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Preliminary characterization of plasmons in low temperature carbon nanotubes

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14. ABSTRACT

The overarching long term objective of this research is to demonstrate control of propagating plasmons in single walled carbon nanotubes (SWCNTs) that have applications to quantum information technologies. Specifically, we will investigate the fundamental limits of plasmon propagation in 1D SWCNTs, which are believed to be governed by Luttinger liquid physics. Luttinger liquid plasmons (LLPs) are fundamental excitations of one-dimensional conductors and have only recently been observed in metallic SWCNTs. During our previous pilot program we successfully demonstrated growth of high quality SWCNTs on top of ultra-flat hexagon boron nitride (hBN) substrates, and successfully demonstrated propagation of IR LLPs using scanning near field optical microscopy (SNOM), being the first group to confirm the reports1,2, that motivated our investigation. Furthermore, in late 2018, LeRoy and Schaibley were awarded a NSF MRI award to purchase a $1.4M cryogenic SNOM instrument, allowing for us to measure the previously unexplored low temperature propagation of plasmons. Due to this new measurement capability, we requested to funding to perform preliminary low temperature measurements on SWCNTs in the cryogenic SNOM. Our hypothesis is that the propagation length of LLPs will be
greatly enhanced at low temperatures, and we will measure this propagation length using a scattering SNOM technique. Due to the COVID 19 pandemic the installation of the cryoneaSNOM was delayed and had to be installed completely remotely due to travel restrictions. Our primary results of this add on award are the successful remote installation of the cryo-neaSNOM at the University of Arizona (UA), demonstration.

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Final Report

Project: Preliminary characterization of plasmons in low temperature carbon nanotubes

PI: John Schaibley, University of Arizona

Co-PI: Brian LeRoy, University of Arizona

(1) Statement of Objectives

The overarching long term objective of this research is to demonstrate control of propagating plasmons in single walled carbon nanotubes (SWCNTs) that have applications to quantum information technologies. Specifically, we will investigate the fundamental limits of plasmon propagation in 1D SWCNTs, which are believed to be governed by Luttinger liquid physics. Luttinger liquid plasmons (LLPs) are fundamental excitations of one-dimensional conductors and have only recently been observed in metallic SWCNTs. During our previous pilot program we successfully demonstrated growth of high quality SWCNTs on top of ultra-flat hexagon boron nitride (hBN) substrates, and successfully demonstrated propagation of IR LLPs using scanning near field optical microscopy (SNOM), being the first group to confirm the reports[1,2], that motivated our investigation. Furthermore, in late 2018, LeRoy and Schaibley were awarded a NSF MRI award to purchase a $1.4M cryogenic SNOM instrument, allowing for us to measure the previously unexplored low temperature propagation of plasmons. Due to this new measurement capability, we requested to funding to perform preliminary low temperature measurements on SWCNTs in the cryogenic SNOM. Our hypothesis is that the propagation length of LLPs will be greatly enhanced at low temperatures, and we will measure this propagation length using a scattering SNOM technique. Due to the COVID 19 pandemic the installation of the cryo-neaSNOM was delayed and had to be installed completely remotely due to travel restrictions. Our primary results of this add on award are the successful remote installation of the cryo-neaSNOM at the University of Arizona (UA), demonstration of low temperature operation, and SNOM imaging of LLPs in the new system at UA.

(2) Research Effort

2.1 Project Background:

The long term application of the proposed research is to develop a single-photon transistor architecture based on plasmons in conducting single-walled carbon nanotubes (SWCNTs) coupled to single quantum emitters (SQEs) in a monolayer semiconductor. A single-photon transistor is a quantum switching device in which the transmission of a single signal photon is controlled by the action of single control

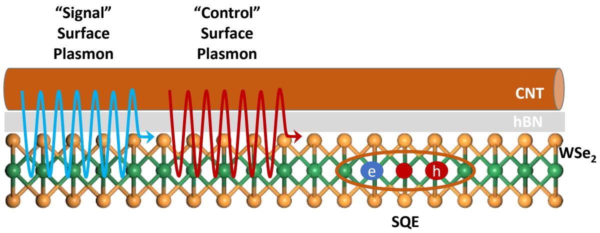

Figure 1: Single-plasmon transistor| A depiction of a single-plasmon transistor based on a SWCNT/hBN/WSe$_2$ heterostructure.

