Electronic Structure of BP Studied by Resonant Soft X-ray Emission Spectroscopy

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The B1s and P2p soft x-ray emission of BP has been measured using monochromatic synchrotron radiation as an excitation source. The band-gap energy was estimated to be about 2.1 eV which is in good agreement with other experiments. The emission bands which reflect the partial density of states in the valence band showed resonant aspects. The spectral profile was interpreted by a momentum conservation approach.

§1. Introduction

The soft x-ray spectroscopy has been used to study the electronic properties of matters for a long time. Recently, progress in tunable monochromatic synchrotron radiation gives the possibility to investigate resonant x-ray emission spectra (XES).[1-3] The resonant feature of x-ray emission in some semiconductor systems, such as diamond, silicon, and cubic BN, has been successfully understood using inelastic x-ray scattering approach in which the radiative decay of the excited state sampled the same point in the Brillouin zone (BZ) as the initial excitation.[4-9]

During the inelastic-light-scattering process, a specific excitation energy selects an unoccupied state at a particular point in the BZ. If the momentum is conserved in the total process the emission transition can only occur from states with the same momentum. The momentum conservation can be written as $q_1 + k_1 = q_2 + k_2 + G$, where q_1 and q_2 are the momenta of incident and emitted photon, k_1 and k_2 are that of the excited electron and the final hole, and G is a reciprocal lattice vector. Since the momenta of soft x-rays are small compared to the BZ, the equation can be reduced to $k_1 = k_2$. The analysis of XES can be used as a photon based band mapping technique. For instance, when a core electron is excited to the X point in the conduction band, an electron which is in the X point of valence band decays during the resonant process.

BP has several interesting physical characters, such as a high melting point, high thermal conductivity, and a wide band gap.[10] To understand the properties, a few experiments[11] and some band structure calculations[12-20] have been carried out. X-ray emission using tunable synchrotron radiation can be a good probe to study the energy-band structure of BP. In the present paper, we have measured the B1s and P2p resonant x-ray emission of BP at the near x-ray absorption edges to obtain information about B2p (P3s and 3d) state.

§2. Experimental

The experiments were performed at beamline BL-3B at the Photon Factory, National Laboratory for High Energy Physics. The beamline comprises a Dragon-type monochromator. The XES were recorded by a grazing-incidence soft x-ray emission spectrometer with a 7 m concave and 1200 l/mm groove density grating with a two dimensional detector in Rowland circle geometry.[21]

The energy scale of the monochromator was calibrated using the photoelectron spectra of the Fermi edge or the 4f level of gold. The energy scale of the soft x-ray emission spectrometer was calibrated by the reflection of incoming x-rays. The x-ray absorption spectra (XAS) were recorded by fluorescence yield mode. The resolution of XES and XAS were about 1 eV. The typical data collecting times were 0.5 h and 1.5 h for the B1s and P2p XES, respectively.

The base pressure of the experimental system was about 3.0×10^{-10} Torr and temperature was room temperature. The single crystals of BP were grown by the high pressure flux method and chemical vapor deposition (CVD) process from B_2H_4 and PH_3.[10]

§3. Results and Discussion

Figure 1 shows (a) B1s XAS (right) and XES (left) excited at 210 eV and 190 eV, and (b) P2p XAS (right) and XES (left) excited at 165 eV and 131 eV. They are compared with Fig. 1(c) the calculated band dispersion curve of BP from ref. 20. The 210 eV-B1s XES and 165 eV-P2p XES spectra can be regarded as non-resonant ordinary fluorescence spectra.

Since XES shows occupied states and XAS shows unoccupied states, the band gap can be estimated from the gap between the top of XES and the bottom of XAS. The
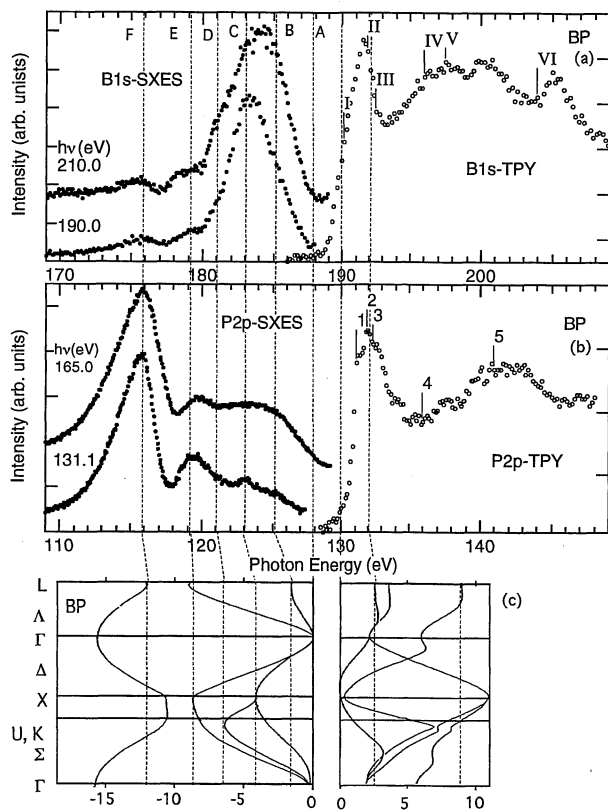

