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Spectroscopy of Nanosphere-Substrate Coupling: The Role of Multipolar Surface Phonon Modes

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With recent advances in monochromators and aberration correctors implemented in scanning transmission electron microscopes, high energy and spatial resolution electron probes become powerful available tools for the characterization of the phonon/vibrational response of nanostructures [1]. For instance, nanoscale local physical properties such as temperature [2, 3], plasmon-phonon coupling factor [4, 5], and phonon density of states can be extracted from EEL spectra through careful quantitative analysis. In particular, phononic interactions of a nanoscale object supported on a thin dielectric support can produce weak inelastic scattering contributions that can be resolved and characterized using EELS. Their understanding can provide physical insights on the complete description of inelastic scattering process and shed light into light-matter interaction process in the infrared range. In this work, we present a detailed analysis of the role of multipolar phonon modes in the coupling between a single nanosphere and a thin dielectric support using vibrational EELS.

We have studied the sphere-film coupling considering different material combinations of the composite system (inset figure 2a) in order to highlight the different physical mechanisms driving the sphere-substrate interaction. Here we focus on amorphous SiO_2 spheres supported on different thin substrates such as Si_3N_4 (extreme weak coupling case), SiO_2 (surface multipolar phonon modes-Fuchs Kliewer coupling case), and amorphous carbon (surface multipolar phonon modes-image charge coupling case). We have collected spatially-resolved EELS data using a monochromated Nion UltraStem electron microscope with a 1.5 - 2 Å probe with energy spread of 10 meV, at 60 kV. Our results reveal that the high energy EELS peak of SiO_2 sphere exhibits different degree of broadening as shown in figure 1a. To better compare the broadening behavior, figure 1b shows the full widths of the EELS peaks at different intensities. Notice that broadening is smaller for the SiO_2-Si_3N_4 case than the other two cases.

In the case of extreme weak coupling, a Si_3N_4 thin film support behaves like a vacuum-like element for silica spheres because its dielectric function (ε) is near 1 in the energy range of the surface phonon modes of silica (from around 132 to 153 meV). As a matter of fact, we have found that the fast electron can excite several multipolar surface phonon modes with energy separations and relative intensities similar to the case for a single SiO_2 sphere in free space (figure 2a). This agrees very well with the simulated spectrum derived from Mie theory by considering up to 49 spherical surface phonon polariton modes. Our finding demonstrates that in order to minimize the interaction with a substrate, the selection of substrate should be carefully done according to its dielectric properties (whether its real part is close to 1) in the resonant energy range of the nanostructure.

In the case of surface multipolar phonon modes-Fuchs Kliewer coupling, we have first considered the dominant interaction between a Frohlich excitation (dipole mode) of the sphere and a Fuchs Kliewer mode of the thin film. As a result of this strong interaction, two new hybrid modes are generated as shown by the energy splitting behavior in the polarizability plot of the composite system (figure 2b) [6]. The contributions of those new hybrid surface modes to the total scattering are also indicated in figure 2c (m^- = 1 and m^+ = 1). Scattering contributions from additional higher order hybrid surface modes (m^+ = 2, 3, 4 …) are needed to account for the total scattering signal, and to properly describe the coupling process between surface phonon interaction.

In the case of surface phonon modes-image charge coupling, we have also noticed the extra broadening with asymmetry in the EELS peak (figure 1). In this scenario we expect that the dipolar mode on the sphere interacts with its own mirror image formed in the substrate creating a new hybrid mode at a lower energy position. Generally speaking, the charge polarization of multipolar surface phonon polaritons on the silica sphere can induce a charge redistribution on the carbon substrate (real dielectric function ~ 2.5) at its resonant energy range [7]. This charge redistribution on the substrate behaves as image multipolar charges and interacts with the charge dipole and multipoles on the sphere, which then creates a new set of hybrid surface phonon polariton modes that characterize the image charge interaction in the composite system. We have also found that those effects are more prominent for substrate with larger dielectric functions.

