Nano-optical Imaging using Scattering Scanning Near-field Optical Microscopy Fehmi Yasin, Advisor: Dr. Markus Raschke, Post-doc: Dr. Gregory Andreev, Graduate Student: Benjamin Pollard Department of Physics, University of Colorado, Boulder, Colorado 80309

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It has long been a goal to achieve higher spatial resolution in optical imaging and spectroscopy. Recently, a concept emerged that combines optical microscopy with scanning probe microscopy, increasing the spatial resolution of optical imaging beyond the diffraction limit. The scanning probe tip's optical antenna properties and the local near-field coupling between its apex and the sample allows for few nanometer optical spatial resolution (Atkin, Berweger, Jones, and Raschke 2012). We investigate a nano-imaging technique, known as scattering scanning near-field optical microscopy (s-SNOM) and image several different materials using said technique. We report our data provide potential paths for future work.

I. INTRODUCTION

Scientists have long studied optical spectroscopy due to its ability to directly interact with the electronic, spin, and lattice excitations in matter. Even the real-time dynamics of elementary interactions can be studied when using ultrafast laser techniques. The problem with optical spectroscopy has always been the diffraction limit which restricts the achievable spatial resolution by the wavelength of the light used. Because of this limitation, optical spectroscopy has never become a primary research tool in solid state physics as it has in other applications such as biological, medicinal, and petrologic.

The desire to combine the spatial resolving power of tip-based scanning probe with the spectroscopic abilities of optics prompted the emergence of tip-enhanced or tip-scattering scanning near-field optical microscopy. In this method, the apex of a sharp (metallic or

semiconducting) scanning probe tip of an atomic-force microscope is illuminated using infrared laser light as shown in Figure 1.



Figure 1. s-SNOM depicted conceptually. The incoming infrared (IR) laser light excites the electrons in the tip and creates a dipole reradiates evanescent waves which reflect off of the sample and interact with the tip. Note that the spatial resolution is now determined by the radius of the tip's apex as opposed to the wavelength of the incoming light. *Note: Image taken from (Atkin, Berweger, Jones, and Raschke 2012).

S-SNOM allows for nanoscale spatial resolution because the spatial resolution is no longer determined by the wavelength of the light, but by the radius of the tip's apex.

In addition to increased spatial resolution, s-SNOM can be used for characterization of materials because it utilizes IR light, which has the characteristic of vibrating molecules at their resonant frequency. If the resonant frequency of a molecule is known, the location of the molecule in the material could be determined which could enlighten us about the formation of certain materials like block-copolymers, and perhaps disband any preconceived notions in favor of data influenced theories of their formation. The application of s-SNOM as a tool for optical nano-imaging could provide nanoscale characterization of correlated and topological matter, vaulting it to the head of future work in optical imaging and in particular, nanoscopy.

II. EXPERIMENTAL

There were two IR lasers used to provide the illuminated IR light necessary in s-SNOM. The first is a CO_2 gas laser which emits light with a wavelength of around 10.6 μ m. The second is called a Quantum Cascade Laser (QCL) and uses a series of semiconductors stacked on one another to tunnel electrons down the stack in order to emit photons. The QCL allows for a wide range of tunable wavelength in the same material system which is useful for two reasons. First, it allows us to image a sample using s-SNOM using multiple wavelengths without having to change the laser. Second, it allows us to probe the sample for certain molecules with known resonance frequencies so that we can image the position of these molecules within nanometer resolution.

The IR laser light illuminates a silicon tip with an apex radius of around 10 nm that is mounted onto the head of a Bruker Innova Atomic Force Microscope (AFM). Using the tapping mode, the tip oscillates vertically with a frequency of around 250 kHz while in contact with the sample and scans the sample, creating a topographical image as shown in the results section of this paper. The tip also couples to the sample as described in the introduction, and these near-field interactions are seen through an MCT (HgCaTe) detector and imaged simultaneously using a Zurich Instruments HF2LI Lock-in Amplifier. If the near-field signal shows an image that has contrasting images, then the molecules are in fact vibrating at a resonant frequency.

