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Effects of Mo Thickness on the Properties of AZO/Mo/AZO Multilayer Thin Films

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Abstract**—**In this paper, we proposed the effects of Mo thickness on the properties of AZO/Mo/AZO multilayer thin films for opto-electronics applications. The structural, optical and electrical properties of AZO/Mo/AZO thin films were investigated. Optimization of the thin films coatings resulted with low resistivity of 9.98×10^{-5} Ω-cm, mobility of 12.75 cm^2/V-s, carrier concentration of 1.05×10^{22} cm^{-3}, maximum transmittance of 79.13% over visible spectrum of 380 – 780 nm and Haacke figure of merit (FOM) are 5.95×10^{-2} Ω^{-1} under Mo layer thickness of 15 nm. These results indicate an alternative candidate for use as a transparent electrode in solar cells and various displays applications.

Keywords**—**Aluminum-doped zinc oxide, AZO, multilayer, RF magnetron sputtering, AZO/Mo/AZO, thin film, transparent conductive oxides.

I. Introduction

TRANSPARENT conducting oxides (TCOs) are materials that can simultaneously exhibit the mutually exclusive properties of conductivity and transparency. TCOs find applications in the optoelectronics industry through use in flat-panel dis-playse.g., liquid crystal displays, solar cells, and electro-magnetic shielding of CRTs used for video display terminals [1–4]. Due to the conductivity of indium tin oxide (ITO) is limited by the mechanism of semiconductor and expensive source from indium, to develop the cheap and high performance TCO films is more needed.

Dielectric-metal-dielectric thin films have been studied in the hope of increased conductivity without significant losses in transmission [5]. Various studies have been done using silver as the sandwiched metal layer [6]. There are some studies on the multilayer thin films were used to fabricate highly transparent conducting oxides applications [7–11], such as ITO/Ag/ITO [12], AZO/Ag/AZO [13] and AZO/Cu/AZO [14]. Besides, AZO thin films as TCO films have most attention, due to the advantages of AZO thin films are cheap, non-toxic and abundant elements [15]. AZO thin films are the wide bandgap semiconductor materials (Eg ≒ 3.4 to 3.9) resulting in the optical transmittance properties in the visible regions. However, the inherent limitation to the increase in conductivity needs to further improve by using the multilayer structure.

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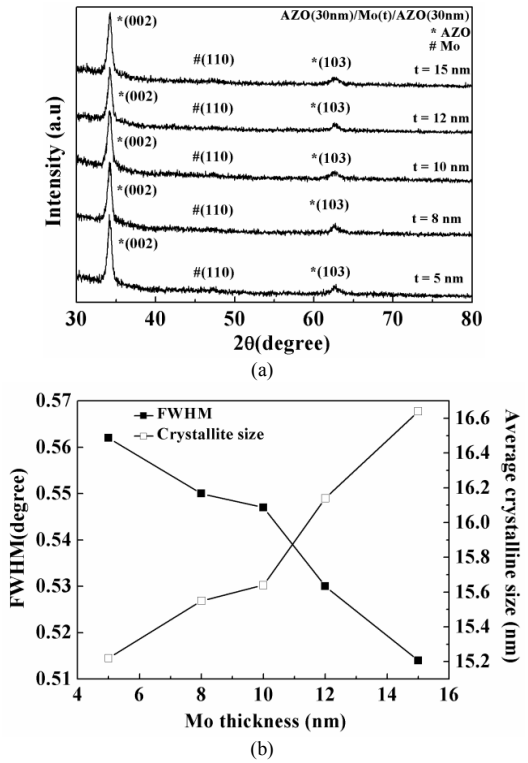
Molybdenum (Mo) has a comparable resistivity, hence, there are also studies documenting the resistance and transmission properties of Aluminum-doped ZnO (AZO) multilayers with molybdenum [16]. However, there are no reports related to AZO/Mo/AZO films for the applications of transparent electrodes. Therefore, in order to improve the conductivity of TCO films, it is necessary to study the structural, optical and electrical properties of the AZO/Mo/AZO films.

