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Visualization of boron distributions on inorganic and organic material surfaces by PEEM

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Visualization of microscopic elemental distributions for a small amount of ingredients in inorganic and organic materials has an essential role in developing new functional features for them, especially where their distributions are inhomogeneous. Electron probe micro analyzer (EPMA) has been widely used in visualization of microscopic elemental distributions on various material surfaces as one of the most popular techniques, by means of combination of a scanning electron microscope and an X-ray fluorescence analyzer [1]. X-ray fluorescence is produced via relaxation of core-holes excited, in this case, by an electron beam, which is therefore element specific in nature. For light elements such as boron (B), however, Auger transition rates are more than 99.9% in their core-hole relaxation processes, which means that detection of trace light elements by X-ray fluorescence has difficulty. In contrast, X-ray absorption spectroscopy (XAS) with total electron yield (TEY) is suitable to detect trace light elements because TEY is proportional to the amount of secondary electrons generated mainly by Auger electrons [2]. The intensity of photoemission electron microscope (PEEM) is also proportional to the TEY intensity when it is used with X-ray as a light source and without both an energy filter and an energy analyzer [3]. One can obtain a local XAS spectrum by plotting intensities in a certain area on a series of PEEM images as a function of X-ray energies. In addition, an elemental distribution image can be obtained as a difference image of two PEEM images measured at X-ray energies of (1) a pre-edge and (2) a peak position above a certain absorption edge.

In this study, we have performed PEEM and TEY measurements at BL5 in HiSOR for inorganic and organic samples in order to investigate microscopic chemical states of trace B atoms in them from fine structures in local- and wide-area-XAS spectra near B *K*-edge and to visualize B distributions on their surfaces. The experimental station of BL5 is equipped with a PEEM III (Elmitec GmbH) and with a manipulator connected to a digital amperemeter for a TEY measurement. As a light source, the second-order X-rays from the monochromator were used because they have higher intensity and energy resolution around B *K*-edge than the first-order X-ray from the monochromator with the same entrance and exit slit widths. All the measurements were performed at room temperature.

As an inorganic sample, we have used a B-doped carbon nano wall (CNW) film on a Si substrate which are newly grown by using a plasma CVD method with a mixture of carbon and B_4C powders. For an estimation of the B concentration of the sample, we have performed photoemission spectroscopy (PES) measurements of C 1s and B 1s core-levels with an angle-resolved PES (ARPES) apparatus at BL5 (the ARPES and the PEEM III chambers have been installed tandemly in the experimetal station). The X-ray energy was set to 634 eV for C 1s and 534 eV for B 1s, respectively, as intending that the kinetic energies of both signals have the same values (about 340 eV) and therefore the probing depth of the photoelectrons the same values (about 0.8 nm [4]). The B concentration was estimated by using the integrated intensities of the core-level spectra (not shown) as about 4 %.

Figure 1 (a) shows that a PEEM image of a B-doped CNW film surface on a Si substrate measured with Hg lamp, showing 2 dimensional local work function distribution for it. The field of view is 150 μm. The PEEM image has flat area and small protrusions. Figure 1 (b) shows plots of averaged intensities per a pixel in squares A (red, protrusion area) and B (green, in flat area) as a function of X-ray energy around B K-edge,

where both squares have a side length of about 21.5 μm. The red and green curves in figure 1 (b) show noisy jagged shapes, probably due to the effect of repeated charging and discharging caused by the (weak) insulating nature of the film (a strong insulating nature will produce just a strong charging effect). Despite of the noisy jagged shapes, strikingly, the blue curve in figure 1 (c) obtained after division of the red one by the green one in figure 1 (b) shows a clear near edge structure which closely resembles the XAS spectrum reported for B_4C bulk [5], revealing existence of B_4C-rich regions on a B-doped CNW film surface. In contrast, XAS spectrum measured by TEY (black curve in figure 1 (c)) has a different spectral shape from the local XAS spectrum for the protrusions and is similar with ones for B-rich boron carbide thin films and B crystalline powders [5], where the TEY-XAS spectrum provides an averaged information of the sample surface from a wide area illuminated by X-ray (the size of X-ray is about 1 x 5 mm^2 on the sample surface). Figure 1 (d) shows a difference image of PEEM images measured with X-rays of 188 and 191 eV. We consider that the bright areas indicate B_4C-rich regions, which seem to roughly correspond to protrusions.

As an organic sample, we are proceeding measurements for a micro-droplet of solidified L-boronophenylalanine (BPA) on a Si substrate which is one of boron delivery drugs developed to use for boron neutron capture therapy (BNCT, a type of radiation therapy for cancer treatment [6]). In addition, we are addressing visualization of boron distribution in cancer cells dosed with BPA in order to obtain useful information for development of a new boron delivery agent which possesses advantages over BPA.

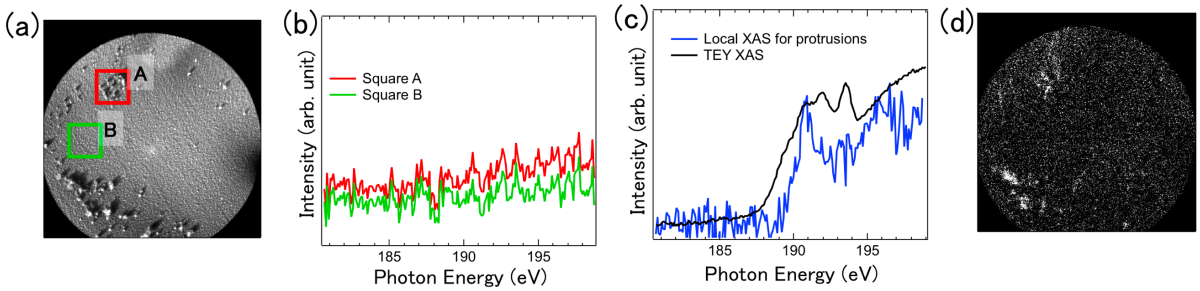

FIGURE 1. (a) PEEM image of a B-doped CNW film surface on a Si substrate measured with Hg lamp. The field of view is 150 μm. (b) Plots of averaged intensities per a pixel in squares A (red, protrusion area) and B (green, in flat area) in (a) as a function of X-ray energy around B *K*-edge, where both squares have a side length of about 21.5 μm. (c) Local XAS spectrum (blue) for the protrusions obtained after division of the red one by the green one in (b) and XAS spectrum (black) measured by TEY where the size of X-ray is about 1 x 5 mm^2 on the sample surface. (d) Difference image of PEEM images measured with X-rays of 188 and 191 eV.

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