SCANNING SCATTERING NEAR-FIELD INFRARED MICROSCOPY: A NEW TOOL FOR THE MAPPING OF FUNCTIONAL GROUPS AT THE TEN NANOMETER SCALE. G. Andreev[1] G. Dominguez[2], Z. Gainsforth[3], A. J. Westphal[3], D. Basov[1], M. H. Thiemens[2], [1]Department of Physics, U.C. San Diego, 9500 Gilman Dr., La Jolla, CA ,[2] Dept. of Chemistry and Biochemistry, U.C. San Diego, [3] Space Sciences Lab, U.C. Berkeley

Introduction: While elemental, chemical, and isotopic analytical techniques have achieved sub-micron spatial resolutions, current mid-infrared (λ=25-2.5 μm) spectroscopic techniques used in the analysis of extra-terrestrial samples are generally limited by the diffraction limit (~ λ). Given that many planetary materials of interest exhibit heterogeneity at the submicron scale, the ability to discriminate between different functional groups is highly desired. Here we describe a new analytical technique that can discriminate between different functional groups at the nano-scale with a minimal amount of sample alteration. This instrument represents a major advance for the analysis of precious returned samples (e.g. Stardust).

Scanning Scattering Near-field Infrared Microscope (S-SNIM): We have implemented an IR mapping system that provides sub-micron scale resolution of substates using scattering near field imaging. Briefly, a modified atomic force microscope (AFM) and coherent radiation are used in combination to provide information about the dielectric properties of a material directly underneath the AFM tip (See Figure 1B). The interaction of a metalized AFM tip with the incident radiation, with frequency omega, creates an oscillating charge distribution on the AFM tip. This charge distribution in turn also induces the formation of a "mirror dipole" in the material directly underneath the AFM tip (See Figure 1A). These charge distributions scatter the incident light and the amount of scattering is a sensitive function of the tip-sample distance and the complex dielectric function of the sample directly underneath the AFM tip.

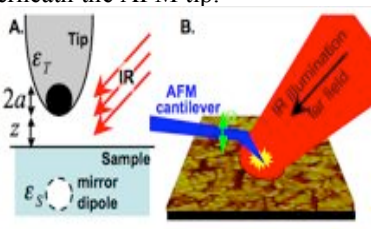


Figure 1. Principles of Operation of S-SNIM. A. AFM tip near the surface of sample. B. Illumination of AFM tip in tapping mode.

Following [1-2], the complex scattering response is given by $\Sigma = se^{i\phi} = E/E_i$,where E_i and E are incident and back scattered fields respectively. A solution of the mirror dipole model yields the following expression:

$$\Sigma = \frac{\alpha(1+\beta)}{1-\alpha\beta/\left(16\pi(a+z)^3\right)} \quad (1)$$

where a is the "radius" of the tip, z is the distance between the tip and the sample, α is determined by the complex dielectric function of the tip, ε_t as: $\alpha = 4\pi a^3 \frac{\varepsilon_t - 1}{\varepsilon_i + 2}$. is determined by the complex dielectric function of the sample ε_s as: $\beta = \frac{\varepsilon_s - 1}{\varepsilon_s + 1}$ (Figure 1A). Eq. (1) establishes that the scattered signal is governed by the dielectric function of the sample at the wavelength of illumination. Therefore Eq. (1) provides the foundation for nano-spectroscopy using S-SNIMs.

Results: We have made near-field maps of a commercially available Si/SiO_2 surface (See Figure 2) with nanoscale features using a using a Quantum Cascade Laser (QCL). Near field images of this substrate are shown in Figure 3 and the spectral response of an SiO_2 region is shown in Figure 4.

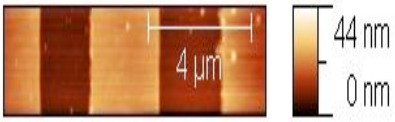


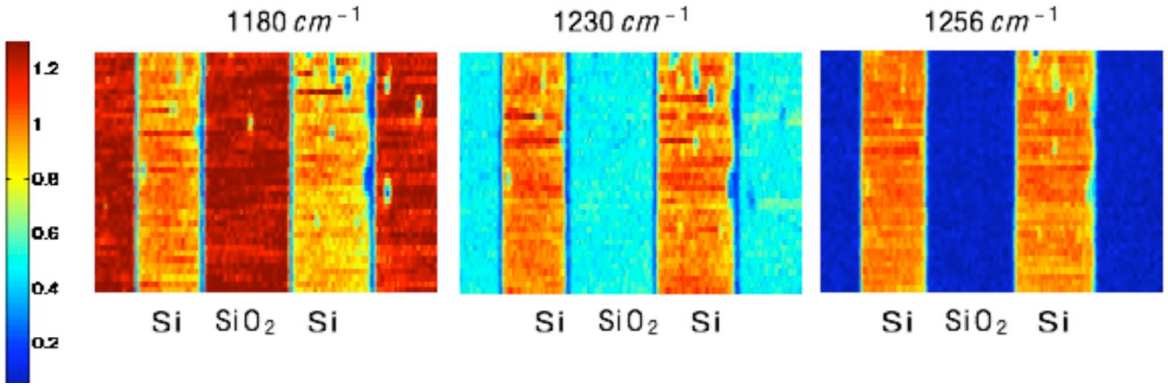
Figure 2. *Silicon (dark orange) and 20 nm thick SiO_2 (light orange) grating. Grating obtained from Anfatec.*

