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Spatially Resolved Vibrational Electron Energy-loss Spectroscopy Across an Abrupt SiO_2/Si Interface

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The detection of vibrational excitations at high spatial resolution with monochromated vibrational electron energy-loss spectroscopy (EELS) can be used to perform local materials characterization on complex geometries. To develop a comprehensive understanding of this technique so that it can be applied to complex materials systems, we need to perform experiments on relatively simple model systems and compare experiment with theory. Recent work on the influence of an abrupt SiO_2/Si interface on the spatially resolved Si-O bond stretch vibrational signal showed a signal in SiO_2 200 nm from the interface due to the long-range Coulomb interaction. At the interface the integrated signal intensity drops to zero. Nanometer spatial resolution is achievable while selecting the interfacial vibrational stretch signal as the electron beam is scanned across the interface. It is also shown that surface coupling must be considered for typical TEM sample thicknesses. Moreover, the energy-loss spectra in SiO_2 can be interpreted using the non-relativistic dielectric theory, while relativistic effects must be considered in Si [1]. In this paper, we explore the experimental spatial variation of the Si-O vibrational modes as the electron probe is scanned across the interface. The experimental spectra are interpreted in terms of the relativistic dielectric theory [2].

A 3 μm layer of SiO_2 on a Si wafer was prepared for STEM EELS analysis by lifting out a focused ion beam (FIB) sample using a Nova 200 NanoLab (FEI) FIB. A NION UltraSTEM 100 aberration-corrected electron microscope equipped with a monochromator was used to perform EELS linescans across the SiO_2/Si interface. The microscope was operated at 60 kV, with probe convergence and collection semi-angles of 30 and 12 mrad respectively. The experimental EELS energy-resolution was 15 meV. Background subtraction and signal integration were performed using the Gatan Microscopy Suite.

Figure 1a is a bright-field (BF) STEM image of the SiO_2/Si interface that shows the position of the interface and the direction of the linescan. A typical background subtracted vibrational energy-loss spectrum observed when the electron beam is positioned in SiO_2 far away from the interface is shown in Figure 1b. The energy-loss spectrum shows three peaks at 58, 98 and 144 meV when the beam is in SiO_2, which correspond to the thin-film Si-O bond-rocking, bond-bending and bond-stretching vibrational signals respectively [3].

Figure 2a shows the experimental spatial variation of the 58 meV Si-O bond-rocking signal overlaid on the spatial variation of the 144 meV signal in SiO_2. The two profiles look very similar which suggests that a begrenzungs type of effect causes the 58 meV integrated signal intensity to drop from its maximum value far away from the interface to zero at the interface [1]. Figure 2b shows the variation in surface contribution with change in thin-film thickness, calculated using Kröger's formula [2]. If the

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sample thickness is of the order of v/ω (v is the electron velocity, ω is the energy-loss frequency), a significant surface contribution is observed in the energy-loss spectra [4]. For 60 kV accelerating voltage, v/ω is ~600 nm for 144 meV and ~1500 nm for 58 meV. This suggests that while there is competing contribution from bulk and surface for the 144 meV signal, only the surface contribution is observed for the 58 meV signal. Experimental spatial variation profiles for the bond-rocking signal as the probe moves into Si and detailed simulations to interpret the experimental energy-loss spectra in Si will be presented [5].

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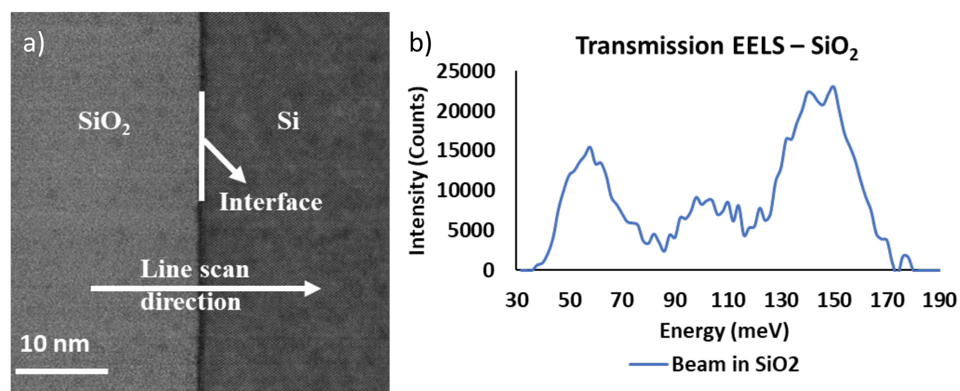

Figure 1. a) BF STEM image of the SiO_2/Si interface showing the direction of linescan. b) Typical experimental vibrational spectra when the beam is positioned far away (~400 nm) from the interface and at the interface.

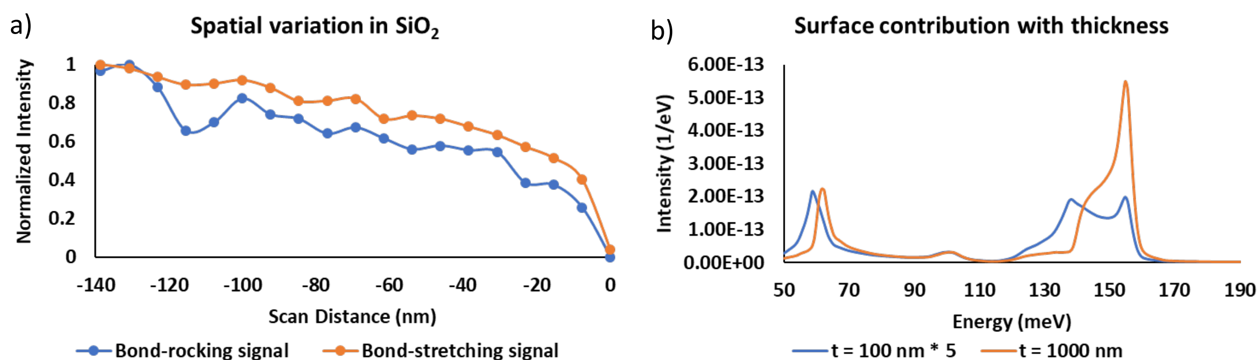

Figure 2. a) Experimental spatial variation of the 58 meV bond-rocking signal overlaid on that of the 144 meV bond-stretching signal in SiO_2. b) Difference in the variation of surface contribution with thickness for the 58 meV and 144 meV signals – calculated using Kröger's formula [2].

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