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Research Paper

Facile Modulation of Electrical Properties on Al doped ZnO by Hydrogen Peroxide Immersion Process at Room Temperature

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Abstract Aluminum-doped ZnO (AZO) thin films were deposited by atomic layer deposition (ALD) with respect to the Al doping concentrations. In order to explain the chemical stability and electrical properties of the AZO thin films after hydrogen peroxide (H_2O_2) solution immersion treatment at room temperature, we investigated correlations between the electrical resistivity and the electronic structure, such as chemical bonding state, conduction band, band edge state below conduction band, and band alignment. Al-doped at ~10 at % showed not only a dramatic improvement of the electrical resistivity but also excellent chemical stability, both of which are strongly associated with changes of chemical bonding states and band edge states below the conduction band.

Keywords: Transparent conducting oxide, Al doped ZnO, Solution immersion treatment, Chemical bonding state, and Electronic structure

I. Introduction

Transparent conducting oxide (TCO) materials has attracted a great amount of attention for the technological realization of the next generation of see-through transparent electronics such as organic light emitting diodes (OLEDs), solar cells, smart windows, thin film transistors (TFTs), flat panels displays (FPDs) and touch screen panels (TSPs) [1,2,3]. In most cases, indium tin oxide (ITO) thin film has been extensively employed as the TCO layer because of this material's excellent electrical and optical properties [4]. However, ITO film has some drawbacks, such as the high cost of indium and its lower wet etch rate compared with those of ZnO or indium gallium zinc oxide (IGZO), which can lead to damage in the active layer [5]. Therefore, alternative TCO films with similar or better properties are needed, and studies have been performed in this area. Recently, aluminum-doped zinc oxide (AZO) film has been intensively studied as a candidate for TCO applications because it has many advantages such as high optical transparency of > 80% in the visible region and low electrical resistivity of ~ 10^{-3} Ω·cm [3,5]. However, the AZO thin film has a small process window because the electrical properties greatly change depending on the doping concentration of Al. Therefore, in order to widen the process window, it is necessary to develop a process capable of decreasing the resistivity of the AZO thin film via a simple post-treatment method. In addition, since most electronic devices have stacked structures, mechanical/chemical stability must be ensured in the process of depositing and etching adjacent layers (e.g. using photolithography or a lift-off process) [5].

In our study, we provide a post-treatment method that can ensure facile modulation of the electrical properties at room temperature of an AZO thin film according to the Al doping concentration; this method also provides information on the chemical stability of the AZO thin film with H_2O_2 solution.

II. Experiment

Using an ALD technique at the substrate temperature of 250ºC, AZO thin films with various Al doping concentrations and with thicknesses of 100 nm were deposited on thermally grown SiO_2 layers on a heavily boron-doped *p*-type Si wafer. The detailed ALD deposition procedure for AZO thin films is provided in our previous report [6]. The doping concentration of Al of the AZO thin films was controlled using changes in the ratio of the supercycle, consisting of the number of cycles of ZnO and Al_2O_3, as shown in Figure 1 (a). For the deposition of AZO thin films, the number of ALD cycles was controlled with Al doping concentrations of 1, 3, 5 and 10 at%. The film compositions were investigated using Rutherford backscattering (RBS) and simulation by the Rump program [7]. Then, all AZO thin films were immersed in 30% hydrogen peroxide (H_2O_2, Sigma Aldrich) for 5 min at room temperature to investigate the effect of H_2O_2 on the chemical stability and electrical properties of the AZO thin

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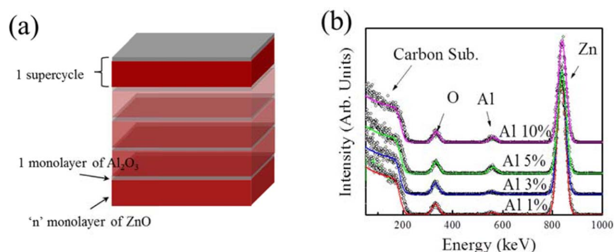

Figure 1. (a) Schematic diagram of AZO thin film stacks deposited with various Al doping concentrations by ALD. (b) RBS spectra for AZO thin films with Al doping concentration.

films. The surface morphology was investigated using atomic force microscopy (AFM). The electrical properties, such as the carrier concentration, Hall mobility and resistivity were examined using a Hall measurements system with a permanent magnet of 0.56 Tesla at room temperature. The chemical bonding states and the composition were also investigated by X-ray photoelectron spectroscopy (XPS) with a pass energy of 23.5 eV and using a monochromatic Al Kα source. The detailed electronic structures, related to changes in the band edge state below the conduction band, were investigated by spectroscopic ellipsometry (SE). In particular, SE measurement was performed by a rotating analyzer system with an auto-retarder in the energy range from 0.74 eV to 6.4 eV, with the incident angles of 65º, 70º and 75º.