Fig. 1. (a) B1s XAS (right) and XES (left) of BP measured at excitaion eneries $h\nu$ = 210 eV and 190 eV. (b) P2p-XAS (right) and XES (left) of BP measured at excitaion eneries $h\nu$ = 165 eV and 131 eV. (c) Band dispesion curve of BP (from ref. 20).

Fig. 2. B1s-XES of BP excited at various photon energies which are indicated on Fig. 1(a).

band-gap energy of BP is estimated to be about 2.1 eV, which is in good agreement with an optical absorption measurement.[12] However the band gap obtained from the band calculation[20] is narrower than the present result. In order to compare the spectra with the calculation, the energy position of the calculated dispersion curve of the occupied states is set to the top of the measured XES as well as that of unoccupied states is set to the bottom of the XAS. We estimated their locations within the uncertainties of the resolution since it is difficult to determine the location of the top of the valence band and the bottom of the conduction band with high accuracy. The dashed lines are guides for eyes which are in correspondence to the high density of state points in the band dispersion curves.

Figure 1(a) shows the B2p components are dominant in the upper valence band but weak in the lower valence band around F. According to the band calculation, the X and L points almost overlap each other at around E, however the intensity of XES is not remarkable. B2s may be dominated at the bottom of the upper valence band. Figure 1(b) shows that the P3s and 3d components extend over the valence band, and the P3s components are dominant in the lower valence band of BP. Structure F does not have a sharp low energy limit. A similar feature in black P has been reported.[22]

In the case of cBN,[8,9] the B1s XAS has a sharp core exciton peak below the conduction band edge. However the B1s XAS of BP has sharp conduction band edge
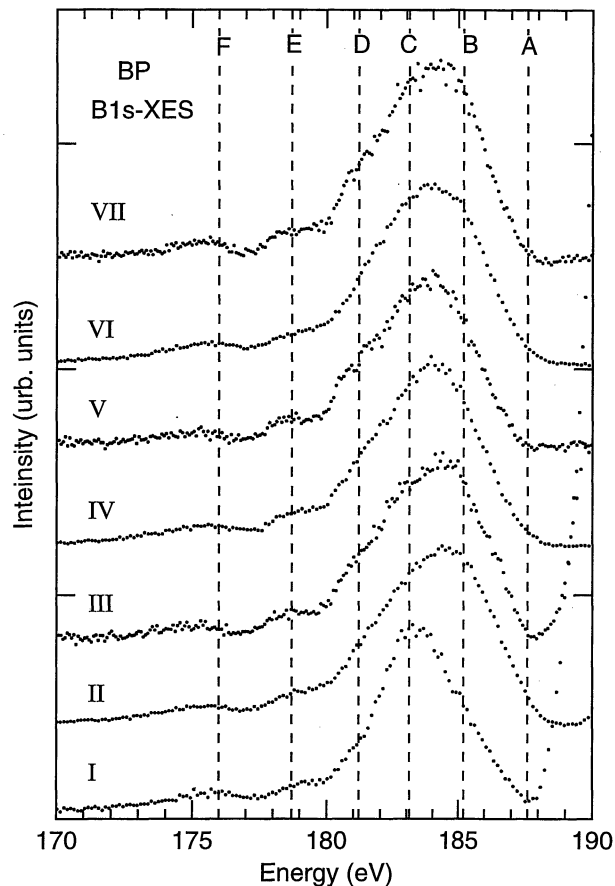
instead of a noticeable single peak. The edge could be attributed to the very dominant B2p state or the core exciton structure at the conduction band bottom. Wentyconvitch et al.[18] has reported that an indirect gap of BP is $\Gamma_{15}^c \to X(\Delta_{min})$, and the lowest conduction state is X_3^c instead of X_1^c as most of the III-V compound semiconductors show. Thus overlap of the two X-points might explain the sharp absorption edge.

