

Investigation of Surface and Bulk Vibrational Modes in SiC Polytypes using Spatially Resolved Monochromated HREELS

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Spatially resolved high resolution electron energy loss in a high energy resolution monochromated EELS system (HERMES) system has attracted a lot of attention after its inception while opening new avenues of research and many unanswered questions. The recent advancements in EELS have made it possible for < 1 nm probe sizes while still managing high probe current of around 10 pA [1]. With this, spatially resolved transmission EELS is possible, paving the way for accurately quantifying bulk vibrational mode energies and distinguishing them from surface modes. [2] It is instructive to begin with a relatively simple system whose vibrational modes can be more precisely studied than other complex systems. We have chosen SiC as the system of choice due to its simple cubic structure in its 3C polytype and hexagonal structure in its 4H and 6H polytypes. Here we discuss only the SiC 6H polytype. SiC vibrational modes have been meticulously studied previously by means of Fourier transform infra-red spectroscopy and Raman spectroscopy. With a well-documented database for the SiC system, we hope to correlate our findings in spatially resolved high resolution EELS. Typically, Raman spectroscopy studies the surface vibrational modes of a material due to the low penetration depth of the laser. Although transmission Raman Spectroscopy [3] is capable of probing bulk modes in a material, it lacks the spatial resolution to map local bulk modes and study thickness and size dependent effects. With our HERMES system, we can show the distinction between surface and bulk modes in a thin high quality thin film single crystal sample as well as increase in scattering probability of bulk modes as a function of thickness.

HREELS measurements were conducted using Nion UltraSTEM 200 at University of California, Irvine, equipped with C3/C5 aberration corrector and high-energy resolution monochromated EELS system (HERMES). The instrument was operated at an accelerating voltage of 60kV with probe convergence and collection semi-angles of 30 and 10 mrad, respectively. Vibrational measurements were carried out by taking a line scan beginning from the vacuum region and ending in the bulk region of the thin film sample. Seven measurements were taken along the path with each measurement consisting of 200 scans at 1s exposure time (Fig 1A). The data set of 200 scans was aligned to account for the ZLP shift, summed to produce a strong coherent phonon signal, and then normalized to the maximum ZLP intensity. Figure 1B shows a log plot of the EEL spectra illustrating vibrational bulk and surface behavior. The phonon signal displayed in (Fig. 2A) was obtained after subtracting a curve that was fitted to the background. We fitted an exponential function $e^{p(x)}$, where $p(x)$ is a fourth-order polynomial [2] for data that was collected in the intersecting and aloof geometries (Fig. 1C).

Our data shows depressed bulk modes that only become more pronounced as the probe is moved on the sample. The backgrounded subtracted phonon modes at each measurement location reveal increasing scattering probability of bulk modes as the probe enters the sample. While in aloof configuration, only a singular surface mode is distinctly present as can be seen in (Fig. 2A). The phonon signal was then deconvoluted into its separate modes. Based on the steady increase in scatter probability (due to increasing

thickness), the first four modes are revealed to be bulk modes while the 115 meV peak is designated to be a surface mode. Examining the gradual increase of these 5 modes from aloof configuration to transmission EELS is evidence for the distinction between bulk and surface modes [4].

References:

- [1] O. L. Krivanek *et al*, Nature **514.7527** (2014), p. 209.
 [2] M. J. Lagos *et al*, Nature **543.7646** (2017), p. 529.
 [3] P. Matousek, A. W. Parker., Applied Spectroscopy **60.12** (2006), p. 1353.
 [4] The authors acknowledge the support of the University of California Irvine Materials Research Institute for the use of TEM facilities.

