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Effect of Plasma Irradiation on Interfacial Nano Layers in Organic/Inorganic Hybrid Structures

有機無機ハイブリッド構造におけるプラズマ照射によるナノ界面層への影響

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Interactions of Ar-O_2 mixture plasma and Zn/Alq3 interface have been investigated on the basis of depth analyses of chemical bonding states via conventional x-ray photoelectron spectroscopy (XPS) and hard x-ray photoelectron spectroscopy (HXPES). The HXPES analyses of Ar-O_2 mixture plasma exposed Zn/Alq3 samples indicated that the oxygen radicals and/or ions from the Ar-O_2 mixture plasma formed oxygen functionalities at the shallower region up to 10 nm from the interface. These results suggest that the Ar-O2 plasma exposure make it possible to control molecular structures of organic semiconductors.

1. Introduction

For fabrication of electronics on polymers or flexible electronics which are expected as next-generation devices, development of low-damage plasma processing technologies is significant. It is of important to control the chemical bonding states in the vicinity of the organic materials surface and at the interface between the organic materials and the deposited films. However, bond-dissociation energies of organic materials for thermal decomposition range from 3.4 eV for the O-C(=O) bond, 3.6 eV for the C-CH_3 bond to 8.4 eV for C=O bond. Thus, in the plasma processes, it is considered that ions, radicals, photons and electrons from the plasma may cause significant degradation of organic materials beneath the surface and the inorganic/organic interface. In order to overcome these problems, low-damage plasma processing technologies with low-inductance antenna (LIA) units [1] have been developed.

In this paper, interactions between plasma with organic semiconductors have been investigated on the basis of non-destructive depth analyses of chemical bonding states at Zn/Alq3 interface. The non-destructive depth analyses of chemical bonding states were carried out using hard x-ray photoelectron spectroscopy (HXPES)

2. Experimental

Schematic diagram of the process chamber is shown in Fig. 1. The LIA consists of a U-shaped antenna conductor (with a 80 mm height and a 70 mm width), which was fully covered with dielectric tubing for complete isolation from the plasma. The chamber had a 500 mm inner diameter and a 200 mm height, which was connected to a diffusion chamber made of stainless-steel vessel with 500 mm inner diameter and 400 mm height. Ar-O_2 mixture plasma was generated via inductive coupling of radio frequency (RF) power at 1000 W (13.56 MHz) with a set of eight LIA units at a gas pressure of 2.6 Pa (oxygen partial pressure = 20%).

Alq3 film was formed on Si substrate using vacuum evaporation. Zn thin film was deposited on Alq3 substrate using magnetron sputtering.

Depth analysis of chemical bonding states was carried out with conventional XPS and HXPES. The HXPES analysis was performed with hard x-ray from a synchrotron at a photon energy of 7940 eV at the national synchrotron radiation facility (SPring-8) of the Japan Synchrotron Radiation Institute. The inelastic mean free path (IMFP) of 7940 eV electrons in organic materials is approximately 18 nm. This feature with HXPES

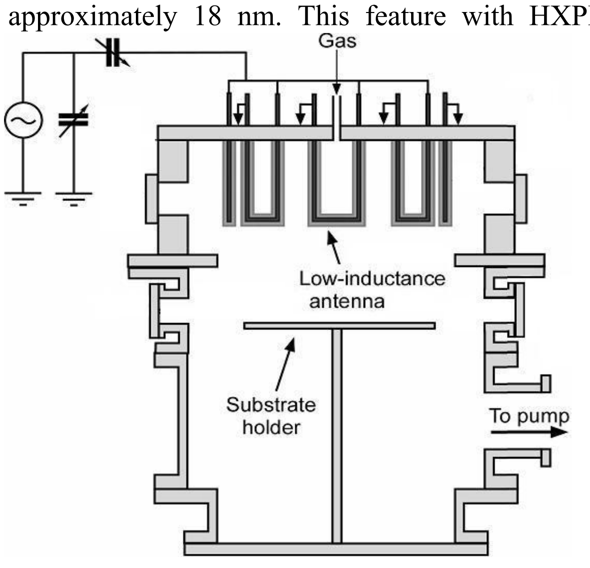

Fig. 1. Schematic diagram of discharge chamber.

makes it possible to evaluate the chemical bonding states at the Zn/Alq3 interface via variation of take-off angle (TOA) for photoelectrons detection from TOA of 88 deg for analysis of deeper region up about 35 nm from the interface down to TOA of 9.6 deg for analysis of shallower region about a few nm from the interface (Fig. 2).

