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Study on Electronic Structure of Au, Ag, and Ca-doped Bathocuproine Layers

Hikaru Kitazume[1], Susumu Toyoshima[1], Takeaki Sakurai[1], Masaru Aoki[2], Shigeru Masuda[2] and Katsuhiro Akimoto[1]

[1]Institute of Applied Physics, University of Tsukuba
1-1-1 Tennodai, Tsukuba, Ibaraki 305-8573, Japan
Phone: +81-29-853-6150 E-mail: sakurai@bk.tsukuba.ac.jp
[2]Department of Chemistry, Graduate School of Art and Science, The University of Tokyo
7-3-1 Hongo, Bunkyo, Tokyo 113-8656, Japan

1. Introduction

The bathocuproine (BCP) buffer layer has a clear effect of improving the electrical properties of organic optoelectronic devices. In organic photovoltaic cells, in particular, the conversion efficiency is greatly improved by inserting a BCP buffer layer between acceptor and metal cathode[1]. The chemical structure of BCP is shown in Fig. 1. BCP is an electron transport material having an energy difference of 3.5 eV between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). There are some reports on the electronic structure between BCP and metal[2]; however, the mechanisms for the improvement of the electrical properties are still unclear. To clarify the interaction between BCP and metal, we have investigated the electronic structures of metal-doped BCP layers by ultraviolet photoelectron spectroscopy (UPS).

2. Experimental

Metal-doped BCP layers (metal: Au, Ag, Ca) were prepared by co-evaporation of BCP and metals on polycrystalline Au on Si(100) wafer. All deposition was done in an ultrahigh vacuum (UHV) system with a base pressure of 2 x 10^{-7} Pa at room temperature. After deposition, the specimens were transferred to UPS measurement chambers while maintaining a vacuum.

The UPS measurements were carried out in a UHV system with a base pressure of 1.6 x 10^{-8} Pa at beamline 11C at KEK Photon Factory. The photon energy was maintained constant at 21.2 eV. The resolution was 300 meV, determined from the width of the Fermi level in the UPS spectrum of Au. The energy scale in the UPS spectra was determined on the basis of Fermi level position of Au substrate.

3. Results and discussion

Figure 2 shows the UPS spectra of (a) Au-, (b) Ag- and (c) Ca-doped BCP layers and the schematic energy level diagrams for these samples are shown in Fig. 3. The thickness of the samples was fixed at 10 nm. The energy positions of the BCP HOMO level in the Au-, Ag- and Ca-doped layers were found to be 3.0, 3.7 and 3.7 eV, respectively. These values were almost constant regardless of the doping concentration. As for the Ag- and Ca-doped BCP layers, the energy position of the LUMO level almost accords with the Fermi level of the substrate. In addition, we observed new peaks named as gap states (GS-1 and GS-2) at around Fermi level which contribute to the improvement of electronic conductivity[2]. For the Au-doped BCP layer, on the other hand, the energy position of LUMO level is higher than that of Fermi level and no gap states were observed in the spectra. Such electronic structures (HOMO level position, gap states) almost coincide with those observed at the interface between undoped BCP layers and metal substrates[3]. These results suggest the electronic structure of metal-doped BCP layer is strongly affected by the interaction between doping metals and BCP.

Figure 4 shows the dependence of doping concentration on the energy position in the electronic states (GS-1, GS-2, HOMO). For Ag-doped BCP layer, the positions of the electronic states were not so varied with increasing the doping concentration. In contrast, the gap states shifted to the higher binding energy side for the heavy Ca-doped BCP layer. The energy shift of the gap states may correlate with the filling of the states by electrons, as illustrated in Fig. 5[4]. Thus, the electrical properties of the metal-doped BCP layer were affected by the doping metals and their concentrations.

3. Conclusions

We have investigated the electronic structure of Au, Ag, and Ca-doped BCP layer. The distribution of their energy states were drastically varied by changing the doping metals. The electronic structures of the metal doped BCP layer almost coincide with those observed at the interface between undoped BCP layers and metal substrates. Therefore, to control the interaction between BCP and metal is a key for improving the electrical properties of the metal-doped BCP layer.