In this paper, we present the obtainment of AZO/Mo/AZO multilayer structures on glass substrates, while retaining transmittance values acceptable for optoelectronics applications. The conduction mechanism as a function of Mo layer thickness and the role of copper on the transmission properties of the films are investigated as well. The AZO/Mo/AZO films were prepared by using the RF magnetron sputtering for top / bottom AZO films and intermediate Mo layer. The average transmittance of 79.13 % in the 300 – 800 nm wavelength region, mobility of 12.75 cm^2/V-s, carrier concentration of 1.05×10^{22} cm^{-3}, low resistivity of 9.98×10^{-5} Ω-cm and Haacke figure of merit (FOM) of 5.95×10^{-2} Ω^{-1} are well obtained at Mo layer thickness of 15 nm. The proper optimization of process parameters and thickness of both Ag and AZO film are critical to achieve a high performance TCO films.

II. Experimental Procedures

The AZO/Mo/AZO tri-layer films were deposited on the glass (corning eagle XG) using an AZO ceramic target (99.9995 % purity, 20 cm diameter, 0.5 cm thickness Al_2O_3 : ZnO = 2 : 98 wt%) and metal Mo targets (99.9995 % purity, 20 cm diameter, 0.5 cm thickness) in a RF magnetron sputter deposition system. The glass substrate was ultrasonically cleaned in acetone, rinsed in deionized water and subsequently dried in flowing nitrogen gas before deposition. The dimension of the glass substrate is $20 \times 20 \times 0.5$ mm^3. The 30 nm thick bottom AZO layer was sputtered on the glass substrate. The sputtering was performed in argon atmosphere with a target to substrate distance of 15 cm. Initially, the sputtering chamber was evacuated to a base pressure of 3×10^{-6} Torr with turbo molecular pump. The deposition of AZO layers was performed in argon (purity: 99.99%) atmosphere and the deposition pressure was maintained at 40 mTorr and the RF power was kept at 250 W and substrate temperature kept at 70 °C. Ar flow ratio of 180 sccm and working pressure of 1.8×10^{-2} Torr. After the sputtering of the bottom AZO layer, Mo layers were deposited on the bottom AZO layer with various thicknesses. For Mo layers, the deposition pressure was maintained at 10 mTorr and the RF power was kept at 100 W and substrate temperature kept at 27 °C. Ar flow ratio of 40 sccm and



(a)

(b)

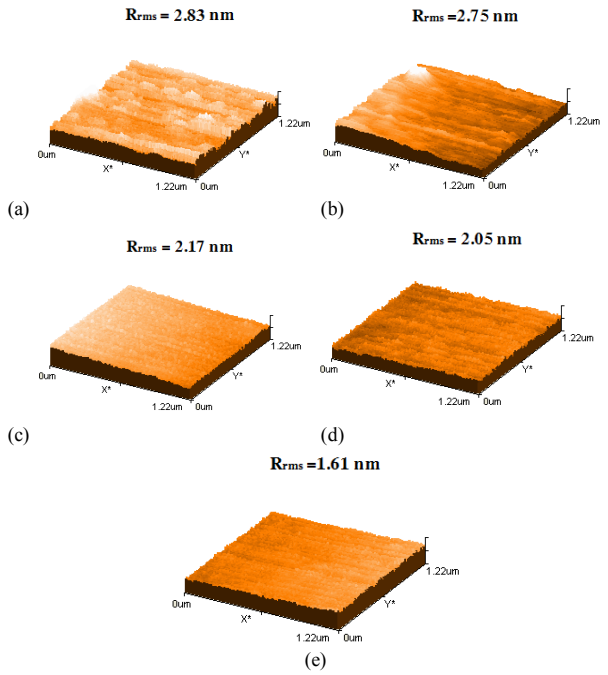
Fig. 1 (a) XRD patterns and (b) full width at half maximum (FWHM) of XRD (002) peaks and the grain size corresponding to the AZO/Mo/AZO films as a function of Mo thickness

working pressure of 4.0 × 10^{-3} Torr. The above-mentioned process conditions are about the best parameters in the experiment for achieving the good opto-electric characteristics.

