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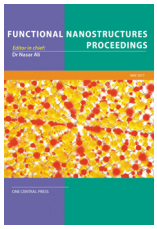

Transmission Electron Microscope Observation of Al- and Ga-doped ZnO Multi-Layer Transparent Conductive Films Fabricated by Wet Process

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ABSTRACT

We fabricated multi-layer aluminum (Al) and gallium (Ga) co-doped ZnO (AGZO) films using a spin-coating method and performed cross-sectional transmission electron microscope and energy dispersive X-ray spectroscopy (TEM-EDS) observations to evaluate the distribution of zinc and oxygen atoms in multi-layer structures. As a result, the multi-layer AGZO films are useful for improving sheet resistance and resistivity because the discontinuous regimes in the first AGZO layer are filled out by the upper AGZO layers. In addition, the distribution of zinc and oxygen atoms in the quadruple-layer AGZO film reveal oscillations, indicating that their distributions are not uniform in each AGZO layer.

I. INTRODUCTION

ZnO films are usually prepared by several techniques such as radio frequency (RF) magnetron sputtering [1], chemical vapor deposition [2], and molecular beam epitaxy [3]. Their fabrication through electrochemical reactions has also been demonstrated, including the sol-gel method [4, 5]. Moreover, the doping effect of aluminum (Al) and gallium (Ga) atoms has been investigated to improve the conductivity of ZnO films fabricated by the sol-gel method [6,7] because the surface roughness of ZnO films fabricated by a wet-process increases, resulting in large sheet resistance.

Very recently, we fabricated Al and Ga co-doped ZnO (AGZO) films by a sol-gel method and found that their resistances improved when the fabrication process of AGZO films was performed twice: double-layer AGZO films [8]. In addition, we found that recoated multilayer AGZO films exhibit very small sheet resistances due to the improved surface roughness [9]. In this paper, we fabricated from single- to quadruple-layer AGZO films and performed cross-sectional transmission electron microscope and energy dispersive X-ray spectroscopy (TEM-EDS) observation to evaluate the distribution of zinc and oxygen atoms in multi-layer structures.

II. EXPERIMENTAL METHOD

Sample fabrication. We fabricated an AGZO precursor solution by the following procedure. First, a $Zn(OAc)_2$, monoethanolamine (MEA) and 2-methoxyethanol mixture was stirred at 50°C for 1 hour. Next, $[Al(NO_3)_3 \cdot 9H_2O]$ and $[Ga(NO_3)_3 \cdot nH_2O]$ were added for Al- and Gadopings, whose density was 2wt%. Then, the AGZO precursor solution films were fabricated on cleaned glass substrates using the spin-coating method. Finally, they were annealed at 550°C and turned into AGZO films [8,9]. The glass substrates were cleaned with a SC-1 method [10] because it is superior for removeing organic matters. For instance, we fabricated a double-layer AGZO film by recoating an AGZO precursor solution on a single-AGZO film and annealing it again. Thus, to fabricate quintuple-layer AGZO films, we recoated and annealed the AGZO precursor solution five times in the same condition.

Experimental setup. TEM-EDS observations were performed using JEM2100F (JEOL). The sheet resistance was evaluated using a 4-point probe measurement system called SR-H1000C. The thickness of the AGZO films was

evaluated using a step profiler (XP-1, Techscience). All of the measurements were performed at room temperature.

III. RESULTS AND DISCUSSION

Figure 1 shows the sheet resistances and the resistivity of the single- to quadruple-layer AGZO films. The resistivity was determined from the value of the sheet resistance multiplied by the film thickness. The thicknesses from the single- to quadruple-layer AGZO films were measured as 35, 40, 42, 60, and 141 nm. The results in Fig. 1 clearly demonstrate that their sheet resistance gradually decreased from single- to triple-layer AGZO films and became minimum in the latter. They also reveal an approximately constant value from triple- to quintuple-layer AGZO films. Moreover, the resistivity becomes minimum in the triple-layer AGZO film. These results indicate that the discontinuous regimes of AGZO films completely disappeared in the triple-layer structure.

