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IZO/Al/GZO multilayer films to replace ITO films

Chongmu Lee · R. P. Dwivedi · Wangwoo Lee · Chanseok Hong · Wan In Lee · Hyoun Woo Kim

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Abstract Multilayer transparent conducting oxide (TCO) film structures have been designed and fabricated to achieve both high conductivity and high transmittance. In this article we report a buffering method and introduction of an aluminum (Al) interlayer to enhance the electrical conductivity of the IZO/Al/GZO/ZnO multilayer film on glass. Hall measurement results show that this multilayer film has a remarkable increase in mobility compared to those without using an Al interlayer. The surface morphology shows a decrease in surface roughness as the Al layer thickness increases. We have shown that the use of a thin Al interlayer enhances the electrical conductivity without sacrificing its optical transmittance much. By optimizing the thickness of the Al layer, the lowest resistivity of $2.2 \times 10^{-4}\ \Omega$ cm and an average transmittance higher than 75% in a range from 400 to 800 nm have been achieved. These properties are acceptable for future TCO applications.

1 Introduction

Transparent conducting oxides (TCOs) are critical components in flat-panel displays, solar cells, window deicers, gas sensors, thin film resistors, photovoltaic devices, liquid crystal displays, organic light emitting diodes (LED) and smart windows [1–4]. Other applications include optical filters, heat mirrors, and low emittance films for advanced glazing, protective, or decorative coatings [5]. Generally tin-doped indium oxide (ITO) is a preferred TCO material for these applications because of its favorable electrical and optical properties. One disadvantage of the use of ITO is its cost. As indium is very rare and expensive (almost US$1400/kg), it is not the most economical choice for mass production of devices utilizing TCO films [3].

Very recently, several groups have realized that sufficiently low resistivity of $1–2 \times 10^{-4}\ \Omega$ cm with high transmittance above 80% in visible range can be obtained by using gallium-doped zinc oxide (GZO) films [6]. The slightly smaller bond length of Ga–O than that of Zn–O is an advantage since it allows minimizing the deformation of the ZnO lattice even in the case of high Ga concentration in GZO [7]. Indium-doped zinc oxide (IZO) has also been reported to be an ideal TCO material for optoelectronic devices, solar cells, and organic LEDs, due to a large work function, a wide transmittance window from 400 to 2,500 nm, and a higher chemical etching rate in comparison with ITO thin films [8]. Amorphous IZO thin films are increasingly replacing ITO for use in transparent conductor applications in manufacturing flat panel displays [9].

There are some reports on improved ITO thin films with a thin ZnO buffer layer or with an ITO/Ag/ITO multilayer [10, 11]. Also quite recently, ZnO was found to be a good buffer layer for the growth of gallium nitride, and a room temperature lasing material [10]. A buffer layer reduces or eliminates undesired interaction between substrate and transparent conducting film. For example, a buffer layer can reduce or eliminate migration of impurities. It can also reduce or eliminate chemical reactions. In general, a buffer

C. Lee (✉) · R. P. Dwivedi · W. Lee · C. Hong · H. W. Kim
Department of Material Science and Engineering, Inha University, 253 Yonghyeon-dong, Incheon 402-751, Republic of Korea
e-mail: cmlee@inha.ac.kr

W. I. Lee
Department of Chemistry, Inha University, 253 Yonghyeon-dong, Incheon 402-751, Republic of Korea

layer isolates transparent conducting film from the substrate [12, 13].

In order to get higher conductivity with higher transparency and multifunctionality, TCOs have been incorporated in multilayer stacks. For example, Kawashima et al. [14] reported that F-doped SnO_2-coated ITO shows improved thermal stability versus ITO with conductivity retained during solar cell processing at 400–600 °C. Martin et al. [3] reported pulsed laser-deposition-derived TCO double layers consisting of Sn-doped CdO, $CdIn_2O_4$, and Cd_2SnO_4,which show higher conductivity than ITO with comparable optical transparency. Furthermore, efforts have been made to develop multilayer TCO consisting of oxide/metal/oxide. These include an early development of ZnO/Ag/ZnO and ITO/Ag/ITO for reactive coatings [15], ITO/CuAg/ITO for low-cost [16] TCO, ZnS/Ag/ZnS for electrochromics [17], and TiO_2/Ag/TiO_2 for dye-sensitized solar cells [18]. Very recently Jyh-Ming et al. [5] have investigated a nano-scaled sandwich multilayer TCO thin film structure consisting of two outer layers of ZnO and an interlayer of an ultra-thin aluminum thin film for the improvement of the electrical conductivity of the ZnO. Therefore, multilayer TCOs structures have the potential to achieve greater functionality than single-layer TCOs by selecting an appropriate layer structure and designing the appropriate properties of component materials [19].