The thickness of the deposited films was measured by an Alpha-step (α-step, Kosaka Laboratory Ltd. ET-4000). Conventional u–2u XRD was carried out in Rigaku (BRUKER D8 ADVANCE) diffractmeter using Cu Kα radiation to investigate the crystallinity and crystal orientation of the films. The variations of surface morphology and root mean square (RMS) roughness as a function of substrate temperature were evaluated using an atomic force microscope (AFM, NT-MDT Solver P47 system). The carrier concentration (n) and Hall mobility (μ) were measured by the Hall measurement (Ecopia HMS 3000). Optical transmittance was measured using a UV–vis–IR spectrophotometer (JASCO V-670) in the range of 300 – 800 nm.

III. Results and Discussions

Fig. 1(a) shows the XRD plots of the AZO/Mo/AZO films as a function of Mo layer thickness. Strong <002> peaks at 34.5° along with <103> were observed for AZO thin films and indicated polycrystalline nature of the thin films. The diffraction peaks <002> intensity of AZO keeps almost the same, because the top and bottom AZO layer thickness was controlled in the thickness of 30 nm. The <110> peaks at 48.5° of Mo layer in the multilayer thin films were observed. For the film with the Mo layer thickness of 5 nm, the <110> peak was not observed suggesting that the Mo layer surface shows the



(a) (b) (c) (d) (e)

Fig. 2 The AFM images of the AZO/Mo/AZO films as a function of Mo layer thickness of (a) 5 nm, (b) 8 nm, (c) 10 nm, (d) 12 nm and (e) 15 nm

non-continuous and poor quality. The results show the good crystallinity and large grain size of Mo layer thickness of 15 nm due to the smallest full width at half maximum (FWHM) [17].

Fig. 1(b) shows the FWHM of XRD (002) peaks and the grain size corresponding to the AZO/Mo/AZO films as a function of Mo layer thickness. The grain size of the AZO/Mo/AZO films as a function of Mo layer thickness was calculated using Scherrer's formulation [18]:

$$D = \frac{0.9\lambda}{\beta\cos\theta} \quad (1)$$

where $\lambda = 1.54\,\text{Å}$ and β = B-b (B is the observed FWHM and b is the instrument function determined from the broadening of the monocrystalline silicon diffraction line). As the Mo layer thickness increases from 5 to 15 nm, the average crystalline size increases from 15.22 to 16.64 nm. Increasing the crystalline size of AZO/Mo/AZO tri-layer films can decrease grain boundary scattering and increase the carrier lifetime for achieving the lower resistivity of the multilayer films [19].

Fig. 2 shows the AFM images of the AZO/Mo/AZO films as a function of Mo layer thickenss. In each case, the scan area shown is 1.22 μm × 1.22 μm. It is found that the thicker the Mo layer thickness in AZO/Mo/AZO film, the smoother the surface morphology. The AZO/Mo/AZO film with 5 nm to 15 nm thick Mo layer shows the root mean square (RMS) roughness of 2.83 nm to 1.61 nm. It can be seen that the RMS roughness of the multilayer films decreases with increasing of the Mo layer thickness due to the Mo layer was changed from distinct islands

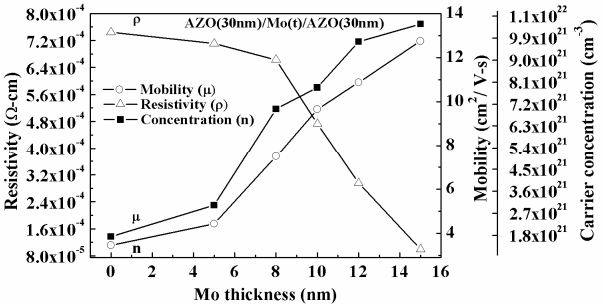


Fig. 3 Electrical resistivity (ρ), Hall mobility (μ) and carrier concentration (n) of the AZO/Mo/AZO films as a function of Mo layer thickness

