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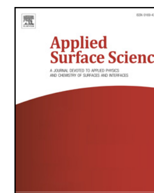

Full Length Article

# Improved moisture stability of thin Ga-doped ZnO films by indium codoping

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ABSTRACT

We studied the effects of indium codoping on the moisture stability of 50- and 100-nm-thick Ga-doped ZnO (GZO) films grown at various oxygen gas flow rates (OFRs) by ion plating with direct-current arc discharge. The results of damp-heat tests at a temperature of 60 °C and a relative humidity of 95% for 500 h showed that, for 100-nm-thick GZO film with 0.75 wt% $In_2O_3$ codoping (GZO:In) grown at an OFR of higher than 10 sccm, the relative change in resistivity (Δρ) was greatly reduced to be less than 10%. Furthermore, Δρ = 7.4% was achieved for 50-nm-thick GZO:In films grown at an OFR of 15 sccm. Δρ is defined as $\Delta\rho = 100\% \times |\rho\text{-}\rho_0|/\rho_0$, where $\rho_0$ and ρ are electrical resistivities before and after the damp-heat tests, respectively. The low resistivity and high transparency of GZO films were retained by indium codoping. No phase segregation of $Ga_2O_3$ and $In_2O_3$ in the GZO:In films was observed by X-ray diffraction and energy-dispersive X-ray spectroscopy in scanning transmission electron microscopy. The water diffusion into GZO film during damp-heat test was blocked in GZO:In film grown at OFR = 15 sccm, which was directly observed by secondary ion mass spectroscopy. All these findings demonstrate that indium codoping is an effective method of improving the moisture stability of thin GZO film of thickness less than 100 nm. This is essential for applications including optoelectronic devices.

## 1. Introduction

Transparent conductive oxide (TCO) films based on Al- or Ga-doped ZnO (AZO or GZO) films have tremendous potential applications in various optoelectronic devices such as flat-panel displays, thin-film solar cells and oxide thin-film transistors [1–6]. ZnO-based TCO films are usually deposited on glass or plastic substrates at a low temperature of 200 °C or even lower. Polycrystalline ZnO-based TCO films commonly become unstable in the presence of moisture [7–12]. An unstable ZnO-based TCO film will show a deterioration of its electrical properties with an increased electrical resistivity when it is exposed to ambient atmosphere, especially under a harsh damp-heat condition. In this paper, in order to evaluate the deterioration of electrical properties of TCO films, the relative change in electrical property is defined as $\Delta E = 100\% \times |E - E_0|/E_0$, where $E_0$ and $E$ are the electrical properties (the resistivity ρ, the carrier concentration $N_e$, the Hall mobility $\mu_H$ and the sheet resistance $R_s$) before and after the damp-heat tests, respectively. The deterioration of ZnO films used as a component in optoelectronic devices will cause performance degeneration and device failure. Even with careful encapsulation, moisture can permeate through substrates or be introduced into devices during a manufacturing process such as wet etching [13–15]. Improving the moisture stability of ZnO-based TCO films is, thus, critical to the long-term reliability of optoelectronic devices.

Over the past decade, many studies have been carried out to improve the moisture stability of ZnO-based TCO films [9,16–18]. One strategy is to introduce an ultrathin metal layer such as Ni or Ti film as the capping layer by post-deposition [17,19]. The ultrathin metal layer is oxidized in the presence of ambient moisture or by an in-situ oxygen plasma treatment. The generated metal oxide prevents the diffusion of oxygen or water molecules into the underlayer and it also modulate the work function of ZnO-based TCO electrode, thereby, improving the device performance. Another feasible strategy is to optimize the deposition conditions or the contents of dopants [16,18,20]. For example, Nakagawara et al. reported that heavy Ga doping could substantially improve the moisture stability of GZO films [16]. By 12.4 wt% Ga doping, an extremely moisture-resistant GZO film with a Δρ of less than 3% was achieved after a damp-heat test for 2000 h (IEC61646 standard: a temperature of 85 °C and a relative humidity of 85%). It should be noted that the excessive Ga doping in GZO film disordered the crystalline structure of GZO film and resulted in a high resistivity due to the dominant grain boundary scattering. This will hamper its wide applications as TCO film. Recently, Zhu et al. have reported a highly moisture- and weak-acid-resistant GZO film codoped with 0.2 wt% titanium dioxide [20]. The relative change in sheet resistance ($\Delta R_s$) was as low as 5.1% after damp-heat test under the conditions of 97% relative humidity at 121 °C for 1 day. Following the semiconductor technology roadmap, the microelectronic industry has benefited

