Practical usefulness of SEM–EDX spectrum subtraction for material identification of individual submicrometer-sized particles on glass substrate

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This paper describes the practical usefulness of scanning electron microscope–energy dispersive X-ray spectroscopy spectrum subtraction for material identification of individual submicrometer-sized particles on glass substrate. Common peaks of glass elements in the spectra from the substrate only, and those from an individual particle on the substrate are used for the normalization of the spectra for subtraction. After demonstrating an experimental example of common dust particles (metals and oxides) on a glass substrate, Monte Carlo simulation was applied to investigate the details of electron scattering and X-ray generation behaviors in individual particles on the substrate. Although limitations on usage and geometrical effect are inevitable, the spectrum subtraction described herein is useful for quick identification of small particles on a glass substrate by reducing pronounced peaks and background from the substrate. Copyright © 2012 John Wiley & Sons, Ltd.

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Introduction

Scanning electron microscope–energy dispersive X-ray spectroscopy (SEM–EDX) is widely used as the first step to analyze a foreign particle in a device formed on glass substrates in liquid crystal display. In such failure analysis, material identification based on a simple quantitative analysis of a particle can provide useful information about a potential source of a foreign particle. Reducing background of glass substrates in the obtained spectrum of tiny particles would, therefore, facilitate identification, especially for elements of the same kind as those in the glass substrate.

There are several reports[1–3] concerning studies of single particles in which substrate effects were not included. Recent approaches to this problem employ Monte Carlo (MC) simulation,[4–11] This report uses NISTMonte MC simulation program[6] because it can model a variety of sample shapes with flexible conditions. Previous reports[2–5] investigated size dependence of X-ray emission from a micrometer-sized standard particle. Available sizes of standard samples such as K309 glass sphere,[3] or K411[4,5] seem to be a possible reason for this size range. Although submicrometer-sized particles were studied for environmental particles,[8–11] they were on a sampling filter of light elements, but not on a glass substrate.

Spectrum subtraction is a well-known technique in data processing, but, to the authors’ knowledge, there are no reports concerning electron probe analysis. It is immediately understood that a simple relation to original composition of a particle is not expected in the subtracted spectrum. Recent SEM/EDX, however, can obtain EDX spectrum from a particle even smaller than 0.1 μm. Therefore, if simpler interpretation of the spectrum becomes available, it would be worth investigating.

The authors studied EDX spectrum from submicrometer-sized particles on a glass substrate and confirmed that spectrum subtraction is useful to reduce a large background from a substrate to enhance material identification. MC simulation was also carried out to study size dependence and the effect of the substrate to learn the basis and limitations of this subtraction processing.

Experiment and spectrum subtraction

A glass slide (Toshinriko Co., Ltd, Japan) was used as a substrate for the experiments. EDX semi-quantitative analysis of this glass showed the composition of Na : Mg : Al : Si : Ca : K : O = 8, 2, 1, 27, 0.4, 2, 59 at.%. Calcined alumina abrasive powders were put on the glass slide, and residues after air blow were used as the sample particles. Edges of freshly broken Al plate were pressed against the glass substrate and the residues were observed. All the samples were coated with about 10 nm of carbon before SEM observation. SEM was conducted by Hitachi S-4700 (Hitachi Ltd, Tokyo, Japan) with an EDAX Phoenix EDS X-ray microanalysis system. The accelerating energy of an electron in all the measurements was 15 keV. The EDS measurement time was 100 s.

