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A Novel Mapping Technique of Oxide Chemical States by Electron Probe Microanalysis

Hideyuki Takahashi and Toyohiko Okumura

Application and Research Center, Electron Optics Division, JEOL Ltd., 3-1-2, Musashino, Akishima, Tokyo, 196 Japan

The O-Kα emission spectra from different types of oxides observed in an electron probe microanalyzer (EPMA) are used for computerized digital mapping. This method enables the chemical state distributions to be mapped with micron resolution. The technique has been applied to copper oxides with different chemical states with considerable success.

***Key words*: electron probe microanalysis, digital mapping, chemical state, O-Kα emission spectra, copper oxides**

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The electron probe microanalyzer (EPMA) is an analytical instrument widely used for the chemical composition analysis of micron sized areas. In practice, quantitative analysis is quite often associated with the observation for the morphology of the sample surface under investigation by secondary electron (SE) imaging and backscattered electron (BE) image, which are also recognized as powerful tools for characterization by EPMA.[1–5]

Furthermore, the potential application of chemical-state analysis with EPMA has recently attracted much attention. This approach is based on the use of the spectral shape of the characteristic X-rays, which closely reflect, for example, crystallographic structures. Typical cases include: the K-emission spectra[6–10] for very light elements B, C, O, N and F; the satellite emission spectra[11] for Mg, Al, Si, P and S; the L-emission spectra[12–14] for transition elements; and the M-emission spectra[15] for rare earth elements.

With respect to the K-emission spectra of very light elements (e.g., O and F), Fialin and Remond[10] tried to elucidate the relationship between the X-ray intensity and the combination of ionic and covalent forces. Sakai et al.[9] also calculated the electron densities of states and energy levels in compounds by a discrete valencial Xα (DVXα) method. Their results allow the peak shapes derived from the calculation to be directly compared with the measured spectra; in the case of O-Kα, their calculation of a cluster of nearest neighbor atoms revealed that anion-anion hybridization plays an important role in the emission of spectral shapes. Discussion on this subject by Remond et al.[14] led to the conclusion that O-Kα is effected by the satellite complex and shake-off of double ionization.

In this paper, we tried to identify the shapes of O-Kα spectra, that reflect the different types of crystal structures in the sample under investigation,[16] by the ratio of the intensities at two specific wavelengths. This led to a novel approach for mapping the chemical state with spatial resolution of micron size.

EXPERIMENTAL

All the data were obtained with a JEOL EPMA JXA-8600 or JXA-8800. Thallium acid phthalate (TAP) was used as a dispersive crystal for the O-Kα emission spectra. TAP has been widely used for the detection of light elements because of its high sensitivity to the K-emission spectra of light elements O to Si with high-energy resolution.[6,14] All the X-ray spectra were digitally recorded by stepping the dispersive crystal. The X-ray map was also digitally recorded for each pixel.

For copper oxides, we tried to identify the O-Kα emission spectra from different stoichiometries by taking the ratio of the intensities at slightly different wavelengths. For analysis in this study, 500×400 pixel points were chosen with a pixel size of 1 μm, covering an area of $500 \times 400\ \mu m^2$. The mapping for the O-Kα X-rays in this case, therefore, was performed using the stage-scan mode. The accelerating voltage was set at 5 kV to minimize the spatial resolution of the X-ray analysis by ensuring a sufficient X-ray count rate.

CHEMICAL STATE MAPPING METHOD

In the usual area analysis in EPMA, the digital signals of X-ray intensity, secondary electrons and/or backscattered electrons are recorded at each pixel for mapping. The area for a map is divided into X-Y pixels by two-dimensional matrices and, at each pixel (position) in computer-controlled digital mapping, the X-ray, secondary and/or backscattered electron signals are recorded. Compared with analogue mapping, digital mapping is more convenient for searching the relationship between X-rays from several kinds of elements. For instance, the recent JXA-8800R allows us to check the selected point using a mouse and directly shows the corresponding X-ray intensities or concentration of certain areas of interest. From a chemical-state analysis point of view, the difference in the peak shape and peak shift have been widely used.

However, when one tries to extend this method to mapping, conventional chemical-state analysis requires each pixel to store hundreds of signal intensities at different wavelengths for identifying the chemical state from the full peak shape. This would be, as a matter of course, extremely time consuming. One of the methods routinely used is to represent the peak shape by superimposing the elementary spectra in order to reduce the number of data stored at each pixel. However, this is not useful for the chemical-state analysis of a complex specimen of practical interest, that includes several different phases, because decomposition of the peak shape to elementary spectra often turns out unsuccessful.

In this situation, therefore, we propose a novel practical mapping method based on the use of the ratio of X-ray intensities at two different wavelengths to represent the difference of the peak shapes. In this method, chemical-state analysis is initially performed to find the two most appropriate specific wavelengths, the intensity ratio of which represents the difference of the chemical states most efficiently. For instance, the wavelengths found for CuO and Cu_2O are, as seen in Fig. 1, 2.367 nm (I_B), corresponding to the major peak, and 2.358 nm (I_A), corresponding to the minor peak. Table 1 shows the ratio of the X-ray intensities at 2.367 and 2.358 nm. According to Remond et al.,[14] this minor peak has been attributed to the satellite line $K\alpha_{3,4}$.

