Effect of oxygen flow rate on physical properties of Al-doped ZnO transparent conducting films prepared by reactive dc magnetron sputtering using metallic Zn:Al target

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Abstract. In this work, Al-doped ZnO transparent conducting thin films were prepared by a reactive dc magnetron sputtering method on slide glass substrate using single metallic Zn:Al (2 wt.% Al) target with the oxygen flow rate 1, 3, 5, 7 and 9 sccm, respectively. From XRD patterns, the films prepared at R(O₂) of 1 sccm showed amorphous characteristics. In contrast, the films prepared at R(O₂) of 3, 5, 7 and 9 sccm showed the preferred orientation (002) plane of hexagonal structure. Surface morphology and diameter of nanocolumns of the films were observed by AFM and FESEM. From transmittance spectra, energy gap value was found to vary between 3.24 and 3.32 eV. Electrical resistivity and Hall effect measurements were performed on the films with van der Pauw configuration. The temperature-dependent conductivity was performed in the range 20-300 K. Three types of conduction mechanisms were expected. Thermally activated band conduction at the high temperature range (250-300 K), Mott variable-range hopping (Mott-VRH) at the low temperature range (100-210 K) and Efros-Shklovskii variable-range hopping (ES-VRH) at the very low temperature range (<100 K) can be found in the films prepared with different oxygen flow rate conditions. Except for the oxygen flow rate at 5 sccm, the behavior of weakly localized electrons was observed. Then, the sets of parameters explaining the properties of localized electrons in each conduction regime were determined. The results indicated that the reactive dc magnetron sputtering using a single metallic Zn:Al (2 wt.% Al) target is suitable for TCO films since it can be easily obtained at low temperatures with good physical properties.

1. Introduction

Thin films of transparent conducting oxides (TCO) based on zinc oxide (ZnO) are supporting for applications in various optoelectronic and energy conversion applications because of they present many advantages such as low material price, abundance, nontoxicity and high chemical stability under the hydrogen plasma as compared to indium oxide doped with tin oxide (ITO). The group IIIA elements such as Ga, Al and In were usually used to dope in ZnO results in a marked reduction in the electrical resistivity value while the optical transparency remains high. Sputtering method commonly used to fabricate high quality of Al-doped ZnO thin films due to high energy bombardment of Ar ions onto the target [1]. Reactive sputtering from metallic alloy targets allows the growth process to be varied to a large condition. The stoichiometric composition in the films can be well adjusted. Moreover, the adhesion between films and substrate can be improved. Guilen and Herrero [2] reported the comparative study...
between continuous dc sputtering and pulsed mid-frequency sputtering techniques for preparing Al-doped ZnO thin films. They found that Al-doped ZnO films obtained from the first technique exhibit a lower resistivity than those obtained from the second one. Al-doped ZnO films can be grown by a variety of methods such as sol-gel, spray pyrolysis, thermal evaporation and sputtering. According to the literature, reactive dc sputtering has drawn significant attention for Al-doped ZnO films growth because this technique could produce high quality thin films, allows synthesis at low temperature closed to room temperature and permits coverage of large substrate. Usually, Al-doped ZnO thin films deposited by magnetron sputtering use ZnO:Al ceramic target. This method has some disadvantages. Firstly, the ZnO:Al ceramic is more expensive. Secondarily, for industrial applications, it is difficult to sinter a large size of ZnO:Al target with high quality and a large ZnO:Al target is easily broken during the sputtering process. In addition, the oxygen flowing is an important parameter that can affect the properties of Al-doped ZnO films prepared by reactive sputtering method. The objective of this work is to prepare the Al-doped ZnO thin films by reactive dc magnetron sputtering method using a metallic alloy Zn:Al (98:2 wt.%) target. The effect of O₂ flow rate on the microstructural and physical properties was systematically examined. Moreover, Electron conduction mechanisms of all films at temperatures below room temperature were explored.