In order to refine sample handling techniques for use in the near-field instrument, we embedded 500 nm glass beads in Embed 812. These samples were ultra-microtomed and sections were imaged using the near-field IR system. A typical S-SNIM image of these SiO_2 nanobeads in epoxy is shown in Figure 5. Over the wavelength region from 1180 cm-1 to 1256 cm-1, we found that Embed 812 did not have any measurable IR resonances. In contrast, despite the non-ideal topography of the SiO_2 beads, the near-field scattering signal increased as the illumination IR beam approached the theoretical resonance for Si-O. These are the first S-SNIM images of SiO_2 in thin (~50 nm) sections.

Discussion: We are currently exploring the instrument's ability to distinguish between SiC and SiO using both the amplitude and phase of the scattered IR beam. Tests using a variety of natural (Renazzo, Tagish Lake) and synthetic (standards) samples are

currently underway . Lastly we emphasize that the analytical technique is expected to be non or minimally destructive. Future work will characterize the alteration of fragile functional groups to determine appropriate sample handling procedures for returned samples.

Figure 3. *Spectral response maps of Si/SiO_2 gratings using Nano-IR system with Daylight Solutions QC laser. Spectral response output shown in Figure 4. The scattered signal (n=3) is normalized to that of Si for calibration. Each rectangle measures 2x10 microns in size. This scan achieved spatial resolutions (pixel size) of 50 nm, although higher resolutions scans of ~ 8nm have also been achieved with this system. Figure taken from publication in prep. detailing this work with SiO_2 standards (Andreev et al., in prep.). Scan time ~ 10 milliseconds per pixel.*



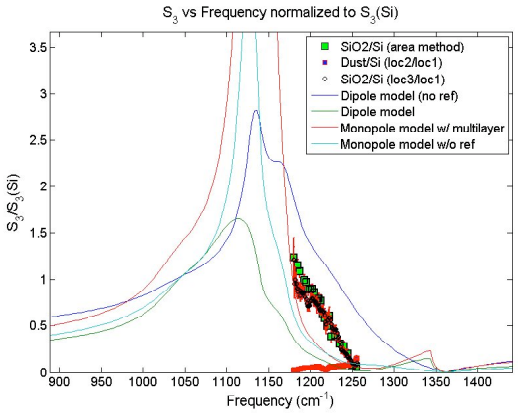


Figure 4. Figure taken from publication in prep. detailing this work with SiO_2 (Andreev et al., in prep.). S_3 refers to the n=3 harmonic in the scattered signal of SiO_2 normalized to the n=3 scattered near field signal from the Si substrate. Dust/Si refers to the scattered signal spectrum acquired in a region of the sample which had a speck of non-sillicate dust and illustrates the specificity of the nanoIR to composition. Various methods of extracting the spectral response of the material were used to obtain the observed spectra. The "area method" averages hundreds of pixels in both SiO2 and Si. The point by point yields the spectral response of individual pixels (loc 1, loc 2, loc 3) and their corresponding regions of interest (Si, Dust, SiO_2) are also shown. There is good correspondence between these two methods, which demonstrate the robustness of the spectral technique at the 50 nm scale. The observed spectral response is consistent with various models of the interaction between the tip and sample near resonance.

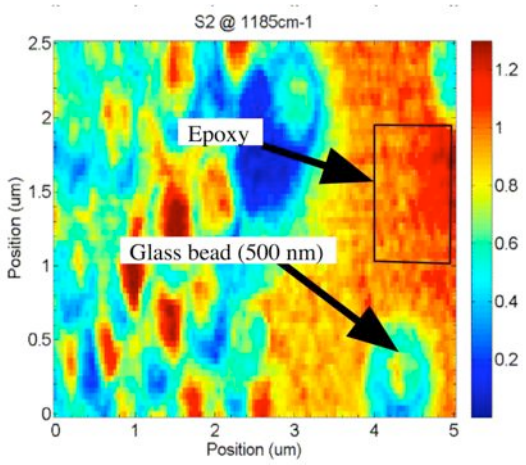


Figure 5. SiO_2 beads embedded in Embed-812 and imaged at 1180 cm^{-1} using the second harmonic of the AFM modulated scattered signal (S_2). Spectral response of epoxy was found to be "flat", while SiO_2 near-field signal increased as l approached resonance.

Acknowledgements: This work was supported by NASA Grant NNX08AI15G.

References: [1] Taubner T., Hillenbrand R., Keilmann F., Journal of Microscopy, 210,311 (2002). [2] R. Kersting, H. T. Chen, N. Karpowicz, G. C. Cho, J. Opt. A: Pure Appl. Opt. 7, S184 (2005) [3] J. M. Gerton et al., Phys. Rev. Lett. 93, 180801 (2004) [4] Andreev G. et al., in prep.