NANOMETER-SCALE TEMPERATURE MEASUREMENTS OF
PHASE CHANGE MEMORY AND CARBON NANOMATERIALS

BY

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DISSEPTION

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ABSTRACT

This work investigates nanometer-scale thermometry and thermal transport in new electronic devices to mitigate future electronic energy consumption. Nanometer-scale thermal transport is integral to electronic energy consumption and limits current electronic performance. New electronic devices are required to improve future electronic performance and energy consumption, but heat generation is not well understood in these new technologies. Thermal transport deviates significantly at the nanometer-scale from macroscopic systems as low dimensional materials, grain structure, interfaces, and thermoelectric effects can dominate electronic performance. This work develops and implements an atomic force microscopy (AFM) based nanometer-scale thermometry technique, known as scanning Joule expansion microscopy (SJEM), to measure nanometer-scale heat generation in new graphene and phase change memory (PCM) devices, which have potential to improve performance and energy consumption of future electronics.

Nanometer-scale thermometry of chemical vapor deposition (CVD) grown graphene measured the heat generation at graphene wrinkles and grain boundaries (GBs). Graphene is an atomically-thin, two dimensional (2D) carbon material with promising applications in new electronic devices. Comparing measurements and predictions of CVD graphene heating predicted the resistivity, voltage drop, and temperature rise across the one dimensional (1D) GB defects.

This work measured the nanometer-scale temperature rise of thin film Ge$_2$Sb$_2$Te$_5$ (GST) based PCM due to Joule, thermoelectric, interface, and grain structure effects. PCM has potential to reduce energy consumption and improve performance of future electronic memory. A new
nanometer-scale thermometry technique is developed for independent and direct observation of Joule and thermoelectric effects at the nanometer-scale, and the technique is demonstrated by SJEM measurements of GST devices. Uniform heating and GST properties are observed for mixed amorphous and crystalline phase GST. However, heterogeneous heating and GST phase distribution are observed for mixed crystalline phases of GST. The properties of GST thin films are evaluated using macroscopic and SJEM measurements. The thermopower of GST thin films depends on the local grain structure and has potential to significantly decrease future PCM energy consumption.

This dissertation presents nanometer-scale thermometry measurements of Joule and thermoelectric effects in new graphene and PCM devices due to defects, interfaces, and grain structure: important for developing future electronics and increasing knowledge of nanometer-scale thermal transport.
This work is dedicated to my family and to Julie.
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CHAPTER 1
INTRODUCTION

Nanometer-scale thermal transport is integral to electronic performance and energy consumption. Microprocessor operating frequency has been limited by nanometer-scale heat dissipation for almost a decade,\textsuperscript{1} and global data center electricity consumption is \(~4-6\%\) of the world’s annual electricity consumption, equivalent to \(~25-30\%\) of the European Union’s annual electricity consumption.\textsuperscript{2} New energy efficient electronic devices are needed to decrease future electronic energy consumption. However, nanometer-scale heat generation is not well understood in new electronic materials and devices.

Thermal transport deviates significantly at the nanometer-scale from macroscopic systems as low dimensional materials, grain structure, interfaces, and thermoelectric effects can dominate heat generation and transport at these small scales. Atomic force microscopy (AFM) based thermometry techniques, such as scanning Joule expansion microscopy (SJEM),\textsuperscript{3} have sufficient resolution to observe and investigate nanometer-scale heat generation. Previous work has used the SJEM technique for direct investigation of nanometer-scale Joule, interface, and thermoelectric effects in new graphene based electronic devices.\textsuperscript{4} Graphene and phase change memory (PCM) devices have the potential to reduce energy consumption and improve performance of future electronics;\textsuperscript{5,6} however, local Joule and thermoelectric effects are not completely understood in these devices. Nanometer-scale thermometry measurements of graphene and PCM devices would improve current comprehension of heat generation in these materials, enabling energy efficient design of future graphene and PCM electronics and increasing current knowledge of nanometer-scale thermal transport.
1.1 – Thermoelectric Transport

Thermoelectric (TE) transport is the reversible transport of thermal energy with charge carriers in a material. Three proportionality constants relate thermal and electrical transport in a material. Electrical conductivity relates carrier flow to a potential gradient. Thermal conductivity relates heat flow to a temperature gradient. The thermopower, Seebeck coefficient, relates TE transport to potential and temperature gradients. Thermal and electrical transport are coupled by irreversible Joule heating (JH) and reversible TE effects. The Seebeck, Peltier, and Thomson effects describe TE transport and have applications in thermocouples and solid-state cooling and power generation.

The Seebeck, Peltier, and Thomson effects describe thermoelectric transport in a material. Electric current is the transport of negative and positive charge carriers, electrons and holes, in a solid; while heat flow is the transport of thermal energy by lattice vibrations, phonons, and charge carriers in a solid. Charge carriers dominate thermal transport in metals, and phonons dominate thermal transport in insulators and most semiconductors. TE transport describes charge carrier or thermal transport due to a temperature or potential gradient. TE transport is well described by MacDonald, which is briefly summarized below. The Seebeck effect describes the potential difference which develops across a material due to a temperature difference at its junctions with dissimilar thermopower materials. The Peltier effect describes the heating and cooling of a junction of dissimilar thermopower materials with carrier flow. The Thomson effect describes the reversible heating or cooling of a material due to carrier flow. The three TE effects scale with bias and are reversible. JH scales with the square of the bias and is irreversible. Peltier and Thomson effects require carrier flow and are therefore coupled with JH.
The magnitude of thermoelectric transport in a material is given by its thermopower. The thermopower of metals is typically low, as only a few electrons at the top of the energy distribution participate in TE transport. The thermopower of semiconductors can be large due to the band gap, as only carriers which cross the band gap are available for electrical or TE transport. Semiconductor TE transport is driven by variations in the density of state due to the applied electric and thermal fields. However, carrier scattering, impurity scattering, and phonon drag also dominate a material’s thermopower, but phonon drag typically occurs at low temperatures. The sign of the thermopower is positive or negative if holes or electrons are the dominant thermoelectric carriers.

Thermoelectric effects have several applications in nanotechnology. The Seebeck effect is utilized in measurements of thin film thermopower by subjecting micrometer-scale device junctions to a temperature gradient and measuring the resultant thermoelectric voltage gradient. Some scanning thermal microscopy (SThM) probes have a thermocouple at the probe tip to measure nanometer-scale temperatures, and SThM probes with integrated heaters have been used to measure the local thermopower across electron and hole doped junctions. The Peltier effect has been observed at the nanometer-scale as heating and cooling of a junction of dissimilar thermopower materials with carrier flow and change in carrier spin. Peltier and Seebeck effects may enable solid-state coolers and power generators, with potential to harvest human waste heat. However, developing thermoelectrics for large-scale energy harvesting faces multiple challenges. Finally, the Thomson effect due to majority and minority carriers has been observed in nanowires subjected to large temperature gradients. Several new electronic materials have large measured thermopowers, and the coupling of optical and thermoelectric effects, the photo-thermoelectric effect, has been observed in 2D (two dimensional) electronic
devices,\textsuperscript{23,26} emphasizing the importance of understanding nanometer-scale thermoelectric transport.

