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Present status of transparent conducting oxide thin-film development for Indium-Tin-Oxide (ITO) substitutes

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Abstract

This paper describes the present status and prospects for further development of transparent conducting oxide materials for use as Indium-Tin-Oxide (ITO) substitutes in the thin-film transparent electrodes of liquid crystal displays (LCDs), currently the largest use of ITO, and, thus, of indium. The best substitute material for the ITO transparent electrodes used in LCDs is impurity-doped ZnO, e.g., Al- and Ga-doped ZnO (AZO and GZO). From resource and environmental points of view, AZO is the best candidate. The most important problems associated with substituting impurity-doped ZnO for the ITO used in LCDs have already been resolved in laboratory trials. Under the present circumstances, (rf and dc)-magnetron sputtering (rf+dc-MS) deposition, both with and without H_2 gas introduction, has been found to be the best deposition method to prepare impurity-doped ZnO thin films for practical use; AZO thin films with a resistivity on the order of 10^{-4} Ω cm were prepared on glass substrates with an approximately uniform resistivity spatial distribution and a thickness above 100 nm. In order to improve the resistivity stability, AZO and GZO thin films co-doped with another impurity have been newly developed. A 50 nm-thick V-co-doped AZO (AZO:V) thin film was stable enough to be acceptable for use in practical transparent electrode applications. However, it seems likely that obtaining a stability comparable to that of ITO using impurity-doped ZnO will be difficult for thin films with a thickness below approximately 30 nm.

Keywords: Transparent conducting oxide; Thin film; ITO; AZO; GZO; LCD; Transparent electrode; Magnetron sputtering

1. Introduction

Indium-Tin-Oxide (ITO) thin films have been practically used as transparent electrodes for most of the various types of liquid crystal displays (LCDs). At present, the indium component of the ITO used in LCDs constitutes the largest use of this material. In addition, the total amount of indium used for flat panel displays, alkaline batteries and thin-film solar cells has been markably expanding in recent years. It is widely believed that a shortage of indium may occur in the near future because of the limited nature of world indium reserves. In addition to the resource availability problem, the price of indium has recently increased by a factor of approximately ten. As a result, a stable supply of ITO may be difficult to achieve for the recently expanding market for LCDs. Therefore, it is important to develop alternatives to the ITO thin-film transparent electrodes used in LCDs. Recently, transparent conducting oxides (TCOs) that contain a reduced amount or no indium have attracted much attention as substitute materials. We have previously noted the importance of Al- and Ga-doped ZnO (AZO and GZO) and $ZnO–In_2O_3–SnO_2$ (or Zn–In–Sn–O) multi-component oxides as substitutes for ITO [1–5]. In this paper, we describe the present status and prospects for further development of these substitute TCO materials for practical use as thin-film transparent electrodes of LCDs. In particular, this review is focused on the remaining problems associated with substituting AZO and GZO for ITO in LCD applications with special emphasis on our proposed solution for the problems.

2. TCO material development of ITO substitutes for LCD applications

Many kinds of TCO thin-film materials have been newly developed in recent years [2–5]; host materials and suitable dopants are shown in Table 1 for typical TCO thin-film materials reported up to now. It should be noted that ITO

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Table 1
Host and associated dopant materials in typical TCO thin films

Binary	Dopant	Resistivity	Toxicity
ZnO	Al, Ga, B, In, Y, Sc,V, Si, Ge, Ti, Zr, Hf,// F	⊙	
CdO	In, Sn	⊙	××
In_2O_3	Sn, Ge, Mo, Ti, Zr, Hf, Nb, Ta, W, Te// F	⊙	×
Ga_2O_3	Sn	Δ	
SnO_2	Sb, As, Nb, Ta// F	○	
TiO_2	Nb, Ta	Δ	
Ternary			
$MgIn_2O_4$		Δ	
$GaInO_3$, $(Ga, In)_2O_3$	Sn, Ge	Δ	
$CdSb_2O_6$	Y	Δ	×
$SrTiO_3$	Nb, La	×	
Ternary	Multi-component	Resistivity	Toxicity
$Zn_2In_2O_5$, $Zn_3In_2O_6$	$ZnO–In_2O_3$ system	○	
$In_4Sn_3O_{12}$	$In_2O_3–SnO_2$ system	○	
$CdIn_2O_4$	$CdO–In_2O_3$ system	○	×
Cd_2SnO_4, $CdSnO_3$	$CdO–SnO_2$ system	○	×
Zn_2SnO_4, $ZnSnO_3$	$ZnO–SnO_2$ system	Δ	
	$ZnO–In_2O_3–SnO_2$ system	○	
	$CdO–In_2O_3–SnO_2$ system	○	×
	$ZnO–CdO–In_2O_3–SnO_2$ system	○	×