2. Materials and methods
The Al-doped ZnO thin films were grown on 25×75 mm² slide glass substrate of 1 mm thickness by dc reactive magnetron sputtering using a high purity Zn:Al (98:2 wt.%) target of 99.999 % with diameter of 2 in. supplied by Kurt J. Lesker Company. The sputtering procedure was carried out in Argon atmosphere with the target to substrate distance of 9 cm. A turbo-molecular pump, back up by a rotary pump, was used to attain a base pressure of 3×10⁻⁵ torr. The reactive gas (O₂ 99.999% purity) and sputtering gas (Ar 99.999 % purity) were introduced in the sputtering chamber separately and were controlled through the gas mass flow meter. The pressure of sputtering chamber during the deposition process was fixed at 2.5×10⁻⁴ torr. The gas flow meter was controlled precisely to allow flow rate of 1-9 sccm and 10-35 sccm for O₂ and for Ar gases, respectively. The sputtering time was 60 min. The microstructure of the films was analyzed with a Brucker D 8 Advance XRD using CuKα radiation. Surface morphology was characterized by Park XE-100 AFM. FESEM images were recorded by JEOL JSM-7610F equipment. The optical transmittance spectra were obtained by UV-Vis Thermo electron corporation (Helios α) spectrophotometer. FTIR spectra in the range between 400 and 4000 cm⁻¹ were obtained by Thermo Scientific Nicolet 6700. The obtained films were studied on the electrical properties by resistivity and Hall effect measurements in the van der Pauw method at room temperature. The temperature-dependent conductivity was measured using the two-probe method in the temperature range of 20-300 K using closed-cycle helium cryostat.

3. Results and discussion
3.1 Structural properties
The combined XRD patterns of ZnO:Al films deposited on slide glass substrates are shown in Figure 1. For O₂ flow rate (R(O₂)) of 1 scmm, no XRD peak of the as-prepared films was observed indicating an amorphous phase. A gradual increase in intensity with an increase in O₂ flow rate reached the maximum value was observed for the films prepared at 5 scmm. The peak corresponded to the reflection of (002) plane of standard JCPDS data card No. 79-207. No other phases were detected. For further increase of R(O₂), its peak intensity reduced and then disappeared at R(O₂) over 9 scmm described to amorphous
phase. Similar behavior was observed in TiO$_2$ films [3]. It may be indicated that too much oxygen content also makes the films become amorphous phase. AFM images of the films fabricated at different O$_2$ flow rates are presented in Figure 2. As R(O$_2$) raised from 1 to 5 sccm, the roughness of films surface raised from 5.1 to 5.5 nm. When R(O$_2$) further increased from 7 to 9 sccm, the surface roughness decreased from 5.2 to 3.7 nm. Interestingly, the columnar grain growth is observed for the films grown with R(O$_2$) of 3, 5, 7 and 9 sccm. From FESEM images (as shown in Figure 3), the average diameter of the nanocolumns was obtained as 34.5, 52.6, 54.4 and 55.8 nm, respectively. It is noticed that the diameter of nanocolumns found in our films prepared by dc magnetron sputtering is slightly bigger than the one of ZnO films prepared by rf reactive sputtering reported earlier [4].

3.2 Optical properties

The optical transmittance data of the films prepared at various O$_2$ flow rates are presented in Figure 4. The energy gap (E$_g$) of sputtered Al-doped ZnO films could be estimated from the relationship between the absorption coefficient (α) and the transmittance. The absorption coefficient is given by $\alpha = \frac{1}{d}\ln(1/T)$ where d is film thickness and T is transmittance. The E$_g$ value can be deduced by

![Figure 1. XRD patterns of Al-doped ZnO films.](image)

![Figure 2. AFM images of Al-doped ZnO films.](image)

![Figure 3. FESEM images of Al-doped ZnO films.](image)
extrapolation of the linear part of the Tauc \((\alpha h\nu)^2 = A(h\nu - E_g)\) plot, as shown in Figure 5, where \(A\) is a constant value and \(h\nu\) is photon energy. The \(E_g\) of the films deposited with \(R(O_2)\) of 1, 3, 5, 7 and 9 sccm was determined to be 3.24, 3.31, 3.32, 3.30 and 3.26 eV, respectively. Figure 6 presents the FTIR data of Al-doped ZnO films at various \(O_2\) flow rates. The peaks with wavenumbers of about 400, 760 and 905 cm\(^{-1}\) are attributed to the stretching vibration of Zn-O bonds, bending of Si-O-Si bonds and C=C stretching mode, respectively [5].

