4. Electronic Structure of Condensed Matters

4-1. Polarization Dependence of Soft-X-Ray Raman Scattering; New Experimental Method to Determine the Symmetry of Electronic Structures

Very recently, soft X-ray Raman scattering (SXRS) experiments have been carried out in highly brilliant synchrotron light sources of the world. This is because it gives important information on the interaction of matter and light [1]. SXRS is known to be a bulk-sensitive and site-selective experimental method for analyzing the electronic states compared to photoelectron spectroscopy. Further, the polarization dependence of SXRS will give new information on the symmetry of the electronic states, because SXRS is a second-order optical process that belongs to the Kramers-Heisenberg formula. We can obtain direct information of the wave function in the ground state.
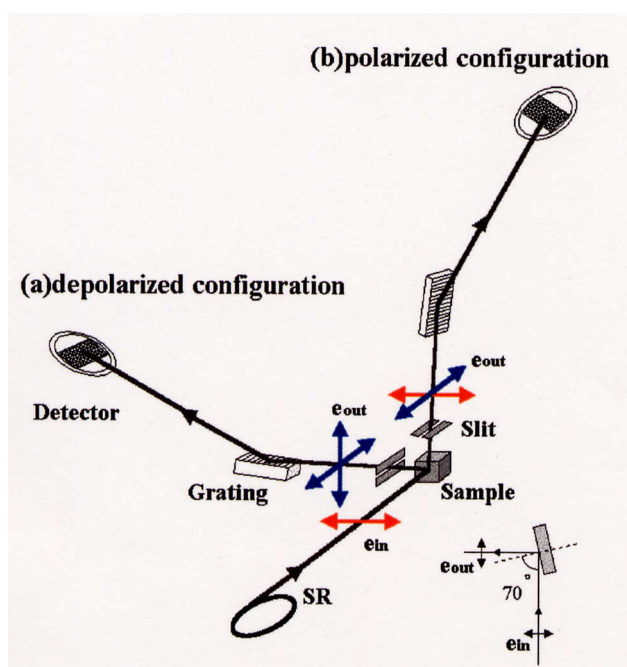
Figure 1 shows how to realize polarization dependence using a soft X-ray source with linear polarization [2] in BL-2C. SXRS is measured in 'depolarized' and 'polarized' configurations. When SXRS is measured in the depolarized configuration, as shown in Fig. 1(a), the polarization vector of the emitted photon rotates by 90° from that of the incident photon. On the other hand, when SXRS is measured in the polarized configuration, as shown in Fig. 1(b), the emitted photon contains the same polarization vector as that of the incident photon.

We carried out SXRS experiments on transition-metal compounds, rare-earth compounds, semiconductors, and ionic compounds. We have studied in what condition we can find the polarization dependence on SXRS.

As an example, Fig. 2 shows the polarization dependence of the Raman scattering of TiO_2 (rutile)

Figure 1.
Experimental setup for the polarization dependence of soft X-ray Raman scattering.
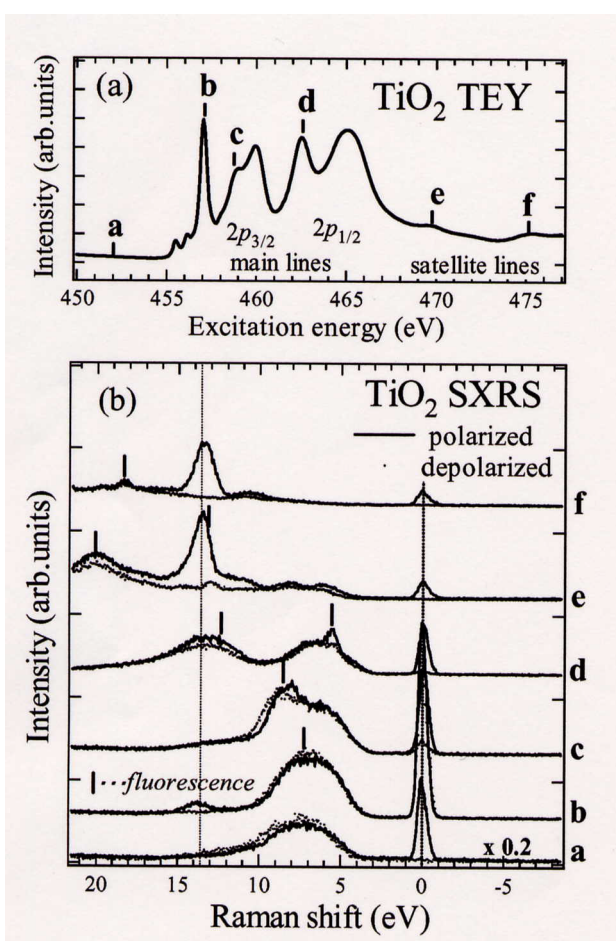

