

REPORT DOCUMENTATION PAGE			Form Approved OMB NO. 0704-0188	
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1. AGENCY USE ONLY (Leave Blank)		2. REPORT DATE 26/04/2005		3. REPORT TYPE AND DATES COVERED Final: 04 Dec 00 - 03 Dec 04
4. TITLE AND SUBTITLE Characterization of Nano-Scale Composites at THz and IR Spectral Region			5. FUNDING NUMBERS DAAD19-01-1-0009	
6. AUTHOR(S) Haim Grebel				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) New Jersey Institute of Technology University Height Newark, NJ 07102			8. PERFORMING ORGANIZATION REPORT NUMBER NNLARO-04-05	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) U. S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211			10. SPONSORING / MONITORING AGENCY REPORT NUMBER 40419.1-EL	
11. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.				
12 a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited.			12 b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) Characterizations of nanostructured carbon nanotube samples have been carried out using Raman and THz spectroscopy.				
14. SUBJECT TERMS Optical Systems.			15. NUMBER OF PAGES 1	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OR REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION ON THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL	

NSN 7540-01-280-5500

Standard Form 298 (Rev.2-89)
Prescribed by ANSI Std. Z39-18
298-102

REPORT DOCUMENTATION PAGE (SF298)
(Continuation Sheet)

NNLARO-04-05

Report Period 04/12/00-03/01/05

1) **List of papers:** See enclosed.

(2) **Scientific personnel supported by this project:** 2 faculty members, 2 Ph.D. students and 1 Postdoc.

(3) **Report of inventions:** None

(4) **Scientific progress and accomplishments:**

- Characterizations of nanostructures at THz frequency range have been conducted.
- Characterizations of nanostructures at infrared (IR) frequency range have been conducted

(5) **Technology transfer:** None

Characteristics of Nanoscale Composites at THz and IR Spectral Regions

Final Report

April 2005

Contract No. DAAD19-01-1-0009

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1. Forward

Interrogation of nano-scale structures is a challenging task when performed with electromagnetic waves because of the large discrepancy between the length scale of the propagating wave (on the order of microns and larger) and the nano-features under study. On the other hand, benefits of such approach are too large to ignore, among which are: non-invasive and *in-situ* assessments. In this project, we applied spectroscopic tools at the terahertz (THz) and infrared (IR) ranges to study nanoscale structures.

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3. List of Appendices, Illustrations and Tables (if applicable)

- “Standard Form 298 (Enclosure 1),” including the following required entries:
- H. Altan, F. Huang, J. Federici, A. Lan, H. Grebel, “Characteristics of nano-scale composites by THz spectroscopy”, *J. Appl. Phys.*, 96, 6685 (2004).

4. Statement of the problem studied

Single Wall Carbon Nanotube (SWCNT) have been the subject of intensive studies in recent years owing to their potential applications in areas such as, electronics, optoelectronics, mechanics, biochemistry for both civilian and military use. However, only a few reports have been made on their THz characteristics.

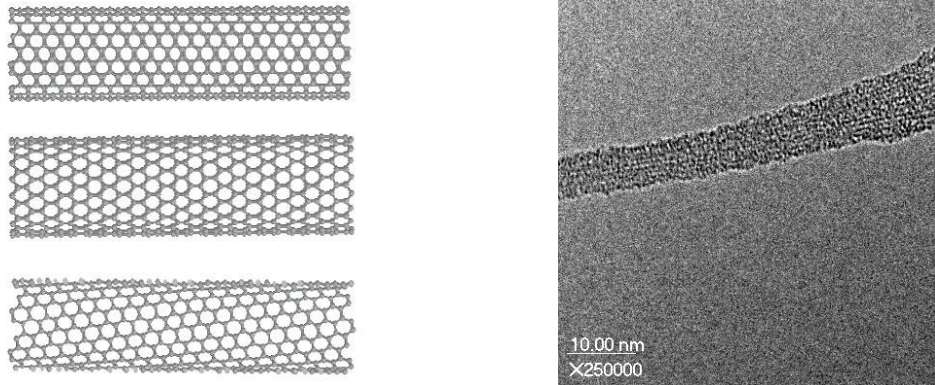


Fig. 1. Left: Structure of SWCNT. **Right:** Transmission Electron Microscope (TEM) picture of a bundle of SWCNT

Photonic crystals have been the subject of intense investigations as well owing to their electromagnetic confining properties. These properties stems from its periodic structure which is on the wavelength scale.