There is a case, however, where the laser does not initially create a dipole in the tip, and that occurs when the laser light is horizontally polarized, as with the CO_2 laser. In this case, we imaged gold antennas of resonant length with the laser wavelength. This horizontally polarized light oscillates the electrons in the antenna, which creates an oscillating dipole in the antenna and couples with the tip which in turn creates a dipole in the tip that then re-radiates the light back through the optical system, which is pictured below.



Figure 2. Here, the path of the IR laser light is shown. The HeNe laser is used to align all of the optics because it emits in the visible spectrum. Note that the CCD camera is used to align the tip, because the light from an overhead camera in the AFM system (not shown) illuminates the tip and then travels down the beam path to the CCD camera which images the tip.

The IR light travels through the wedge beam combiner and then travels down a path of optics approximately three meters long in order to increase the diameter of the beam. The light then spits and travels to the piezo mirror and also to the AFM tip where it scatters and returns down the same path, recombining with the light that reflects off of the piezo mirror after passing through the beam splitter one more time, and then it enters the MCT detector as shown.

III. THEORETICAL

The detector couples to the Zurich Lock-in Amplifier which takes the incoming waves and multiplies them by a sine wave that is of the same frequency that we want to measure (the frequency of the tip oscillation). The lock-in amplifier then integrates over a time which cancels all of the unwanted frequencies because by multiplying by a sine wave, you essentially multiply by 1 or -1, and only the wave that is in phase with the multiplied reference (sine) wave and has the same frequency will be multiplied by 1 consistently [1*1 or (-1)*(-1)]. The s-SNOM system also uses a technique called pseudo-heterodyne, which is the purpose of the piezo mirror shown in Figure 2. Essentially, the mirror oscillates through space a certain distance, altering the phase of the incoming wave that recombines with the scattered light from the tip. This change in phase causes the two waves recombining to interfere either destructively or constructively. The mathematics will not be discussed here, but for more information, check the references.





2 µm Fig. 5 2nd Harmonic s-SNOM near-field image

2.0 1.0

0.1

These figures each depict two antennas that are separated at the center of the image. It is important to note that in the near-field image, the two ends are dark. This occurs because as the electrons oscillate in the antennas, they oscillate similarly to a classical oscillator. That is to say that the electrons spend more time at the ends of the antennas than in the center. Theoretically, the higher the harmonic s-SNOM image, the higher the resolution, but the lower the signal

strength. After the 3rd harmonic, the loss of signal strength is generally too much to justify the slight resolution gain.





Fig. 6 Topographical image for block-copolymers PMMA and PS





Fig. 8 3rd Harmonic s-SNOM near-field image with 5.714 µm wavelength IR light

These figures display images of the block-copolymers Poly-methyl methacrylate (PMMA) and Polystyrene (PS) in the micelle formation meaning that the PS clump together while the PMMA form a boundary around the PS. This formation occurs when there is much more PMMA than PS. PMMA contains carbonyl bonds which have a resonant wavelength of $5.780 \mu m$. Figure 7 clearly shows a contrasting image because it is at a frequency near the resonant frequency of the carbonyl, whereas Figure 8 does not have a high contrast image because it is too far from the resonant frequency of the carbonyl bonds.

In Figure 9 below, the block-copolymers are in a worm formation. This formation occurs when there are relatively the same amount of PS polymers to PMMA. We theorize that the polymers tend to form layers where the PMMA and PS are stacked on top of each other. However, as shown in the PS-like spectrum below, there is a slight increase in phase near the resonant frequency of carbonyl, suggesting that some PMMA also exists there. Perhaps our theory of formation needs modification.



Fig. 9 Upper left: PS-like spectrum showing the contrast in the area shown in the lower left image [as compared to the silicon substrate (bright white strip] that we believe to contain PS as opposed to PMMA. Upper right: PMMA spectrum showing the contrast from the area in the lower right image that we believe to contain PMMA. As it should, the phase spectrum peaks at the resonant frequency of the carbonyl, which exists in PMMA.

V. CONCLUSION

Scientists will continue to strive for higher resolution techniques to image the nano-world in order to explore that which we have never been able to in such detail as now. As new techniques are engineered and innovated, s-SNOM might eventually become outdated. But currently, it is a state of the art technique that takes advantage of both the imaging of scanningprobe microscopy and the characterization potential of IR imaging. Both characteristics are important for future advances in microscopy, nanoscopy, and potentially picoscopy.

References

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