

Chemical Mapping by Energy-filtering Transmission Electron Microscopy

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We report a chemical map by using electrons with an energy-loss corresponding to a specific peak of near-edge fine structure by an energy-filtering transmission electron microscopy. The possibility of distinguishing elements in different chemical states is a prominent advantage of the chemical mapping compared to the ordinary elemental mapping.

Keywords : Energy-loss / EFTEM / ELNES / Elemental map / EELS

Electron energy-loss spectroscopy (EELS) is a powerful technique to analyze the elemental composition and electronic structure at local area of materials. In particular, the energy-loss near-edge structure (ELNES) appearing in a core-loss spectrum has useful information about the chemical bond around an excited atom. Such features in ELNES can be used for observation of energy-filtering image specific to a particular type of chemical bond, which is called chemical mapping.

There are two approaches to get a chemical map: one is done by combining the EELS with a scanning transmission electron microscopy (STEM). The other one is based on a recently developed energy-filtering transmission microscopy (EFTEM).[1] The first chemical map based on the EFTEM method has been reported by Krivanek who observed unstained polystyrene particles in a polyethylene matrix using the π^* -plasmon peak.[2] In the present work, we report the first map using core-loss intensity by the EFTEM method.

Energy-filtering images were observed by a high-voltage electron microscope (JEOL ARM-1000) equipped with an energy filter of Gatan (GIF) under the column of the microscope.[3] Specimen for observations was fine particles of lead chromium oxide (PbCrO_4) covered with a thin amorphous silicate (SiO_2). The size of fine particles were about 200nm and the thickness of amorphous SiO_2 film was about 10nm. Ordinary elemental map was observed using electrons lost energy corresponding to an O K-edge with an energy-selecting slit of 20eV width, which was set at $547 \pm 10 \text{eV}$.

For chemical mapping, the oxygen K-edge ELNES peak located at 529eV loss-energy, which is specific to the fine particles, was used. Because this peak was rather sharp, the width of energy-selecting slit was chosen to be 8eV. The magnification was 42,500 times on a slow-scan CCD camera with the pixel size of $24 \times 24 \text{mm}^2$.

In the elemental distribution image, the image of O is

STATES AND STRUCTURES —Crystal Information Analysis—

Scope of research

Structures of materials and their structural transition associated with chemical reactions are studied through the direct observation of atomic or molecular imaging by high resolution microscopy. It aims to explore new methods for imaging with high resolution and for obtaining more detailed chemical information. The following subjects are studied: direct structure analysis of ultrafine crystallites and ultrathin films, crystal growth and adsorption states of organic materials, and development on high resolution electron microscopy as well as electron energy-loss spectroscopy.



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contributed from both regions because oxygen atoms are contained in the PbCrO_4 particles and also the SiO_2 films. The aim of chemical mapping is to visually discriminate both materials in the oxygen map by means of the difference of oxygen K-edge ELNES. Fig.1 shows the ELNES spectra of oxygen K-edge taken from each region of the fine particles or the amorphous SiO_2 films. These spectra were measured by the image mode with an entrance aperture of 1mm, so that the diameter of selected area was 40nm. The ELNES features are different from each other, which indicates that the chemical bonding around oxygen atoms is different between PbCrO_4 particles and amorphous SiO_2 films.

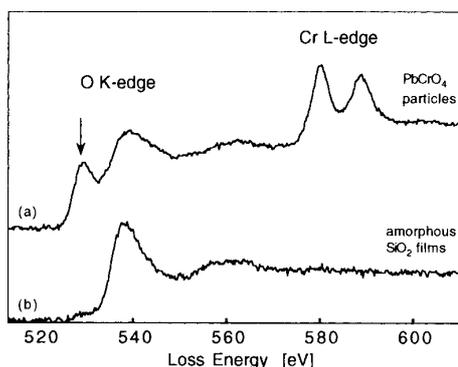


Figure 1 Energy-loss near-edge structure of oxygen K-edge measured from fine particles (a) and amorphous SiO_2 films (b).

The most prominent difference is the appearance of the first peak at 529eV (indicated by the arrow) in the spectrum of particles. This peak is characteristic to the chromium oxide ion, $(\text{CrO}_4)^{2-}$, in which a six-valence chromium ion (Cr^{6+}) is tetrahedrally surrounded by four oxygen atoms. According to the electronic structure of the $(\text{CrO}_4)^{2-}$ cluster, the LUMO is a bound antibonding state which consists of 3d orbital of the chromium ion and some amount of 2p orbital of oxygen atoms. Such mixing of 2p orbital of oxygen allows the transition from 1s core level to the LUMO. Therefore, the first peak at 529eV can be attributed to the transition to the LUMO. The second broad peak centered at 538eV is due to the transition to the unoccupied antibonding states formed by the chromium 4s and 4p orbitals and oxygen 2p orbitals.

In contrast to the above, the first peak at 529eV was not observed in the spectrum of SiO_2 films. The $(\text{SiO}_4)^4-$ cluster has the same tetrahedral symmetry as the $(\text{CrO}_4)^{2-}$ cluster. However, the energy gap between the HOMO and the LUMO of $(\text{SiO}_4)^4-$ cluster is about 10eV which is quite large compared to that of $(\text{CrO}_4)^{2-}$ cluster (3.3eV), so that the peak around 538eV in the spectrum of amorphous SiO_2 films is attributed to the transition to the LUMO.

The existence of the peak at 529eV clearly demonstrates the different properties of chemical bond around oxygen atoms in both materials; this peak relates to the existence of the Cr 3d orbital near the Fermi level. Such the difference can be used for the chemical mapping. Fig.2(a) shows the energy-filtering image formed by electrons with an energy-loss of

529 \pm 4eV. In this image only the PbCrO_4 particles are observed. Fig.2(b) shows the energy-filtering image formed by electrons with an energy-loss of 538 \pm 4eV, in which the particles and the amorphous SiO_2 films are both observed because of the equal contributions to this peak from both regions as shown in spectra of Fig.1.

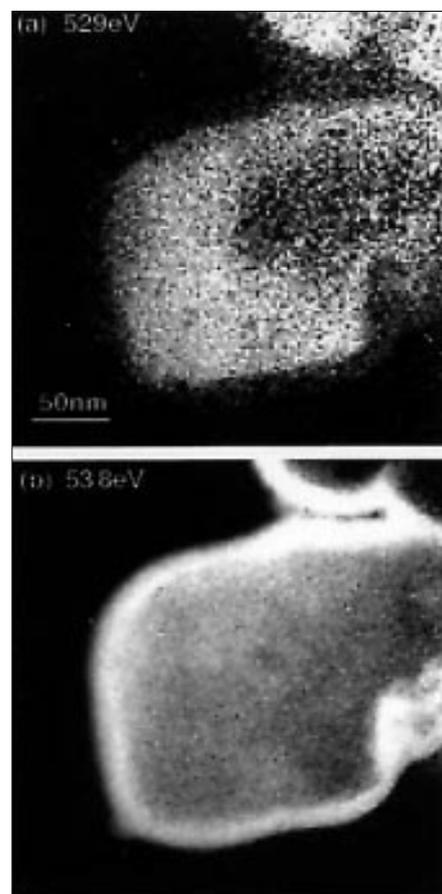


Figure 2 Chemical maps formed by electrons with the energy-loss of (a) 529 \pm 4eV and (b) 538 \pm 4eV.

The above results establish that the chemical mapping is useful to individualize the different chemical phase.[4] The present result proves that the chemical mapping at a resolution of several nanometer is available in practical way.

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