photon. Such a device has been highly sought after for applications in quantum information processing, where quantum nonlinear optics can be used to perform logic operations[3-6]. Single photon transistors require that the incident photons strongly interact with a highly nonlinear medium, such as a few level atom-like system, which saturates when it absorbs a single photon. The primary challenge limiting the development of single photon transistors is the coupling strength between a photon and the nonlinear medium. Over the past decade, there has been significant progress in developing trapped-atom and atom-cavity systems capable of observing single-photon nonlinearities, which have typically required trapping of atoms in vacuum chambers and elaborate optical cavity designs to overcome the primary challenge of the required strong light-atom coupling. The team is pursuing a nanoscale solid-state architecture, inspired by the theoretical work of Chang *et. al*[3], which showed that plasmons confined to nanoscale waveguides are ideal for realizing solid-state single-photon transistors. Our goal is to investigate the fundamental small-size limit for nanoscale waveguides, by confining the plasmons to single SWCNTs and then integrating them with nonlinear atom-like systems (Figure 1).

2.2 Results from pilot program:

In year one of the pilot program, our experimental efforts (Schaibley and LeRoy) focused on the fabrication of ultra-clean SWCNTs on hBN substrates. We pursued two different approaches: 1) drop casting of SWCNTs in solvent, and 2) direct growth of SWCNTs on hBN using chemical vapor deposition (CVD). In both approaches, the 10-50 nm thick hBN was obtained by mechanical exfoliation from bulk crystals (provided by Watanabe and Taniguchi). The drop cast method was successful in obtaining SWCNTs on hBN with an appropriate density; however, we found that removing the surfactant was unreliable, resulting in SWCNTs with significant contamination. The contamination was evidenced by non-uniform atomic force microscopy (AFM) heights along the tube length. Due to this contamination, we decided to pursue direct CVD growth of SWCNTs on hBN substrates. Our theoretical efforts have

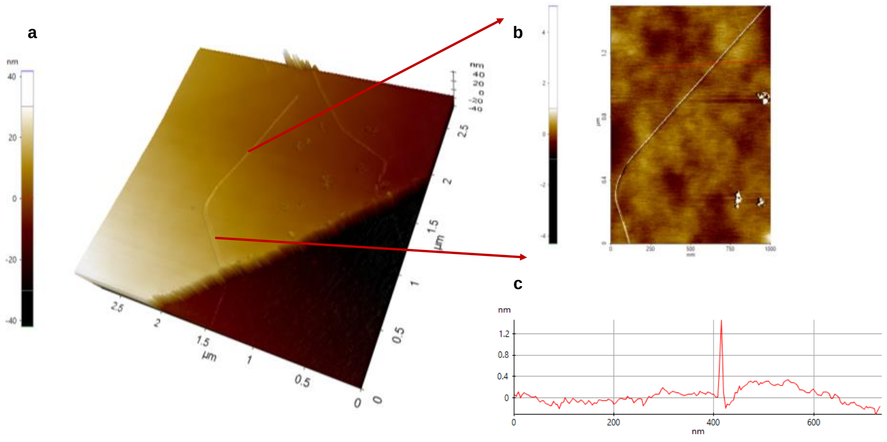

Figure 2: SWCNT on hBN| a) AFM height image of a SWCNT grown on hBN via CVD. b) Higher resolution AFM of a) The red line shows the location of the line cut which is plotted in c).

focused on understanding optical and near IR SPPs in doped metallic carbon nanotubes using the model described below.

2.2.1 CVD Growth of SWCNTs on hBN

We have developed a reliable fabrication process to grow SWCNTs on hBN. hBN was exfoliated on pre-cleaned SiO_2(90nm)/Si substrates. Once hBN flakes with thickness 10-50 nm were identified with an optical microscope, the substrates were spin-coated with two layers of poly (methyl methacrylate) PMMA and baked at 160 ^{0}C. Using electron beam lithography, small rectangular patterns were written on the edges of the hBN flakes to allow targeted dispersion of catalysts for carbon nanotube growth. The catalyst was prepared from a solution of 10 mg of MoO_2, 30 mg of Al_2O_3 and 40 mg $Fe(NO_3)_3$ dispersed in 30 ml of methanol. The precursor was drop cast on to the patterned area of hBN/SiO_2. After dispersion of the precursors, the substrates were baked at 170 ^{0}C for 8 minutes to remove the remaining solvent.

