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Total electronic structure analysis by EELS & SXES based on transmission electron microscopy

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Hihg energy-resolution spectroscopy methods basd on transmission electron microscopy is imperative for characterizing new functional materials with nm-scale spatial resolution. A high energy-resolution electron energy-loss spectroscopy (EELS) gives us information of the dielectric properties and the partial density of states (DOS) of the conduction band (unoccupied states). Together with the DOS of the conduction band, the DOS of the valence band (occupied states by boding electrons) is necessary to understand the whole electronic structure of a material. The information is included in the joint DOS of the conduction and valence bands, which can be derived from a valence-loss spectrum by using the Kramers-Kronig analysis. However, it is usually difficult to deduce the valence DOS from the joint DOS. Photoelectron spectroscopy gives us the total DOS of the valence band of a material. However, the method is difficult to be combined with a conventional transmission electron microscope (TEM). Soft-X-ray emission spectroscopy (SXES) gives information of the partial DOS of the valence band. This method can be combined with a conventional TEM, because soft-X-ray emission can be induced by electron beam illumination. An energy resolution better than 1 eV may be necessary for obtaining fine structures of the DOS of the valence band, because the energy spread of the valence band is usually from 5 eV to 10 eV.

A development of a SXES instrument attached to a TEM of JEM2000FX presented us that a DOS of the valence band can be obtained from a specified small specimen area [1,2]. The spectrometer has commercialized recently for a conventional analytical TEM [3]. It is composed of laminar-type varied-line-spaced (VLS) gratings, a back-illumination & non-coated type CCD detector and X-ray collection mirrors. The measurable energy is from 60 eV to 1200 eV (basic version). Figure 1 shows an Al L-emission (valence bands→$L_{2,3}$-shell, 72 eV) spectrum. Obtained by a spectrometer attached to a TEM of JEM2200FS. An energy resolution of 0.2 eV was obtained at the Fermi edge of the spectrum.

For applications to materials science, it is important to extend the measurable energy range to higher energy region. As a first step, a new VLS grating has designed and manufactured for the spectrometer. It can measure up to 2.4 keV. The first-type has designed as an Au-coated replicated-type VLS grating. This type of grating is suitable for mass-production. The character of the grating is a wide working energy region from 500eV to 2400eV but a low diffraction efficiency of less than 1%. Thus, a multi-layer-coated VLS grating (Mo/C), which has a character of a high reflection efficiency of about 10 % with a narrow effective energy region of about 50 eV, has designed as a second one. Figure 2 shows Pt M-emission spectrum showing two peaks of Mα(2050eV) and Mβ(2127eV) obtaied by a spectrometer attache to a TEM of JEM2010 [4]. A FWHM value of the Mα peak was 13 eV.

Figure 3 shows a combination of B K-excitation (EELS) and B K-emission (XES) of h-BN with an arbitral relative intensity. Two spectra are placed according to the experimentally determined energy. Calculated energy band diagrams are also shown. It should be noted that an additional separation of about 2 eV between the valence band and the conduction band is introduced by a comparison of the calculated band diagram and the spectra. This indicates that the calculation, a local density approximation, evaluated the bandgap energy of h-BN smaller than that of real material by an amount of 2 eV. The imaginary part of the dielectric function ε_2 derived from a valence electron excitation spectrum by using Kramers-Krong analysis is shown as an inset. From a comparison with the EELS/XES spectrum and the ε_2, the peak A was assigned to $\pi\rightarrow\pi^*$ transitions around M, L, K and H points at Brillourin zone boundary. The shoulder structure B was assigned to $\pi\rightarrow\pi^*$ transitions around M point. The peak C was assigned to $\sigma\rightarrow\sigma^*$ transitions around Γ and L points [5].

References

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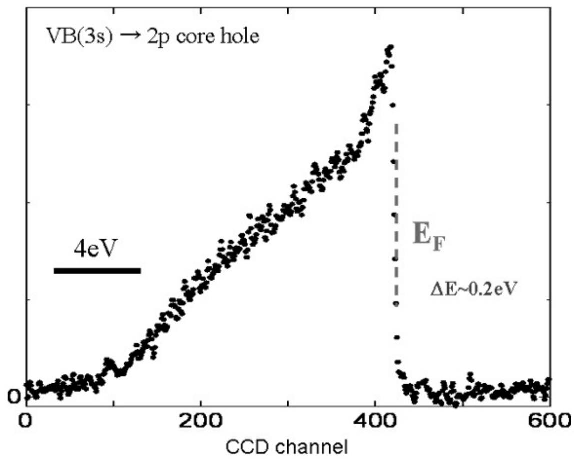

Fig.1 Al L-emission spectrum. The Fermi edge shows an energy resolution of 0.2 eV.

