

Proceeding of ICNM - 2009

1st International Conference on Nanostructured Materials and Nanocomposites (6 – 8 April 2009, Kottayam, India)

Published by : Applied Science Innovations Private Limited, India.
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Stability of Electrical Properties in Transparent Conducting ZnO Thin Films for Transparent Electrode Applications

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Abstract : The present status and prospects for further development of transparent conducting impurity-doped ZnO thin films for use as ITO substitutes for transparent electrode applications are presented with particular focus on the stability of electrical properties in the transparent conducting films under various oxidizing environments. The stability of resistivity of Al- or Ga-doped ZnO (AZO or GZO) thin films prepared with a thickness in the range from approximately 20 to 2000 nm on glass substrates by various deposition techniques were tested in air environments at high temperatures and/or high humidity. The resistivity in AZO and GZO thin films prepared with a thickness of less than approximately 100 nm considerably increased in oxidizing environments. For the purpose of improving the resistivity stability of these transparent conducting thin films, a new technique that co-dopes AZO with another impurity has been demonstrated.

1. Introduction :

Transparent conducting oxide (TCO) thin films are necessary for applications as the transparent electrode used in most optoelectronic devices such as flat panel displays, thin-film solar cells and touch panels. Although many kinds of TCO materials have been developed up to now, only a limited number of materials such as impurity-doped zinc oxide (ZnO), indium oxide (In_2O_3) and tin oxide (SnO_2) are in practical use for conventional transparent electrode applications [1-4]. In particular, Sn-doped In_2O_3 (commonly called ITO) thin films have been widely used for most transparent electrode applications because ITO is the best material in regard to obtainable low resistivity and suitability for practical applications. Nevertheless, some problems have become more apparent recently with the scarcity and, therefore, high cost of indium as well as environmental issues such as the toxicity of ITO powder [5,6]. As an ITO substitute, impurity-doped SnO_2 must be deposited or heat treated at high temperatures in order to obtain transparent conducting thin films with a low resistivity; however, these thin films exhibit higher stability in oxidizing environments at high temperatures and in acid and alkaline solutions than ITO or impurity-doped ZnO [1]. As for impurity-doped ZnO, it is a low cost, abundant

and nontoxic material that can be deposited as a thin film with low resistivity on low temperature substrates. However, for use in oxidizing environments as well as in acid and alkaline solutions, impurity-doped ZnO thin films are less stable than ITO or impurity-doped SnO_2 thin films, whereas in reducing environments, the impurity-doped ZnO thin films are more stable than the others [7,8]. Thus, the use of TCO materials for specialized applications requires consideration of various factors such as material cost, toxicity of material, stability of various properties in thin films and suitability of film deposition.

In this paper, we describe the stability of electrical properties in transparent conducting polycrystalline ZnO thin films prepared on glass substrates for transparent electrode applications by various deposition techniques. Because the resistivity in impurity-doped ZnO thin films prepared with a thickness of less than approximately 100 nm considerably increased in oxidizing environments, a new impurity-co-doping technique has been demonstrated.

2. Stability of Resistivity :

2.1 Oxidizing environment at high temperatures

Minami et al. were the first to report that the resistivity of transparent conducting non-doped ZnO (ZO) films considerably increased in oxidizing environments at temperatures above about 150°C [9,10]. In addition, they first reported that resistivity stability can be successfully improved in transparent conducting ZnO films doped with a donor impurity such as Al or Ga [9,11]. It has been also reported that the resistivity stability of Al- or Ga-doped ZnO (AZO or GZO) thin films in various environments at a high temperature was lower than that of ITO or impurity-doped SnO_2 thin films [11-16]; it should be noted that the obtained resistivity stability was considerably dependent on the film deposition conditions as well as the kind and content of doped impurity [11,17,18]. In particular, the resistivity stability of AZO and GZO thin films in oxidizing environments at a high temperature was relatively low.