![Figure 4. Transmittance spectra of Al-doped ZnO films.](image)

![Figure 5. The plot of \((\alpha h\nu)^2\) vs photon energy (hv) of Al-doped ZnO films.](image)

### 3.3 Electrical properties

The observed variation in electrical properties of ZnO films doped with Al as a function of \(O_2\) flow rates is shown in Figure 7. It is noted that the electrical resistivity of the films firstly reduced 28.30 down to a minimum value at \(1.11 \times 10^{-3} \ \Omega \cdot \text{cm}\) with \(O_2\) flow rate raised from 1 to 5 sccm. As \(O_2\) flow rate raised from 7 to 9 sccm, the resistivity raised from \(4.05 \times 10^{-3}\) to \(5.20 \times 10^{-2} \ \Omega \cdot \text{cm}\). The carrier concentration initially increased with an increase \(O_2\) flow rate up to 5 sccm, reached a maximum value of \(4.55 \times 10^{21} \ \text{cm}^{-3}\) and then decreased with an increase in \(O_2\) flow rate. The variation of the mobility curve displayed similar behavior to the resistivity curve. It is also interesting to note that the films prepared at \(R(O_2)\) of 5 sccm revealed the lowest resistivity as well as the highest carrier concentration values. Figure 8(a) depicts the Arrhenius plot of \(\ln \sigma\) and \(10^3/T\) for the films deposited at \(R(O_2)\) of 7 sccm. As seen in Figure 8(a), the graph cannot display the linear portion in the whole measured temperature region of 20-300 K. It suggested that the electron conduction is not dominated by the only one mechanism. In the temperature region of 250-300 K, the thermally activated allowed-band conduction became important. Then, the activation energy value for the films prepared at \(R(O_2)\) of 1, 3, 7 and 9 sccm, evaluated from the slope of the plot in Figure 8(b), were 14.80, 1.73, 5.52 and 2.77 meV, respectively. Such low activation energy values possibly can be attributed to the formation of shallow impurity levels below the conduction band edge [6]. With a continuous increase in \(R(O_2)\), the broadening of the impurity band has appeared. The impurity band finally overlaps with the conduction band forming a degenerate semiconductor like situation resulting into metal-semiconductor transition as observed in the films prepared at \(O_2\) flow rate of 5 sccm discussed below. For the temperature region of 100-210 K, the conduction of electron is dominated by variable-range hopping process proposed by Mott (abbreviated as Mott-VRH) because the plot of \(\ln(\sigma T^{1/2})\) against \(T^{-1/4}\) was found to be linear as shown in Figure 8(c). The conduction of the Mott-VRH process is given by

\[
\ln\left(\sigma T^{1/2}\right) = -\left(T_{0,Mott}/T\right)^{1/4} + \ln \sigma_{0,Mott}
\]

where \(T_{0,Mott}\) measures the degree of disorder in the films [7]. The important parameters of the Mott-VRH process for the films prepared at \(R(O_2)\) of 1, 3, 7 and 9 sccm extracted from the Mott-VRH equation are listed in Table 1. For the lower
temperature region (40-90 K), we took up the Efros-Shklovskii variable-range hopping process (ES-VRH) to explain the electron conduction mechanism. A fitting of lower temperature data to ES-VRH expression as
\[ \ln(\sigma T) = -\left( \frac{T_{0,ES}}{T} \right)^{1/2} + \ln \sigma_{0,ES} \] is shown in Figure 8(d) where \( T_{0,ES} \) is an ES characteristic temperature coefficient [7]. The parameters of the ES-VRH process extracted from ES-VRH expression are tabulated in Table 3. Except for \( R(O_2) \) of 5 sccm, the resistivity value obeyed very well with the weakly localized electron regime presented by the expression \[ \rho=1/(\sigma_0 + a T^{1/2}) + b T^2 \] [8].