In summary, we have performed EELS studies in sphere-film composite systems and investigated different mechanisms driving interactions between surface phonons. The coupling leads to generation of new hybrid/mixed modes resulting in broader resonances. This study highlights the role of the multipolar surface phonon polariton coupling in sphere-substrate systems in the nanoscale, and it reveals experimentally the underlying physics of various surface phonon polariton interactions [8].

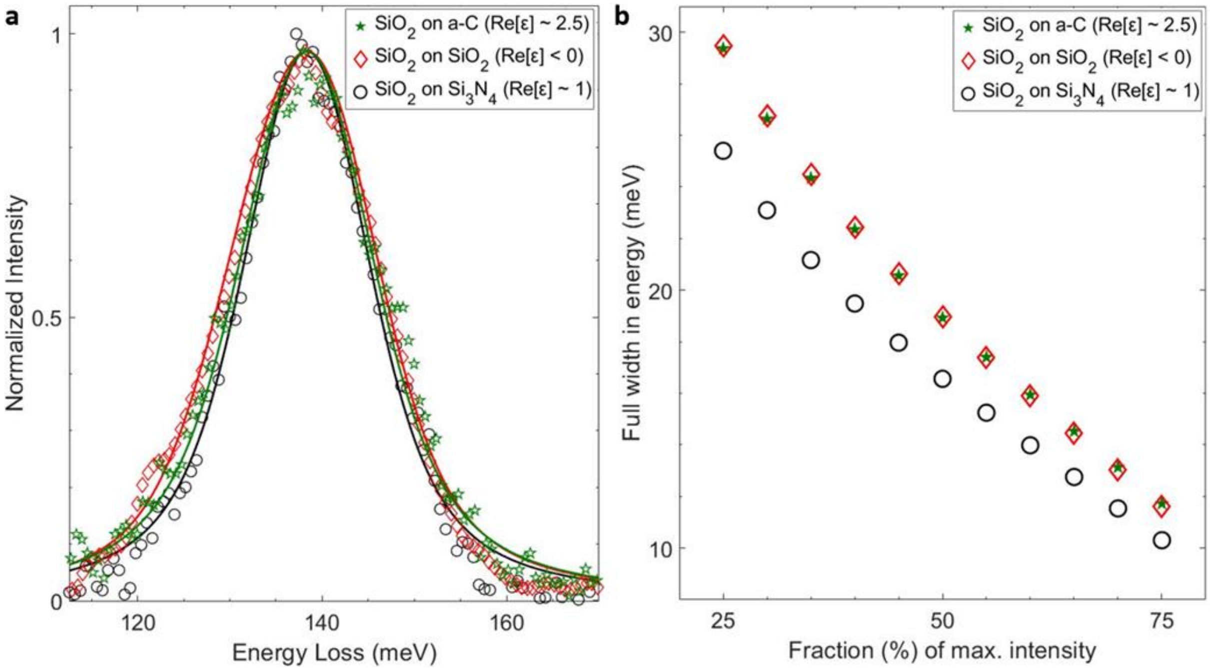

Figure 1. (a) Background subtracted, normalized, and aligned experimental EEL spectrum obtained for an amorphous SiO2 sphere of radius 150 nm supported on different dielectric substrates (indicated in the inset) of thickness ranging between 10 to 15 nm. (b) A plot of full widths from 25% to 75% of the maximum intensity for spectra shown in a. Error bars in energy ~ 1 meV.

