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Atomic Resolution Vibrational Spectroscopy with On-Axis Detector Geometry

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Atomic-scale characterization of vibrational modes in materials can greatly improve our understanding of ionic and atomic diffusion, heat transport, phase transformations, and surface chemical reactions. The detection of vibrational modes with monochromated vibrational electron energy-loss spectroscopy (EELS) in a scanning transmission electron microscope (STEM) opens up the possibility to probe such excitations with high spatial resolution. The electron interactions associated with the excitation of vibrational modes can be discussed in terms of dipole and impact scattering as was done for *high-resolution* electron energy-loss spectroscopy (HREELS) by Ibach and others [1]. Dipole scattering is associated with the long-range Coulomb field which excites vibrational modes by polarizing the medium while impact scattering is associated with short-range interactions with the nucleus and atomic electrons. Recent work on the influence of an abrupt SiO_2/Si interface on the spatially resolved Si-O bond stretch vibrational signal showed that the electron probe can sense the interface from a distance of 200 nm in SiO_2 due to the dipolar character of the Si-O vibrational mode [2]. This delocalization in the vibrational signal can be suppressed either by selectively probing chemical bonds with no ionic character or non-dipole vibrational modes like acoustic phonons or symmetric-stretch modes in ionic materials. In this paper, we demonstrate that it is possible to achieve atomic spatial resolution with individual vibrational modes in Si, which has completely covalent bonding character, and in SiO_2, which has mixed ionic and covalent bonding character, in the conventional on-axis STEM EELS geometry.

A conventional cross section Si sample in the [110] zone axis orientation was prepared by dimpling and milling. A second sample was prepared for vibrational EELS experiments across the SiO_2/Si interface by lifting out a FIB lamella from an oxidized Si wafer. STEM-EELS analysis on all samples was performed using a NION UltraSTEM 100 aberration-corrected electron microscope equipped with a monochromator, operated at 60 kV. The probe convergence semi-angle was 28 mrad, and a 1 mm spectrometer entrance aperture was used corresponding to a collection semi-angle of 12 mrad. A dispersion of 1 or 2 meV per channel was used to record all spectra. Aberration correction of the magnetic lenses up to the fifth order produced probes of ~0.12 nm diameter with beam currents of ~100 pA. During the monochromated experiment, the beam current was ~10 pA, and the energy resolution was 15 meV.

Fig. 1a shows the conventional on-axis spectrometer geometry for EELS in the STEM employed in this work. Fig. 1b shows a monochromated ADF image of the Si dumbbells and the position of the EELS linescan. The monochromated probe size was ~0.17 nm, which wasn't small enough to resolve the Si atoms forming the dumbbell. Fig. 1c shows the background subtracted vibrational energy-loss spectra at every 0.06 nm between the points marked in the Fig. 1b. There are very significant differences in the spectral shape and intensity as the probe changes position. The spectrum shows two peaks when the probe is between dumbbell columns; one at 62 ±2 meV with a width of approximately 16 meV and a

weaker broader feature centered at about 43 ± 2meV. The higher energy peak corresponds to optical phonons near the center of the Brillouin zone whereas the lower energy peak corresponds to optical and acoustic phonons at the Brillouin zone boundary, as can be ascertained from the blue (high-energy) and red (low-energy) bands in the Si phonon dispersion curves, shown in Fig. 1d. When the probe is on the column (position 4), only one peak is apparent with energy about 58 meV and width of 22 meV. As the probe continues to move off the column, it becomes narrower and shifts back to approximately 62 meV (positions 5 and 6). The integrated intensity of the peak on the column is approximately 3 times the intensity between the columns and shows a spatial resolution of better than 0.2 nm for both the high and low energy peaks. Experimental observations from Si and SiO_2 will be discussed in more detail [4].

References:

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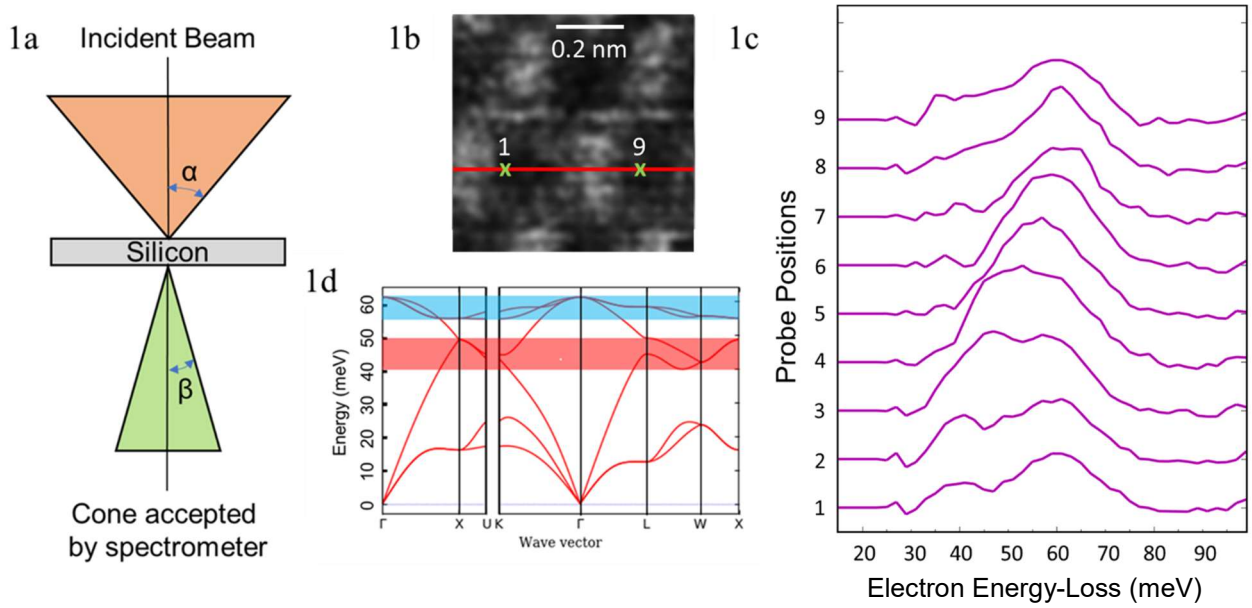

Figure 1. (a) Schematic diagram showing the STEM EELS acquisition geometry used in experiment with α = 28 mrad and β = 12 mrad. (b) ADF image of Si dumbbells with the red line indicating position of EELS linescan acquisition. (c) Raw spectra at 9 individual probe positions all separated by 0.06 nm along the linescan between the labels 1 and 9 shown in b. (d) Dispersion surfaces in for Si – blue and red shaded areas corresponds to peaks in the density of states on the upper branches from 55 – 62 meV (optical) and on a lower branch from 41 – 48 meV (optical and acoustic) [3].

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