If the size of a particle on the substrate is small enough, an \( I_{\text{obs}} \) (E) spectrum obtained from the particle could be assumed as a superposition of the following individual spectra

\[
I(E)_{\text{obs}} = a \cdot I(E)_{\text{particle}} + b \cdot I(E)_{\text{substrate}}
\]

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where \( I(E)_{\text{particle}} \) and \( I(E)_{\text{substrate}} \) are a spectrum from a particle kept in a vacuum without a substrate and one from a substrate without a particle. The coefficients \( a \) and \( b \) are correction factors that include electron backscattering for the particle, absorption, and fluorescence in the particle and substrate. Precisely, these are functions of the energy, \( E \), and also depend on the shape of a particle. The approximation should be valid under very limited conditions. However, as information on elements, namely detection of X-ray peaks, is useful in the first step of material identification, subtraction between \( I(E)_{\text{obs}} \) and \( I(E)_{\text{substrate}} \) is performed per the following formula. Hereafter, \( I(E)_{\text{obs}} \) is assumed to include peaks of the glass substrate, as the particle is relatively small, so electrons penetrate into the substrate.

\[
I(E)_{\text{diff}} = I(E)_{\text{obs}} - k^2 I(E)_{\text{substrate}}
\]

where \( k \) is a constant given by the procedure described in the succeeding text. If this subtraction works well with an appropriate \( k \) value for the whole energy range, \( I(E)_{\text{diff}} \) should have reduced peaks for glass elements. To determine the \( k \) value in Eqn (2), peaks of a glass element (Ca–K, Si–K, or Mg–K) in both \( I(E)_{\text{obs}} \) and \( I(E)_{\text{substrate}} \) are used to normalize the glass element peaks in \( I(E)_{\text{substrate}} \). Hereafter, these glass peaks are referred as reference peaks. In the energy interval of the interest \([3.40, 4.00] \text{ keV}\) for Ca–K, \([1.60, 1.90] \text{ keV}\) for Si–K, and \([1.15, 1.40] \text{ keV}\) for Mg–K, the reference peaks in \( I(E)_{\text{obs}} \) and \( I(E)_{\text{substrate}} \) are assumed to have a linear background and Gaussian peak distribution \( A \exp \left[ -\frac{E-E_p}{\sigma} \right] + CE + D \), where \( A, B, C, \) and \( D \) are fitting parameters, and \( E_p \) is the energy of the reference peak. Fitting of the parameters was performed for one reference peak with nonlinear least-squares estimates in R language.\(^{12} \) The area of this Gaussian peak is given as \( S = \sqrt{\pi} A / \sqrt{B} \). After calculating the peak areas \( S_A \) in \( I(E)_{\text{obs}} \) and \( S_b \) in \( I(E)_{\text{substrate}} \), \( k \) value for Eqn (2) is given by the ratio \( S_A / S_b \).

Measured and subtraction-processed spectra for Al₂O₃ and Al are shown in Fig. 1. In the figures, \( I_{\text{obs}} \) is a spectrum obtained from an individual particle on a glass substrate, and \( I_{\text{sub}} \) is one from the substrate for which the measurement point is >100 \( \mu \text{m} \)-distant from the particle. \( I_{\text{diff_x}} \) is a subtracted spectrum using Eqn (2) for an \( x \)-peak as the reference peak. Several peaks of glass elements, such as Ca–K, Si–K, and Mg–K, are used as reference peaks because the particle material is usually not known beforehand. Although the details in the subtracted spectra are different, Al–K and O–K peaks are dominant in the subtracted spectra, so we can see the particle primarily consists of Al and O. This tendency is basically maintained, even when \( k \) values are changed for different reference peaks. However, it also demonstrates that negative peaks in the subtracted spectrum appear depending on a \( k \) value. If the spectrum has a large negative peak, such a spectrum should be neglected for the identification. O–K in Fig. 1(b) is also seen although it is not expected for a metal Al particle.

**Discussions**

As demonstrated in the examples earlier, small contributions from a particle in the original spectrum \( I_{\text{obs}} \) can be enhanced in the subtracted spectrum. Identification is not easy in the original spectrum if the particle contains the same elements as those in a glass substrate (e.g., Na, Mg, Si, Al, Ca, and O). Although the spectra of glass substrate \( I_{\text{sub}} \) in Fig. 1(a) and (b) should be the same if all the experimental conditions are the same, the O–K peak in Fig. 1(a) is smaller than that of Fig. 1(b). The reason of the difference is not clear. For a larger size particle, this subtraction is not necessary, as peaks of the particle are clearly identified. Information similar to this subtraction processing can be estimated by a comparison of ZAF correction results for \( I_{\text{obs}} \) and \( I_{\text{sub}} \). However, as small peaks can be easily found in the subtracted spectrum, the subtraction processing makes analysis more reliable. Unlike MC simulation that needs tens of minutes to complete the calculation and comparison with experimental results, this subtraction processing can be made quickly for identification purposes.
of the material during an SEM/EDX measurement. Moreover, the obtained information on the material may help the improvement of EDX measurement conditions such as electron beam energy and a beam size so as to get a better spectrum for identification.