The PMMA was washed off by soaking it in acetone for 40 minutes and 5-10 min in methanol respectively. Consequently, the substrates were transferred to a CVD growth furnace. The samples were heated to 900 ^{0}C while Ar gas was flowing at a rate of 990 ml/min. The CNT growth was started after the temperature reacheed 900 ^{0}C, by flowing H_2 at a rate of 710 ml/min and CH_4 at 900 ml/min. The total growth time for the SWCNTs was 10 minutes. After the growth was complete the samples were cooled at a rate of 5 degrees/min while Ar gas was flowing. An example of an ultra-clean SWCNT grown on hBN is shown in Figure 2.

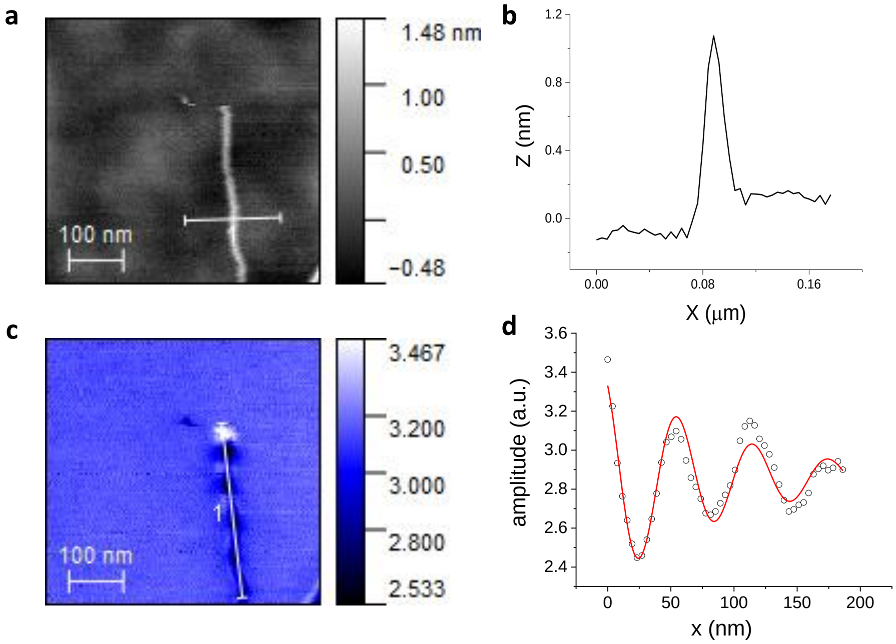

Figure 3: LLP propagation in SWCNTs| a) AFM topography of a SWCNT. b) CNT diameter from the line cut in a). c) SNOM amplitude for excitation wavelength of 10 μm. d) Amplitude oscillation along the tube in c).

2.2.2. Propagation of IR surface plasmons in SWCNTs

Through our collaboration with neaspec GmbH, we demonstrated propagation of LLPs at room temperature using a scattering-SNOM technique. Here, an IR (10 µm) laser is focused onto the metalized SNOM tip, which serves both to launch plasmons and to scatter them back to free space photons. The scattered light is recorded as the sample is scanned under the tip. The AFM topography and line cut are shown in Figure 3a-b, and the corresponding scattering-SNOM image is shown in Figure 3c. Figure 3c shows clear plasmon oscillations along the SWCNT whose line cut is shown in Figure 3d. By fitting the data with an exponentially decaying sine function $Ae^{-\frac{2\pi x}{Q\lambda_p}}\sin(\frac{4\pi x}{\lambda_p})$, we obtain a plasmon wavelength of 120 nm and a Q factor of ~20, where $A, x,$ and λ_p are the amplitude, position and wavelength of the plasmon.