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enormously from the scaling down in the device dimensions. TCO electrodes of 100 nm thickness or even much smaller thickness have been widely adopted in the present electronic devices, such as thin-film transistors in displays [14,21,22]. To date, most of the reported moisture-resistant ZnO-based TCO films have been much thicker than 100 nm. The moisture stability of 100-nm-thick or even thinner ZnO-based TCO film is still a huge challenge. In our previous work, we found that 0.25 wt% $In_2O_3$ codoping could improve the moisture stability of GZO film with a thickness > 300 nm [23,24]. Our further research showed the improved moisture stability of indium codoped GZO (GZO:In) film even though the GZO:In film has a thickness of 100 nm or smaller. As shown in Fig. S1 in Supplementary material, 0.75 wt% $In_2O_3$ codoping could provide us with a GZO:In film showing a perfect moisture stability regardless of oxygen gas flow rate (OFR) introduced into the deposition chamber, in the range from 12 to 15 sccm (sccm denotes standard cubic centimeters per minute), which is an optimized range for Hall mobility, as shown in Fig. 3(a). In this study, we will demonstrate that 0.75 wt% $In_2O_3$ codoping is an effective method to achieve moisture resistant 50-nm-thick GZO films.

## 2. Experimental

GZO and 0.75 wt% $In_2O_3$ codoped GZO:In films were deposited on alkali-free glass substrates (Corning, EAGLE XG) at 200 °C by ion plating with dc-arc discharge using a pressure-gradient-type plasma gun [18]. Sintered GZO tablets (Hakusui Tech) containing 3.0 wt% $Ga_2O_3$ (99.9% purity) with and without 0.75 wt% $In_2O_3$ (99% purity) codoping were used as targets. During the deposition, the flow rate of argon gas (Ar) was fixed at 140 sccm. Oxygen gas was introduced into the deposition chamber to compensate for oxygen deficiency. OFR was varied from 0 to 25 sccm. Other details of the growth conditions have been reported in our previous papers [2,18]. For both GZO and GZO:In films, the deposition rates increased with increasing OFR. The film thickness was controlled by adjusting the deposition time, which was calibrated by a trial growth before the formal deposition. Film thickness was measured using a surface profilometer (Alfa-Step, IQ). In this paper, the film thickness is 100 ± 5 nm if without special emphasis.

The surface morphologies were characterized by atomic force microscopy (AFM: JEOL, JSPM-5200). The crystal structures of GZO and GZO:In films were characterized by x-ray diffraction (XRD) using Cu $K_\alpha$ ($\lambda$ = 1.5422 Å) radiation (Rigaku, ATX-G). Electrical properties (the resistivity ρ, the carrier concentration $N_e$ and the Hall mobility $\mu_H$) of films were determined by room-temperature Hall effect measurements using an Accent HL-5500 system. The magnetic field strength was 0.505 Tesla. The samples were cut to 1 × 1 $cm^2$ size, and ohmic contacts were formed by tiny indium dots placed at the four corners on the sample surface. Damp-heat tests were performed at a temperature of 60 °C and a relative humidity of 95% for 500 h [18]. Optical transmittance and reflection spectra were measured in the wavelength range from 200 to 2500 nm using Hitachi U4100 with an incidence angle of 5°. Cs-corrected scanning transmission electron microscopy (STEM) analysis was performed by Hitachi HD-2700 using an accelerating voltage of 200 KV. This STEM was fitted with two windowless X-$Max^N$ 100 TLE (Oxford Instruments) silicon drift detectors for energy-dispersive X-ray spectroscopy (EDX) measurement. This EDX detector can provide enough counts to achieve a sufficient precision for imaging changes on the 0.1 wt% level. The spatial resolution of EDX is about 1 nm when an accelerating voltage of 200 KV is used. To quantitatively estimate the water diffusion into GZO and GZO:In films after damp-heat test, hydrogen depth profiles were determined by secondary ion mass spectroscopy (SIMS) measurements using a $Cs^+$ ion beam as the primary beam (Evans Analytical Group).