III. Result and Discussion

Figure 1(b) shows that the RBS spectra of the AZO thin films containing 1, 3, 5 and 10 at% of Al deposited on a carbon substrate accurately matched the target Al concentrations, which will hereafter be indexed as AZO 1%, AZO 3%, AZO 5% and AZO 10%, respectively. The electrical properties of the AZO thin films with H_2O_2 solution immersion treatment were investigated by Hall measurement at room temperature. Figure 2 (a) shows the resistivity of the AZO thin films before and after H_2O_2 solution immersion treatment with respect to the Al doping concentration, while Table 1 summarizes the detailed electrical resistivity values. First, the AZO thin film has an optimum electrical resistivity at an Al doping concentration of 3%, which is reasonable behavior comparing to previous reports [3,5]. After the H_2O_2 solution immersion treatment, the electrical resistivity of the AZO thin films decreased regardless of the Al doping concentration. In particular, when the Al doping concentration was 10%, it is obviously seen that the resistivity most strongly decreased compared with the other Al doping concentrations. Figure 2(b) shows the electrical properties of the AZO 10% film before and after H_2O_2 solution treatment. As can be seen in Figure 2 (b), the decrease in the resistivity of AZO 10% is more closely related to the increase in the carrier concentration rather than it is to the electron mobility. Therefore, the

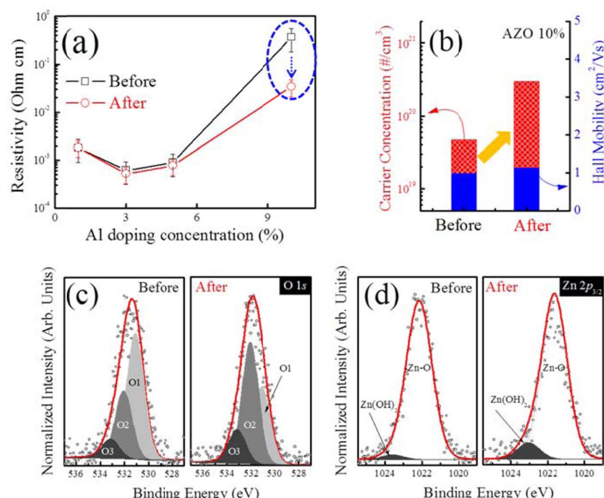

Figure 2. (a) Electrical resistivity of AZO thin films before and after H_2O_2 solution treatment with respect to the Al doping concentration. (b) Change of carrier concentration and mobility, and deconvoluted XPS spectra, of (c) O 1*s*, (d) Zn 2*p*$_{3/2}$ with an AZO 10% thin film before and after H_2O_2 solution treatment.

Table 1. Electrical resistivity of AZO thin films before and after H_2O_2 immersion treatment with respect to the Al doping concentration

Al doping concentration (%)	H_2O_2 immersion treatment (Ω·cm)	
	Before	After
1	1.79×10^{-3}	1.82×10^{-3}
3	6.10×10^{-4}	5.16×10^{-4}
5	8.91×10^{-4}	7.67×10^{-4}
10	3.64×10^{-1}	3.39×10^{-2}

remarkable changes in resistivity of AZO thin film can be associated with the carrier generation by defect states such as oxygen vacancies, which are affected by the H_2O_2 solution treatment. More discussion is provided below to consider the chemical bonding state and the electronic structure. The chemical bonding states were observed by XPS; Figure 2(c) and (d) shows the changes in the O 1*s* and Zn 2*p*$_{3/2}$ spectra. Using Ar ion at 500 V, XPS spectra were measured after eliminating surface contamination by adsorbed OH, C, H_2O, etc. For detailed analysis of the chemical bonding states, the O 1*s* and Zn 2*p*$_{3/2}$ spectra were carefully normalized and de-convoluted with three different Gaussian peaks. The three representatively assigned peaks from low binding energy relate to the oxygen state in the metal-oxide lattices (O1), the oxygen deficient state (O2), and the chemisorbed or dissociated oxygen states or OH− impurities (O3) [8]. The relative area of the oxygen deficient bonding states (O2) dramatically increases after H_2O_2 solution immersion treatment. In addition, two representatively assigned peaks of low binding energy and high binding energy are related to the Zn 2*p*$_{3/2}$ binding energy in the zinc-oxygen (Zn-O) bond and the $Zn(OH)_2$. These XPS results demonstrate that the AZO

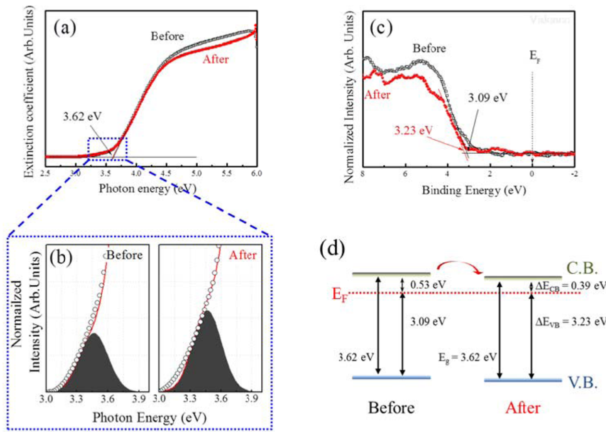

Figure 3. (a) Optical extinction coefficient spectra, (b) enlargement of the extinction coefficient spectra for band edge state below conduction band, (c) valence band spectra, and (d) schematic energy-level diagrams reflecting the relative energy position of the Fermi level (E_F) for an AZO 10% thin film before and after H_2O_2 solution treatment.

thin films after H_2O_2 solution treatment have larger oxygen related defects due to the oxygen deficient bonding states, which contribute to the increase of the carrier concentration. Moreover, the hydrogen atoms bonded to the surface oxygen atoms may increase the surface conductivity [9].

