Journal of Alloys and Compounds 522 (2012) 69–73

Contents lists available at SciVerse ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

# Dependence of the properties of sputter deposited Al-doped ZnO thin films on base pressure

Deok-Kyu Kim[a,*], Hong-Bae Kim[b]

[a] *Advanced Development Group, Samsung LED Co. Ltd., Yongin 446-711, Gyeonggi, Republic of Korea*
[b] *Division of Electronics and Information Engineering, Cheongju University, Cheongju 360-746, Chungbuk, Republic of Korea*

A R T I C L E I N F O

*Article history:*
Received 7 November 2011
Received in revised form 5 January 2012
Accepted 15 January 2012
Available online 28 January 2012

*Keywords:*
Al-doped ZnO
Base pressure
RF magnetron sputtering
Zn—O bond
Oxygen vacancy
Figure of merit

A B S T R A C T

Al-doped ZnO (AZO) thin films were prepared on glass substrates by RF magnetron sputtering at room temperature. The dependence of electrical, structural, and optical properties on the base pressure was investigated. The lower base pressures for AZO thin film deposition resulted in improved electrical conductivity owing to an increase in the carrier concentration and mobility, giving a resistivity as low as $7.3 \times 10^{-4}\ \Omega$ cm. The improved conductivity is attributed to increased Zn—O bond formation and a subsequent increase in oxygen vacancies as the base pressure is reduced. The average transmittance of all the thin films deposited was above 84% in the visible spectrum. With decreasing base pressure, the figure of merit for the AZO thin film improved linearly. The control of base pressure plays a major role in the subsequent properties of AZO thin films deposited at room temperature.

© 2012 Elsevier B.V. All rights reserved.

## 1. Introduction

Al-doped ZnO (AZO) has several potential applications as a transparent conducting oxide (TCO) electrode in solar cells, light emitting diodes and transparent thin film transistors [1–3]. It has attracted attention because its high optical transmittance and low electrical resistivity. AZO is a nontoxic, low-cost, abundant material, with higher thermal stability, and it is less susceptible to hydrogen plasma processing damage than the more widely used indium tin oxide (ITO). AZO can also be deposited at lower temperatures, leading to TCO applications that are sensitive to process temperature. AZO thin films can be prepared by various methods such as RF magnetron sputtering [4], pulsed laser deposition [5], and chemical vapor deposition [6]. RF magnetron sputtering is the preferred deposition method because it offers room-temperature processing and easy control of the electrical properties of films by adjusting processing parameters such as RF power, working pressure and substrate temperature [7–9]. Although the effects of varying the parameters in RF magnetron sputtering upon film deposition have been reported by several researchers, no previous studies have reported on the electrical properties of AZO thin films deposited in a regime where differing base pressures have been applied. Previous work on ITO thin films has suggested that chamber base pressure prior to film deposition affects the resistivity of films deposited in the manner [10–12].

In this study, we determined how chamber base pressures impacts on the structural, optical, and electrical properties of AZO thin films deposited at room temperature using RF magnetron sputtering. We also investigated the effect of chemical bonding on the film properties by an XPS study.

## 2. Experimental procedure

AZO thin films were deposited on glass substrates (Corning 1737) using an RF magnetron sputtering system. A 3-in AZO ceramic target (mixed with 2 wt% $Al_2O_3$) was loaded on the cathode 55 mm from the substrate stage. The substrate surfaces were cleaned in an ultrasonic bath for 10 min with acetone, methanol, and deionized water, and then blown dry with nitrogen before being loaded into the sputtering system. The sputter chamber was evacuated using a turbomolecular pump before introducing the sputtering argon gas, which was oxygen-free and of high purity. The base pressure was varied to following values: $0.8 \times 10^{-6}$ Torr, $2.0 \times 10^{-6}$ Torr, and $4.0 \times 10^{-6}$ Torr. In order to minimize possible plasma damage to the substrates, a low RF power of 25 W was used. The deposition process was performed in an Ar mass-controlled flow of 60 sccm at a deposition pressure of $2.0 \times 10^{-2}$ Torr. The AZO thin films were deposited at room temperature with a thickness of 250 nm.

