The Study of Tip-Induced Deformations in Single-Walled Carbon Nanotubes Using Tip-Enhanced Near-Field Raman Spectroscopy

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SUMMER NANOTECHNOLOGY STUDY PROGRAM JAPAN

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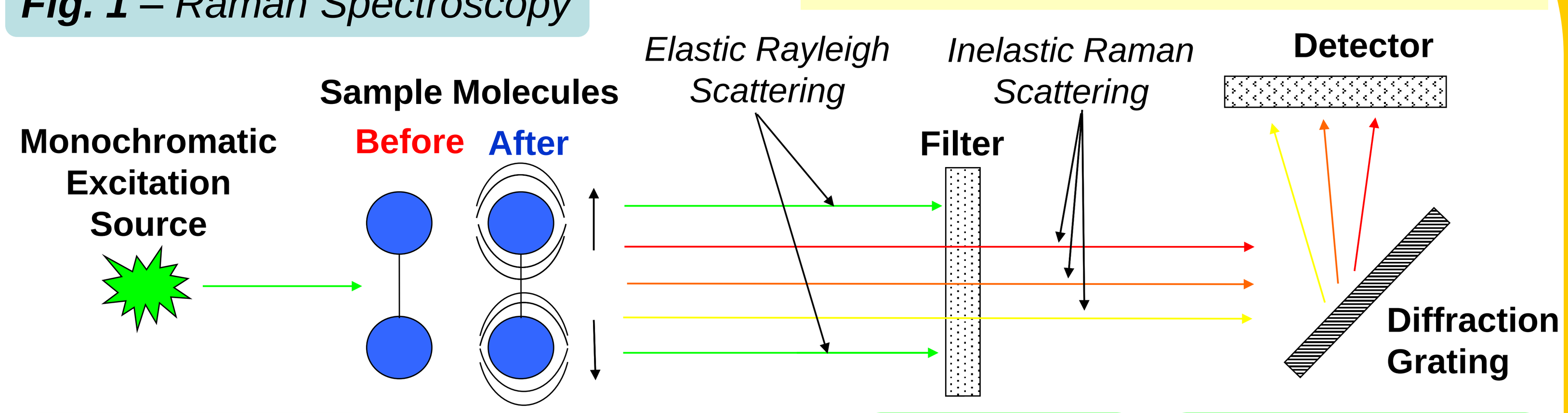
BACKGROUND

Raman Spectroscopy

Fig. 1 – Raman Spectroscopy



Carbon Nanotubes (CNT)

- Possess electronic and vibrational properties which are dependent on the CNTs' chirality (detected with Raman spectroscopy)

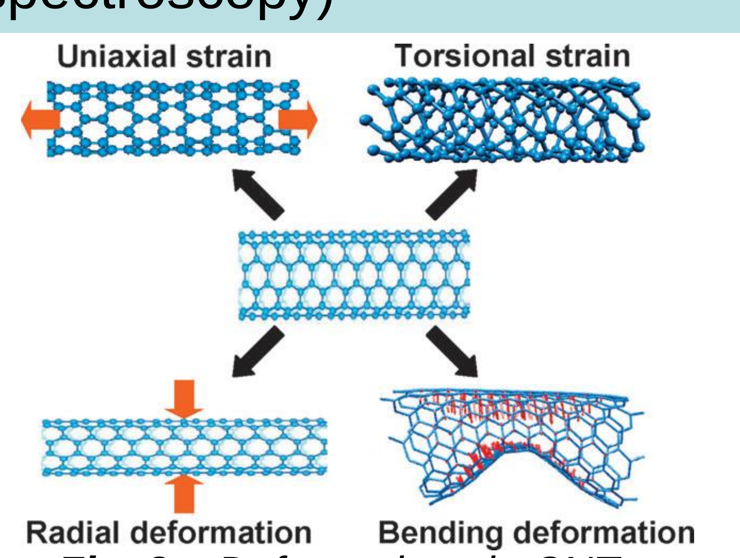


Fig. 3 – Deformations in CNT
Z. Liu, et. al., Chem. Comm.2009, 6902 (2009).