The origin of O–K peak for Al particle in Fig. 1(b) was investigated with NISTMonte (MC simulation) for a cubic Al particle of the size L on glass substrate. The glass composition used in the MC simulation was obtained with semi-quantitative analysis. In the MC simulation, the accelerating energy was 15 keV and a 1 nm-diameter beam was focused on the center of the particle. The number of electron trajectories was 10,000 in each simulation. In Fig. 2, the simulated spectra of Al cubic particle (L = 200 nm), glass substrate, and the subtracted spectra using Si–K and Ca–K as the reference peaks were shown. The subtraction procedure is the same as the one described for experimental spectra of Fig. 1. The subtracted spectra \( I_{\text{diff Ca–K}} \) and \( I_{\text{diff Si–K}} \) were obtained with Eqn (2) using Ca–K and Si–K peaks as the reference. Even for pure Al, O–K peak cannot be canceled in the subtracted spectrum. The direct comparison of the simulated spectra indicates that Si–K and Ca–K peaks in the particle spectrum are slightly weaker than those of a glass substrate, and O–K peak is slightly larger in the particle spectrum. As a result, small O–K peak that appears in the subtracted spectrum in Fig. 1(b) is considered to be an artifact because of this subtraction processing. Although O–K remains in the subtracted spectrum in this simulation, it has been confirmed that the O–K peak intensity is smaller compared with Al–K peak, so the difference on the peak ratio (Al–K/O–K) between Al and Al2O3 (data not shown) particles is clearly seen as in an experimental comparison of Fig. 1(a) and (b). In failure analysis, information on residual material, (whether it is metal or oxide) is important in order to identify the root cause of the defect. As glass contains large amounts of oxygen, this cannot be easily determined based solely on the original spectrum \( I_{\text{observ}} \), especially for a small particle on a glass substrate.

Monte Carlo simulation was performed for an individual particle on a glass substrate to study size dependence of peak intensity behavior in the subtracted spectrum. Figure 3 shows size dependence of Al–K and O–K peak intensities (a) without, and (b) with the glass substrate. In Fig. 3(a) without the substrate, both Al and O peaks increase almost linearly up to \( L = 1000 \) nm. This pseudo-linear relation of Al–K peak intensity could be roughly explained as follows: The MC simulation showed that the average length \( l \) of trajectories in the particle was 216 nm for a cubic Al2O3 particle (\( L = 200 \) nm), and the average electron energy at the exit surface from the particle was 13.9 keV. According to reference,\(^{[1]} \) ionization cross-section of Al–K shell for 15 keV electron is about \( 8 \times 10^{-20} \) cm\(^2\) (which corresponds to a mean free path length \( \lambda = 28 \) \( \mu \)m for the ionization in Al2O3). Under the condition of relatively large \( \lambda \) compared with \( l \), the Al–K X-ray intensity \( I_{\text{al-K}} \) would be approximately proportional to the average trajectory length \( l \) in the particle as in a thin film approximation. And the average trajectory length \( l \) in the particle has an approximately linear relation to the particle size \( L \) as the trajectories form a cone shape envelope in the submicrometer-sized particle. X-ray intensity \( I_{\text{al-K}} \) then has a pseudo-linear relation to the particle size \( L \).

