Nanocomposite Thermoelectric Materials

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ABSTRACT

We have studied the thermoelectric properties of nanoscale silicon spheres embedded within a germanium host. Our theory has identified that 10nm diameter spheres, with the densest possible packing, has the potential to improve thermoelectric efficiency 10x. If cost effective fabrication methods are found, this will enable a multitude of technological applications.

THERMOELECTRICITY

In any material, heat is conducted via two carriers; phonons and electrons. Thermoelectricity is simply a heat induced electrical potential, whereby electrons or holes are driven across a thermal gradient, producing a current.

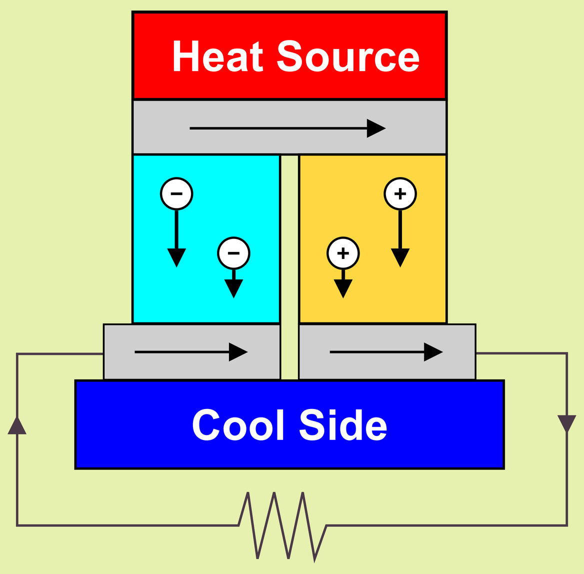

Figure 1. A thermoelectric circuit configured as an electrical generator. N and P-doped thermoelectrics are placed across a heat gradient, driving electrons and holes to recombine, generating a current.

NANOCOMPOSITES

Much like a traditional composite, a nanocomposite is comprised of two or more materials assembled to form a functionally distinct material. Typically, nanoscale sheets, wires or particles are dispersed into a bulk material, forming an artifical structure with significantly altered properties.

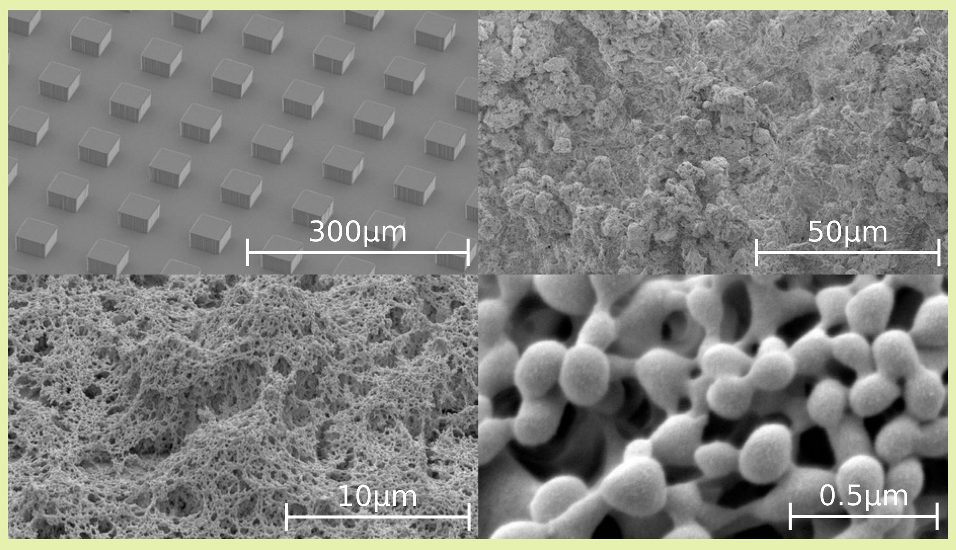

Figure 2. A STEM image of a nanocomposite at several different scales [1]

APPLICATIONS

Thermoelectric materials have the potential to revolutionise electricity generation and refridgeration methods. They are both simple to use and incredibly reliable; apply a heat gradient for electricity, apply electricity for cooling. Currently, their efficiency limits their use to space probes, where reliability is vitally important. But with the potential advancements of nanocomposite design, we could see utilisation in heat recovery systems, refridgeration and combined photovoltaic solar thermal systems.

