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14. ABSTRACT The experimental focus of the research project was the further development of time-domain thermoreflectance (TDTR) as a high-throughput and nearly universal method for the measurement of the thermal conductivity of materials. The scientific focus of this project was on understanding i) the lower-limits to the thermal conductivity of disordered layered crystals, multilayers, and superlattices; and ii) the distribution of heat carrying phonons in conventional semiconductor alloys.					
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Thermal Conductivity of Novel Thermoelectric and Nanostructured Functional Materials
by Time-Domain Thermoreflectance, ONR grant no. N00014-07-1-0190

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A. Project description

The search for materials with improved efficiency for direct thermal-to-energy conversion is wide-ranging, encompassing superlattices, nanowires, nanoparticle assemblies, and layered crystals prepared by modulated elemental reactants. There is a great need for accurate and convenient measurements of the thermal conductivity of these novel materials. The experimental focus of the research project was the further development of time-domain thermoreflectance (TDTR) as a high-throughput and nearly universal method for the measurement of the thermal conductivity of materials. The scientific focus of this project was on understanding i) the lower-limits to the thermal conductivity of disordered layered crystals, multilayers, and superlattices; and ii) the distribution of heat carrying phonons in conventional semiconductor alloys.

B. Technical Approach

Thin film, nanowire, nanostructured, and more conventional bulk thermoelectric materials were prepared by our collaborators: the research groups of Profs. D. Johnson (U. Oregon), T. Sands (Purdue), L. Samuelson (Lund, Sweden), D. Jena (Notre Dame), C. Vineis (MIT), and A. Majumdar (UC-Berkeley). Thermal conductivity measurements were performed at the U. of Illinois using time-domain thermoreflectance (TDTR); we have recently advanced the state-of-the-art of TDTR data collection and analysis and can rapidly evaluate data for a wide range of compositions, multilayer periods, and deposition and annealing conditions. We use ion beam irradiation to systematically vary the chemical abruptness of interfaces and introduce point defects. Rutherford backscattering spectrometry is used to measure elemental composition.

C. Research Highlights

Nitride superlattices. In collaboration with the group of Depdeep Jena at U. Notre Dame, we completed a study of the thermal conductivity of AlN/GaN superlattices grown by plasma-assisted MBE. These materials are extremely well characterized and the mobility of the two-dimensional electron gas at the AlN/GaN interface provides an interesting tool for evaluating the interface roughness. Ion-beam irradiation of short period superlattices enabled critical tests of theories of the heat transport by introducing point-defects; we fit the data for a wide range of superlattice period, temperature, and point defect density with a single model based on frequency dependent scattering of phonons by interfaces. We also completed a study of the thermal conductivity, elastic constants, and composition of

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metal-semiconductor nitride superlattices (ZrN/ScN and ZrWN/ScN) grown by the group of T. Sands using pulsed-laser deposition. Thermal conductivities are strongly suppressed by phonon scattering at interfaces.

Disordered layered materials . In collaboration with David Johnsons group, we explored the lower limit of the lattice thermal conductivity of nanostructured Bi_2Te_3 -based materials. Growth of multilayers using the method of elemental reactants allowed us to reduce the grain size of homogenous Bi_2Te_3 to a few nanometers; in this limit, the thermal conductivity approaches the predicted minimum thermal conductivity. A Debye-Callaway model for the phonon scattering rates fits the experimental data for a range of grain sizes 1–100 nm well and shows that extremely small scattering lengths on the order of 20 nm are needed to significantly suppress the lattice thermal conductivity. Ultralow thermal conductivities (conductivities below the predicted minimum thermal conductivity) can be achieved by combining the effects of alloying and turbostratic disorder in a multilayer structure.

Nanodot superlattices based on PbTe. In the original publication by the MIT/Lincoln-Lab group, the extraordinarily high ZT of PbTe-PbSe nanodots superlattices was attributed to extremely low lattice thermal conductivity. We measured the through-thickness lattice thermal conductivity of a large set of samples grown at Lincoln Laboratories for a wide range of periods, composition, growth temperatures, and growth rates. All of our measurements approach the lattice thermal conductivity of bulk homogenous $\text{PbTe}_{1-x}\text{Se}_x$ alloys with the same average composition. Based on our measurements of thermal conductivity and our collaborators measurements of Seebeck coefficient and electrical conductivity on the same samples, the highest ZT at room temperature is 0.6, a factor of 4 smaller than originally reported.

Semiconductor nanowires composites. Semiconductor nanowires have low lattice thermal conductivity but need to be incorporated into composite materials to produce practical thermoelectrics. The thermal conductivity of InAs nanowires/PMMA composite materials, however, shows a pronounced dependence on the modulation frequency using the time-domain thermoreflectance measurement. (Samples were synthesized and fabricated by the groups of Samuelson and Linke.) Through experiment and finite-element modeling, we have confirmed that the low frequency limit of the TDTR data corresponds to the effective medium behavior.

D. Publications that cite N00014-07-1-0190

1. Yee Kan Koh, Yu Cao, David G. Cahill, and Debdeep Jena, “Heat transport mechanisms in superlattices,” *Adv. Funct. Mater.* **19**, 610–615 (2009).
2. Vijay Rawat, Yee Kan Koh, David G. Cahill, and Timothy D. Sands, “Thermal conductivity of (Zr,W)N/ScN metal/semiconductor multilayers and superlattices,” *J. Appl. Phys.* **105**, 024909 (2009).