## 3. Results and discussion

Fig. 1(a)–(d) show the AFM surface morphologies of typical GZO and GZO:In samples grown at OFR = 0 sccm. It shows that GZO:In film has a much smoother surface with larger grains than GZO film grown under the same conditions. Fig. 1(e) shows the root-mean-square roughness (Rq) of GZO and GZO:In films as a function of OFR. Except for the films grown at OFR = 0 sccm, the Rq values for both GZO and GZO:In films decrease with increasing OFR. In addition, an obvious decrease in surface roughness is observed in GZO:In films grown at OFRs lower than 10 sccm in comparison with GZO films. At OFRs of higher than 10 sccm, both GZO and GZO:In films have flat surfaces with Rq values of less than 0.5 nm. It has been widely reported that dopants such as Ga and Ti atoms could act as surfactants and would smooth the surfaces of ZnO-based TCO films [20,25,26]. The decrease in surface roughness of GZO:In films might be explained as a result of the enhanced surfactant effect from indium dopants.

Fig. 2(a) and (b) show the typical out-of-plane ($2\theta/\omega$) and in-plane ($2\theta_\chi/\phi$) XRD scans of GZO and GZO:In films grown at OFR = 20 sccm, respectively. These data show both GZO and GZO:In films have the wurtzite structure with a preferential *c*-axis-oriented columnar grain structure perpendicular to the substrate surface. In addition, no peak indicating the segregation of $Ga_2O_3$ or $In_2O_3$ is observed in the XRD spectra of GZO and GZO:In films. Fig. 2(c) shows the full widths at half maximums (FWHMs) of rocking curves for (0002) peaks as a function of OFR. The FWHM for GZO:In film is larger than that of the corresponding GZO film when OFR is lower than 15 sccm. The FWHM of GZO:In film sharply falls with further increasing OFR. This unusual phenomenon is caused by the deterioration of GZO:In target after long-time sublimation under a high OFR condition. When the target deterioration happened, we found that the sputtered surface of GZO:In target changed from the normal gray white to slightly black. To confirm this, we used a fresh GZO:In target to deposit sample at OFR = 20 sccm. As a result, the FWHM of the sample grown with the fresh target locates near the dotted line in Fig. 2(c), which is the guide for the eyes showing

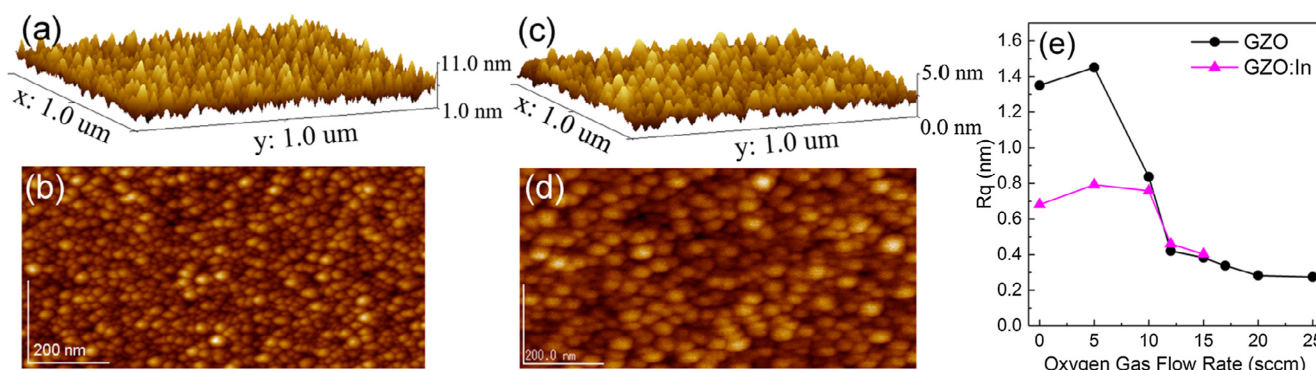


**Fig. 1.** AFM images of (a and b) GZO and (c and d) GZO:In films grown at OFR = 0 sccm. (a) and (c) are the three dimensional AFM images of the corresponding samples below. (e) Root-mean-square roughness (Rq) of GZO and GZO:In films as a function of OFR. All the films are 100-nm-thick.

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