Strain field and coherent domain wall effects on the thermal conductivity and Kapitza conductance in Bismuth Ferrite

Patrick E. Hopkins
Assistant Professor
University of Virginia
phopkins@virginia.edu
patrickehopkins.com

Brian M. Foley
University of Virginia

Carolina Adamo, Darrell G. Schlom
Cornell University

Linghan Ye, Bryan Huey
University of Connecticut

Brady Gibbons
Oregon State University

Stephen R. Lee, Doug Medlin, Harlan Brown-Shaklee, Jon F. Ihlefeld
Sandia National Labs
Ferroelectrics and related materials can have low thermal conductivities
  • Complex phonon spectra
  • Soft modes
  • Anisotropy
  • What role do internal boundaries/structures play??

Grain boundaries: SrTiO$_3$

\[
\tau_j = \left[ \frac{1}{\tau_a} + \frac{1}{\tau_{gb}} + \frac{1}{\tau_{fb}} \right]^{-1}
\]

\[
= \left[ BT \omega_j^2 \exp\left(-\frac{C}{T}\right) + \frac{v_j}{d_{avg}} + \frac{v_j}{170 \times 10^{-9}} \right]^{-1}
\]

What about domain boundaries/strain?

Grain boundaries = incoherent

Ferroelectric domain boundaries = coherent and strained
• Domains and domain walls in BiFeO$_3$

• Time domain thermoreflectance (TDTR)

• Domain effects on thermal transport in BiFeO$_3$

• “Domain wall” Kapitza conductance – phonon-strain field scattering
Layered structures can exhibit ultralow thermal conductivity.

**Ex. Sr$_2$Nb$_2$O$_7$**

Perovskite-like layers

SrO layer


“Coherent” interfaces – BiFeO$_3$ domains

- Domain boundaries – other types of coherent interfaces
- Reactive molecular-beam epitaxy: 30 nm BiFeO$_3$ films on SrTiO$_3$ substrates

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Domain characterization - PFM

- Standard domain imaging not sufficient
- Require quantification of domain boundaries
- Vector (angle-resolved) PFM: 2 steps
  - Out-of-plane (normal) z-direction
  - In-plane y-direction
  - Rotate specimen 90 degrees

Domain boundary quantification

• Growth on vicinal substrate results in different domain structure
• Virtually all 71 deg. domain walls
• **4 variant**: 16 $\mu$m domain wall/$\mu$m$^2$
• **2 variant**: 11 $\mu$m domain wall/$\mu$m$^2$

Time domain thermoreflectance (TDTR)

- Thermal conductivity of series of BiFeO$_3$ films with different domain structures

- Can measure thermal conductivity of thin films and substrates ($\kappa$) separately from thermal boundary conductance ($h_K$)
- Nanometer spatial resolution (~10’s of nm)
- Femtosecond to nanosecond temporal resolution
- Noncontact
Domain effects on *effective* thermal conductivity

- Effective thermal conductivities of BiFeO$_3 < 2.5$ W m$^{-1}$ K$^{-1}$
- Presence of domain walls reduces $\kappa$ by $\sim 30\%$

- *Strain fields from domains are scattering phonons* *(previous speaker)*

Domain effects Kapitza conductance

- 4 variant: $D = 16 \mu m$ domain wall/\(\mu m^2\)
- 2 variant: $D = 11 \mu m$ domain wall/\(\mu m^2\)

$$h_K = \frac{\kappa_0}{D \left( \frac{\kappa_0}{\kappa} - 1 \right)}$$

- Strain fields from coherent domain boundaries can scatter phonons like domain boundaries
- Coherent domain walls offer as much resistance as 10 nm of SiO\(_2\)

Domain engineering of thermal properties

Single Crystalline Pb\([Zr_xTi_{1-x}]O_3\) (PZT) – A LOT OF DOMAINS!

More domains and smaller domains at boundaries

Domain scattering stronger than alloy scattering

Schmitt et al. JAP 101, 074107 (2007)

- Domains boundaries scatter phonons
- Coherent strain fields have similar effects as incoherent grain boundaries

\[
\frac{1}{\tau_{\text{domain wall}}} = \frac{\nu}{d_{\text{domain wall}}}
\]

**Young Investigator Program**
Single vs. poly PZT

Thermal Conductivity of polycrystalline PZT films

Thermal Conductivity of single-crystalline PZT films

[Graphs showing the thermal conductivity of single and polycrystalline PZT films as a function of mole percent PbTiO$_3$.]
TDTR sensitivities – effective thermal conductivity

FIG. 2. TDTR sensitivity calculations based on 2 and a two- or three-layer thermal model (dashed and solids lines, respectively). Assuming a three-layer system (50 nm Pt/30 nm BiFeO$_3$/SrTiO$_3$), we have very low sensitivity to $C$ of the BiFeO$_3$ compared to $\kappa$ of BiFeO$_3$ or $h_K$ at the Pt/BiFeO$_3$ interface. Therefore, we can treat this system as a two layer system (Pt/SrTiO$_3$) and fit $h_K$ between the Pt films and SrTiO$_3$ substrate to determine the effective thermal conductivity of the BiFeO$_3$. Note we are extremely sensitive to $h_K$ between the Pt films and SrTiO$_3$ using this approach, as indicated by the dashed line.