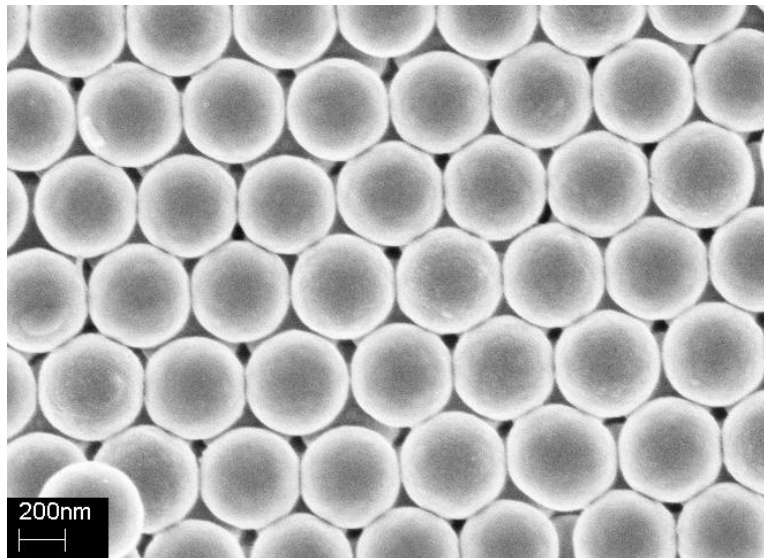


Fig. 2 Synthetic opal: colloidal version of photonic crystal

Our goal is to combine these two systems into one and characterize them via Raman and THz spectroscopy.

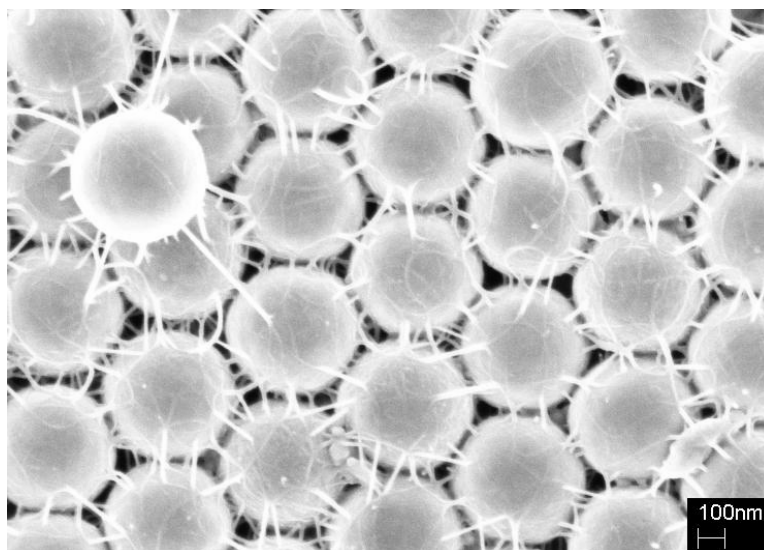


Fig. 3. SWCNT within colloidal photonic crystal

5. Summary of the most important results

5.1 Raman Spectroscopy

Raman spectroscopy is a widely used technique for the characterization of solids by their optical phonon frequencies [1]. Surface-Enhanced Raman Scattering (SERS) is a modified version of this technique; the usually weak signal of a non-resonant, spontaneous Raman line is amplified via coupling of the Raman-active, optical phonons with localized electric fields. The probed molecule or, solid is adsorbed on a rough metallic silver, gold or, copper surface in order to enable such amplification [2]. A large local electric field is induced in the metal layer when the surface is comprised of sharp features, and a local signal amplification of up to six orders of magnitude is typically measured and predicted by simulations [3,4]. Another method of inducing local charge fields is through surface charge waves (surface plasmons) where momentum conservation is achieved by means of a grating [5]. Here we present angular-dependent back-reflection data from bundled single-wall carbon nanotubes (SWNT) deposited on silver and gold coated, ordered array of silica spheres. The Raman spectra of SWNT are now well understood to be resonance-enhanced via van Hove singularities induced by their one-dimensional electronic states. Conventional SERS results for SWNT have been reported on random silver particles [6-9], but interactions with a periodic metallic surface in SERS experiments are unknown, and especially when they are coupled with resonantly enhanced Raman scattering from van Hove singularities in the electronic density-of-states.

