

SCANNING NEAR-FIELD INFRARED MICROSCOPY

Edward S. Gillman

Jefferson Lab

12000 Jefferson Avenue

Newport News, VA 23606

Commonly, location specific chemical identification by means of vibrational spectroscopy in the infrared region is largely restricted to samples of macroscopic dimensions, on the order of one to several microns; the scale of the examined area is completely determined by the diffraction limit of the incident radiation. However, chemical identification at length scales less than the diffraction limit is possible using a scanned probe technique, the Scanning Near-Field Infrared Microscope (SNFIM). Using a scanned probe technique in the near-field, resolution of chemical features on the order of $\lambda/20$ or ≈ 100 nm can be achieved. An overview of previous experimental results using a free electron laser (FEL) and more conventional infrared sources will be discussed. Recent results from the SNFIM experiment at Jefferson Lab will also be presented.

INTRODUCTION

Vibrational spectroscopy in the mid-infrared region ($400 - 4000 \text{ cm}^{-1}$) is a widely used tool for quantitative and qualitative chemical identification in a variety of disciplines. The technique relies on the intramolecular vibrational absorption to reveal molecular or submolecular concentrations and discriminate between different chemical states based on the line shape or "fingerprint" of the resonance. The spatial resolution of vibrational spectroscopies is normally diffraction limited; the smallest area that can be resolved is of the order of 1 to several microns in size, comparable to the wavelength of the electromagnetic radiation that is absorbed. Optical resolution better than the diffraction-limited case is possible with a near-field scanning optical microscope (NSOM); the enhanced resolution of the NSOM is due to the fact that it relies on near-field probing rather than beam focusing (1,2,3). Thus a NSOM that utilizes absorption of mid-infrared light as the contrast mechanism can in principle make chemical assignments to nanoscale features.

Near-field vibrational spectroscopic methods have been investigated previously and contrast has been observed from near-field Raman scattering and infrared absorption (4,5,6,7,8,9). Near-field methods that rely on Raman scattering are fundamentally limited by the small scattering cross-section, typically $\sigma \approx 10^{-30} \text{ cm}^2$. In the absence of unusually

large scattering cross-section and/or surface enhancement of Raman scattering (SERS), near-field measurements utilizing Raman scattering as the contrast mechanism will depend critically on developments that enhance the signal-to-noise ratio and do not compromise the spatial resolution of the near-field probe (10,11). On the other hand cross-sections for infrared adsorption are significantly greater than for Raman scattering. This has stimulated the interest in near-field optics and probes by a number of groups. Near-field infrared microscopes that use aperture probes formed from optical fibers of various types as well as apertureless approaches have been reported in the literature (6,7,8,10,11,12,13,14,15).

The apertureless approach is notable since such probes allow for significantly higher spatial resolution than is possible with optical fibers due to the limitation of the optical throughput for mid-infrared radiation. In this technique a metallic coated scanning probe microscope (SPM) cantilever tip acts as an antenna and in the presence of an electromagnetic field serves as a field-concentrating scattering center (16). The signal observed from this experiment consists of a large background due to scattering directly from the cantilever tip, which has superimposed on it scattering due to the interaction of the tip and the sample in the near-field. The signal derived from the interaction of the tip and the sample depends on the tip geometry, the distance of the tip from the sample and the dielectric properties of the tip and the sample. The background due to scattering directly from the cantilever tip can be reduced using a lock-in amplifier when the reference signal is equal to the resonant frequency of the cantilever.

This paper reports on the first experimental results obtained from the apertureless scanning near-field infrared microscope (SNFIM) at the Jefferson Lab FEL user facility of near-field infrared images of 2-amino-nitrotoluene (MNA) vapor deposited on a Si(100) substrate. Details about the parameters of the FEL are published elsewhere (17). The FEL is still a valuable resource for this experiment because it is one of the few continuously tunable laser sources in the mid-infrared region with sufficient brightness.

EXPERIMENTAL

The SNFIM used for these experiments is based on a commercially available scanning probe microscope (SPM) (JEOL JSPM-4200) operated in a non-contact tapping mode. This instrument has a fixed cantilever and utilizes a piezoelectric sample scanner to control the position of the sample. Commercially available silicon cantilevers coated with gold (MikroMasch) served as the atomic force probe as well as the apertureless probe for the near-field infrared measurements. The beam from the FEL was focused on the cantilever tip with a CaF₂ lens. The position of the beam on the cantilever tip was precisely controlled with a five-axis picomotor stage. The forward scattered radiation was collected with a peltier-cooled PbSe detector (Cal Sensors). The output of the PbSe detector was fed into a RF lock-in amplifier (SRS 844). An external oscillator that was used to drive the cantilever provided an external reference for the lock-in amplifier. The resonant frequency of the cantilevers was \cong 350 KHz; the frequency varied slightly with each individual cantilever.

