate made by DC sputtering was investigated. The electrical, optical and micro-structural characteristics of MZO thin films made using different deposition parameters was also studied. XRD analysis showed that all the films exhibited strong (0 0 2) MZO preferential orientation. It was found that the average visible light transmittance of all the MZO thin films was about 70%. The resistivity was $6.02 \times 10^{-3}$ Ω-cm and electron mobility, from the Hall effect, was 39 cm²/Vs.

The figure shows the optical transmittance curves with different deposition times and sputtering power. A little decrease of the transmittance is observed with the increase of the deposition times and the decrease of flow rate of Ar. The average transmittance in the visible range decreases from 80 to 70% with the increase of deposition times and sputtering power.

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1. Introduction

Thin transparent conductive oxide films can have transmittance of 80% or more within the visible light range (380–760 nm), as well as high conductivity and low resistivity ($1 \times 10^{-3} \ \Omega \cdot \text{cm}$ or less). TCO films have good electrical properties, high transparency, low resistivity, and are easy to manufacture in bulk at low cost. The most commonly used thin films are indium oxide ($\text{In}_2\text{O}_3$), tin oxide ($\text{SnO}_2$), and zinc oxide ($\text{ZnO}$). $\text{In}_2\text{O}_3$ and $\text{SnO}_2$ are n-type semiconductors, but $\text{ZnO}$ can be either n- or p-type, and this is determined by the dopant used [1–3].

Electronics circuitry on flexible substrates has become very common in recent years. The technology is used for flat panel displays, touch panels, solar cells, and very many other products that need circuitry on a thin flexible substrate. The resulting digital products can be very thin, lightweight, impact resistant, flexible, of large size, and relatively inexpensive. Glass on the other hand is fragile and the manufacture of large pieces of glass with a good finish, which is thin and flat enough for the purpose is difficult and expensive. Soft plastic film is meeting the market demand for less expensive electronic products and replacing glass for a large number of applications.

To make a conductive film with good transparency to light in the visible light spectrum, the gap width of the selected semiconductor material needs to be larger than that of visible light. The wavelength range of visible light is between 400 and 800 nm and this means the band gap width of the semiconductor material needs to be more than 3 eV, to be suitable for use as a transparent conductive film. However, it is possible to combine a range of different transparent conductive film materials, such as indium, tin, cadmium, and zinc oxides and some other semiconductors to make a film. The combination of different transparent conductive materials can be changed using different processing parameters. Such a combination can allow the electrical, optical, chemical, and physical properties of the films to be adjusted to give a degree of transparency that a single conductive film material cannot reach. To improve electrical conductivity, some of the impurities are often doped into the oxide or added during heat treatment. The most commonly used materials are tin-doped indium oxide (ITO) [4–6], fluorine doped tin oxide, aluminum doped zinc oxide (AZO) [7–11], and gallium-doped zinc oxide (GZO) [8,9], all of which have received attention in many prominent publications.

In these experiments, MZO ($\text{ZnO}$: Mo = 98: 2 wt%) thin films were deposited on a PI substrate with specific size by pure argon insertion using DC sputtering. The optical and surface properties of the transparent conductive film were studied to determine the most suitable surface properties to produce a conductive film of sufficient transparency for the intended use. The structure of ZnO thin films is mainly composed of ZnO. The crystal structure is unaffected by the Mo doping and has the same Wurzite hexagonal structure as that of pure ZnO, the six sides of the hexagon showing the densest accumulation.