The film electrical properties were measured at room temperature using a Hall measurement system (ECOPIA HMS-3000). X-ray photoelectron spectroscopy (XPS, THERMO VG SCIENTIFIC MultiLab2000) was used to investigate chemical bonding. The crystal properties of the different AZO thin films were inspected using X-ray diffraction (XRD, Phlilips X'pert), employing Cu Kα (λ = 1.5406 Å) radiation. The optical properties were analyzed using a spectrophotometer (JASCO UV/VIS/NIR) in the wavelength range of 250–1000 nm.

* Corresponding author. Tel.: +82 10 8222 7669; fax: +82 43 229 8461.
*E-mail address:* maruchi111@naver.com (D.-K. Kim).

0925-8388/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2012.01.078

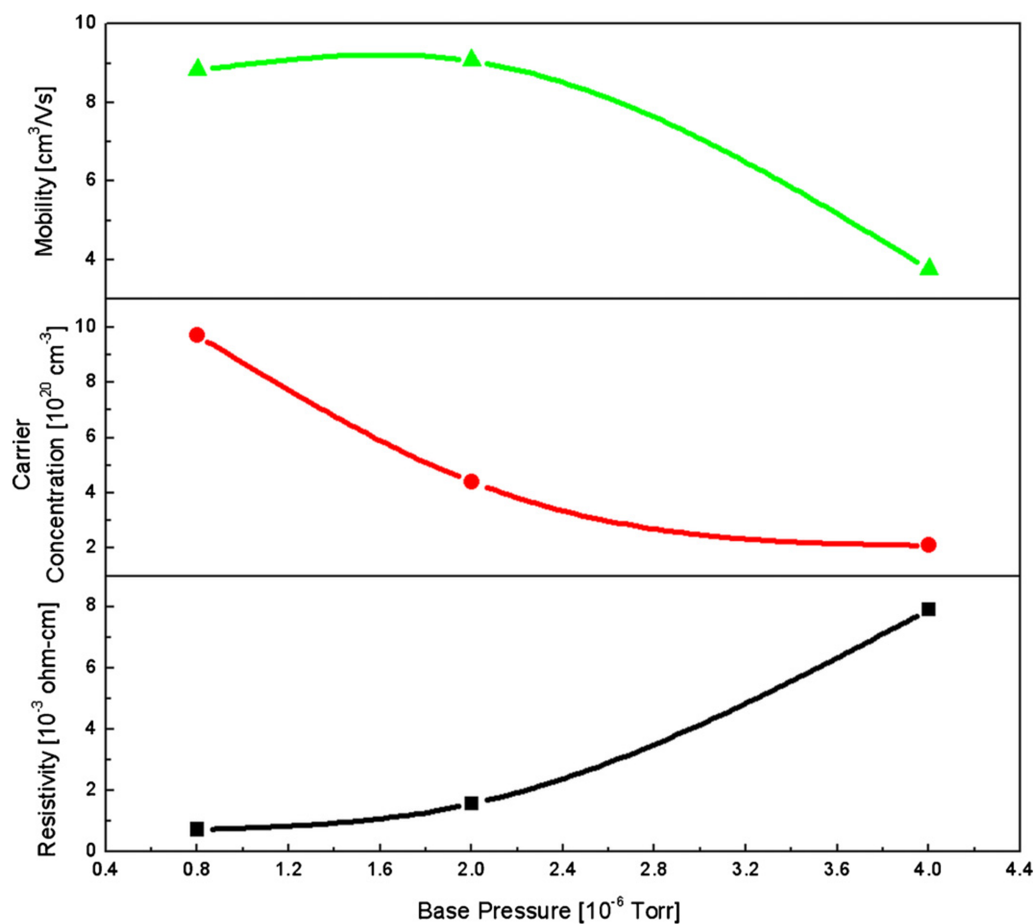


**Fig. 1.** Electrical resistivity, carrier concentration and mobility of AZO thin films deposited on glass substrates at room temperature as a function of the base pressure.