As a part of efforts to develop multilayer TCO thin films, we have investigated multilayer thin film consisting IZO/Al/GZO/ZnO film on the glass substrate using RF and DC sputtering techniques. To our knowledge, such combination for a multilayer TCO have not been yet properly investigated. Here ZnO film acts as a buffer layer over the glass substrate. In this study, the optical transmittance and electrical resistance of IZO/Al/GZO/ZnO film on the glass substrate have been investigated and compared with that of the single ITO–glass system.

2 Experimental

The IZO/Al/GZO/ZnO multilayers films were deposited at room temperature on glass substrates (Corning 1737F) by a sequential RF sputtering of ZnO, GZO (Ga_2O_3: 3 wt%, ZnO:97 wt%), IZO (In_2O_3: 10 wt%, ZnO: 90 wt%) and DC sputtering of Al (Al purity: 99.999% Al). Prior to each deposition, the target was cleaned by sputtering in an argon atmosphere for 10 min. The substrates were isolated from the plasma by a shutter during the pre-sputtering. The glass substrates were previously cleaned with a washing agent (commercial detergent and deionized water) before loading. For each film deposition process sequence, the chamber is initially evacuated to a base pressure of 1×10^{-6} Pa. The distance between the substrate and the target was fixed at 7 cm and the RF power was maintained at 150 W for AZO and IZO, 70 W for ZnO, respectively, for all RF sputter-deposition processes. Structure analyses were performed by using an X-ray diffractometer (Rigaku 2500 PC) based on Cu Kα radiation. The surface morphology and the film thickness of each layer were measured by scanning electron microscopy (SEM) and atomic force microscopy (AFM), respectively. The electrical resistivity, free carrier concentration and Hall mobility were determined by using a Hall effect measuring system (HEM-2000) using the van der Pauw method. Optical transmission through the film was measured in the wavelength range from 300 to 1,000 nm by means of a UV/VIS spectrophotometer.

3 Results and discussion

Figure 1 shows the resistivities, the carrier concentrations and the carrier mobilities of IZO/Al/GZO/ZnO multilayer films with different Al thicknesses. The thicknesses of the Al layers were varied from 5 to 20 nm. It is apparent from this figure that the sheet resistance decreases rapidly from 5 to 15 nm and has reached to the lowest value of 1.02×10^{-4} Ω cm for the Al interlayer thickness of 15 nm and then increases as the Al layer thickness increases. A comparison of the sheet resistance of the whole multilayer system in Fig. 1 with that of the Al layer leads to a conclusion that the conductivity of the multilayer is mainly due to the metal Al layer, as the electrical conductivity of an Al metal layer is almost 100 times higher than those of IZO and GZO layers. However, the main function of the GZO and IZO layers in the multilayer is to enhance transmission in

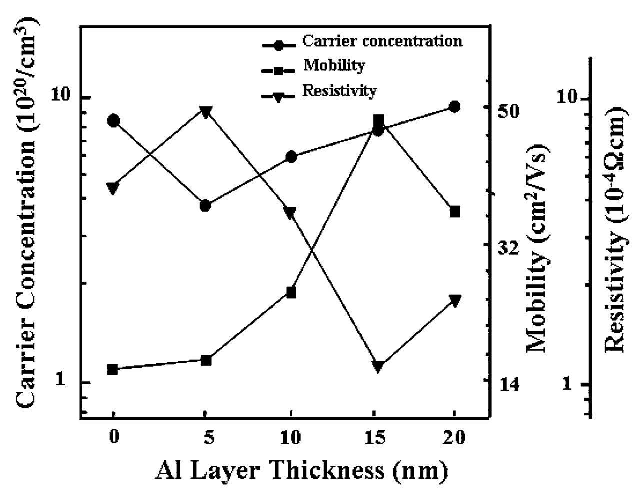

Fig. 1 Dependence of the carrier concentration, the carrier mobility and the resistivity of the IZO/Al/GZO/ZnO multilayer film on the thickness of the Al interlayer

the visible spectral range rather than conductivity. An increase in the thickness of the Al layer is not allowed beyond a certain level for high transmittance. As the thickness of the Al layer increases, the transmittance of the multilayer system decreases and the reflection increases as the film becomes a mirror. Optimization of the thickness of each layer including the Al interlayer is necessary for maximum transmittance [20].

