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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. 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 revealed 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, 2], chemical vapor deposition (CVD) [3, 4], and molecular beam epitaxy (MBE) [5, 6]. Their fabrication through electrochemical reactions has also been demonstrated, including the sol-gel method [7, 8]. 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 [9-13] 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 [14]. In addition, recoated multi-layer AGZO films exhibit very small sheet resistances due to the improved surface roughness [15]. In this paper, we fabricated from single- to quadruple-layer AGZO films and performed crosssectional transmission electron microscope and energy dispersive X-ray spectroscopy (TEMEDS) 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 Ga-dopings 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 [14, 15]. The glass substrates were cleaned with a SC-1 method [16] because it is superior for removing 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. We evaluated the thickness of the AGZO films was evaluated using a step profiler (XP-1, Techscience). All measurements were performed at room temperature.

III. RESULTS AND DISCUSSION

First, we fabricated the single- and double-layer AGZO films and observed their 3-dimensional figures using AFM. Figure 1 shows the AFM images of the two samples: their surfaces and cross-sectionals. They clearly have wrinkled surfaces. From the cross-sectional AFM image of the double-layer film, the surface roughness was clearly not improved by recoating an AGZO precursor solution on a single-AGZO film. Cross-sectional TEM-EDS observation, however, clearly shows that the double-layer AGZO film is obviously connected under the wrinkled surface, resulting in smaller resistivity than the single-layer AGZO film [15].

Figure 2 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. We measured the thicknesses from the single- to quadruple-layer AGZO films as 35, 40, 42, 60, and 141 nm. The results in Fig. 2 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 the AGZO films completely disappeared in the triple-layer structure. Note that the transmittance of the triplelayer sample exceeded 90% in the entire visible light regime [15]. This means that the triplelayer AGZO film is the best condition for fabricating transparent conductive AGZO film because transparent conductive films require that their transmittance exceed 90% in the visible light regime [17, 18].

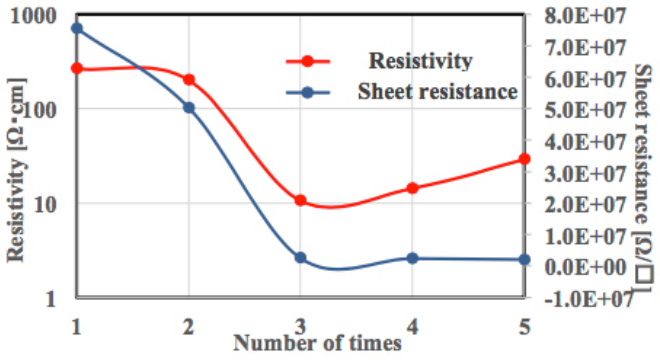

Figure 2 Resistivity (red line) and sheet resistance (blue line) of samples from single- to quintuplelayer AGZO films fabricated on glass substrates cleaned using SC-1 method.

Figure 3 shows a cross-sectional TEM image of the quadruple-layer AGZO film. A striped pattern was clearly observed in all the observed ranges and has five periods of bright and dark layers. This suggests that the quadruple-layer AGZO film was successfully fabricated. However, the periods of bright and dark layers indicate that in each AGZO film, the distribution of the zinc and oxygen atoms is not uniform. Thus, we must evaluate the distributions of Zn and O atoms in it.