Recently, it was found that the resistivity stability in transparent conducting AZO and GZO thin films in various environments at a high temperature considerably degraded as the film thickness was decreased below approximately 100 nm, irrespective of the deposition method used. In addition, it has been reported that the increase in resistivity associated with a decrease of film thickness is always observed in transparent conducting ZnO and impurity-doped ZnO thin films [17-20]. As an example, typical heat-treated temperature dependencies of resistivity are shown in Figs. 1(a) and 1(b) for transparent conducting AZO and GZO thin films, respectively, prepared with various thicknesses and tested in an air environment at high temperatures (maintained for 30 min at each temperature). These AZO and GZO thin films were prepared with an Al content (Al/(Al+Zn) atomic ratio) and a Ga content (Ga/(Ga+Zn) atomic ratio) of approximately 3.3 at.% on glass substrates at a temperature of 200°C by a pulsed laser deposition (PLD) [21]. As can be seen in Figs. 1(a) and 1(b), AZO and GZO thin films prepared on substrates at 200°C with a thickness above approximately 100 nm were sufficiently stable for practical use in an air

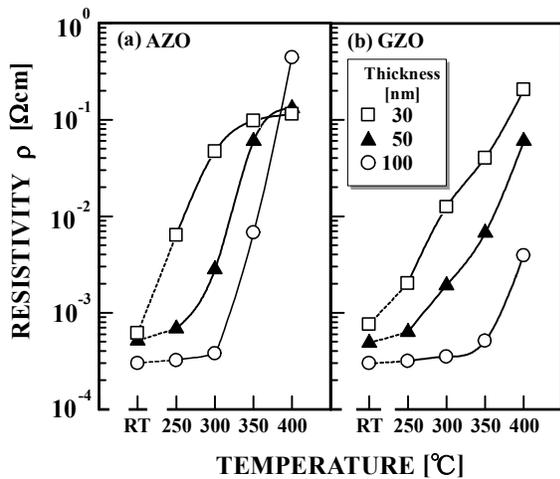


Fig. 1 Typical heating temperature dependencies of resistivity for (a) AZO and (b) GZO thin films prepared with various thicknesses: 30(□), 50(▲) and 100(○) nm.

environment at a temperature up to approximately 250°C. As can be seen, the onset of a more rapid increase in resistivity with increased ambient temperature occurred at lower temperatures as the film thickness was decreased, in particular, below approximately 50 nm. Although the obtained resistivity stability in AZO and GZO thin films exhibited a tendency to improve slightly when the doped impurity content was increased, the obtainable resistivity in the resulting as-deposited thin films also always increased with the impurity content. In addition, it was found that the resistivity stability of AZO thin films was lower than that of GZO thin films prepared under the same deposition conditions, irrespective of the deposition techniques used.

It should be noted that most transparent electrodes used in liquid crystal displays (LCDs) require preparation with a thickness in the range from about 35 to 200 nm on substrates at a temperature around 200°C as well as ability to withstand exposure for 30 min to an

air environment at a temperature up to about 250°C. In addition, transparent electrodes used in plasma display panels (PDPs) require stable operation even when exposed for about 30 min to an air environment at a temperature of about 500°C. As described above, the resistivity of AZO and GZO thin films prepared with a thickness below approximately 50 nm increased even in an air environment with a 30 min. exposure at a temperature of 250°C; consequently, very thin films may be unsuitable for use as the transparent electrode in LCDs. Transparent conducting AZO and GZO films may also be unsuitable for use as the transparent electrode in PDPs.

The resistivity increase associated with increases in the heating test temperature up to approximately 350°C are mainly attributable to decreases of both carrier concentration and Hall mobility. For example, Figs. 2(a) and 2(b) show heating test temperature dependencies of carrier concentration and Hall mobility, respectively, for the AZO thin films prepared with a thickness of 100, 50 and 30 nm shown in Fig. 1(a). It was found that the increased resistivity resulting from the heating test of thin films in an air environment at a temperature up to approximately 300°C could be returned to near the initial resistivity of the as-deposited films by a heat treatment in a hydrogen gas environment at a temperature up to 400°C. Thus, the resistivity increase in AZO and GZO thin films found after heat testing at temperatures up to approximately 300°C was mainly attributable to grain