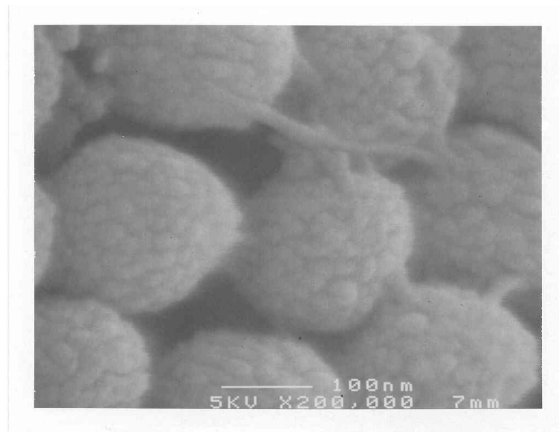


Fig. 4. Single wall carbon nanotubes on a silver-coated, ordered array of 200 nm silica spheres (opal)

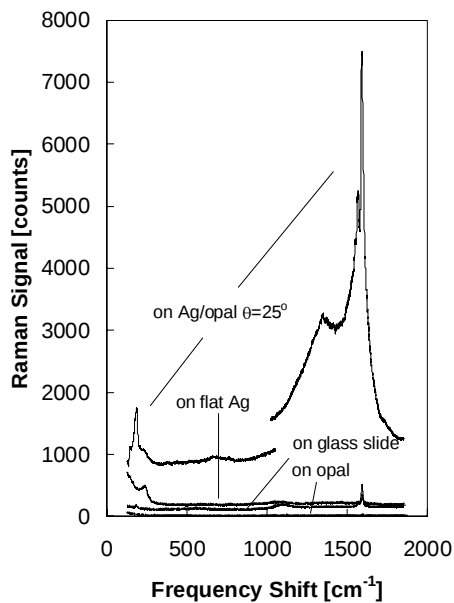


Fig. 5. Comparative Raman spectra from SWCNT on various substrates. Note signal enhancement when deposited on silver coated opal.

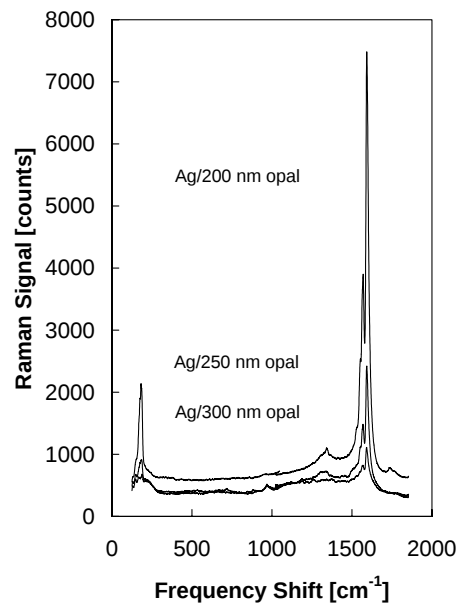


Fig. 6. SCWNT on silver-coated, order arrays of silica spheres: the effect of sphere's diameter

5.2 THz wave Spectroscopy

The concept of enhanced interactions between charge carriers and local electric fields can be extended to the THz range. In our ongoing work in THz technology, we have shown that sharp, singular features in THz radiator structures show an enhanced localized emission of THz radiation with higher total power than is possible with standard structures [reference]. One of our fabricated structures is shown in Fig. 7a. The sharp feature in the antenna structure leads to larger time-dependent currents in the structure's photoconductive gap region and consequently more

intense THz radiation. In other ongoing work, we have shown [12] that small metallic structures (apertures in metallic films) have an enhanced evanescent electric field in the immediate vicinity of the structure. The enhanced evanescent field, as shown in Fig. 7b, has been incorporated into a novel near-field THz probe with a state-of-the-art spatial resolution of 7 microns in the THz range. [13]



Fig. 7. (a) Photograph of THz generating/ detecting structure. The bright features are gold on top of an epilayer of low-temperature GaAs (LT-GaAs) which acts as a fast photoconductive switch. The sharp features of the structure concentrate the local electric field leading to enhanced THz transmission. (b) Simulation of the THz electric field amplitude . Note the concentration of the evanescent electric field in the immediate vicinity of the aperture.

Such antennas were used in our visible pump/THz probe spectroscopy to study the underlying physical processes of carrier transport within nanostructures such as SWCNT. Our THz experimental setup is shown in Fig. 8. From the change in the sample's far-infrared transmission subsequent to photo-excitation, carrier dynamics such as inter-valley scattering, mobility, carrier relaxation times, and mean-free-path can be deduced.

