Transparent conducting zinc-co-doped ITO films prepared by magnetron sputtering

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Zn-co-doped ITO films have been prepared by dc magnetron sputtering using powder targets. Zn-co-doped ITO films with a practical etching rate as well as a low resistivity were obtained; in particular, etching rate could be controlled by varying the Zn content doped into ITO. In addition, a resistivity of 2-3×10^{-4} Ω cm was obtained in Zn-co-dped ITO films prepared with a Sn content of 9.3 at.% and a Zn content of 0-34.1 at.% under optimized target preparation and sputter deposition conditions. The spatial distribution of electrical properties on the substrate surface in Zn-co-doped ITO films was considerably affected by the Zn content. A relatively uniform distribution of electrical properties was obtained in films prepared with a Zn content in the range of 15-34.1 at.%.

Keywords: Magnetron sputtering, ITO, Zn co-doped ITO, thin films, etching rate, transparent conducting oxide

1. Introduction

Transparent conducting oxide (TCO) films produced using binary compounds such as SnO_2, In_2O_3 and ZnO doped with an impurity are in practical use [1]. In particular, Sn-doped In_2O_3 (ITO) is a leading material for TCO film applications. Most ITO films are prepared by dc magnetron sputtering using a sintered oxide target [2].

However, recent developments in large area flat panel displays and large area thin-film solar cells frequently require improvements in the electrical, optical and chemical properties of ITO thin films used as transparent electrodes. Besides the preparation of ITO films having lower resistivity, for example, control of the etching rate of the films is necessary. In addition, nonuniformity of spatial resistivity distribution on the substrate surface in ITO film deposition using magnetron sputtering remains an unsolved problem [3].

Recently, new transparent conducting oxide films using ternary compounds such as Zn_2SnO_4 [4], $ZnSnO_3$ [5], $MgIn_2O_4$ [6], $Zn_2In_2O_5$ [7] and $In_4Sn_3O_{12}$ [8] have been reported. Some of the problems mentioned above may be resolved by these materials. However, it is difficult to control the etching rate of transparent conducting oxide films produced with binary and ternary compounds. In addition to the use of ternary compounds, we have proposed the use of multicomponent oxides such as ZnO-In_2O_3 [9], In_2O_3-SnO_2 [10], $Zn_2In_2O_5$-$In_4Sn_3O_{12}$ [11] and $MgIn_2O_4$-$Zn_2In_2O_5$ [12].

The use of multicomponent oxides [9-14], whose physical and chemical properties can be controlled by changing their chemical compositions, may resolve the above problems. As an extension of our previous work, we now propose the use of impurity-co-doped oxides for transparent conducting films.

In this paper, we demonstrate the modification of both the spatial resistivity distribution on the substrate surface and the etching rate of Zn-co-doped ITO films prepared by dc magnetron sputtering.

2. Experimental

The films were prepared by conventional dc planar magnetron sputtering [15] using a slightly pressed powder target: Al holder with a diameter of 120 mm. A mixture of In_2O_3, SnO_2 and ZnO powders (purity, 99.99%) calcined at 1000 °C in an Ar gas and/or at 400 °C in an Ar+10% H_2 mixed gas atmosphere for 5 h was used as the target. The ITO films were prepared using an ITO powder target with the following content, Sn/(In+Sn) atomic ratio (SnO_2 added to the In_2O_3 powder), held constant at 9.3 atomic%; the Zn-co-doped ITO (ITO:Zn) films were prepared using a powder target with the following content, Zn/(In+Zn) atomic ratio (ZnO added to the ITO powder), varied in the range of 0 to 34.1 at.%.

Substrates of Corning 7059 glass were placed parallel to the target surface. Sputtering deposition was carried out with a power of 50 W at sputter gas pressures of 0.2-0.4 Pa in an Ar gas or Ar+O_2 mixed gas atmosphere. Substrate temperatures were lower than 200 °C. Film thickness, about 100 nm, was measured using a conventional surface roughness detector with stylus. The deposition rate of 10 nm/min was relatively independent of the powder composition. Electrical resistivity and Hall mobility were measured using the van der Pauw method. The composition (metal element content, or the atomic ratio) of sputtered films was measured by energy dispersive X-ray (EDX) spectroscopy. The composition of deposited films was found to be approximately equal to that in the target.

3. Results and discussion

A. *Zn content dependence of electrical properties*

Figure 1 shows resistivity, carrier concentration and Hall mobility as functions of the Zn content for ITO and ITO:Zn films prepared using ITO targets with a Zn content of 0 to 34.1 at.%. These films were prepared at a substrate temperature of about 200 °C and an Ar+O_2 gas total pressure of 0.2 Pa with an O_2 gas partial pressure of 4.0×10^{-3} Pa.

