

Depth-resolved electronic structure analysis of IGZO/SiO₂ interface by two-dimensional photoelectron spectroscopy

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1. Introduction

Amorphous InGaZnO (*a*-IGZO) is a transparent amorphous oxide semiconductor (TAOS), which is transparent to visible light owing to its wide band gap. The *a*-IGZO has high channel mobility (μ_{ch}) compared with the amorphous silicon (*a*-Si) TFTs. Moreover, it is fabricated by low temperature process. Therefore, it has been expected as a material of thin film transistors (TFTs) [1, 2] and transparent electronics [3, 4] for next-generation displays. It has been reported that an annealing process is needed for *a*-IGZO to improve its TFT characteristics [2], and the change of bonding state in *a*-IGZO by an annealing is one of the topics for discussion.

Display-type spherical mirror analyzer (DIANA) is the powerful tools for analyzing the depth profile of electronic structures with element selectivity [5]. The DIANA enables two-dimensional angle-resolved measurements by the spherically-symmetric electronic field as shown in Fig. 1. Unlike conventional photoelectron spectrometer which requires sample and/or analyzer rotation, the DIANA with very large acceptance angle of $\pm 60^\circ$ enables acquisition of depth information with one shot.

In this study, we have investigated the annealing effect for *a*-IGZO/SiO₂ interface from the depth-resolved electronic structure analysis by DIANA.

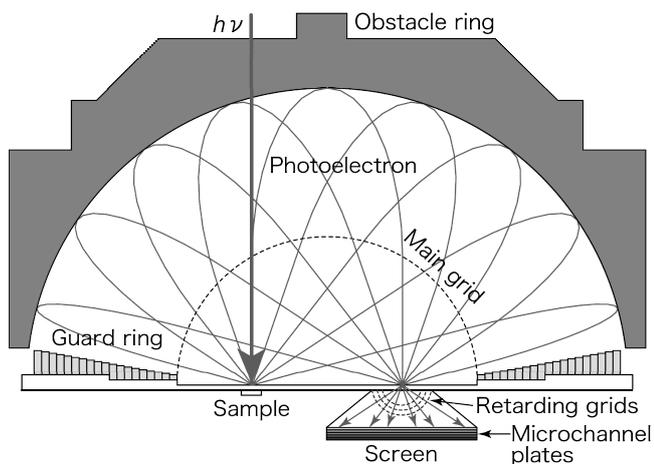


Fig. 1 Schematic illustration of display-type spherical mirror analyzer (DIANA). Spherically-symmetric electronic field is applied between main grid and obstacle rings. Angular distribution of photoelectrons from samples is projected on the screen without distortion.

2. Experimental

The *a*-IGZO film was deposited on the high doped p-type Si substrates (conductivity=0.002-0.004 Ωcm) with thermally oxidized SiO₂ layer (100 nm) by radio-frequency (RF) magnetron sputtering using follow conditions: 5% O₂ in Ar gas, 0.6 Pa, and room temperature (RT). The wedged *a*-IGZO layer as shown in Fig. 2 was fabricated by wet-etching process in HCl aq (0.02 mol/l). The wedged *a*-IGZO samples were annealed in the atmospheric condition (AT, N₂:O₂ = 4:1) at 300°C for 2 hours. The non-annealed (NA) and annealed (AT) samples were compared.

The experiments were performed at the circularly-polarized soft-X-ray beamline BL25SU in SPring-8, Japan, and the DIANA was used for the emission-angle-resolved measurements. The constant-final-state X-ray photoelectron spectra (CFS-XPS) were measured to keep the length of photoelectron free path from each element the same [8]. Therefore, each photoelectron has same escape depth, and it is useful for analyzing depth profile. The spectra of the grazing emission angles are mainly from surface region, while those of the surface normal direction are more sensitive to the bulk region. The intensity of photoelectrons having kinetic energy of 600 eV was measured. The photon energy was scanned from 600 to 780 eV for In 4d and Ga 3p core levels and from 1130 to 1150 eV for O 1s core level measurements.

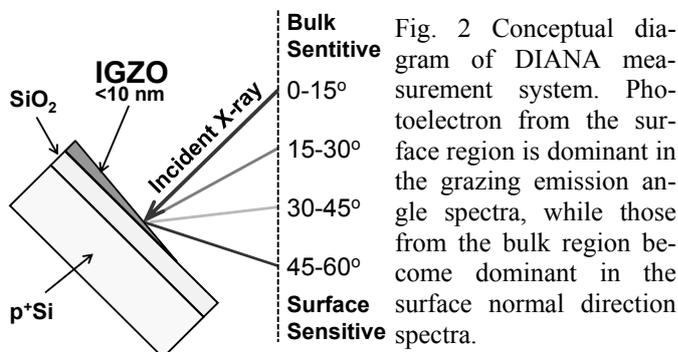


Fig. 2 Conceptual diagram of DIANA measurement system. Photoelectron from the surface region is dominant in the grazing emission angle spectra, while those from the bulk region become dominant in the surface normal direction spectra.

3. Results and Discussion

The near-interface CFS spectra normalized by each peak top of NA and AT samples are shown in Fig. 3. Each peak was disaggregated to the angle integrated spectra at 0-15°, 15-30°, 30-45°, and 45-60°. Note that low-angle

spectra includes bulk region, and high-angle spectra is sensitive to surface region. The In 4d peaks shifted toward lower binding energy side by AT annealing, and it was observed that each In 4d peak shifted to low energy direction with increasing the measurement angle. On the other hand, the Ga 3p shifts toward higher binding energy side by the annealing, and it was indicated that each Ga 3p shifted to high energy direction with increasing the measurement angle. These chemical shifts implied that the electron density around In atoms increased, but that around Ga atoms decreased by the annealing and increasing the measurement angle. In general, a metal peak shows a chemical shift to higher binding energy by bonding with oxygen. The intermediate peak shift originates from combination of varying proportion of several ionized metal peaks. It is implied that Ga-O bonds increased but In-O bonds decreased from the results in Fig. 3. We consider that this recombination is related to the carrier density and stability of IGZO film. Zn peak analysis is now underway.