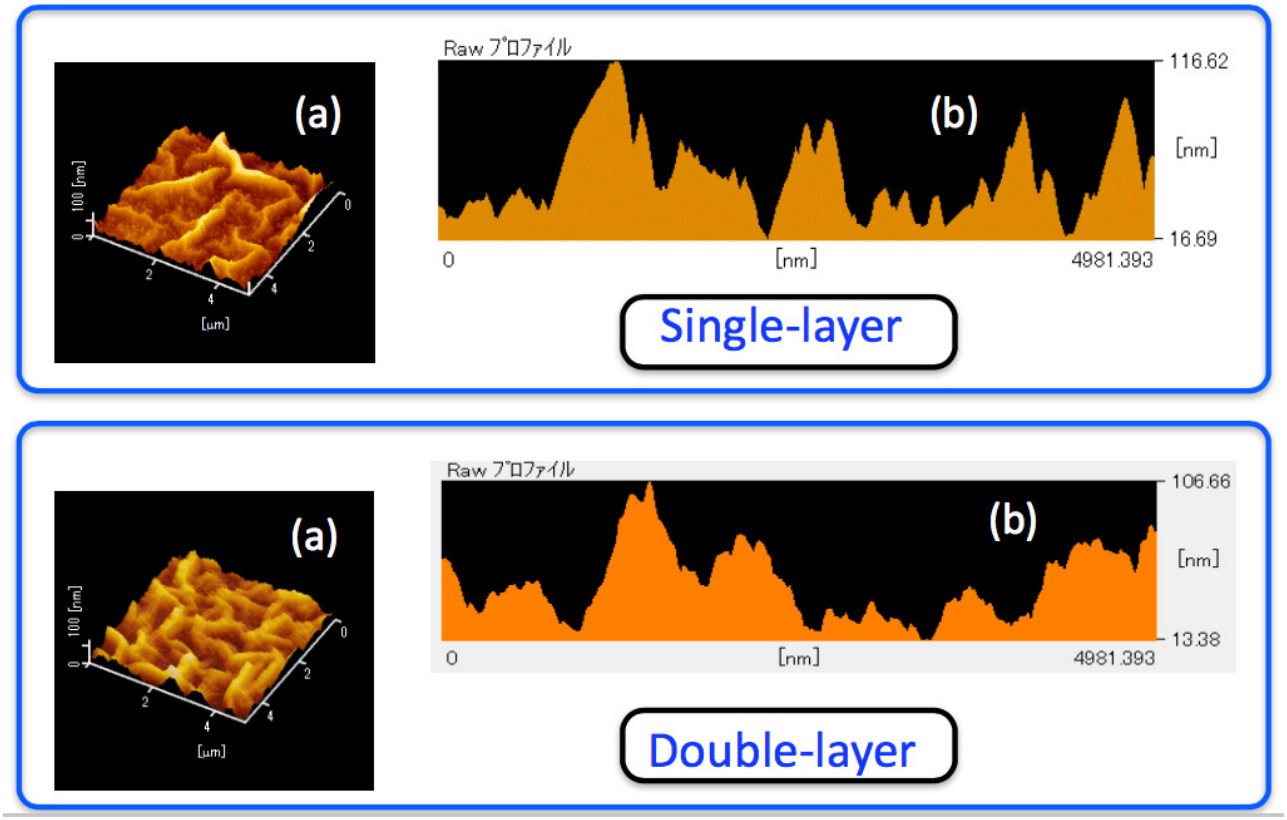

Figure 1 AFM images of the single- and double-layer AGZO films: (a) their surfaces and (b) crosssectional images.

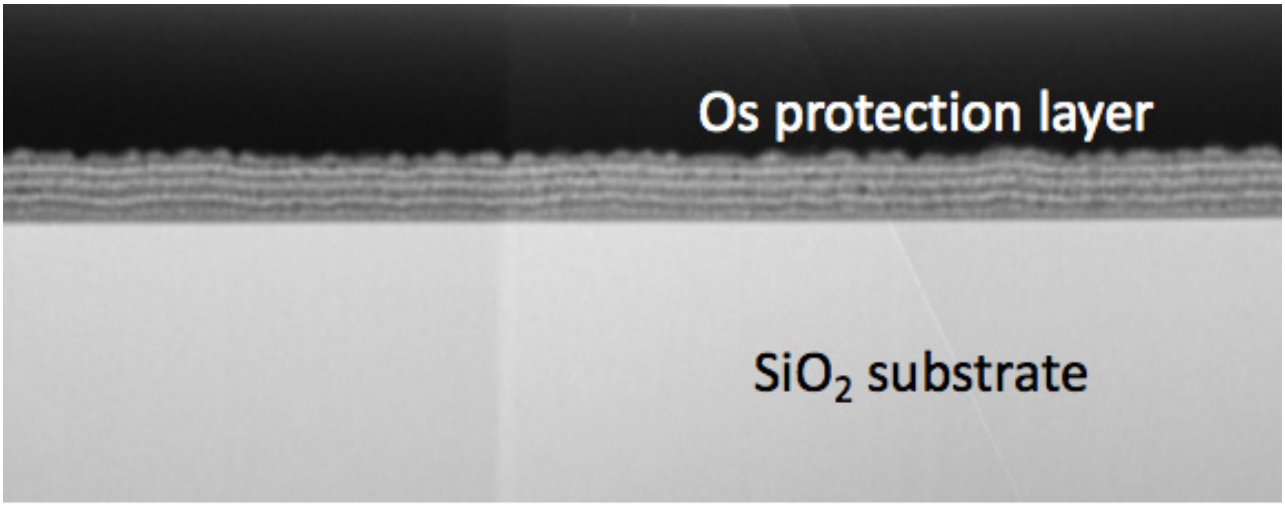

Figure 3 Cross-sectional TEM image of quadruple-layer AGZO film. Five periods of bright and dark layers correspond to fabricated quadruple-layer AGZO film.

