Ceramic-based Ultra-High-Temperature Thermocouples in Harsh Environments

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Collaborating with

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Outline

1. Introduction of Project Team Members
2. Short Background on Thermocouples
3. Discussion of Technical Aspects of the Project
4. Comments and Questions
Project Team: Members

Morgan State University
- Yucheng Lan (PI).
- Numbers of grad: 1; Numbers of undergrad: 2.

University of Wyoming
- Dr. Hertanto Adidharma (co-PI) and Dr. Maohong Fan (co-PI)
- Numbers of student: 1
High-Thermoelectric Performance of Nanostructured Bismuth Antimony Telluride Bulk Alloys
Bed Poudel, et al.
Science 320, 634 (2008);
DOI: 10.1126/science.1156446

Structure Study of Bulk Nanograined Thermoelectric Bismuth Antimony Telluride
Yucheng Lan, Bed Poudel, Yi Ma, Dezhi Wang, Mildred S. Dresselhaus, Gang Chen, and Zhifeng Ren
Nano Lett., 2009, 9 (6), 1419-1422; DOI: 10.1021/nl900329v • Publication Date (Web): 25 February 2009
Downloaded from http://pubs.acs.org on April 28, 2009

Increased Phonon Scattering by Nanograins and Point Defects in Nanostructured Silicon with a Low Concentration of Germanium
Department of Physics, Boston College, Chestnut Hill, Massachusetts 02167, USA
Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA
Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA
(Rceived 26 November 2008; published 14 May 2009)

The mechanism for phonons scattering by nanograins and point defects in nanostructured silicon (Si) and the silicon germanium (Ge) alloy and their thermoelectric properties are investigated. We found that the thermal conductivity is reduced by a factor of 10 in nanostructured Si in comparison with bulk crystalline Si. However, nanosize interfaces are not as effective as point defects in scattering phonons with wavelengths shorter than 1 nm. We further found that a 5% at. % Ge replacing Si is very efficient in scattering phonons shorter than 1 nm, resulting in a further thermal conductivity reduction by a factor of 2, thereby leading to a thermoelectric figure of merit of 0.95 for Si0.95Ge0.05 similar to that of large-grained Si0.95Ge0.05 alloys.

DOI: 10.1126/science.1156446 PACS numbers: 73.40.Hq, 81.05.Et

Enhancement of Thermoelectric Figure-of-Merit by a Bulk Nanostructuring Approach
By Yucheng Lan, Austin Jerome Minnich, Gang Chen, and Zhifeng Ren
Nano Letters is published by the American Chemical Society. 1155 16th Street, N.W., Washington, DC 20036 www.nanoletters.org

Recently a significant figure-of-merit (ZT) improvement in the most-studied existing thermoelectric materials has been achieved by creating nanograins and nanostructures in the grains using the combination of high-energy ball-milling and a direct-current-induced hot-press process. Thermoelectric transport measurements, coupled with microstructure studies and theoretical modeling, show that the ZT improvement is the result of low lattice thermal conductivity due to the increased phonon scattering by grain boundaries and structural defects. In this article, the synthesis process and the relationship between the microstructures and the thermoelectric properties of the nanostructured thermoelectric bulk materials with an enhanced ZT value are reviewed. It is expected that the nanostructured materials described here will be useful for a variety of applications such as waste heat recovery, solar energy conversion, and environmentally friendly refrigeration.

Recently, a number of studies reported high performance of thermoelectric materials. Since the thermoelectric effect was discovered by Jean Charles Athanase Peltier in 1834, solid state energy conversion between heat and electric-ality has been achieved by creating nanograins and nanostructures in the grains using the combination of high-energy ball-milling and a direct-current-induced hot-press process. Thermoelectric transport measurements, coupled with microstructure studies and theoretical modeling, show that the ZT improvement is the result of low lattice thermal conductivity due to the increased phonon scattering by grain boundaries and structural defects. In this article, the synthesis process and the relationship between the microstructures and the thermoelectric properties of the nanostructured thermoelectric bulk materials with an enhanced ZT value are reviewed. It is expected that the nanostructured materials described here will be useful for a variety of applications such as waste heat recovery, solar energy conversion, and environmentally friendly refrigeration.

where S, a, k, and T are the Seebeck coefficient, the electrical conductivity, the thermal conductivity, and the absolute temperature at which the properties are measured, respectively. The efficiency of a thermoelectric device is directly related to ZT. For power generation, the efficiency ε is

$\eta = \frac{T^2}{k T + a C}$

and for air-conditioning and refrigeration, the coefficient of performance is

$\text{COP} = \frac{T}{T - T_{amb}} \frac{1}{\sqrt{1 - \frac{T}{ZT T_{amb}}}}$
Ag-base thermal sensors at nanoscale.

CdS-based thermal history sensing.

Thermal sensors.

Setaram TAG 24-24 simultaneous digital thermoanalyzer.

- Hitachi S-5500 cold field-emission scanning electron microscope.
- Physical Property Measurement System (PPMS).
- Scintag PAD-V high precision automated X-ray diffractometer, Rigaku MiniFlex desktop X-ray diffractometer.
- Atomic force microscopes (AFM).
- LECO HR-1B-2 hydrothermal system.
Project Team: Facilities at UW

- FEI G2-F20 TEM.
- FEI FEG450 SEM with EDS.
- DXR2Xi Raman Imaging Microscope.
- SmartLab X-ray diffractometer.
- MFP-3D Origin AFM.
- Thermogravimetric Analyzers (TGA).
Background: Thermoelectrics

Luigi Galvani (1737 – 1798) and experiment frog legs. Italian physicist. Pioneer of bioelectricity.