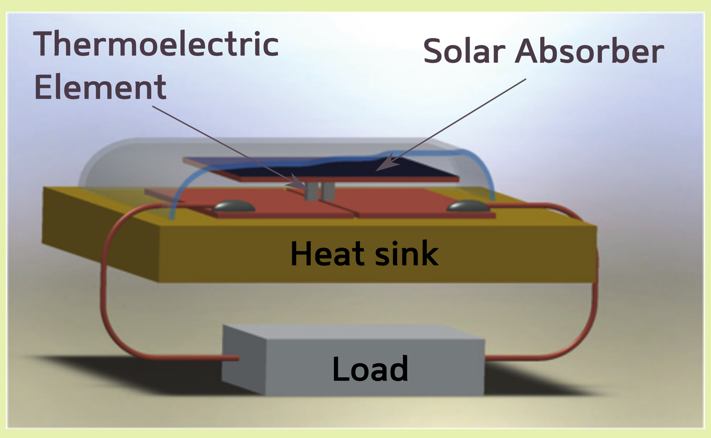

Figure 3. A solar thermal thermoelectric panel design. Sunlight heats the solar absorber, producing a thermal gradient across the two thermoelectric elements, generating a current across the load.

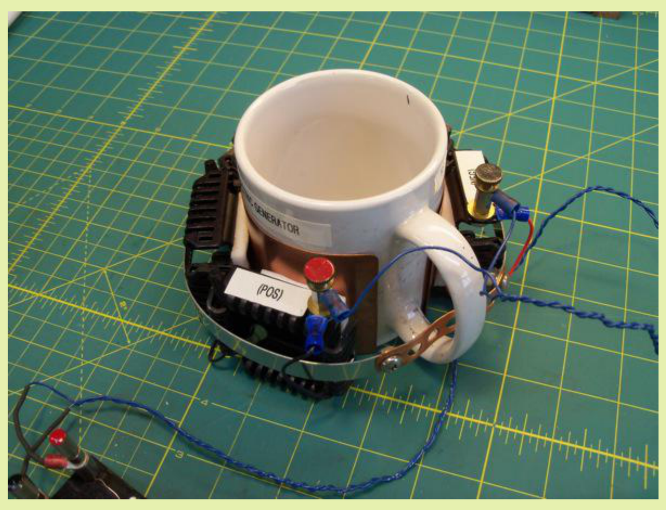

Figure 4. A prototype coffee cup heat recovery system. A thermal gradient between the heat sinks and the cup lights a small bulb, demonstrating the versatility of thermoelectric generators.

PHONON HEAT CONDUCTION

A core aim of our project is the reduction of phonon thermal conductivity (K_{ph}) via nanocomposite structuring. A reduction in K_{ph} will increase the total thermoelectric efficiency, as described by the figure of merit (ZT):

$$ZT = \frac{S^2 \sigma T}{K_{el} + K_{ph}}$$

Equation 1:
Defines the thermoelectric figure of merit (ZT) ∝ conversion efficiency. Seebeck coefficient (S), electrical conductivity (σ), temperature (T), thermal conductivity of electrons (K_{el}) and phonons (K_{ph}).

We investigated two different composite theories; the effective medium approximation (EMA) [2] and the phonon hopping model [5]. From our analysis, the phonon hopping model neglected crucial thermoelectric properties, so we adopted the EMA model.

