Journal of the Physical Society of Japan
Vol. 71, No. 7, July, 2002, pp. 1761–1764

π Emission Anomaly in the N 1*s* Resonance Emission from Hexagonal BN: Effects of the Core Hole Potential

Noboru MIYATA*, Mihiro YANAGIHARA, Masamitsu WATANABE[1], Yoshihisa HARADA[1] and Shik SHIN[1,2]

Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577
[1]*RIKEN/SPring-8, 1-1-1 Kouto, Mikazuki-cho, Sayo-gun, Hyogo 679-5148*
[2]*Institute for Solid State Physics, University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8581*

(Received May 25, 2001)

N 1*s* resonance emission spectra in hexagonal BN was measured with high energy resolution at an undulator beamline. It was found that π emission is very weak in the spectator emission, while both π and σ components are present in the normal emission. This π emission anomaly has been explained in terms of the Coulombic effect of the core hole on the localized N $2p_z$ valence orbital. The π emission anomaly is quite analogous to the case of the B 1*s* resonance emission observed in the previous study.

KEYWORDS: hexagonal boron nitride, N 1*s* emission, π emission, localized *p* orbital, core hole
DOI: 10.1143/JPSJ.71.1761

1. Introduction

Soft-X-ray emission (SXE) spectra yield direct information about the partial density of states of a valence band because of the dipole selection rule and small dispersion of the core level. They also include information about relaxed intermediate states with a core hole present. It is well understood that the sudden generation of a core hole plays an essential role in the soft-X-ray spectroscopies.[1)] For example, the configuration interaction in the core excited state is important in the X-ray photoemission processes as well as in the X-ray emission processes in the transition metal and rare-earth compounds, where the localized *d* or *f* orbitals take part in the screening of the core hole potential through hybridization with the valence bands.[2)] In these cases the localized property of the *d* and *f* orbitals is essential. Yanagihara *et al.*[3)] observed a core hole effect for outer-shell electrons in hexagonal boron nitride (h-BN), which is a delocalized *s–p* electron system. The h-BN is an insulator with a direct band gap of about 5.8 eV.[4)] It has a layer structure very similar to graphite. It exhibits a sharp feature due to a core exciton at the B 1*s* absorption threshold.[5,6)] When a B 1*s* exciton is created, the core hole radiatively decays by spectator emission or by direct recombination. In spectator emission, the core hole is filled by a valence electron rather than by the excitonic electron. When the core hole is filled by a valence electron without an excitonic electron, the radiative decay is referred to as normal emission. They investigated the anisotropy of the spectra and the polarization degree of the B 1*s* emission in h-BN. It was found that the π emission component was absent or very weak in the spectator emission, while both π and σ components were present in the normal emission. Noba *et al.*[7)] successfully explained this π emission anomaly in terms of the Coulombic effect of the core hole on the localized B $2p_z$ orbital and the configuration interaction in the outer-shell electron system.

In the proposed model core exciton states and localized valence orbitals are essential. The bottom of the conduction band in h-BN consists of mainly the B $2p_z$ orbital. We actually observe a dominant peak due to the B 1*s* core exciton. Though the ratio is lower than B $2p_z$, the N $2p_z$ component also contributes to the conduction bottom. Thus we can expect that h-BN has a spectral feature due to a core exciton at the N 1*s* absorption threshold. In this study we have investigated the N 1*s* emission spectra in h-BN to confirm the core hole effect. We have observed the same π emission anomaly for the N 1*s* emission as observed for the B 1*s* emission. In this paper we present and discuss the results in terms of the Coulombic effect of the core hole on the localized N $2p_z$ state.

