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Present status and future prospects for development of non- or reduced-indium transparent conducting oxide thin films

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ABSTRACT

This paper surveys the recent progress and prospects for further development of indium–tin-oxide (ITO) substitute materials for practical use as thin-film transparent electrodes. The best, and only practical, indium-free candidate for an alternative material to ITO is impurity-doped ZnO such as Al- or Ga-doped ZnO (AZO or GZO). Presented here are newly developed impurity-doped ZnO thin-film deposition techniques, suitable for practical use, that reduce resistivity as well as improve the uniformity of the resistivity distribution using oxidization-suppressing magnetron sputtering deposition methods. Also presented are descriptions concerning the observed increase in resistivity of impurity-doped ZnO thin films resulting from exposure to long-term testing in a high humidity environment (air at 90% relative humidity and 60 °C) as well as the increase in resistivity associated with a decrease of film thickness. The resistivity stability of AZO thin films could be considerably improved by co-doping another impurity.

1. Introduction

Transparent conducting oxide thin films are necessary for use as transparent electrodes in flat panel displays such as liquid crystal displays (LCDs), plasma display panels, electronic paper displays and organic light-emitting-diodes (OLEDs), thin-film solar cells (*e.g.*, silicon and compound semiconductors) and touch panels. At present, indium–tin-oxide (ITO) thin films prepared by magnetron sputtering deposition methods are in practical use for most thin-film transparent electrode applications. It should be noted that the indium in the ITO used in LCDs constitutes the largest use of this material, approximately 80% of the total [1]. In addition to the currently expanding market of the indium, as ITO, used for transparent electrode applications, the amount of indium used in $CuInGaSe_2$ thin-film solar cells has been dramatically expanding in recent years [2]. As a result, there are serious problems associated with this expanding market for indium, especially ITO, as a stable supply may be difficult to achieve because of the high cost and scarcity of indium. In addition to the resource availability problem, the toxicity of indium compound (including ITO) powders has been recently reported [3]. Therefore, it is important to develop substitute materials for ITO transparent electrodes and/or to develop technology for reducing indium usage in transparent electrodes [4–7]. For the purpose of eliminating the requirement for ITO as thin-film transparent electrodes used in LCDs, in particular, it is necessary to develop an alternative material that contains a reduced amount or no indium.

In this paper, we survey the recent progress and prospects for further development of ITO substitute materials for practical use as thin-film transparent electrodes.

2. Substitute materials for ITO transparent electrodes

For most transparent electrode applications, it is necessary to deposit transparent conducting oxide thin films on various substrates at a temperature below approximately 200 °C, except for applications such as amorphous silicon solar cells and plasma display panels, as indicated in Table 1. In addition, various applications often impose specific restraints on the properties of thin-film transparent electrodes. For example, polycrystalline ITO thin films prepared by dc magnetron sputtering deposition have been practically used as transparent electrodes for most types of LCDs and touch panels; the nature of specifically suitable properties is affected complexly by the display's size and type as well as the manufacturing process used. However, most of the manufacturing processes involve proprietary technologies. For example, current conventional LCDs (TFT-LCD) are operated with either a vertical alignment (VA) or in-plane switching (IPS) mode. In LCDs, ITO transparent electrodes must be prepared at a temperature below approximately 200 °C with a low resistivity on the order of 10^{-4} Ω cm, as listed in Table 1. In addition to a deposition substrate temperature below approximately 200 °C, applications for VA-type LCDs and touch panels require transparent electrodes with a thickness below approximately 50 nm. For the above applications, we have previously noted the feasibility of substituting polycrystalline impurity-doped ZnO and amorphous multi-component oxides that contain a reduced amount of indium for ITO [4–8]: $ZnO–In_2O_3$ and zinc indates ($Zn_2In_2O_5$ and $Zn_3In_2O_6$), $In_2O_3–SnO_2$ and indium

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Table 1
Property requirements in various transparent electrode applications

Applications		Substrate material	Deposition temperature [°C]	Film thickness [nm]	Resistivity [Ω cm] (sheet resistance [Ω/□])
LCD	TFT side	Glass	≈200	35–140	$4–5\times10^{-4}$ (30–120)
	CF side	Glass	<200	120–160	$1.6–3.6\times10^{-4}$ (16–30)
PDP		Glass	≈200 after 550	150–200	$2.0–3.0\times10^{-4}$ (<20)
OLED		Glass plastic film	<200	100–150	$2.0–4.0\times10^{-4}$ (<40)
Touch panel		Plastic film	150–180	10–30	(250–500)
CIGS solar cell		Glass	<200	1000–2000	on the order of 10^{-4} (<10)
a-Si solar cell		Glass	500–600	800–1000	on the order of 10^{-4} (<10)