Table 1.1: Summary of nanometer-scale thermometry techniques

<table>
<thead>
<tr>
<th>Technique</th>
<th>Measurement</th>
<th>Lateral resolution</th>
<th>Advantages</th>
<th>Disadvantages</th>
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<tr>
<td><strong>Micrometer-scale thermistors</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3-omega (3ω)</td>
<td>Vertical thin-film thermal properties</td>
<td>Not applicable</td>
<td>Simple fabrication, accurate measurements</td>
<td>Difficult implementation, no lateral resolution</td>
</tr>
<tr>
<td>Suspended platform</td>
<td>Lateral thermal conductivity</td>
<td>Not applicable</td>
<td>Direct interpretation of measurements</td>
<td>Difficult fabrication</td>
</tr>
<tr>
<td>Supported platform</td>
<td>Lateral thermal conductivity</td>
<td>Not applicable</td>
<td>Simple fabrication</td>
<td>Complicated modeling required</td>
</tr>
<tr>
<td><strong>Optical techniques</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Infrared thermometry (IR)</td>
<td>Thermal emissivity</td>
<td>~10 μm</td>
<td>Non-contact, minimal sample preparation, direct temperature measurements</td>
<td>Low resolution</td>
</tr>
<tr>
<td>Raman thermometry</td>
<td>Raman peak shift due to temperature change</td>
<td>~1 μm</td>
<td>Non-contact, minimal sample preparation, measure equilibrium distributions</td>
<td>Requires calibration of Raman peaks, low temperature sensitivity</td>
</tr>
<tr>
<td>Pump-probe techniques</td>
<td>Vertical thin-film thermal properties</td>
<td>~10 μm</td>
<td>Non-contact, nanometer-scale vertical resolution</td>
<td>Requires careful preparation of surface, difficult implementation</td>
</tr>
<tr>
<td><strong>High resolution optic techniques</strong></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Luminescent thermometers</td>
<td>Temperature-dependent particle emission</td>
<td>~100 nm</td>
<td>High temperature sensitivity</td>
<td>Difficult implementation</td>
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<tr>
<td>Near-field scanning optical microscopy (NSOM)</td>
<td>Focuses evanescent waves using sharp probe tip</td>
<td>~100 nm</td>
<td>High resolution, limited by probe tip size</td>
<td>Can require vacuum, unknown heat generation</td>
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<tr>
<td>Scanning electron microscopy (SEM) techniques</td>
<td>Temperature dependence of back-scattered electrons</td>
<td>~10 nm</td>
<td>High resolution</td>
<td>Difficult sample preparation and interpretation of results</td>
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<tr>
<td><strong>Scanning probe microscopy (SPM) techniques</strong></td>
<td></td>
<td></td>
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<tr>
<td>Scanning thermal microscopy (SThM)</td>
<td>SPM probe with integrated temperature sensor</td>
<td>~100 nm</td>
<td>Direct temperature measurements, high resolution</td>
<td>Complex probe fabrication, unknown tip-sample heat transfer</td>
</tr>
<tr>
<td>Scanning Joule expansion microscopy (SJEM)</td>
<td>Device periodic thermo-mechanical expansion</td>
<td>~50 nm</td>
<td>Simple device fabrication, high resolution</td>
<td>Complicated modeling required</td>
</tr>
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1.2 – Nanometer-Scale Thermal Metrology

Nanometer-scale thermal metrology techniques can be grouped by micrometer-scale thermistor,\textsuperscript{27,28} optical,\textsuperscript{29} and scanning thermal microscopy (SThM)\textsuperscript{30,31} measurements. Research activity in these fields has focused on measuring thermal properties, heat flow, and temperature fields of nanometer-scale devices. Current nanometer-scale thermal measurements balance measurement implementation, spatial resolution, and accuracy. Table 1.1 provides an overview of the nanometer-scale thermometry techniques discussed in this section.

Micrometer-scale thermistors measure thermal properties of nanometer-scale materials.\textsuperscript{27,28} The large size of micrometer-scale thermistors limits the measurement’s lateral spatial resolution. Measurements use optical or electron-beam (e-beam) patterned metal lines as Joule heaters and thermometers. Micrometer-scale thermistor measurements include 3-omega (3\(\omega\)),\textsuperscript{27} suspended platform,\textsuperscript{28} and supported platform\textsuperscript{32} techniques. The 3\(\omega\) technique biases a metal line with a sinusoidal waveform and measures its associated temperature rise, which depends on the sample thermal resistance.\textsuperscript{27,33,34} The vertical thermal diffusivity of a thin film can be determined from the 3\(\omega\) technique if the input power, metal temperature, and substrate properties are known.\textsuperscript{33} Suspended and supported platform techniques measure the lateral thermal resistance of a nanometer-scale sample. Suspended platforms use two isolated thermal reservoirs at different temperatures which are connected by the sample.\textsuperscript{28} The reservoirs are composed of suspended thin insulator films with metal heaters and thermometers to control and measure the temperature rise of each reservoir. Reservoirs can have additional metal lines contacting the sample for thermoelectric measurements.\textsuperscript{35} The sample thermal conductance can be determined if the input power and temperature rise of each reservoir is known\textsuperscript{36} as the suspended platform isolates heat flow across the sample. Recent work has used suspended
platforms and a scanning electron microscopy (SEM) beam to locally heat the sample and measure the sample thermal conductance with nanometer-scale resolution. Supported platform techniques are similar to suspended platform techniques. Both techniques use separate metal heaters and thermistors to measure sample thermal conductance. Fabrication of supported platforms is simpler than suspended platforms, but accurate modeling is required to account for additional heat flow into the substrate. A semi-suspended platform, fabricated by a back-side etch, has advantages of both platform based techniques and can measure the anisotropic thermal conductivity of thin films.

Optical techniques are used to map device temperature and determine thin film thermal properties. Optical techniques include infrared (IR) thermometry, Raman thermometry, and pump-probe and time-domain thermal reflectance (TDTR) methods. These techniques are typically non-contact and non-destructive. IR thermometry measures sample IR emissivity for direct temperature measurements, but is diffraction limited to ~10 μm lateral resolution. Raman thermometry measures the shift in Raman peaks of a sample with temperature and is diffraction limited to ~1 μm lateral resolution. Accurate Raman thermometry measurements require calibration of the sample’s Raman peak-shifts, but Raman thermometry enables measurements of carrier and phonon populations of the device. IR and Raman thermometry do not require complicated sample preparation, and have been used to study Joule heating in heated cantilevers, graphene devices and carbon nanotubes (CNTs) devices. Raman thermometry has also been used to measure sample thermal conductivity. Pump-probe and TDTR techniques measure the nanometer-scale thermal diffusivity of thin films. A laser pulse is used to heat and measure sample temperature with picosecond time resolution. The sample surface must be well prepared and characterized as the temperature is measured by the change
in surface reflectivity. The high time resolution of TDTR can measure nanometer-scale, vertical heat diffusion of a sample. Sample preparation for TDTR can be easier than other methods, but experimental set-up and analysis is difficult.\textsuperscript{31,33,43}

The lateral resolution of optic based techniques can be improved to sub-1 \( \mu m \) using luminescent thermometers, near-field scanning optical microscopy (NSOM), and scanning electron microscopy (SEM) techniques.\textsuperscript{29} Luminescent thermometers utilize the temperature-dependent emission properties in nanometer-scale particles such as fluorescents,\textsuperscript{39} dyes,\textsuperscript{29} and vacancies.\textsuperscript{48} NSOM utilizes a sharp probe to focus evanescent electromagnetic waves to obtain sub-100 nm resolution,\textsuperscript{43} but NSOM often requires vacuum conditions.\textsuperscript{29} Local heating due to field enhancement in NSOM and nano-particle luminescent is also not well understood.\textsuperscript{39,43} SEM techniques obtain nanometer-scale resolution by measuring the temperature dependence of back-scattered electrons\textsuperscript{49,50} or measuring small changes in sample thermo-mechanical expansion.\textsuperscript{29} However, sample preparation and measurement interpretation can be difficult for SEM techniques.