In order to understand the electronic structure of the AZO 10% thin film before and after H_2O_2 solution treatment, in such aspects as band gap and band edge states, the extinction coefficient spectra were measured by SE, as shown in Figure 3(a). Except for the slight change of the area of the conduction band above the photon energy of 4.5 eV, no significant change of the electronic structure of the AZO 10% thin film was observed to result due to H_2O_2 solution treatment. However, the band edge state below the conduction band dramatically increased after H_2O_2 solution treatment, as shown in Figure 3(b). These changes coincided with the increase of the oxygen deficient state (O2) and the $Zn(OH)_2$ state, as determined by XPS analysis; the increase of these two states is related to the increase of the unoccupied states within the band gap and can generate the charge carrier concentration. Figure 3(c) and (d) shows the valence band spectra and the schematic energy-level diagram for the AZO 10% film before and after H_2O_2 solution treatment. Noticeable changes are the relatively narrow conduction band offset (ΔE_{CB}) between the conduction band minimum and the Fermi level, which could be related to an increase in the carrier density according to the following equation: $n = N_c e^{-(E_C - E_F)/kT}$, where N_C is the effective density of states near the conduction band minimum and k is the Boltzmann constant [10]. Therefore, the decrement of the electrical resistivity of the AZO 10% thin film after H_2O_2 solution treatment may be explained by the increase of the carrier concentration, which is induced by changes of the electronic structure such as the increase of the band edge states and the reduction of the conduction band offset, caused by the increase of the oxygen deficient bonding states. Finally, in order to confirm the chemical stability of the AZO thin film after H_2O_2 treatment according to the Al doping concentration, the change of the surface roughness was analyzed by AFM measurement, as shown in Figure 4. As the Al doping concentration increased, the surface roughness increased from 0.7 nm to 1.92 nm. The surface roughness of the AZO thin film after H_2O_2 solution treatment increased to up to 5% of the Al doping concentration. On the other hand, Al doping concentration at 10% showed excellent chemical stability. This increase in chemical stability could be attributed to the increase in the amount of highly stable Al_2O_3 in the AZO thin film, which would reduce the etching effect of ZnO by the H_2O_2 solution [11].

IV. Conclusions

In summary, we evaluated the electrical properties and chemical stability of AZO thin films before and after H_2O_2 solution treatment with respect to the Al doping concentration. The resistivity of all AZO thin films was found to decrease after H_2O_2 solution treatment. Especially, the resistivity of the AZO 10% thin film was found to

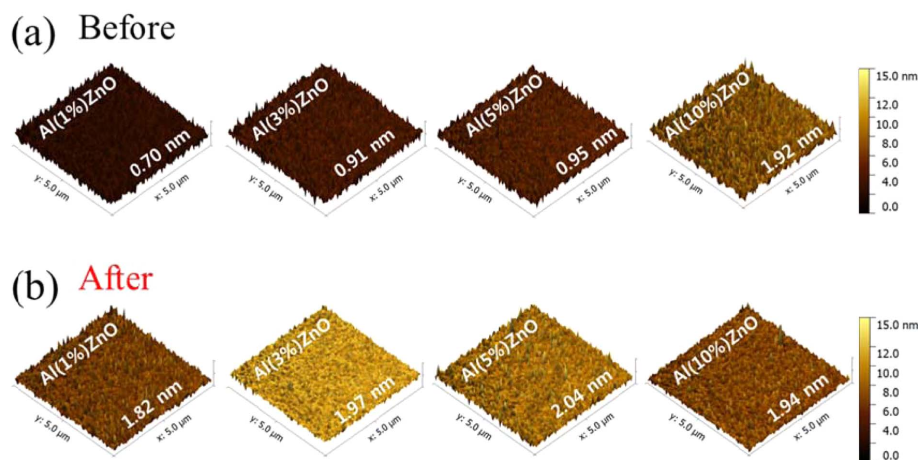

Figure 4. Surface morphology of AZO thin film (a) before and (b) after H_2O_2 solution treatment with respect to the Al doping concentration.

decrease 10 times from 3.64×10^{-1}Ω·cm to 3.39×10^{-2} Ω·cm. Based on chemical bonding state and electronic structure analysis, it was found that with increasing oxygen deficiency state and band edge state the decrease of the resistivity of the AZO 10% thin film is strongly correlated with the carrier concentration after H_2O_2 treatment. In addition, the higher the Al doping concentration, the more the chemical stability of the AZO thin film increases due to the decrease in the etching effect of ZnO, which has a relatively low chemical stability, and also due to the very high chemical stability of Al_2O_3.

Acknowledgments

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