A metal-semiconductor transition was appeared at 50 K. The corresponding parameters \( \sigma_0 \), \( a \) and \( b \) obtained from the curve fitting (not shown here) were \( 5.01 \times 10^{-3} \) (\( \Omega \cdot \text{cm} \)), \( 4.35 \times 10^{-2} \) (\( \Omega \cdot \text{cm} \cdot \text{K}^{-1/2} \)) and \( 2.44 \times 10^{-8} \) (\( \Omega \cdot \text{cm} \cdot \text{K}^{-2} \)) which they are closed to the values reported earlier in ZnO:Al (2 wt.%) [8].

**Figure 6.** FTIR spectra of Al-doped ZnO films.

**Figure 7.** Value of \( \rho \), \( n \) and \( \mu \) as a function of \( R(O_2) \) for Al-doped ZnO films.

**Figure 8.** (a) Plot of ln\( \sigma \) versus 10\(^3\)/T in range 20-300 K, (b) Plot of ln\( \sigma \) versus 10\(^3\)/T in range 250-300 K, (c) Plot of ln(\( \sigma T^{1/2} \)) versus T\(^{-1/4} \) and (d) Plot of ln(\( \sigma T \)) versus T\(^{-1/2} \) for Al-doped ZnO films prepared at 7 sccm.

**Table 1.** Parameters of Mott-VRH at low temperature range of Al-doped ZnO films.

| \( R(O_2) \) (sccm) | \( \sigma_{0,Mott} \) (S/cm) | \( T_{0,Mott} \) (10\(^3\) K) | \( N_0(E_F) \) (10\(^{22}\) cm\(^{-3}\) eV\(^{-1} \)) | \( R_{hop,Mott} \) (nm) | \( W_{hop,Mott} \) (meV) | \( R_{\xi,Mott} \) (\( \xi = \frac{\hbar}{e} \)) |
|---|---|---|---|---|---|---|
| 1 | \( \frac{1.87 \times 10^{-4}}{} \) | 2.04 | 1.95 | 5.35 | 24.60 | 7.99 |
| 3 | \( \frac{1.81 \times 10^{-2}}{} \) | 2.46 | 1.62 | 5.67 | 8.08 | 5.67 |
| 7 | \( \frac{3.70 \times 10^{-2}}{} \) | 3.56 | 1.12 | 6.14 | 9.21 | 1.03 |
| 9 | \( \frac{8.72 \times 10^{-1}}{} \) | 2.22 | 1.79 | 5.46 | 8.49 | 0.81 |

**Table 2.** Parameters of ES-VRH at very low temperature range of Al-doped ZnO films.
4. Conclusion

Thin films of Al-doped ZnO compound were fabricated on glass substrate by dc reactive sputtering using single metallic Zn:Al (2 wt.%) target. The effect of O₂ flux rate on the microstructural, morphological, optical and electrical properties of the obtained films was systematically investigated. The Al-doped ZnO thin films belonging to hexagonal structure with (002) preferred orientation were appeared at R(O₂) values of 3, 5, 7 and 9 sccm. The surface roughness in the range of 3.7-5.5 nm was observed by AFM. From FESEM images, the average size of the nanocolumns was estimated in the range of 34.5-55.8 nm. From transmittance spectra, energy gap value was found to vary between 3.24 and 3.32 eV. It was shown that three kinds of conduction behavior, for the films prepared at 1, 3, 7 and 9 sccm, can be determined such as thermally activated allowed-band conduction at high-temperature range (250-300K). For the temperature range of 100-210 K, the electron conduction mechanism is governed by the Mott-VRH process. For very low temperatures (<100 K), ES-VRH process is dominated. Except for R(O₂) at 5 sccm, the behavior of weakly localized electrons was observed. Some important parameters corresponding to thermally activated allowed-band conduction, Mott-VRH and ES-VRH conduction mechanisms were determined. These parameters would be useful to achieve further optimization of the performance of TCO films. The results demonstrated that the structural and physical properties of the as-prepared films obviously depended on R(O₂).

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