Figure 2.
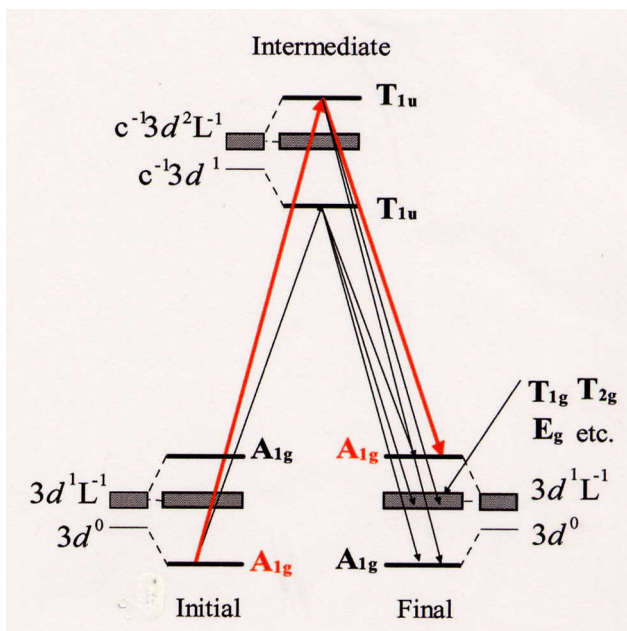Polarization dependence of the soft X-ray Raman scattering of TiO_2.

Figure 3.

Schematic energy-level diagram and soft X-ray Raman scattering process (arrows) in TiO_2. c^{-1} and L^{-1} represent a core hole and a ligand hole.

[3]. One can find a strong polarization dependence at a 14-eV Raman shift, as shown by the red curve. Figure 3 shows a schematic diagram of the electronic states of TiO_2 based on a localized electron picture. It is shown that the initial and final states are the bonding and antibonding states between the $3d^0$ and $3d^1L^{-1}$ configurations, where $3d^1L^{-1}$ represents a Ti3d electron and a ligand hole. The polarization dependence of the SXRS spectra can be well elucidated by using Kramers-Heisenberg formula, as shown by the arrows in Fig. 3. We find that the existence of the A_{1g} mode in solids is important for the polarization dependence in SXRS. In this study, it is shown that the electronic structures of TiO_2 cannot be elucidated by the band calculation because the 14-eV Raman band energy is too large, but can be well elucidated by the localized electron model. Although TiO_2 (rutile) has no 3d electron, it is found that the electron correlation effect plays an essential role in the electronic states. The polarization dependence of SXRS is very useful for knowing the electronic structure of materials.

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4-2. Evidence for the Existence of a Nitrogen-Substituted Graphite Structure by the Polarization Dependence of NEXAFS

Recently, carbon nitride (CN_x) has attracted much attention because of its characteristic properties; for example, a theoretical prediction that the β-C_3N_4 phase would be as hard as diamond has been reported by Cohen et al. [1] Beside this material, many kinds of crystal phases have also been proposed [2]. Graphite-like CN_x, one of the hypothetical materials, is interesting as an electronic material due to its promising semiconducting property. However, despite considerable efforts to synthesize CN_x materials, there are only a few reports concerning direct observations of graphite-like CN_x, because most of the synthesized CN_x films are amorphous, having variety of possible local structures and long-range order is lacking. In order to clarify the local structures, we measured the NEXAFS spectra of CN_x films synthesized by ion implantation.

