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Extended Abstract of PSA-19

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Characterization of Al-doped ZnO thin films by laboratory-based hard X-ray photoelectron spectroscopy system

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The highly transparent conductive Al-doped ZnO thin films were characterized by the laboratory-based hard X-ray photoelectron spectroscopy system using monochromatic Cr Kα line as an excitation X-ray source. The Al 1*s* core spectra of dopants can be measured in practically high throughput. The area intensity was proportional to the doping contents. The peak position of Al 1*s* systematically shifted to low binding energy with increasing the Al content. It was suggested that some correlations with the carrier concentration in AZO thin films.

1. Introduction

X-ray photoelectron spectroscopy (XPS) is widely used surface analysis technique to investigate chemical states and electronic structure of materials. Al Kα soft X-ray with the photon energy of 1486.6 eV is conventionally used as excitation in laboratory-based XPS systems. Hard X-ray photoelectron spectroscopy (HAXPES) has been developed in synchrotron radiation facilities [1] and attracted much attentions because of relatively deep probing depth. Owing to this, we can expect intrinsic bulk chemical states without any surface treatments. Recently, HAX-PES systems using Cr Kα [2] or Ga Kα [3] X-ray sources have been developed for laboratory usage.

Al-doped ZnO (AZO) is one of important materials for optoelectrical applications because of high conductivity and high transparency, and the AZO thin film is used as transparent electrodes in solar cells. In the AZO thin films, there still remaining several issues like as thermal stability, improvement of conductivity, carrier compensation, and so on. It is necessary to characterize the chemical state of dopant Al to understand electrical properties of AZO films and to raise performance of the solar cells. However, there are few reports of Al in AZO characterized by HAXPES. In this study we employed laboratory-based HAXPES system to characterize Al dopants in AZO thin films.

2. Experimental

The AZO thin films with different doping content of Al were deposited on glass substrates by a direct current magnetron sputtering. ZnO ceramic targets containing 0.5, 1, 2, 3 wt % of Al_2O_3 were used. XPS spectra were measured by a custom-made laboratory-based HAXPES system consists of monochromatic Cr Kα and Al Kα X-ray sources with photon energies of 5414.9 eV and 1486.6 eV (ULVAC-PHI), respectively, and a wide acceptance angle electron analyzer (Scienta Omicron, EW4000).

3. Results and discussion

Figures 1a and 1b show Al 2*p* core spectra of the AZO (1 wt%) thin films measured using Al Kα and Cr Kα lines, respectively. Here, we kept accumulation time of ~20 min for comparison, corresponding to 10 times scans under commonly used measurement conditions. We can see that the Al 2*p* spectrum measured using Cr Kα is extremely week compared to the case of Al Kα, mainly due to smaller photoionization cross section of subshells at high energy excitations [4]. Instead, we can measure Al 1*s* core spectra with comparable intensity to the Al 2*p* measured using Al Kα as shown in Fig. 1c.

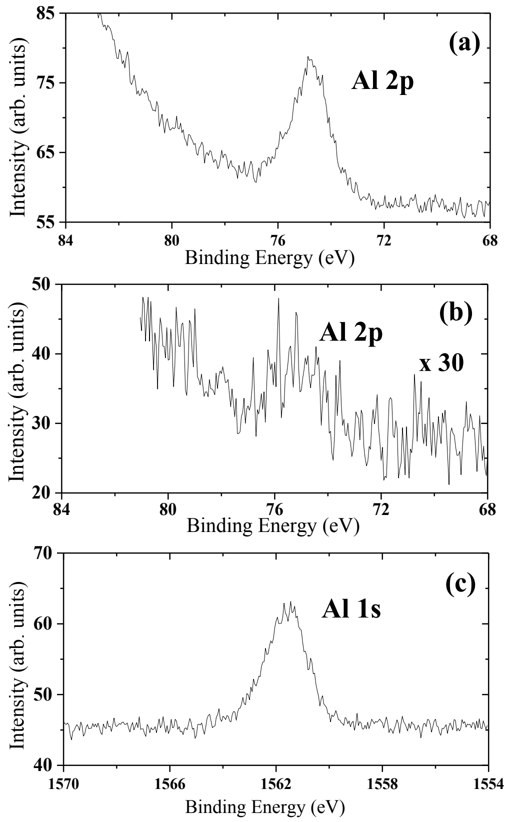

Fig. 1 Al 2*p* spectra of AZO measured using (a) Al Kα and (b) Cr Kα, and (c) Al 1*s* spectra measured using Cr Kα.

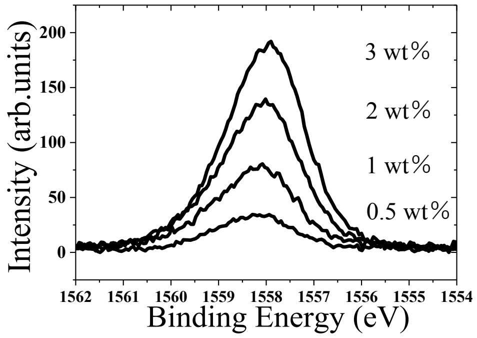

Fig. 2 Al 1*s* core spectra of AZO thin films.

In addition to the practical throughput, the Al 1*s* core spectra showed very flat background, while the Al 2*p* measured by Al Kα showed background largely increasing toward high binding energy side. Such background strongly influences its analysis when the signal is week. The availability of deeper core level is another advantage of HAXPES to avoid overlapping with other contributions. Accordingly, it is reasonable to measure Al 1*s* instead of Al 2*p* using HAXPES system especially for such low concentration regime.

Next, the Al concentration dependence of the Al 1*s* spectra were examined by HAXPES using Cr Kα line. The carrier concentration increased with increasing the Al content. However, the carrier concentration saturated at high doping content. The HAXPES spectra entirely shifted to high binding energy. This is because the fermi level changes depending on the carrier concentrations. In order to compare core level spectra, we selected the sample with lowest carrier concentration as a reference. Then, the HAXPES spectra of all samples were entirely shifted so as to match the top of valence band with the reference sample.

Figure 2 shows the Al 1*s* HAXPES spectra of the AZO films after shifted. The background was subtracted. Firstly, the area intensity of the Al 1*s* spectra was proportional to the doping content of Al. Moreover, the peak position slightly shifted toward lower binding energy with the increase of Al content. It was reported that there exist different chemical states of Al in AZO films with different binding energy [5]. The shift may suggest appearance of Al ions with different chemical state in AZO. The Al 1*s* spectra were separated into two peaks. It was found that the intensity of peak at higher binding energy showed strong correlation with the carrier concentration. The appearance of peak at low binding energy may related to deactivated dopants resulting in the saturation of carrier concentration with increasing the Al content.

4. Summary

The transparent conductive AZO films were characterized by the laboratory-based HAXPES system. The Al 1s spectra were measured even for relatively low doping content in practical throughput. The relationship between electrical properties and chemical states of dopant Al could be further discussed after overall characterization of the AZO thin films.

5. References

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