

Relaxation Process of the Excited State and Selection Rule in the Soft X-ray Emission of Si and cBN

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The soft X-ray emission spectra of Si and cubic boron nitride (cBN) are compared in the Si2*p*- and B1*s*-core exciton regions because inversion symmetry is lost and the band gap is extremely large for cBN although both crystal structures are very similar. The background in the soft X-ray emission spectrum of Si is much larger than that for cBN but becomes extremely weak as the excitation energy becomes low and the Raman process becomes dominant compared with the fluorescence process. The background is found to be mainly formed by electron excitation from the valence band to the conduction band. The Raman spectrum is similar to the absorption spectrum in cBN, while those of Si are quite different from each other. It is shown that the centrosymmetry is important in the selection rule of Raman scattering. In resonant Raman scattering the selection rule partly breaks down due to the lattice relaxation process that emits an ungerade phonon in the intermediate state.

Keywords: soft X-ray emission; Raman scattering; fluorescence; silicon; cubic boron nitride.

1. Introduction

Very recently the inelastic light-scattering process has been found in soft X-ray emission spectra by using synchrotron radiation (Nordgren, 1994; Ederer *et al.*, 1994), while fluorescence spectra are dominant when excited by traditional X-ray or electron sources. It is important to understand the conditions under which inelastic light scattering becomes strong, since fluorescence and inelastic light-scattering processes coexist in soft X-ray emission spectroscopy (SXES). In the case of diamond (Ma *et al.*, 1992), inelastic light scattering contributes to about half of the C1*s*-SXES spectra, while it is dominant in B1*s*- and N1*s*-SXES of cubic boron nitride (cBN) (Agui *et al.*, 1997). Since it is a two-photon process, inelastic light scattering corresponds to a type of well known Raman scattering. When the intermediate state is a real state it is called resonant Raman scattering. When it is a virtual state it is called normal Raman scattering. Of course, this process converges to the resonant process when the virtual state approaches the real state (Shin *et al.*, 1996).

The electron wavevector conservation model has been found recently in the SXES of diamond (Ma *et al.*, 1992; Johnson & Ma, 1994), graphite (Skytt *et al.*, 1994) and Si (Rubensson *et al.*, 1990; Miyano *et al.*, 1993; Shin *et al.*, 1996; Eisebitt *et al.*, 1996). This process is a type of resonant Raman scattering where the wavevector of the produced core hole is the same as that of the excited electron within the small wavevector of the photon. Thus an inelastic light-scattering study provides us with a great deal of fruitful information on the interaction of matter with light.

Very recently normal Raman spectra have been clearly observed in Si even in the energy region below the $L_{2,3}$

absorption edge (Shin *et al.*, 1996). The resonant Raman effect is also observed above the $L_{2,3}$ absorption edge. It is quite interesting that the line shape changes when the regime changes from the normal to the resonant Raman process. A microscopic viewpoint will be needed to solve this problem in the Raman processes.

Here, the SXES spectra of Si and cBN have been compared at several photon energies. The first aim of this study is to understand the origins of the relaxation processes in the excited state of SXES, which will clarify the difference between the normal and resonance Raman and fluorescence processes. The second aim is to understand the selection rule of the Raman spectra in the soft X-ray region. The selection rule in the soft X-ray Raman process will provide us with essential information on the photon energy dependence of the SXES spectra.

2. Experimental

The optically polished (100) surface of an Si crystal and the cleaved (111) surface of an undoped cBN crystal were used for the measurements. The samples were cooled to below 30 K in order to suppress the phonon effect in the SXES process.

Soft X-ray emission measurements were carried out by the SXES system (Shin *et al.*, 1995), which is installed at beamline BL-19B at the Photon Factory, KEK, Japan. The Revolver undulator (Isoyama *et al.*, 1989) and the VLM19 monochromator (Fujisawa *et al.*, 1996) with a varied-line-spacing plane grating (central groove density 2400 lines mm⁻¹) were used as the excitation light source.

