Photoemission study of IBr graphite intercalation compound using synchrotron radiation light source

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Abstract

We measured the photoemission spectra of IBr graphite intercalation compound (IBr-GIC) with stage-2 and stage-4 structures at 16 K with incident photon energies $h\nu$ = 40-200 eV. The peak positions of the I 4d and Br 3d core-levels are unchanged for the stage-2 and stage-4 IBr-GICs. Partial density-of-states of the I 5p and Br 4p states in the valence bands have been evaluated by resonant photoemission spectroscopy. These spectra indicate significant hybridization between the host and the guest IBr in the van der Waals gap.
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1. Introduction

A graphite intercalation compound with iodine monobromide, IBr-GIC, is an acceptor-type material, where some charge transfer from the host graphite layers to the guests in the van der Waals (vdW) gaps occurs [1]. We have conducted angle-resolved photoemission spectra (ARPES) of IBr-GIC using incident light with $h\nu$= 122 eV, and found that the dispersive bands are mainly derived from the C 2s and 2p valence states [2]. However, less is known about the electronic states of the IBr guests in the vdW gaps.

In this study we measured core-level and valence-band photoemission (PES) spectra of the stage-2 and stage-4 IBr-GIC using synchrotron radiation to elucidate the electronic states of IBr.

2. Experimental

IBr-GIC samples were prepared by a two-bulb method with 105-105 °C and 91-51 °C for the stage-2 and stage-4 samples, respectively. Highly oriented pyrolytic graphite (HOPG) and Kish graphite were used as host materials. Chemical composition of the sample was determined from the mass variation before and after the intercalation. The repeat distance I_c along the c-direction was evaluated by powder x-ray diffraction. We obtained $C_{18(1)}$IBr and I_c = 10.55(2) Å for the stage-2 GIC, and $C_{42(2)}$IBr and I_c = 17.2(1) Å for the stage-4 GIC.

Angle-integrated PES measurements with photon energies $h\nu$ = 40-200 eV were carried out on the beamline BL-7 of a compact electron-storage ring (HiSOR) at Hiroshima Synchrotron Radiation Center (HSRC), Hiroshima University with a high-resolution hemispherical electron-energy analyzer (SES100, GAMMADATA-SCIENTA) [3]. The PES spectra were obtained by integrating photoemission intensities over ±3.5 degrees from the surface normal. The total energy resolution was
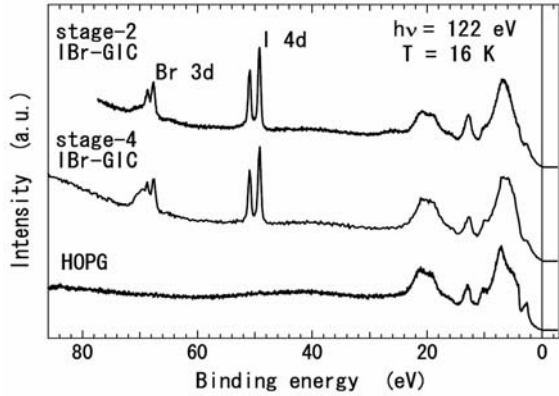
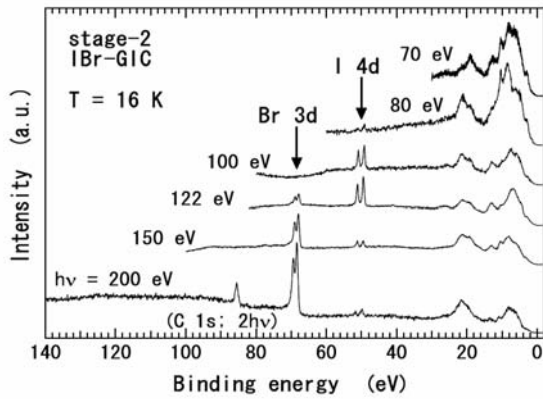Fig. 1. EDC curves of HOPG, the stage-4 and stage-2 IBr-GICs at 16 K using hν = 122 eV.