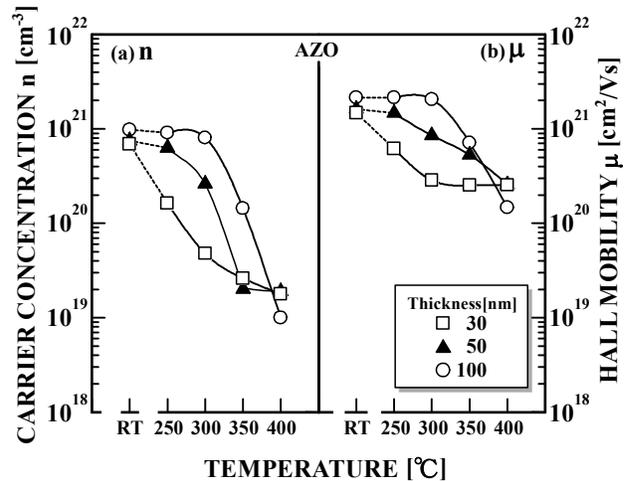


Fig. 2 Typical heating temperature dependencies of (a) carrier concentration and (b) Hall mobility for AZO thin films prepared with various thicknesses: 30(□), 50(▲) and 100(○) nm.

boundary scattering resulting from the decreases of both carrier concentration and Hall mobility that followed oxygen being adsorbed on the surface of grain boundaries [22]. However, the crystallinity of these thin films was found to be clearly improved by heat treatment at approximately 400°C, whereas the crystallinity of these thin films remained unchanged when heat tested at a temperature up to approximately 300°C. As a result, the behavior of carrier concentration and Hall mobility in the heating tests at temperatures in the range from 350 to 400°C may be attributable to an improvement of crystallinity in these thin films.

As mentioned above, we have reported that the resistivity stability of ZnO thin films at high temperatures could be improved by doping an impurity

such as Al or Ga [9-11] and, in addition, the chemical stability of transparent conducting AZO and GZO thin films could be improved by co-doping another impurity such as Cr, V, Co or Mn [23,24]. In addition to chemical stability, we have recently reported that the resistivity stability in transparent conducting AZO and GZO thin films could be improved by co-doping another impurity such as V or In [6,25]. Figure 3 shows typical heating test temperature dependencies of resistivity change, shown as normalized resistivity (referenced to the initial resistivity ρ_{in} of as-deposited films), for transparent conducting V-co-doped AZO (AZO:V) thin films prepared with various V contents (V/(V+Zn) atomic ratio) and a thickness of 100 nm; heating tests were conducted in an air environment for 30 min at each temperature. The above AZO and AZO:V thin films were prepared with an Al content of approximately 3.3 at.% and a V content of 0.0, 0.15, 0.25 or 0.4 at.% on glass substrates at a temperature of 200°C by PLD [21]. As can be seen in Fig. 3, the increase in resistivity associated with increasing heat test temperature was lessened by increasing the V co-doping content. It was found that similar resistivity stability improvement could also be obtained in In- or Sn-co-doped AZO thin films. Therefore, it can be concluded that the resistivity stability of AZO thin films for use in an air environment at high temperatures could be improved by using transparent conducting AZO:X thin films, *i.e.*, AZO thin films co-doped with an appropriate impurity (X).

2.2 Long-term use in moist environments

It should be noted that long term exposure to an air

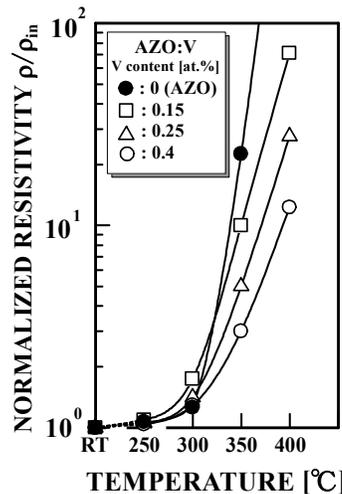


Fig. 3 Typical heating temperature dependence of resistivity change for AZO:V thin films prepared with a thickness of 100 nm and various V contents: 0(●), 0.15(□), 0.25(△) and 0.4(○) at.%.