Alessandro Volta (1745 – 1827) and a voltaic pile. Italian physicist and chemist. Pioneer of electricity and power.
Background: Seebeck Effect

Thomas Johann Seebeck (1770 – 1831). German physicist. Discover of thermoelectric effects.

$$\Delta V = S(T_h - T_c)$$

$S$: Seebeck coefficient; $V$: electromotive force (Seebeck voltage); $T_h$: temperature of hot end; $T_c$: temperature of cold end.

Background: Alloy-based Thermocouples

<table>
<thead>
<tr>
<th>Type</th>
<th>Combination*</th>
<th>Temperature range (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E</td>
<td>chromel – constantan</td>
<td>-50 – 740</td>
</tr>
<tr>
<td>J</td>
<td>Fe – constantan</td>
<td>-40 – 750</td>
</tr>
<tr>
<td>K</td>
<td>chromel – alumel</td>
<td>-200 – 1350</td>
</tr>
<tr>
<td>M</td>
<td>82%Ni / 18%Mo – 99.2%Ni / 0.8%Co</td>
<td>1400</td>
</tr>
<tr>
<td>N</td>
<td>Nicrosil / Nisil</td>
<td>-270 – 1300</td>
</tr>
<tr>
<td>T</td>
<td>copper – constantan</td>
<td>-200 – 350</td>
</tr>
</tbody>
</table>

*: by weight. T: Temperature range (°C).

<table>
<thead>
<tr>
<th>Type</th>
<th>Combination*</th>
<th>Temperature range (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>70%Pt / 30%Rh – 94%Pt / 6%Rh</td>
<td>50 – 1820</td>
</tr>
<tr>
<td>R</td>
<td>87%Pt / 13%Rh – Pt</td>
<td>0 – 1600</td>
</tr>
<tr>
<td>S</td>
<td>90%Pt / 10%Rh – Pt</td>
<td>630 – 1600</td>
</tr>
<tr>
<td>C</td>
<td>95%W/5%Re – 74%W/26%Re</td>
<td>2329</td>
</tr>
<tr>
<td>D</td>
<td>97%W/3%Re – 75%W/25%Re</td>
<td>2490</td>
</tr>
<tr>
<td>G</td>
<td>W – 74%W/26%Re</td>
<td>2,300</td>
</tr>
<tr>
<td>P</td>
<td>55%Pd/31%Pt/14%Au – 65%Au/35%Pd</td>
<td>500 – 1400</td>
</tr>
</tbody>
</table>

*: by weight. T: Temperature range (°C).
Background: High-Temperature Alloy-based Thermocouple Assemblies

- Cost. Noble metals, such as Pt and Rh, are used.
- Slow responsive.
- Bulky.
Background: Seebeck Coefficient and Semiconducting Thermoelectric Materials

\[ S = \frac{8\pi^2 \kappa_B^2}{3e h^2} m^* T \left( \frac{\pi}{3n} \right)^{2/3} \]

- \( S \) is Seebeck efficient.
- \( \kappa_B \) is the Boltzmann constant.
- \( m^* \) is the effective mass the carrier.
- \( T \) is temperature.
- \( e \) is the unit charge.
- \( h \) is the Planck’s constant.
- \( n \) is the carrier concentration.

Background: Advanced Semiconducting Thermoelectric Materials

Top: Bi$_2$Te$_3$ thermoelectric nanocomposites with its microstructures.

Bottom: Microstructures of Si$_{95}$Ge$_5$ thermoelectric nanocomposites.

Nanostructured thermoelectric materials.

A new kind of semiconducting thermocouples working in harsh environments:

- High stability at high temperature.
- Resistance to oxidization, erosion, and shock.
- Simple structure and easy maintenance.
- Low Cost.
Project: Semiconducting Thermoelectric Ceramic

Seebeck coefficient $S$ of proposed semiconducting ceramic.

Predicated $emf$ of proposed thermocouples.

Working at high temperatures, with high chemical stability and high erosion resistance.
Project: Relevancy to Fossil Energy

Bowen Steam Plant. A coal-fired power station in Georgia.

- Coal combustion at $1,300 - 1,700 \degree C$.
- Coal-fired thermal power plant: emit $CO_2$, $SO_2$, $NO_x$, solid waste under high temperature / high pressure.
- Overall coal plant efficiency: $32 - 42 \%$. Efficiency: $35 - 38 \%$ at $570 \degree C$ and $170$ bar, $42 \%$ at $600 \degree C$ and $220$ bar, $48 \%$ at $600 \degree C$ and $300$ bar.

Thermal sensors work under harsh environment to control temperature accurately. The proposed thermocouples will be good substitutes.

en.wikipedia.org; coalhandlingplants.com
Project: Milestones and Schedule

- Ceramic *synthesis* and structural *characterization*.
- Seebeck *coefficient* measurements of semiconducting ceramics.
- Fabrication of *thermocouples* and *emf* measurements.
- *Stability* characterization of thermocouples

Budget: $500K.
COVID-19 and pandemic
Comments and Questions ?