2. Experimental

The h-BN sample was prepared from original powder of 99.7% purity. It was pressed and then sintered at about 2000°C. The *c* axis was confirmed to be highly oriented. It was cut with faces parallel to the *c* axis into a size of $10 \times 10 \times 5$ (thickness) mm^3. The sample was stripped off with vinyl tape to obtain fresh surface immediately before mounted in the vacuum chamber. The SXE experiments were carried out at the beamline 2C of the Photon Factory. A varied-line-spacing plane grating monochromator[8)] coupled with an undulator as its light source provided intense monochromatic soft X-rays. The energy width of the excitation light was 0.4 eV at 400 eV. The SXE spectrum was recorded using a soft-X-ray Raman scattering spectrometer.[9)] It was rotated on the axis of the incident light without breaking the vacuum. In the ‘‘polarized’’ configuration the series of the grating and the detector was positioned vertically above the sample. The *c* axis of the sample was oriented horizontally normal to the incident light. The sample was irradiated on the lateral face parallel to the *c* axis. Therefore, both the π and σ emission components were observed in the polarized configuration. The resolution of the spectrometer was 0.4 eV at 400 eV. An excitation spectrum of the total photoelectron yield was measured as an absorption spectrum in the N 1*s* edge region. The energy width of the primary monochromator was narrowed to 0.1 eV in this case. A total SXE yield spectrum was also measured for reference data.

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*E-mail: miyata@tagen.tohoku.ac.jp

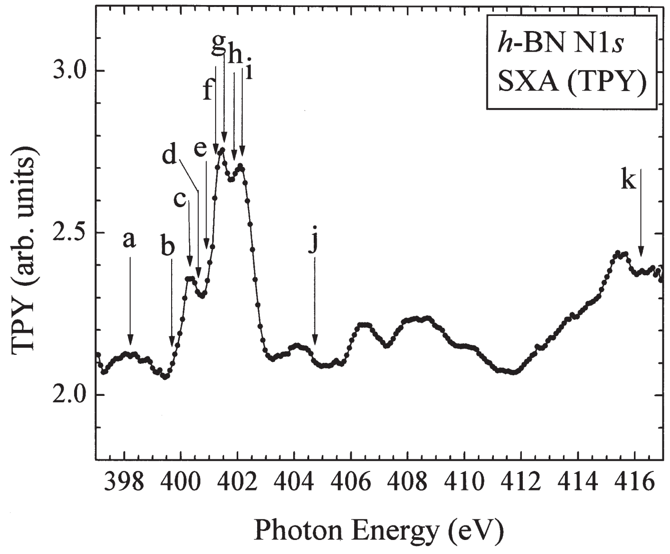


Fig. 1. N 1*s* absorption spectrum of h-BN obtained by total photoelectron yield. The excitation energy for N 1*s* SXE is also illustrated with the arrows.

3. Results

Figure 1 shows the absorption spectrum obtained by total photoelectron yield near the N 1*s* absorption edge. A remarkable structure with three peaks appears just above 400 eV, and broad peaks can be seen around 407 eV and 416 eV. According to Ma *et al.*[10] the peak at 401.5 eV is a resonance of the N $2p_z$ orbital, while the broad peaks around 407 eV and the peak at 416 eV are due to resonances of the N $2p_{xy}$ orbitals. As for the total SXE yield spectrum also measured in this study, absorption onset appeared at 401 eV and no structure was observed below 401 eV, though the S/N ratio was not enough. The difference in the degree of peak appearance between the two spectra may originate from the excitation energy dependence of the relaxation processes. The small peak at 400.3 eV in the total photoelectron yield spectrum may be due to the N 1*s* core exciton as has been expected. The binding energy of the exciton is estimated to be about 1.0 eV, which is smaller than that of the B 1*s* core exciton. This result is consistent with the calculation of Robertson.[11] In Fig. 1 are also illustrated the energy positions with alphabetical arrows to obtain the N 1*s* SXE spectra in the present study. Excitation above 401 eV yields normal emission because the N 1*s* electron is excited into the conduction band, while stimulation at 400.3 eV yields spectator emission.

