Preparation of Aluminum doped Zinc Oxide Thin Films on Glass Substrate by Sparking Process and Their Optical and Electrical Properties

A Sukee, E Kantarak, P Singjai*
Department of Physics and Materials Science, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand
Email: pisith.s@cmu.ac.th

Abstract. Aluminum doped Zinc Oxide (AZO) nanoparticle thin films were deposited on glass substrates by a double tip sparking process. The effect of Al doped ZnO on electrical and optical transmittance properties were studied. The doping ratios of Al into ZnO were 3, 5, 7, 13 and 22 %. SEM images indicated particle size decreased with increasing the Al content after annealing. Raman spectra results of AZO films associated with the hexagonal structure. AZO films have an average transmittance in visible region at 60 %. The energy gap increased with increasing Al content. The minimum resistivity was found at 5 % of Al doping for AZO film.

1. Introduction

Zinc Oxide (ZnO) is a great interesting material due to their advantage in widely range of technology applications, low coat, non-toxic, resource availability and high physical/chemical stability. It is a wide bandgap semiconductor, which has direct band gap width of 3.37 eV [1]. In order to improve electrical and optical properties, ZnO film has been doped with many metal elements. Impurity doping such as Al, In, Ga, B affected to high electrical conductivity [2]. Among these elements, Al doped ZnO are considered as an alternative for transparent conducting oxide material (TCO) for solar cell and light-emitting diodes (LEDs) [3]. The atomic substitution of Al to Zn in ZnO crystal structure has occurred a free electron in conduction band, which provides a reduction in its electrical resistivity [4]. This material exhibits high transparency and low resistivity [5]. The AZO thin films have been prepared by various methods such as sol-gel processing [6], magnetron sputtering [7], and atomic layer deposition [8]. These methods have been done under controlled environment that leads to complicate in the process and high cost. Moreover, sparking process is a method to fabricate the thin films [9]. The advantages of this technique are a simple, cost effective, and a single step preparation.

In the present study, we report the AZO thin films deposited on glass substrate by a sparking process. Effect of Al doped ZnO on optical and electrical properties were investigated.

2. Experimental detail

AZO films were deposited on a rotating glass substrate by double tip sparking process. Zn (purity 99.99%, diameter 0.38 mm) and Al (purity 99.99%, diameter 0.5 mm) wires were placed as the main tips and the doping tips, respectively. The sparking process was done for 5 min under flowing argon (Ar) atmosphere with a flow rate of 0.5 L/min at room temperature. The doping ratio of Al to Zn was controlled by sparking energy using a different capacitor (C) paralleled Al doping tips. The capacitances...
of paralleled Zn was fixed at 40 nF while those of Al were varied by 0.5, 1.1, 1.5, 3.1, and 4.7 nF. The as-samples were annealed at 400 °C for 60 min.

The thin films were observed by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). The chemical structure of AZO films were measured by Raman spectroscopy. Optical transmittance property of the thin films was recorded in a wavelength range of 300-800 nm using uv-vis spectroscopy. The electrical property were measured by a standard four probe technique with silver paste contact.

Figure 1. Schematic diagram of two tip sparking process under flowing Ar atmosphere.

Figure 2. Equivalent circuit of a sparking process.

3. Results and discussion

3.1 The morphologies and chemical structure of AZO films

Figure 3 a-f show the SEM surface morphologies of un-doped and Al doped ZnO thin films prepared by the sparking process. The different energy (E=CV^2/2, at the same breakdown voltage (V)) of Zn and Al resulted different Al content and the film thickness as illustrated in Table 1. It is noticed that the agglomerated particle size decrease with increasing the Al content after the annealing treatment.

Figure 4 shows the Raman spectra of annealed AZO films. All samples present the Raman shift of 333 cm⁻¹ (multiphonon mode) and 438 cm⁻¹ (E₂ high mode) [10], which associated with O sublattice vibrations of a typical ZnO hexagonal structure. The peak at 275 cm⁻¹ is an additional mode caused by oxygen vacancy and impurities defects [10]. Besides, the Raman spectra of Al doped ZnO shows another vibration mode at 578 cm⁻¹. This peak is a longitudinal optical (LO) scattering mode that resulted from higher carrier concentration [11].