The sample was scanned using the piezoelectric scanner and two images were collected simultaneously, the deflection of the cantilever vs. x-y position (topographic

image) and the output of the PbSe detector vs. x-y position (near-field infrared image). Atomic force feedback from the SPM insured that the probe remained in the near-field without making contact with the sample while the images were obtained. In these experiments careful control of the FEL power is critical. The FEL can easily supply too much power to the cantilever. In extreme cases this immediately vaporizes the cantilever, but in less extreme cases the mechanical properties of the cantilever can be changed enough to drive it out of resonance resulting in loss of force feedback. During the measurements the whole experimental setup was purged with nitrogen to prevent additional attenuation of the FEL and scattered infrared radiation due to H₂O and CO₂.

Figure 1 shows the images collected from the SNFIM at 5140nm of vapor deposited MNA/Si(100). Arrows in the infrared images indicate areas of high contrast, which can be correlated with features in the topographic images. The areas of high contrast are attributed to enhanced infrared absorption. The dots in the infrared images are $\cong 800$ nm or $\lambda/6.5$. The elongated structure in the infrared image is $\cong 450$ nm across or $\lambda/12$. A second, essentially identical set of images was obtained at the same wavelength approximately ten minutes after the first images (bottom two images), which attests to the stability of the experimental setup during this measurement.

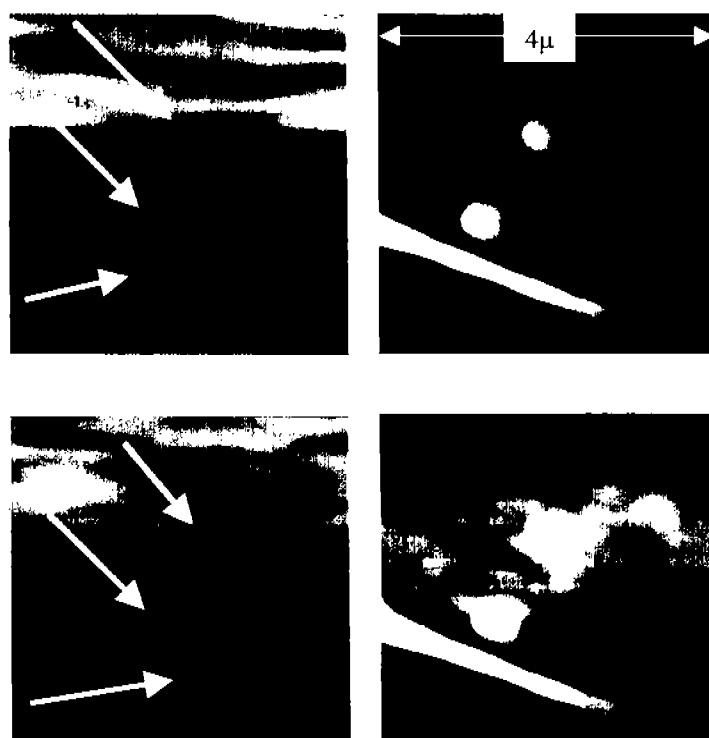


Figure 1 Images of MNA/Si(100) showing infrared contrast at 5140 nm (left) and topography (right) from the FEL SNFIM experiment. The upper two scans are from the initial measurement and the bottom two scans are from a second measurement made approximately ten minutes after the first measurement. Areas of infrared contrast (indicated by arrows) can be correlated with areas of high contrast in the topographic scans.

DISCUSSION

This experiment has demonstrated infrared contrast at a single wavelength, 5140 nm. Future experiments are planned that will discriminate infrared absorption at different

wavelengths. This will be the key to using this technique successfully for chemical identification on a nanoscale. Positioning the tip on a nanoparticle in the scan and continuously varying the wavelength of the FEL will allow chemical identification of nanoparticle in a manner analogous to Scanning Tunneling Spectroscopy (STS), which has been used to identify single molecules (18,19).

Although the images collected clearly demonstrate that optical resolution of features is possible with a mid-infrared SNFIM, controversy exists as to whether this is purely an optical response. As the images are collected the tip is constrained to move by a non-optical distance-control mechanism, atomic force feedback from the SPM. With this mechanism there exists the possibility that the z motion of the probe can couple to the purely optical information of the image, creating a "tip artifact" (20). In other words, the optical information may be dependent on the path that the tip follows during the scan. Unfortunately the images presented here cannot completely rule out this possibility. Further experiments are planned with infrared absorbers buried below the surface, so that topographic and optical signals can be completely decoupled.

CONCLUSIONS

The first images from the SNFIM at the Jefferson Lab were observed. Infrared contrast at 5140 nm from MNA/Si(100) is shown with sub-wavelength resolution. These experiments show the promise of extending the applicability of the SNIFIM technique to an area of great practical importance, chemical identification of nanoscale structures.

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