environment of transparent conducting impurity-doped ZnO thin films prepared on low temperature substrates with a thickness less than approximately 50 nm even results in a gradual increase of resistivity at room temperature. It has been recently reported that the resistivity of transparent conducting AZO and GZO thin films prepared with a thickness in the range from 30 to 200 nm on glass substrates at a temperature below 200°C always increased with exposure time when tested for a long time in an air environment at a high humidity, irrespective of deposition techniques used [26,27]. In particular, the resistivity stability degraded markedly as

the film thickness was decreased below approximately 100 nm. However, the obtained resistivity stability in impurity-doped ZnO thin films was considerably dependent on the deposition technique and deposition conditions used as well as the kind and content of doped impurity [28,29]. As an example, Fig. 4 shows resistivity as a function of exposure time in a high-relative humidity test environment (air at 90% relative humidity and 60°C) for AZO and GZO thin films prepared at a substrate temperature of 200°C with various thicknesses by dc magnetron sputtering. These AZO and GZO thin films were prepared on glass substrates at a temperature of 200°C with an Al content of approximately 3.3 at.% and a Ga content of approximately 7.3 at.%. As can be seen in Fig.4, impurity-doped ZnO thin films with a thickness below approximately 50 nm were very unstable, *i.e.*, an increase of resistivity to very high levels with exposure to the high-relative humidity test environment. The obtainable resistivity stability of both AZO and GZO thin films was found to exhibit a tendency to improve with increases in the content of doped impurity; unfortunately, this increase in the content of the doped impurity resulted in increasing the obtained resistivity in these thin films. In addition, as can be seen in Fig. 4, the increase of resistivity with exposure time found in AZO thin films was lower than that in GZO thin films, regardless of thickness. It was also found that the resistivity stability of AZO thin films showed a tendency to be higher than that of GZO thin films prepared under the same deposition conditions and the same film thickness, irrespective of deposition techniques used. As described above, the low resistivity stability found in transparent conducting AZO and GZO thin films prepared with a thickness of approximately 100 nm or less may preclude their use as transparent

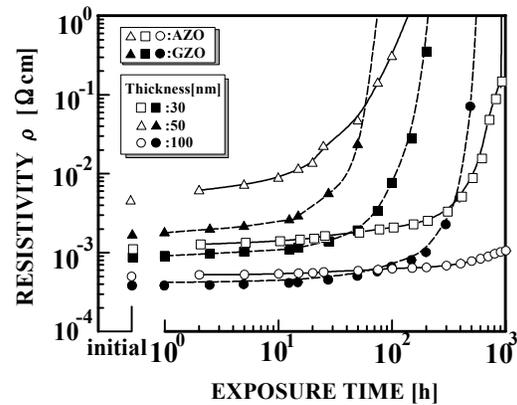


Fig. 4 Resistivity as a function of exposure time for AZO (open) and GZO (solid) thin films prepared with various thicknesses: 30(□), 50(△) and 100(○) nm.

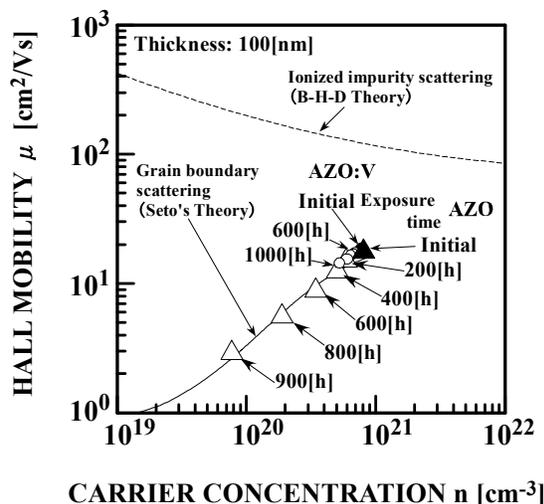


Fig. 5 Resistivity as a function of exposure time for AZO (open) and AZO:V (solid) thin films prepared with a thickness of 50(Δ) or 100(○) nm.

electrodes in LCDs.