Our TDTR sensitivity calculations for this three layer system are shown in Fig. 2 as the solid lines. Our thermal model that we use for these sensitivity calculations has been discussed in detail elsewhere.

Note that an ideal sensitivity is very dynamic throughout the entire range of pump-probe delay times (i.e., not flat). For this three layer analysis, our TDTR measurements are always more sensitive to the thermal boundary conductance between the Pt and BiFeO$_3$ and the thermal conductivity of the BiFeO$_3$ than the heat capacity of the BiFeO$_3$. At longer time delays, we begin to become more sensitive to the BiFeO$_3$ heat capacity, but at these time delays the sensitivity to the thermal boundary conductance and thermal conductivity also increases and overwhelms the sensitivity to the heat capacity of the thin BiFeO$_3$ film. As our measurements have very low...
Conductance measurements

FIG. 3. Measured conductances from our TDTR data using a two-layer model. The conductances determined from the Pt/BiFeO$_3$/SrTiO$_3$ are represented by the filled symbols and the thermal boundary conductance measured from our Pt/SrTiO$_3$ calibration samples is shown by the unfilled squares. The data in Fig. 3 of the manuscript are derived by multiplying the conductance from the Pt/BiFeO$_3$/SrTiO$_3$ by the thickness of the BiFeO$_3$ (30 nm).

sensitivity to the heat capacity of the 30 nm BiFeO$_3$ films, we can treat this system as a two-layer system (Pt/SrTiO$_3$) and fit our TDTR data via the thermal boundary conductance between the Pt film and SrTiO$_3$ substrate to determine the conductance of the 30 nm BiFeO$_3$ film. As shown in Fig. 2 by the dashed line, our measurements are very sensitivity to K between the Pt and SrTiO$_3$, yielding low uncertainty.

Therefore, the values reported in this manuscript are determined from fitting our TDTR data to a two-layer model by iterating the thermal boundary conductance between the Pt transducer film and the SrTiO$_3$ substrate. These resulting conductances are shown in Fig. 3. The effective thermal conductivities of the BiFeO$_3$ films reported in Fig. 3 in the manuscript are derived by multiplying the conductances of the Pt/BiFeO$_3$/SrTiO$_3$ samples (filled symbols) by the thicknesses of the films (30 nm). Note that this conductance actually represents three thermal pathways: the thermal boundary conductance between the Pt transducer and the BiFeO$_3$ film, the thermal conductiv...
Reciprocal space mapping

Fig. 4. Reciprocal space mapping of the 103 peaks in 30 nm thick BiFeO$_3$ films grown on (001)-oriented SrTiO$_3$ with (a) 4 domain variants, (b) 2-domain variants and (c) a single domain variant.

Due to the epitaxial growth of the BiFeO$_3$ and high quality and coherency of the interface, we are minimally sensitive to this BiFeO$_3$/SrTiO$_3$ conductance since the thermal boundary conductance is very high at epitaxial interfaces, as we mentioned previously. To estimate the thermal boundary conductance between the Pt and BiFeO$_3$ film, we measure the thermal boundary conductance between a Pt transducer and a single crystalline SrTiO$_3$ substrate. These measurements are shown in Fig. 3 (unfilled squares), and are roughly half an order of magnitude greater than the conductance measured on the Pt/BiFeO$_3$/SrTiO$_3$ samples. Due to the surface quality of the BiFeO$_3$ films owing to the epitaxial growth, the Pt/BiFeO$_3$ thermal boundary conductances are most likely similar to those at the Pt/SrTiO$_3$ interfaces. Therefore, we can conclude that our conductances measured in the Pt/BiFeO$_3$/SrTiO$_3$ samples are primarily dominated by the thermal conductivity of the BiFeO$_3$ films, resulting in the effective thermal conductivities reported in Fig. 3 of the manuscript.
“Coherent” interfaces – Domain boundaries

- Domain boundaries – other types of coherent interfaces
- BiFeO$_3$ domains can be engineered with substrate vicinality

Exact (001) SrTiO$_3$

4° miscut toward [100]

4° miscut toward [110]

Slide courtesy of Chang-Beom Eom and Jon Ihlefeld
BiFeO$_3$ film growth

- Reactive molecular-beam epitaxy: 30 nm BiFeO$_3$ films on SrTiO$_3$ substrates
- Phase-pure
- Smooth surface and interface
- Crystallinity limited by substrate (SrTiO$_3$)

Does this make sense?

- Coherent domain wall scatters phonons like incoherent grain boundary?
- What’s the mechanism???

**Attenuation (Akhieser):**

\[
\frac{1}{\tau_{\text{Akhieser}}} \propto \omega^2
\]

**Rayleigh:**

\[
\frac{1}{\tau_{\text{impurity}}} \propto \omega^4
\]

**Incoherent (like a grain boundary):**

\[
\frac{1}{\tau_{\text{grain}}} \propto \frac{v}{d_{\text{grain}}}
\]