Transparent conducting impurity-co-doped ZnO:Al thin films prepared by magnetron sputtering

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Abstract

This report describes the effects of impurity-co-doping on transparent conducting Al-doped ZnO (AZO) films prepared by DC magnetron sputtering using a target composed of dopant powder added to a mixture of ZnO and Al₂O₃ powder. The chemical stability of transparent conducting AZO films could be improved by co-doping Cr or Co without significantly altering the original electrical and optical properties. A reduction in etching rate, as well as a low resistivity of 3.0 × 10⁻⁴ Ω cm, was obtained in transparent conducting AZO:Cr films prepared using Zn powder added into the oxide target with an Al₂O₃ content of 2 wt.% and a Cr₂O₃ content of 1 wt.%. In addition, a reduction in etching rate, as well as low resistivity, was obtained in transparent conducting AZO:Co films prepared with an Al₂O₃ content of 2 wt.% and a CoO content of 0.5–2 wt.% or a CoCl₂ content of 1.5–3 wt.% © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Recent developments in optoelectronic device systems require control of the physical and/or chemical properties of transparent conducting oxide (TCO) films used as transparent electrodes. For the purpose of obtaining a TCO film suitable for specialized applications, several approaches have been reported recently. For example, some of the required properties may be attained by the recent development of new TCO materials using ternary compounds, such as Zn₅SnO₄ [1], ZnSnO₃ [2], MgIn₂O₄ [3], Zn₂In₂O₅ [4] and In₇Sn₂O₁₂ [5]. However, alterations in the physical and chemical properties of TCO films have been limited by the intrinsic properties of the TCO material used. We have reported on the applicability of new materials consisting of multicomponent oxides composed of combinations of binary and/or ternary compounds, such as ZnO–In₂O₃ [6], In₂O₃–SnO₂ [7], Zn₂In₂O₅–In₃Sn₂O₁₂ [8] and MgIn₂O₄–Zn₃In₂O₅ [9]. The use of multicomponent oxides [10–12], the physical and chemical properties of which can be controlled by changing their chemical compositions, may produce TCO films suitable for specialized applications. In addition to the use of multicomponent oxides, we have recently proposed the use of In₇Sn₂O₁₂ co-doped with Sn and Zn (Zn-co-doped ITO) for TCO films. Control of the etching rate, as well as low resistivity, was obtained in Zn-co-doped ITO (ITO:Zn) films [13]; the etching rate could be increased as the Zn content doped into ITO was increased.

Transparent conducting ZnO films doped with an impurity, such as Al or Ga [11,14], have recently attracted much attention as an alternative to ITO films, which are widely used but are expensive materials. Although ZnO films are abundant and inexpensive, they are more chemically unstable than ITO films. For example, ZnO films can easily be etched in acid and alkaline solutions; the etching rates for these etchants are higher than those for ITO. These high etching rates may often be a disadvantage for applications with a patterning process. Therefore, an improvement in chemical stability is required before ZnO films can be used for many applications. In this paper, we demonstrate an improvement in the chemical stability of ZnO films co-

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doped with Al and Cr or Co and prepared by DC magnetron sputtering.

2. Experimental

The films were prepared by conventional DC planar magnetron sputtering using a powder target: a mixture of ZnO, Al2O3 and Cr2O3 or CoO (or CoCl2) powders (purity, 99%) calcined at 900–1000°C in an Ar gas atmosphere for 1 h and pressed into an Al holder with a diameter of 120 mm [15]. The Al-doped ZnO (AZO) films were prepared using a ZnO + Al2O3 powder target with the Al content (Al2O3 added to the ZnO powder) held constant at 2 wt.%; the Cr- or Co-co-doped AZO (AZO:Cr or Co) films were prepared using a powder target with the dopant content [Cr2O3 or CoO (or CoCl2) added to the ZnO powder] varied in the range 0–15 wt.%. The powder in the targets was completely replaced for every deposition. Corning 7059 glass substrates were placed parallel to the target surface. After presputtering for 10–60 min, sputtering deposition was carried out with a power of 50 W at a sputter gas pressure of 0.2 Pa in a pure Ar gas atmosphere. The substrate temperature was 200°C.

Film thickness ranged from 200 to 400 nm, measured using a conventional surface roughness detector with a stylus. The deposition rate was approximately 16 nm/min. The chemical composition in deposited films as determined by energy dispersive X-ray spectroscopy (EDX) analyses, specifically, the doped impurity contents [impurity/(Zn + impurity) atomic ratio], was found to be approximately equal to that present in the target used. Electrical resistivity and Hall mobility were measured using the van der Pauw method. Etching tests using acid and alkaline solutions were carried out in 0.2 mol/l HCl and 3.0 mol/l KOH at 20°C, respectively.

3. Results and discussion

3.1. Effect of Cr-co-doping on AZO films

It has been reported that AZO films prepared by DC magnetron sputtering can be produced with a resistivity as low as 3–5 × 10⁻⁴ Ω cm, but the resistivity exhibits a spatial distribution on the substrate surface [15]. Also, the resistivity obtainable and its distribution are strongly dependent on the deposition conditions, as well as on the oxygen content in the oxide target used [15–18]. In addition, oxygen introduced into the Ar gas atmosphere did not improve the resistivity or its distribution in conventional DC magnetron sputtering using an oxide target. Likewise, in the present study, the introduction of oxygen was found to be ineffective in lowering the resistivity of AZO films prepared by DC magnetron sputtering using an oxide powder target.