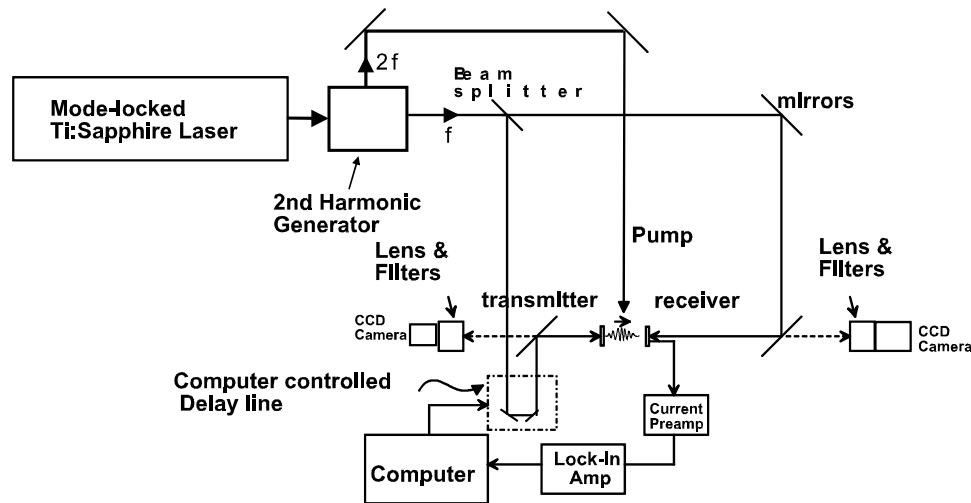


Fig. 8. Experimental configuration of "standard", visible pump/probe THz spectroscopy. A second harmonic generation module can be used to generate blue light for photoexcitation of nanocluster films.

Such spectroscopic system was applied to SWCNT and the differential transmission was measured (Fig. 9). The use of a non-contact visible pump-THz probe technique, the differential THz spectra of SWCNT and ion implanted Si nanoclusters exhibited the existence of photoinduced states. A photoinduced free-carrier Drude or Drude-Smith model was not consistent with the magnitude of the transmission value changes. A better fit was obtained when incorporating Lorentzian-like discrete states. The SWCNT data was consistent with a single Lorentz state in the measured frequency range. The flatness of the ion-implanted Si nanocluster spectra indicated either the presence of a broad Lorentz state in the 0.2-0.7 THz range or, the presence of a much broader Lorentz peak outside of our spectral range [14].

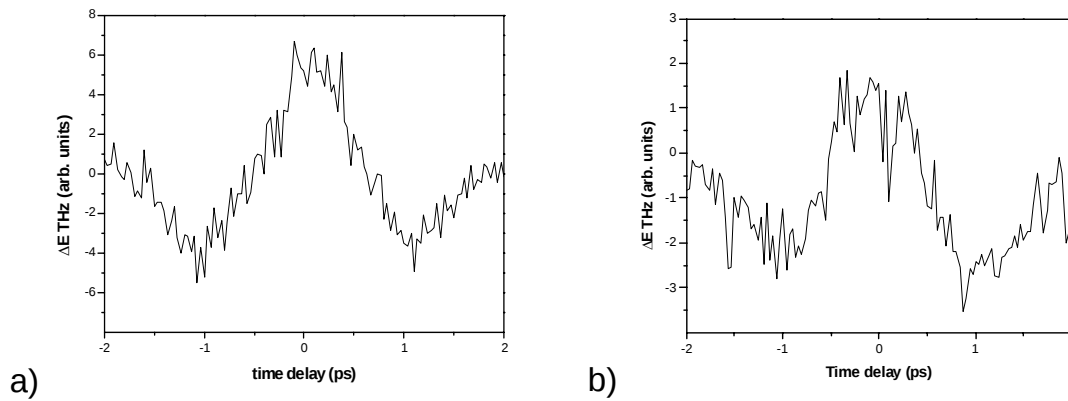


Fig. 9. Differential THz transmission of SWCNTs on quartz substrates. The two curves are taken from two different sample locations.