Fig. 2. The I 4d and Br 3d core-level PES spectra of the stage-2 IBr-GIC at 16 K using different photon energies, hν = 70-200 eV.

set to 20-100 meV. Samples were cleaved in the atmosphere and transported to an analyzer chamber (P < 1×10^{-10} Torr) and cooled to 16 K. The value of the binding energy E_B was defined referring to E_F, which was calibrated by the Fermi edge of an evaporated Au film.

3. Results and discussion

Figure 1 shows wide range PES spectra of the stage-4 and stage-2 IBr-GICs using hν = 122 eV. Here the host is HOPG. Double peaks at E_B = 49.2 and 50.9 eV are derived from I 4d core-levels, and those at E_B = 67.7 and 68.7 eV from Br 3d core-levels. These binding energies are almost the same for the stage-4 and stage-2 IBr-GICs, suggesting that the chemical bonds of IBr are similar. On the other hand, comparing the present I 4d spectra with those in an IBr molecule, the binding energies are smaller by ~8 eV in the IBr-GICs [4]. This chemical shift suggests a significant hybridization between IBr in vdW gap and the host graphite layers. We will discuss the hybridization effects with the results of resonant PES spectra later.

The intensities of I 4d and Br 3d are strongly dependent on hν over the range of 70-200 eV, but their positions are almost unchanged (Fig. 2). When lowering hν, Br 3d core-level intensities show a monotonic decrease and vanish at hν < 100 eV, while I 4d intensities show maxima at hν = 100~120 eV,
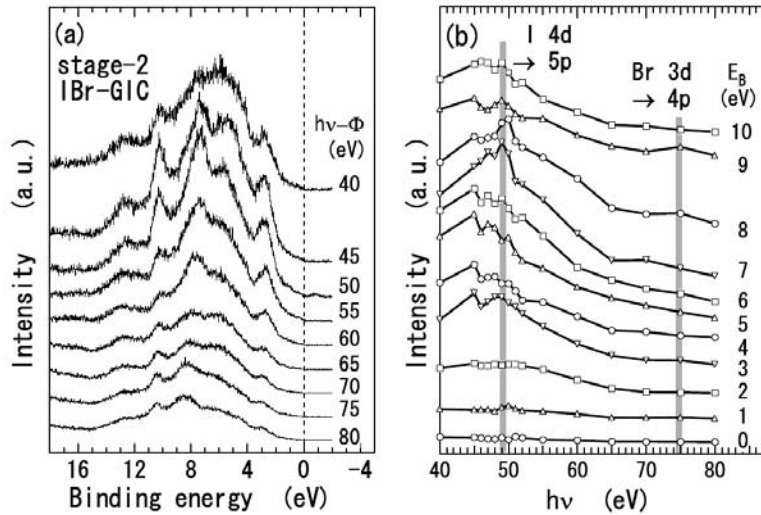

Fig. 3. (a) Variation in the valence-band spectra of the stage-2 IBr-GIC at 16 K using different photon energies hν = 40-80 eV. (b) Constant-initial-state spectra of the stage-2 IBr-GIC at E_B = 0-10 eV in steps of 1 eV.
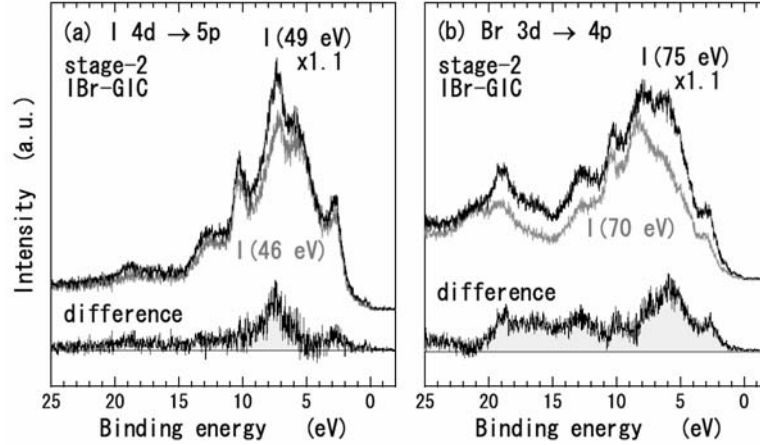
Fig. 4. (a) Partial density-of-states of the I 5p valence states and (b) those of Br 4p ones evaluated from the differences between on- and off-resonance spectra of the stage-2 IBr-GIC at 16 K.

followed by a decrease. This intensity variation is derived from $h\nu$ dependence of the photoionization cross-section (σ) of I 4d and Br 3d states [5].