The experiments were performed at the BL-11A station. CN_x thin films were synthesized in situ by nitrogen-ion implantation in highly oriented pyrolitic graphite (HOPG) to avoid the effect of contamination. Ion implantation was performed at room temperature and at 3.0 keV energy. The ion fluence was 1.7×10^{15} ions/cm^2. After the procedure, thin films were annealed for 3 min. The polarization dependence of NEXAFS spectra was observed for samples with different annealing temperatures (T= 840 and 1100°C).

Figure 4 shows the N 1s NEXAFS spectra of CN_x film. In this figure, the solid and broken curves show the results at grazing incidence ($\theta = 10°$) and at normal incidence ($\theta = 90°$), respectively. Three discrete π^* resonances (a, b, and c) were observed at energies of 398.3, 399.5, and 400.7 eV, respectively. For peaks a and c, the π^* resonances are enhanced at grazing incidence and suppressed at normal incidence. This polarization dependence is similar to that of the π^* resonance in the C 1s
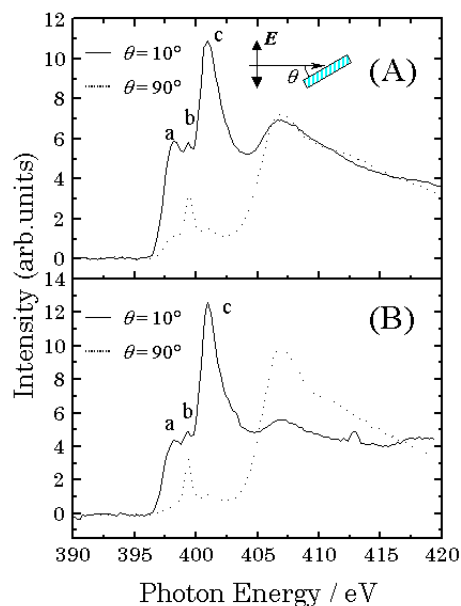

Figure 4.
N 1s NEXAFS spectra of CN_x films annealed at (A) 840°C and (B) 1100°C. The solid and dotted lines indicate the spectra for grazing ($\theta = 10°$) and normal ($\theta = 90°$) incidence, respectively.

NEXAFS spectra of HOPG [3]. Furthermore, a close inspection shows that the intensity of peak c is especially enhanced as the annealing temperature increases. On the other hand, peak b shows an opposite polarization dependence to that of the other peaks. These results indicate that all of the peaks originated from different local structures.

Considering the coordination number of carbon atoms, three kinds of local structures at the nitrogen site can be candidates for the origins of the π^* resonances. Namely, for the cases of one, two, and three carbon coordination, we can image a cyanic structure, a pyridine-like structure, and a graphite-like structure, respectively. Among them, the pyridine-like and graphite-like structures can have a graphitic orientation. Since the cyanic group is bonded with the graphite plane by a single C-C bond, this structure is expected to have an orientation which is nearly upright to the graphite plane. Also, as mentioned above, peak c is especially enhanced by annealing. We consider that this is caused by a
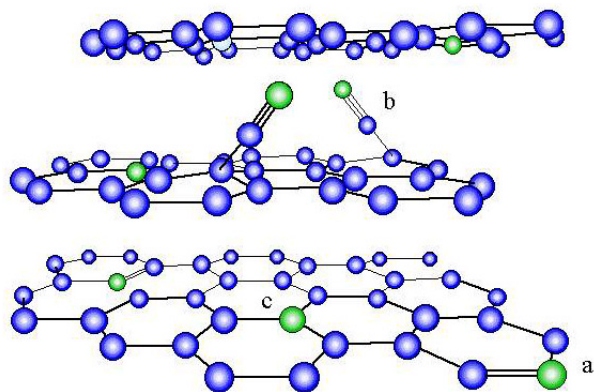
structural change of the graphite crystal. If a graphite crystal damaged by ion implantation is recovered by annealing, pyridine-like structures should change to graphite-like structures. This means that the graphite-like structures should increase by the annealing procedure. Therefore, we have concluded that peaks a, b, and c can be assigned to pyridine-like, cyanic, and graphite-like structure, respectively [4, 5].

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