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Effects of substrate temperature and Zn addition on the properties of Al-doped ZnO films prepared by magnetron sputtering

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ABSTRACT

Al-doped ZnO (AZO) films prepared at different substrate temperature and AZO films with intentional Zn addition (ZAZO) during deposition at elevated substrate temperature were fabricated by radio frequency magnetron sputtering on glass substrate, and the resulting structural, electrical, optical properties together with the etching characteristics and annealing behavior were comparatively examined. AZO films deposited at 150 °C showed the optimum electrical properties and the largest grain size. XPS analysis revealed that AZO films deposited at elevated temperature of 450 °C contained large amount of Al content due to Zn deficiency, and that intentional Zn addition during deposition could compensate the deficiency of Zn to some extent. It was shown that the electrical, optical and structural properties of ZAZO films were almost comparable to those of AZO film deposited at 150 °C, and that ZAZO films had much smaller etching rate together with better stability in severe annealing conditions than AZO films due possibly to formation of dense structure.

1. Introduction

Transparent conducting oxide (TCO) films are materials which are highly transparent to visible light and electrically conducting. TCO films, especially indium tin oxides (ITO, Sn doped In_2O_3) have been widely used in many applications such as transparent electrodes of flat panel devices, solar cells and IR reflectors [1]. Recently doped ZnO films with Al, Ga or In have attracted much attention as an alternative material of ITO due to their good advantages of the low electrical resistivity similar to ITO and the low material cost [2,3]. However, practical applications of ZnO films have been limited due to the instability in the atmosphere. The instability of ZnO related TCO in atmosphere was attributed to the chemisorption of oxygen species at the grain boundaries, which traps the free carriers and leads to an increase of potential barrier at the grain boundaries [4]. It has been shown that the instability could be dramatically improved by doping extrinsic donors, but these doped ZnO thin films still showed instability when exposed to air at elevated temperature [5–8]. Besides the thermal stability in ambient, thermal stability of ZnO layer in vacuum may also be required for some applications such as front contacts in Cu(In, Ga)Se_2 based superstrate solar cells, in which the absorber layer is deposited onto ZnO layer at temperature higher than 500 °C [9–11]. Although it has been shown that the highly stable epitaxial ZnO layer with very low electrical resistivity could be obtained by chemical vapor deposition [12], it is worth of examining the possibility of improving the thermal stability in doped ZnO films grown by magnetron sputtering technique because of its wide usage in fabrication of TCO films.

In this study, Al-doped ZnO (AZO) films were deposited with varying substrate temperature by conventional radio frequency (rf) magnetron sputtering, and their electrical, optical, structural and compositional properties were examined. Also, AZO films with intentional Zn addition (ZAZO) were prepared by co-sputtering of AZO and Zn targets at elevated substrate temperature, and their corresponding properties were analyzed. By adopting severe post heat treatment in ambient and vacuum, the relative thermal stability of the AZO and ZAZO films was examined. Also, the differences in initial etching behavior and etching rate were tested by performing the surface texturing in diluted 0.5% HCl solution.

2. Experimental details

Al-doped ZnO films were deposited on glass substrates (Corning Eagle 2000) by radio frequency (13.56 MHz) planar magnetron

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sputtering. The base pressure in the chamber was below 5×10^{-7} Torr, and the sputtering deposition was carried out at a pressure of 1.2 mTorr unless otherwise specified. The distance between the target and the substrate was 60 mm, and the substrate rotated at a constant speed of 12 rpm during sputtering. The substrate temperature varied from room temperature (RT) to 450 °C. Deposition of AZO films at varying substrate temperature was carried out by sputtering of 2-in. $ZnO:Al_2O_3$(2 wt.%) target with rf power of 50 W. Zn-added AZO films were deposited at 450 °C by co-sputtering of $ZnO:Al_2O_3$(2 wt.%) and pure Zn targets. Zn addition was done by varying the power ratios (P_{Zn}/P_{total}) of 0.14, 0.27 and 0.46, while total power applied to two targets were fixed at 110 W. In the following, AZO films deposited at different temperature will be denoted as AZO_X, where the subscript 'X' designates the corresponding substrate temperature. And the three Zn-added AZO films will be denoted as $ZAZO_{14}$, $ZAZO_{27}$ and $ZAZO_{46}$ to designate the ZAZO films deposited at P_{Zn}/P_{total} of 0.14, 0.27 and 0.46, respectively. Annealing experiment was carried out in rapid thermal processing chamber at 500 °C in ambient and at 550 °C in vacuum for 30 min.

Film thickness was measured by a surface profilometer (KLA-tencor, ASIQ) after etching away part of the film with diluted HCl solution. The film thicknesses were 277 ± 34 nm. The electrical resistivities, Hall mobilities, and carrier concentrations were determined from Hall-effect measurement using a Van der Pauw method with indium contact pads at room temperature. The structural analysis was carried out by an X-ray diffraction (XRD, Rikaku, ATX-XRD) measurement (Cu Kα, θ–2θ scan mode). X-ray photoelectron spectroscopy (XPS) spectra were recorded with Phi 8000 spectrometer using Al Kα (1486.6 eV) radiation. The spectra were referenced to the surface impurity C 1s line (284.6 eV) binding energy. The quantitative analysis was done by using XPS spectra obtained at depth of about 40 nm from the film surface. The optical transmission and reflection spectra were obtained from a UV–vis spectrophotometer (PerkinElmer, Lambda 35) in wavelength ranges of 250–1100 nm.