![Fig. 1. Resistivity (○), carrier concentration (□) and Hall mobility (Δ) as functions of Cr2O3 content for AZO:Cr films.](image)

Fig. 1 shows resistivity (ρ), carrier concentration (n) and Hall mobility (μ) as functions of the Cr content for AZO:Cr films prepared using AZO (Al2O3 content of 2 wt.%) targets with a Cr2O3 content of 0–5 wt.% These films were prepared with presputtering for 10 min at a substrate temperature of approximately 200°C and sputtering at an Ar gas pressure of 0.2 Pa with a DC power of 50 W using a powder target calcined at 900°C. The film thickness of AZO:Cr films prepared with a Cr2O3 content of 0–3 wt.% was approximately 350 nm. Resistivity increased from the minimum value, obtained in an AZO film, as the Cr2O3 content was increased. The arrow noted in Fig. 1 indicates the subsequent point that could not be shown, because the resistivity increased markedly as the Cr2O3 content was increased above 3 wt.% As is evident in Fig. 1, the resistivity change is attributable to changes in both n and μ.

The dependence of etching rate (R_e) on the Cr2O3 content in HCl and KOH solutions is shown in Fig. 2 for AZO:Cr films. The chemical stability in both HCl and KOH solutions improved, i.e. the etching rates decreased as the Cr2O3 content was increased. Thus, with Cr-co-doping into AZO films, the chemical stability improved, but the resistivity increased. It is well known that chemical stability, represented here as etching rate, usually improves as the crystallinity of conventional TCO films is improved [10,19]. Fig. 3 shows X-ray diffraction patterns as a function of the Cr2O3 content for the AZO:Cr films shown in Fig. 1. The AZO film was c-axis-oriented perpendicular to the substrate surface, as evidenced from a strong (0002) and weak
(0004) diffraction peaks. The intensity of these peaks decreased gradually as the Cr$_2$O$_3$ content was increased up to approximately 3 wt.%, and then decreased markedly as the Cr$_2$O$_3$ content was further increased. Since the crystallinity of AZO:Cr films, estimated from the X-ray diffraction intensity, actually decreased as the Cr$_2$O$_3$-co-doped content was increased, the improvement in the chemical stability of AZO:Cr films cannot be related to the crystallinity.

Fig. 4 shows optical transmission spectra as a function of the Cr$_2$O$_3$ content for AZO:Cr films. The transmittance in the visible range decreased gradually as the Cr$_2$O$_3$ content was increased up to approximately 3 wt.%, markedly decreasing as the Cr$_2$O$_3$ content was further increased. This decrease in transmittance is explained by the fact that a transition metal element such as Cr exhibits optical absorption in the visible range. Despite this, an average transmittance above 89% in the visible range was obtained for AZO:Cr films prepared with a Cr$_2$O$_3$ content of up to 3 wt.%.

### 3.2. Effect of Zn introduction on AZO:Cr films

As is evident in Figs. 1 and 3, $\mu$, $n$ and the crystallinity decreased in AZO:Cr films as the Cr$_2$O$_3$ content was increased. These results suggest that electrical conduction in AZO:Cr films is mainly dominated by grain boundary scattering [11,20]: The decrease in both $\mu$ and $n$ is caused by oxygen adsorption at the grain boundary. Thus, the resulting resistivity increase with increasing Cr$_2$O$_3$ content may be ascribed to excessive oxygen in the chamber during the AZO:Cr film deposition. In the deposition of AZO:Cr films, a reduction in oxygen gas content in the chamber could lower the resistivity by suppressing this oxygen adsorption. Since it is difficult to control the oxygen gas content in the chamber during sputter deposition using a pure Ar gas atmosphere, the sputter deposition of AZO:Cr films was carried out using Zn powder added to the oxide powder targets.

Fig. 5 shows $\rho$, $n$ and $\mu$ as functions of the Zn content for AZO:Cr films prepared using AZO (Al$_2$O$_3$ and Cr$_2$O$_3$ contents of 2 and 1 wt.% respectively) targets with a Zn content of 0–20 wt.%. These films, with a thickness of approximately 330 nm, were prepared at a substrate temperature of approximately 200°C and an Ar gas pressure of 0.2 Pa with a DC power of 50 W. The resistivity decreased as the Zn content was...
increased up to approximately 8 wt.%; it then remained relatively unchanged at the minimum resistivity as the Zn content was further increased. This change in resistivity was attributed to that of \( \mu \). However, the crystallinity of AZO:Cr films prepared with a Zn content of 4–20 wt.% was relatively independent of the Zn content. It should be noted that a resistivity as low as \( 3.0 \times 10^{-4} \, \Omega \, \text{cm} \) was obtained in AZO:Cr films prepared with a Zn content of 8 wt.%.