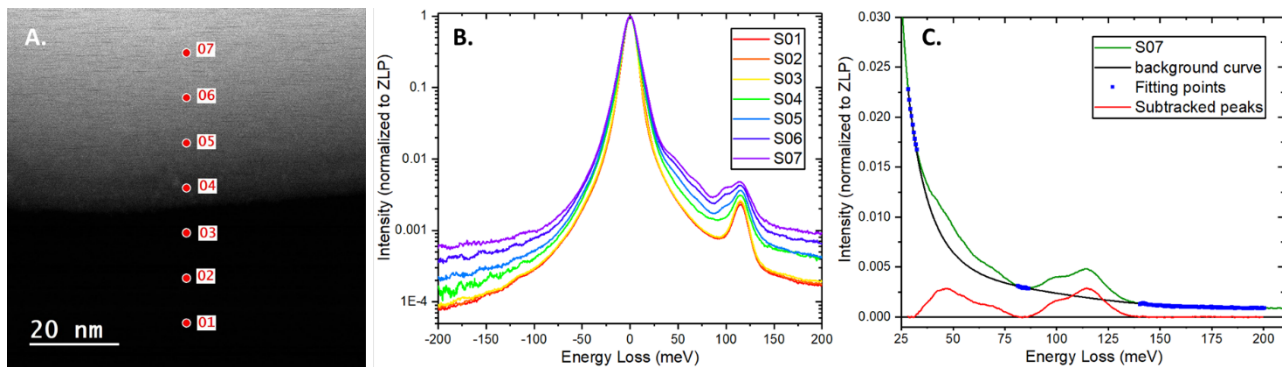


Figure 1. Profile showing the spatial variation of the vibrational signal. a. HAADF image of an SiC-6H-vacuum sample viewed in cross-section; the yellow arrow indicates the direction of the line scan **b.** Log plot of the EEL spectra at locations depicted in **a** showing surface and bulk phonon modes **c.** background subtraction curve shown with subtracted phonon modes along with triple range fitting

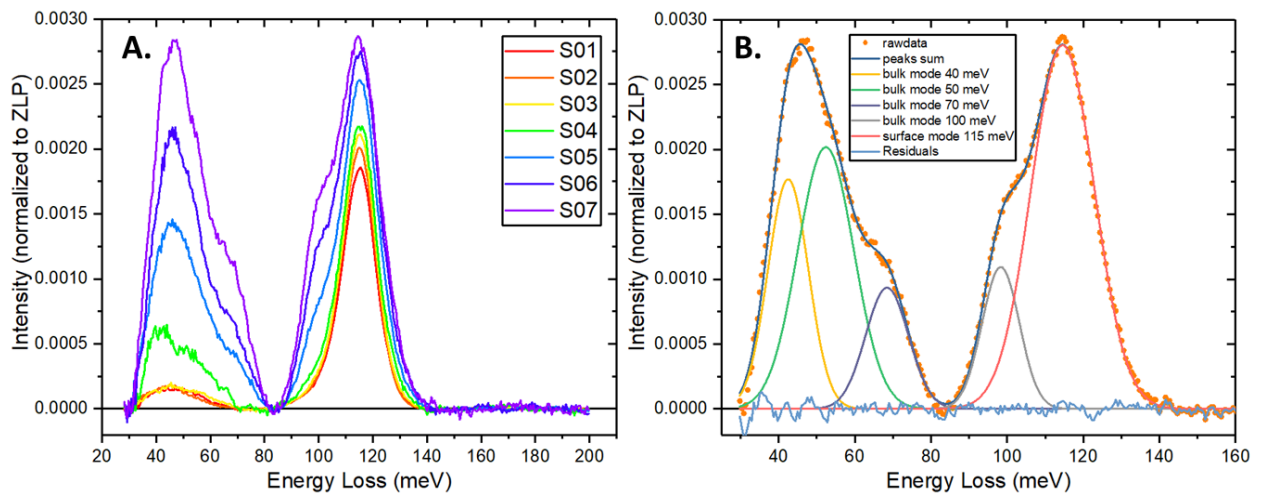


Figure 2. Background subtracted signal a. background subtracted phonon modes at locations depicted in **Figure 1. a.**, **b.** Peak separation of phonon modes separating bulk modes from the surface mode