2. Experimental Principles and Methods

2.1. Sputtering Principle

There are very many ways of producing thin films. In addition to electroplating methods, the first to be used, there are DC and RF sputtering, AIP, evaporation, spinning, sol–gel, chemical vapor deposition (CVD), and metal organic chemical vapor deposition (MOCVD). DC sputtering was used in this study.
2.2. DC Sputtering

In a DC sputtering system a plasma is generated by an inert gas in a vacuum chamber in a high-voltage electric field, Argon is typically used. Ions of the atomized gas (Ar+) will strike a cathode target and dislodge atoms, some small number of which will be energetic enough to travel in straight lines and impact the surface of the substrate where they will form a coating [12]. Sputtering is similar to general vacuum coating because the design factor is the mean free path. The mean free path is the distance that the gas particles will travel before meeting another particle in the vacuum chamber. The distribution and direction of travel of the Ar+ ions, and other atoms present, is random and so the mean free path of all the particles will not be the same. However, the difference will not be too great and an average mean free path can be calculated:

\[
\lambda = \frac{kT}{\pi \sqrt{2D^2P}}
\]

where \( \lambda \) is the mean free path, \( k \) is the constant, \( D \) is the molecular diameter, \( T \) is the absolute temperature, and \( P \) is the gas pressure. Together these make the distance from the cathode to the substrate and the system pressures the key factors affecting sputtering [13].

The main advantage of the DC sputtering method is that as the dissociation rate of the working gas is increased the greater the number of ions sputtered and higher the coating rate. However, in this method the target material consumption rate is relatively high and the target needs frequent replacement [14].

2.3. Experimental Method

Pieces of PI (Polymide) flexible substrate cut to an appropriate size were cleaned ultrasonically in ethanol for 10 min, rinsed in deionized water, blown dry and further dried in an oven at 100 °C for an hour. DC argon sputter coating with MZO was carried out with different set of parameters: Power at 100, 80, and 60 W, for 20, 30, and 40 min. No substrate heating was used and oxygen was totally excluded from the chamber.

3. Results and Discussion

3.1. Thickness of the MZO Films

Growth of the crystalline MZO transparent conductive film increases with sputtering power and time, and thickness of the conductive film vs. power and time is shown in Table 1. From the table it can be seen that the maximum thickness, 161.43 nm, was reached using a power of 100 W for 40 min.

3.2. The Electrical Properties of the MZO Films

The electrical properties of the sputtered MZO thin films are shown in Table 2. The lowest resistivity was \( 6.02 \times 10^{-3} \) Ω-cm, also achieved with a sputtering power of 100 W for 40 min.
Table 1. Deposit parameters and thickness of MZO thin films.

| Sputtering power (W) | Sputtering time (min) | Thickness (nm) |
|---------------------|----------------------|----------------|
| 60                  | 20                   | 38.63          |
| 80                  | 20                   | 71.63          |
| 100                 | 20                   | 85.54          |
| 60                  | 30                   | 65.59          |
| 80                  | 30                   | 97.64          |
| 100                 | 30                   | 131.81         |
| 60                  | 40                   | 90.24          |
| 80                  | 40                   | 131.77         |
| 100                 | 40                   | 161.43         |

Table 2. Electrical properties of MZO as a function of different process parameters.

| Sputtering power (W) | Sputtering time (min) | Mobility (cm²/Vs) | Resistivity (Ω-cm) | Carrier concentration (cm⁻³) |
|---------------------|----------------------|------------------|-------------------|-----------------------------|
| 60                  | 20                   | 1.58 x 10¹       | 2.16 x 10⁰        | 4.39 x 10¹⁷                |
| 80                  | 20                   | 1.78 x 10¹       | 2.63 x 10⁻⁴       | 3.49 x 10¹⁹                |
| 100                 | 20                   | 1.77 x 10¹       | 1.55 x 10⁻⁴       | 4.59 x 10¹⁹                |
| 60                  | 30                   | 2.57 x 10¹       | 3.57 x 10⁻⁴       | 3.74 x 10¹⁹                |
| 80                  | 30                   | 2.59 x 10¹       | 8.84 x 10⁻⁴       | 1.53 x 10²⁰                |
| 100                 | 30                   | 2.74 x 10¹       | 8.13 x 10⁻⁴       | 1.97 x 10²⁰                |
| 60                  | 40                   | 3.60 x 10¹       | 2.80 x 10⁻⁴       | 6.17 x 10¹⁹                |
| 80                  | 40                   | 3.78 x 10¹       | 6.22 x 10⁻⁴       | 2.64 x 10²⁰                |
| 100                 | 40                   | 3.90 x 10¹       | 6.02 x 10⁻⁴       | 3.04 x 10²⁰                |