SThM techniques measure temperature fields and thermal properties with nanometer-scale lateral resolution.\textsuperscript{30,31,51,52} SThM is a scanning probe microscopy (SPM) based technique which utilizes specialty fabricated SPM probes to measure temperature using a thermocouple tip, an integrated thermistor, or changes in cantilever strain.\textsuperscript{31,43} The nanometer-scale lateral resolution of SThM has measured defect heating in graphene,\textsuperscript{53} the thermopower of GaAs electron-hole junctions,\textsuperscript{16} and the temperature rise of plasmonic structures during operation.\textsuperscript{54} Applications of SThM techniques are limited by the ability to fabricate sufficiently sharp tips and unknown heat transfer between the cantilever tip and sample surface.\textsuperscript{39,43,52} Several techniques have been proposed to overcome and understand cantilever-sample heat transfer including
alternating and direct current excitation of a heated cantilever,\textsuperscript{55} operation in vacuum,\textsuperscript{56-58} and creating a thermocouple at the tip-sample interface.\textsuperscript{59} Vacuum SThM can reach \textasciitilde10 nm lateral resolution,\textsuperscript{56,57} and integrating a carbon nanotube (CNT) on a SThM tip can measure sample thermal conductivity with \textasciitilde30 nm lateral resolution.\textsuperscript{60} SThM probes also have applications in nanometer-scale topography measurements,\textsuperscript{61,62} thermal analysis,\textsuperscript{52} and fabrication.\textsuperscript{31,52,63} Coupling SThM with NSOM can measure nanometer-scale, temperature-dependent IR surface absorption,\textsuperscript{64} and coupling SThM with a scanning tunneling microscopy (STM) has potential to measure electron orbital temperatures.\textsuperscript{65} However, difficult probe fabrication and complex cantilever-sample heat transfer limits the application of SThM, despite the variety of applications and high spatial resolution.

1.3 – Scanning Joule Expansion Microscopy

Scanning Joule expansion microscopy (SJEM) is an atomic force microscopy (AFM) based nanometer-scale thermometry technique.\textsuperscript{3,4,66,67} SJEM is capable of high spatial (sub-50 nm) and temperature (\textasciitilde100 mK) resolution measurements.\textsuperscript{4,68} SJEM operates by biasing and Joule heating a device with a periodic waveform, and an AFM cantilever in contact with the surface measures the resultant periodic sample thermo-mechanical expansion. A lock-in amplifier at the heating frequency records the surface expansion. The sample is typically coated in a polymer with a large coefficient of thermal expansion (CTE), such as Poly(methyl methacrylate) (PMMA), to amplify the measured surface expansions and protect the device during SJEM measurements.\textsuperscript{3,4} Coupling SJEM measurements with finite element analysis (FEA) models allows for prediction of the nanometer-scale stresses and temperature field of the device.\textsuperscript{4,67,69}
Measurement techniques using periodic heat sources to measure temperature or sample thermo-mechanical expansion have existed for ~35 years. In 1978, Wickramasinghe and colleagues studied micrometer-scale photoacoustics using a laser heat source and an acoustic lens to induce and measure sample thermo-mechanical expansions. Subsequent studies measured the periodic temperature rise of the sample due to periodic heating from optical beams. In 1982, a phase-sensitive laser measured device thermo-mechanical expansions with ~2 μm lateral resolution due to periodic Joule heating. A similar method measured Joule heating in a bipolar inverting gate four years later. In 1989, a scanning tunneling microscopy (STM) technique accomplished nanometer-scale thermometry using the tip-sample interface as a thermocouple to measure sample temperature due to periodic heating from a laser. Then in 1998, Majumdar and Varesi invented SJEM using an AFM cantilever to measure sample thermo-mechanical expansions due to periodic Joule heating. Subsequent techniques have utilized periodic heating of a SThM probe to measure polymer thermo-mechanical expansion and SThM thermometry to measure thermal waves due to periodic Joule heating of buried metal lines.

Many studies have improved and implemented the SJEM technique to investigate nanometer-scale heating in microelectronics. Majumdar and Varesi initially showed SJEM measurements were due to thermo-mechanical surface expansions and not due to thermally induced cantilever bending, acoustic waves from the surface expansion, piezoelectric forces, or electrostatic forces between the tip and sample. Subsequent work studied Joule heating of micrometer-scale metal lines to demonstrate the SJEM technique. The work of Cannaerts and colleagues investigated the roles of cantilever stiffness and electrostatic forces in the SJEM technique, and they calibrated their SJEM measurements using a metal thermistor. Their work
enabled the study of current crowding and grain boundary heating in a cobalt-nickel silicide device.\textsuperscript{81} SJEM accuracy has also been verified by comparison with optical interferometry and SThM measurements,\textsuperscript{82} and SJEM measurements have investigated thermal stresses in interconnects due to sinusoidal and pulsed biases.\textsuperscript{83} Tiedemann, Fakhri, and colleagues coupled vertical and lateral SJEM measurements and 3D (three dimensional) FEA modeling to investigate thermo-mechanical strains in metal lines.\textsuperscript{67,84} The accuracy of their technique was verified by comparison with SThM measurements to predict the thermo-mechanical stresses of a multi-layered interconnect structure.\textsuperscript{85} Coupling SJEM measurements and FEA modeling of thin Au lines verified the Wiedemann-Franz law.\textsuperscript{86} SJEM measurements of transistors includes observations of hot-spot movement of in-plane gate transistors with gate bias;\textsuperscript{87} defect induced hot-spots in CNT transistors;\textsuperscript{68,88,89} and Joule heating, current crowding, and thermoelectric effects in graphene transistors.\textsuperscript{4} The ease of implementation and high spatial resolution make SJEM an appealing technique to study nanometer-scale thermal transport.\textsuperscript{4,30}

1.4 – Graphene Devices

Graphene\textsuperscript{90} is an atomically-thin material composed of hexagonal carbon rings with exceptional electrical,\textsuperscript{5} optical,\textsuperscript{91} mechanical,\textsuperscript{92} and thermal\textsuperscript{47} properties. The combination of these properties has promising applications for current microelectronics.\textsuperscript{93} Graphene can also be developed for new analog transistors,\textsuperscript{94-96} high-electron mobility transistors (HEMTs),\textsuperscript{97} tunneling transistors,\textsuperscript{98} micro-electrical-mechanical systems (MEMS) devices,\textsuperscript{99} gas sensors,\textsuperscript{100} window defrosters,\textsuperscript{101} and flexible and transparent electronics.\textsuperscript{102}

Large-scale graphene can be grown by chemical vapor deposition (CVD).\textsuperscript{103} CVD graphene is typically fabricated by flowing a hydrocarbon gas mixture over a metal foil at an
elevated temperature,$^{104}$ and then the graphene is transferred from the metal foil to the choice substrate, typically Si/SiO$_2$. Predominately monolayer graphene grows on Cu foils due to the low solubility of carbon in Cu. Meter-scale monolayer graphene sheets have been fabricated using this method.$^{105}$ Large area graphene can also be obtained from sublimation of Si from a SiC surface.$^{106,107}$ However, applications of SiC sublimated graphene are limited due to difficulty of transferring graphene from the SiC substrate.