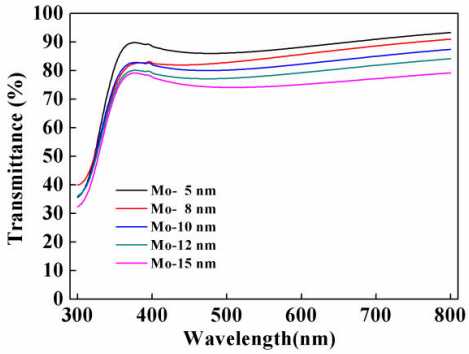


Fig. 4 Optical transmittance spectra of the AZO /Mo/AZO films as a function of Mo layer thickness

to continuous film. Surface roughness is one of the important properties of the TCO thin films for many opto-electronics applications, because the smooth structure can reduce the scattering of incident light, which makes the contribution to increase the transmittance [20].

Fig. 3 shows the electrical resistivity, mobility and carrier concentration of the AZO/Mo/AZO films as a function of Mo layer thickness. As the Mo thickness increases from 5 to 15 nm, the resistivity decreased from 7.44×10^{-4} Ω-cm to 9.98×10^{-5} Ω-cm. Changes in resistivity between 5 nm and 15 nm Mo films can be attributed to transition of Mo atoms from distinct islands to continuous film. The decrease in resistivity can be observed the changes in carrier concentration and mobility. The carrier concentration and mobility increases with increasing Mo layer thickness. The Mo layer could inject electrons into AZO layer and reduce the resistivity of the AZO/Mo/AZO structure. To compare the carrier concentration of the AZO thin films is around 10^{21} cm^{-3} [21], the carrier concentration of AZO/Mo/AZO structure with 15 nm Mo is increased by around ten orders of magnitude to 1.047×10^{22} cm^{-3}. For the change of Hall mobility, many scattering mechanisms have been reported [22, 23]. The highest mobility at a critical Mo thickness of 15 nm for the AZO/Mo/AZO film is around 12.75 cm^2/V-s. Fig. 4 shows the optical transmittance spectra of the AZO/Mo/AZO films as a function of the Mo layer thickness. The optical transmittance of glass substrate is about 90% over the visible range of wavelength. Transmittance spectra of the multilayer films were decrease on thickness of Mo layer increase. The transmittance of the AZO/Mo/AZO structure depends on the

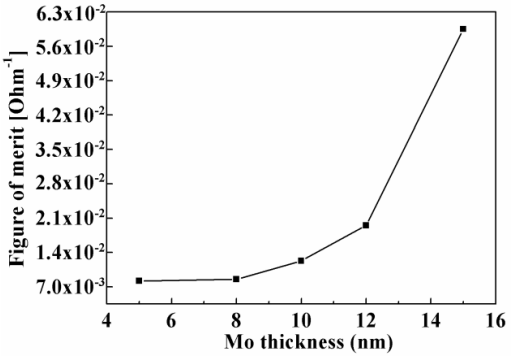


Fig. 5 Figure of merit of the AZO/Mo/AZO films as a function of Mo layer thickness

thickness of Ag layer. The average transmittance of the AZO/Mo/AZO films with Mo layer thickness of 5, 8, 10, 12 and 15 nm show the value of 85.4%, 82.1%, 79.7%, 76.8% and 73.4% in the visible region. The transmittance peaks shows around 380 nm of all AZO/Mo/AZO films. In the short wavelength region, the transmittance is affected by light absorption caused by inter-band electronic transitions [24]. Therefore, the transmittance decreases with increasing Ag layer thickness, more electrons are available for inter-band transitions and result in more light absorption. Fig. 5 shows the figure of merit (FOM) for the AZO/Mo/AZO films as a function of Mo layer thickness. The FOM (φ_{TC}) is calculated for the AZO/Mo/AZO films as follows [25]

$$\varphi_{TC} = T_{av}^{10} / R_s \tag{2}$$

where

$$T_{av} = \frac{\int T(\lambda) f(\lambda) d\lambda}{\int f(\lambda) d\lambda} \tag{3}$$