After a preliminary investigation to choose the two intensities (I_A and I_B), the actual mapping is performed by taking two maps with the intensities I_A and I_B at the relevant wavelengths (λ_A and λ_B, respectively), followed by a final map with the ratio I_A/I_B. Since this method does not require each pixel to store the data of the full spectra of the peak shape under investigation, mapping can be performed much faster, and the chemical-state distribution visualized in different colors on a CRT. In the case of the copper oxides shown in Fig. 1, conventional chemical analysis requires 100 data points to describe the peak shape. This means that the present method enables chemical-state mapping to be performed in only 1/50 of the time needed for the conventional method. In practice, chemical-state mapping using the present method took 10 h and, therefore, 21 days (500 h) by the conventional method. From a practical point of view, it should also be noted that the ratio (I_A/I_B) is represented by taking the major peak intensity (I_A) as the numerator since the ratio is larger than unity. This makes it very easy to select the color level threshold in pseudo-color mapping.

RESULTS AND DISCUSSION

Hereafter, an application of the present approach for chemical-state mapping is presented. Figure 2(a) shows the secondary electron and backscattered electron images of a copper sheet whose surface was partially oxidized. In the backscattered electron image, the dark part represents the more oxidized regions. In the case of CuO, as seen in Fig. 1, the ratio of X-ray intensities between A and B is 1.00, and in the case of Cu_2O, the ratio is 2.93. Mapping with these two X-ray intensities was performed by setting the WD spectrometer at position A (2.358 nm) and then at position B (2.367 nm), and the images displayed in color on a CRT. The X-ray ratio at each pixel point was calculated and the ratio of the two intensities was also represented in color, as shown in Fig. 2(b). The green or yellow color levels are close to 1, corresponding to CuO, and red corresponds to Cu_2O. This mapping makes it possible to distinguish the different chemical states of oxygen, enabling the degree of oxidation to be represented by the variation in color from green to red.

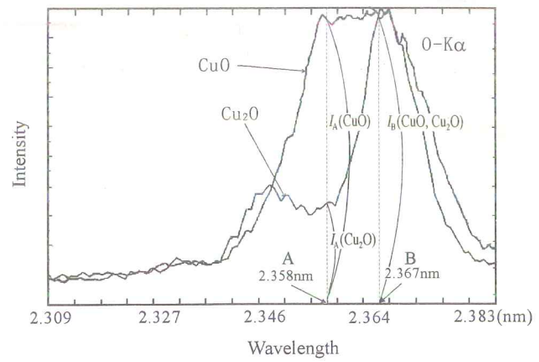

Fig. 1. The O-Kα emission spectra of CuO and Cu_2O. The dotted lines represent the specific wavelengths, 2.358 nm and 2.367 nm, to identify each spectrum.

Table 1. The ratio of X-ray intensity at 2.367 nm to 2.358 nm in the O-Kα spectra of Cu_2O and CuO.

Oxides	I_B (2.367 nm)/I_A (2.358 nm)
Cu_2O	2.93
CuO	1.00

CONCLUSIONS

This study has demonstrated a novel practical approach to chemical-state mapping, focusing on the identification of oxides of different phases. This approach enables the chemical-state mapping of oxides of different phases to be displayed in different colors on a CRT with considerable success. The results are summarized as follows:

1. O-Kα peak shapes obtained using a TAP crystal were identified by the intensity ratio of two specific wavelengths according to their crystal structures.
2. The ratio mapping of the X-ray intensities enabled the chemical-state distribution to be displayed as different colors on a CRT, leading to a more comprehensive understanding of the chemical state of the local area under observation.

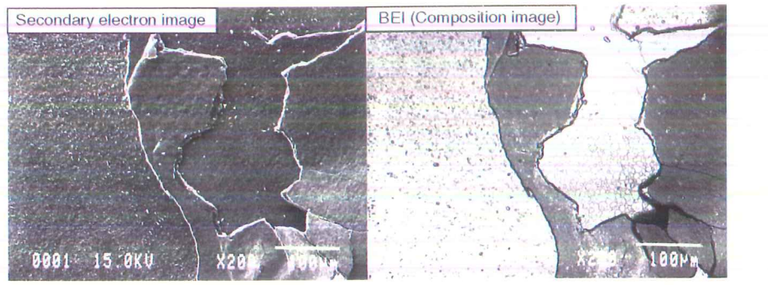

Fig. 2. Secondary electron and backscattered electron images (a), and chemical-state distribution of O-Kα obtained from the ratio mapping at two wavelengths (b) for an oxidized copper specimen.

This digital ratio mapping allows the assessment of the proportion of different phases by observing the areas corresponding to relevant chemical states, shedding further insight into the reaction procedures in specimen preparation.

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