## 3. Results and discussions

Electrical parameters such as electrical resistivity ($\rho$), carrier concentration ($n$), and mobility ($\mu$) of the AZO thin films as measured by the Hall system are shown in Fig. 1. All the films showed n-type behavior, as confirmed from the signature of Hall coefficient. With decreasing initial base pressure, the electrical resistivity decreases whilst both the carrier concentration and the mobility increase. These results are similar to those obtained for ITO thin films deposited by magnetron sputtering [10]. The best electrical properties were obtained at $0.8 \times 10^{-6}$ Torr: $\rho$ of $7.3 \times 10^{-4}\,\Omega$ cm, $n$ of $9.7 \times 10^{20}$ cm$^{-3}$, and $\mu$ of 8.82 cm$^3$/Vs. The measured decrease in the resistivity is due to an increase both in the carrier concentration and in the mobility. We suggest that the resistivity is mainly affected by the mobility when the base pressure is decreased from $4 \times 10^{-6}$ Torr to $2 \times 10^{-6}$ Torr (so-called first decrease), whereas the change is mostly influenced by the carrier concentration when the base pressure is decreased from $2 \times 10^{-6}$ Torr to $0.8 \times 10^{-6}$ Torr (so-called second decrease). This conduction behavior under differing base pressure is discussed in detail later in the text.

To investigate the influence of chemical state on the electrical properties, the XPS spectra of each element in the AZO thin films were analyzed. All atomic spectra were calibrated by using the hydrocarbon C 1 s peak at 284.6 eV as a reference. The Zn $2p_{3/2}$ and Al $2p_{3/2}$ core lines (not shown here) exhibit a highly symmetric shape centered at 1021.79 eV and 74 eV, respectively, which corresponds to Zn—O bonds and Al—O bonds in AZO [13]. No metallic Zn or Al with binding energies of 1021.5 eV [14] and 72.7 eV [15] was observed. This confirms that Zn and Al exist only in oxidized states. The O 1s spectra show asymmetrical features (Fig. 2) for films deposited at different base pressures. For a careful analysis of this asymmetrical behavior, the O 1s peak of AZO was fitted with 90% Gaussian and 10% Lorentzian mixed lineshape functions. These O 1s core level features can be deconvoluted into three components at binding energies of 529.9 eV, 531.35 eV, and 532.6 eV. The fitted results indicate that each component has a full width at half maximum (FWHM) of less than 1.9 eV. The low and medium energy components are related to $O^{2-}$ with the different binding structures. It has been previously reported that for $O^{2-}$ions in