stannates ($In_4Sn_3O_{12}$) and Zn–In–Sn–O multi-component oxides with an appropriate composition. In these examples, the ratio of In to the sum total amount of the other metal elements is higher than about 50 at.%. In particular, amorphous multi-component oxides such as ZnO–In_2O_3, In_2O_3–SnO_2 and Zn–In–Sn–O, without or with the addition of gallium or magnesium, may be suitable for transparent electrode applications used in flat panel displays such as OLEDs [8]. The use of these multi-component oxide materials can reduce the amount of indium nearly by half. However, this level of reduction may yet be insufficient. As a result, we have previously noted that the best, and only practical, indium-free candidate for an alternative material to ITO is impurity-doped ZnO such as Al- or Ga-doped ZnO (AZO or GZO), as evidenced from the obtained properties [4–7]. In particular, the best thin-film material is AZO due to its low obtainable resistivity [9] and the low cost and non-toxicity of the source materials. Nevertheless, there are some remaining problems associated with substituting impurity-doped ZnO for ITO.

3. Impurity-doped ZnO transparent electrodes

3.1. Preparation by magnetron sputtering

In transparent electrodes used for LCDs, polycrystalline ITO thin films with high stability and low resistivity are prepared not only by a deposition on substrates at a temperature around 200 °C but also by a postannealing on the resulting amorphous ITO thin films at a temperature around 200 °C. However, it should be noted that the latter film preparation technique is unsuitable for impurity-doped ZnO thin films deposited by magnetron sputtering because of the difficulties of depositing amorphous films evenly on low temperature substrates and of decreasing sufficiently the resistivity of as-deposited polycrystalline films with postannealing at a temperature around 200 °C. With regard to recent advances in deposition techniques for impurity-doped ZnO thin films, a resistivity of 4.4×10^{-4} Ω cm was obtained in a GZO thin films prepared with a thickness of 30 nm by vacuum arc plasma evaporation (VAPE) [10]. However, the difficulties associated with AZO depositions, especially the control of film thickness on large area substrates, must be resolved for the practical use of VAPE methods with a high deposition rate [11–13]. Therefore, we have previously noted the importance of using magnetron sputtering depositions as the only currently suitable practical preparation technique when applying transparent conducting impurity-doped ZnO thin films as transparent electrodes for LCDs [4–7]. However, substituting impurity-doped ZnO for ITO using magnetron sputtering depositions currently involves some remaining problems associated with resolving the thickness dependency of the resistivity and the non-uniform distribution of resistivity.

It should be noted that the obtainable properties of transparent conducting impurity-doped ZnO thin films prepared by magnetron sputtering are considerably affected by the apparatus and the deposition conditions as well as the sintered oxide target used. A particularly serious problem is that most of the commercially available oxide targets are unsuitable for obtaining a sufficiently low obtainable resistivity with a uniform spatial distribution on the substrate [7]; the non-uniform resistivity distribution results in an increase of the obtainable resistivity in impurity-doped ZnO thin films deposited on moving large area substrates used for practical applications. Therefore, improving the resistivity distribution is necessary to obtain lower resistivity impurity-doped ZnO thin films suitable for use as alternatives to ITO transparent electrodes [6,7,14]. As an example, the two typical resistivity distributions shown in Fig. 1 for both (a) AZO and (b) GZO thin films deposited on a substrate placed parallel to the disk target surface by a dc magnetron sputtering (dcMS) apparatus use different commercially available AZO and GZO targets (a diameter of 150 mm), respectively; the solid data points indicate the film resistivity resulting from the use of the better one of the targets. All of the thin films were deposited on a glass substrate at a temperature of 200 °C with a dc power of 200 W. As can be seen in Fig. 1, the resistivities obtained at the substrate locations that correspond to the target erosion area were higher than those at the substrate locations

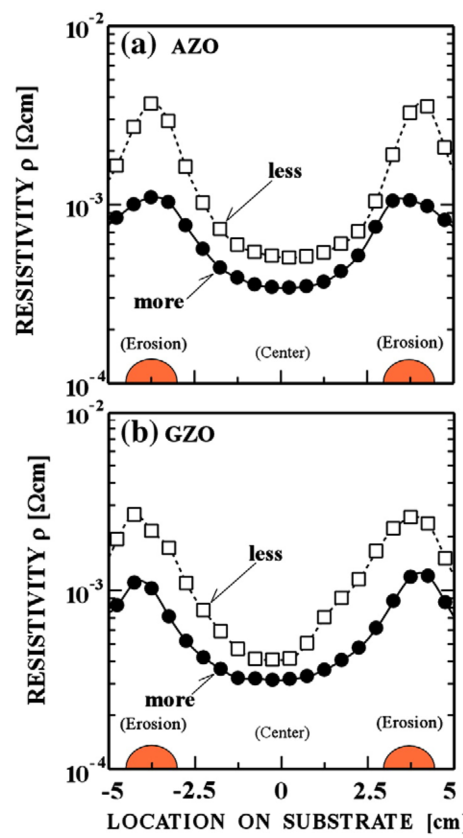

Fig. 1. Resistivity spatial distributions for (a) AZO and (b) GZO thin films prepared by dcMS using more (solid) or less (open) oxide targets.