and Rs is the sheet resistance. f(λ) is the luminous spectral efficiency function defining the standard observer for photometry [26] and T(λ) is the measured transmittance of the AZO/Mo/AZO films. The range of λ is set from 300 to 800 nm. It can be seen that the best FOM ($=5.95 \times 10^{-2}$ Ω^{-1}) is obtained when the Mo layer with 15 nm is continuous to electron conduction. The sheet resistance of 13.31 Ω/sq and the average transmittance values of 73.4% over the visible region are well obtained in the AZO/Mo/AZO film with Mo layer thickenss of 15 nm. The photonic function is a measure of the sensitivity of the human eyes. The method gives a more realistic estimate of the actual merit of the AZO/Mo/AZO films for transparent electronics.

IV. Conclusion

In this paper, the AZO/Mo/AZO thin films were prepared by RF magnetron sputtering. We have investigated the structural, optical and electrical properties of thin films with Mo layer thickness of 5, 8, 10, 12 and 15 nm. The low resistivity of 9.98 × 10-5 Ω-cm, mobility of 12.75 cm2/V-s, carrier concentration of 1.05 × 1022 cm−3, maximum transmittance of 79.13% and

figure of merit of 5.95 × 10-2 Ω-1 were obtained at Mo layer of 15 nm and AZO layer of 30 nm. These results made the AZO/Mo/AZO films be a good candidate for future transparent conductive electrode applications.

