

Chemical State Mapping of Amorphous Carbon Films by Soft X-ray Emission Spectroscopy

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Soft X-ray emissions, which originate from electronic transitions from valence bands (bonding electron states) to inner-shell electron levels, inform us energy states of bonding electrons if those energies are analyzed with an energy resolution better than 1 eV. Thus, soft-X-ray emission spectroscopy (SXES) based on electron microscopy should be a hopeful method to evaluate bonding states of identified small specimen areas. SXES can apply to metal, semiconductor and insulator materials under a conventional vacuum condition of electron microscopes. One drawback is its low detection efficiency. Then, a commercial SXES spectrometer, which was composed of varied line spacing (aberration corrected) gratings and an area detector, was designed as an attachment for EPMA/SEM [1], which can use a larger probe current than that of TEM. As EPMA/SEM are operated at a lower accelerating voltage than that of TEM, bonding states of irradiation sensitive materials can be investigated. Here, SXES imaging of chemical state mapping of carbon atoms of amorphous carbon nitride (a-CN_x) films and diamond like carbon (DLC) films are presented [2,5].

a-CN_x films show a controllability of photoconductivity and UV luminescence by a change of the content of nitrogen x [3,4]. First, high energy-resolution EELS was applied at 80 kV. It was notice a change of valence electron excitation spectra due to irradiation damage. Then, EPMA-SXES was applied at 5 kV. At the voltage, any change of carbon K-emission spectrum intensity was not detected. Figure 1(a) shows a carbon K-emission spectrum of a-CN_x (2nd order), which shows two peak structure [2]. 3rd order N K-emission intensity is also seen. Peak energies of A and B are the same with those of graphite (sp²-σ bonding) and diamond (sp³-σ bonding). a-CN_x film with a smaller x showed a smaller B intensity. Thus, inclusion of N induces a presence of sp³-bonding. This is also linked with an increase of macroscopic electrical resistivity of those films. Figure 1(b) and (c) show intensity distribution of energy windows of I_A and I_B, indicated in Fig.1(a). Pixel size is 1.2 μm². The intensity variation in left and right figures correspond to variations of sp²-C and sp³-C bonding signals, respectively. Thus, a brighter pixel area in the right figure includes a larger amount of sp³-bonding. This experimental result shows that the high energy-resolution soft X-ray mapping with an appropriate energy window can show not only elemental distribution but also chemical bonding state distribution of bulk materials [2].

Figure 2(a) shows 2nd order C K-emission spectrum of a DLC film formed on Si wafer. From XPS analysis of C-1s energy level, this film was assigned to have a ratio of sp³-C/sp²-C=2.42. C K-emission spectra of graphite and diamond are also shown for comparison. As the DLC film composed of sp³-C and sp²-C, the peak energy of C-K emission of this DLC film is placed between those of graphite (sp²-C) and diamond (sp³-C). When setting energy windows of 139-141 eV for sp³-C and 130-143 eV for all C-K intensity and calculate a ratio of I(139-141eV)/I(130-143eV), a distribution image of sp³-C is obtained as shown in Fig.2(b). The ratio variates ±6% within the imaged area. This map shows an amount of sp³-C bond variate in a few μm scale [5].

References:

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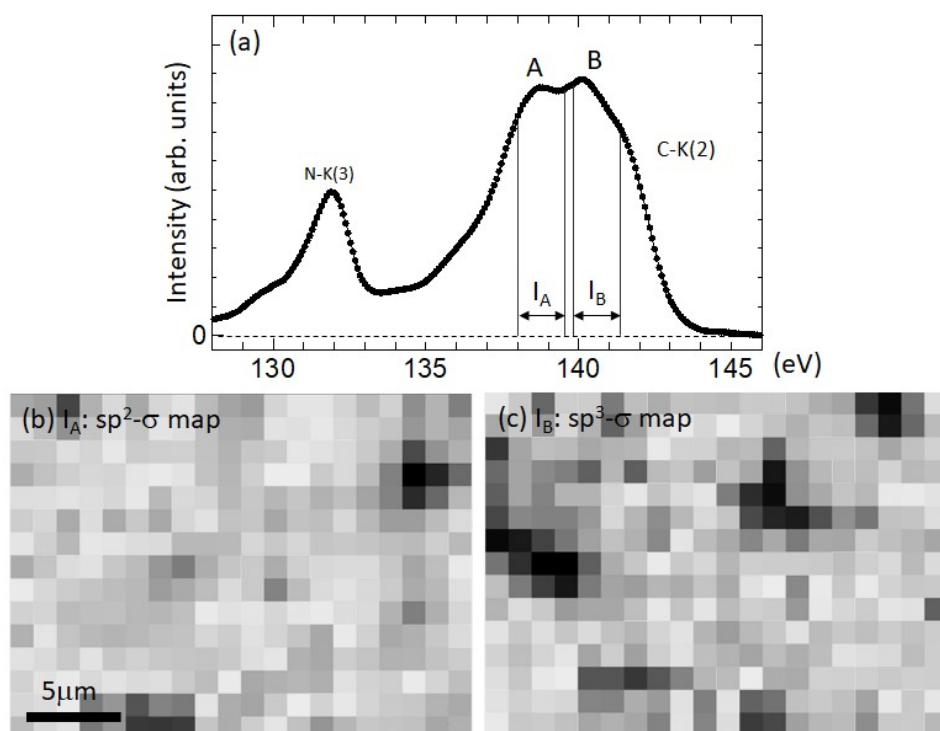


Figure 1. (a) 2nd order C K-emission spectrum of a-CNx, (b) and (c) respectively show intensity distributions of I_A (sp^2 - σ bonding) and I_B (sp^3 - σ bonding) indicated in (a).

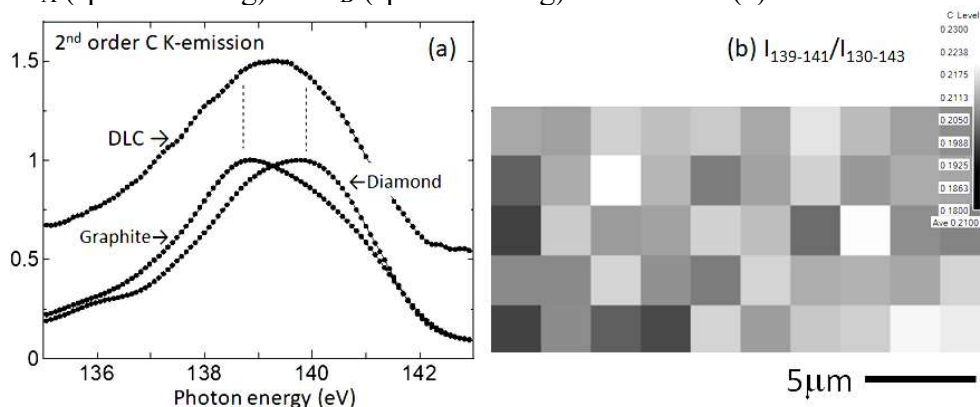


Figure 2. (a) 2nd order C K-emission spectra of a DLC film, graphite and diamond, (b) spatial variation of a ratio $I(139-141)/I(130-143)$.