The properties of graphene are degraded by the presence of grain boundaries (GBs) and wrinkles in polycrystalline, CVD grown graphene.$^{108-111}$ Grain boundaries form between graphene grains during growth, and wrinkles result from the growth and transfer process. The hexagonal carbon rings of graphene grains are interrupted by pentagon-heptagon carbon rings which form at the GB between two graphene grains.$^{108}$ Predictions show the angle between the two grains can increase or decrease graphene strength,$^{111}$ but measurements have shown graphene strength is the same$^{112}$ or decreases$^{108}$ with GBs. Non-equilibrium Green’s function calculations show the GBs decrease graphene thermal conductivity.$^{110}$ Electrical measurements of polycrystalline graphene show the GB has insignificant$^{108,113}$ to significant$^{114,115}$ impact on graphene electrical performance, and STM studies show the GB can form small, resistive electron-hole junctions.$^{116,117}$ Simulations predict GBs have little intrinsic resistance, but adsorbents at the GB cause a local increase in GB resistivity.$^{118}$ Measurements have shown the GB resistance depends on the formation of the graphene domains during growth.$^{109}$ Measurements have also shown wrinkles in CVD graphene can locally degrade graphene electronic transport,$^{119}$ but wrinkles are typically less resistive than GBs.$^{120}$ Current research has focused to improve CVD graphene quality by increasing graphene grain size and reducing the presence of graphene GBs. High quality CVD graphene can be obtained by inductive heating of
the Cu foil\textsuperscript{121} using smooth Cu foil\textsuperscript{122,123} or creating a vapor trap with the Cu foil\textsuperscript{124}. Further investigation on graphene growth and the role of GBs and wrinkles in graphene transport are required to produce high quality graphene.

Graphene performance is also limited by the quality of the graphene-metal contact\textsuperscript{4,125-127}. The finite graphene-metal interface resistivity causes current crowding\textsuperscript{125-127} and localized Joule heating\textsuperscript{4} at the interface. The effect is well-known in CNTs\textsuperscript{128-130} and silicon devices\textsuperscript{7,131}. Recent work has decreased the graphene-metal contact resistivity by patterning cuts in graphene,\textsuperscript{132} sandwiching graphene between metal contacts,\textsuperscript{133} and contacting only the edge of the graphene.\textsuperscript{134} Graphene also has a large thermopower,\textsuperscript{24,26,135,136} and Peltier heating and cooling has been observed at the graphene-metal contact.\textsuperscript{4} Understanding thermoelectric effects in graphene may lead to self-cooling electronics,\textsuperscript{4} infrared thermocouples,\textsuperscript{137} and photoresponsive memory devices.\textsuperscript{138} Graphene thermopower is typically studied by scanning photocurrent microscopy (SPCM) due to the observable photo-thermoelectric effect in graphene,\textsuperscript{26,139,140} and studies have shown the thermopower of CVD graphene varies locally due to inhomogeneity in the graphene structure.\textsuperscript{141,142} Knowledge of current crowding and thermoelectric effects at graphene-metal contacts are important for the design of future graphene electronics.\textsuperscript{4}

Little is currently known of nanometer-scale heating of CVD grown graphene. Previous work has examined the micrometer-scale temperature rise in graphene devices.\textsuperscript{41,42,45,47,143,144} Raman thermometry of graphene devices has investigated Joule heating\textsuperscript{41} and phonon-carrier coupling.\textsuperscript{42} IR measurements of exfoliated graphene have investigated micrometer-scale graphene hot-spots corresponding to the graphene minimum carrier density,\textsuperscript{45,143} and subsequent IR measurements of CVD graphene observed additional and unexplained hot-spots in the device.\textsuperscript{144} High resolution SThM measurements have investigated graphene ballistic and
diffusive transport\textsuperscript{145} and Joule heating of defects in CVD graphene.\textsuperscript{53} Our previous work with exfoliated graphene observed nanometer-scale Joule and Peltier effects at graphene-metal contacts.\textsuperscript{4} These previous studies provide insight into heating of CVD graphene. However, direct observation and knowledge of nanometer-scale Joule heating of CVD graphene channels, contacts, wrinkles, and grain boundaries is currently lacking.

1.5 – Chalcogenide Based Phase Change Memory

Chalcogenide based phase change memory (PCM) has potential to be a universal memory technology improving electronic performance.\textsuperscript{6} Data in Ge\textsubscript{2}Sb\textsubscript{2}Te\textsubscript{5} (GST) based PCM are stored by the large change in electrical resistivity between the amorphous and crystalline phases.\textsuperscript{6} Ovshinsky discovered the phase switching phenomenon of chalcogenide materials and realized the potential for PCM technology over 45 years ago.\textsuperscript{146} However, chalcogenide materials were initially used for optical data storage.\textsuperscript{25,147} Chalcogenide based PCM has developed over the last ten years,\textsuperscript{148} and Samsung recently demonstrated 8 Gb PCM devices.\textsuperscript{149} Current PCM research has demonstrated a fast (sub-nanosecond),\textsuperscript{150} low power (femtojoule),\textsuperscript{151-153} and non-volatile\textsuperscript{6} memory technology with potential to replace DRAM and Flash memory in future electronic devices.\textsuperscript{6,154}

Data in PCM are stored by the change in material properties with material phase.\textsuperscript{6,25} The majority of PCM research has investigated GST devices, but many studies have adjusted the GST stoichiometry to tune device properties for specific applications.\textsuperscript{155} GST exists in amorphous, face-centered cubic (fcc), and hexagonal close-packed (hcp) phases. Annealing amorphous GST results in the fcc phase with a $10^2$-$10^4$ decrease in resistivity,\textsuperscript{6} and increased annealing transforms the fcc phase into a ten times less resistive hcp phase.\textsuperscript{25,156} Previous work
has shown the electrical contact resistivity also decreases from the amorphous to fcc to hcp phase.\textsuperscript{157-159} GST thermal conductivity increases from the amorphous to crystalline phase,\textsuperscript{38,160} with the hcp phase having the highest thermal conductivity due to significant electron contribution to heat conduction.\textsuperscript{160,161} However, thermal interface conductance is dominated by phonons for all GST phases.\textsuperscript{161} GST thermopower decreases from the amorphous to fcc to hcp phase.\textsuperscript{32} Amorphous and fcc GST exhibit a negative temperature coefficient of resistance (TCR), similar to semiconductors, and hcp GST exhibits a positive TCR, similar to metals.\textsuperscript{162}

Electrical switching between GST phases is typically driven by Joule heating. Biasing a PCM bit causes local Joule heating and anneals amorphous GST to a crystalline phase, known as the SET operation. A short current pulse can quickly heat and melt-quench crystalline GST to the amorphous phase, known as the RESET operation.\textsuperscript{6} The speed of PCM operation is limited by the SET operation,\textsuperscript{150} and the power consumption of PCM is dominated by the RESET operation.\textsuperscript{152} The interplay of thermal and electrical effects in the SET and RESET operations\textsuperscript{163,164} and the role of surrounding materials on GST phase change\textsuperscript{15,38,165} are not well understood. GST electrical and thermal interfaces are important for heat generation and thermal confinement of GST devices\textsuperscript{151,166-168} and could reduce PCM programming power.\textsuperscript{166,167,169} The Peltier,\textsuperscript{170} Seebeck,\textsuperscript{32} and Thomson\textsuperscript{171} effects have been shown to contribute to phase change, and the large thermopower of fcc phase GST\textsuperscript{32,162,172} has potential to significantly reduce GST power consumption.\textsuperscript{173}

Proper PCM device design is crucial for fast, low power, and high-density memory. Decreasing the active PCM volume will increase PCM operation speed and decrease power consumption\textsuperscript{174} by decreasing the device thermal time constant and volume of phase change material. Initial PCM devices were vertical structures with a thin film of GST sandwiched
between two electrodes. Then, lateral GST devices were fabricated by sputtering and patterning thin film GST across two electrodes. Lateral devices are encased in an insulator and have improved thermal confinement. Cross-bar memory structures feature a thin film of GST sandwiched between two perpendicular metal lines, and the cross-bar structure can isolate very small volumes of GST if small contacts, such as CNTs, are used. Other attempts to decrease PCM size and power consumption include using co-polymer lithography to pattern small areas of GST and high thermopower Si contacts to enhance PCM thermoelectric effects.