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REFERENCES

[1] G. Golan, A. Axelevitch, B. Gorenstein and A. Peled, "Novel type of indium oxide thin films sputtering for opto-electronic applications," Applied Surface Science, vol.253, pp.6608-6611, 2007.
[2] Betz U, Kharrazi, Olsson M, Marthy J, Escola M F and Atamny F, " Thin films engineering of indium tin oxide: Large area flat panel displays application," Surf. Coat. Technol. , Vol. 200, pp. 5751-5759, 2006.
[3] D. Arai, M. Kondo, A. Matsuda, "Reduction of light-induced defects by nano-structure tailored silicon solar cells using low-cost TCO substrates," Sol. Energ. Mater. Sol. Cell, vol. 90, pp. 3174–3178, 2006.
[4] T. Hino,Y. Ogawa and N. Kuramoto, "Preparation of functionalized and non-functionalized fullerene thin films on ITO glasses and the application to a counter electrode in a dye-sensitized," Carbon , vol. 44, pp. 880–887, 2006.
[5] Jin-A Jeong,Yong-Seok Park and Han-Ki Kim, "Comparison of electrical, optical, structural, and interface properties of IZO/Ag/IZO and IZO/Au/IZO multilayer electrodes for organic photovoltaics", J. Appl. Phys. vol. 107, pp. 0233111, 2010.
[6] D.R. Sahu , Shin-Yuan Lin and Jow-Lay Huang, "Investigation of conductive and transparent Al-doped ZnO/Ag/Al-doped ZnO multilayer coatings by electron beam evaporation," Thin Solid Films, vol. 516, pp. 4728-4732, 2008.
[7] Y.S. Jung, Y.W. Choi, H.C. Lee, D.W. Lee, "Effects of thermal treatment on the electrical and optical properties of silver-based indium tin oxide/metal/indium tin oxide structures," Thin Solid Films, vol. 440, pp. 278–284, 2003.
[8] Y. Aoshima, M. Miyazaki, K. Sato, Y. Akao, S. Takaki, K. Adachi, "Development of silver-based multilayer coating electrodes with low resistance for use in flat panel displayers," Jpn. J. Appl. Phys. Vol. 39, pp. 4884-4889, 2000.
[9] E. Ando and M. Miyazaki, "Moisture resistance of the low-emissivity coatings with a layer structure of Al-doped ZnO/Ag/Al-doped ZnO," Thin Solid Films, vol. 392, pp. 289, 2001.
[10] D. R. Sahu and J. L. Huang, "Characteristics of ZnO/Cu/ZnO multilayer films on copper layer properties," Applied Surface Science, vol. 253, pp. 827-832, 2006.
[11] X. Liu, X. Cai, J. Mao, C. Jin, "ZnS/Ag/ZnS nano-multilayer films for transparent electrodes in flat display application," Appl. Surf. Sci., vol. 183, pp. 103, 2001.
[12] Jin-A Jeong, Han-Ki Kim., "Low resistance and highly transparent ITO/Ag/ITO multilayer electrode using surface plasmon resonance of Ag layer for bulk-heterojunction organic solar cells," Solar Energy Materials & Solar Cells, vol. 93, pp. 1801–1809, 2009.
[13] S. Sutthana, N. Hongsith, S. Choopun, "AZO/Ag/AZO multilayer films prepared by DC magnetron sputtering for dye-sensitized solar cell application," Current Applied Physics, vol. 10, pp. 813–816, 2010.
[14] Y.P. Wang, J.G. Lu, X. Bie, Z.Z. Ye, X. Li, D. Song, X.Y. Zhao, W.Y. Ye, "Transparent conductive and near-infrared reflective Cu-based Al-doped ZnO multilayer films grown by magnetron sputtering at room temperature," Applied Surface Science, vol. 257, pp. 5966–5971, 2011.
[15] M. Fahland, P. Karlsson, C. Charton, "Low resistivity transparent electrodes for display on polymer substrates," Thin Solid Films, vol. 392, pp.334-337, 2001.
[16] G. Gordillo, F. Mesa, and C. Calderon, "Electrical and Morphological Properties of Low Resistivity Mo thin Films Prepared by Magnetron Sputtering," Brazilian Journal of Physics, vol. 36, pp. 982, 2006.
[17] X.T. Hao, L.W. Tan, K.S. Ong and F. Zhu, "High-performance low-temperature transparent conducting aluminum doped ZnO thin films and applications," Journal of Crystal Growth, vol. 287, pp. 44, 2006.
[18] B.D. Cullity, "Elements of X-ray Diffraction, " 2nd ed, Addison-Wesley, New York, chap.3, pp. 102, 1978.
[19] Hung-Wei Wu, Ru-Yuan Yang, Chin-Min Hsiung, Chien-Hsun Chu, "Effects of Ar Flow on the Optoelectronic Characteristics of Aluminum-doped Zinc Oxide (AZO) Thin Films Prepared by RF Magnetron Sputtering," International Symposium on Computer Consumer and Control," pp. 309-312, 2012.
[20] [20] M. Suchea, S Christoulakis, N. Katsarakis, T. Kitsopoulos and G. Kiriakidis, "Comparative study of ZnO and Al-doped ZnO transparent thin films grown by DC magnetron sputtering", Thin Solid Films, vol. 515, pp. 6562-6566, 2007.
[21] M. Bender, W. Seelig, C. Daube, H. Frankenberger, B. Ocker, and J. Stollenwerk, "Dependence of oxygen flow on optical and electrical properties of DC-magnetron sputtered ITO films," Thin Solid Films, vol. 326, pp. 72-77, 1998.
[22] Z.L. Pei, C. Sun, M.H. Tan, J.Q. Xiao, D.H. Guan, R.F. Huang, L.S. Wen, "Optical and electrical properties of direct-current magnetron sputtered ZnO:Al films," J. Appl. Phys. Vol. 90, pp. 3432, 2001.
[23] A. Indluru, T.L. Alford, "Effect of Ag thickness on electrical transport and optical properties of indium tin oxide/Ag/indium tin oxide multilayers", J. Appl. Phys. vol.105, pp. 123528, 2009.
[24] Park K C, Ma D Y and Kim K H., "The physical properties of Al doped zinc oxide films prepared by RF magnetron sputtering," Thin Solid Films. vol. 305, pp. 201-209, 1997.
[25] K. Sivaramakrishnan, N. D. Theodore, J. F. Moulder and T. L. Alford, "The role of copper in ZnO/Cu/ZnO thin films for flexible electronics," J. Appl. Phys. vol. 106, pp. 063510, 2009.
[26] G. Haacke, "New figure of merit for transparent conductors", J. Appl. Phys. vol. 47, pp. 4086–4089, 1976.