The P2p XAS also has a sharp absorption edge, however the P3s components are not dominant at the bottom of the conduction band. Even if it has core exciton state, the contribution might be small. There is a plateau between 1 and 2, and their interval is about 0.9 eV. The P2p spin-orbit splitting in black P has been reported to be 0.87 eV.[23] Therefore, the feature 1 and 2 of the P2p XAS are attributed to the P2p spin-orbit splitting. Though Nemoshkalenko and Aleshin reported that the full valence bandwidth of BP was roughly to be at most 17 eV by using an e-gun as an excitation source.[11] We have estimated the upper, lower valence band, and total band widths to be about 9, 5, and 16 eV in BP, respectively, which show a good agreement with the prediction of the local density approximation.[20] These values are smaller than those of cBN,[8] that is consistent with the prediction from the band calculation.[20]

Figure 2 shows the B1s resonant XES of BP which were excited at the various photon energies. The selected excitation energies are indicated by the numbers on the B1s XAS in Fig. 1(a), and spectrum-6 was excited
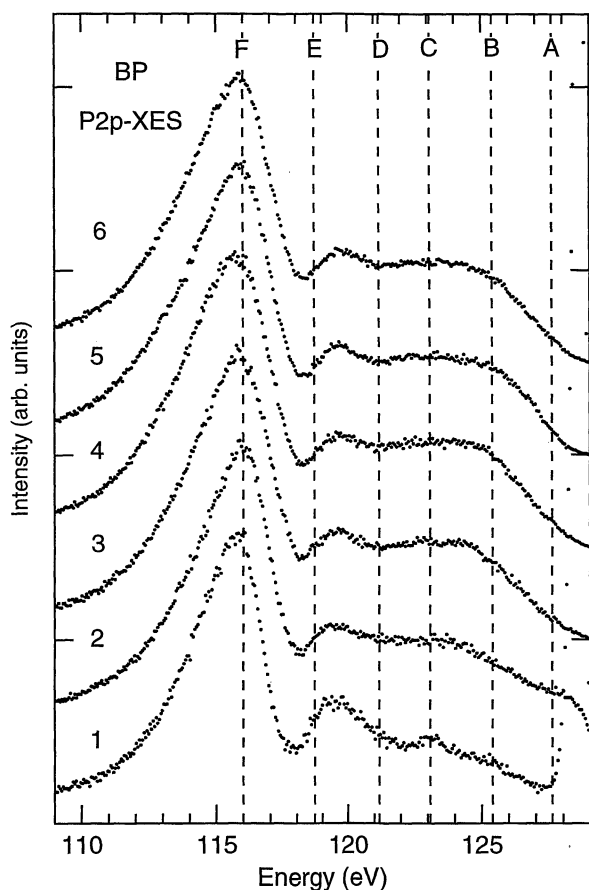
Fig. 3. P2p-XES of BP excited at various photon energies which are indicated on Fig. 1(b).

at 165 eV. The spectra were nomalized to have the same height at B or C. When the excitation energy was close to the edge of the conduction band, the edge A was covered with the direct recombination of incoming x-rays. Structure C is clearly observed in spectrum-I and structure B is more obvious in spectrum-II than in the other spectra.

Figure 3 shows the P2p resonant XES of BP excited at the various photon energies. The selected excitation energies are indicated by the numbers on the P2p XAS in Fig. 1(b). The peak height of the spectra was normalized at F. Spectrum-1 seems to have a sharper profile. Specially structure C is clearly observed. The excitation energy of 1 excites only the $2p_{3/2}$ core-level and the excitation energies of above 2 excite both the $2p_{3/2}$ and $2p_{1/2}$ levels. The overlap of the transition to the two core-levels makes the spectra broad above the excitation energy of 2. Energy dependence of P2p-XES of BP is not so clear because of the overlap of the transitions due to the 2p spin orbit splitting.

In the case of cBN, the excitation energy dependence was explained by the momentum conservation approach.[8,9] We interpret the spectra of BP on the analogy of cBN using the ability to prove the band structure of a solid by investigating the excitation dependence of the XES. The profile of the energy distribution curves of the valence band of BP are similar to that of cBN. The band calculation shows that the bottom of the conduction band is Δ_{min}, which is close to the X-point.

Structure C of B1s spectrum-1 is enhanced when a core electron is excited to the bottom of the conduction band. Indeed structure C is attributed to the X-point in the valence band. Also in comparison with the band dispersion curve, structure B is attributed to the L-point which is enhanced at the excitation energy of II. Thus, the structure of II is assigned to the L-point in the conduction band. Also structure D is a rise at the excitation energy of V, indeed they have a same symmetry. It is attributed to the U, K points comparing to the band dispersion curves. Energy difference between A and I is 2.1 eV, and that between A and II is 4.5 eV. Those can mean the Γ-X and Γ-Γ transition respectively. Those values are in good agreement with the other measurements.[12] Among various band structure calculations of BP, the local density of approximation method shows good agreement with the experimental results except the band gap.

§4. Conclusions

The B1s and P2p soft x-ray emission and absorption spectra of BP has been measured. The band-gap energy was estimated to be about 2.1 eV. The XES showed resonant aspects. The excitation energy dependence of XES was interpreted by a momentum conservation approach, and the high symmetry points were attributed.

Acknowledgement

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