

Final Report

May 25, 2007

Title: Quantitative tunneling spectroscopy of nanocrystals
Grant: DE-FG02-02ER45956
Institutions: Georgia Institute of Technology and Oak Ridge National Laboratory
PIs: P. N. First (GT), T. G. Schaaff (ORNL), and R. L. Whetten (GT)
Start Date: 01-Dec-2001
End Date: 30-Nov-2005
Unexpended Funds: None

The proposed goals of this collaborative work (*First* and *Whetten* at Georgia Tech, *Schaaff* at Oak Ridge National Lab) were to systematically characterize the electronic structure and dynamics of 3-dimensional metal and semiconducting nanocrystals using scanning tunneling microscopy/spectroscopy (STM/STS) and ballistic electron emission spectroscopy (BEES). During the grant period, substantial effort also was devoted to the development of epitaxial graphene (EG), a very promising materials system with outstanding potential for nanometer-scale ballistic and coherent devices (“graphene” refers to one atomic layer of graphitic, sp^2 -bonded carbon atoms [or more loosely, few layers]). In *First’s* lab, the latter effort became the main focus of this nanoscience research. Funding from this DOE grant was critical for the initial development of epitaxial graphene for nanoelectronics.

Graphene research has become one the busiest subfields of condensed matter physics since our 2004 publication [1], and epitaxial graphene has attracted the attention of electronics industry giants Intel and IBM. References [1] and [2] were (apparently) the first transport measurements performed on epitaxial graphene. These works clearly demonstrated the potential of the material for large-scale integrated ballistic and coherent nanoelectronics. Because of its basis in carbon, and the ability to pattern the material with standard nanolithography techniques, EG could ultimately provide a platform for molecular- and nanocrystal-based electronic devices.

Personnel

The following students received funding from this grant for portions of their Ph.D. research:

1. A. Y. Ogbazghi (Ph.D. in Physics, 2005)
Thesis title: *Conductance through Nanometer-scale Metal-to-Graphite Contacts*.
Employment: Intel Corp., Portland, OR.
2. Sameh Dardona (Ph.D. in Physics, 2006)
Thesis title: *Energy Relaxation and Hot-electron Lifetimes in Single Nanocrystals*.
Employment: United Technologies Research Center, East Hartford, CT.
3. Tianbo Li (Ph.D. in Physics, 2006)
Thesis title: *Characteristics of Graphite Films on Silicon- and Carbon-Terminated Faces of Silicon Carbide*.
Employment: Spansion, Inc., Sunnyvale, CA.

4. Ryan Price (Ph.D. in Chemistry, 2006)
Thesis title: *Nanocrystalline Gold Arylthiolate Molecules*.
Employment: Postdoc, Georgia Tech.
5. Jianfei Shao (Ph.D. in Physics, 2006)
Thesis title: *STM/STS and BEES Study of Nanocrystals*.
Employment: Spansion, Inc., Sunnyvale, CA.

One Postdoctoral scientist was employed:

1. Dr. T. P. Bigioni (Physics): Upgrades to low-temperature STM instrument, student training and STM experiments (April 2002–September 2002).

Undergraduates who participated in this research were: David Pilkington (Summer 2002, REU, U. Florida); Burt Betchart (Summer 2003, REU, Oberlin); Harrison Caudill (Georgia Tech, 2003-5), Michael Hadsell (Georgia Tech, 2004).

Research Highlights

Referenced publications and Theses are listed in the *Publications* section. Journal publications are attached in the order they are referenced. Theses can be downloaded from the URL listed in the reference.

- Correlation of nanocrystal core mass with STM height [3].
- Synthesis of new nanocrystal compounds [4, 5, 6, 7].
- Elucidation of mass spectra from laser desorption ionization [8, 9].
- Correlation of energy gaps with nanocrystal core mass (to be published).
- Discovery of high impedance and confined electronic states at a metal/graphite interface [10] (and tbp).
- Atomic-scale imaging with a liquid metal STM tip [10] (and tbp).
- Growth and characterization of epitaxial graphene [1, 2, 11, 12, 13].
- Measurement of carrier mobilities and coherence lengths in EG [1, 2].
- Observation of quantum confinement in EG ribbons [2].
- Demonstration of electrostatic gating in EG [1].
- Proposal for a new nanoelectronics paradigm based on EG [1] (and patent).
- Calculation and physical picture of the conditions for a Brewster angle in negative index materials [14].

- Development of a new STM-based single-nanocrystal technique for measurements of electron relaxation rates in nanocrystals [15, 16] (and *tbp*).
- Rate equation modeling of the tip-nanocrystal-substrate tunneling process, and prediction of subthreshold BEES current [16].