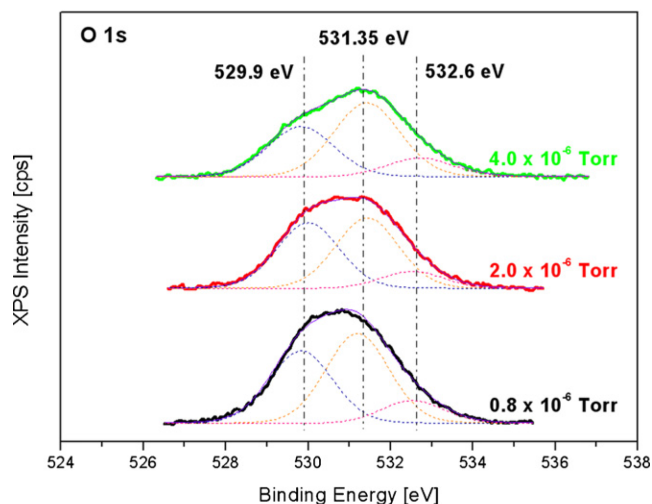


**Fig. 2.** O 1s XPS spectra of AZO thin films under various base pressures.

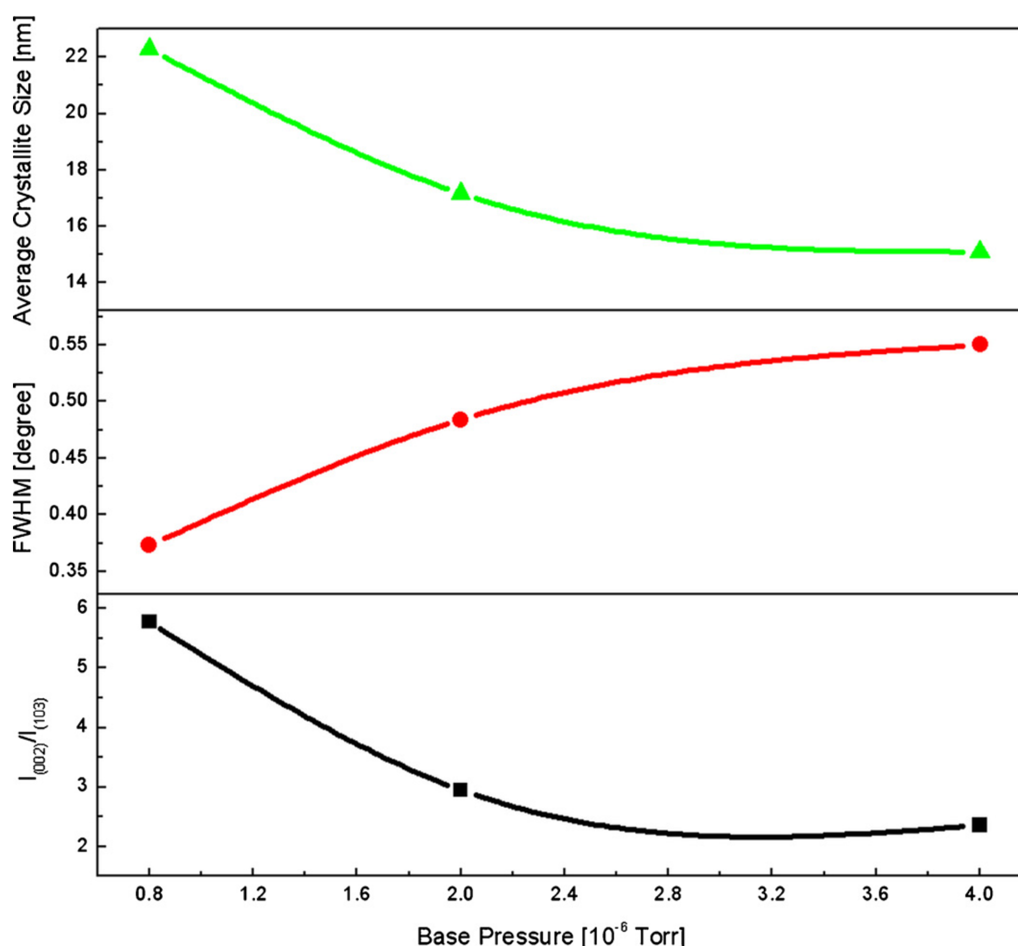


**Fig. 3.** XRD results of AZO thin films as a function of the base pressure.

AZO thin films with a full stoichiometric arrangement of Zn or Al atoms, there is a peak located at 529.9 eV (low binding energy) [16]. $O^{2-}$ ions located in oxygen-deficient regions in AZO thin films give a peak at 531.35 eV (medium binding energy) [17]. The high binding energy peak at 532.6 eV originates from adsorbed species such as $O_2$, $H_2O$, and CO owing to surface hydroxyl groups [18]. The relative changes in intensity of the low and medium binding energy components therefore indicate the degree of O—Zn bonding and oxygen vacancies, respectively. The intensity of O—Zn bonding increases at the first decrease in the base pressure and saturates at the second decrease. The intensity of the peak in oxygen-deficient areas is constant at the first decrease but increases at the second decrease. The formation of the O—Zn bonds was initially enhanced at the first decrease of the base pressure and then an oxygen deficiency was promoted at the second decrease. These behaviors are consistent with the conduction characteristics mentioned above. At the first decrease of the base pressure, the mobility increases owing to an improvement in crystallinity, as is evident from the O—Zn bonding. At the second decrease, the carrier concentration is enhanced by an increase in oxygen vacancies. Both these mechanisms cause a reduction of the resistivity with a reduction in base pressure. Low base pressure generally minimizes the effect of residual gases such as $N_2$, $O_2$, and $H_2O$ in the process chamber. Rogozin et al. have reported that the increase in the amount of impurities with increasing the base pressures leads to a chemical reduction in the ITO thin film, resulting in the formation of non-stoichiometric structures [10]. Lee et al. have reported increase in the measured lattice constant for films deposited at higher sputtering base pressures, which they attributed to the interstitial or substitution incorporation of impurities from residual gases into the lattice [11]. On the basis of the large number of O—Zn bonds at intermediated pressures, we suggest that the reduced impurity levels result in better structure; in contrast, at the lowest pressure, there is some measure of reduction, which results in the formation of oxygen vacancies. The change between crystallinity and oxygen deficiency with decreasing the base pressure is attributed to behavior of $H_2O$, which start to reduce at high vacuum condition (<$10^{-6}$ Torr) [19]. These experimental data show that base pressure is an important factor in determining the nature of bonding in AZO thin films and that it has implications for the conductivity of AZO thin films deposited at room temperature.