Table 3. Optical transmittance for MZO films.

| Sputtering power (W) | Sputtering time (min) | Thickness (nm) | Average transmittance (%) |
|---------------------|----------------------|----------------|---------------------------|
| 60                  | 20                   | 38.63          | 59.27                      |
| 80                  | 20                   | 71.63          | 53.62                      |
| 100                 | 20                   | 85.54          | 51.40                      |
| 60                  | 30                   | 65.59          | 56.50                      |
| 80                  | 30                   | 97.64          | 52.49                      |
| 100                 | 30                   | 131.81         | 50.51                      |
| 60                  | 40                   | 90.24          | 55.23                      |
| 80                  | 40                   | 131.77         | 52.24                      |
| 100                 | 40                   | 161.43         | 60.33                      |

Figure 1. MZO transmittance.
3.3. Transmittance of the MZO Thin Films

The average optical transmittance of the sputtered MZO thin films is shown in Table 3 and Figure 1. It can be seen from the table that the transmittance decreases slightly as the film gets thicker. However, the transmittance finally increases at 100 W for 40 min. The reason for this is that the quality of the sputtering achieved under these conditions is better. This behavior is explained in the XRD analysis section. However, when compared to the PI substrate itself, the transmittance of the PI substrate shows little difference.

Figure 2. Surface features of MZO thin films with different deposit parameters.
Figure 3. AFM 3D images of MZO under different deposit parameters.

Table 4. MZO surface roughness.

| Deposit Parameters | RMS (nm) |
|-------------------|----------|
| 60 W 20 min       | 4.87     |
| 60 W 30 min       | 2.89     |
| 60 W 40 min       | 2.11     |
| 80 W 20 min       | 4.98     |
| 80 W 30 min       | 4.26     |
| 80 W 40 min       | 2.45     |
| 100 W 20 min      | 7.31     |
| 100 W 30 min      | 4.28     |
| 100 W 40 min      | 3.37     |
3.4. **MZO Thin Film Surface Morphology**

The MZO thin films were examined by both Scanning (SEM) and Atomic Force (AFM) microscopy. SEM magnification was 50,000× and the surface roughness and graining can be seen clearly in Figure 2. The AFM images in Figure 3, more clearly shows the roughness and surface grain morphology.

As the sputtering power and time is increased the film becomes thicker and the SEM images show that the surface grains become more compact. The roughness value can be easily determined by examination of the AFM images where it can be seen that as the sputtering power goes up the roughness value increases. However, roughness finally decreases at 100 W for 40 min. Table 4 shows the roughness values of the MZO transparent conductive film made under the different parameters.

3.5. **XRD Analysis of the MZO Thin Films**

XRD was used to determine if the crystal growth direction of the conductive film was along the C-axis. It can be seen from the peaks in the graph in Figure 4 that the strongest growth is clearly in the (0 0 2) direction. This means the crystal growth is vertical to the substrate surface. Although there are secondary growth peaks at (1 0 1), (1 0 2), and (1 0 3) these are comparatively weak. The crystal growth of the MZO thin film is on the C-axis, perpendicular to the substrate. Figure 4 also clearly shows that as the sputtering power increases, so do the diffraction peaks. This means the crystal orientation also increases along the C-axis. In other words more sputtering power gives better MZO crystal formation and orientation to the conductive thin film.

4. **Conclusion**

The results show that the thickness of the MZO transparent conductive film increases with a higher sputtering power and longer time, the thicker film gives better electrical properties,
but the average transmittance declines. However, it should be noted MZO films can reach a resistivity of $6.02 \times 10^{-3}$ Ω·cm with an average transmittance of 46.3% at a sputtering power of 100 W for 40 min.

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**Disclosure statement**

No potential conflict of interest was reported by the authors.

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