2.2.3 Theory of SPPs in SWCNTs

Our theoretical efforts during the pilot program (lead by García de Abajo) focused on understanding of plasmons in SWCNTs. This includes a careful investigation of Fabry-Perot (FP) resonances that occur due to reflections of SPPs within the SWCNT. These resonances are important for our project because they effect the dispersion of plasmons. Here, we consider the lowest order resonance of a 1 eV doped metallic SWCNT. Figure 4a depicts the geometry used in the model, where we consider a SWCNT with length L, thickness t and diameter D. Figure 4b-c show the scattering cross section (σ) of the FP resonances as a function of tube length L. We see that for short tubes on order of L=10 nm, the FP resonance occurs near 0.6 eV. For the long tubes ~ 2000 nm, we see that the FP resonance occurs below 10 meV. Figure 5 shows the dispersion relation for plasmons, again for the case of 1 eV Fermi energy where the longitudinal k-vector ($k_{//}$) is determined by the relationship $k_{//} = \pi/L$. We see that for longer tubes, the dispersion becomes nearly continuous, whereas short tubes (large k-vectors) take on discrete values. These results motivated the use of SWCNTs longer than 1 µm and Fermi energy above 1 eV.

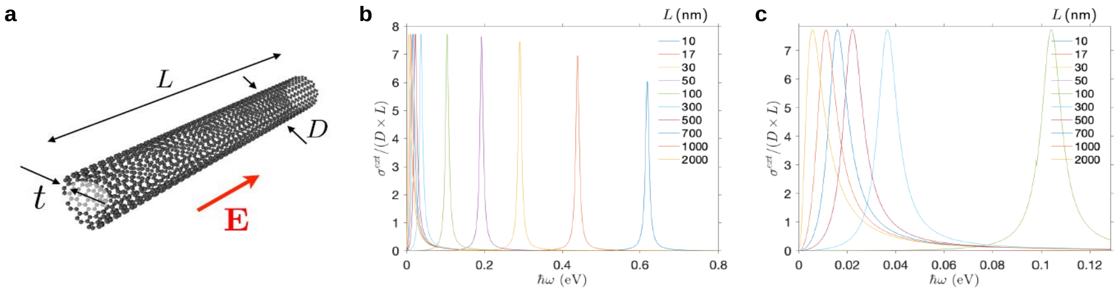

Figure 4: Fabry-Perot Resonances in SWCNTs| a) Depiction of SWCNT geometry. b) Scattering cross section (σ) of SWCNTs is plotted as function of energy for tubes of different lengths (L). c) Zoom in of the low energy resonances shown in b).

2.3. Experimental Plan:

To date, the measurements of LLPs in SWCNTs on hBN have focused on IR plasmons (corresponding to free space wavelength on order of 6-10 µm) at room temperature under ambient conditions. One key figure of merit, the propagation length of plasmons is characterized by the Q factor. At room temperature this Q-factor is on order of 20 (see Figure 3c-d), consistent with previous reports[1,2]. At 10 µm excitation, this limits the propagation length of plasmons to ~ 2 µm, but it is not currently understood how the-Q factor scales with temperature and plasmon energy, warranting further experimental investigation. Indeed, it is likely that the propagation length will significantly increase with lowered sample temperature, evidenced by a recent report of ~5 fold increase in the plasmon propagation length in graphene at liquid nitrogen temperatures[7]. In order to investigate the fundamental limit of plasmon propagation, we will directly measure the Q-factor of plasmons at temperatures down to 10 K. At low temperature, we expect to observe significantly longer propagation lengths due to reduced scattering, potentially enabling the demonstration of plasmons over long (several micron) length scales. In addition, we will explore the propagation of NIR/visible wavelength plasmons, and how they couple to SQEs in 2D materials.

