Exploring Phonon Signals by High Energy / High Spatial Resolution EELS

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Using the High Energy Resolution Monochromated EELS-STEM (HERMES) instrument we have developed [1] together with a Gatan Enfinium spectrometer retrofitted with extra-stable power supplies [2], we now achieve sub-20 meV resolution in electron energy loss spectra (EELS) acquired in >1 s. We have also been able to improve the rate of the decay of the zero loss peak (ZLP) such that tail intensities of <4x10-4 of the ZLP maximum have been recorded at energy losses as small as 100 meV.

Besides the high energy resolution and minimized tail ZLP, HERMES provides several new capabilities, including: 1) spatial resolution – we can record full-resolution spectra from sample areas as small as a few Å; 2) flexibility – we can also record spectra from areas as large as 10 μm, and attain an angular resolution of ~1 μrad (using a camera length setting of ~1 km); 3) angular acceptance – we can attain a good energy resolution with EELS acceptance angles of ±30 mrad and greater; and 4) brightness – we use a bright cold field emission (CFE) gun, and can therefore extract appreciable signals from Å-sized areas. Taken together, these capabilities promise that signals not accessible in electron microscopy before are about to become available. Here we explore phonon spectroscopy; in a related contribution at this meeting, we explore detecting H and other light elements by energy-filtered HADF imaging [3].

Fig. 1 illustrates how important signals have up to now been "hidden in plain sight" – obscured by a broad zero loss peak. The solid green spectrum was recorded in 0.13 s at 60 keV, with no sample, and with the beam passing through the monochromator but the energy-selecting slit retracted. The ZLP FWHM is ~250 meV, typical of tungsten CFE operated with a total emission current <1 μA. The red (line) spectrum was recorded with the slit in, in 0.1 s, and shows FWHM of 14 meV. It demonstrates the ~20x improvement in energy resolution that's readily available with our system.

The blue spectrum in Fig. 1 was recorded from a ~2 nm Ø area in SiO_2, in a single acquisition of 10 s duration, with a beam current of ~10 pA, probe convergence angle of ±12 mrad and collection angle also ±12 mrad. Its ZLP (not shown) had a FWHM of ~17 meV. The optical phonon peak visible at 140 meV energy loss had a peak intensity of ~1x10^{-4} (above background) relative to the zero loss peak, a level the tail of the unmonochromated ZLP only decays to at about 1.7 eV. The energy of the phonon peak is in good agreement with the energy of the strongest feature normally observed in infrared spectra of SiO2, at 1100 cm^{-1}. (To convert cm^{-1} to meV, divide by 8.)

The phonon signal is due to two types of interactions: a short-range and a long-range one. Fig. 2 demonstrates that both types of signals can appear in a single line scan. Fig. 2(a) shows a high-angle

annular dark field (HAADF) image of the examined area in a Si-SiO₂ sample, with the scan line used for collecting EELS data marked. The scan started in the Si, went through the SiO_2 layer, and ended in the vacuum outside the sample. Fig. 2(b) shows the integrated intensity of the background-subtracted SiO_2 phonon peak (as a fraction of the ZLP intensity) in a series of 100 spectra recorded in 10 s each, taken as the beam progressed along the line. The figure also shows the sample thickness, determined by taking the ratio of the intensity of energy losses, recorded separately up to 180 eV, to the ZLP, and assuming a mean free path of 72 nm for SiO_2. Two sample areas are especially interesting: the Si–SiO_2 interface, where the phonon intensity goes to zero ~3 nm inside the Si and builds up only gradually inside the SiO_2, and the SiO_2–vacuum interface, which shows an initial sharp drop-off and then a long decay tail stretching tens of nanometers outside the sample. The long tail suggests that phonon spectroscopy can be carried out in the STEM with an aloof beam, thus avoiding damage in radiation-sensitive samples.

We have also recorded optical phonons in several other materials, measured the phonon energy varying with the scattering angle and the probe position, and observed an enhancement of the short-range signal at high scattering angles. Results illustrating these phenomena will be shown at the meeting.

References:
[1] OL Krivanek et al., Microscopy **62** (2013) 3-21.
[2] OL Krivanek et al., Proceedings 2013 EMAG meeting, in print (2014).
[3] TC Lovejoy et al., these proceedings (2014).
[4] We gratefully acknowledge the use of facilities within the LeRoy Eyring Center for Solid State Science at
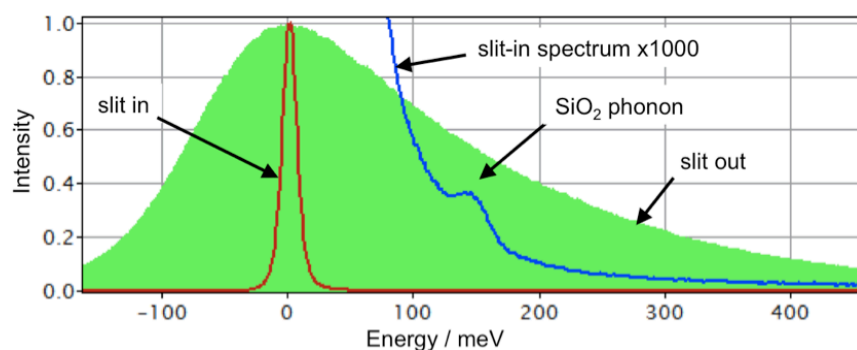ASU, and grants NSF MRI-R2 #0959905, DE-SC0004954 and DE-SC0007694.

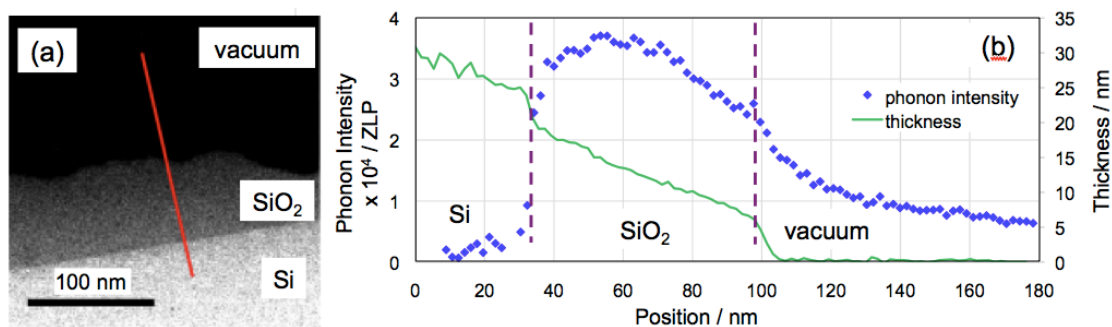**Figure 1.** EEL spectra recorded with the monochromator slit out (green) and in (red and blue).

Figure 2. Variation of the phonon signal intensity in a line profile taken from Si via SiO_2 into vacuum. 60 keV, 10 pA probe current. (a) HAADF image showing profile location. (b) Profile showing the phonon intensity and the sample thickness. Sample courtesy Dr. John Bruley, IBM.