Heat generation and phase change of thin film GST is not well understood. Scaling GST films to small dimensions is essential for realizing low power, fast, and high density memory devices. Previous work has indirectly observed the temperature rise of GST devices by measuring the change in GST resistance with device heating or measuring the location of the amorphous-crystalline boundary after device operation. Other studies have directly examined GST phase change using scanning electron microscopy (SEM) during device operation but without direct temperature measurements. The models used to predict the temperature and performance of thin film GST devices may be inaccurate as knowledge of the properties of sub-25 nm thin GST films is still incomplete. Recent work has shown thin film and mixed phase GST has anisotropic thermal properties. However, little is known of the properties of mixed phase GST, and mixed phase GST has potential for high-density, multi-bit memory and neuromorphic applications. Knowledge of heat generation and the properties of thin film and mixed phase GST are crucial to enabling new PCM technologies and developing low power PCM devices.
1.6 – Dissertation Overview

The implementation of new energy efficient graphene and PCM electronic devices requires knowledge of nanometer-scale thermal transport in these materials. This dissertation reports the development and use of a nanometer-scale thermometry technique, known as SJEM, to investigate local Joule and thermoelectric effects in graphene and GST devices. Chapter 2 shows SJEM measurements of Joule heating in CVD graphene and investigates the local temperature rise at graphene grain boundaries and wrinkles. Chapter 3 develops the SJEM technique for independent and direct observation of nanometer-scale Joule and thermoelectric effects. Chapter 4 measures uniform Joule, interface, and thermoelectric effects in 25 nm thin, lateral GST devices. Chapter 5 measures the properties of sub-25 nm thin, mixed phase GST films and investigates heterogeneous Joule and thermoelectric effects in lateral GST devices. SJEM measurements can resolve nanometer-scale Joule and thermoelectric effects due to defects, interfaces, and grain structure of graphene and PCM devices, important for developing future electronics and increasing current knowledge of nanometer-scale thermal transport.
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CHAPTER 2
DIRECT OBSERVATION OF RESISTIVE HEATING AT GRAPHENE WRINKLES
AND GRAIN BOUNDARIES

2.1 – Introduction

Graphene, a monolayer of hexagonally arranged carbon atoms, has been the subject of intense research due to its thinness (~3.4 Å), unique linear band structure,\textsuperscript{1,2} and micron-scale quasi-ballistic electrical and thermal transport at room temperature.\textsuperscript{3,4} Graphene applications typically rely on material growth by chemical vapor deposition (CVD) on metal substrates.\textsuperscript{5} This process can produce graphene up to meter dimensions,\textsuperscript{6} but typically of a polycrystalline nature, with the sheet being made up of a patchwork of grains connected by grain boundaries (GBs).\textsuperscript{7} In addition, various transfer processes from the metallic growth substrate onto other substrates (e.g. SiO\textsubscript{2}, BN, plastics) can lead to wrinkling of the monolayer material.\textsuperscript{8} Not surprisingly, the presence of GBs and wrinkles are expected to degrade the thermal,\textsuperscript{9} electrical,\textsuperscript{10,11} and mechanical\textsuperscript{12} properties of graphene. Recent work has measured the electrical resistance of graphene GBs,\textsuperscript{10-17} which is important as transport across GBs influences the overall electrical performance of graphene devices grown by CVD.\textsuperscript{7} However, the associated temperature rise resulting from nanometer-scale resistive heating of GBs is currently unknown. Understanding this aspect is important not only from a graphene device (e.g. reliability) perspective, but also as an exquisite platform to directly connect the technology of high-resolution thermometry tools with the science of atomic-scale heat generation in the context of a realistic device.

In this chapter, we measured the nanometer-scale temperature rise in CVD grown hexagonal graphene grains using scanning Joule expansion microscopy (SJEM),\textsuperscript{18-21} a thermometry technique based on atomic force microscopy (AFM). We specifically study the
resistive heating at graphene wrinkles and GBs, giving insight into the coupled electrical and thermal properties of such nanoscale defects. We observe a small temperature rise at wrinkles and a larger temperature rise at GBs (150-300 % greater than the surrounding graphene) due to the finite GB resistivity and to non-uniform current flow across GBs, visualized here with nanometer-scale resolution.

2.2 – Graphene Device Fabrication

Graphene was grown on 125 μm thick Cu foil by atmospheric pressure chemical vapor deposition (APCVD) similar to previous reports. The Cu foil was electropolished in concentrated H₃PO₄, and the foils were then annealed for 1 hour at 1000 °C under 500 sccm flow of 2.5% H₂ in Ar. The growth was performed by addition of 8 sccm 0.1% CH₄ for 90 min.

Graphene was transferred to the 90 nm SiO₂/Si substrates by coating one side of the Cu foil with a bilayer of poly(methyl methacrylate) (PMMA), 495 K A2 and 950 K A4, at 3000 rpm followed by a 200 °C bake for 2 min. An O₂ plasma etch of the graphene backside is performed prior to overnight exposure to the Cu etchant (Transcene CE-100). The resultant PMMA/graphene film is transferred to a series of rinses to remove residual metal particles and etchants. The film is then transferred onto the receiving substrate and left to dry in ambient conditions before removing the supporting PMMA in a 1:1 methylene chloride to methanol solution for 20 min. As a final step, the samples undergo a 400 °C anneal under 500 sccm Ar and 100 sccm H₂ flow to remove residual PMMA.

Electron beam (e-beam) lithography was used to pattern contacts for the graphene devices. Suitable devices were located using optical microscopy by finding isolated hexagonal graphene grains which coalesced forming a grain boundary. First, e-beam lithography was used
to pattern a region around each lead to remove undesired graphene by O$_2$ plasma etching. Then, e-beam lithography was used to pattern electrical contacts. Electrical contacts were deposited by e-beam evaporation of 1/70 nm of Cr/Pd. Fabrication was completed by spin coating the samples with 55-70 nm of PMMA for the SJEM measurement.$^{19,20}$

**Figure 2.1:** Raman spectroscopy measurements of Device 1. The measurements shown were typical of all devices. An amorphous carbon baseline is present from $\sim$1100-1500 cm$^{-1}$. The full-width at half-maximum (FWHM) of the 2D peak is $\sim$25 cm$^{-1}$ indicating monolayer graphene.

Figure 2.1 shows a typical Raman spectrum of the graphene used in this study. We note a large amorphous carbon baseline at $\sim$1100-1500 cm$^{-1}$ due to unstitched areas of carbon, wrinkles in the graphene grain, or leftover polymer residue from the transfer which carbonized during the anneal. The amorphous carbon baseline was present on other samples transferred with PMMA, poly(bisphenol A carbonate), and poly(lactic acid) (PLA) scaffolds.$^{25}$ The baseline persists on all samples, regardless of the transfer scaffold used, suggesting that it originates during the CVD growth process. Regardless, the presence of the amorphous carbon baseline does not allow us to determine quantitatively if the graphene is monolayer from solely the 2D/G peak ratio ($I(2D)/I(G)$). Therefore, we measured the full width at half maximum (FWHM) of the 2D band and found it to be $\sim$25 cm$^{-1}$ which implies the graphene is monolayer.$^{26,27}$ We also do not observe a pronounced nucleation point from our Raman scans, which would indicate bilayer graphene, or
additional optical absorption peaks from turbostratic graphene. These observations support the conclusion that the graphene is monolayer.

Figure 2.2 shows a schematic of the SJEM experiment. A sinusoidal waveform with amplitude $V_{DS}$ was applied to the device at frequency $\omega = 61$-230 kHz. The sinusoidal waveform generates resistive heating within the device. The resulting thermo-mechanical expansions of the sample were measured by the laser, photodiode, and AFM cantilever in contact with the surface. A lock-in amplifier at $2\omega$, with a bandwidth of 4-125 Hz, recorded the peak-to-peak surface expansion $\Delta h$. The measured $\Delta h$ can be related to the device temperature rise $\Delta T$ using FEA modeling. A constant back-gate voltage $V_G = 0$ V was applied to control the carrier concentration of the graphene sheet for all experiments.