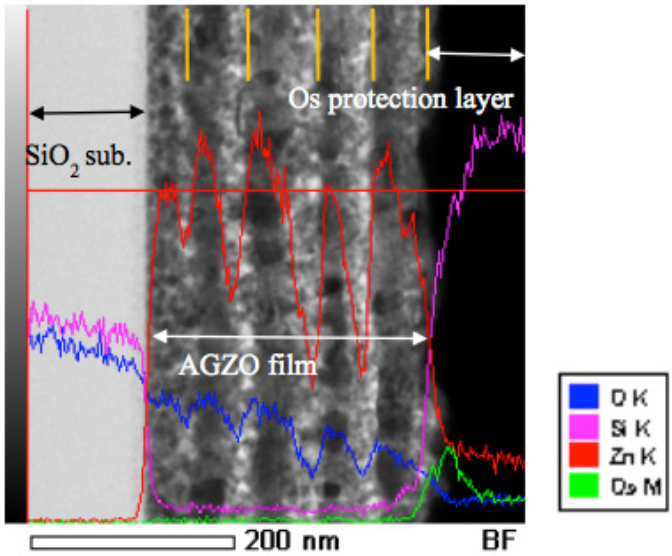

Figure 4 Expanded cross-sectional TEM image of quintuple-layer AGZO film and corresponding EDS analysis. Five yellow lines are eye-guides to separate the stacked five layers. EDS analysis indicates four atom distributions: zinc (red), oxygen (blue), silicon (pink), and osmium (green). Sample was covered by Os protection layer. SiO2 substrate was cleaned by SC-1 method.

Figure 4 shows an expanded cross-sectional TEM image of the quadruple-layer AGZO film and corresponding EDS analysis. Cross-sectional EDS observation 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, suggesting that it is the quadruple-layer AGZO film. However, the quantities of Zn and O atoms in the bright layers are smaller than those in the dark layers, which leads to the larger transparent quantities of electrons. 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, the 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 the samples fabricated by other methods, RF magnetron sputtering, CVD, and MBE, the large resistance of the solution-processed AGZO films is most likely caused by the inhomogeneous distribution of Zn and O atoms. Therefore, we cannot conclude that the SC-1 substrate cleaning method improves the sheet resistance of the AGZO films. Further study is needed that uses the SC-1 substrate cleaning method to improve the sheet resistances; the optimal conditions in terms of the amounts of ammonia, hydrogen peroxide, and pure water plus their temperatures must be determined to improve the sheet resistance of multi-layer AGZO films.

IV. SUMMARY

The fabrication of multi-layer AGZO films is useful to improve the sheet resistance of solution-processable films. In addition, we evaluated the distribution details of Zn and O atoms in quadruple-layer AGZO film by TEM-EDS observations and found that their distributions are not uniform. This result suggests that for improving the resistivity of the solution-processed AGZO films, their optimal fabrication conditions must be identified for the uniform distribution of Zn and O atoms.

V. ACKNOWLEDGEMENT

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VI. REFERENCES

[1] K. Kim, K. Park, and D. Ma, J. Appl. Phys. **81** (1997) 7764.
[2] Y. Hu, J. Li, N. Chen, C. Chen, T. Han, and C. Yu, J. Appl. Phys. **121**, 085302 (2017).
[3] G. Aanon, R. Rup, and A. Mansingy, Thin Solid Films, **190** (1990) 284.
[4] J. Hu and R. Gordon, J. Appl. Phys. **72**, 5381

(1992).

[5] Y. Deesirapipat, M. Fujita, M. Sasajima, C. Antarasena, and Y. Horikoshi, Jpn. J. Appl. Phys., **44**, 5150 (2005).

[6] X. Shen, H Zhou, Y. Li, J. Kang, J. Zheng, S. Ke, Q. Wang, and H. Wang, Opt. Lett. **41**, 4895 (2016).

[7] M. Izaki and T. Omi, Appl. Phys. Lett., **68** (1996) 2439.

[8] Y. Takahashi, M. Kanamori, A. Kondoh, H. Minoutia, and Y. Ohya, Jpn. J. Appl. Phys., **33** (1994) 6611.

[9] M. Ohyama, H. Kozuka, and T. Yoko, J. Am. Ceram. Soc., **81** (1998) 1622.

[10] K. Cheong, N. Muti, and S. Ramanan, Thin Solid Films, **410** (2002) 142.

[11] W. Tang and DC. Cameron, Thin Solid Films **238**, 83 (1994).

[12] M. Jun, S. Park, and J. Koh, Nanores. Lett. **7**, 639 (2012).

[13] K. Ravichandran, N. Begun, S. Snega, and B. Sakthivel, Mat. Manu. Proc. **31**, 1411 (2016).

[14] Y. Morita, A. Emoto, and N. Ohtani, Mol. Crys. and Liq. Crys. **641**, 111 (2016).

[15] Y. Morita and N. Ohtani, EM-NANO 2017, **PO3-54** (June 2017), also in Jpn. J. Appl. Phys., in press.

[16] W. Kern: J. Electrochem. Soc. **137** (1990) 1887.

[17] G. Gordillo and C. Calderon, Sol. Energy Mater. Sol. Cells **69**, 251 (2001).

[18] M. Oztas and M Bedir, Thin Solid Films **516**, 1703 (2008).