Extended Abstract of PSA-19

O-38

Hard X-ray photoelectron spectroscopy of transparent conductive heavily doped ZnO thin films

Hisao Makino,[1,2,*]
[1] *Department of Electrical and Photonic System Engineering, Kochi University of Technology, 782-8502, Japan*
[2] *Research Institute of KUT, Kochi University of Technology, 782-8502, Japan*
*corresponding author's e-mail: makino.hisao@kochi-tech.ac.jp

(Received: June 26, 2019; Accepted: July 16, 2019)

Transparent conductive Al-doped ZnO thin films have been investigated by hard X-ray photoelectron spectroscopy using a laboratory-based XPS system equipped with a Cr Kα X-ray source. The dependences of the carrier concentration were studied. The core and valence band spectra showed tail-like satellite structures at high binding energy side strongly depends on the carrier concentration. The in-gap states near the Fermi level showed a broad feature extended below the conduction band minimum estimated by the photoluminescence.

1. Introduction

Heavily doped ZnO is one of important materials for optoelectronic application as transparent electrodes. In this decade, the transport properties of transparent conductive thin films have attracted much attention. It is important to study the electronic structures near the Fermi level E_F to understand the transport properties. The hard X-ray photoelectron spectroscopy (HAXPES) has been recognized as powerful technique to investigate intrinsic electronic properties owing to its relatively larger probing depth [1]. In this study, we have investigated transparent conductive Al-doped ZnO (AZO) thin films by the HAXPES.

2. Experimental

The AZO thin films with a thickness of 100 nm were deposited on silica glass substrates by DC magnetron sputtering (ULVAC, CS-L) at a substrate temperature of 200 °C. ZnO ceramic targets containing 0.5, 1 and 2 wt % of Al_2O_3 were used for the deposition. HAXPES measurements were performed using a custom-made XPS system equipped with monochromatic focused X-ray sources of Cr Kα (5414.9 eV) and Al Kα (1486.6 eV) (ULVAC PHI) and a wide acceptance angle electron analyzer (Scienta Omicron, EW4000). The HAXPES spectra were measured at a take-off angle of 85° from the sample surface. Electrical properties of the films were characterized by Hall effect measurements. Optical absorption and photoluminescence spectra were measured for comparison.

3. Results and discussion

Table 1 summarize the electrical properties of the AZO films. The resistivity decreased with increasing the Al doping content due to the increase of carrier concentration. These characteristics are commonly observed in electrical properties in AZO thin films.

Table 1 Resistivity ρ, Hall mobility μ, and carrier concentration N of AZO thin films deposited on silica glass.

	$ZnO:Al_2O_3$ wt%	ρ 10^{-4} Ωcm	μ cm^2/Vs	N 10^{20} cm^{-3}
#1	0.5	16.2	27.4	1.41
#2	1	8.03	27.1	2.87
#3	2	7.52	20.9	3.97

The HAXPES spectra in the Zn 2*p*, O 1*s*, and valence band regions of the AZO films are shown in Fig. 1a, 1b, and 1c, respectively. Since the HAXPES spectra entirely shifted to higher binding energy side due to the increase of carrier concentration, all the spectra were plotted against the relative binding energy measured

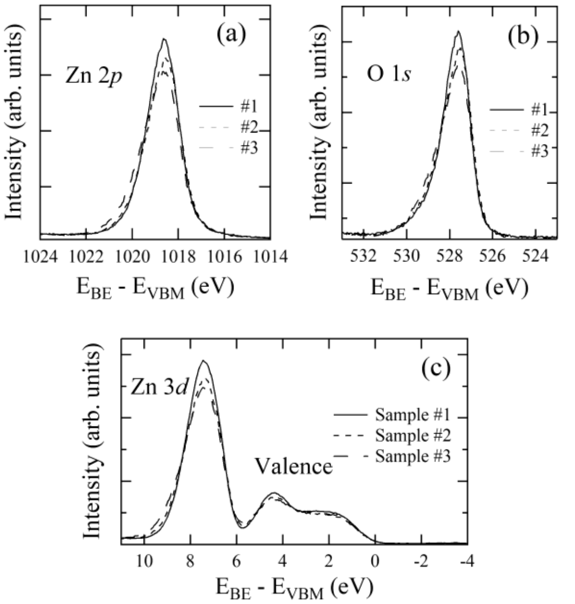

Fig. 1 HAXPES spectra of AZO thin films in the Zn 2*p* (a) and the O 1*s* (b) core regions and valence band region (c).