3. Results and discussion

3.1. Decay channel of the excited state

Figs. 1(a), 1(b) and 1(c) show the SXES spectra of silicon. The excitation photon energies are 145, 99.7 and 99.5 eV, respectively. The spectrum in Fig. 1(a) was measured at an excitation photon energy higher than the Si $L_{2,3}$ threshold and mainly consists of the fluorescence spectrum (Shin *et al.*, 1996). The two strong structures have been assigned to the high density of state structures around the $L_{2'}$ and L_1 points in the Brillouin zone of the valence band. The SXES spectrum in Fig. 1(b) was measured at the excitation photon energy of the Si L_3 core exciton that can be the resonant state of Raman scattering (Shin *et al.*, 1996). The small structure at ~ 4 eV and the large structure at 8.5 eV are assigned to the X_4 and X_1 structures of the valence band in the Brillouin zone. This spectral change has been elucidated by the electron wavevector conservation

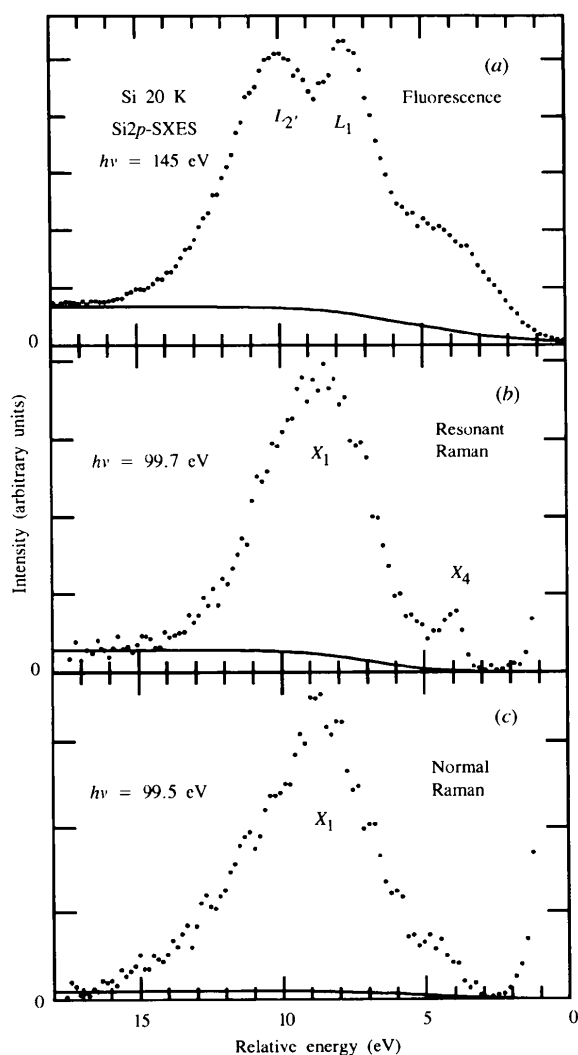


Figure 1

The $L_{2,3}$ -SXES spectra of Si measured at various photon energies: (a) an energy well above the $L_{2,3}$ threshold, (b) the energy at the core exciton, and (c) the energy corresponding to excitation to the virtual states below the L_3 core exciton. The abscissa is the relative photon energy.

model of the core hole and the excited electron because the core excitation is formed around the X_1 - Δ conduction band minimum (Chelikowsky & Cohen, 1976; Weng, Rez & Batson, 1990). On the other hand, Fig. 1(c) shows the normal Raman spectrum measured at the excitation photon energy of the virtual state below the $L_{2,3}$ threshold. Although the X_1 band remains, the X_4 band becomes very weak. The abscissa of Figs. 1(b) and 1(c) represents the Raman shift, *i.e.* the energy difference from the excitation photon energy to the soft X-ray emission energy. The abscissa of Fig. 1(a) is the relative energy, *i.e.* the energy difference from 99.7 eV.

