High performance Zintl phase TE materials with embedded nanoparticles

Ali Shakouri and Zhixi Bian
EE, Univ. of California Santa Cruz
Susan Kauzlarich
Chemistry, Univ. of California Davis
In collaboration with
Sabah Bux, Jean-Pierre Fleurial; JPL
Lon Bell; BSST, Amerigon

Acknowledgement:
NSF-DOE,
ONR, DARPA DSO

DOE Thermoelectric Applications Workshop, San Diego; 4 January 2011
Thermoelectric figure of merit, $ZT$

Power factor

$$ZT = \frac{S^2 \sigma}{\kappa T}$$

$S$: Seebeck coefficient

$\sigma$: Electrical conductivity

$\kappa$: Thermal conductivity (e + phonon)

Example: Si-doped (InGaAs)$_{0.8}$(InAlAs)$_{0.2}$
Seebeck-conductivity trade-off

Doped Bulk Semiconductor

\[ \text{Energy} \]

\[ \text{Density of States} \]

- \( E_f \) High doping
- \( E_f \) Low doping

Deg. Semiconductor/Metal + Energy Filter (Thermionic emission)

=> Potential to reach \( ZT \sim 4-5 \) (with \( k_{\text{lattice}} \sim 1 \text{W/mK} \))

ErAs Semi-metal Nanoparticles embedded in InGa(Al)As Semiconductor Matrix

- Erbium is co-deposited at a growth rate which is a fixed fraction of the InGaAlAs growth rate (MBE growth)
- Solubility limit is exceeded $\rightarrow$ islands are formed (2-3nm ErAs)

Josh Zide, Art Gossard and Chris Palmstrøm (UCSB and Delaware)
Electrical conductivity and Seebeck (theory/experiment)

**Electrical Conductivity**

- Si-doped InGaAlAs
- 0.6% ErAs:InGaAlAs

**Seebeck**

- 0.6% ErAs:InGaAlAs
- Si-doped InGaAlAs

J. Zide et al., J. Appl. Phys. 2010

The nanoparticle material is not optimized.
Electron mobility in embedded nanoparticle material

Theory

Mobility (cm$^2$ V$^{-1}$ s$^{-1}$)

0.08% ErAs

0.6%

Si-doped InGaAs
Er-doped InGaAs

Carrier density (cm$^{-3}$)

Je-Hyeong Bahk et al. 2010
Thermal conductivity reduction

Si-doped InGaAlAs

0.6% ErAs:InGaAlAs

UCSB, UCSC, UC Berkeley
Thermoelectric figure-of-merit

Largest measured ZT~1.33 at 800K

ErAs:InGaAlAs

n-InGaAlAs (control)


The majority of ZT enhancement is from thermal conductivity reduction. 5% power factor enhancement at 800K.
ErAs:InGa(Al)As thick growth approach

Hong Lu, Art Gossard, UCSB
Nanoparticle scattering optimization

Power factor, n-type InGaAs at 600K

Optimal: $Q=1e$, $a=1.5$ nm

~ 40% enhanced
Silicide nanoparticles in SiGe

300K
3.4% nanoparticles

Silicon

Si$_{0.5}$Ge$_{0.5}$

NiSi$_2$

Ge

Predictions:
ZT (300K) $\sim$ 0.5
ZT (900K) $\sim$ 1.8

Natalio Mingo et al. Nano Letters 2009
Frequency contributions to thermal conductivity in presence of Iron silicide nanoparticles at 300K

Alloy

Natalio Mingo 2009 (unpublished)
Nanoparticles in $\text{Mg}_2\text{Si}_x\text{Sn}_{1-x}$

Synthesis and Characterization of Mg$_2$Si/Si

Susan Kauzlarich’s Group
Tanghong Yi
UC Davis
And
Jean-Pierre Fleurial’s Group
Sabah Bux
JPL

Part of this work was performed at the Jet Propulsion Laboratory, California Institute of Technology under contract with the National Aeronautics and Space Administration.
Synthesis Goals

- Develop non-toxic Zintl phase magnesium silicide alloys with embedded nanoparticles
- Optimizing the matrix alloy composition and the nanoparticles for maximum thermoelectric figure-of-merit in 500K ~ 800K range
Synthesis

\[ 2\text{MgH}_2 + (1+x)\text{nano Si(Bi)} \rightarrow \text{Mg}_2\text{Si}/x\text{Si(Bi)} \]
\( (x = 0\%, 1.25\%, 2.5\%, 5\%) \)

Crystallite~ 50 nm
Particle size ~200 nm
Powder X-ray Diffraction

2.5 mol% Si
5 mol% Si
Transport properties

Sabah Bux and Jean-Pierre Fleurial (JPL)

- TY79: MgH$_2$ + bulk Si = 2.25:1
- TY81: MgH$_2$ + nano Si = 2.2:1
- TY95: MgH$_2$ + nano Si = 2:1
- TY101: MgH$_2$ + nano Si = 1.95:1

Transport properties

Sabah Bux and Jean-Pierre Fleurial (JPL)

Nano-Si inclusions (1% to 5%)
• Demonstrated n-type Mg$_2$Si via a new synthetic method (MgH2 + Si) with naturally occurring Si nanoparticle inclusions.

• Preliminary measurements of thermoelectric properties by JPL

• Carrier concentration changes vs nanoinclusions needs to be studied

• Further characterization of the pressed pellets is necessary to determine if the nanoinclusions are isolated and randomly distributed.

• Further efforts are underway to reduce particle size along with optimization of carrier concentration.

Actual ZT $\sim 1$
(see e.g. Nanostructured Thermoelectrics: Big Efficiency Gains from Small Features, Vineis et al. Advanced Materials 2010)

Difficulty
- Non-active barrier layers: Broido and Reinecke PRB ‘01, Mahan, etc.
- Improvement “per conduction channel” is 40-60% - Kim et Lundstrom J. Appl. Phys. 105, 034506 (2009)
Solar Cells (Efficiency + Cost $\rightarrow \$/W)

An inconvenient truth about thermoelectrics

Cronin Vining, Nature Materials 2009
Material cost of TE power generation system

Current TE modules

2nd generation TE modules

3rd generation TE modules

Cross over

Air cooling (Aluminum heat sink)

Water cooling (microchannels)

Today’s TE power generation cost: $1-2/W

Potential to bring this down to: $0.1/W

See K. Yazawa’s presentation on Wednesday

K. Yazawa and A. Shakouri, International Mechanical Engineering Congress Nov. 2010
Acknowledgement

Senior Researchers: Zhixi Bian, Kaz Yazawa, James Christofferson

Postdocs/Graduate Students: Je-Hyeong Bahk, Tela Favaloro, Phil Jackson, Kerry Maize, Hiro Onishi, Paul Abumov, Oxana Pantchenko, Amirkoushyar Ziabari, Bjorn Vermeersch, Gilles Pernot, Shila Alavi

Collaborators: John Bowers, Art Gossard, Chris Palmstrom (UCSB), Tim Sands (Purdue), Rajeev Ram (MIT), Venky Narayanamurti (Harvard), Arun Majumdar (Berkeley), Josh Zide (Delaware), Lon Bell (BSST), Natalio Mingo (CEA/UCSC), Susan Kauzlarich (Davis), Sabah Bux, Jean-Pierre Fleurial (NASA JPL)