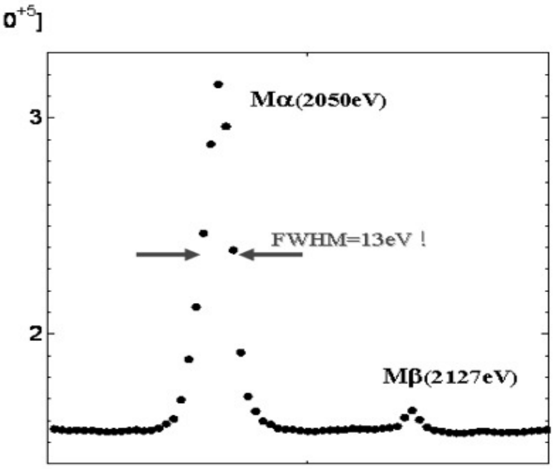

Fig.2 Pt M-emission spectrum. The FWHM value of Mα is 13 eV.

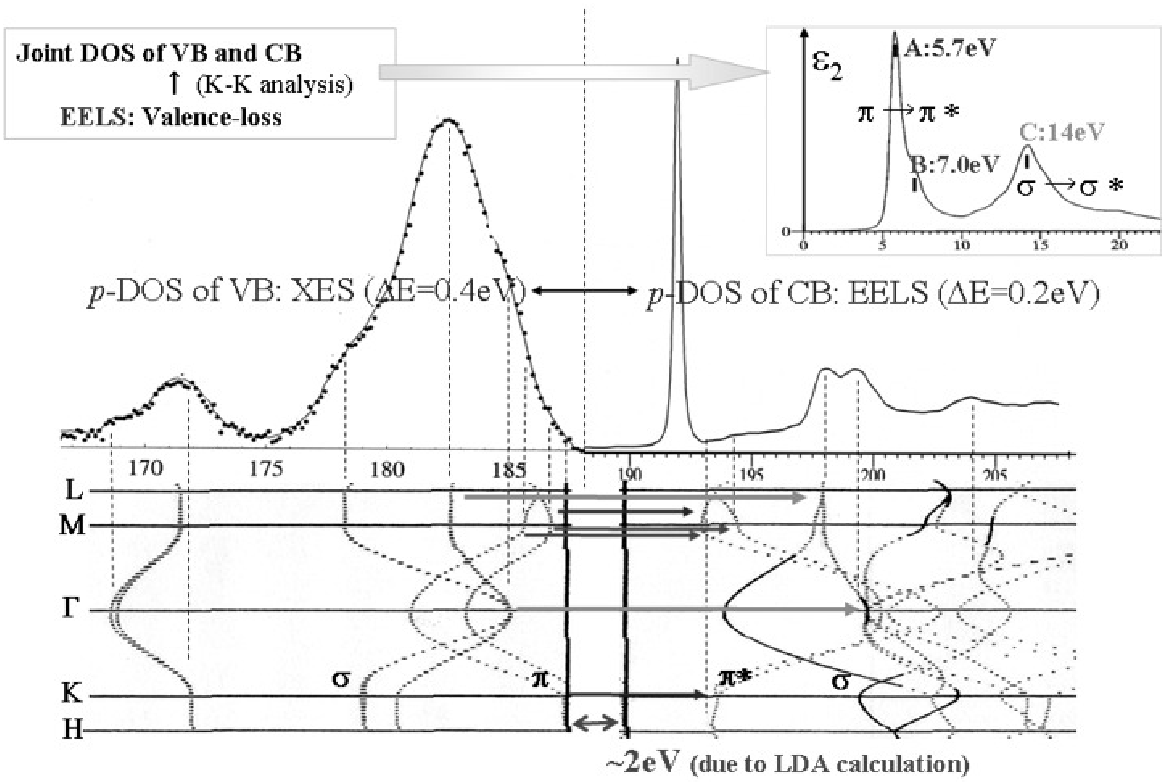

Fig.3 EELS&XES spectra of h-BNcompared with a theoretical band calculation.