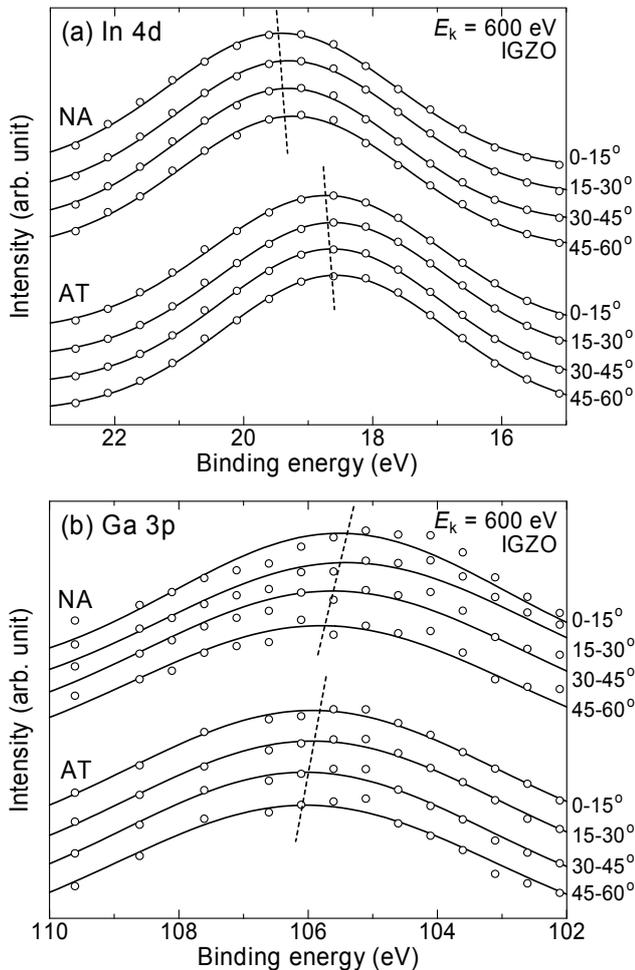


Fig. 3 Angle-resolved In 4d and Ga 3s peaks in CFS spectra of NA and AT samples.

Figure 4 shows the normalized O 1s spectra for the NA and the AT annealed samples. The O 1s peak of each sample shifted toward lower binding energy direction with in-

creasing the measurement angle. These results suggest that M(metal)-O bonds increased by becoming sensitive to the surface. From the discussion on Fig. 3, the possible causes of the O 1s peak shift toward low energy are the increase of Ga-O bonds. On the other hand, each O 1s peak shift by the annealing was little. We expect that the entire number of M-O bonds did not change, for example In-O bonds decreased but the Ga-O bonds increased. This is considered as the reason why the O 1s peak shifts after annealing were small. We will investigate the depth profile of X-ray absorption near edge structures (XANES) on *a*-IGZO/SiO₂ interface as a future work.

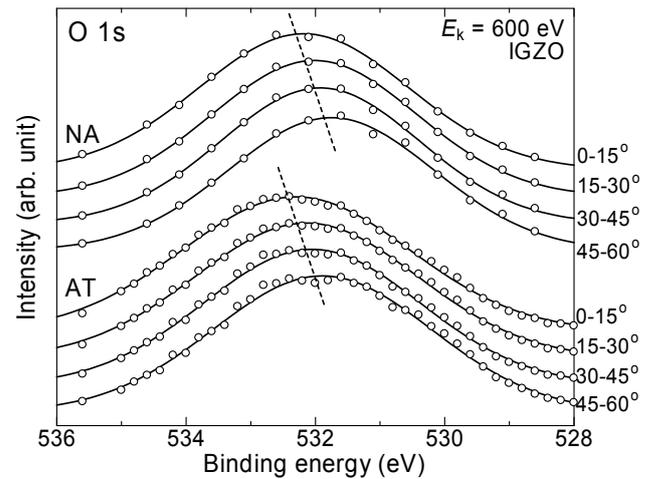


Fig. 4 Angle-resolved O 1s peaks in CFS spectra of NA and AT samples.

4. Conclusions

In conclusion, CFS-XPS of non-annealed and annealed samples were observed. It is suggested that Ga-O bonds increased and In-O bonds decreased, especially on the surface region. We concluded that this reconstitution of bonds was one of the annealing effects to improve TFT characteristics. We showed that DIANA is useful for investigating the depth-resolved electronic structure.

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References

- [1] K. Nomura, H. Ohta, A. Takagi, T. Kamiya, M. Hirano, and H. Hosono, *Nature*, **432**, p. 488, (2004).
- [2] T. Kamiya, K. Nomura, and H. Hosono, *Soc. Technol. Adv. Mater.*, **11**, 044305, (2010).
- [3] W-B. Im, Y-E. Kim, T-S. Kim, Y-B. Ha, and K-B. Kim, *SID Symposium Digest of Technical Paper*, **41**, 245 (2011)
- [4] H-H. Hsieh, T-T. Tsai, C-M. Hu, C-L. Chou, S-F. Hsu, Y-C. Wu, C-S. Chuang, L-H. Chang, and Y. Lin, *SID Symposium Digest of Technical Paper*, **42**, 1 (2011).
- [5] H. Daimon, *Rev. Sci. Instrum.*, **59**, 545, (1988)