One finds that the background increases at a higher binding energy (lower photon energy) at ~ 15 eV, as shown in Fig. 1(a). It seems that the SXES bands have an energy tail to higher binding. The solid lines in Figs. 1(a), 1(b) and 1(c) show the estimated backgrounds, as discussed later. These low photon energy tails cannot be elucidated by the one-electron band structure. Livins & Schnatterly (1988) have already suggested that a broad energy tail exists below the main SXES bands and assigned it to the electron excitation from the valence band. They pointed out the analogy to the shake-up process in the photoemission process and calculated the line shape of the background. Here, in order to estimate the background intensity, we tentatively suppose that the background is in proportion to the intensity integrated above the emitted photon energy, as in the secondary electrons of the photoemission spectra, because the emitted photon loses its energy in proportion to the number of the valence electron excitation to the conduction band, as shown schematically in Fig. 3(a). Thus,

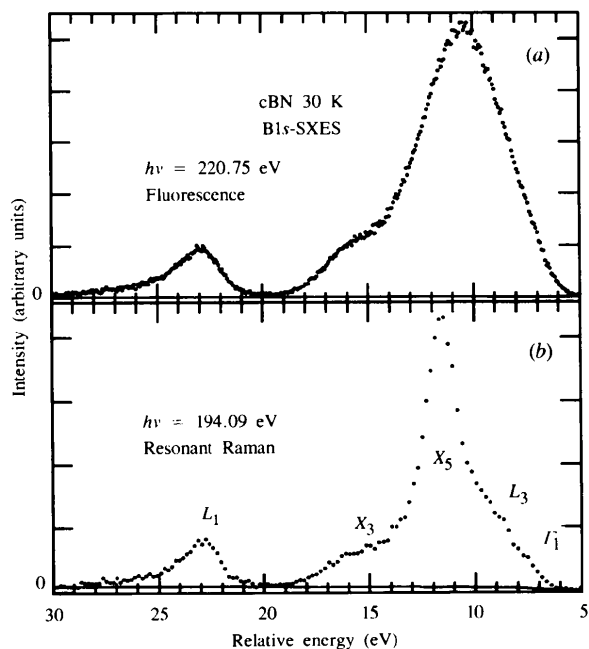


Figure 2

The B1s-SXES spectra of cBN measured at various photon energies: (a) at an energy high above the B1s threshold, and (b) at the B1s threshold energy. The abscissa is the relative photon energy.

the solid lines in Figs. 1(a), 1(b) and 1(c) are estimated as the backgrounds. The large background spectrum shown in Fig. 1(a) decreases from Fig. 1(a) to Fig. 1(c) as the excitation energy decreases. The number of the valence electron excitation seems to be in proportion to the lifetime of the core hole. Because the lifetime for Raman scattering is shorter than that for fluorescence, it is within reason that the background intensity decreases as the Raman process increases from Fig. 1(a) to Fig. 1(c).

On the other hand, Figs. 2(a) and 2(b) show the excitation energy dependence of the B1s-SXES spectra of cBN. They are excited to the higher conduction band and at the conduction band threshold. The abscissa of Fig. 2(b) represents the Raman shift. The abscissa of Fig. 2(a) is the relative energy, *i.e.* the energy difference from 194 eV. In the case of cBN, the backgrounds of the SXES spectra are always very weak at any excitation photon energies.

Thus we pay attention to the remarkable contrast found in the background spectra of SXES between Si and cBN. Of course, the electron excitation from the valence band to the conduction band strongly depends on the band-gap energy. The band gaps of Si and cBN are ~ 1.1 and 6.3 eV, respectively, so that it is within reason that the electron relaxation effect is negligible in cBN. Thus, the background spectrum in cBN is very weak while that of Si is rather strong.