3. Yee Kan Koh, Suzanne L. Singer, Woochul Kim, Joshua M. O. Zide, Hong Lu, David G. Cahill, Arun Majumdar, Arthur C. Gossard, "Comparison of the 3ω method and time-domain thermoreflectance for measurements of the cross-plane thermal conductivity of epitaxial semiconductors," *J. Appl. Phys.* **105**, 054303 (2009).
4. Yee Kan Koh, C. J. Vineis, S. D. Calawa, M. P. Walsh, and David G. Cahill, "Lattice thermal conductivity of nanostructured thermoelectric materials based on PbTe," *Appl. Phys. Lett.* **94**, 153101 (2009).
5. Catalin Chiritescu, David G. Cahill, Clay Mortensen and David C. Johnson, and Paul Zschack, "Lower limit to the lattice thermal conductivity of nanostructured Bi₂Te₃-based materials," *J. Appl. Phys.* **106**, 073503 (2009).
6. Ann I. Persson, Yee Kan Koh, David G. Cahill, Lars Samuelson, and Heiner Linke, "Thermal conductance of InAs nanowire composites," *Nano Lett.* **9**, 4484–4488 (2009).

E. 2008 publications that cite the previous grant number N00014-05-1-0250

1. Seongwon Kim, Jianmin Zuo, Ngoc Nguyen, David C. Johnson, David G. Cahill, "Structure of layered WSe₂ thin films with ultralow thermal conductivity," *J. Mat. Res.* **23**, 1064–1067 (2008).
2. Catalin Chiritescu, David G. Cahill, Raimar Rostek, Harald Böttner, Colby Heide-
man, Qiyin Lin, Clay Mortensen, Ngoc T. Nguyen and David Johnson, "Low thermal
conductivity in nanoscale layered materials synthesized by the method of modulated
elemental reactants," *J. Appl. Phys.* **104**, 033533 (2008).

F. Ph.D. thesis supported by N00014-07-1-0190

- Catalin Chiritescu, "Ultralow thermal conductivity in layered disordered crystalline materials," U. Illinois, Urbana, IL, April 2010.
- Yee Kan Koh, "Heat transport by phonons in crystalline materials and nanostructures, U. Illinois, Urbana, IL, July 2010.

G. 2008–2010 invited conference presentations that report work supported by N00014-07-1-0190

1. D. G. Cahill, "Thermal conductivity of phase change materials and the thermal conductance of interfaces," MRS Spring Meeting, San Francisco, CA, March 24–27, 2008.
2. D. G. Cahill, "Pushing the boundaries of the thermal conductivity of materials," 6th US-Japan Joint Seminar on Nanoscale Transport Phenomena—Science and Engineering, Boston, MA July 13–16, 2008.
3. D. G. Cahill, "Pushing the boundaries of the thermal conductivity of materials," International Conference on Thermoelectrics, Corvallis, OR, August 4–7, 2008.

4. D. G. Cahill "Ultralow thermal conductivity in disordered layered crystals," MRS Spring Meeting, San Francisco, CA, April 13–16, 2009.
5. D. G. Cahill, "Thermal conductivity control with thin films," International Conference on Metallurgical Coatings and Thin Films, San Diego, CA, April 27–30, 2009.
6. D. G. Cahill and Yee Kan Koh, "Do embedded nanodots make better thermoelectrics?," International Conference on Thermoelectrics, Freiburg, Germany, July 27–30, 2009.
7. D. G. Cahill, "Phonon lifetimes in Si from 50 GHz to 15 THz," MRS Fall Meeting, Boston, MA, November 30–December 3, 2009.
8. D. G. Cahill, "Thermal conductance of interfaces and ultralow thermal conductivity," 37th Conference on the Physics and Chemistry of Surfaces and Interfaces, Santa Fe, NM, January 10–14, 2010.
9. D. G. Cahill, "Thermal energy conversion and control," AAAS Annual Meeting, San Diego, CA, February 18–22, 2010.
10. D. G. Cahill, "Ultralow thermal conductivity in nanostructured materials," Workshop on Transport in Nanostructured Materials, Lawrence Berkeley Laboratory, Berkeley, CA, April 1–2, 2010.
11. D. G. Cahill and Yee Kan Koh, "Nanostructures and the lattice thermal conductivity of thermoelectric materials," MRS Spring Meeting, San Francisco, CA, April 5–9, 2010.

H. 2008-2009 contributed presentations that report work supported by N00014-07-1-0190

1. Y. K. Koh, Y. Cao, D. G. Cahill, and D. Jena, "Thermal conductivity reduction by interface roughness in $(\text{AlN})_x\text{-(GaN)}_y$ superlattices." 2008 March Meeting of the APS, New Orleans, LA, March 10–14.
2. Y. K. Koh and D. G. Cahill, "Lattice thermal conductivity of nanostructured thermoelectric materials based on PbTe," MRS Spring Meeting, San Francisco, CA, April 14–17, 2009.
3. M. L. Scullin, J. Ravichandran, S. Mukerjee, Y. K. Koh, D. G. Cahill, J. Moore, A. Majumdar, and R. Ramesh, "High-temperature thermoelectric performance of $\text{Sr}_{1-x}\text{La}_x\text{TiO}_{3-d}$," MRS Spring Meeting, San Francisco, CA, April 14–17, 2009.