Quantitative analyses of damp-heat-induced degradation in transparent conducting oxides

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ABSTRACT

A complete understanding of the reliability for ZnO-based transparent conducting oxides is essential for actual applications in photovoltaic devices or displays requiring long-term stability. The stability and degradation mechanisms under a controlled damp-heat environment (humid and hot atmosphere) for sputter-deposited aluminum-doped zinc oxide (ZnO:Al) thin films were quantitatively studied. The continuous degradations of carrier concentration and mobility with the Fermi-level shift were observed, and this behavior was resolved by separating the changes in the carrier-transport characteristics of the intragrain and grain boundary. By correlating the temperature dependence of electrical characteristics with x-ray photoelectron spectroscopy, the degradation is well explained by the increase of chemisorbed OH^- in the grain boundaries.

1. Introduction

Transparent conducting oxides (TCOs) have been widely used for various applications requiring their optoelectronic multi-functionalities, such as photovoltaic devices, liquid crystal displays (LCD), organic light-emitting diodes (OLED), touch panels, etc. [1–9]. Among various TCOs, ZnO-based TCOs have recently received intense interests to replace commercially used indium tin oxide (ITO) or fluorine-doped tin oxide (FTO) due to their low cost, abundance, and non-toxicity. Furthermore, excellent light-scattering properties can be achieved via sputter deposition and surface texturing by wet-chemical etching, particularly for front TCOs in silicon thin-film solar cells, which suggest a great potential toward effective light trapping for enhancing power-conversion efficiencies [10].

However, the environmental stability is still an unsolved problem especially when exposed to harsh environment, which prevents the ZnO-based TCOs from actual applications in devices requiring long-term stability [11–16]. For this reason, great efforts have been dedicated to understand environmental reliability, though previous research has mainly focused on methodological and technical aspects. Thus, very little is known about the essential degradation mechanisms.

In this work, quantitative investigation on degradation behavior in a controlled damp-heat (DH) environment (humid and hot atmosphere) is introduced for aluminum-doped ZnO (ZnO:Al) thin films. The electrical degradation behavior was thoroughly analyzed in aspects of both energy-level shifts in band diagrams and changes in carrier-transport characteristics of the intragrain and grain boundary separately. Also, the correlation between the degradation behavior and nanostructural change was resolved.

2. Experimental details

ZnO:Al thin films were deposited on Corning Eagle XG glasses by rf magnetron sputtering using the ZnO:Al targets doped with 1.6 wt% Al_2O_3. The sputtering was performed under an Ar atmosphere at 400 °C, with an rf power of 75 W and an operating pressure of 5 mTorr. For comparison, ZnO thin films were prepared without any doping. After deposition, the ZnO:Al films were exposed to a damp-heat atmosphere of a relative humidity of 85% and a temperature of 85 °C, for up to 800 h.

The Hall resistivity of thin films was measured by four-point probe, and the carrier concentration was estimated from the Hall measurement (HL5500PC: BIO-RAD) using a van der Pauw method at 300 K. The Hall-carrier mobility was deduced from the relation

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$\rho = 1/ne\mu$, where ρ, n, e, and μ are the resistivity, carrier concentration, electron charge, and carrier mobility, respectively. Transport characteristics were investigated from the temperature dependence on electrical properties in the range of 80–340 K.

The crystallinity of the ZnO:Al films were analyzed by x-ray diffraction (XRD, New D8 Advance: Bruker). The change in conduction-band filling was investigated with the optical bandgap (E_g^{op}) estimated from the UV/vis absorption spectra (Lambda 35: Perkin-Elmer). The infrared reflectance was investigated to separately analyze the electrical characteristics of the intragrain and grain boundary by Fourier-transform infrared spectrometer (FT-IR, IFS 66v/S: Bruker). The chemical state and Fermi-level shift of the ZnO:Al films were analyzed by x-ray photoelectron spectroscopy (XPS, AXIS-HSI: KRATOS).

3. Results and discussion

Fig. 1 shows the changes in electrical properties of the ZnO:Al thin films as a function of DH exposure. The continuous degradation behavior of the Hall resistivity was observed initially from $\sim 6.7 \times 10^{-4}$ to $\sim 1.9 \times 10^{-3}\,\Omega$ cm after 800 h. Note that the degradation is related to the decrease of both carrier mobility and carrier concentration with the DH exposure.

To characterize the carrier-concentration degradation, the optical bandgap was estimated by Tauc's relation [5]:

$$\alpha^2 \propto (h\nu - E_g^{op}), \tag{1}$$

where α is the absorption coefficient, $h\nu$ is the photon energy, and E_g^{op} is the optical bandgap (Fig. 2). The E_g^{op} values are reduced initially from 3.73 eV to 3.60 eV after 800-h DH exposure. To compare the band structure and illustrate the effect of conduction-band filling, the E_g^{op} from the nondegenerate ZnO
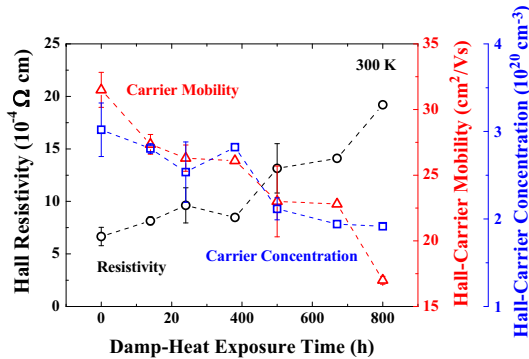
sample was also acquired to be 3.26 eV. The conduction-band filling was quantitatively estimated to be ~ 0.59 eV and ~ 0.43 eV for 0-h and 800-h DH exposure, respectively, from the Burstein–Moss model [17,18]:

$$E_F - E_{CB} = \left(\frac{\hbar^2}{2m_e^*}\right)(3\pi^2 n)^{2/3}, \tag{2}$$

where E_F, E_{CB}, n, and m_e^* are, respectively, the Fermi level, conduction-band minimum, carrier concentration, and effective electron mass ($\cong 0.28m_e$ where m_e is the electron rest mass [19]).

To correlate the energy-level shifts of E_g^{op} and the carrier-concentration degradation, the XPS core-level spectra of Zn 2p were analyzed as shown in Fig. 3(a). For the pristine ZnO:Al compared to ZnO, the upshift of the Fermi level by ~ 0.6 eV is shown due to the electron population within the conduction band. After the DH treatment of 800 h, the Fermi energy is decreased by ~ 0.1 eV, which is well correlated with the E_g^{op} analyses and conduction-band filling deduced from Eq. (2).

The O 1s peaks of the ZnO:Al films were also analyzed to identify the chemisorbed hydroxyl groups in humid atmosphere, as shown in Fig. 3(b). With two XPS peaks at ~ 530.9 eV (O^{2-} binding with Zn or substitutional Al) and ~ 532.5 eV (OH^- in metal-OH bonds [20,21]), the integrated-intensity ratio of OH^-/O^2 was $\sim 23\%$ for the initial ZnO:Al film, while the ratio significantly increases to $\sim 44\%$ after the DH exposure of 800 h. This result clearly indicates the increase of chemisorbed OH^- with the exposure to the humid environment, probably along the grain boundaries which are easy diffusion paths for the OH^- species [22]. The full-width at half maximum (FWHM) of the XRD patterns was unchanged as shown in Fig. 4. This result supports that the crystallinity of the ZnO:Al thin films are hardly affected by the DH environment, and the degradation centers are located mainly along the grain boundaries due to the hydroxyl groups [23].

Based on the observations such as the Fermi-level shift (~ 0.10 eV from Fig. 3(a)), optical-bandgap energy ($\sim 3.73-\sim 3.60$ eV from Fig. 2), and change in conduction-band filling ($\sim 0.59-\sim 0.43$ eV from Fig. 1 and Eq. (2)), the energy-level shifts

Fig. 1. Hall resistivity, carrier mobility, and carrier concentration of ZnO:Al films as a function of damp-heat (DH) exposure time.
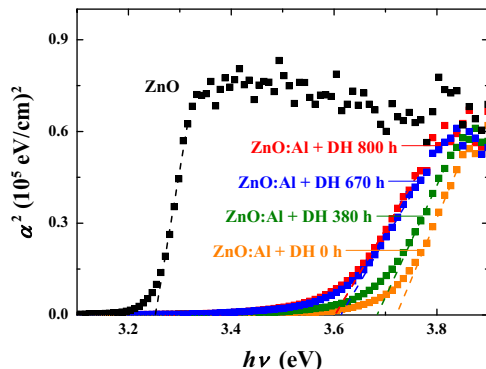

Fig. 2. Plot of α^2 vs. $h\nu$ near the bandedge for ZnO:Al films at various DH exposure times. For comparison, the absorption from nondegenerate ZnO is also included.
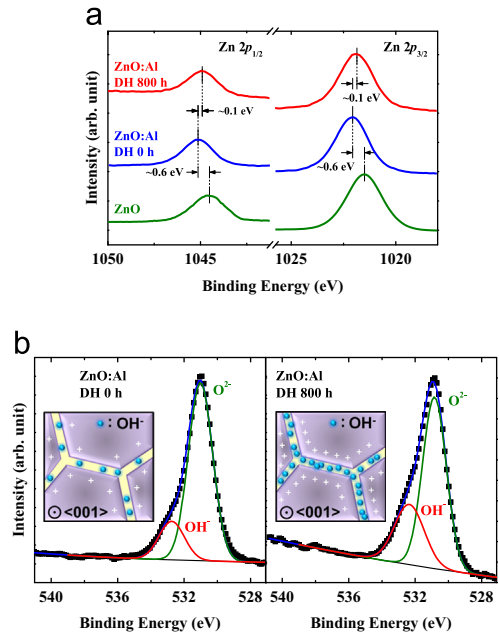

Fig. 3. Comparison of the XPS core-level spectra of the ZnO and ZnO:Al films with and without DH exposure. (a) The Zn 2p peak and (b) deconvoluted O 1s peak of the films. Each inset shows a scheme of the chemisorbed hydroxyl groups along the grain boundaries and accumulated positive carriers towards the depleted regions at the given DH exposure condition.