: ⊙Very good, ○: Good, Δ: Average, ×: Bad, ××: Very bad.

transparent electrodes used in LCDs have been prepared on amorphous substrates such as glass by dc magnetron sputtering deposition. In addition, preparation at a temperature below 200 °C along with the feasibility of obtaining low resistivities on the order of 10^{-4} Ω cm and thicknesses of approximately 15 to 100 nm are required when fabricating most types of LCDs. Therefore, under the present circumstances, it is difficult to use practically cadmium oxide-based and titanium oxide-based TCO materials [6,7] because of the toxicity of cadmium and the required high temperature heat-treatment, respectively, as indicated in Table 1 by a cross. In titanium oxide and titanium oxide-based TCO thin films, a deposition and heat-treatment at a high temperature above about 300 °C and/or an epitaxial growth on a single crystal substrate are necessary in order to obtain a low resistivity on the order of 10^{-4} Ω cm [7–9]. In addition, there is a patterning problem. Of the remaining materials, three kinds of binary compounds (ZnO, In_2O_3 and SnO_2) and multi-component oxides composed of any combination of these binary compounds or ternary compounds may possibly be usable practically for transparent electrode applications in LCDs. We have previously noted the feasibility of decreasing the use of indium by substituting multi-component oxides that contain a reduced amount of indium, e.g., $ZnO–In_2O_3$, $In_2O_3–SnO_2$ and Zn–In–Sn–O, composed of any combination of ZnO, In_2O_3 and SnO_2 [2–5]. Table 2 summarizes the obtained properties of reduced-indium LCD-suitable TCO materials composed of multi-component oxides. These properties could be obtained in thin films prepared under optimized deposition conditions by magnetron sputtering (MS) and vacuum arc plasma deposition (VAPE) methods [2–5]. $ZnO–In_2O_3$ and zinc indates, $In_2O_3–SnO_2$ and indium stannate, and Zn–In–Sn–O multi-component oxides with an appropriate composition are possible candidates for use as transparent electrodes in LCDs. The resulting amount of indium used in these materials is reduced to approximately half, a possibly insufficient amount.

Another solution is indium-free materials such as ZnO, SnO_2 and $ZnO–SnO_2$ multi-component oxides[1–5]. However, impurity-doped SnO_2 and SnO_2-based materials are unsuitable for use in LCDs because of the difficulty of producing low-resistivity films in depositions on low temperature substrates [10]. In addition, there is a problem of patterning. As a result, at present, the best, and only practical, indium-free candidate for an alternative TCO material is impurity-doped ZnO. We have previously noted the importance of substituting transparent conducting AZO and GZO thin films for ITO [1,3–5]. In particular, AZO is suitable for use in LCDs.

3. Problems associated with substituting AZO and GZO for ITO

Many problems associated with substituting transparent conducting AZO and GZO thin films for ITO transparent electrodes in LCD applications have to be overcome. Although it is believed that most of these problems can be resolved eventually, at present, the most important remaining problems are the development of thin-film preparation techniques suitable for LCD applications and the improvement of stability in various environments of thin films with a thickness below approximately 100 nm [5,11,12]. Practical thin-film preparation techniques suitable for LCD fabrication processes must achieve the following minimum requirements: transparent conducting AZO and GZO thin films with a thickness of approximately 50 nm deposited with a resistivity on the order of 10^{-4} Ω cm at a high deposition rate on a large area substrate and a temperature below 200 °C. In addition, further requirements may include improving the stability in various environments. Although preparation techniques such as pulsed laser depositions (PLD) that can prepare AZO thin films with a low resistivity on the order of 10^{-5} Ω cm [13] have been reported, the above requirements most probably limit the applicable preparation methods to only MS deposition [14–16] and VAPE [17–19]. However, the difficulties associated with AZO depositions and achieving stability in thin films with a thickness below 50 nm must be resolved for the practical use of VAPE methods. Therefore, it can be concluded that MS deposition methods are the only suitable practical preparation techniques when using

Table 2
Obtained properties of reduced-indium TCO materials

TCO	In content [at.%]	Deposition temperature [°C]	Resistivity ρ [Ω cm]
$ZnO–In_2O_3$	50–80	RT	$2.9–3.5\times10^{-4}$
$In_2O_3–SnO_2$	50–90	RT	$4.5–5.5\times10^{-4}$
Zn–In–Sn–O	50–57	RT	$4.5–8.5\times10^{-4}$