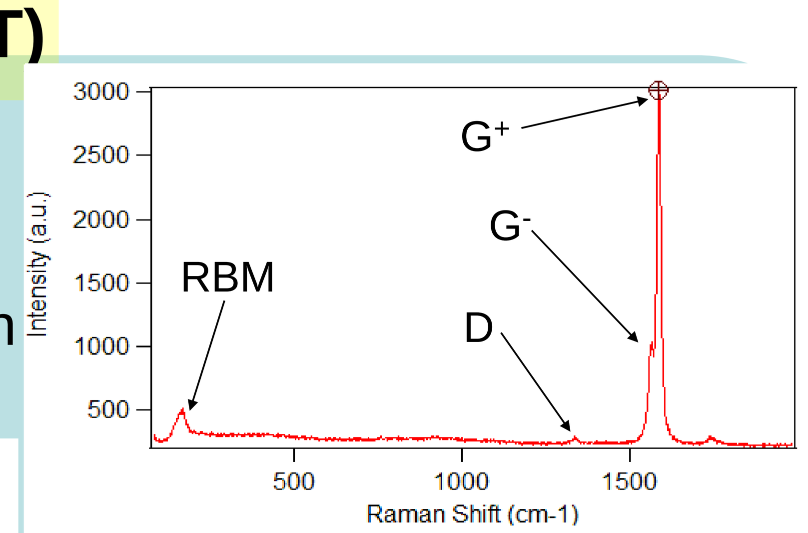


Fig. 2 – Raman Spectrum of CNT

- Deformations alter the CNTs' energy band structure thereby altering their characteristics
- Shifts in the phonon modes result from these alterations

Significance

- **Far-field Raman Spectroscopy** has **low spatial resolution ~300nm** – (*due to diffraction limit of propagating light* $d = \lambda/2$)
  Tip-Enhanced Raman Spectroscopy (TERS) can achieve a spatial resolution of less than 30nm
- **Raman Scattering** is **very weak** compared to **Rayleigh Sct.** (**~1 in 10 million photons** in a scattering event are Raman!)
- **Manipulation of CNTs** could cause **loss in Raman intensity**
  TERS increases the Raman Scattering response by a factor of 10^0 - 10^4