For the purpose of resolving the resistivity stability problem, we demonstrated that the stability of AZO and GZO thin films could be improved by improving crystallinity and controlling chemical composition by varying the kind and amount of doped impurity as well as co-doping with another impurity. As mentioned above, the resistivity stability of AZO and GZO thin films for use in oxidizing environment at a high temperature could be improved by co-doping another impurity such as V, Sn or In. In addition to the above, we have recently reported that the resistivity stability in AZO and GZO thin films for use in a high-relative humidity environment could be improved by co-doping another impurity such as V or In [6,25]. As an example, Fig. 5 shows the effect of co-doping vanadium on the resistivity stability in AZO thin films in a high humidity environment (air at 90% relative humidity and 60°C). The resistivity as a function of V content is shown in Fig. 5 for both AZO and AZO:V thin films prepared by PLD with various thicknesses on glass substrates at a temperature of 200°C: Al content of approximately 4 at.% and V content of approximately 0.2 at.%.

It has been reported that the electrical conduction of transparent conducting impurity-doped ZnO thin films with a carrier concentration on the order of 10^{19} to 10^{21} cm^{-3} is dominated by not only ionized impurity scattering, but also grain boundary scattering [2,22,30]. It was found that the increase of resistivity with test time can be ascribed to decreases of both carrier concentration and Hall mobility. As an example, the relationship between carrier concentration (n) and Hall mobility (μ) as a function of test time is shown in Fig. 6 for AZO and AZO:V thin films prepared by PLD with a thickness of approximately 100 nm and an Al content of approximately 4.0 at.% and a V content of approximately 0.25 at.%. The μ - n relationship suggests that electrical conduction is mainly dominated by grain boundary scattering [22]. In addition to the experimental results, the theoretical μ - n relationship calculated by Seto's formula [22,31] for mobility dominated by grain boundary scattering is shown with solid lines in Fig. 6. The good agreements shown suggest that the adsorption

of oxygen on the grain boundary surface of polycrystalline AZO and AZO:V thin films is enhanced in a high humidity environment. In addition, the V co-doping could suppress the adsorption of oxygen on the grain boundary surface. As a result, it can be concluded that the 100 nm-thick AZO:V thin film is stable enough to be acceptable for use in practical transparent electrode applications such as LCDs. However, in regard to impurity-doped ZnO films that are thinner than approximately 50 nm, we believe that the resistivity increase is mainly dominated by oxygen adsorption on the surface of the film rather than the grain boundary. In particular, at the film surface, the potential barrier created by adsorbed oxygen prevents electron transport.

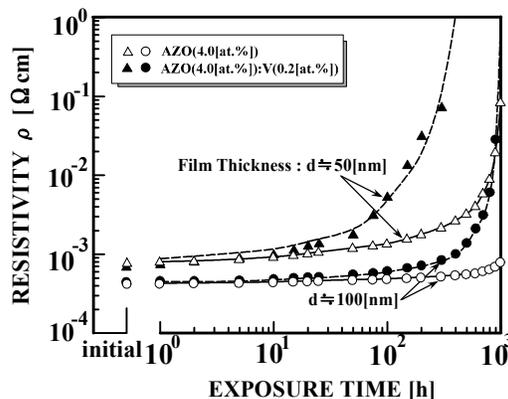


Fig. 6 Experimental μ - n relationships as functions of exposure time for AZO (Δ) and AZO:V (○) thin films prepared with a thickness of approximately 100 nm. Theoretically calculated μ - n relationships are indicated by lines.

This effect may be enhanced as the thickness is decreased. As a result, impurity-doped ZnO thin films with a thickness below approximately 50 nm are unstable, even when co-doped with another impurity. In particular, it seems likely that attaining a level of stability comparable to that of ITO will prove difficult with ZnO films that are thinner than approximately 50 nm.

At present, transparent conducting thin films prepared with impurity-doped ZnO such as AZO and B-doped ZnO (BZO) are in practical use as transparent electrodes for $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ (CIGS) thin-film solar cells. The demand for impurity-doped ZnO transparent electrodes has also grown for Si and compound semiconductor thin-film solar cells. A high stability of resistivity is necessary, even with long term exposure to an oxidizing environment at high temperatures up to about 300°C, for the practical use of impurity doped ZnO thin films as transparent electrodes in thin-film solar cells. However, the resistivity increase resulting from oxygen adsorption on grain boundary and thin film surfaces will continue to be a problem because the increase in resistivity in oxidizing environments may be caused by thermally activated chemical reactions. The resistivity stability in transparent conducting impurity-doped ZnO thin films must be evaluated for long term use in oxidizing environments. In addition, it is necessary to prove whether newly developed transparent conducting films prepared with AZO, GZO and BZO by co-doping another impurity such as V or In are sufficiently suitable for long term practical use.