In order to derive I 5p and Br 4p contributions to the valence bands of IBr-GIC, we have carried out resonant photoemission experiments in the I 4d-5p and Br 3d-4p excitation regions. Figure 3(a) shows valence-band spectra of the stage-2 IBr-GIC using different photon energies, $h\nu$ = 40-80 eV. Clear enhancement is observed at $h\nu$= 50 eV, which is related to the I 4d-5p absorption. The constant-initial-state spectra of stage-2 IBr-GIC are shown in Fig. 3(b), where the photoemission intensity at fixed E_B is plotted as a function of $h\nu$. Clear resonance enhancement is observed around $h\nu$ = 49 eV in the I 4d-5p excitation region, which takes place as a result of the interference effect of two processes of $(4d)^{10}(5p)^n$ + $h\nu$ $\rightarrow$ $(4d)^{10}(5p)^{n-1}$ + ε_p and $(4d)^{10}(5p)^n$ + $h\nu \rightarrow (4d)^9(5p)^{n+1} \rightarrow (4d)^{10}(5p)^{n-1}$ + ε_p, where ε_p represents an emitted 5p state. Similar but smaller enhancement is observed around $h\nu$ = 75 eV in the Br 3d-4p excitation region. The Br 3d-4p-resonance effect is more clearly seen in the PES spectra in Fig. 4 (b).

Partial density-of-states (PDOS) of I 5p and Br 4p in the valence bands were evaluated from the differences between on- and off-resonance spectra of the stage-2 IBr-GIC. The obtained I 5p and Br 4p PDOSs are illustrated in Figs. 4(a) and (b), respectively. In order to compensate for the $h\nu$ dependence of σ, we multiplied the on-resonance spectra by 1.1. From the obtained PDOS spectra, I 5p states are located mainly at E_B = 2.7 and 7.5 eV. In the case of Br 4p states, on the other hand, besides the spectral features located at 2.7 and 5.5 eV, one can see a broad spectral feature over the range of 12-19 eV. The Br 4p states have broader widths than the I 5p states. This indicates that the Br 4p states hybridize more strongly with host valence states, which is consistent with the larger electronegativity of Br. This hybridization should correspond to a charge transfer from the host graphite layers to IBr in the vdW gap.

In the ARPES spectra of the stage-2 IBr-GIC, we found new spectral features at 3-11 eV, besides dispersions derived from the host [2]. Based on the present results, these states are attributed to I 5p and Br 4p derived states.

4. Conclusions

We have measured core-level and valence-band photoemission spectra of the stage-2 and stage-4 IBr-GIC. The binding energies of the I 4d and Br 3d states are the same for the stage-2 and stage-4 IBr-GIC, and have larger binding energy compared with those of IBr molecules. By means of resonant PES, PDOS spectra of I 5p and Br 4p states were successfully obtained. We found strong hybridization between graphite and IBr, and could identify new states found in the ARPES measurements.

References

[1] K. Kobayashi *et al*., J. Phys. Soc. Japan. 68 (1999) 2006.

[2] H. Negishi *et al*., J. Phys. Chem. Solids (2006) in press.

[3] H. Sato *et al*., Phys. Rev. B 68 (2003) 35112.

[4] J.N. Cutler *et al*., Phys. Rev. Lett. 67 (1991) 1531.

[5] J-J.Yeh, Atomic Calculation of Photoionization Cross-Sections and Asymmetry parameters, Gordon and Breach, New York, 1993.