Fluorescence is caused by the relaxation process after the absorption process has taken place. The lattice relaxation and the valence electron excitation processes have been proposed as relaxation processes in the soft X-ray region. Figs. 3(a) and 3(b) show schematic diagrams of both processes. It is well known that the phonon frequency is comparable with the lifetime broadening of the core hole of light elements in the soft X-ray energy region. In the case of semiconductors the number of the valence electron excitation is in proportion to the inverse band-gap energy, $1/E_{\text{gap}}$. O'Brien *et al.* (1993) observed the lattice relaxation effect in the SXES spectra of SiO₂, Al₂O₃ and MgO in the energy region below 100 eV. The phonon side band is also observed in the SXES spectrum of diamond (Ma *et*

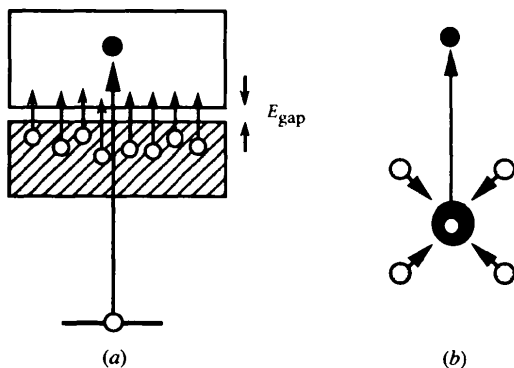


Figure 3
Schematic diagram of the relaxation processes of the excited state that are caused by (a) valence electron excitation and (b) lattice distortion.

et al., 1993). If compounds consisting of light elements have a high phonon frequency, the lattice relaxation effect is essentially important.

The lattice relaxation effect must play an essential role in the fluorescence process of cBN because it has a high phonon frequency. In cBN the Raman and fluorescence spectra coexist in the SXES spectra even above the threshold (Agui *et al.*, 1997), while fluorescence spectra are dominant in Si above the threshold (Shin *et al.*, 1996). The microscopic mechanism of the lattice relaxation effect is not yet well understood in the soft X-ray region, though it is well established in the visible-light region.

3.2. Selection rule of soft X-ray Raman scattering

Figs. 4(a) and 4(b) show a comparison between the resonant Raman and the ϵ_2 (Phillipp & Ehrenreich, 1959) spectra of Si. The abscissa of the Raman spectrum represents the Raman shift. The ordinate is the SXES intensity divided by the fourth power of the emission photon energy. The abscissa of the ϵ_2 spectrum is the absorption photon energy, which should be compared with the Raman shift energy. The strong structure by the transition from the X_1 valence band to the lowest X_1 conduction band is not found at ~ 8.5 eV in the ϵ_2 spectrum, but the X_4 structure at ~ 4 eV is found in both spectra. It is known that the transition from the $\Gamma_{25'}$ to Γ_{15} points is around the lowest direct transition. The electroreflectance spectrum (Aspnes

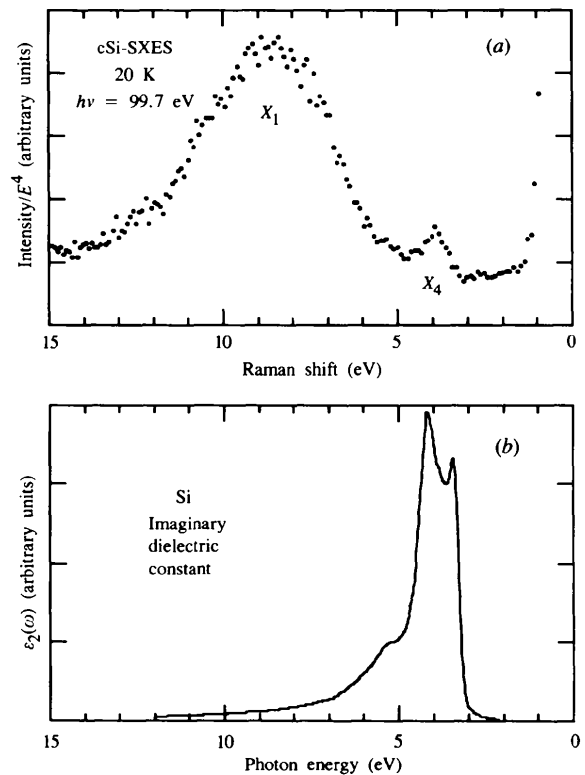


Figure 4
(a), (b) A comparison between the Raman and the VUV absorption (Phillipp & Ehrenreich, 1959) spectra of Si. The ordinate is the SXES intensity divided by the fourth power of the photon energy.

