Ultralow thermal conductivity and the thermal conductance of interfaces

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• Thermal conductivity and interface thermal conductance.
• Advances in time-domain thermoreflectance.
• Amorphous limit to the thermal conductivity of materials.
• Ultralow thermal conductivity: beating the amorphous limit in disordered layered crystals.
• On-going work on understanding and extending the physics.
Interfaces are critical at the nanoscale

- Low thermal conductivity in nanostructured materials
  - improved thermoelectric energy conversion
  - improved thermal barriers

- High thermal conductivity composites and suspensions
Interfaces are critical at the nanoscale

- High power density devices
  - solid state lighting
  - high speed and power electronics
  - nanoscale sensors

TEM micrograph of tunneling magnetoresistive sensor (view from “air bearing side”) M. Kautzky (Seagate)
Thermal conductivity and interface thermal conductance

- Thermal conductivity $\Lambda$ is a property of the continuum

\[ \mathbf{J} = -\Lambda \nabla T \]

\[ \Lambda = \frac{1}{3V k_B T^2} \int_0^\infty \langle \mathbf{J}(t) \cdot \mathbf{J}(0) \rangle \, dt \]

- Thermal conductance (per unit area) $G$ is a property of an interface

\[ \mathbf{J} = G \Delta T \]

\[ G = \frac{1}{A k_B T^2} \int_0^\infty \langle q(t) q(0) \rangle \, dt \]
Both properties are difficult to understand and control because they are integral properties.

For example, simplest case of thermal conductivity where resistive scattering dominates

$$\Lambda = \frac{1}{3} \int C(\omega) \nu(\omega) l(\omega) \, d\omega$$

$C(\omega) = \text{heat capacity of phonon mode}$

$\nu(\omega) = \text{group velocity}$

$l(\omega) = \text{mean-free-path}$
Time domain thermoreflectance since 2003

- Improved optical design
- Normalization by out-of-phase signal eliminates artifacts, increases dynamic range and improves sensitivity
- Exact analytical model for Gaussian beams and arbitrary layered geometries
- One-laser/two-color approach tolerates diffuse scattering

Clone built at Fraunhofer Institute for Physical Measurement, Jan. 7-8 2008
Optical constants and reflectivity depend on strain and temperature.

Strain echoes give acoustic properties or film thickness.

Thermoreflectance gives thermal properties.

Graph showing a decay curve with labels for TaN and MgO layers.
Time-domain Thermoreflectance (TDTR) data for TiN/SiO$_2$/Si

- reflectivity of a metal depends on temperature
- one free parameter: the “effective” thermal conductivity of the thermally grown SiO$_2$ layer (interfaces not modeled separately)
Our first steps in a search for a solid-state heat switch...

**Epitaxial VO\(_2\)/sapphire**

- Large temperature oscillations activate latent heat contributions to the heat capacity
- Contrast in thermal conductivity is only 50%. Need larger contrast between “off” and “on”
Interface thermal conductance: Factor of 60 range at room temperature

\[ \Lambda = \frac{L}{G} \]

\( \Lambda = 1 \, \text{W m}^{-1} \, \text{K}^{-1} \)
Can we beat the amorphous limit of the thermal conductivity $\Lambda_{\text{min}}$ with interfaces?

- Einstein (1911): random walk of thermal energy
- Not good for crystals: Debye (1914)
- but does work for amorphous solids, Birch and Clark (1940); Kittel (1948)
- and crystals with strong atomic-scale disorder, Slack (1979); Cahill and Pohl (1988).

$$\Lambda_{\text{min}} = 0.40 k_B n^{2/3} (\nu_\ell + 2\nu_\ell)$$

**High T limit**
Einstein (1911)

- coupled the Einstein oscillators to 26 neighbors
- heat transport as a random walk of thermal energy between atoms; time scale of $\frac{1}{2}$ vibrational period
- did not realize waves (phonons) are the normal modes of a crystal
Works well for homogeneous disordered materials

- amorphous
- disordered crystal
Layered disordered crystals: WSe$_2$ by “modulated elemental reactants”

- Deposit W and Se layers at room temperature on Si substrates
- Anneal to remove excess Se and improve crystallinity
- Characterize by RBS, x-ray diffraction (lab sources and Advanced Photon Source) and TEM
Cross-sectional TEM of 60 nm thick WSe$_2$

Seongwon Kim and Jian Min Zuo
Thermal conductivity of $\text{WSe}_2$

- 60 nm film has the lowest thermal conductivity ever observed in a fully dense solid. Only twice the thermal conductivity of air.

