

Present State of TEM-SXES Analysis and its Application to SEM aiming Chemical Analysis of Bulk Materials

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X-ray emission spectroscopy is widely used as a practical tool for compositional analysis of local specimen area and elemental mapping analysis in electron microscopes. X-rays with energy more than a few keV are dominantly due to electronic transitions between inner-shell electron levels. Those characteristic X-ray energies are useful for assignment of elements. On the other hand, X-rays originate from electronic transitions from valence bands (VB, bonding electron states) to inner-shell electron levels inform us energy states of bonding electrons. The energy of this latter X-ray ranges in ultrasoft or soft X-ray region from about 0.01 to a few keV. Since K-emissions of light elements and L-emissions of 3d transition elements are in this energy region, soft X-ray emission spectroscopy (SXES) based on electron microscopy (EM) can be a sensitive tool for elemental and chemical identifications. Thus, various applications are expected through this approach. We have developed and tested the SXES instruments by attaching to TEM, EPMA, and SEM. The spectrometers have an energy range of 50-4000eV by using four varied-line-spacing (aberration corrected) gratings [1,2,3]. This SXES spectrometer informs us energy states of VB from specified specimen areas in electron microscopy, which is hardly obtained by EELS and EDS.

Applications of TEM-SXES instrument to carbon and boron materials have revealed characteristic energy distribution of bonding electrons [4]. Figure 1 shows carbon K-emission (V.B.→K-shell) spectra of monomer-C₆₀ crystal and two types of polymerized-C₆₀ (3-dimensional C₆₀, 3D-C₆₀) crystals, which were produced by a high-temperature and -pressure treatment of monomer-C₆₀. Each structure unit reported by X-ray structure analysis is shown as an inset. It can be seen that peak structures observed for π -bonding and the σ -bonding states in monomer-C₆₀ (bottom) become broad in polymerized-C₆₀ materials without an apparent change of those energy positions. Finally, not only those peak structures but also the characteristic dip structure between the π -bonding and the σ -bonding states in monomer-C₆₀ disappear in the most polymerized-C₆₀ crystal (top). Furthermore, the intensity maximum of the spectrum of the most polymerized-C₆₀ placed in the between those of graphite and diamond. Thus, this most polymerized-C₆₀ material loses a character of C₆₀-molecule and would be considered to be formed by sp² and sp³ bonding network. This TEM-SXES instrument was also applied to zeolite-templated-carbon, which was expected to have carbon network different from that of amorphous carbon. The carbon K-emission spectra showed that the material is formed by curved carbon network, sp², partly formed by sp³ bonding [5].

From the point of view of applying this SXES analysis for a wide variety of materials, examination of bulk specimens other than dedicated thin specimens for TEM is plausible. It can be realized by applying

the spectrometer to a conventional scanning electron microscope (SEM). Figure 2 shows Al L-emission (VB \rightarrow 2p) spectra of bulk specimens of intermetallic compounds of Al₂Au, and AlCo together with a spectrum of pure Al for comparison [6]. The Al L-emission intensity distribution represents partial density of states (DOS) of VB of Al with *s+d* symmetry due to the dipole selection rule. Emission intensities of Co M_{2,3}(3p)-M_{4,5}(3d) transitions in AlCo spectrum and Au N_{5,6}(4f)-O_{4,5}(5d) transitions in Al₂Au spectrum are also observed. It is clearly seen that intensity distributions of the compounds are different from that of aluminum. It should be due to different band structure originated from different crystal structures of Al (FCC), AlCo (CsCl-type), and Al₂Au (CaF₂-type). A peak at 72 eV of AlCo is due to a hybridization of Al-3d and Co-3d. The smooth tail of the bottom part of VB from 60 eV to 66 eV can be assigned to the DOS of a parabolic Al 3s-band around the Brillouin zone center. The energy region between the two structures indicated in the figure corresponds to energy region of hybridization of Al-3p and Co-3d orbitals. This explains why the region forms a shallow dip, because 3p component of VB cannot contribute to this spectrum due to the dipole selection rule. The spectrum of Al₂Au shows characteristic intensity profiles due to interaction between Al and Au-5d orbitals. The smooth intensity profile at the bottom of VB also was assigned to parabolic Al-3s band around the Brillouin center.

References:

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Figure 1. Carbon K-emission spectra of monomer-C₆₀ crystal and two types of polymerized-C₆₀ (3-dimensional C₆₀, 3D-C₆₀) crystals. Not only the peak structures in π - and σ -bands but also the characteristic dip structure between the π -bonding and the σ -bonding states in monomer-C₆₀ disappear in the most polymerized-C₆₀ crystal (top).

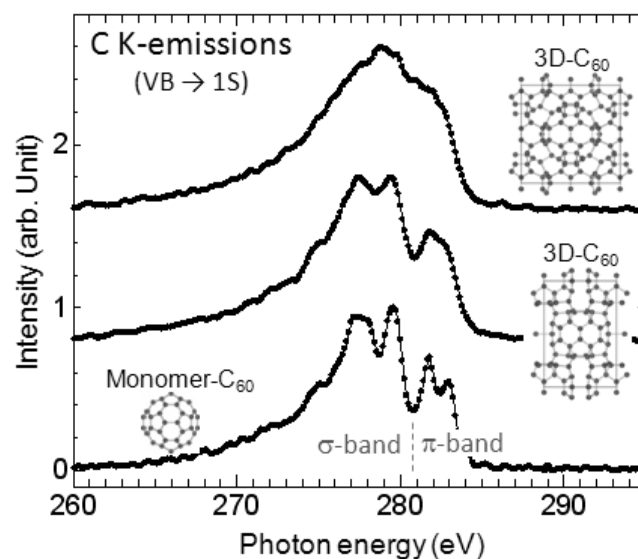
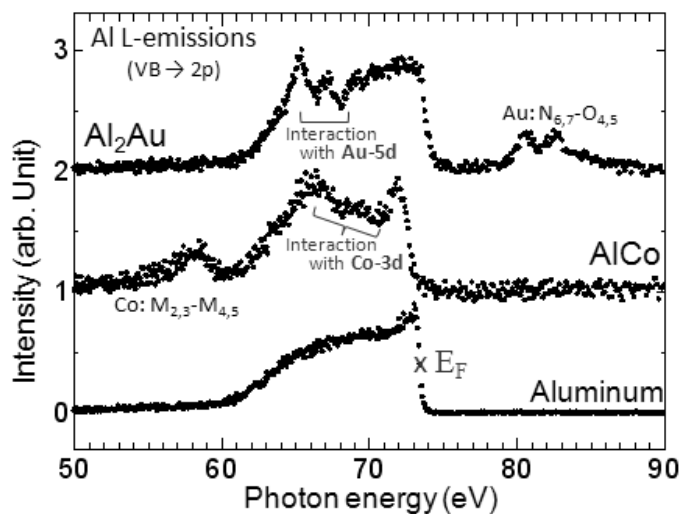


Figure 2. Al L-emission (V \rightarrow B_{2p}) spectra of bulk specimens of intermetallic compounds of Al₂Au, AlCo, and aluminum. Different intensity distributions of the materials should be due to different band structures originate from different crystal structures.