The crystalline structure of the AZO thin films was analyzed by XRD. Fig. 3 shows XRD curves for the AZO thin films. All three films have a strong crystalline peak located at the $2\theta$ position of 34.4° and a weak crystalline peak at 62.8°, which correspond to the (0 0 2) peak and (1 0 3) peak, respectively, regardless of the base pressure. This indicates that all the AZO thin films are polycrystalline with a hexagonal structure and have a well-defined *c*-axis orientation perpendicular to the substrate. No data for an $Al_2O_3$ phase is found, which implies that Al atoms substitute Zn in the hexagonal lattice, Al ions may also occupy the interstitial sites of ZnO or that Al segregates to the non-crystalline region in the grain boundary and forms Al—O bonds [20]. The intensity ratio of the (0 0 2) and (1 0 3) peaks, which is $I_{(0\,0\,2)}/I_{(1\,0\,3)}$, becomes stronger with decreasing base pressure. In case of $0.8 \times 10^{-6}$ Torr, the intensity of (0 0 2) peak is 5.7 times that of the (1 0 3) peak, which indicates highly *c*-axis oriented crystallographic growth. The FWHM of AZO thin films with decreasing base pressure, implying an enhancement in the

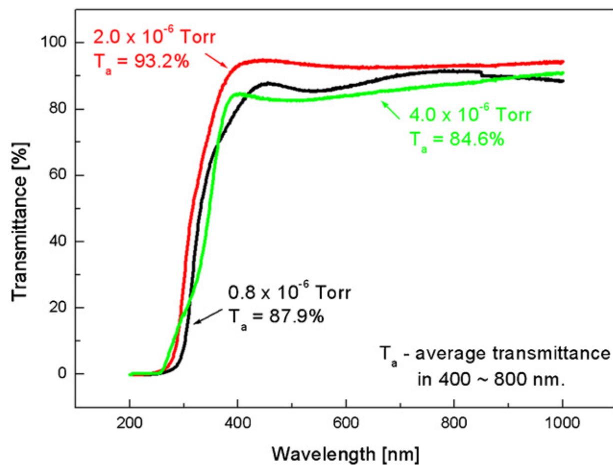


**Fig. 4.** Optical transmittance spectra in light wavelength of AZO thin films under various base pressures.

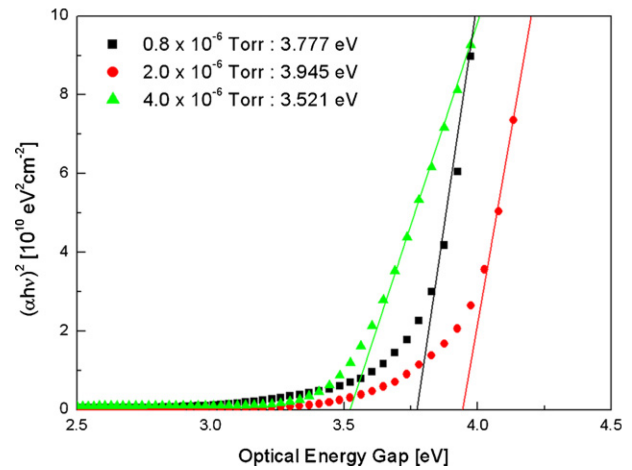


**Fig. 5.** Variation of the optical energy bandgap for AZO thin films as a function of the base pressure.

crystallinity. It suggests that low base pressure improves crystallinity owing to reduced incorporation of impurity atoms into the AZO films. These results agree with those of the XPS study, mentioned above. According to Scherrer's formula [21], the average crystallite size, which is the length of the crystal in the direction of the *d*-spacing, can be calculated using the FWHM. In line with this, our data suggest that the average crystallite size increases when the films are deposited from low base pressure, giving rise to more crystalline films.

Fig. 4 shows the transmittance spectra of AZO thin films of 250 nm thickness prepared at different base pressures in the 200–1000 nm wavelength region. In the visible spectrum, all the AZO thin films are highly transparent (>80% on average). The average transmittance ($T_a$) in the visible wavelength region (400–800 nm) increases and then decreases as the base pressure decreases. The highest transmittance (93.2%) was obtained for the film deposited at moderate base pressure, $2.0 \times 10^{-6}$ Torr. This, together with the conductivity results mentioned earlier, confirms