- A factor of 6 less than the calculated amorphous limit for this material.
Ion irradiation of WSe$_2$

MD simulation of 1 MeV Kr impact on Au

- Heavy ion irradiation (1 MeV Kr$^+$) of 24 nm WSe$_2$ film.
- Novel behavior: ion damage causes the thermal conductivity to increase.
Digression: ion bombardment of a superlattice (with Y. Cao and D. Jena)

- 2.3 MeV Ar ion irradiation of GaN and \((\text{AlN})_4\text{nm}-(\text{GaN})_5\text{nm}\)
- Lines are Debye-Callaway models assuming phonon Rayleigh scattering scales linearly with ion dose.
- Fit gives \(\Gamma = 1\) at an ion dose of \(10^{14}\text{ cm}^{-2}\)
• MD work by Bodapati and Keblinski (RPI)

• Original LJ model of WSe$_2$ gives 0.06 W/m-K independent of length-scale

• Conclusion: physics is general, not specific to some detail of the WSe$_2$ bonding or microstructure
Conclusions from theoretical work (Hu and Keblinski, unpublished)

- Analysis of the participation ratio: phonon localization is not significant.
- Analysis of mode polarization: incoherent grain boundaries create diffusive but non-propagating vibrational modes. (stacking faults are not sufficient)
- Key to ultralow thermal conductivity is disorder in combination with anisotropy, i.e., an “anisotropic glass”.
- Interface resistance between 2D crystalline sheets? Lowering of the effective density of states for modes diffusing perpendicular to the sheets?
Back to experiment: Can we lower the conductivity even further?

• Synthesize misfit layered compounds by elemental reactants method (Johnson and co-workers)
  - WSe$_2$/PbSe
  - MoSe$_2$/PbSe
• Interface density does not matter. Conductivity determined by composition not interface density.
Incredibly low thermal conductivity (far below the amorphous limit) in the disordered, layered crystal WSe$_2$.

- Combination of disorder (random stacking of sheets) and anisotropy (large differences in vibrations within and across the sheets) appears to be the key.
- How far can we push this using other types of interfaces?
- Can we reproduce this physics in materials with good electrical conductivity for thermoelectric energy conversion?
- Can we reproduce this physics in refractory oxides for thermal barriers?
I. Is anisotropy a key factor?

- Use “pressure tuning” to modify anisotropy
  - Mica as demonstration (not disordered)
- Low thermal conductivity in Dion Jacobson layered oxide
  - 60% of minimum thermal conductivity,
  - suppression is consistent with anisotropy but source of disorder is unknown at this time
Use pressure as a variable

- Muscovite mica is a layered (but not disordered) crystal
- Elastic anisotropy is a factor 3; thermal conductivity anisotropy is a factor of 8

*Diamond anvil cell*
Time-domain stimulated Brillouin scattering (picosecond interferometry)
Pressure tuning of elastic anisotropy

- Cross-plane elastic constants are more anharmonic and stiffen more rapidly with pressure.
- $C_{33}$ (cross-plane) measured by picosecond interferometry (time domain Brillouin scattering); Gruenisen constant is $\gamma \approx 4$.

Hsieh, Chen, Li, Cahill, Keblinski, PRB (2009)
Pressure tuning of thermal conductivity of mica

Hsieh, Chen, Li, Cahill, Keblinski, PRB (2009)
Low thermal conductivity in a layered oxide

70 nm film grown by pulsed laser deposition

Cahill, Melville, Schlom, Zurbuchen, APL 2010
II. What can pressure dependence tell us about thermal conductance of interfaces?

- “Classical” models (DMM, AMM) for interface thermal conductance do not include physics of the interface itself: phonon transport is only a function of the properties of the two solids.

- Elastic constants and phonon spectrum of typical materials do not change much between 0 and 10 GPa.

- But interface bonding might be weak and highly anharmonic
II. What can pressure dependence tell us about thermal conductance of interfaces?

- Work in progress.
  a) Al deposited on native oxide of SiC
  b) Al deposited *in-situ* on SiC cleaned in high vacuum at 1000°C
Big picture summary

- Powerful experimental tools for probing “nanoscale thermal transport”
  - Measuring thermal conductivity of novel, thin layer materials, is no longer (in most cases) a research project in itself; can focus on the materials and the physics.

- Conventional wisdom about the lower limit of the thermal conductivity of dense (non-porous) solids is not correct.
  - Compelling “race to the bottom” to find even lower conductivity solids

- Pressure dependence is providing a new “knob” to turn for experiments on heat transport at the nanoscale