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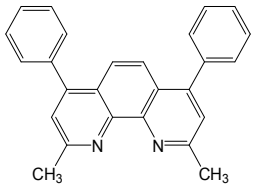

Fig.1 Chemical structure of BCP.

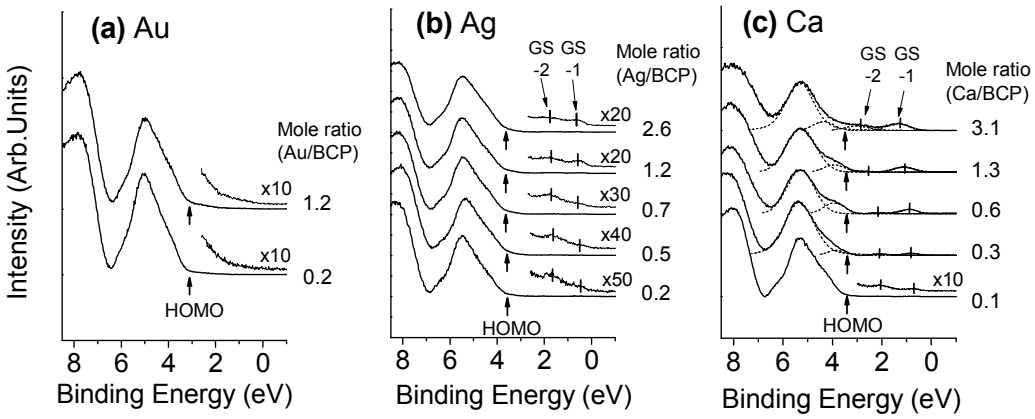

Fig.2 UPS spectra for (a) Au, (b)Ag, and (c) Ca-doped BCP layers.

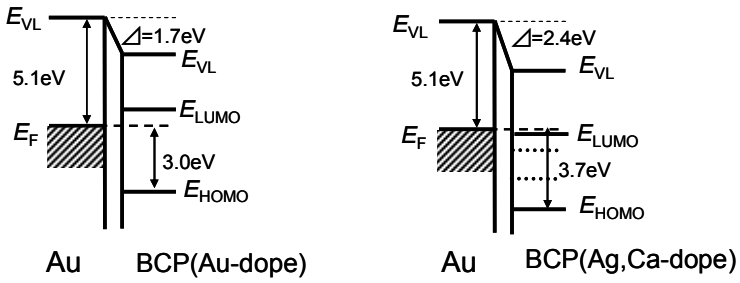

Fig.3 Energy level diagrams for metal-doped BCP layers (E_{LUMO}-E_{HOMO} = 3.5 eV).

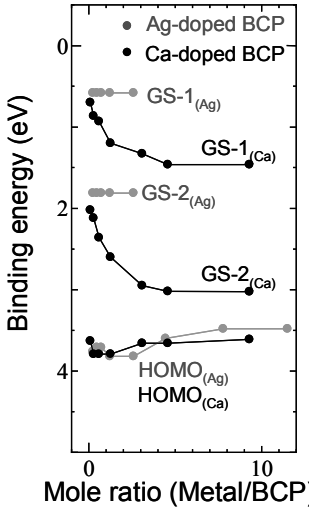

Fig.4 Dependence of doping concentration (Ag and Ca) on the energy position in the electronic states.

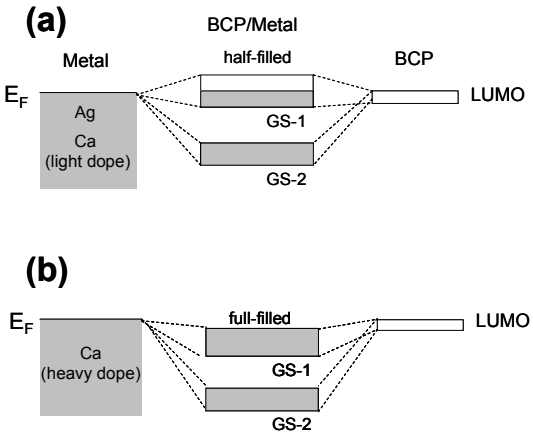

Fig.5 Schematic energy level diagrams for metal-doped BCP layers; (a) Ag, Ca (light dope), (b) Ca (heavy dope).