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The resistivity increased from the minimum value, obtained in an ITO film, as the Zn content was increased. In particular, the resistivity markedly increased as the Zn content was increased from 0 at.%, reached a maximum at a Zn content of about 7.6 at.%, and then even more rapidly decreased as the Zn content was further increased, reaching a minimum at a Zn content of about 11 at.%. The resistivity change was attributed to changes of both carrier concentration and Hall mobility.

The Hall mobility markedly decreased as the Zn content was increased up to 7.6 at.%, reached a minimum at about 7.6 at.%, and then rapidly recovered to a high mobility at about 11 at.% as the Zn content was further increased. With further increases of Zn contents, the Hall mobility decreased gradually. Figure 2 shows X-ray diffraction patterns as a function of the Zn content for the ITO and ITO:Zn films shown in Fig.1. A peak near 31°, which corresponds to the diffraction from the In_2O_3 lattice, was observed for films prepared with a Zn content of 0 to 7.6 at.%. However, ITO:Zn films prepared with a Zn content above 9 at.% were amorphous. The X-ray diffraction analyses show that the Zn content dependence of Hall mobility, shown in Fig.1, is not related to the crystallinity of deposited films.

As with the Hall mobility, the carrier concentration, in general, decreased gradually as the Zn content was increased; similarly, it decreased drastically at Zn contents around 7.6 at.%. It is well known that a free electron acting as a carrier in ITO films is caused by two kinds of donors: a native defect such as an oxygen vacancy and a Sn^{4+} ion on a substitutional site of an In^{3+} ion [1,2]. Therefore, the drastic decrease of carrier concentration obtained in crystallized ITO:Zn films prepared with Zn contents around 7.6 at.% is possibly related to the following two origins: oxidation enhancement of films and carrier compensation due to doped Zn acting as an acceptor.
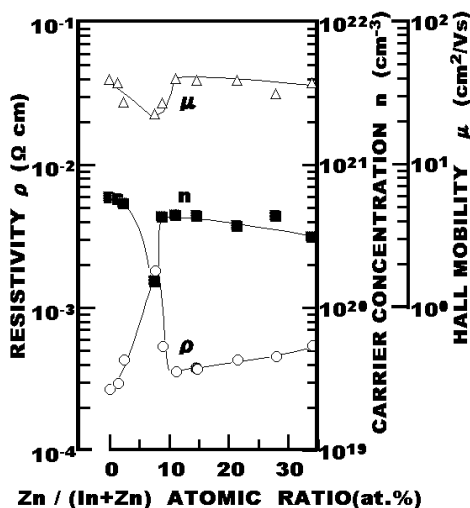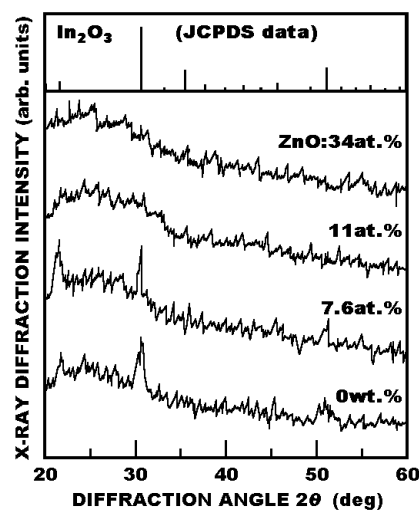

Fig.2. X-ray diffraction patterns for ITO:Zn films prepared with different Zn contents.

The former may be caused by the increasing amount of oxygen in the sputter chamber as the content of ZnO added to the ITO target was increased, because the oxygen sputtering rate for In_2O_3 is higher than that for ZnO [16]. Consequently, the decrease of carrier concentration may be caused by either extinction of oxygen vacancies or free electron trapping due to the adsorption of oxygen on the grain boundary and/or the surface of films.

The latter may be explained by the doping of Zn into In_2O_3 which may cause carrier compensation when a Zn^{2+} ion occupies the site of an In^{3+} ion. Although the decrease of carrier concentration with increases of Zn content up to 7.6 at.% can be explained by a mechanism where Zn acts as an acceptor, it may be difficult to apply this explanation to the decrease of Hall mobility.