3.2 The optical property of AZO films

Figure 5 shows the optical transmittance spectra of the samples in the wavelength range of 300-800 nm at room temperature. All samples have an average transmittance in visible region at 60 %. It is clear that the transmittance increased with increasing the doping ratio of Al. Moreover, a blue shift of the absorption edge was observed in the doped films [8]. It probably caused by the energy gap turning that resulting from Al content in ZnO.
Table 1. The Al doping ratio and the films thickness.

| sample | Capacitance Zn : Al (nF) | Al doping (atomic %) | Thickness (µm) |
|--------|--------------------------|----------------------|----------------|
| 1      | 40 : -                   | 0                    | 0.950          |
| 2      | 40 : 0.5                | 3                    | 1.136          |
| 3      | 40 : 1.1                | 5                    | 0.972          |
| 4      | 40 : 1.5                | 7                    | 1.174          |
| 5      | 40 : 3.1                | 13                   | 1.110          |
| 6      | 40 : 4.7                | 22                   | 0.956          |

For calculation the energy gap ($E_g$), Tauc Method is used to evaluate the energy gap of the samples using formulas as follows [7]:

$$(a h \nu)^2 = C(h \nu - E_g)$$

where $C$ is a constant, $E_g$ is the energy gap, $h \nu$ is photon energy. $\alpha$ is absorption coefficient and can calculate from transmittance by $\alpha = -\ln T / d$, where $T$ is the transmittance and d is the film thickness. The relationship curves of $(a h \nu)^2$ and $h \nu$ were plotted. A linear extrapolation, the point value of fitted line and x axis is $E_g$ as shown in Figure 6.

The energy gap of the films were $3.34 - 3.59$ eV. It is clearly seen that energy gap increased with increasing the Al doping ratio. The energy gap turning can be explained by Burstein-Moss effect that is related to the electron carrier density. It can be described in the equation as follows [8]:

$$E_g = E_{g0} + \Delta E_g^{BM} = E_{g0} + \frac{h^2}{8m_e^*} \left( \frac{3}{\pi} \right)^{2/3} n_e^{2/3}$$

where $E_{g0}$, $\Delta E_g^{BM}$, $n_e$, $h$ and $m_e^*$ are the intrinsic forbidden band width, band gap increment caused by Burstein-Moss effect, electron carrier density, Planck’s constant and effective electron mass in conduction band, respectively. Substitution of Al$^{3+}$ to Zn$^{2+}$ in the AZO films, the extra $e^-$ from Al$^{3+}$ makes the electron carrier density increases [4], that resulted in the increasing of $E_g$ in the AZO films as illustrated in the inset of Figure 6.
3.3 The electrical property of AZO films

The resistivity of AZO films was measured by standard technique with a standard four probe technique with silver paste contact at room temperature. The resistivity was calculated the equation as follows:

\[
\rho = \frac{RA}{h} \text{ (}\Omega \text{cm) }
\]

where \( \rho \) is the volume resistivity, \( A \) is the effective area of the measuring electrode, \( h \) is the film thickness, and \( R \) is the resistance.

![Figure 7. Resistivity of AZO films for different Al content.](image)

The resistivity result of AZO films is shown in Figure 7. It decreased at a small amount of Al doping as compared to the un-doped sample. As mentioned above, Al\(^{3+} \) provides extra free electron into the system. In contrast, the increase doping levels affected to increase the resistivity of doped films that may be due to an increasing of insulator Al\(_2\)O\(_3\) concentration [6, 8]. However, the optimum of Al doping level was found at 5% in AZO film.

4. Conclusion

Un-doped and Al doped ZnO thin films were deposited on glass substrate by the double tip sparking process. The morphologies, chemical structure, optical and electrical properties were investigated. Raman spectra results of AZO films associated with the hexagonal structure. AZO films have an average transmittance in visible region at 60% and the band gap energy increased with increasing Al content. The electrical property measurement showed that the minimum resistivity was found at 5% of Al doping for AZO film.

References

[1] Mahroug A, Boudjadar S, Hamrit S and Guerbous L 2014 Mater. Lett. 134 248
[2] Nunes P, Fortunato E, Tonello P, Braz Fernandes F, Vilarinho P and Martins R 2002 Vacuum 64 281
[3] Shahedi Z and Jafari M R 2016 Appl. Phys. A 123 98
[4] Maldonado F and Stashans A 2010 J. Phys. Chem. Solids 71 784
[5] Raghu P, Srinatha N, Naveen C S, Mahesh H M and Angadi B 2017 J. Alloys Compd. 694 68
[6] Zhou H M, Yi D Q, Yu Z M, Xiao L R and Li J 2007 Thin Solid Films 515 6909
[7] Wang X and Zhang Y 2017 Mater. Lett. 188 257
[8] Zhai C H, Zhang R J, Chen X, Zheng Y X, Wang S Y, Liu J, Dai N and Chen L Y 2016 Nanoscale Res. Lett. 11 407
[9] Kumpika T, Thongsuwan W and Singjai P 2008 Thin Solid Films 516 5640
[10] Montenegro D N, Hortelano V, Martínez O, Martínez-Tomás M C, Sallet V, Muñoz-Sanjose V and Jiménez J 2013 J. Phys. D: Appl. Phys. 46 235302
[11] Liu Y, Zhang H, An X, Gao C, Zhang Z, Zhou J, Zhou M and Xie E 2010 J. Alloys Compd. 506 772