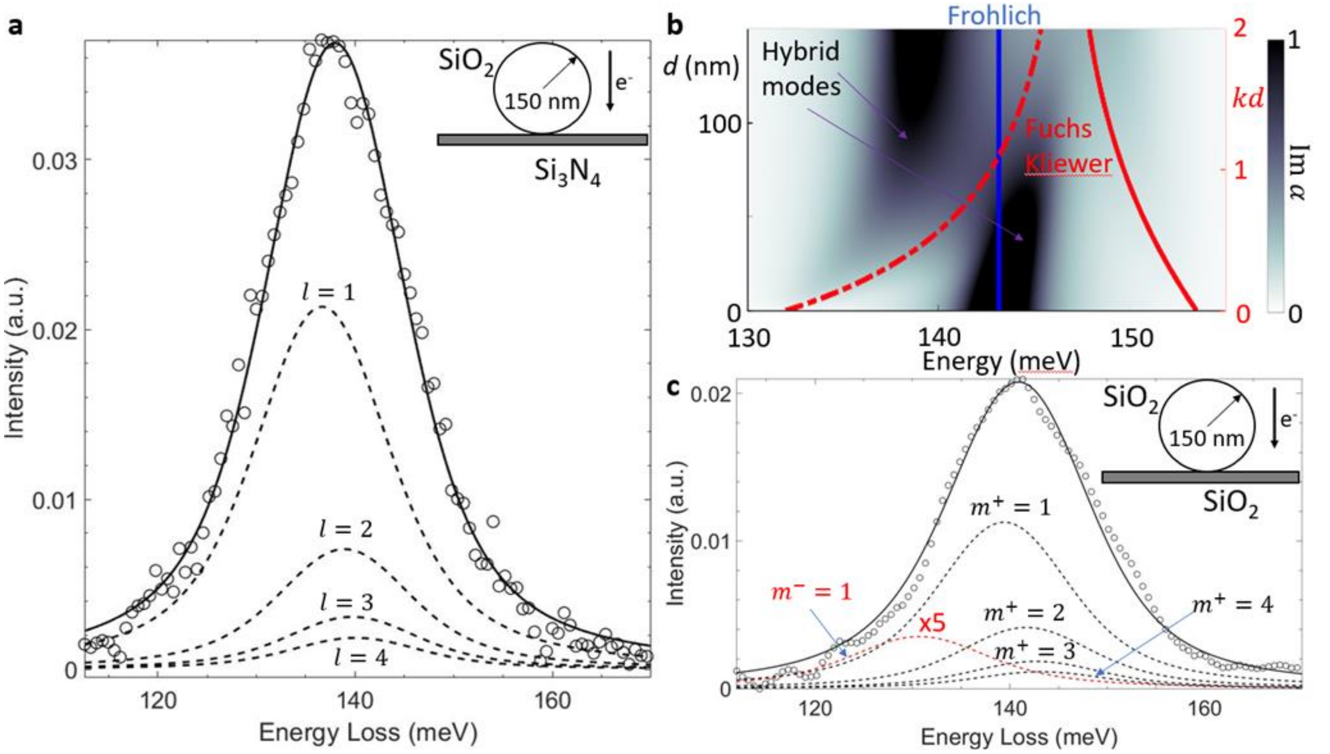

Figure 2. (a) Fitting analysis of the experimental EEL spectrum of an a-SiO_2 sphere supported on 10 nm thick Si_3N_4 substrate, acquired in a configuration shown in the inset. $l = 1$ dotted curve represents the inelastic scattering intensity from the dipolar mode, other l's denotes higher order multipole modes. Contributions up to $l = 4$ are shown for simplicity (b) Imaginary part of the normalized polarizability (Im α) along the direction of the electron beam trajectory for a silica sphere on silica thin substrate of thickness d. Red lines represent the Fuchs Kliewer dispersion with different wavevectors k. The blue solid line indicates the Frohlich mode energy. (c) Fitting analysis of the experimental EEL spectrum of an a-SiO_2 sphere supported on approximately 10 nm thick a-SiO_2 substrate. Red ($m^- = 1$) and black dotted lines ($m^+ = 1, 2, 3, 4$) are scattering intensities from the lowest order, and the higher order hybrid surface phonon polariton modes respectively. Contributions up to $m^+ = 4$ are shown for simplicity.

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