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MULTIVARIATE STATISTICAL ANALYSIS OF SPECTRUM LINES FROM Si_3N_4 GRAIN BOUNDARIES

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It is well known that the high-temperature properties of polycrystalline Si_3N_4 ceramics are strongly influenced by the nanometer-scale glassy phase at the grain boundaries. We have recently analyzed the variation of the near-edge fine structure (ELNES) of the Si-$L_{2,3}$ edges using a combination of TEM spectrum-line acquisition with an imaging filter and multivariate statistical analysis.

The glassy phase at the Si_3N_4 grain boundaries is easily damaged by the the fine probes usually used in scanning transmission electron microscopy to acquire ELNES data. Thus an alternative method using a Gatan imaging filter (GIF), called TEM spectrum-line analysis, was used. In this mode,[1] energy-loss spectra are dispersed along one axis of the CCD detector, while the orthogonal axis displays the spatial variation across the interface. In this mode, a slotted washer is used as the GIF entrance aperture, with its minor axis parallel to the energy-dispersion direction of the spectrometer. To ensure that the grain boundary to be analyzed was edge on, the Si_3N_4 grain was carefully oriented so that the appropriate $(10\bar{1}0)$ lattice fringes were parallel to the dispersion direction and the minor axis of the slit, as shown in Fig. 1a. The magnification calibration was performed with these 0.66 nm lattice fringes. The interface of interest is then translated into position, as shown in Fig. 1b. The calibration for the grain boundary shown in Fig. 1b, acquired at 42,000× microscope magnification, resulted in a spectrum line of ~30 nm width with ~0.27 nm sampling frequency for the spectrum line shown in Fig. 2. The spectrum line was acquired for 120 s with a collection half-angle of 1.9 mrad, at an energy dispersion of 0.1 eV / pixel.

A portion of the spectrum line of 64 spectra (17.3 nm) by 943 channels (94.3 eV) was selected for multivariate statistical analysis (MSA). The MSA method separates the components of the spectrum-lines that are specific to matrix and interface without any a priori assumptions about the shape or spatial extent of these components.[2,3] A logarithmic plot of the information content of the principle components of the analysis identified by MSA is shown in Fig. 3. The exponential variation of most of these eigenvalues is consistent with Poisson counting statistics (noise). MSA identifies one component of the variance above this noise level. A plot of the average of the 64 spectra, E_0, is shown in Fig. 4, along with E_1, the significant component of the variation. [Note that the scale for E_1 is expanded 2× that for E_0.] The amplitudes of these two components are shown in Fig. 5. The average signal level per spectrum, C_0, shows a dip in the vicinity of the grain boundary; the amplitude of the significant component of the variation, C_1 (shown on a scale expanded 20× that for C_0), shows a sharp peak at the boundary with a FWHM of 4 pixels or ~1.1 nm. This chemical width compares well with the structural width shown in the bright field image, Fig. 1b. Spectra reconstructed from E0 and E1 for the matrix and the grain boundary are shown in Fig. 6. The matrix spectrum has been shifted vertically to allow both spectra to be visible. The arrows mark the regions of the grain boundary spectrum that are different from that of the matrix. This technique will be used to correlate variations in grain boundary chemistry and bonding with the observed performance of Si_3N_4 ceramics.

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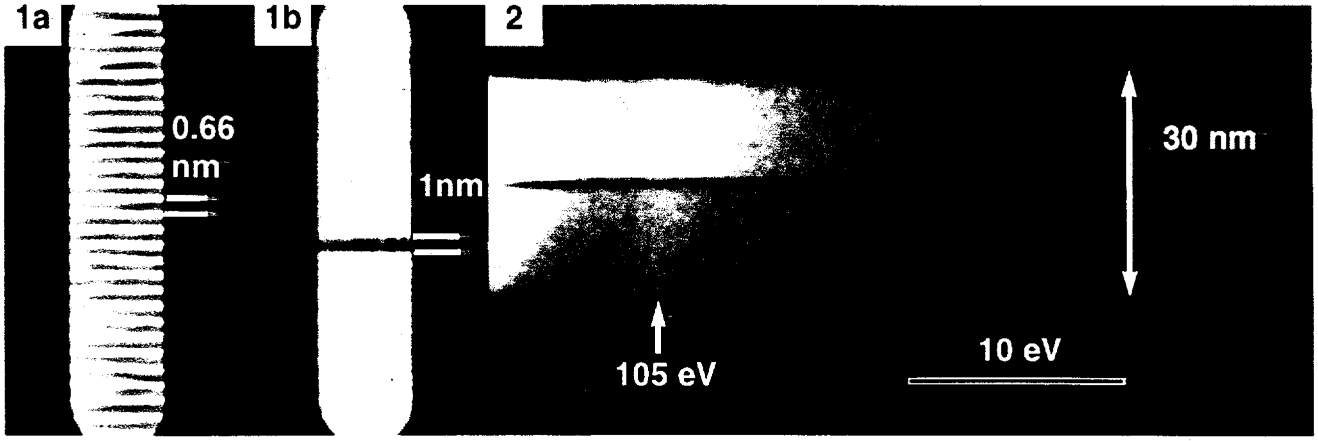