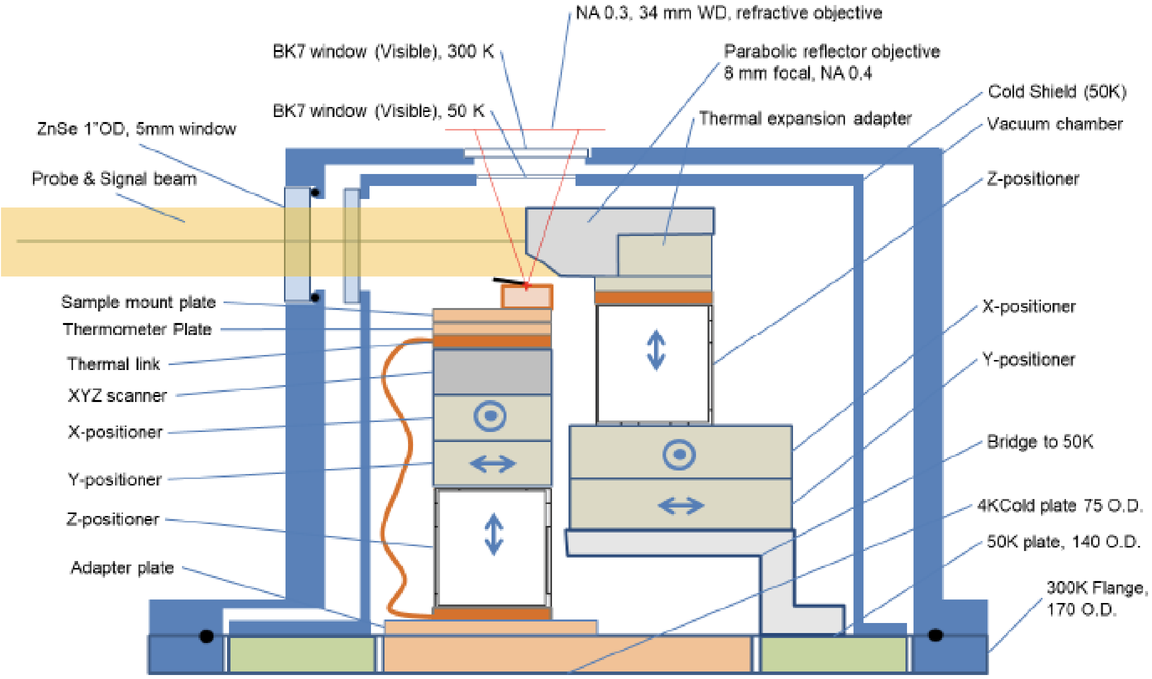

Figure 5: Schematic of the cryogenic SNOM design.

We will carry out these experiments in a cryo-neaSNOM from neaspec GmbH which was successfully installed at the University of Arizona. The basic system layout is shown in Figure 5 with two separate optical paths to the sample location: the first for basic AFM tip positioning; and the second for the probe and signal path. The entire SNOM system sits on a cold finger of the cryostat, on top of an optical table, allowing free-space coupling of external lasers/light sources and detectors: making the cryo-neaSNOM highly customizable for a wide array of researcher needs and advanced research training. The recently installed cryo-neaSNOM includes several unique modes of operation including: spatially resolved nano-FTIR; near-field mapping with both visible and near-infrared sources; confocal Raman and PL imaging; and tip-enhanced Raman spectroscopy (TERS) and PL. We will utilize these highly novel measurement tools to explore plasmon propagation at temperatures down to 10 K and wavelengths up to 1.7 eV.

2.4. Results from 2020 add-on grant

2.4.1 Remote installation of cryo-neaSNOM at UA

The primary objective of this add-on project was to obtain preliminary measurements of SWCNTs in the new cryo-neaSNOM installed at the University of Arizona (UA). The cryo-neaSNOM is a complex instrument with numerous components (cryostat, AFM, light sources, detectors) that must be assembled and aligned. Because of this, the instrument has always previously been installed by neaspec technicians, which was our initial plan. However, due to the COVID-19 pandemic, the instrument which was initially scheduled to be installed at UA in spring/summer of 2020 was delayed, and travel from Germany was not possible. After negotiating with neaspec GmbH, we developed a remote installation strategy, and the instrument was shipped to UA in fall of 2021 and installed. Figure 6 shows the cryo-neaSNOM installed in the UA lab. Figure 7 shows the test acceptance data imaging an SiO2-Si test grid sample at room temperature. Figure 7a shows the AFM topography and Figure 7b shows the near field scattering SNOM amplitude signal at 10 µm.