Embedding a generic particle in a homogenous host, periodically perturbs the thermal conductivity. We assume the particle-host interface scatters phonons diffusely and is described by the acoustic mismatch model [6]. For spherical particles, the EMA simplifies to:

$$\frac{k_e}{k_h} = \frac{k_p(1+2\alpha) + 2k_h + 2\varphi[k_p(1-\alpha) - k_h]}{k_p(1+2\alpha) + 2k_h - \varphi[k_p(1-\alpha) - k_h]}$$

Equation 2:
Defines phonon thermal conductivity (k_e) of a spherical macrocomposite. Thermal conductivity of the host (k_h) and particle (k_p), thermal boundary resistance (α), volume fraction of particle to host per unit cell (φ).

For nanocomposites, the EMA needs to be modified to account for increased scattering in and around particles. The modified-EMA (mEMA) [3] model introduces these scattering terms, reducing k_p & k_h and increasing ZT.

Finally, we investigated the effect of specular interface scattering [4], reworking the thermal boundary resistance. We found this had a negligible effect on k_{ph} (see Figure 5) so we decided to use the simpler mEMA.

Assumptions

- Crystals described by Debye's isotropic continuum model
- Optical phonon effects are negligable
- Nanoparticle diameter is greater than phonon wavelength
- Interfaces scatter phonons diffusely

ELECTRICAL TRANSPORT

We derived from first principles all the electrical properties to complete our ZT expression. Of particular importance is the temperature dependent Fermi level (E_F), defined here for an extrinsic semiconductor [7]:

$$E_F = E_g + \frac{3}{4}kT\ln\left(\frac{m_h^*}{m_e^*}\right) + kT\sinh^{-1}\left(\frac{N_d - N_a}{2\sqrt{U_c U_v}\exp - \frac{E_g}{2kT}}\right)$$

Equation 3:
Defines the Fermi level (E_F) of an extrinsic semiconductor.
Band gap (E_g), hole & electron effective mass (m*), donor & acceptor dopant concentration (N_d), effective conductance & valence band (U_c)

To find S, σ and K_{el}, first you must determine the number of electrons by integrating the Fermi-Dirac distribution with the density of states. This leads to many Fermi integrals, which cannot be solved exactly.

Using a numerical method, such as Simpson's rule, a near complete solution could be found. At high temperatures, the Fermi integrals can be approximated by taking an asymptotic limit, leading to [8]:

$$S = \frac{k}{e}\left(\frac{2E_F}{kT} - \left(P + \frac{5}{2}\right)\right)$$

$$K_{el} = \frac{k^2}{e^2}\left(P + \frac{5}{2}\right)\sigma T$$

Equations 4 & 5:
Defines the Seebeck cofficient (S) and electrical thermal conductivity (K_{el}) for a generic conductor. Electrical conductivity (σ), temperature (T), power factor for phonon-carrier scattering (P) = -½ for acoustic phonons

Through similar logic, electrical conductivity (σ) can be found.

We are unaware of a nanocomposite theory of electrical transport, so as a basic initial model we took a weighted average of all constituant variables. This is a valid assumption if the electron wavelength is much greater than the nanoparticle diameter; the electron will 'see' the composite material as a homogenous structure.

Assumptions

- Nanoparticles are smaller than typical electron wavelength
- Only consider acoustic phonons
- Diameter of nanoparticle spheres greater than 10nm

RESULTS

All models discussed above are calculated for 10nm silicon particles embedded within a germanium host. EMA models show a surprisingly constant temperature dependence as shown in Figure 7. This can be traced back to the dominance of diffuse phonon scattering at particle interfaces.

From our analysis, it is clear that maximising the particle's surface area per unit volume (interface density) is key to minimising the phonon thermal conductivity. So far, it appears to have no effect on the electrical transport, thus at 0.3 volume fraction, a 10x increase in ZT could be realised.