METHOD

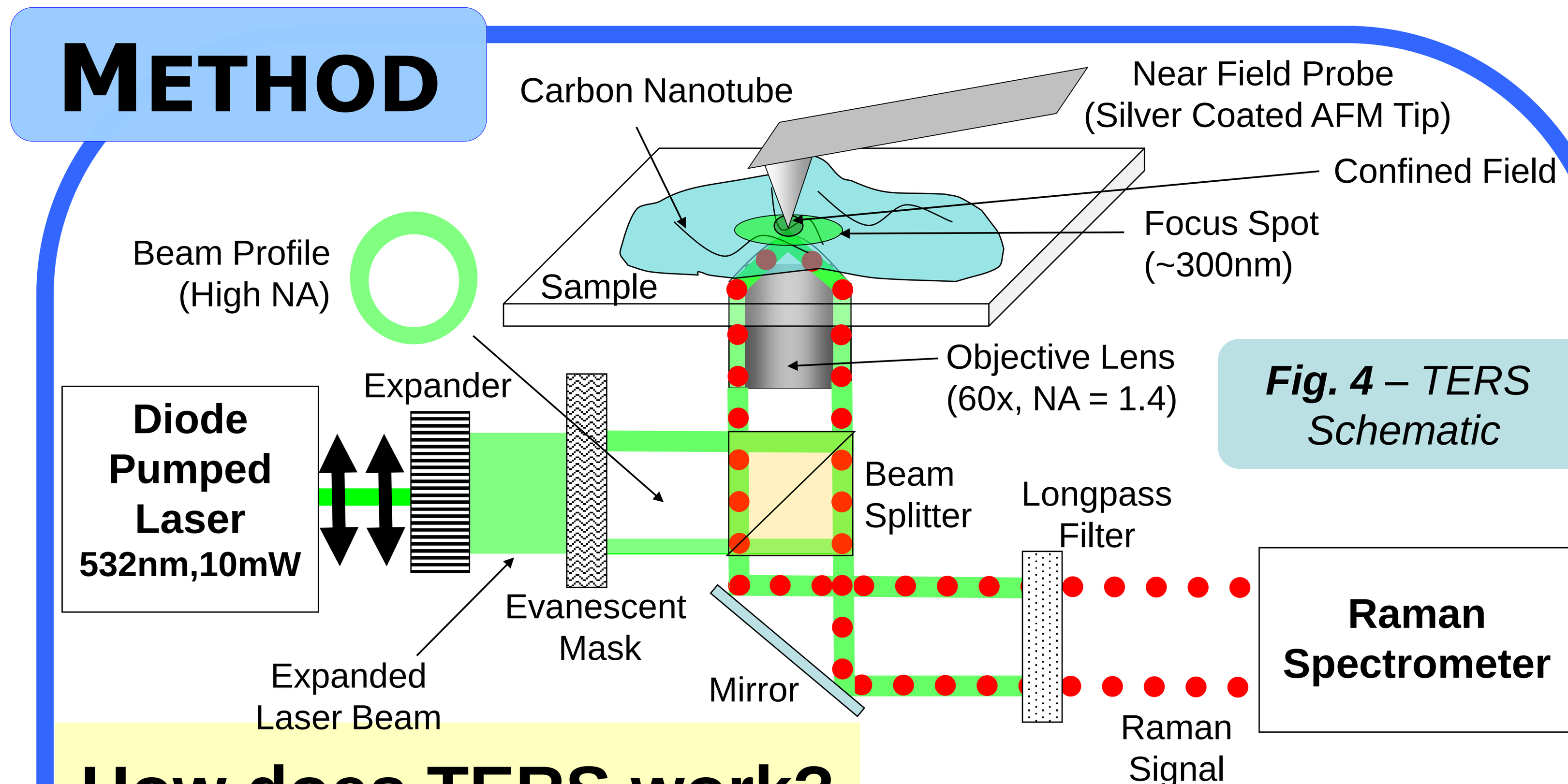


Fig. 4 – TERS Schematic

How does TERS work?

- ***Evanescent illumination*** decreases the spot size of the laser confining the illuminated region of the sample
- **High NA p-polarized component** of the laser increases the electromagnetic field along the metallized tip
- Propagating photons are captured and confined at the apex of the hovering conical ***silver coated silicon tip*** due to coupling with localized ***surface plasmon polaritons***

Process

1 Spincoated and then baked **CoMoCAT SWCNT** onto glass slides

2
- Used an **AFM-Raman System** comprised of a SII AFM system and Nikon Optical Microscope
- **Far-field image** of the SWCNT was taken by raster scanning the sample with the setup in Fig. 4 but ***with the tip and evanescent mask removed***

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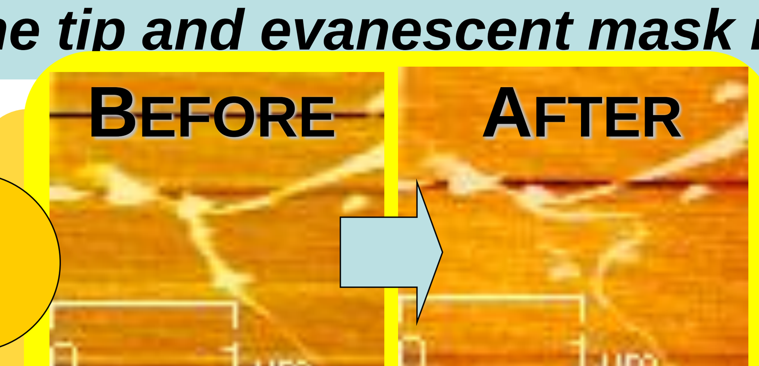


Fig. 5 – AFM Image of Tip-Induced Deformation in CNT

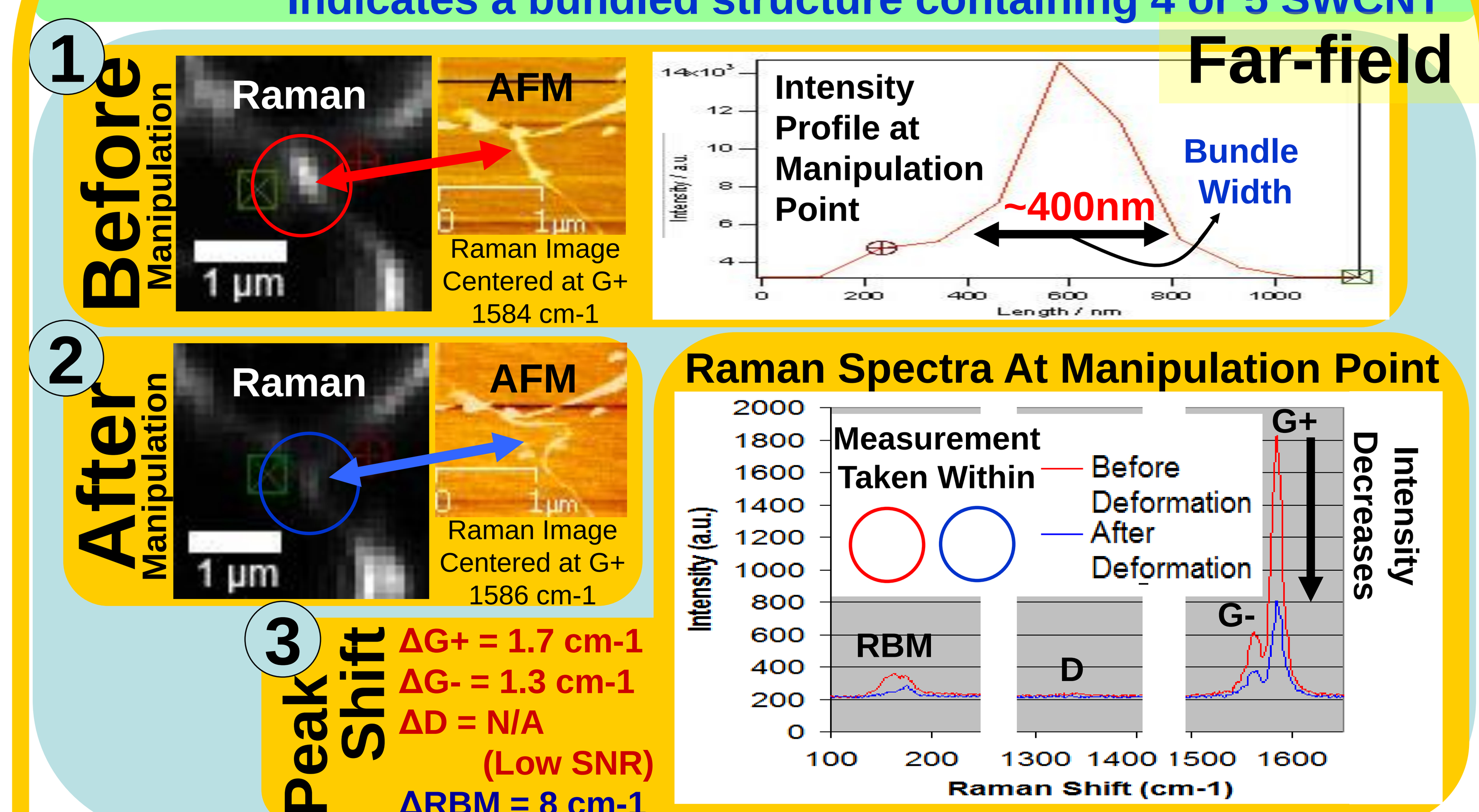
Using a silicon **Dynamic Force Microscopy (DFM)** tip, a ***~430 nm horizontal defect*** was introduced

