Detecting Exotic Vibrational States at Interfaces by Electron Microscopy

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Due to the continued minimization of microelectronic devices, thermal interface conductance (TIC) becomes increasingly imperative to dissipate the heat flux generated in integrated circuits and prolong their lifetime. The conventional phonon gas model theory fails to describe the thermal properties at interfaces. Recently, local interfacial phonon modes, which are absent in the phonon structure of bulk counterparts, have been theoretically predicted to play a significant role in promoting heat transport across semiconductor interfaces [1]. However, such emerging modes are challenging to detect due to the lack of effective tools to investigate local vibrational spectra with at least nanoscale resolution. Compared to optical spectroscopies, the state-of-the-art monochromated electron energy-loss spectroscopy (EELS) in the advanced scanning transmission electron microscope (STEM) offers few meV energy resolution, enabling a powerful space- and angle-resolved vibrational spectroscopy [2]. This approach has been applied to reveal vibrational states localized at crystalline imperfections such as point defects [3] and stacking faults [2]. Here we show two cases to utilize this vibrational EELS method to explore interfacial phonon modes at (1) Si–Ge heterojunction and (2) MoS_2-WSe_2 heterostructure.

Si-Ge interface is a model system for studying TIC because of relatively low lattice mismatch and wide applications in the electronics. Fig. 1a displays an atomic resolution STEM image of a high-quality interface in an epitaxially grown Si-Ge heterojunction. We first employed a space-resolved condition with a large convergence semi-angle (33 mrad) to probe the local vibrational spectra as shown in Fig. 1b. The Si and Ge spectra exhibit prominent longitudinal/transverse optical (LO/TO) phonon peaks at about 60 meV and 34 meV respectively, as well as low-energy acoustic phonon modes. Strikingly, there are extra signals at 48 meV (11.6 THz) in the interface space, which cannot be ascribed to the bulk phonon modes of either Si or Ge or be fitted by their linear combination [4]. The line-scan results reveal that the 48-meV mode is confined to within a few nanometers of the interface. To consider the phonon dispersion relation, angle-resolved vibrational spectra (Fig. 1c) with a small convergence semi-angle (3 mrad) also validate the occurrence of the interfacial phonon modes in the similar energy range at Γ point of the first Brillouin zone (BZ). First-principles calculations further point out that this exotic mode is indeed correlated with local atomic vibrations at the interface and could contribute to 5% of total TIC.

In the second case, we adapted a similar strategy to detect local vibrational states in a two-dimensional MoS_2-WSe_2 lateral heterostructure (Fig. 2a), which forms a monolayer p-n junction. Fig. 2b plots line-scan vibrational spectra across the interface acquired under a space-resolved condition, which reflect the phonon density of states (PDOS) throughout the entire BZ. To improve the signal-to-noise ratio, we divided all spectra into three groups via k-means clustering [5] and then obtained averaged WSe_2, interface, and MoS_2 spectra in Fig. 2c. After peak separation, the peak positions in the MoS_2 and WSe_2 regions agree with those in the corresponding calculated PDOS curves, despite a few weak peaks (nonshaded in Fig. 2c) caused by delocalization effect. However, the interface spectrum contains two peaks at 27.9 and 41.1 meV, which are absent in the PDOS curves of bulk MoS_2 and WSe_2 [5]. These

modes are assigned to interfacial phonon modes based on the first-principles calculations, and may alter the phonon transport across the interface.