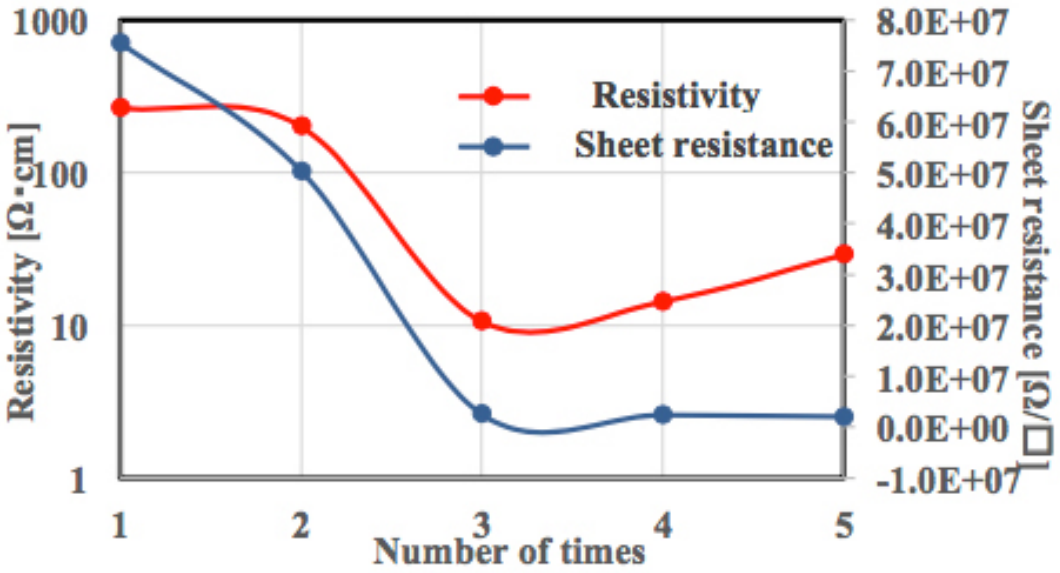

Figure 1 Cross-sectional TEM-EDS image of quintuple-layer AGZO film, indicating four atom distributions: oxygen, silicon, zinc, and osmium. SiO_2 substrate was cleaned by SC-1 method.

Figure 2 shows a cross-sectional TEM image of the quadruple-layer AGZO film. A striped pattern was clearly observed, containing five periods of bright and dark layers. This implies that the quadruple-layer AGZO film was successfully fabricated. However, in each AGZO film, the distribution of the zinc and oxygen atoms is not uniform. Cross-sectional EDS observation that displays the distribution of four atoms, zinc (Zn), oxygen (O), silicon (Si), and osmium (Os). The Zn atoms are clearly concentrated in the five-period structure. This suggests that it is the quadruple-layer AGZO film. However, the quantities of the Zn and O atoms in the bright layers are smaller than those in the dark layers. In particular, the bright layer is located on the right side in each AGZO layer. Thus, the Zn and O atoms are concentrated more on the left side in each AGZO layer. This result clearly shows that in each AGZO layer, Zn and O atoms are concentrated more on the side closer to the substrate. Since the resistivity of the solution-processed ZnO films exceeds that of samples fabricated by other methods, RF magnetron sputtering, chemical vapor deposition, and molecular beam epitaxy, the large resistance of the solution-processed AGZO films is most likely caused by the inhomogeneous distribution of Zn and O atoms.

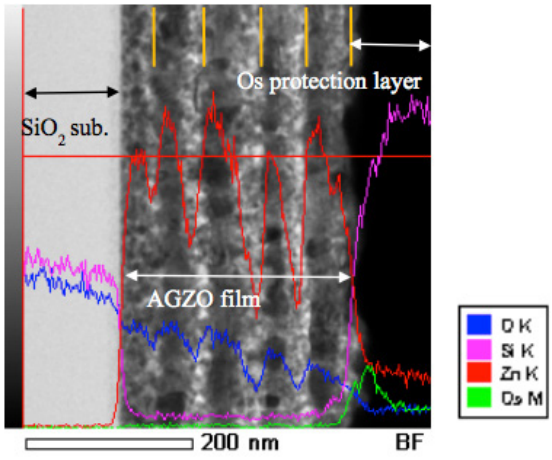

Figure 2 Cross-sectional TEM-EDS image of quintuple-layer AGZO film, indicating four atom distributions: zinc (red), oxygen

(blue), silicon (pink), and osmium (green). Sample was covered by Os protection layer. SiO_2 substrate was cleaned by SC-1 method.

IV. SUMMARY

Multi-layer AGZO films are useful to improve sheet resistance. However, we found that the distribution of the Zn and O atoms is not uniform. This result suggests that for improving the resistivity of solution-processed AGZO films, the fabrication conditions of AGZO films must be identified for the uniform distribution of the Zn and O atoms.

V. REFERENCES

[1] K. Kim, K. Park, and D. Ma, J. Appl. Phys. **81** (1997) 7764.
[2] G. Aanon, R. Rup, and A. Mansingy, Thin Solid Films, **190** (1990) 284.
[3] Y. Deesirapipat, M. Fujita, M. Sasajima, C. Antarasena, and Y. Horikoshi, Jpn. J. Appl. Phys., **44**, 5150 (2005).
[4] M. Izaki and T. Omi, Appl. Phys. Lett., **68** (1996) 2439.
[5] Y. Takahashi, M. Kanamori, A. Kondoh, H. Minoutia, and Y. Ohya, Jpn. J. Appl. Phys., **33** (1994) 6611.
[6] M. Ohyama, H. Kozuka, and T. Yoko, J. Am. Ceram. Soc., **81** (1998) 1622.
[7] K. Cheong, N. Muti, and S. Ramanan, Thin Solid Films, **410** (2002) 142.
[8] Y. Morita, A. Emoto and N. Ohtani, Mol. Crys. and Liq. Crys, **641** (2016) 111.
[9] Y. Morita and N. Ohtani, EM-NANO 2017, **PO3-54** (June 2017).
[10] W. Kern: J. Electrochem. Soc. **137** (1990) 1887.