Figure 2.2: Schematic of scanning Joule expansion microscopy (SJEM) measurements. An AFM cantilever in contact with the surface measures thermo-mechanical expansion of the sample due to periodic resistive heating of the device. From top to bottom the device is composed of 55-70 nm PMMA, 70 nm Pd, a graphene monolayer, and 90 nm SiO$_2$ on a highly p-doped Si substrate.
2.3 – Finite Element Analysis Model

A three dimensional (3D) frequency domain electro-thermo-mechanical finite element analysis (FEA) model was developed to simulate graphene device behavior and interpret SJEM measurements. The heat diffusion and Poisson equations are shown in Eqs. 2.1 and 2.2.\(^{28,29}\)

\[
\rho_d c_p \frac{\partial T}{\partial t} = \nabla k \nabla T + \sigma (\nabla V)^2 \tag{2.1}
\]

\[
\nabla \sigma \nabla V = 0 \tag{2.2}
\]

The density, heat capacity, thermal conductivity, electrical conductivity, temperature, and voltage are given by \(\rho_d, c_p, k, \sigma, T,\) and \(V.\) Equations 2.3 and 2.4 show the expected voltage and thermal waveforms for the SJEM measurements.

\[
V = V_{0\omega} + V_{1\omega} \cos(2\omega t) \tag{2.3}
\]

\[
T = T_{0\omega} + T_{1\omega} \cos(2\omega t) + T_{2\omega} \cos(2\pi 2\omega t) \tag{2.4}
\]

The subscripts denote the amplitude of \(V\) and \(T\) at the zero, first, and second harmonics. The frequency of the applied bias \(\omega = 61-230\) kHz for all experiments. The peak-to-peak graphene temperature rise is \(\Delta T = 2|T_{2\omega}|.\) We applied \(V_{0\omega} = 0\) V which implies \(T_{0\omega} = 0\) K for a Joule heated device. The Fourier transform of Eqs. 2.1-2.4 yields Eq. 2.5.

\[
\begin{bmatrix}
  k & 0 & 0 & 0 & 0 \\
  0 & k & 0 & 0 & 0 \\
  0 & 0 & k & 0 & 0 \\
  0 & 0 & 0 & \sigma & 0 \\
  0 & 0 & 0 & 0 & \sigma
\end{bmatrix}
\begin{bmatrix}
  T_{0\omega} \\
  T_{1\omega} \\
  T_{2\omega} \\
  V_{0\omega} \\
  V_{1\omega}
\end{bmatrix}
=-
\begin{bmatrix}
  \sigma (\nabla V_{0\omega})^2 + 0.5\sigma (\nabla V_{1\omega})^2 \\
  2\sigma (\nabla V_{1\omega} \nabla V_{0\omega}) - i\pi \rho_d c_p T_{1\omega} \omega \\
  0.5\sigma (\nabla V_{1\omega})^2 - i\pi \rho_d c_p T_{2\omega} 2\omega \\
  0 \\
  0
\end{bmatrix} \tag{2.5}
\]

Equation 2.5 was coded into the PDE physics and coupled with thermo-mechanical physics in COMSOL. Transforming and solving the equations in the frequency domain reduced computation time and convergence issues.\(^{20}\)
Figure 2.3: (a) Top and (b) side view of model geometry. The PMMA is modeled as a cylinder covering the SiO$_2$ and graphene surface with two additional PMMA rectangles on top of the Pd electrodes as shown. The PMMA has a minimum overhang of ~200 nm over the Pd electrodes to reduce the mesh intensity. (b) Side view of the model center about the x-axis. The schematic is not to scale.

Figure 2.3 shows the 3D FEA model geometry. Device geometry was modeled from optical images and the e-beam lithography pattern of the device. The model consisted of 55-70 nm PMMA, 70 nm Pd, 1 nm graphene, and 90 nm SiO$_2$ on top of a 200 μm diameter, 100 μm tall Si cylinder. The large domain was chosen to be larger than the Si thermal penetration length. The graphene was modeled 1 nm thick to decrease computation time, and all graphene properties were adjusted by the graphene thickness. The thermal properties of the graphene do not significantly affect the simulations. The minimum mesh size was ~100 nm, larger than the measurement resolution.

Figure 2.3 also shows the boundary conditions for the 3D FEA model. The device is biased at the contacts, and has a heat sink at the bottom as shown. The top surfaces are not mechanically constrained. All other surfaces are electrically and thermally insulated and mechanically constrained.
Table 2.1: Electro-thermo-physical properties of materials used in the simulation. From left to right the listed properties are the thermal conductivity, density, heat capacity, coefficient of thermal expansion, Poisson’s ratio, and elastic modulus.

<table>
<thead>
<tr>
<th>Material</th>
<th>$k$ (W m$^{-1}$ K$^{-1}$)</th>
<th>$\rho_d$ (kg m$^{-3}$)</th>
<th>$c_p$ (J kg$^{-1}$ K$^{-1}$)</th>
<th>$\alpha_{CTE}$ (K$^{-1} \times 10^6$)</th>
<th>$\nu$</th>
<th>$E$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphene</td>
<td>300</td>
<td>2,100</td>
<td>710</td>
<td>-5</td>
<td>0.2</td>
<td>1000</td>
</tr>
<tr>
<td>Pd</td>
<td>30</td>
<td>12,000</td>
<td>244</td>
<td>11.8</td>
<td>0.39</td>
<td>121</td>
</tr>
<tr>
<td>PMMA</td>
<td>0.18</td>
<td>1,200</td>
<td>1,500</td>
<td>50</td>
<td>0.35</td>
<td>3</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>1.4</td>
<td>2,220</td>
<td>745</td>
<td>0.5</td>
<td>0.17</td>
<td>64</td>
</tr>
<tr>
<td>Si</td>
<td>80</td>
<td>2,330</td>
<td>712</td>
<td>2.6</td>
<td>0.28</td>
<td>165</td>
</tr>
</tbody>
</table>

Table 2.1 lists the thermophysical properties used in the model. We set the electrode resistivity to zero for the current model. Therefore, the FEA model directly simulated the device resistance $R$, without simulating additional lead resistance. The model does not include the effects of wrinkles or temperature dependent graphene properties.

2.4 – Fitting Measurements and Predictions

Fitting FEA simulations and SJEM measurements of $\Delta h$ yielded the graphene device properties and temperature rise. The FEA model varied the graphene resistivity $\rho$, graphene-Pd contact resistivity $\rho_C$, and grain resistivity $\rho_{GB}$. The best fit between measurements and simulations was found by the largest coefficient of determination $r^2$ (typically $>0.75$) between the measured and simulated $\Delta h$ with a simulated device resistance $R$ similar to measurements.

The measured graphene resistance $R$ and voltage drop $V_{DS}$ was calculated from two terminal resistance measurements. We calculated and subtracted the resistance and voltage drop of the Pd leads from the two terminal measurements. We prepared two sets of samples, and we found the Pd resistivity of each to be $\sim2.5 \times 10^{-7}$ and $\sim5.0 \times 10^{-7}$ Ω m, similar to our previous work. Devices with higher resistivity Pd leads had higher simulated $\rho_C$ indicating low quality Pd. We note that varying the Pd thermal conductivity between 15-30 W m$^{-1}$ K$^{-1}$, calculated from
the Wiedemann-Franz law, did not significantly change the simulations. The model did not account for wrinkles or temperature dependent graphene resistivity. Unknown probe resistance and contact resistance of our home-built atomic force microscopy (AFM) probe station introduced additional uncertainty in our measurements. Therefore, we adjusted the simulated $\Delta h$ by -20 to +10 % depending on the device and bias condition to account for these discrepancies.