Presentations

1. “Metal/Graphite Contacts,” A.Y. Ogbazghi, C. Berger, W.A. de Heer, and P.N. First, 62nd Annual Physical Electronics Conference, Atlanta, GA, June 12, 2002.
2. “STM/STS Measurements on Au Nanocrystals,” T.P. Bigioni, L.E. Harrell, T.G. Schaaff, R.L. Whetten, and P.N. First, 62nd Annual Physical Electronics Conference, Atlanta, GA, June 14, 2002.
3. “Conductance through small-area gallium/graphite contacts,” A. Y. Ogbazghi, W. A. de Heer, and P. N. First, March Meeting of the American Physical Society, Austin, TX, March 4, 2003.
4. “Self-assembled gold clusters exhibiting size dependent electronic and optical properties,” R. C. Price, T. G. Schaaff, and R. L. Whetten, POSTER, Workshop on Bio-Inspired Processes for Design, Assembly, and Repair of Electromagnetic and Structural Composites, August 19-20, 2003, Atlanta, GA
5. “Novel arylthiolate/gold nanoclusters,” R. C. Price, T. G. Schaaff, and R. L. Whetten, POSTER, South-Eastern Regional Meeting of the American Chemical Society, November 17th, 2003, Atlanta, GA
6. “Evidence for 2D electron gas behavior in ultrathin epitaxial graphite on a SiC substrate,” Claire Berger, Zhimin Song, Tianbo Li, Phillip First, Jean Bellissard, Walt de Heer, March Meeting of the American Physical Society, Montreal, Quebec, March 22, 2004.
7. “Transition from Coulomb to molecular charging in tunneling spectra of gold nanocrystals,” T. P. Bigioni, T. G. Schaaff, R. L. Whetten, and P. N. First, March Meeting of the American Physical Society, Montreal, Quebec, March 25, 2004.
8. “Synthesis of size quantized arylthiol/gold nanocrystals,” R. C. Price, T. G. Schaaff, and R. L. Whetten, POSTER, 227th American Chemical Society National Meeting, March 28-April 1, 2004, Anaheim, CA
9. “Criteria for a Brewster angle in negative-index materials,” Ceji Fu, Phillip N. First, and Zhuomin M. Zhang, March Meeting of the American Physical Society, Los Angeles, CA, March 21–25, 2005.
10. “Growth and Characterization of Ultrathin Epitaxial Graphite films on Silicon Carbide,” Tianbo Li, Asmerom Y. Ogbazghi, Xuebin Li, Zhimin Song, Claire Berger, Walt A. de Heer,

and Phillip N. First, March Meeting of the American Physical Society, Los Angeles, CA, March 21–25, 2005.

11. “STS and BEES Study of Semiconductor Nanocrystals,” (Poster), Jianfei Shao, Sameh Dardona, Alex Schill, Qusai Darugar, Phillip First, Mostafa El- Sayed, March Meeting of the American Physical Society, Los Angeles, CA, March 21–25, 2005.
12. “Tunneling Microscopy and Spectroscopy of Semiconductor Nanocrystals,” (Poster), S. Dardona, J. Shao, A. Schill, Q. Darugar, M. El-Sayed, and P. N. First, March Meeting of the American Physical Society, Los Angeles, CA, March 21–25, 2005.
13. “Fabrication and characterization of nanopatterned ultrathin epitaxial graphite films,” Zhimin Song, Xuebin Li, Tianbo Li, Claire Berger, Phillip First, and Walter A. de Heer, 2006 APS March Meeting, Baltimore, MD, March 13, 2006.
14. “Simulation of tunneling I-V curves from gold nanocrystals,” Jianfei Shao and Phillip N. First, 2006 APS March Meeting, Baltimore, MD, March 13, 2006.
15. “Electronic Structure of Ultra-thin Graphite,” Gey-Hong Gweon, Elizabeth Rollings, Shuyun Zhou, Bongjin Mun, Alexei Fedorov, P. N. First, W. A. de Heer, and Alessandra Lanzara, 2006 APS March Meeting, Baltimore, MD, March 13, 2006.
16. “Ballistic Electron Emission Spectroscopy Studies of Gold Nanocrystals,” Sameh Dardona, Jianfei Shao, Ryan Price, Robert Whetten, and Phillip N. First, 2006 APS March Meeting, Baltimore, MD, March 13, 2006.
17. “Characterization of Graphene Films and Ribbons on Silicon Carbide,” Tianbo Li, Asmerom Ogbazghi, Xuebin Li, Zhimin Song, Claire Berger, Walt de Heer, and Phillip N. First, 2006 APS March Meeting, Baltimore, MD, March 14, 2006.
18. “Hydrogen etching and graphitization of 4H- and 6H-SiC,” Xuebin Li, Zhimin Song, Tianbo Li, Claire Berger, Phillip N. First, Walter de Heer, 2006 APS March Meeting, Baltimore, MD, March 15, 2006.
19. “Highly Ordered Graphene for Two Dimensional Electronics,” Rui Feng, J. R. Hass, E. H. Conrad, X. Li, C. Berger, W. A. de Heer, T. Li, P. N. First, and C. A. Jeffrey, 2006 APS March Meeting, Baltimore, MD, March 17, 2006.