Figure 2 shows the N 1*s* SXE spectra obtained by excitation in the N 1*s* edge region, where the excitation energy is designated by the respective spectra. As for the normal emission spectra, excited above 401 eV, each has a similar feature; a dominant sharp peak at 394.6 eV and a broad band with three small peaks at 385 eV, 390 eV, and 393 eV. The former peak is attributed to the N $2p_z$ states, and referred to as π emission. The latter peaks are associated with the N $2p_{xy}$ states,[11,12] and referred to as σ emission. This result is quite consistent with that of Tegeler *et al.*[13] From the spectra it is concluded that the N 1*s* normal emission has both π and σ emission components. On the other hand, the spectra of the spectator emission, obtained at 400.6 and 400.3 eV, show a drastic change from the normal emission. The dominant feature is that the π emission peak lowers and the σ emission peaks slightly shift towards low energy in the spectator emission. The result concerning π emission is not due to the experimental geometry because we never fail to observe π emission if it is emitted in the polarized configuration. We are now able to draw a conclusion that the π emission component is very weak in the N 1*s* spectator emission while both π and σ components are present in the normal emission. Thus the π emission anomaly was also ascertained in the N 1*s* spectator emission for h-BN as well as the B 1*s* spectator emission.[3]

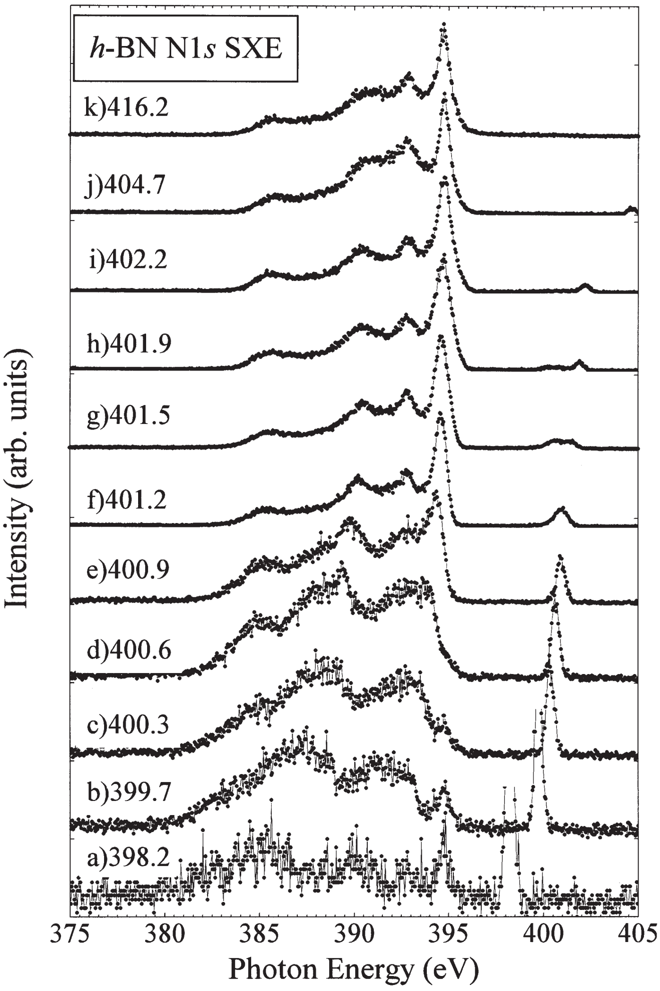


Fig. 2. N 1*s* resonance emission spectra of h-BN. The excitation energy is indicated by the respective spectra.

4. Discussion

The π emission anomaly in the N 1*s* spectator emission can be discussed by analogy with that in the B 1*s* spectator emission. We should refer to the theory of resonant inelastic X-ray scattering[14] since the spectral profile depends on the excitation energy near the core threshold. The conservation of the crystal momentum during the absorption-emission process is deduced from it. When the incident photon energy is tuned to about 401 eV for h-BN, the absorption process with the N 1*s* electron excitation occurs near the K–H symmetry points of the Brillouin zone.[11] At these points, the bottom of the conduction band and the top of the valence band are composed of the π band. According to the theory,