From Fig. 1 it is also clear that the carrier mobility increases from 16 to 45 $cm^2 V^{-1} s^{-1}$ and correspondingly the resistivity decreases from 9×10^{-4} to 2.2×10^{-4} Ω cm as the Al layer thickness is increased from 5 to 15 nm. Yet, reverse is the case as the Al layer thickness is increased further. Increasing the mobility of charge carriers in a TCO material will allow the conductivity to increase without compromising the transparency, thereby enhancing the overall performance of the TCO material. A strong increase in carrier mobility by increasing the Al thickness may be related to the change in film morphology. It may be due to a decrease in grain boundary scattering in the film. Another reason may be owing to a decrease in quantum size effect as the quantum confinement effect degrades carrier transport and hence degrades the mobility, when the film thicknesses are decreased below a certain level [21]. In general, the resistivity of a film is determined by carrier concentration and mobility. Since the increase rate in carrier mobility (300%) shown in Fig. 1 due to the use of an Al interlayer is higher than those compared with the increase in carrier concentration (200%), it is clear that the improved electrical property is mainly due to the increase in mobility [22]. The reduction in electrical resistivity due to the use of an Al interlayer can also be explained as below. The total resistance (R_s) of a multilayer is a combination of the resistances of four consecutive layers in parallel as follows:

$$\frac{1}{R_s} = \frac{1}{R_{ZnO}} + \frac{1}{R_{GZO}} + \frac{1}{R_{Al}} + \frac{1}{R_{IZO}} \quad (1)$$

Since R_{Al} is much less than other resistances. The total resistance$R_s$would have a much lower value for a multilayer film with an Al interlayer than for that without an Al interlayer.

Dependence of the transmittance of the multilayer in the visible region on the Al layer thickness is shown in Fig. 2. The experimental data presented in this work contain the transmission of the multilayer including the glass substrate. A metal is normally opaque. However, if a metal film is extremely thin, it is transparent. The film shows various degrees of optical transmittance in the visible light region, and the transmittance decreases as the Al layer thickness is increased. The fluctuation in the transmittance of the film is probably caused by the interference between different

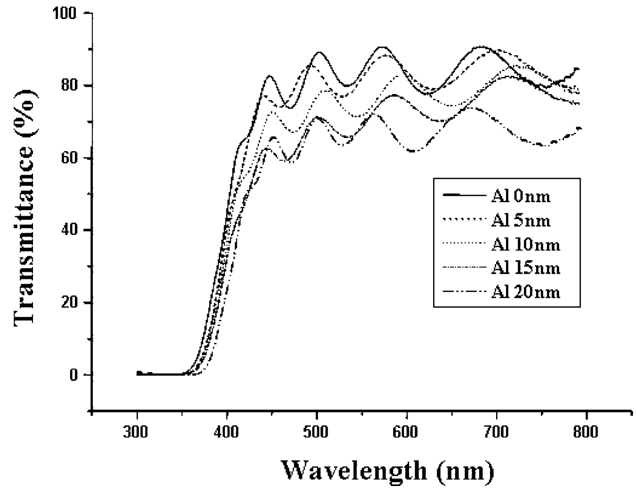

Fig. 2 Optical transmittance spectra for IZO/Al/GZO/ZnO multilayer thin films with different Al interlayer thicknesses

layers. The presence of the Al layer slightly deteriorates the transmittance but this film still gives respectable transmittances higher than ~75%.

The surface roughnesses of IZO/Al/GZO/ZnO multilayer films with different Al layer thicknesses were subsequently investigated by using AFM and the resulting surface roughness are shown in Fig. 3. The measured root mean square (RMS) surface roughness were approximately 8.3, 7.0, 1.8, and 1.0 nm for samples for Al = 5, 10, 15, and 20 nm, respectively. It is known that an increase in the surface roughness may cause deterioration of the electrical and optical properties [22]. The multilayer film with a thicker Al interlayer shows a smoother surface and