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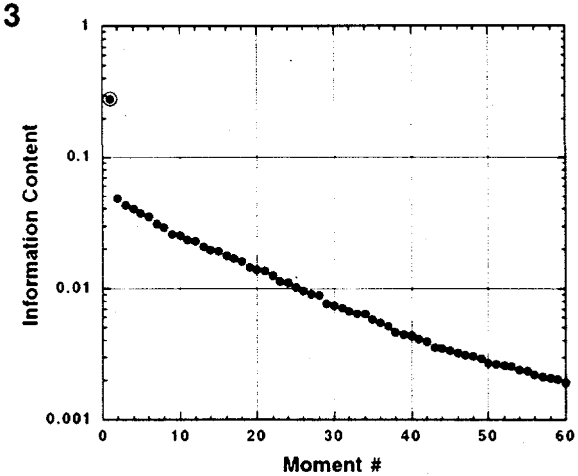

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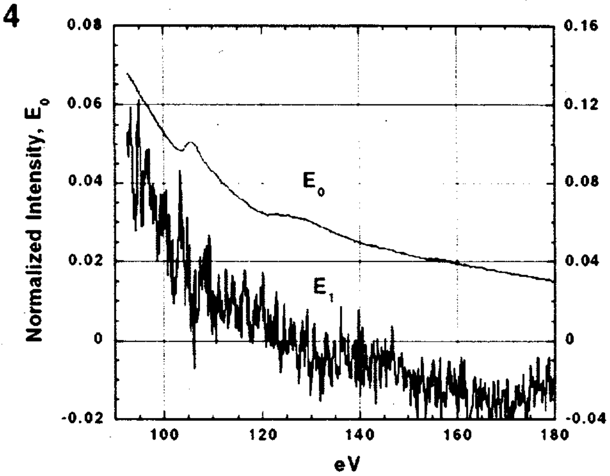

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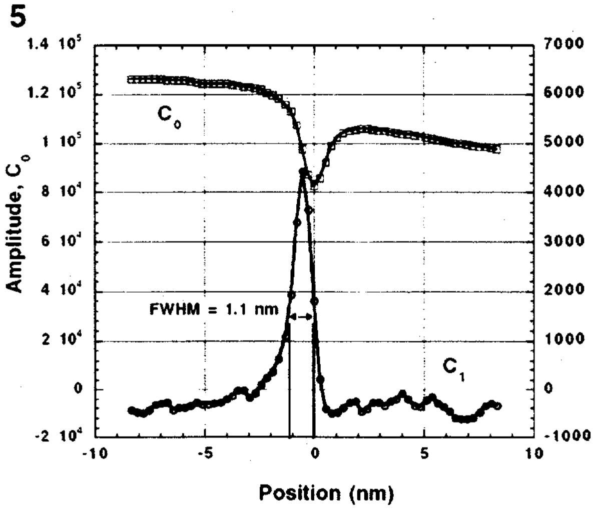

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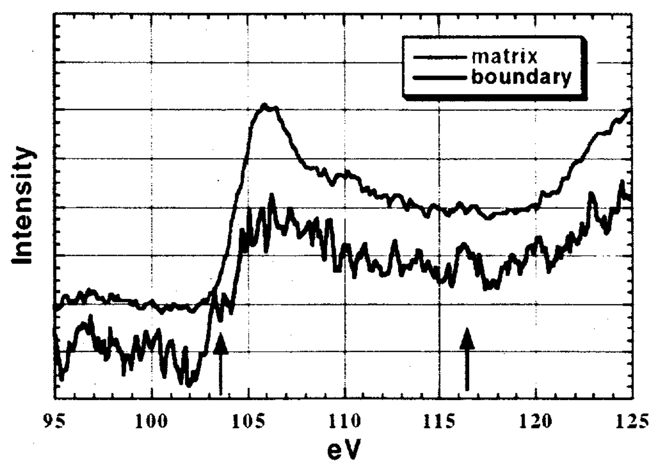

FIG. 1 -Bright-field GIF images of the specimen, as seen through slotted-washer entrance aperture: (a) Si_3N_4 lattice fringes used for magnification calibration and grain boundary orientation; (b) edge-on grain boundary.

FIG. 2 -GIF image of spectrum-line acquired from grain boundary shown in Fig. 1b.

FIG. 3 -Logarithmic plot of information content of principle components identified by MSA.

FIG. 4 -Plots of average spectrum (E_0) and significant component of the variation (E_1).

FIG. 5 -Plots of amplitudes of components shown in Fig. 4, as a function of position.

FIG. 6 -Background-subtracted spectra reconstructed for matrix and grain boundary.

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