The FEA simulations underestimate the graphene-Pd contact resistivity $\rho_C$ due to inexact modeling of the graphene-Pd contact. Optical measurements were used to estimate the graphene shape for the FEA models. The limited resolution of optical measurements of the graphene before depositing the Pd may have caused us to underestimate the amount of graphene under the Pd contacts in the FEA model, which increases the simulated current crowding and contact heating. We also assume the PMMA has a square, stepped profile at the Pd edge, instead of the measured smooth and conformal PMMA coating. Therefore, we simulate a thicker PMMA layer at the Pd edge. Figure 2.3 also shows we model a 200 nm thick overhang of PMMA at the electrode edge, which is larger than the ~100 nm thick PMMA overhang experimentally observed.\textsuperscript{19} We were unable to simulate a thinner PMMA overhang. The thicker PMMA layer at the Pd edge would increase the simulated $\Delta h$ at the contacts. The inaccurate modeling of the graphene shape and PMMA coating for the Pd electrodes would increase the simulated contact heating and $\Delta h$ at the contacts. Therefore, a lower simulated $\rho_C$ was required to match the measured contact heating and $\Delta h$ at the contacts. The simulated contact resistance did not significantly affect the simulated device resistance.
Figure 2.4: (a) Optical image of Device 1 with two hexagonal graphene grains connected by a grain boundary (GB). The image has been adjusted to improve contrast. Light areas are the Pd electrodes and the substrate is SiO$_2$/Si. (b) Measured SJEM surface expansion $\Delta h$ as a color overlay on the device topography with PMMA coating. SJEM operates by biasing the device with a sinusoidal voltage waveform with amplitude $V_{DS}$ to resistively heat the device, and the AFM measures the resulting thermo-mechanical expansion of PMMA covering the device. The measured $\Delta h$ is proportional to the device temperature rise $\Delta T$ and is related by a FEA model.$^{19,20}$

2.5 – Resistive Heating of a Graphene Grain Boundary

Figure 2.4 shows an optical image of typical GB device used in this chapter, labeled as Device 1, and the surface thermo-mechanical expansion $\Delta h$ measured by SJEM overlaid onto the device topography during operation. The spatial and temperature resolution of our SJEM measurements are $\sim 50$ nm and $\sim 0.2$ K, respectively, based on our previous reports.$^{19,21}$ The peak-to-peak graphene temperature rise $\Delta T$ is proportional to the measured $\Delta h$, and the two are related
by finite element analysis (FEA) modeling.\textsuperscript{19,20} The hexagonal graphene shape and GB are evident from the measured $\Delta h$ in Figure 2.4. We also observe a decrease (increase) in $\Delta h$ as the graphene device \textit{laterally} expands (contracts) due to its hexagonal shape, creating a non-uniform current density throughout the device. The measured $\Delta h$ increases 100-200 % at the GB near the device center ($x \approx 0 \, \mu m$) compared to the graphene sheet due to (1) localized Joule heating from the presence of the GB with finite resistivity $\rho_{GB}$ and (2) the laterally constricting device shape. Simulations discussed below show <25 % increase in $\Delta h$ at the GB compared to device center due to the constricting graphene shape, thus we attribute the majority of the measured $\Delta h$ increase to the GB resistivity $\rho_{GB}$. Figure 2.4(b) also reveals a local increase (~25 %) in $\Delta h$ at a wrinkle, discussed below.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2_5.png}
\caption{Simulated $\Delta h$ and $\Delta T$ of Device 1 for $\rho_{GB} = 0 \, \Omega \, \mu m$ (a,b) and $\rho_{GB} = 180 \, \Omega \, \mu m$ (c,d) for $V_{DS} = 2.34 \, V$. The grain boundary is located at $x \approx 0 \, \mu m$. The simulation results shown in (c) and (d) are the same as Figs. 2.7(c) and (d).}
\end{figure}
Figure 2.5 shows the simulated $\Delta h$ and $\Delta T$ of Device 1 due to the device geometry and the presence of a grain boundary with finite resistivity $\rho_{GB} \neq 0$. The constriction of the graphene grains at the GB causes an increase in current density and Joule heating at the GB. Figures 2.5 (a) and (b) show the increased current density at the GB causes $<25\%$ and $<50\%$ increase in the simulated $\Delta h$ and $\Delta T$ at the GB compared to the graphene sheet. The simulated $V_{DS}$ for Figs. 2.5(a) and (b) was decreased to account for the lack of simulated grain resistance. Figures 2.5(c) and (d) show the same device with a resistive GB and show a 100-200% and 150-300% increase in the simulated $\Delta h$ and $\Delta T$ at the GB, relative to the graphene sheet. The additional simulated increase in $\Delta h$ and $\Delta T$ of Figs. 2.5(c) and (d) compared to Fig. 2.5(a) and (b) is due to the presence of a resistive GB. The simulated $\rho_{GB} = 180 \, \Omega \, \mu m$ was obtained from fitting measurements and simulations of Device 1 at $V_{DS} = 2.34 \, V$, shown in Fig. 2.7. Fitting measurements and simulation at other bias conditions yielded $\rho_{GB} = 60-180 \, \Omega \, \mu m$ with the average and deviation of the simulated $\rho_{GB}$ reported in Table 2.2.

2.6 – Resistive Heating of a Single Grain Device

Next, we turn to our AFM and SJEM measurements of a single grain graphene device with wrinkles but without a GB. Figures 2.6(a) and (b) show the measured $\Delta h$ and second resonance amplitude $A_2$ of such a device. Figure 2.6(b) shows $A_2$ measurements from dual alternating contact AFM measurements, described below, which contrasts the graphene from the surrounding SiO$_2$.\textsuperscript{31,32} The labeled wrinkle in Fig. 2.6(b) has a height of 3-12 nm which varies along its length. We observe no increase in the measured thermal expansion along the wrinkle, and, therefore, we do not expect a large increase in $\Delta T$ at this wrinkle. This observation agrees with recent theoretical work suggesting that tall (>5 nm) wrinkles have low electrical resistance.\textsuperscript{8}
The measured thermo-mechanical expansion $\Delta h$ at the contacts is due to current crowding at the graphene-metal interface.\textsuperscript{19}

![Image](image_url)

**Figure 2.6:** (a) Measured $\Delta h$ of single domain graphene device. (b) Second resonance amplitude $A_2$ image of device, which is sensitive to the sample surface properties.\textsuperscript{31,32} Wrinkles are seen as white lines across the graphene sheet, with one labeled for reference. The image is tilted counterclockwise by $\sim 63^\circ$ with respect to (a), and the red arrow shows the $x$-axis direction. Pd electrodes are shown with lighter contrast at the top-right and bottom-left. (c) and (d) Simulated thermal expansion $\Delta h$ and temperature rise $\Delta T$ of the device.

Dual alternating contact, or bimodal, AFM measurements can enhance the material contrast of an AFM image due to changes in surface mechanical properties.\textsuperscript{32} The AFM cantilever is excited at the first and second resonances. The amplitude of the first resonance is held constant and used in the AFM feed-back loop to measure sample topography. The second resonance amplitude $A_2$ and its phase are recorded as the AFM cantilever raster scans the surface.
Previous work has shown the second resonance has increased sensitivity to surface mechanical properties\(^\text{32}\) and can identify monolayer from bilayer graphene.\(^\text{31}\) In this chapter we post-process our AFM data by subtracting the average SiO\(_2\) \(A_2\) signal from each line scan. This process improves the image contrast and creates a uniform image by adjusting for changes of the AFM cantilever tip due to interaction with debris or tip wear while scanning.