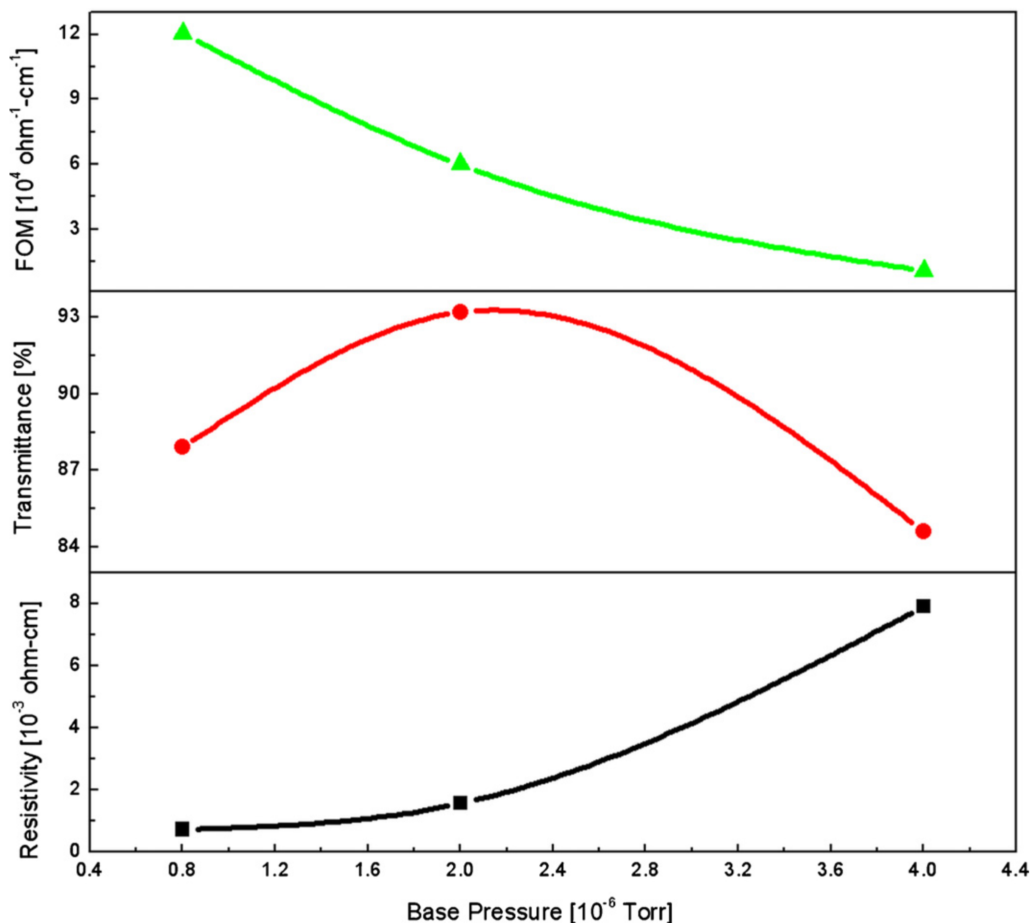


**Fig. 6.** Effect of the base pressure on the figure of merit of AZO thin films.

that the AZO thin films prepared under these conditions are highly suitable for application to thin film optical devices. The absorption edge, which is related to the optical energy gap, shifts toward shorter wavelength and then back to the longer wavelength with a decrease in base pressure. The optical energy gap ($E_g$) of the thin films was calculated by using the value of $\alpha$ in the following equation for direct band semiconductors [22]: $\alpha(h\nu) = C(h\nu - E_g)^{1/2}$, where $h$ is Planck's constant and $\nu$ is the frequency of the incident photon; $C$ is independent of frequency. The optical absorption coefficient ($\alpha$) is defined as $\alpha = \ln(1/T)/d$, where $d$ is the thickness of the AZO thin films [23]. Fig. 5 shows the plots of $(\alpha h\nu)^2$ versus the optical energy gap. The energy gap can be obtained from the intercept of the linear absorption edge part with the energy axis. When $(\alpha h\nu)^2$ is zero, then the photon energy is equal to the optical energy gap. As was seen in the transmittance spectra, the optical energy gap increases and then decreases with a decrease in the base pressure. The highest optical energy gap of 3.945 eV was observed for in $2.0 \times 10^{-6}$ Torr. In general, the increasing carrier concentration correlates well with the widening of the bad gap, which is related to the Burstein–Moss shift and is due to filling of states at the bottom of the conduction band, which results in an increase in the band gap [24,25]. However, a decrease in the band gap to 3.521 eV for $N > 3.407 \times 10^{20}$ cm$^{-3}$ in $2.0 \times 10^{-6}$ Torr can be attributed to a basic change in the band structure of the material [26]. For device application, a band gap of >3 eV is required, which is already exhibited by the films synthesized in this study [27].

To confirm the suitability of the AZO thin film as TCOs, the figure of merit (FOM), which is a ratio of optical properties to electrical properties, was calculated; the results are given in Fig. 6. The FOM was calculated using the following equation: $\Phi = T/\rho$, where $T$ is the average transmittance in the visible spectrum and $\rho$ is the resistivity of AZO thin film [28]. With decreasing base pressure, the FOM of the AZO thin film increases linearly, in line with electrical conductivity, data, which influences the FOM to a greater extent than the optical transmittance. The highest FOM value was found to be $12 \times 10^4$ $(\Omega\,\text{cm})^{-1}$, achieved at a base pressure of $0.8 \times 10^{-6}$ Torr. This high FOM for the AZO thin films deposited at room temperature implies that they are suitable for application as transparent contacts in various optoelectronic devices.

## 4. Conclusion

In this study, the properties of sputtered AZO thin films deposited at different base pressures were investigated. It was found that the base pressure is a critical factor influencing the properties of the films. The AZO films deposited at low base pressure showed the best crystallinity, lowest resistivity, and highest FOM. The optical properties of AZO thin films were less affected by the base pressure. The conductivity behavior as a function of base pressure is attributed to enhanced Zn—O bond formation and oxygen vacancy formation with a reduction in the pressure. Therefore, we conclude that the control of base pressure is an important factor in the fabrication of AZO transparent electrodes for optoelectronic devices.