For 15 keV electrons incident on an Al2O3 particle, the \( \phi(\mu z) \) curves of generated and emitted Al–K X-ray for a single particle indicate the absorption effect increases proportionally with size. For example, a 2% decrease in X-ray emission due to absorption is observed for the size \( L = 100 \) nm, and becomes 15% for \( L = 1000 \) nm. On the other hand, the average trajectory length in a particle is observed to fit better with quadratic increase for the size in submicrometer-size range. Cross-section for Al–K ionization also increases for the particle size due to deceleration of electrons along the path. Therefore, the origin of the pseudo-linearity dependence of X-ray peak intensity in this size range is considered to be the balance of these factors. More detailed investigations are needed and will be reported elsewhere.

**Figure 2.** Monte Carlo simulation of subtracted spectra for Al cubic particle (size: \( L = 200 \) nm) on a glass substrate. \( I_{\text{diff Ca–K}} \) and \( I_{\text{diff Si–K}} \) are subtracted spectra using Ca–K and Si–K peaks as the reference.

**Figure 3.** Monte Carlo simulation of size (\( L \)) dependence of Al–K and O–K peak for a cubic Al2O3 without a glass substrate (a) and on a substrate (b). Al–K indicates a peak value corrected by subtracting the peak value of a glass substrate from that of a particle on a glass substrate.
In Fig. 3(b) with a glass substrate, Al–K at \( L = 10 \text{ nm} \) has significant intensity as the glass contains Al. Therefore, if the contribution of glass is subtracted, the curve, which is plotted as “Al–K” is almost identical to that of Al–K in Fig. 3(a) with no substrate. On the other hand, O–K behaves differently, mainly due to the O–K generation at the glass surface and strong absorption.

To investigate the contribution of backscattering from a substrate to X-ray generation in a single particle, size dependence of \( \delta \) ratio defined as Eqn (3) was calculated by MC simulation for Al–K in a film and a cubic particle with and without a substrate.

\[
\delta(x) = \frac{I_{Al}(x)_{\text{film with substrate}} - I_{Al \text{ substrate}}}{I_{Al}(x)_{\text{without substrate}}}
\]

where \( I_{Al}(x)_{\text{film with substrate}} \): Al–K peak value from a particle on a substrate or without a substrate, \( x \): thickness of a film (t) or a size (L) of a cubic particle, \( I_{Al \text{ substrate}} \): Al–K peak value of a glass substrate without a film/particle. Figure 4 shows the thickness dependence of the ratios, \( \delta_{\text{film}} \) and \( \delta_{\text{particle}} \) calculated for Al–K from an Al\(_2\)O\(_3\) film and a cubic particle. For a cubic particle, \( \delta_{\text{particle}} \) is almost 1 for the size range from 10 nm to 10 \( \mu \text{m} \), whereas \( \delta_{\text{film}} \) of a film starts from around 1.4 then gradually decreases to 1. These results indicate that backscattered electrons have little chance of reverting back to a particle. In a film, on the other hand, electrons backscattered from glass generate X-rays again at points distant from the incident point so that \( \delta_{\text{film}} \) becomes larger than one. This diffusion feature of backscattered electrons and strong forward scattering in individual submicrometer-sized particles is considered to be a basis of spectrum superposition of Eqn (1).

Monte Carlo simulation is the only accurate method to analyze a particle composition on a substrate. However, there may be error sources in the simulation, which are due to ambiguities in experimental parameters such as local compositional change in a substrate including contamination, surface tilt, roughness etc. Subtraction processing might also be effective to reduce such factors, as they could be partially offset by spectrum subtraction using an experimental substrate spectrum.

**Conclusions**

This paper describes SEM–EDX spectrum subtraction for material identification of submicrometer-sized particles on a glass substrate. It was applied to common dust particles on glass substrates and showed a clear difference between subtracted spectrum of Al\(_2\)O\(_3\)-particle and that of Al. Although there are limitations concerning usage and interpretation, because the strong peaks and background from a substrate can be significantly reduced, the spectrum subtraction described herein is useful for quick identification of tiny individual particles on a glass substrate. Monte Carlo simulation showed that backscattered electrons from substrate have a minimal effect on X-ray generation in individual submicrometer-sized particles on a glass substrate. This is the basis of the expected spectrum superposition in the particle size range.

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**References**