3. Conclusion :

The resistivity stability of transparent conducting impurity-doped ZnO thin films in various oxidizing environments was described. Al- or Ga-doped ZnO (AZO or GZO) thin films with a thickness in the range from approximately 20 to 2000 nm were prepared by various deposition techniques on glass substrates and used for stability tests. The resistivity stability in an air environment at high temperatures was improved in transparent conducting AZO thin films by co-doping another impurity (X) (AZO:X). It was found that a 100 nm-thick AZO:V thin film is stable enough to be acceptable for practical use as transparent electrodes for liquid crystal displays, even in air environments at a high humidity and/or a high temperature ; for use. However, impurity-doped ZnO thin films with a thickness less than approximately 50 nm are unstable, even when co-doped with another impurity. It seems likely that attaining a level of stability comparable to that of ITO will prove difficult.

References :

- [1] H.L. Hartnagel et al., *Semiconducting Transparent Thin Films*, Institute of Physics Publishing, Bristol, Philadelphia, 1995.
- [2] T. Minami, *MRS Bull.* 25 (2000) 38.
- [3] T. Minami, *Semicond. Sci. Technol.* 20 (2005) S35.
- [4] C. G. Granqvist et al., *Thin Solid Films* 411 (2002) 1.
- [5] D. S. Ginly et al., *MRS Bull.* 26 (2000) 15.
- [6] T. Minami et al., *Thin Solid Films*, 517 (2008) 1474.
- [7] S. Major et al., *Appl. Phys. Lett.*, 49 (1986) 394.
- [8] T. Minami et al., *Thin Solid Films* 176 (1989) 277.
- [9] T. Minami et al., *Jpn. J. of Appl. Phys.*, 23 (1984) L280.
- [10] T. Minami et al., *Thin Solid Films* 111 (1984) 167.
- [11] S. Takata et al., *Thin Solid Films* 135 (1986) 183.
- [12] T. Minami et al., *Thin Solid Films*, 193/194 (1990) 721.
- [13] H. Nanto et al., *J. of Appl. Phys.*, 63 (1988) 2711.
- [14] T. Minami et al., *Jpn. J. of Appl. Phys.*, 33 (1994) L1693.
- [15] T. Minami et al., *Jpn. J. of Appl. Phys.*, 34 (1995) L971.
- [16] T. Minami et al., *J. Vac. Sci. Technol.*, A 17 (1999) 1822.
- [17] T. Minami et al., *Jpn. J. of Appl. Phys.*, 25 (1986) L776.
- [18] H. Sato et al., *J. Vac. Sci. Technol.*, A 11 (1993) 2975.
- [19] T. Minami et al., *Thin Solid Films* 124 (1985) 43.
- [20] T. Minami et al., *Jpn. J. of Appl. Phys.*, 24 (1985) L781.
- [21] H. Tanaka et al., *J. Vac. Sci. Technol. A* 22 (2004) 1757.
- [22] T. Minami et al., *Mat. Res. Symp. Proc.*, 666 (2001) F1.3.1.
- [23] S. Suzuki et al., *Thin Solid Films*, 434 (2003) 14.
- [24] T. Minami et al., *Thin Solid Films*, 398-399, (2001) 53.
- [25] T. Minami, *Thin Solid Films*, 516 (2008) 5822.
- [26] T. Minami et al., *phy. stat. sol.*, (RRL) 1 (2007) R31.
- [27] T. Minami, *Thin Solid Films*, 516 (2008) 1314.
- [28] T. Minami et al., *phys. stat. sol.*, (a), 205 (2007) 255.
- [29] T. Miyata et al., *Thin Solid Films*, 516 (2008) 1354.
- [30] T. Minami et al., *J. Cryst. Growth*, 117 (1992) 370.
- [31] J.Y.W. Seto, *J. Appl. Phys.*, 46 (1975) 5247.