4 **Far-field** (as in step 2) and **near-field** (using the setup of Fig. 4 with the tip constantly over the focal point) images of the manipulated SWCNT were taken

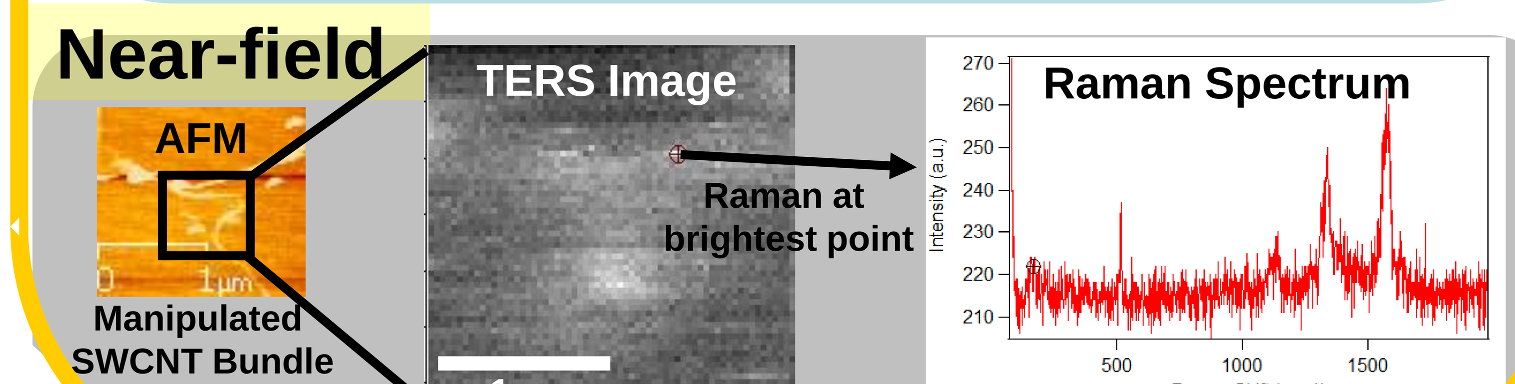
RESULTS

Manipulation region was about 5 nm wide - determined with DFM
Indicates a bundled structure containing 4 or 5 SWCNT

Far-field



Near-field



CNT manipulation could not be discerned from TERS Image

CONCLUSION

- **TERS** was *not supported* by results, but it still exists
- **Proved** the ***necessity of TERS*** because:
  1. **~5nm** bundle was measured **~400nm** using Far-field
  2. D-band was **indiscernible from noise** after defect
- **RBM peak shift** could indicate a shift in the orientation of the bundled CNTs or change in CNT band structure

Future Work

- Work with a single CNT strand instead of bundle
- Obtain data showcasing TERS enhancement
- Develop new opto-electric devices using the SWCNT structural deformation relation to electronic structure

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