## References


[1] S.W. Cho, Y.T. Kim, W.H. Shim, S.Y. Park, K.D. Kim, H.O. Seo, N.K. Dey, J.H. Lim, Y.S. Jeong, K.H. Lee, Y.D. Kim, D.C. Lim, Appl. Phys. Lett. 98 (2011) 023102.
[2] C.H. Kuo, C.L. Yeh, P.H. Chen, W.C. Lai, C.J. Tun, J.K. Sheu, G.C. Chi, Electrochem. Solid-State Lett. 11 (2008) H269.
[3] K.S. Jang, H.S. Park, S.W. Jung, N.V. Duy, Y.K. Kim, J.H. Cho, H.W. Choi, T.Y. Kwon, W.B. Lee, D.Y. Gong, S.M. Park, J.S. Yi, D.Y. Kim, H.J. Kim, Thin Solid Films 518 (2010) 2808.
[4] D.K. Kim, H.B. Kim, J. Alloys Compd. 509 (2011) 421.
[5] M.Y. Zhang, G.J. Cheng, Appl. Phys. Lett. 98 (2011) 051904.
[6] W.H. Kim, W.J. Maeng, M.K. Kim, H.J. Kim, J. Electrochem. Soc. 158 (2011) D495.
[7] S.Y. kuo, K.C. Liu, F.I. Lai, J.F. Yang, W.C. Chen, M.Y. Hsieh, H.I. Lin, W.T. Lin, Microelectron. Reliab. 50 (2010) 730.
[8] C.H. Tseng, W.H. Wang, H.C. Chang, C.P. Chou, C.Y. Hsu, Vaccum 85 (2010) 263.
[9] R. Wen, L. Wang, X. Wang, G.H. Yue, Y. Chen, D.L. Peng, J. Alloys Compd. 508 (2010) 370.
[10] A.I. Rogozin, M.V. Vinnichenko, A. Kolitsch, W. Moller, J. Vac. Sci. Technol. A 22 (2004) 349.
[11] B.H. Lee, I.G. Kim, S.W. Cho, S.H. Lee, Thin Solid Films 302 (1997) 25.
[12] M.G. Zebaze Kana, E. Centurioni, D. Iencinella, C. Sumonte, Thin Solid Films 500 (2006) 203.
[13] L. Li, L. Fang, X.J. Zhou, Z.Y. liu, I. Zhao, S. Jiang, J. Electron Spectrosc. Relat. Phenom. 173 (2009) 7.
[14] M.N. Islam, T.B. Ghosh, K.L. Chopra, H.N. Acharya, Thin Solid Films 280 (1996) 20.
[15] C.D. Wagner, W.M. Riggs, L.E. Davis, J.F. Moulder, G.E. Muilenberg, Handbook of X-ray Photoelectron Spectoscopy, PerkinElmer Corporatio, Eden Prairie, Mn, 1979, pp. 50–51.
[16] V.I. Nefedov, M.N. Firsov, I.S. Shaplygin, J. Electron Spectrosc. Relat. Phenom. 26 (1982) 65.
[17] J.C. Fan, J.B. Goodenough, J. Appl. Phys. 48 (1977) 3524.
[18] S. Major, S. Kumar, M. Bhatnagar, K.L. Chopra, Appl. Phys. Lett. 40 (1986) 394.
[19] K.D. Vargheese, G.M. Rao, T.V. Blasubramanian, S. Kumar, Mater. Sci. Eng. B 83 (2001) 242.
[20] X.T. Hao, L.W. Tan, K.S. Ong, F. Zhu, J. Cryst. Growth 287 (2006) 44.
[21] B.D. Cullity, Elements of X-ray Diffraction, Addison-Wesley, Reading, MA, 1978, p. 102.
[22] J.I. Pankove, Optical Processes in Semiconductors, Dovr, New York, 1976.
[23] H.R. Fallah, M. Ghasemi, A. Hassanzadeh, H. Steki, Mater. Res. Bull. 42 (2007) 487.
[24] L. Burstein, Phys. Rev. 93 (1954) 632.
[25] T.S. Moss, Proc. Phys. Soc. Lond. Ser. A 382 (1954) 775.
[26] E. Aperathitis, M. Bender, V. Cimala, G. Ecke, M. Modreamu, J. Appl. Phys. 94 (2003) 1258.
[27] C.G. Granqvist, A. Hultake, Thin Solid Films 411 (2002) 1.
[28] H.A. Mohamed, J. Phys. D: Appl. Phys. 40 (2007) 4234.