& Studna, 1972) shows that the transition from X_4 to X_1 is located at ~ 4.3 eV. There is an energy difference of ~ 0.3 eV between the Raman shift and the ε_2 spectrum. In the case of the Raman spectrum the conduction band minimum is located along the Δ line near the X point. Thus, the vertical transition on the Δ line may be lower than that on the X point by ~ 0.3 eV.

It is interesting that the X_1 band is not found in the ε_2 spectrum. Furthermore, the X_4 band in the Raman spectrum becomes weak as the resonant Raman process tends towards the normal Raman process. This X_4 band finally disappears in normal Raman scattering (Shin *et al.*, 1996). Thus, these facts suggest that the normal Raman and the ε_2 spectra in Si have a different selection rule.

On the other hand, the VUV ε_2 and the soft X-ray Raman spectra are very similar in cBN. Figs. 5(a) and 5(b) show a comparison between the ε_2 spectrum (Yokohama *et al.*, 1989) and the Raman spectrum excited at the conduction band threshold. The abscissa of the Raman spectrum represents the Raman shift. The strongest structure is located at ~ 11.5 eV and is assigned to be X_5 (Agui *et al.*, 1997). The structures at ~ 9 and 16 eV that are assigned in SXES are also seen in the ε_2 spectrum. Thus, Si and cBN show a remarkable contrast in the comparisons between the Raman and the ε_2 spectra.

Here, one should remember that the selection rule between the normal Raman and the absorption spectrum has been

studied for a long time by ordinary laser Raman scattering in the visible-light region. The centrosymmetry of the crystal provides important and basic information on the selection rule (Shin, Tezuka, Sugawara & Ishigame, 1991). In the case of centrosymmetric crystals the dipole mode is the ungerade mode and the Raman mode is the gerade mode. The dipole and Raman modes are complementary to each other, as shown by Fig. 6(a). In the case of non-centrosymmetric crystals, some modes are allowed for both measurements, as shown by Fig. 6(b). The crystal structure of Si belongs to O_h^7 that has the centrosymmetry. On the other hand, the crystal structure of cBN has T_d^2 symmetry that has no centrosymmetry, though the B and N ions of cBN have the same atomic configurations as that of Si.

In fact, the transition from the X_1 valence band to the X_1 conduction band in Si is a totally symmetric transition, so that the X_1 band is Raman active. On the other hand, the transition from the X_4 valence band to the X_1 conduction band is dipole-allowed but is not Raman active. Thus, it is within reason that the X_4 band is very weak in the normal Raman scattering process. Here, there is a problem that the X_4 band is observed in the resonant Raman process, though it disappears in normal Raman scattering. It is well known that the Raman selection rule often breaks down in the resonant Raman process, because the symmetry of the intermediate state as well as the symmetries of the initial and final states contribute to resonant Raman scattering.

Group theory indicates that the X_4 point in the Brillouin zone of the sp^3 bands in the diamond-type crystal structure has p symmetry and the X_1 points have sp symmetry of the atomic orbitals. When the L_3 core exciton in Si is made, the excited electron in the conduction band has s symmetry, because the core hole has p symmetry. Thus, only the

