Radiation Damage and Spatial Resolution in the EXELFS of Inorganic Materials

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EXELFS, the extended energy loss fine structure superimposed on the high energy loss side past an inner-shell electron excitation in an EELS spectrum, contains quantitative information about the local structure around the scattering atom from which the core electron is excited, similar to that contained in the x ray absorption fine structure (XAFS) [1]. Main advantages of the EXELFS technique over XAFS include the relative ease in the former to study the local environments of low Z elements coupled to the higher spatial resolution, imaging and diffraction capabilities of the TEM.

Radiation damage to the sample caused by the energetic electron beam, however, has been an important concern to whether EXELFS can be safely applied to study materials at the nanometer scale. To investigate this question we chose to study Al, SiC and MgO as representatives of three different classes of binding: metallic, covalent and ionic, with the belief that these should exhibit different sensitivities to different mechanisms of radiation damage and hence will be fair representatives of a wide variety of materials.

We recorded EXELFS spectra at the Al, Si, C, Mg and O K-edges as a function of electron dose, either by increasing the electron flux or by reducing the illuminated area of the specimen. All the experiments were done in a Philips 430 TEM equipped with a LaB_6 filament and with a 666 GATAN parallel detector EELS spectrometer. Data were collected in the diffraction mode with a nominal camera lenght of 250 mm and a 3 mm entrance aperture to the GATAN spectrometer. Data collection was divided in seven time intervals and data scans within each interval were aligned and added on-line. The different intervals were needed to monitor any time dependent changes in the EXELFS due to either radiation damage or changes in experimental conditions. A total of 10^6 counts were acquired at each current condition to achieve sufficient counting statistics. The highest electron current attained in our experiments was $I = -12.4nA$ and the smallest probe size used was $0.5\mu m$ in radius, given a maximum current density of $J \approx 10^{23} e^-/(sec\ m^2)$. We could not observed any radiation damage in the Al and SiC samples, even after accumulating 10^6 counts at the highest current density and smallest area (highest dose). For the MgO case, however, even though the EXELFS did not show any time dependent changes, changes were evident in the diffraction pattern (DP) as well as in the image after a total dose of $J\Delta t \approx 3 \times 10^{26} e^-/m^2$ was administered to the sample. A uniform ring pattern passing through the single crystal spots appeared in the DP and dark spots about 100Å in size appeared in the image. After corroborating that no changes ocurred in the EXELFS signal of each material as a function of time, the different groups were aligned and summed together. The EXELFS data were analyzed in a way described previously [2] using XAFS theory, and excellent agreement with the known structures was obtained. XAFS theory can be used to analyze the EXELFS provided the dipole approximation is satisfied. This requires that $q_m a_0 \lesssim 0.2$ (q_m is the maximum momentum transfer in the inelastic scattering and a_0 the radius of the K-shell electron [3]), which can be obtained by a proper choice of collection geometry in the TEM.

Table. 1 summarizes the main findings of this work and the parameters used in determining the validity of the dipole approximation and the ultimate spatial resolution attainable. The spectrometer acceptance semiangle , $\theta_m = 6$ mrad, is determined by the camera length and the spectrometer entrance aperture (diffraction mode). The maximum wave number transfered is given by $q_m = \sqrt{(q_{m,\perp})^2 + (w/v)^2}$; $q_{m,\perp} = \frac{2\pi}{\lambda}\theta_m = 1.5\text{Å}^{-1}$ is the maximum transverse momentum transfer, $\lambda = 0.0251$Å is the 200 KeV electrons wavelength, $\hbar w$ is the energy loss and v is the velocity of the incoming electrons. w/v is given 500 eV above the edge. $a_0 \approx \sqrt{\hbar/(2\ w_0 m_e)}$ is the radius of the K shell electron, $\hbar w_0$ being its binding energy and m_e its mass. $J\Delta t$ is the total dose needed to accumulate 10^6 counts at the given edge using a probe $0.5\mu m$ in radius and the highest current density. Δt is about 1 hr. at the Al and Si K-edges and about 15 min. at the C and O K-edges. $J\Delta t_{max}$ is the threshold doses for radiation damage. For Al and SiC these values are taken from the literature (we could not observe any damage at the doses used to record the EXELFS because a field emission gun is required to observe damage in a reasonable time exposure). For MgO we use for the threshold the value at which we started seeing changes in the image and DP, even though the EXELFS did not show changes and the nature of the changes are presently unknown. The ultimate probe size achievable is estimated from improvements in collection efficiency (a factor of two when going from 3mm to 5mm spectrometer entrance aperture for edges where the validation of the dipole approximation is not compromised) and by improvements in counting rates attainable with a faster computer (a factor of six if our Macintosh IIci is replaced by a Power Macintosh).

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TABLE I.

Ultimate probe size for EXELFS

Edge	ω/v (Å^{-1})	$q_m a_0$	JΔt(e/m^2)	JΔt_{max}(e/m^2)	Ultimate probe radius
Al (metal)	1.45	0.1	3.4×10^{26}	10^{28} [a]	250 (Å)
Si (SiC)	1.7	0.104	3.8×10^{26}	5×10^{27} [b]	384 (Å)
C (SiC)	0.57	0.186	8×10^{25}	5×10^{27} [b]	256 (Å)
O (MgO)	0.68	0.139	1.2×10^{25}	3×10^{26} [c]	400 (Å)
Mg (MgO)	1.31	0.107	3×10^{26}	3×10^{26} [c]	1300 (Å)

[a]Ref. 4

[b]Ref. 5

[c]Our measurements