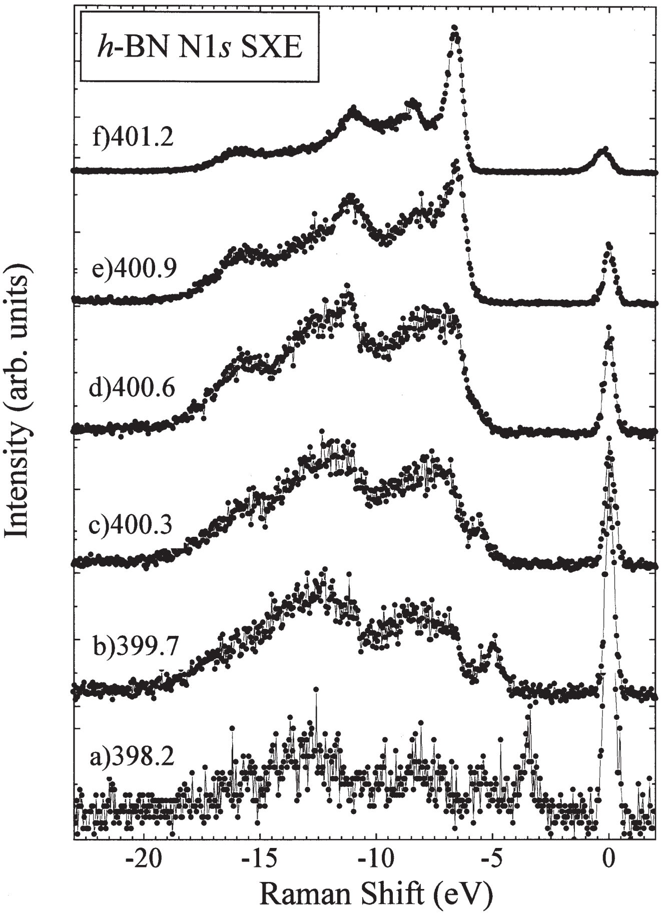
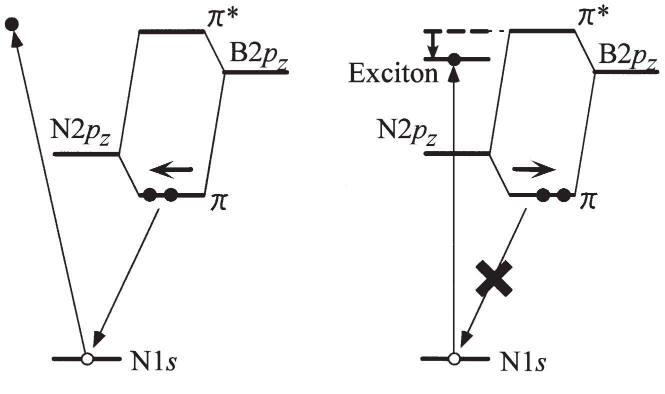


Fig. 3. N 1s resonance emission spectra of h-BN as a function of the Raman shift with regard to the elastic scattering.



(a) Normal (b) Spectator

Fig. 4. Illustration of the core hole effect for normal emission (a) and spectator emission (b). The π and π^* bands are schematically shown as the bonding and the antibonding states of the N and B 2p_z orbitals.

we would have observed a spectrum enriched with the π emission component. However, the obtained spectra show quite the opposite tendency. Besides, as the electron-phonon coupling is strong in h-BN, the momentum conservation is a minor effect.[14)] The spectra obtained below the resonance excitation should be discussed from the view point of Raman scattering.[15)] Figure 3 illustrates the spectra shown in Fig. 2 as a function of the Raman shift, the origin of which is the elastic scattering. The three peaks observed in normal and spectator emission lose their intensity as the excitation shifts from the resonance. Besides, a new broad peak appears at a Raman shift of about -12 eV in the spectrum of 400.3 eV. The origin of the broad peak has not been assigned. The spectator emission appears under excitation into the core exciton state, which is a real state. Thus it is difficult to interpret the spectator emission in terms of the Raman scattering. Our result should be attributed to another effect.