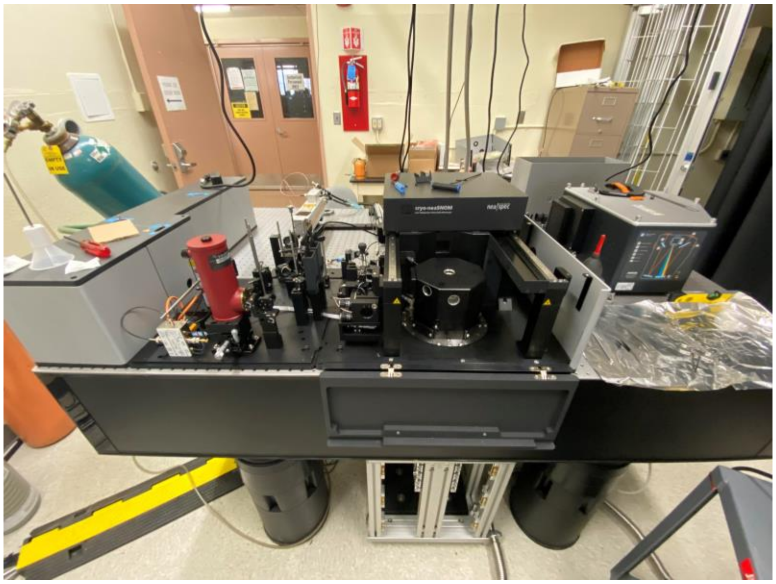

Figure 6: cryo-neaSNOM installed at University of Arizona.

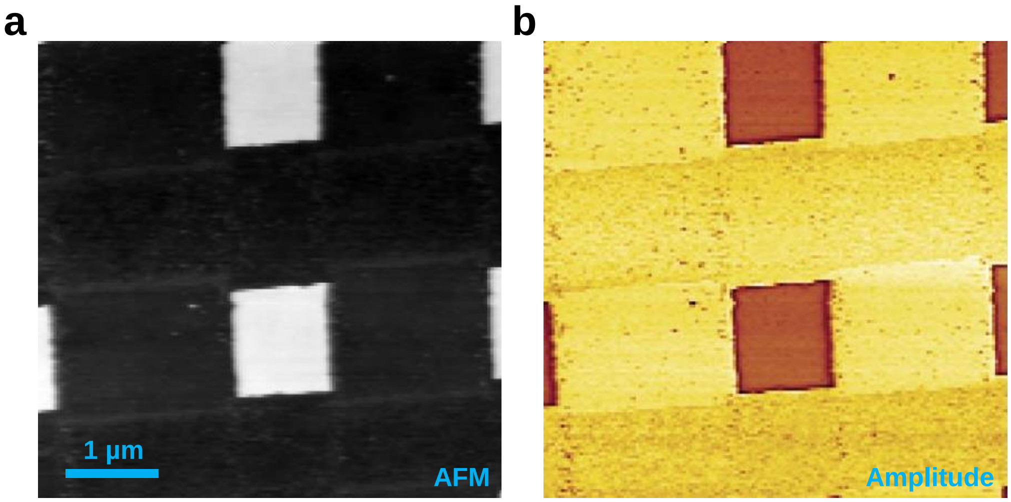

Figure 7: a) AFM topography image and b) near field scanning amplitude of SiO_2- Si test grid imaged by the cryo-neaSNOM at room temperature at the University of Arizona.

2.4.2 Demonstration of SNOM operation and Q control at low temperature

The basic operation mode of the cryo-neaSNOM have been successfully (Figure 7a-b) tested and are at or below the factory acceptance levels. In early spring 2020, Schaibley sent a graduate student to the neaspec headquarters in Germany to perform preliminary characterization of SWCNTs at low temperature. During these tests, it was discovered that neaspec's standard low temperature SNOM tips were unable to launch plasmons in SWCNTs due to a larger tip radius. These tips had been chosen by neaspec because they exhibited a lower Q-factor than their standard SNOM tips, a challenge which is associated with low temperature AFM measurements. This experimental challenged prompted the development of a novel FPGA based Q-factor control system which was developed for the UA cryo-neaSNOM system and is now installed in the lab at UA.

The **low temperature** operation and factory acceptance specifications of the cryo-neaSNOM have been demonstrated at UA. Figure 8 shows the acceptance test data imaging an SiO_2-Si test grid sample at 10 K. Figure 8a shows the AFM topography and Figure 8b shows the near field scattering SNOM amplitude signal at 10 µm. These data were recorded using the new FPGA based Q control system that was developed for the UA system.