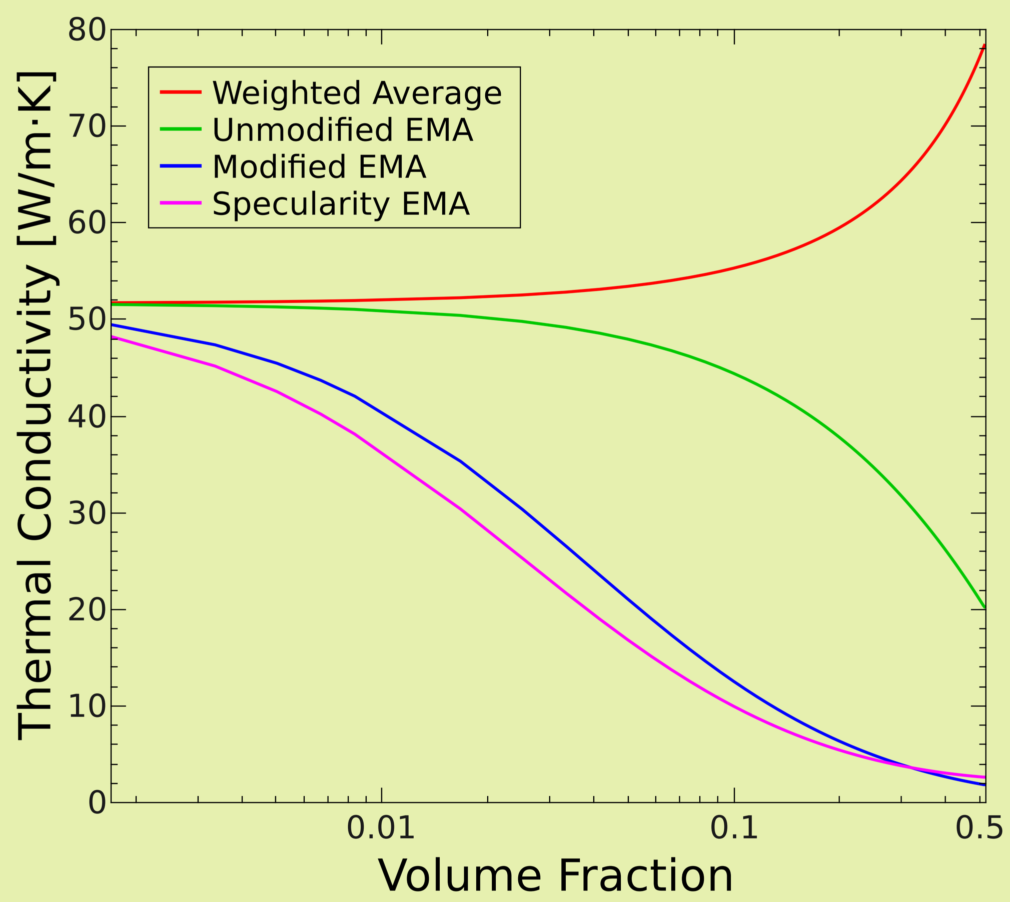

Figure 5. A comparison between 4 different composite K_{ph} models. 0.1 volume fraction corresponds to 90% Ge, 10% Si. Each model considers progressively smaller size scales, with increasing complexity.