In the initial state of normal emission wavefunction of the excited electron extends over the conduction band, while in the case of spectator emission the excited electron is localized to form a core exciton, consequently screening the core hole. Our result is interpreted in terms of the core-hole effect on the localized 2p_z orbitals and the configuration interaction (hybridization) in the outer-shell electron system. The π orbital is essentially nonbonding, while the σ orbital, originated from the sp^2 hybridized orbitals, contributes to the bonding. According to the calculations of the band structures,[4,11,12,16,17)] the width of the π band is small as compared with that of the σ band. In the ground state, the upper part of the valence band is the π band which is primarily composed of the N 2p_z orbital, while the bottom of the conduction band is the π^* band primarily composed of the B 2p_z orbital. On the other hand, the σ band is composed of the B 2p_{xy} and N 2p_{xy} orbitals with equal weight, which extends over the layer. In other words, several π electrons exist in the vicinity of the N site, and σ electrons are also present with a high probability. If a N 1s electron is excited into the conduction band (normal emission), the effect of the Coulomb attraction is dominant particularly for the π orbital because of its localized property, while it is almost negligible for the σ orbitals for the extended property.[6)] The N 2p_z orbital is pulled down from the π^* band at the core hole site due to the attractive Coulomb force. As a result, the N 2p_z is mixed to a larger extent in the π orbital of the valence band at the core hole site as shown in Fig. 4(a). This is nothing but the polarization of the outer-shell electrons induced by the core hole. Therefore, we observe π as well as σ emission in normal emission. The excitonic electron occupies the core exciton level, which is attracted by the core hole as shown in Fig. 4(b). This electron repels the π electrons out of the N site with the repulsive Coulomb force. Consequently, mixing of the N 2p_z component into the valence band is suppressed (Coulomb blocking effect). Thus we observe spectator emission with less π component. The π emission anomaly has been observed in the N 1s emission as well as in the B 1s emission for h-BN, which provides an evidence for the core hole effect on the localized 2p_z valence orbitals.

Compared with the case of the B 1s emission, the π emission anomaly seems more remarkable in the N 1s emission. As π electrons exist close to the N site in the ground state, the Coulomb interaction of the π electrons with the core hole and the excitonic electron will be stronger on the N site. Therefore, in the case of normal emission the Coulombic attraction between the N 1s core hole and the π electrons makes the overlap of their wavefunctions larger, and the π emission component grows higher. In the case of spectator emission, the Coulombic repulsion of the excitonic electron will be more dominant on the N site. These reasons may explain remarkable π emission anomaly in the N 1s

emission qualitatively.

One of the prediction of our model is that the π^* state will be occupied with a finite probability in the intermediate state of the normal emission by the shake-up effect. As a result, a satellite peak will appear in the vicinity of the N 1*s* core exciton emission. Actually we can see a small peak at about 400.5 eV in the spectrum of 401.5 eV in Fig. 2. It also seems that the small peak could be due to the exciton emission because of the energy position. This point will be made clear by observing the predicted satellite structure in the N 1*s* photoelectron spectrum.

Now we discuss the σ emission component in normal and spectator emission by comparing the spectra of 401.2 eV and 400.6 eV shown in Fig. 2. The spectrum of 400.3 eV is not employed as spectator emission because the S/N ratio is a little lower and another feature appears as described above. With regard to the spectral shape of the peaks at 385 eV and 390 eV spectator emission has a sharper feature than normal emission. This result also agrees with the case of B 1*s* emission. We also conclude that the feature is closely correlated with the lifetime of the two excited states. On the other hand, the σ emission band in spectator emission shifts towards the low energy side as compared with the normal emission. The spectator shift is originated from the energy difference between the final states of spectator emission (valence exciton) and normal emission (free electron–hole pair). The spectator shift was estimated to be about 0.8 eV from the shift of the remarkable peak at 390 eV. It is fairly close to the binding energy of the N 1*s* core exciton, about 1.0 eV.

5. Conclusion

N 1*s* resonance emission in h-BN was investigated using high-intensity synchrotron radiation. It was ascertained that π emission is very weak in the N 1*s* spectator emission, while both π and σ components are present in the normal emission. This π emission anomaly has been explained in terms of the Coulombic effect of the core hole on the localized N $2p_z$ valence orbital by analogy with that in the B 1*s* spectator emission. The π emission anomaly observed in both the B and N 1*s* spectator emission offers evidence for the core hole effect on the localized $2p_z$ valence orbitals.

Acknowledgments

We would like to thank Prof. Kayanuma and Prof. Tanaka of Osaka Prefecture University for discussion about the experimental results. The SXE experiments were carried out under the approval of the Photon Factory Program Advisory Committee (Proposal 98G238). This work was also supported in part by Grant-in-Aid for Scientific Research (C) (Contract No. 11640306) from Japan Society for the Promotion of Science.

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