Patents

1. “Patterned thin film graphite devices and method for making same,” U.S. patent no. 7,015,142, issued March 21, 2006. Based on U.S. Provisional Patent Application Serial No. 60/477,997, filed June 12, 2003, entitled “Integrated and discrete electronic components from structured thin graphitic materials,” W. A. de Heer, C. Berger, and P. N. First, (GTRC ROI no. 2756).

Publications

- [1] C. Berger, Z. Song, T. Li, X. Li, A. Y. Ogbazghi, R. Feng, Z. Dai, A. N. Marchenkov, E. H. Conrad, P. N. First, and W. A. de Heer. “Ultrathin epitaxial graphite: 2d electron gas properties and a route toward graphene-based nanoelectronics.” *J. Phys. Chem. B* **108** (52), 19 912–19 916 (2004).
- [2] C. Berger, Z. Song, X. Li, X. Wu, N. Brown, C. Naud, D. Mayou, T. Li, J. Hass, A. N. Marchenkov, E. H. Conrad, P. N. First, and W. A. de Heer. “Electronic confinement and coherence in patterned epitaxial graphene.” *Science* **312** (5777), 1191–1196 (2006).
URL <http://www.sciencemag.org/cgi/content/abstract/312/5777/1191>
- [3] T. P. Bigioni, T. G. Schaaff, R. B. Wyrwas, L. E. Harrell, R. L. Whetten, and P. N. First. “Scanning tunneling microscopy determination of single nanocrystal core sizes via correlation with mass spectrometry.” *J. Phys. Chem. B* **108** (12), 3772–3776 (2004).
- [4] T. G. Schaaff and A. J. Rodinone. “Preparation and characterization of silver sulfide nanocrystals generated from silver(i)-thiolate polymers.” *J. Phys. Chem. B* **107** (38), 10 416–10 422 (2003).
- [5] R. Price and R. Whetten. “All-aromatic, nanometer-scale, gold-cluster thiolate complexes.” *J. Am. Chem. Soc.* **127** (40), 13 750–13 751 (2005).
URL http://pubs3.acs.org/acs/journals/doi/lookup?in_doi=10.1021/ja053968+
- [6] R. C. Price and R. L. Whetten. “Raman spectroscopy of benzenethiolates on nanometer-scale gold clusters.” *J. Phys. Chem. B* **110** (44), 22 166–22 171 (2006).
- [7] R. C. Price. *Nanocrystalline Gold Arylthiolate Molecules*. Ph.D. thesis, Georgia Institute of Technology (2006).
URL <http://hdl.handle.net/1853/14051>
- [8] T. G. Schaaff. “Metastable ions produced in laser desorption of gold : thiolate cluster compounds.” *Rapid Commun. Mass Spectrom.* **17** (22), 2567–2570 (2003).
- [9] T. G. Schaaff. “Laser desorption and matrix-assisted laser desorption/ionization mass spectrometry of 29-kda au : Sr cluster compounds.” *Anal. Chem.* **76** (21), 6187–6196 (2004).
- [10] A. Y. Ogbazghi. *Conductance through Nanometer-scale Metal-to-Graphite Contacts*. Ph.D. thesis, Georgia Institute of Technology (2005).
URL <http://hdl.handle.net/1853/6872>
- [11] J. Hass, R. Feng, T. Li, X. Li, Z. Zong, W. A. de Heer, P. N. First, E. H. Conrad, C. A. Jeffrey, and C. Berger. “Highly ordered graphene for two dimensional electronics.” *Appl. Phys. Lett.* **89** (14), 143106 (2006).
URL <http://link.aip.org/link/?APL/89/143106/1>

- [12] E. Rollings, G.-H. Gweon, S. Zhou, B. Mun, J. McChesney, B. Hussain, A. Fedorov, P. First, W. de Heer, and A. Lanzara. “Synthesis and characterization of atomically thin graphite films on a silicon carbide substrate.” *J. Phys. Chem. Solids* **67** (9-10), 2172–2177 (2006).
URL <http://www.sciencedirect.com/science/article/B6TXR-4KMYG9D-4/2/add010fd01538519>
- [13] T. Li. *Characteristics of Graphite Films on Silicon- and Carbon-Terminated Faces of Silicon Carbide*. Ph.D. thesis, Georgia Institute of Technology (2006).
URL <http://hdl.handle.net/1853/14024>
- [14] C. Fu, Z. M. Zhang, and P. N. First. “Brewster angle with a negative-index material.” *Appl. Opt.* **44** (18), 3716–24 (2005).
- [15] S. I. Dardona. *Energy Relaxation and Hot-electron Lifetimes in Single Nanocrystals*. Ph.D. thesis, Georgia Institute of Technology (2006).
URL <http://hdl.handle.net/1853/11604>
- [16] J. Shao. *STM/STS and BEES Study of Nanocrystals*. Ph.D. thesis, Georgia Institute of Technology (2006).
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