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

Hyun-Woo Park and Kwun-Bum Chung*
Division of Physics and Semiconductor Science, Dongguk University, Seoul 04620, Korea

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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$_2$O$_2$) 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 have 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$_2$O$_2$ solution.

II. Experiment

Using an ALD technique at the substrate temperature of 250°C, 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$_2$O$_3$, 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$_2$O$_2$, Sigma Aldrich) for 5 min at room temperature to investigate the effect of H$_2$O$_2$ on the chemical stability and electrical properties of the AZO thin
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 65°, 70° and 75°.

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 H₂O₂ 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 H₂O₂ solution immersion treatment with respect to the Al doping concentration. 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 H₂O₂ 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 H₂O₂ 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 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 H₂O₂ 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 1s and Zn 2p₃/₂ spectra. Using Ar ion at 500 V, XPS spectra were measured after eliminating surface contamination by adsorbed OH, C, H₂O, etc. For detailed analysis of the chemical bonding states, the O 1s and Zn 2p₃/₂ 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 H₂O₂ solution immersion treatment. In addition, two representatively assigned peaks of low binding energy and high binding energy are related to the Zn 2p₃/₂ binding energy in the zinc-oxygen (Zn-O) bond and the Zn(OH)₂. These XPS results demonstrate that the AZO

| Al doping concentration (%) | H₂O₂ immersion treatment (Ω·cm) |
|--------------------------|-------------------------------|
| 1                        | Before 1.79 × 10⁻³ 1.82 × 10⁻³ |
| 3                        | Before 6.10 × 10⁻⁴ 5.16 × 10⁻⁴ |
| 5                        | Before 8.91 × 10⁻⁴ 7.67 × 10⁻⁴ |
| 10                       | Before 3.64 × 10⁻¹ 3.39 × 10⁻² |

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thin films after H$_2$O$_2$ 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$_2$O$_2$ 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$_2$O$_2$ solution treatment. However, the band edge state below the conduction band dramatically increased after H$_2$O$_2$ solution treatment, as shown in Figure 3(b). These changes coincided with the increase of the oxygen deficient state (O$_2$) 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$_2$O$_2$ solution treatment. Noticeable changes are the relatively narrow conduction band offset ($\Delta E_{CB}$) 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:

$$n = N_C e^{(E_F - E_C)/kT}$$

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$_2$O$_2$ 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 decrease 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$_2$O$_2$ 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$_2$O$_2$ 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$_2$O$_3$ in the AZO thin film, which would reduce the etching effect of ZnO by the H$_2$O$_2$ solution [11].

IV. Conclusions

In summary, we evaluated the electrical properties and chemical stability of AZO thin films before and after H$_2$O$_2$ solution treatment with respect to the Al doping concentration. The resistivity of all AZO thin films was found to decrease after H$_2$O$_2$ solution treatment. Especially, the resistivity of the AZO 10% thin film was found to

![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$_2$O$_2$ solution treatment.](image)

![Figure 4. Surface morphology of AZO thin film (a) before and (b) after H$_2$O$_2$ solution treatment with respect to the Al doping concentration.](image)
decrease 10 times from $3.64 \times 10^{-1} \Omega \cdot \text{cm}$ to $3.39 \times 10^{-2} \Omega \cdot \text{cm}$. 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$_2$O$_2$ 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$_2$O$_3$.

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