In addition, if Zn acts as an acceptor, it is difficult to account for the increase of carrier concentration and its high value observed for films prepared with Zn contents above 7.6 at.%, as shown in Fig.1. We suggest that this observed increased carrier concentration with a high value is related to the formation of ternary compounds, for example, $Zn_2In_2O_5$ composed of ZnO and In_2O_3.[7] It has been reported that $Zn_2In_2O_5$ films prepared by magnetron sputtering exhibit a high carrier concentration as well as a high Hall mobility [7,9]. As described above, the drastic increase of resistivity may be explained by oxygen enhancement rather than Zn acceptor mechanisms.

B. ITO:Zn films prepared under optimized conditions.

In order to clarify the effect of oxidation enhancement, we prepared ITO:Zn films with Zn contents of 1 to 28 at.% using magnetron sputtering with special efforts undertaken to suppress oxidation during the film deposition. Oxidation suppression was attempted by changing the kind and partial pressure of sputter gas, the sputter gas pressure and the calcined condition of target powder.

Fig.1. Resistivity ( ) , carrier concentration (■) and Hall mobility( ) as functions of Zn content for ITO:Zn films prepared under the same preparation condition.

For example, ITO:Zn films were prepared in a pure Ar gas atmosphere using a target calcined at 1000 °C. In addition, films were prepared in a pure Ar atmosphere using a target calcined at 1000 °C in an Ar atmosphere after being calcined at 400 °C in an Ar+H$_2$ (10%) atmosphere. As the result of tests to obtain minimum resistivity films prepared with various Zn contents, low resistivity ITO:Zn films which are relatively independent of the Zn content could be obtained. Resistivity, carrier concentration and Hall mobility as functions of Zn content are shown in Fig.3 for ITO and ITO:Zn films prepared under the optimized conditions. Resistivities of 2-3×10^{-4} Ωcm were obtained in ITO and ITO:Zn films prepared with a Zn content of 0 to 28 at.%.

It is well known that the etching rate of ITO films prepared by magnetron sputtering is strongly affected by the sputter deposition conditions. For example, the etching rate of crystalline ITO films in a HCl solution is lower than that of amorphous films [17]. Figure 4 shows the etching rate as a function of the Zn content for ITO:Zn films prepared at a substrate temperature of 200 °C. The etching test was carried out in 1.0M HCl at 25 °C.

The etching rate in 1.0M HCl was strongly dependent on the Zn content in ITO:Zn films, whereas the ITO film remained unetched. The etching rate of ITO:Zn films prepared with a Zn content above 7.6 at.% markedly increased: about 25 nm/min with a Zn content of 11 at.%. It should be noted that Zn-co-doping facilitates the etching of crystallized films. Therefore, the increase of etching rate with increasing Zn content seen in Fig.4 is mainly related to the effect of the Zn added into ITO films, *i.e.,* a result of the chemical properties of Zn.

Figure 5 shows optical transmission spectra for ITO:Zn films prepared with different Zn contents. An average transmittance above 85% in the visible range was obtained for all films.
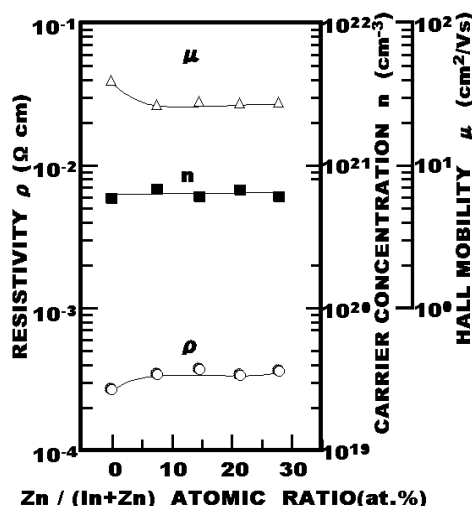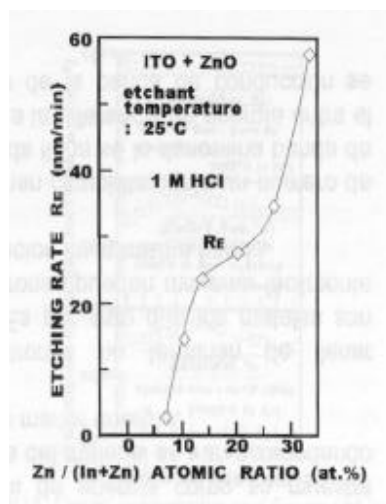

Fig.4. Etching rate as a function of Zn content for ITO:Zn films.

The absorption edge energy of ITO:Zn films prepared with a Zn content up to 7.6 at.% can be explained by taking into account the Burstein-Moss effect [18,19] and many body effects [20, necessary to take into account not only these effects but also the band-gap energy of the In$_2$O$_3$-Zn$_2$In$_2$O$_5$ 21] for the band-gap energy of In$_2$O$_3$.