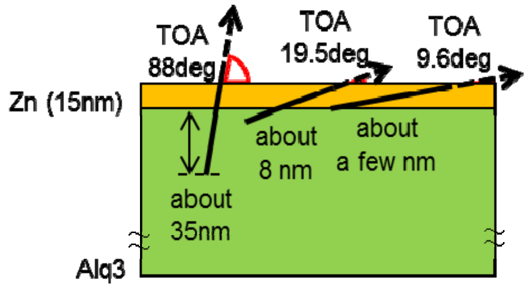

Fig.2. Schematic diagram of HXPES measurement

3. Results

Fig. 3 shows HXPES C 1s spectra of Zn/Alq3 samples; (a) without plasma exposure and (b) with plasma exposure as a parameter of TOA. For analysis of deeper region up about 35 nm from the interface, TOA was set at 88 deg. And For analysis of shallower regions up about 8 nm and a few from the interface, TOA were set at 19.5 deg and 9.5 deg. As shown in Fig. 2(a), after the deposition process of Zn thin film, O=C-O bond increased significantly at shallower regions about a few nm from the interface. These results indicated that the sputter process cased degradation of molecule structure at the interface. The HXPES C 1s spectra measured at a TOA = 88 deg showed insignificant change after the Ar-O_2 mixture plasma exposure. Whereas, the HXPES C1s spectra measured at TOA = 19.5 deg and TOA = 9.5 deg showed significant increase in O=C–O bond after the Ar-O_2 mixture plasma exposure. These results indicated that new oxygen functionalities are formed by the Ar-O_2 mixture plasma exposure at the interface. These results suggest that oxygen radicals and/or ions make it possible to control molecular structures at the interface.

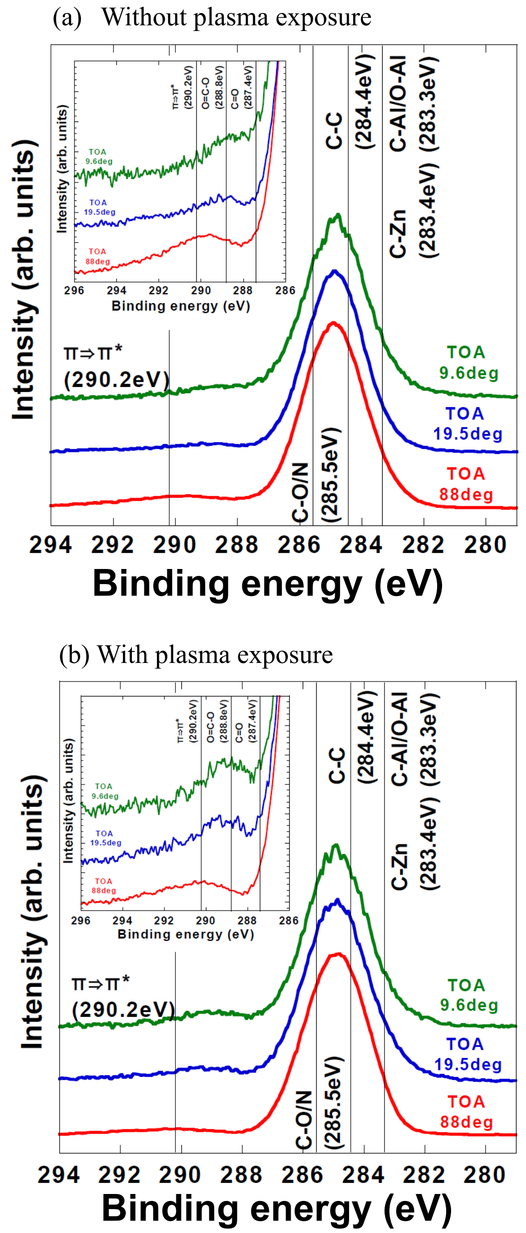

Fig.3. Variation of C1s HXPES spectrum of Zn/Alq3 films (a) without and (b) with Ar-O_2 mixture plasma exposure.

4. Conclusions

Interactions between plasma with organic semiconductors have been investigated on the basis of non-destructive depth analyses of chemical bonding states at Ar-O_2 mixture plasma exposed Zn/Alq3 interface. The HXPES analyses of Ar-O_2 mixture plasma exposed Zn/Alq3 samples indicated that the oxygen radicals and/or ions from the Ar-O_2 mixture plasma formed oxygen functionalities at the interface.

Acknowledgments

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References

[1] Y. Setsuhara et al., Surf. Coat. Technol. **174 – 175** (2003) 33.