Both cases demonstrate that the semiconductor interfaces exhibit exotic interfacial vibrational states, which are spatially localized near interfaces and boost local heat transport across interfaces. Our work paves an avenue to studying emerging vibrational modes at various interfaces and provides guidance to manipulating thermal interface transport for semiconductor and power electronic devices [6].
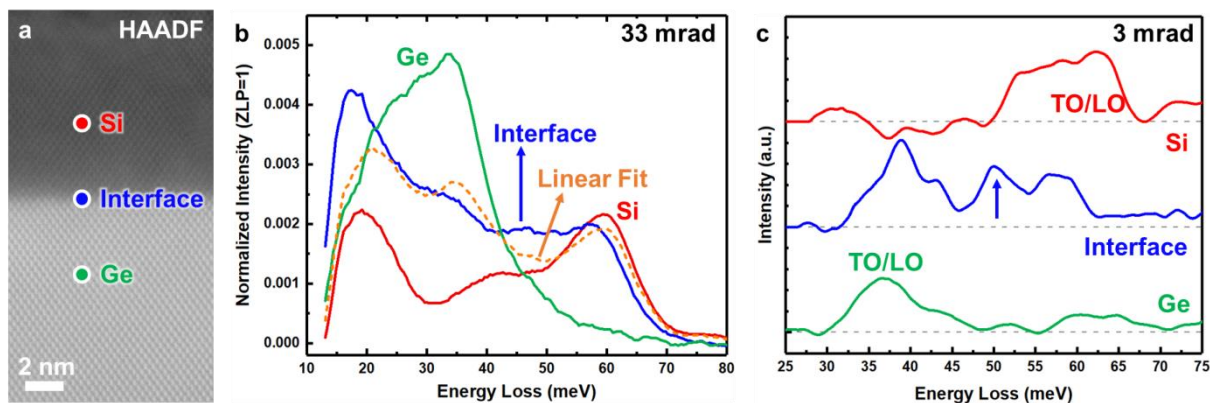
Figure 1. Vibrational spectra of the Si-Ge epitaxial heterostructure. (a) STEM image at the interface through [110] zone axis. **(b)** Space-resolved vibrational spectra of Si, Ge, and interface acquired from corresponding regions in (a). The orange dashed curve is a linear regression fitting of interface spectrum from a linear combination of Si and Ge spectra. **(c)** Local angle-resolved vibrational spectra of Si, Ge, and interface. Three dashed horizontal lines are the zero baseline.
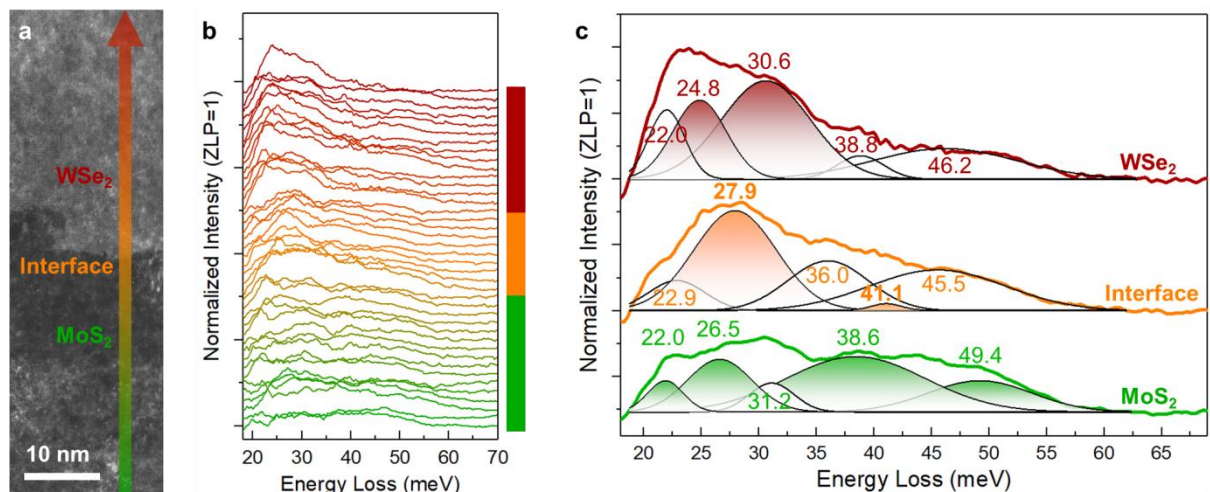

Figure 2. Space-resolved vibrational spectra of monolayer MoS_2-WSe_2 heterointerface. (a) STEM image of the heterointerface. **(b)** Vibrational spectra acquired from MoS_2 (green) through the interface region (orange) to WSe_2 (brown). **(c)** Average vibrational spectra of three corresponding regions, overlapped with fitted Gaussian peaks and peak positions.

References:

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