However, for films prepared with a Zn content of 7.6 to 34.1 at.%, it is multicomponent system, which is from 3.6 to 2.9 eV [7].
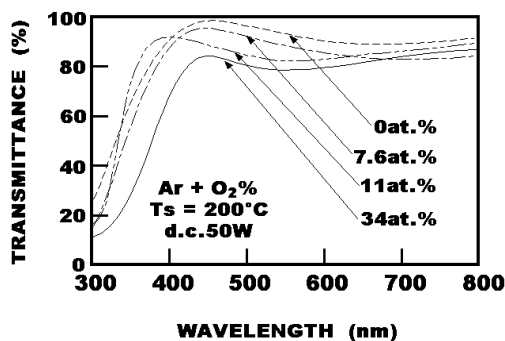

Fig.5. Optical transmission spectra as a function of Zn content for ITO:Zn films.

C. Spatial distributions of electrical properties

Figures 6, 7 and 8 show typical Zn content dependence of the spatial distributions of resistivity, carrier concentration and Hall mobility, respectively, for ITO:Zn films prepared under the optimized preparation conditions. The distances of 5 cm and around 1-2 and 8-9 cm in these figures indicate locations on the substrate that correspond to the center and the erosioned area of the target, respectively.

The thickness of films deposited on the substrate at locations from 0 to 10 cm varied slightly, within ±10%; however, the film thickness dependence of resistivity was negligibly small. ITO and ITO: Zn films prepared with a

Fig.3. Resistivity ( ),carrier concentration(■) and Hall mobility( ) as functions of Zn content for ITO:Zn films prepared under the optimized preparation condition.

Zn content up to about 7.6 at.% exhibited a large resistivity distribution. The distribution of resistivity is mainly related to that of carrier concentration. Increased resistivity and decreased carrier concentration were found at locations on the substrate corresponding to the erosioned area.

As described above, the decreased carrier concentration found at locations on the substrate corresponding to the erosioned area can be related to the enhancement of oxidation at such locations resulting from a nonuniform distribution of oxygen reaching the substrate [8,22,23]. In contrast, a uniform resistivity distribution could be obtained in ITO:Zn films prepared with Zn contents above about 15 at.%. The obtained uniform distributions of resistivity are related to the creation of ITO-$Zn_2In_2O_5$ multicomponent system films.

4. Conclusions

Highly transparent and conductive Zn-co-doped ITO (ITO:Zn) thin films were prepared with a Zn content of 0 to 34.1 at.% by conventional dc magnetron sputtering. A resistivity of $2\text{-}3\times10^{-4}$ Ωcm was obtained in ITO:Zn films prepared under optimized conditions with a Zn content of 0-28 at.%. The etching rate of ITO:Zn films in a HCl solution could be controlled by the Zn content in the films; ITO:Zn films prepared with a Zn content of 7.6-34.1 at.% were easily etched in a 1.0 M HCl solution.

The spatial resistivity distribution was affected by the Zn content of the target; films prepared with Zn contents above about 15 at.% exhibited a uniform spatial resistivity distribution. The lowering of resistivity as well as the improvement of spatial resistivity distributions are attributed to the decreased amount of oxygen in the sputter chamber that resulted from using a reduced oxide target and controlling the sputter gas
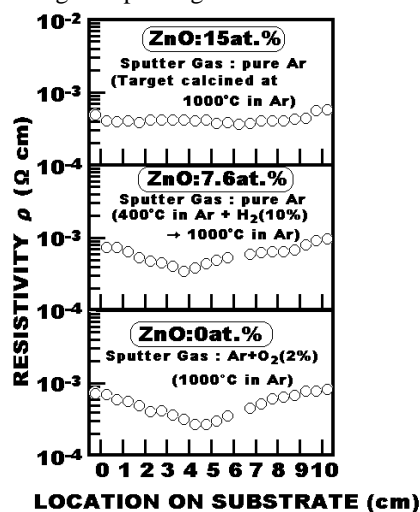

Fig.6. Resistivity as a function of location on the substrate atmosphere.of ITO:Zn films prepared under different preparation conditions.
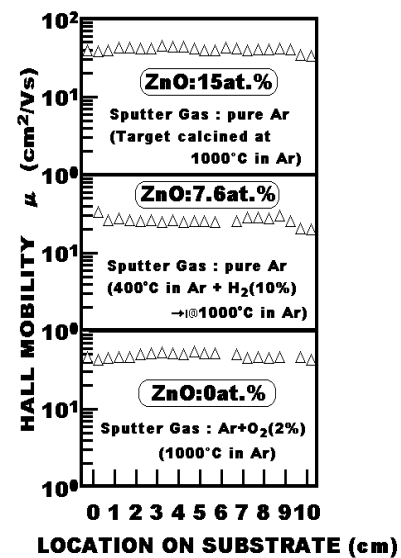