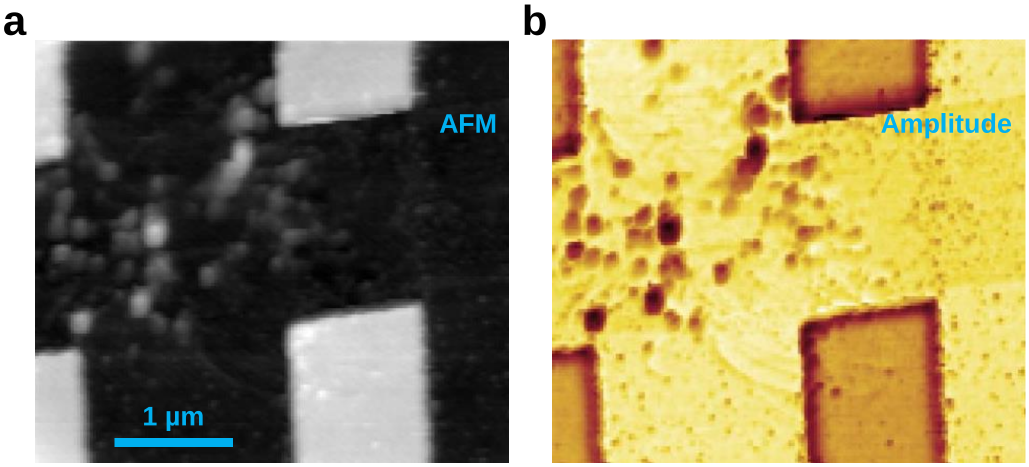

Figure 8: a) AFM topography image and b) near field scanning amplitude of SiO_2- Si test grid imaged by the cryo-neaSNOM at **10 K** at the University of Arizona.

2.4.3 Preliminary characterization of SWCNT plasmons at University of Arizona

The primary objective of this project is to image plasmons in SWCNTs. Figure 9 shows example data from a SWCNT on hBN imaged at in the UA cryo-neaSNOM with 10 µm excitation. Figure 9a shows the AFM topography, Figure 9b(c) shows the near field scattering SNOM amplitude (phase) signal at 10 µm. The amplitude signal is proportional to the reflectivity and the phase is proportional to the absorption. In both amplitude and phase, we observe clear plasmon oscillations consistent with a plasmon wavelength of 120 nm. These measurements were performed at room temperature and exhibit Q factors similar to those previously reported. At present, we are performing the initial low temperature measurements of LLPs to investigate their expected enhanced propagation lengths.

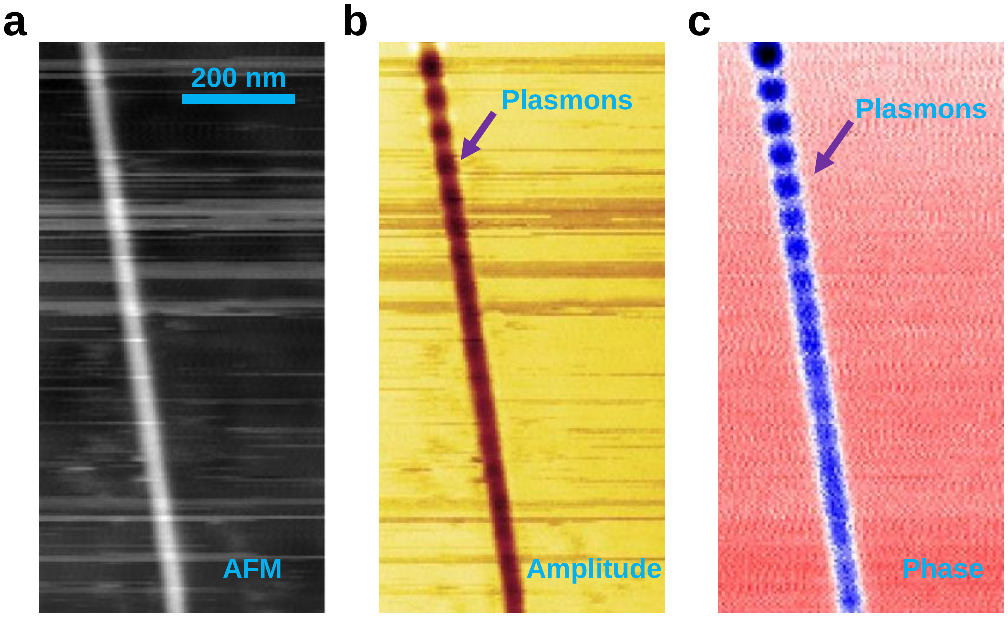

Figure 9: a) AFM topography image and b) near field scanning amplitude and c) near field scanning phase of SWCNT on hBN imaged by the cryo-neaSNOM at **room temperature** at the University of Arizona.

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