6. Listings of all publications and technical reports supported under this grant

6.a. THz papers and book chapters published in peer-reviewed journals

- John Federici and Haim Grebel, "Characterization of nanoscale composites at THz and IR spectral regions", *Int. J. of High Speed Elec. and Sys.*, **13**, 969-993 (2003);
- J. F. Federici and H. Grebel, "Characteristics of Nano-Scale Composites at THz and IR Spectral Regions", *Sensing Science and Technology at THz Frequencies, Volume II. Emerging Scientific Applications & Novel Device Concepts*, ed. D. Woodard, M. Shur, W. Loerop., 2004;
- H. Altan, A. Lan, F. Huang, J. F. Federici, and H. Grebel, "Optical and electronic characteristics of single walled carbon nanotubes and silicon nanoclusters by terahertz spectroscopy," *J. Appl. Phys* **96**(15) (2004)

6.a.1. Related papers citing the grant

- H. Grebel, "Surface Enhanced Raman Scattering - phenomenological approach", *J. Opt. Soc. Am (JOSA) B*, **21**, 429-435 (2004).
- Aidong Lan, Yan Zhang, Xueyan Zhang, Zafar Iqbal and Haim Grebel, "Is molybdenum necessary for the growth of single-wall carbon nanotubes from Co?" *Chem. Phys. Letts*, **379**, 395-400 (2003).
- H. Han, S. Vijayalakshmi, A. Lan, Z. Iqbal, H. Grebel, E. Lalanne and A. M. Johnson, "Linear and nonlinear optical properties of carbon nanotubes within an ordered array of silica spheres", *Appl. Phys. Letts*, **82**, 1458-1460 (2003).
- AiDong Lan, Zafar Iqbal, Abdelaziz Aitouchen, Matthew Libera, and Haim Grebel, "Growth of small diameter single-wall carbon nanotubes within an ordered array of nanosize silica spheres", *Appl. Phys. Letts*. **81**, 433-435 (2002)

6.b. Papers published in non-peer-reviewed journals or in conference proceedings

- H. Altan, A. Lan, F. Huang, J. F. Federici, and H. Grebel, "Characteristics of Nanocomposites using THz spectroscopy," CLEO 2004
- H. Altan, A. Lan, F. Huang, J. F. Federici, and H. Grebel, "Characteristics of Nanocomposites using THz spectroscopy," *Proc. SPIE* **5268**, 53 (2004).
- H. Altan, A. Lan, F. Huang, J. F. Federici, and H. Grebel, "Characteristics of Nanocomposites using THz spectroscopy," *Proc. SPIE* **5070**, 53 (2003)
- H. Altan, A. Lan, F. Huang, J. F. Federici, and H. Grebel, "Characteristics of Nanocomposites using THz spectroscopy," *SPIE-Photonics East* 2003
- J. F. Federici, H. Altan, F. Huang, and H. Grebel, "Characteristics of nano-scale composites at THz and IR spectral regions," *The International Symposium on Spectral Sensing Research (ISSSR)* 2003, Santa Barbara, CA June 2003.

6.c. Papers presented at meetings, but not published in conference proceedings

6.d. Manuscripts submitted, but not published

- H. Altan, A. Sengupta, J. F. Federici, H. Grebel, and D. Pham, "Characteristics of 200 mm diameter Si_{1-x}Ge_x, SiO₂ and HfO₂ on p-type silicon wafers using THz spectroscopy," submitted to *Phys. Rev. B*, 2005.

6.e. Technical reports submitted to ARO

- NNLARO 04-01 Attachment, *Characteristics of Nanoscale Composites at THz and IR Spectral Regions*, an interim report

- NNLARO 11-01 Attachment, Characteristics of Nanoscale Composites at THz and IR Spectral Regions, an interim report
- NNLARO 12-02 Attachment, Characteristics of Nanoscale Composites at THz and IR Spectral Regions, an interim report

7. List of all participating scientific personnel showing any advanced degrees earned by them while employed on the project

- Hakan Altan, Ph.D

8. Report of Inventions (by title only)

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- [13] O. Mitrofanov, M. Lee, J. W. P. Hsu, I. Brenner, R. Harel, J. Federici, J. D. Wynn, L. N. Pfeiffer, and K. West "Collection Mode Near-Field Imaging with 0.5 THz Pulses", submitted to *IEEE J. Sel. Top. in Quant. El.*
- [14] H. Altan, A. Lan, F. Huang, J. F. Federici, and H. Grebel, "Optical and electronic characteristics of single walled carbon nanotubes and silicon nanoclusters by terahertz spectroscopy," *J. Appl. Phys* **96**(15) (2004)