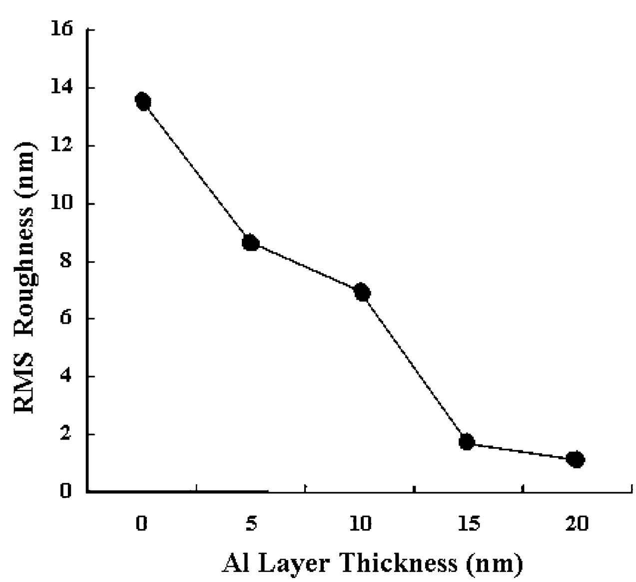

Fig. 3 The RMS surface roughness of the IZO/Al/GZO/ZnO multilayer thin film as a function of the Al interlayer thickness

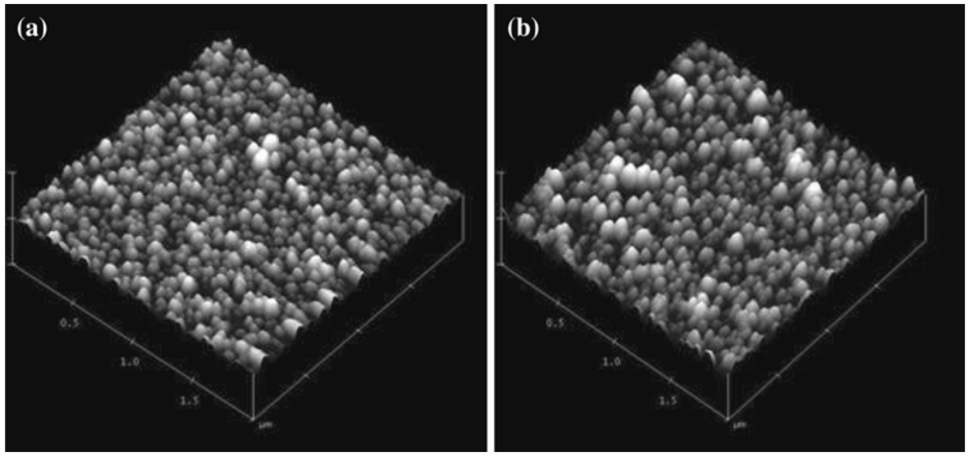

Fig. 4 The AFM images of the surfaces of the IZO/Al/GZO/ZnO multilayer films (**a**) with and (**b**) without an Al interlayer (10 nm thick)

becomes rougher as the Al layer thickness is decreased. From the AFM images shown in Fig. 4a and b, it is evident that introduction of an Al interlayer makes the film surface smoother.

The X-ray diffraction patterns for multilayer films with different Al thicknesses are shown in Fig. 5. The IZO/GZO/ZnO film deposited without an Al interlayer does not show any sharp peak. Films with different Al layer thicknesses exhibit different XRD patterns. The film with an Al interlayer thickness of 5, 10, or 15 nm shows Al(111) and Al(200) peaks besides ZnO and In_2O_3 peaks. The low ZnO(002) peak and the smooth diffraction curve for the film without an Al interlayer tells us that the IZO film is amorphous. In contrast to that film, the films with an Al interlayer have a sharp ZnO(002) peak and several other peaks. This difference in the diffraction curve between the two suggests that the Al layer has an effect of enhancing the crystallinity of the IZO overlayer. No distinct difference is, however, noted for different Al layer thicknesses, which suggests that a thick Al underlayer is not necessary for the IZO overlayer to be crystallized. An Al underlayer as thin as 5 nm can play a role of a seed layer for the growth of a crystalline IZO film.

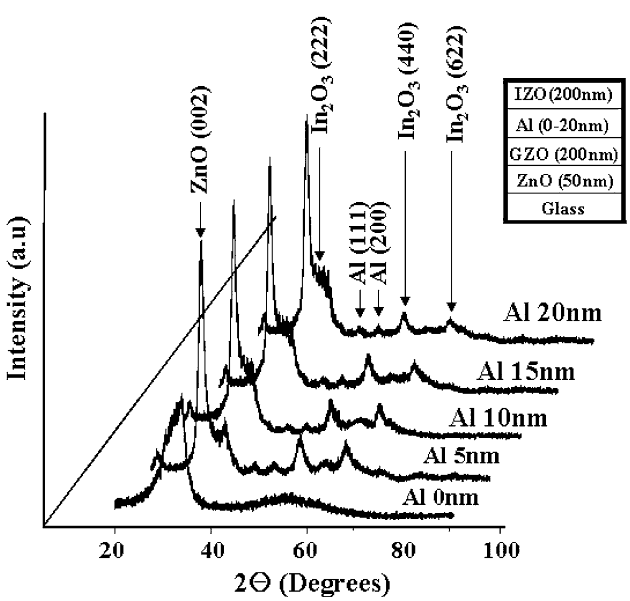

Fig. 5 XRD patterns of IZO/Al/GZO/ZnO multilayer thin films with different Al interlayer thicknesses