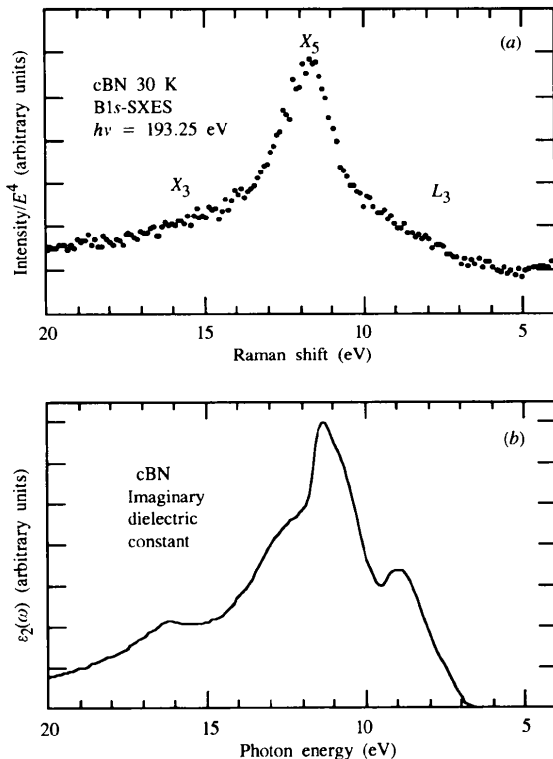


Figure 5
(a), (b) A comparison between the soft X-ray Raman and the VUV absorption (Yokohama *et al.*, 1989) spectra of cBN. The ordinate is the SXES intensity divided by the fourth power of the photon energy.

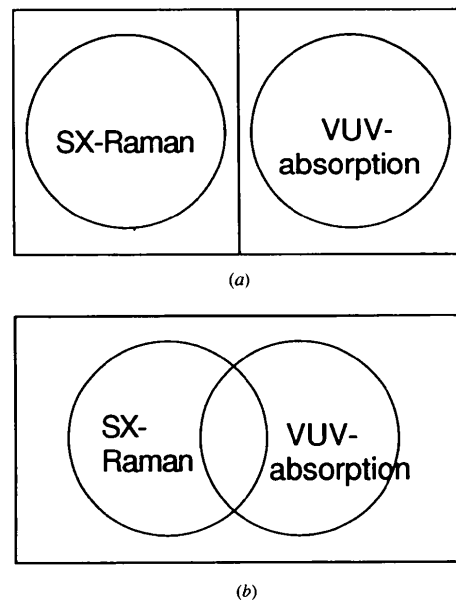


Figure 6
Schematic diagram of the selection rule between the soft X-ray Raman and the dipole transition for (a) centrosymmetric and (b) non-centrosymmetric materials.

valence electron that has s symmetry in the X_1 point goes to the core hole. In this scheme, the transition from X_4 to the core hole is forbidden, because the X_4 point has p symmetry. Thus, the parity must change in the intermediate state only when it is at the resonant state. As discussed in the relaxation process of Fig. 3, the valence electron and lattice relaxation processes can be considered for the SXES process. If there is a valence electron relaxation, there is a large energy shift corresponding to a band-gap energy of ~ 1.1 eV. However, such an energy shift is not observed in the X_4 band. Thus, it is within reason that the lattice relaxation must play an important role in the excited state. Because the phonon relaxation that emits an ungerade phonon can change the parity, an X_4 point might have some intensity at the resonance state through the change of the symmetry by the lattice relaxation process in the intermediate state. It is enough to consider only the symmetries of the initial and final states in the case of the normal Raman process, so that the X_4 band is forbidden in this case.

4. Conclusions

The background intensity in the lower energy tail of the SXES spectrum has been estimated in Si and cBN. The background of B1s-SXES of cBN is very small. The Si2p-SXES of Si is strong but decreases drastically as the SXES process moves from the fluorescence to the Raman processes. The relaxation process is considered to be valence electron excitation to the conduction band. The centrosymmetry is important in the selection rule for soft X-ray Raman and ϵ_2 spectra. The selection rule is complementary for the centrosymmetric material, Si, while both spectra are similar for the non-centrosymmetric material, cBN. At the resonant state an ungerade phonon plays an important role since it changes the parity symmetry in the intermediate state.

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