An average transmittance of above 87% in the visible range was obtained in AZO:Cr films prepared with a Zn content of 0–20 wt.%. In addition, etching rates in HCl and KOH solutions were relatively independent of the Zn content up to approximately 12 wt.%. The Zn content dependence of \( R_e \) in HCl and KOH solutions is shown in Fig. 6 for AZO:Cr films. For the etching test in HCl solution, AZO:Cr films prepared with a Zn content of 0–20 wt.% exhibited an \( R_e \) of 7–8 nm/s, and that in a KOH solution remained low, approximately 1 nm/s, in the Zn content range of 0–12 wt.%. In contrast, the \( R_e \) in KOH markedly increased as the Zn content was increased above 16 wt.% Therefore, it can be concluded that the introduction of Zn during sputter deposition is beneficial for AZO:Cr film preparation; AZO:Cr films prepared with a Zn content of 8–12 wt.% showed resistivity as low as \( 3 \times 10^{-4} \, \Omega \, \text{cm} \), as well as an etching rate that was lower than that of AZO films.

### 3.3. Effect of Co-co-doping on AZO films

Figs. 7 and 8 show resistivity and etching rates in HCl and KOH solutions as functions of the Co content for AZO:Co films prepared using AZO targets co-doped with CoO and CoCl\(_2\), respectively. After presputtering for 60 min, these films were prepared at a substrate temperature of approximately 200°C and an Ar gas pressure of 0.2 Pa with a DC power of 50 W using powder targets calcined at 1000°C. The resistivity
obtained for the resulting AZO films was higher than that for the AZO:Cr films shown in Fig. 1. This difference in resistivity obtained for AZO films is ascribed to differences in sputter deposition conditions. As is evident in Figs. 7 and 8, the resistivity of AZO:Co films was relatively independent of CoO or CoCl₂ content of in the range 0–2 wt.%, before increasing as the content was increased further. In order to obtain lower resistivity, we attempted AZO:Co film preparation using a powder target with added Zn. In contrast to the results with AZO:Cr films, the introduction of Zn into AZO:Co films proved fruitless: the resulting resistivity increased as the Zn content was increased.

The etching rate in HCl solution, in general, decreased as the CoO or the CoCl₂ content was increased up to approximately 3 wt.%; that in the KOH solution continued to decrease as the CoO or CoCl₂ content was increased further. A reduction in etching rate, as well as a low resistivity of 5–6 × 10⁻⁴ Ω cm, was obtained in transparent conducting AZO:Co films prepared with an Al₂O₃ content of 2 wt.% and a CoO content of 1 wt.% under optimized sputter deposition conditions, using Zn powder added into the oxide powder targets. In addition to Cr impurity co-doping, AZO:Co thin films were prepared. A reduction in etching rate, as well as a low resistivity of 3.0 × 10⁻⁴ Ω cm, was obtained in transparent conducting AZO:Cr films prepared with an Al₂O₃ content of 2 wt.% and a Cr₂O₃ content of 1 wt.% with optimized sputter deposition conditions, using Zn powder added into the oxide powder targets. In addition to Cr impurity co-doping, AZO:Co thin films were prepared. A reduction in etching rate, as well as a low resistivity of 5–6 × 10⁻⁴ Ω cm, was obtained in transparent conducting AZO:Co films prepared with an Al content of 2 wt.% and a CoO content of 0.5–2 wt.% or a CoCl₂ content of 1.5–3 wt.%.

It can be concluded that the chemical stability of transparent conducting AZO films can be improved by co-doping with Cr or Co without significantly altering the original electrical and optical properties.

4. Conclusions

Impurity-co-doped transparent conducting Al-doped ZnO (AZO) films were prepared by conventional DC magnetron sputtering using a target composed of dopant powder added to a mixture of ZnO and Al₂O₃ powders. The resistivity of AZO:Cr films increased gradually as the Cr₂O₃ content was increased up to 3 wt.%; it increased markedly with further increases in Cr₂O₃ content. However, the etching rate of AZO:Cr films in HCl solution decreased markedly as the Cr₂O₃ content was increased to approximately 3 wt.%, continuing to decrease with further increases in Cr₂O₃. In addition, the etching rate in KOH solution was also found to decrease markedly as the Cr₂O₃ content was increased above approximately 1 wt.%. A reduction in etching rate, as well as a low resistivity of 3.0 × 10⁻⁴ Ω cm, was obtained in transparent conducting AZO:Cr films prepared with an Al₂O₃ content of 2 wt.% and a Cr₂O₃ content of 1 wt.% with optimized sputter deposition conditions, using Zn powder added into the oxide powder targets. In addition to Cr impurity co-doping, AZO:Co thin films were prepared. A reduction in etching rate, as well as a low resistivity of 5–6 × 10⁻⁴ Ω cm, was obtained in transparent conducting AZO:Co films prepared with an Al content of 2 wt.% and a CoO content of 0.5–2 wt.% or a CoCl₂ content of 1.5–3 wt.%. It can be concluded that the chemical stability of transparent conducting AZO films can be improved by co-doping with Cr or Co without significantly altering the original electrical and optical properties.

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