doi:10.1017/S1431927610053766
Microsc. Microanal. 16 (Suppl 2), 2010
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Electron Diffraction Spectral Imaging and Multivariate Statistical Analysis for Structural Mapping of Amorphous and Nano-Crystalline Composites

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Spectral imaging (SI) techniques that collect point-spectra at a two-dimensional array of points have been used widely to collect a full spectral datasets for comprehensive chemical microanalysis. Energy-dispersive X-ray spectra (EDS) are now commonly used in scanning electron microscopy (SEM) and scanning transmission electron microscopy (STEM) as the point-spectra [1, 2]. The EDS-SI dataset can be analyzed by multivariate statistical analysis (MSA) techniques beyond principal components analysis (PCA), providing us with statistically-derived compositional phase maps in complex multi-phase materials [2]. In this work, we demonstrate a similar, but new method to provide structural mapping based on MSA analysis of a SI-like dataset that uses an interference function derived from an electron nano-probe diffraction pattern as the "point-spectrum". Our method is particularly applicable in structural mapping of amorphous and nano-crystalline composites that contain individual phases that may have very small or no difference in the chemical composition among them.

The electron diffraction SI (ED-SI) data collection consists of scanning a nano-electron probe over the specimen and recording diffraction pattern by a CCD camera from each specimen position. From each diffraction pattern, an interference function, F(q), can be derived. The F(q) has been employed in pair distribution function (PDF) or radial distribution function (RDF) analysis of amorphous films and nanoparticles, and is directly related to the RDF function by the Fourier transformation [3-5]. Figure 1 shows the steps involved in deriving the F(q) function in our method. We have been using this approach to study RDF functions for nanoparticles from materials such as Au and ZnO [6]. In the MSA approach, the raw spatially-resolved diffraction data matrix D is factored into two contributions, one containing the diffraction characteristics (S) of the species and one contains their respective spatial abundances (C), which can be represented as the matrix product $D=CS^T$, where the superscript T denotes a matrix transpose. This factorization can be performed by PCA, with use of the rotation by the VARIMAX procedure to maximize the spatial simplicity of C [7]. In applying MSA approach to analysis of the derived F(q)-SI dataset, the linear model approximation is assumed, that is the diffraction pattern from a mixed phase is a linear combination of individual pattern weighted by volume fraction of the phase.

As an example of this approach, we examined a SiN_x/SiO_2 multilayer film formed on a Si substrate. The specimen was prepared with FEI DB-235 FIB/SEM. The ED-SI data were acquired on an FEI Tecnai F30-STEM, operated at 300kV. An approximately parallel electron probe of about 8 nm diameter formed with a 10 μm condenser aperture, was used to form diffraction patterns, and the patterns were recorded at camera length 200 mm by a slow scan 1kx1k GATAN CCD camera. Fig.2a is a bright field image of the multilayer in cross-section. A rectangular box of dimensions 200 nm x 100 nm shows the region of the ED-SI with sampling pixels of 16x8 used for SI collection. The ED-SI dataset consisted of 128 diffraction patterns. The PCA eigenanalysis of F(q)-SI dataset indicated there were 7 non-noise factors, and two of seven the considerably more significant than the rest. Fig.2b shows these two most significant components and structural maps of the two components obtained from the PCA analysis. The two components were found to correspond to the averaged F(q)

https://doi.org/10.1017/S1431927610053766 Published online by Cambridge University Press

for the SiN_x and SiO_2 phases, respectively. Using the PCA derived components, the RDF functions corresponding to the SiN_x and SiO_2 phases can also be calculated. The details of the method and its application to structural mapping of nano-crystalline composites will be reported in our future publication [6, 8].

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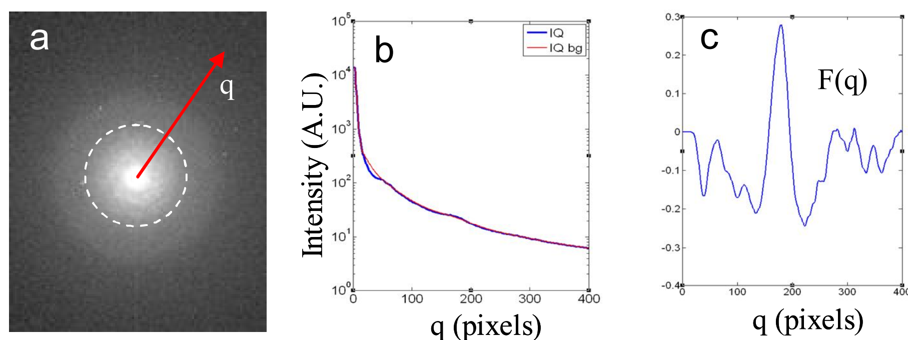

Fig.1. Nano-electron diffraction in (a) was first filtered to remove the x-ray counts and followed by calculating rotational average about the center beam to obtain the intensity as a function of q (defined as $4\pi\sin(\theta)/\lambda$), IQ, in (b). The background IQ_bg in (b) can be obtained by modeling or a fitting procedure; (c) the interference function F(q) was derived by q∗(IQ/IQ_bg-1) (See ref. 5).

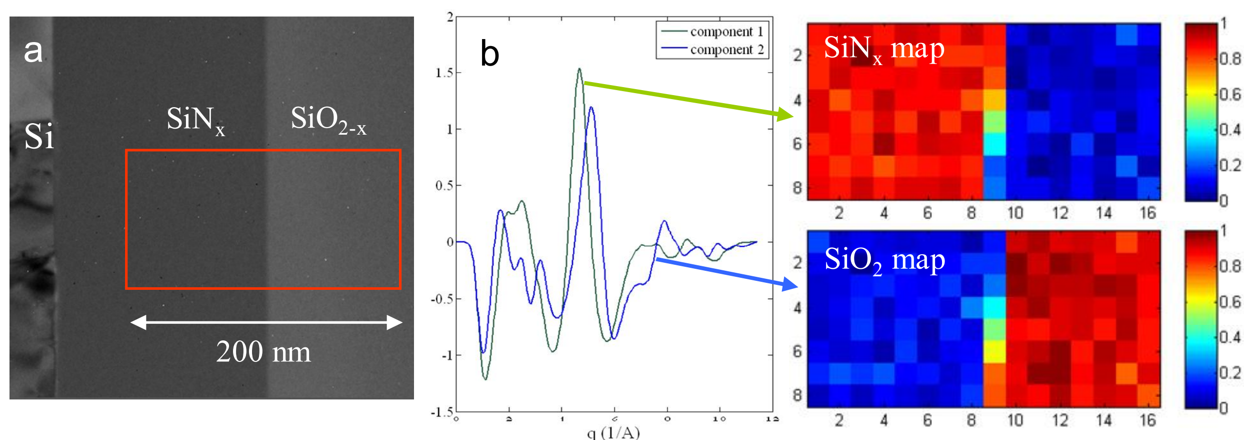

Fig.2. (a) Bright-field TEM micrograph showing a rectangular area of 200x100nm, where ED-SI dataset was taken; (b) Two most significant components obtained by PCA analysis of F(q)-SI dataset, along with the maps of the two components corresponding to SiN_x and SiO_2 phase, respectively.

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