Fig.7. Hall mobility as a function of location on the substrate of ITO:Zn films prepared under different preparation conditions.
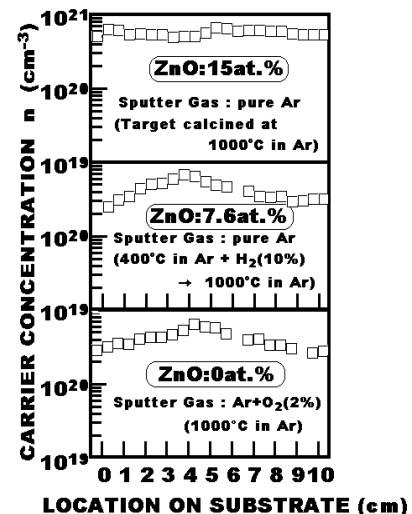

Fig.8. Carrier concentration as a function of location on the substrate of ITO:Zn films prepared under different preparation conditions.

Acknowledgements

References

[1]   H.L.Hartnagel, A.L.Dawar, A.K.Jain and C.Jagadish, Semiconducting Transparent Thin Films, Institute of Physics Publishing Bristol and Philadelphia, (1995) 134 and 219.

[2]   R.Bel Hadj Tahar, T.Ban, Y.Ohya and Y.Takahashi,. Appl. Phys., **83,** 2631 (1998).

[3]   S.Ishibashi, Y.Higuchi, Y.Ota and K.Nakamura, J.Vac. Sci. Technol., **A8,** 1403 (1990).

[4]   H.Enoki and J.Echigoya, Phys. Stat. Sol. (A), **132,** K1(1992).

[5]   T.Minami, H.Sonohara, S.Takata and H.Sato, Jpn. J. Appl. Phys., **33**, L1693(1994).

[6]   N.Ueda, T.Omata, N.Hikuma, K.Ueda, H.Mizoguchi, T.Hashimoto, H.Kawazoe, Appl. Phys. Lett., **61**, 1954(1992).

[7]   T.Minami, H.Sonohara, T.Kakumu and S.Takata, Jpn. J. Appl. Phys., **34**, L971(1995).

[8]   T.Minami, Y.Takeda, S.Takata and M.Ishii, Thin Solid Films, **308-309**, 13(1997).

[9]   T.Minami, T.Kakumu and S.Takata, J. Vac. Sci. Technol. **A 14**, 1704(1996).

[10] T.Minami, T.Kakumu, K.Shimokawa and S.Takata, Thin Solid Films, **317**, 318(1998).

[11] T.Minami, T.Miyata and T.Yamamoto, Surf. Coat. Technol., **108-109**, 583(1998).

[12] T.Minami, S.Takata, T.Kakumu and H.Sonohara, Thin Solid films, **270**, 22(1995).

[13] T.Minami, J. Vac. Sci.Technol. **A 17**, 1765(1999).

[14] X.Wu, T.J.Coutts and W.P.Mulligan, J. Vac. Sci. Technol., **A 15**, 1057(1997).

[15] T.Minami, H.Sato, H.Imamoto and S.Takata, Jpn. J. Appl. Phys., **31**, L257(1992).

[16] S.Major, S.Kumar, M.Bhatnagar and K.L.Chopra, Appl. Phys. Lett., **49**, 394(1989).

[17] J.E.A.M. van den Meerakker, P.C. Baarslag, W.Walrave, T.J.Vink, J.L.C. Daams, Thin Solid Films, **226**, 152(1995).

[18] E.Burstein, Phys. Rev., **93**, 775(1954).

[19] T.S.Moss, Proc., Phys. Soc., London **B67**, 775(1954).

[20] T.Minami, H.Nanto and S.Takata, Jpn. J. Appl. Phys., **24**, L605 (1985).

[21] Z.C.Jin, I.Hamberg and G.C.Granqvist, J. Appl. Phys. **64**, 5117(1988).

[22] K.Ichihara, N.Inoue and M.Okubo, Thin Solid Films, **245**, 152(1994).

[23] T.Minami, Y.Takeda, T.Kakumu, S.Takata and I.Fukuda, J. Vac. Sci. Technol., **A 15**, 958(1997).