4 Conclusion

We have performed experiments to improve the electrical and optical property of IZO/Al/GZO/ZnO multilayer film for display applications. It was found that the properties, especially the optical and electrical properties of the multilayer film depend strongly on the Al interlayer thickness. We have optimized and developed high quality transparent conducting IZO/Al/GZO/ZnO multilayer film comparable to that of state of the art of ITO and other commercially available TCOs. The Al thin film exhibited visible light transmittances due to its ultra-thin thickness. The transmittance of this multilayer higher than 75% and the electrical resistivity as low as $2.2 \times 10^{-4}\,\Omega\,\mathrm{cm}$ was obtained using the IZO/Al/GZO/ZnO multilayer films.

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References

1. MRS Bulletin 25(2005), Special Issue on Transparent Conducting Oxides Edited by D.S. Ginley 2002
2. H. Hosono, H. Ohta, M. Orita, K. Ueda, M. Hirano, Vac. 66, 419 (2002)
3. E.J.J. Martin, M. Yan, M. Lane, J. Ireland, C.R. Kannewurf, R.P.H. Chang, Thin Solid Film **461**, 309 (2004)
4. K.Y. Zeng, F.R. Zhu, J.Q. Hu, L. Shen, K.R. Zhang, H. Gong, Thin Solid Films **443**, 60 (2003)
5. J.-M. Tingw, C.-K. Lin, J. Am. Ceramic Soc. **89**(12), 3676 (2006)
6. M. Osada, T. Sakemi, T. Yamamoto, Thin Solid Film **494** 38 (2006)

7. V. Assuncao, E. Fortunato, A. Marques, H. Aguas, I. Ferrira, M.E.V. Costa, R. Martins, Thin Solid Films **427** 401 (2003)
8. G. Hu, B. Kumar, H. Gong, E.F. Chor, P. Wu, App. Phys. Lett. **88**, 101901 (2006)
9. Burag Yaglioglu, H.-Y. Yeom, D. C. Paine, Appl. Phys. Lett. **86**, 261908 (2005)
10. X.W. Sun, L.D. Wang, H.S. Kwok, Thin Solid Films **360**, 75 (2000)
11. G. Fang1, Dejie Li, Bao-Lun Yao, Instit. Phys. Publish., J. Phys. D: appl. Phys. **35**, 3096 (2002)
12. Patent by Schulz Stephen C, 12-19-2006, application-10/216507, 3 M Innovative Properties Company (St Paul, MN)
13. J.-S. Hong, B.-R. Rhee, H.-M. Kim, K.-C. Je, Y.-J. Kang, J. Sun Ahn, Thin Solid Films **467**, 158 (2004)
14. T. Kawashima, T. Ezure, K. Okada, H. Matsui, K. Goto, N. Tanabe, J. Photochem. Photobiol.-A **164**, 199 (2004)
15. E. Kusano, J. Kawaguchi, K. Enjoiji, J. Vac. Sci. Technol. A. **4**(6), 2907 (1986)
16. M. Bender, W. Seelig, C. Daube, H. Frankenberger, B. Ocker, J. Stollenwerk, Thin Solid Films **326**, 67 (1998)
17. S. Ito, T. Takeuchi, T. Katayama, M. Sugiyama, Chemical Materials C (2003)
18. G. Leftheriotis, S. Papaefthimiou, P. Yianoulis, Solid State Ionics **136–137**, 655 (2000)
19. Yu Yang et al App. Phys. Lett. **89**, 051116 (2006)
20. D.R. Sahu, J. Huang, Thin solid films **515**, 876 (2006)
21. I. Lauer D.A. Antoniadis, IEEE Electron Dev. Lett. 26, 5 (2005)
22. Byeong Yun Oh, M.-C. Jeong, D.-S. Kim, W. Lee, J.-M. Myoung, J. Cryst. Growth **281**, 475 (2005)