

INFRARED PHONON FINGERPRINTING OF NANOCRYSTALS THROUGH BROADBAND NEAR-FIELD SPECTROSCOPY.

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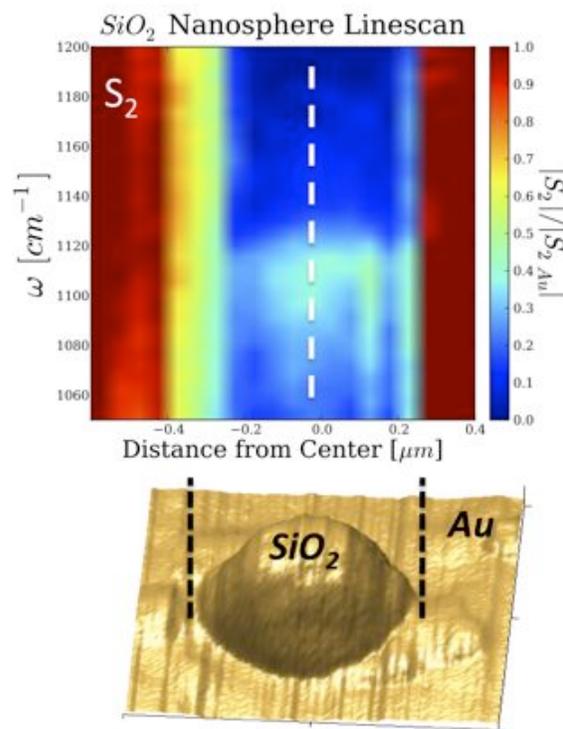
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Summary: Near-field infrared spectroscopy has recently been demonstrated with the ability to resolve optical properties of sub-wavelength sample areas across a broad range of infrared frequencies [1]. This method holds promise for the direct identification of sub-wavelength chemical composition in nanostructured and heterogeneous samples. We apply this technique to the study of phonon-resonant silicon carbide nanocrystals and silicate nanospheres tens of nanometers in size using a scattering mode scanning near-field optical microscope (s-SNOM) coupled to a pulsed broadband infrared laser source and FTIR spectrometer.

Measurements of nanocrystal near-field spectra in the range of 700-1300 cm^{-1} are obtained with this technique and evaluated in comparison with near-field spectra of bulk silicate and silicon carbide. Material properties are calibrated with ellipsometry, X-ray diffraction and e-beam techniques. A detailed analytic model of the probe-sample near-field interaction is applied for the identification of nanoscale resonant size effects. Work is in progress to correlate spectral signatures of nanoparticle crystal defects with transmission electron microscopy measurements of lattice structure in individual particles.

Experimental Setup: An apertureless scattering-mode scanning near-field optical microscope (s-SNOM) was utilized for the phase identification of nanoscale crystals through near-field spectroscopy. The microscope operates by focusing collimated infrared laser light on a metallic tapping-mode AFM probe, confining radiation at the probe's 20 nanometer tip apex. The confined field locally polarizes the surface of a sample, which mutually interacts with the probe tip. Material contrasts modulate charge separation within the tip, providing material sensitivity through the intensity and phase of back-scattered radiation [2]. Background-free detection is accomplished by demodulating the back-scattered radiation signal at harmonics of the AFM tapping frequency [3].

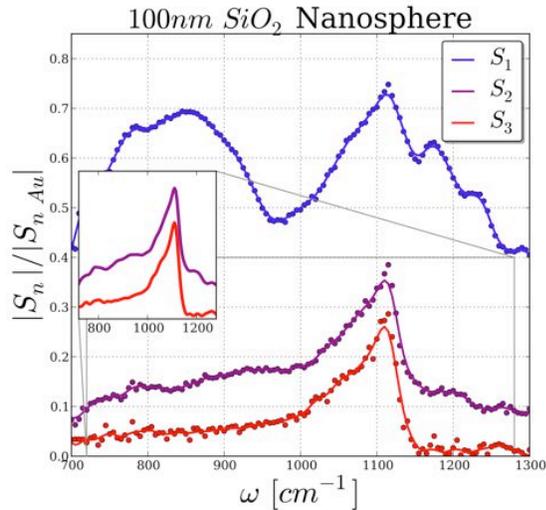
A femtosecond pulsed mid-infrared laser source provides broadband illumination tunable across 700-1400 cm^{-1} , while a translating mirror in Michelson interferometer configuration produces an interferogram from the back-scattered signal. This enables FTIR point- or linescan-spectroscopy with 10 nm spatial resolution and 3 cm^{-1} spectral resolution [4]. By nor



-malizing near-field spectra to featureless reference materials such as gold for each alignment of the apparatus, spectroscopic characterization becomes both reproducible and quantitative.

Nanoparticle Spectroscopy: The sensitivity of near-field spectroscopy is used to measure the optical properties of silicate and silicon carbide nanoparticles in comparison with their bulk counterparts [5]. This investigation is critical for the development of non-destructive sub-diffraction identification procedures applicable to presolar grains and nanocrystals, such as those sought amongst geological and extraterrestrial samples [6].

60 nm diameter ball-milled silicon carbide nanoparticles and 50-150 nm colloidal silicate nanospheres were deposited on gold substrates, then individually identified with AFM and characterized through near-field spectroscopy. Fig. 3 displays the AFM topography, spectral linescan, and near-field spectra for one such 100 nm silicate nanosphere. Appropriate control of the near-field probe position and illuminating laser power allows these particles to be rendered immobile and measured non-destructively.



Theoretical Analysis: We analytically predicted near-field spectra obtained for nanoparticle and substrate samples using a realistic model of the tip-sample interaction derived from electrodynamics. Modeling results confirm successful “phonon fingerprinting” of individual nanoparticles according to their material dielectric properties. In practice, best-fit effective dielectric properties might be extracted from samples by comparing modeling results with measured near-field spectra.

We calibrated our model through comparison with the near-field spectra of bulk silicon carbide and silicon dioxide wafers, applying knowledge of their infrared optical constants measured directly with ellipsometry. Bulk silicon carbide crystallinity was verified by electron channeling.

Size Effects and Defect Signatures: Size-effects due to nano-scale phonon confinement were evaluated systematically using these techniques by comparing near-field measurements for identically shaped silicate nanospheres of diameters ranging from 50 to 150 nanometers. Whereas the precise “failure point” of bulk optical constants in nanometric geometries has been tenuously suggested in conventional Raman spectra of nanoparticle ensembles, our measurements show direct sensitivity to bulk-nanoscale transition effects, including the red-shifting and asymmetrization of infrared phonon resonance peaks with decreasing particle size [7, 8].

Nanocrystals found amongst in-situ samples are hardly expected to be ideally spherical or uniformly crystalline. To evaluate spectroscopic evidence of defects, X-ray diffraction and transmission electron microscopy measurements will be used to characterize silicon carbide particles for which near-field spectra were obtained.

Effects of this sort have never before been identified in isolated individual nanoparticles, marking significant step toward nanoscale structural and chemical sensitivity with direct application to the analysis of returned samples.

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