from the valence band maximum (E_{BE} - E_{VBM}). In the core level spectra, the intensity of main peak decreased and a tail like satellite feature at the high binding energy side appeared with increasing the carrier concentration. The similar tendency was also observed in the valence band spectra (Fig. 1c). These features are same as the Ga-doped ZnO thin films [2]. Such the characteristics in transparent conductive films have been discussed in relation with the excitation of the plasmon of conduction electrons [2, 3], although origin of the tail like satellite feature is not fully understood yet.

Fig. 2 show the HAXPES spectra of the AZO films (1wt%) neat the E_F, which is determined by the E_F of Au as a reference. We can see that a broad in-gap state deeply extends about 2 eV below the E_F. To further study the broad in-gap state, we measured optical absorption and photoluminescence spectra as shown in the bottom of Fig. 2. The absorption edge corresponding to the excitation from the valence band to the empty states of the conduction band shifts to high energy due to the Burstein-Moss effect [4]. On the other hand, the photoluminescence spectra reflect population of electrons filling in the conduction band. The band edge emission can be attributed to recombination of charge carrier electrons in the conduction band merged with the impurity states of dopants. Based on the consideration, we deduced the conduction band minimum E_{CBM} as shown in Fig. 2. The comparison implies that the broad in-gap states extended below the E_{CBM} cannot be explained only by the filled states in the conduction band. One possible explanation is due to the plasmon as explained in the core and valence band spectra, however, the contribution is too large. Another possible explanation is existence of some localized states below the E_{CBM}. The excitations from the in-gap states to the E_F may cause the tail-like satellite features observed in the core and valence band spectra.

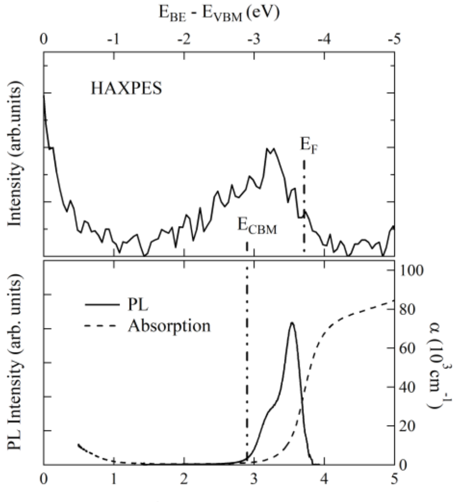

Fig. 2 HAXPES, photoluminescence, and optical absorption spectra of the AZO thin film (1wt%).

4. Summary

We have studied heavily Al-doped ZnO thin films by the laboratory base HAXPES system. The electronic structure near the E_F was compared among the different spectroscopic characterization methods. The core and valence band spectra showed specific characteristic of satellite structure strongly dependent on the carrier concentration. The broad in-gap state observed in the HAXPES spectra is not consistent with the photoluminescence spectra and cannot be simply explained by the filled states in the conduction band.

5. Acknowledgement

This work was partially supported by JSPS KAKENHI Grant Number 17K06356.

6. References.

[1] Y. Takata *et al.*, Appl. Phys. Lett. **84**, 4310 (2004).
[2] H. Song *et al.*, Appl. Surf. Sci. **433**, 1148 (2018).
[3] F. Borgatti *et al.*, Phys. Rev. B **97**, 155102 (2018).
[4] E. Burstein, Phys. Rev. **93**, 632 (1954).