3. Results

The structural properties of films were examined by XRD in θ–2θ scan mode, and the XRD profiles are shown in Fig. 1(a). For all the films, XRD profiles showed only strong peak from (0 0 2) plane, indicating that all the films exhibit typical hexagonal wurzite structure with (0 0 2) preferred orientation. The best crystallinity was observed for the AZO_{150} film. Above 150 °C, the intensity of (0 0 2) peak decreased rapidly with increasing substrate temperature, and eventually the peak intensity of AZO_{450} film went down to 10% of AZO_{150} film. It is notable that small addition of Zn into AZO_{450} film resulted in substantial increase of (0 0 2) peak intensity, yielding almost the same intensity for $ZAZO_{27}$ and $ZAZO_{46}$ films as AZO_{150} film. In Fig. 1(b), the variations in the grain size and the (0 0 2) peak position are plotted as a function of the substrate temperature. The average grain size d was estimated from the full width at half maximum (FWHM) of the (0 0 2) peak according to the Sherrer formula $d = k\lambda_{Cu\ K\alpha}/\Delta(2\theta)\cos\theta$ with $\lambda_{Cu\ K\alpha} = 1.540562$ Å and $k = 0.9$. As was the case of (0 0 2) peak intensity, the average grain size was the largest for AZO_{150} film, and decreased with increasing substrate temperature. For ZAZO films, the average grain size increased with increasing P_{Zn}/P_{total}, but the largest grain size of about 28 nm was still smaller than AZO films deposited at low substrate temperature. The c-axis lattice parameter evaluated from the (0 0 2) peak position also showed large dependence on the substrate temperature. AZO film deposited at RT and higher temperature than 350 °C had relatively large c-axis lattice parameters. Addition of Zn caused the c-axis lattice parameter to decrease.

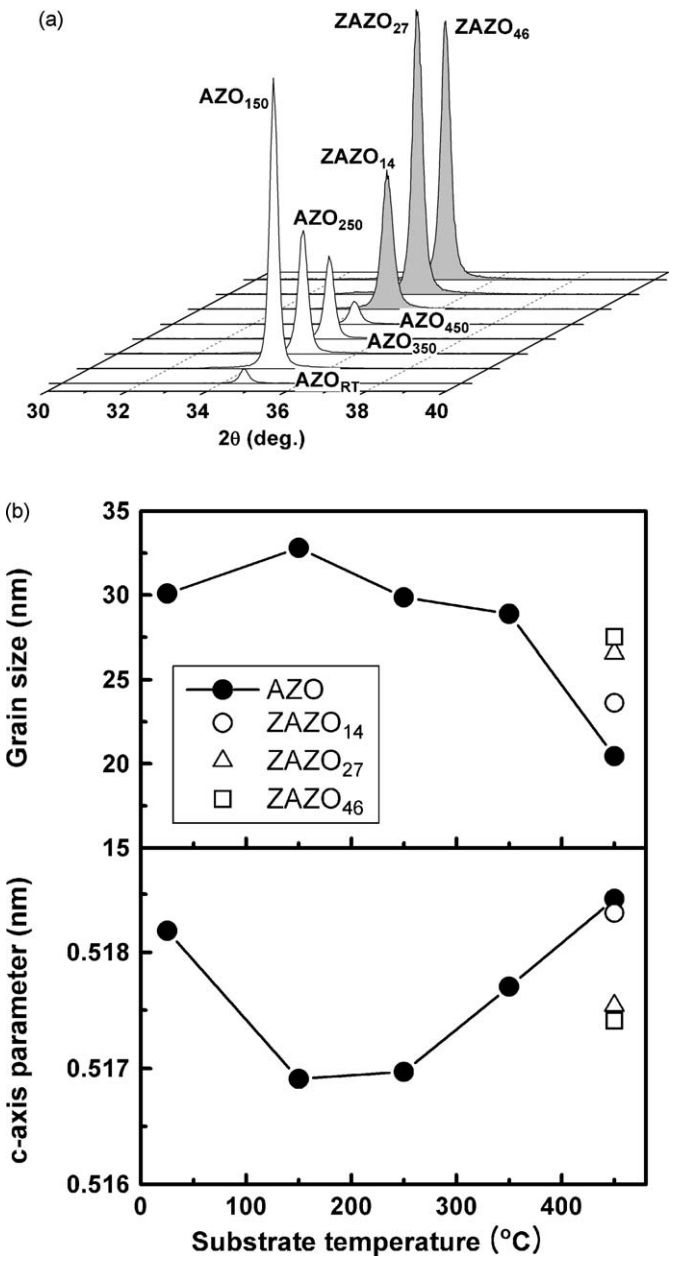

Fig. 1. (a) XRD profiles of AZO and ZAZO films. (b) Variation of grain size and c-axis lattice parameter in AZO and ZAZO films.

Fig. 2 summarizes the electrical resistivity (ρ), Hall mobility (μ_H) and free carrier concentration (n) of AZO and ZAZO films. The lowest electrical resistivity of $3.9 \times 10^{-4}\ \Omega$ cm was observed for AZO_{150} film. Above this temperature, both the Hall mobility and the carrier concentration decreased with increasing deposition temperature, resulting in very high resistivity for AZO_{450} film. Zn-added ZAZO films showed much improved electrical properties than AZO_{450} film, but the Hall mobility and especially the carrier concentration were still slightly lower than those obtained for AZO_{150} film. It is interesting to note that they had similar electrical properties regardless of P_{Zn}/P_{total} unlike the structural properties which showed rather gradual change with increasing P_{Zn}/P_{total}.

Fig. 3(a) and (b) represent the transmission spectra of selected samples and the variation of the absorption coefficient (α) averaged in visible range of 400–800 nm, respectively. The absorption coefficients were evaluated from the measured transmittance and reflectance by using relationship which is