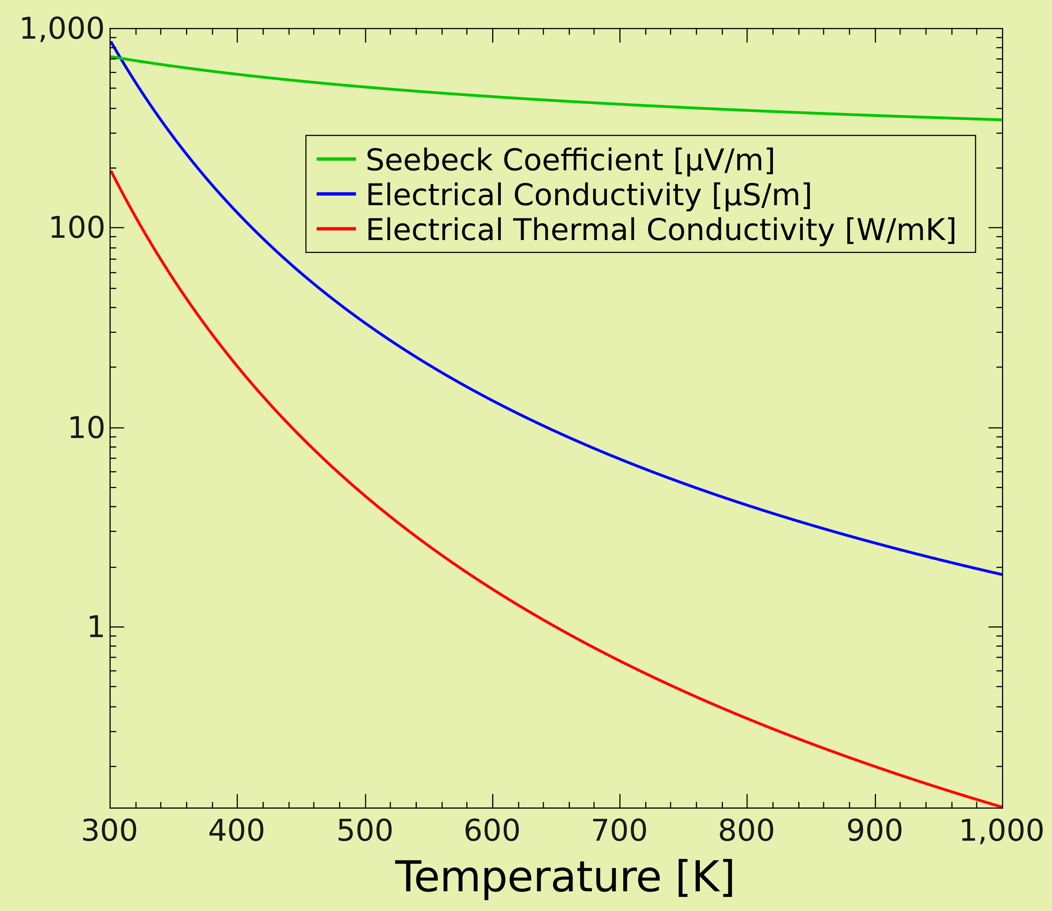

Figure 6. Calculated electrical transport properties for a 70-30 GeSi composite. Negative slopes suggest a higher thermoelectric efficiency can be obtained at room temperature. See key for y-axis dimensions.

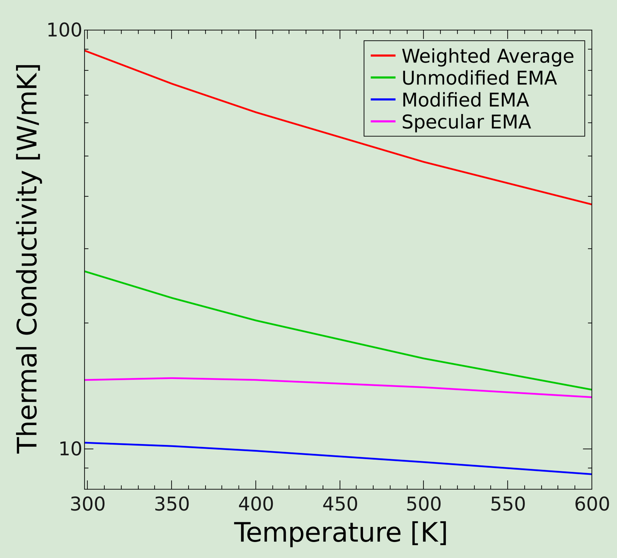

Figure 7. Temperature dependence of 4 different composite K_{ph} models. Temp independent particle size scattering terms dominate.

FUTURE WORK

- Numerically solve Fermi integrals to improve temp range & accuracy
  - Planning to use Fortran to implement simpsons rule
- Create a nanocomposite theory of electrical transport
  - May be possible to use the EMA approach
- Find temperature dependent variables (band gap etc) and calculate ZT
- Derive an expression for the total efficiency of a thermoelectric generator
  - Is the 10x ZT improvement able to be translated to a real application
- Investigate the effects of non-spherical particle shapes
  - Particularly a 3D tesselating shape, to maximise interface density

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