Figures 2.6(c) and (d) show the simulated \(\Delta h\) and \(\Delta T\) for the single grain graphene device. Fitting the measured and simulated \(\Delta h\) for two measurements each at \(V_{DS} = 0.54, 1.12,\) and 1.67 V yields the bulk graphene resistivity \(\rho = 0.11 \pm 0.01\ \Omega \mu m\) (sheet resistance\(^\text{33}\) \(R_S \approx 330\ \Omega/\text{sq.}\)) and graphene-metal contact resistivity\(^\text{19}\) \(\rho_C = 280 \pm 90\ \Omega \mu m^2\). These values are in-line with previous studies of monolayer graphene and graphene-metal contacts on SiO\(_2\).\(^\text{19,33}\) The model matches measurements with a coefficient of determination \(r^2 = 0.78 \pm 0.06\) for all \(V_{DS}\) and yields a total device resistance \(R = 388\ \Omega\), close to the measured 371 \(\Omega\).

2.7 – Resistive Heating of Device 1

We now return to a more in-depth investigation of AFM and SJEM measurements of Device 1 which had a single GB. Figures 2.7(a) and (b) show the measured \(\Delta h\) and \(A_2\) of two coalesced graphene grains, the same device with one GB as in Fig. 2.4. Figure 2.7(a) shows a large, 100-200 % increase in \(\Delta h\) at the GB. Figure 2.7(b) also reveals multiple wrinkles, most being 1-3 nm tall and oriented parallel to the current flow direction (along the \(x\)-axis). However, the wrinkles show no measureable increase in \(\Delta h\) in Fig. 2.7(a). We only measure a 25 % increase at one wrinkle (2-3 nm tall), which rests at a \(\sim 56^\circ\) angle to the current flow direction. However, the measured \(\Delta h\) is \(\sim 4\) times larger at the GB than the wrinkle, indicating the GB has a greater (detrimental) influence on device performance.
Figure 2.7: (a) Measured $\Delta h$ of Device 1 from Fig. 2.4. The large $\Delta h$ measured at $x \approx 0 \, \mu m$ is due to Joule heating at the GB. Joule heating of a wrinkle is also evident. (b) Measured $A_2$ image of device, tilted clockwise by $\sim 35^\circ$ from (a). Red arrow shows $x$-axis direction and the Pd electrodes are shown with lighter contrast at the top-left and bottom-right. Wrinkles are evident as white lines across the graphene. (c) and (d) Simulated $\Delta h$ and $\Delta T$ of the device, including only the GB which had stronger resistive heating than the wrinkles.

Figures 2.7(c) and (d) show the simulated $\Delta h$ and $\Delta T$ for Device 1. Fitting the measured and simulated $\Delta h$ for two measurements each at $V_{DS} = 0.56, 1.13, 2.34$, and $2.95 \, V$ yields bulk graphene resistivity $\rho = 8.3 \pm 0.1 \times 10^{-2} \, \Omega \, \mu m$ (sheet resistance $R_s \approx 250 \, \Omega/$sq.), grain boundary resistance $\rho_{GB} = 120 \pm 60 \, \Omega \, \mu m$, and graphene-contact resistivity $\rho_{C} = 30 \pm 10 \, \Omega \, \mu m^2$. (The contact resistivity is underestimated) The GB resistivity $\rho_{GB}$ is commonly defined per unit width, here the width of the GB being about $4.7 \, \mu m$ for Device 1. One can also define an effective GB length $\ell = \rho_{GB}/R_s \approx 490 \, nm$ for Device 1, corresponding to the length of graphene channel that would yield the same resistance as the GB. (The longer the effective GB length,
the larger the resistive contribution of the GB to the total resistance of the device.) Wrinkles were shown to have a small effect on Δ$h$ and were not included in the simulation. The model matches measurements well ($r^2 = 0.89 \pm 0.03$) and predicts the total device resistance $R = 481 \, \Omega$, close to the measured value of 471 Ω. Figure 2.7(d) shows the simulated $\Delta T$ increases ~150 % at the GB center and ~300 % at the GB edge compared to the middle of the graphene grains. The ~150 % rise is due to $\rho_{GB}$, and the ~300 % rise is due to $\rho_{GB}$ plus the additional effects of current crowding near the grain edges.

2.8 – Resistive Heating of Device 2

Figures 2.8(a) and (b) show the measured Δ$h$ and $A_2$ of two coalesced graphene grains, Device 2. The analysis of Device 2 is similar to Device 1 of Section 2.7 and duplicate details are omitted here. Figure 2.8(a) shows a ~10-50 % increase in Δ$h$ at the GB. An increase in Δ$h$ of ~10-40 % is measured along two (1-2 nm tall) labeled wrinkles in Fig. 2.8(a). The two wrinkles rest at an angle 51 and 79 ° to the carrier flow direction (along the x-axis). We do not observe an increase in Δ$h$ at other wrinkles (1-4 nm tall) oriented parallel to the current flow direction.

Figures 2.8(c) and (d) show the simulated Δ$h$ and Δ$T$ for Device 2. Fitting the measured and simulated Δ$h$ for two measurements each at $V_{DS} = 0.35, 0.47, 1.03, \text{and } 1.72 \, \text{V}$ yields $\rho = 6.3 \pm 0.8 \times 10^{-2} \, \Omega \, \mu \text{m}$ ($R_S \approx 190 \, \Omega/\text{sq}$), $\rho_{GB} = 8 \pm 8 \, \Omega \, \mu \text{m}$, and $\rho_C = 25 \pm 10 \, \Omega \, \mu \text{m}^2$. The model matches simulations with a coefficient of determination $r^2 = 0.89 \pm 0.02$ and simulates the device resistance $R = 213 \, \Omega$, close to the measured 196 Ω. Figure 2.8(d) shows the simulated Δ$T$ increases ~10-30 % at the GB.
Figure 2.8: (a) Measured $\Delta h$ of Device 2. The large $\Delta h$ measured at $x \approx 0 \, \mu m$ is due to Joule heating of the GB. Joule heating of two wrinkles are also evident. (b) Measured $A_2$ image of device tilted counterclockwise by $\sim 32^\circ$ from (a). Red arrow indicates the $x$ axis direction, and the Pd electrodes are shown with lighter contrast at the bottom-left and top-right. Wrinkles are evident as white lines across the graphene. (c) and (d) Simulated $\Delta h$ and $\Delta T$ of the device.

2.9 – Resistive Heating of Device 3

Figures 2.9(a) and (b) show the measured $\Delta h$ and $A_2$ of two coalesced graphene grains, Device 3. The analysis of Device 3 is similar to Device 2 of the Section 2.7 and repeated details are omitted here. Figure 2.9(a) shows a large 50-300 % increase in $\Delta h$ at the GB. Figure 2.9(b) shows multiple wrinkles (1-6 nm tall) orientated perpendicular to the current flow direction (along the $x$-axis). No increase in $\Delta h$ is observed at each wrinkle. However, the high wrinkle density makes it difficult to discern if all or none of the wrinkles experience uniform heating.
Figures 2.9(c) and (d) show the simulated $\Delta h$ and $\Delta T$ for Device 3. Fitting the measured and simulated $\Delta h$ for two measurements each at $V_{DS} = 0.95, 1.45,$ and $1.9$ V yields $\rho = 0.1 \pm 0.01 \ \Omega \ \mu m$ ($R_s \approx 300 \ \Omega/$sq.), $\rho_{GB} = 150 \pm 30 \ \Omega \ \mu m$, and $\rho_{C} = 130 \pm 25 \ \Omega \ \mu m^2$. The model simulates $\Delta T$ increases $\sim 100$-$300\%$ at the GB. We note the model under estimates $\Delta h$, and therefore $\Delta T$, at the GB edges due to the limited ($\sim 100$ nm) mesh resolution, and we expect the actual $\Delta T$ to be larger than FEA simulations.

**Figure 2.9:** (a) Measured $\Delta h$ of Device 3. The large $\Delta h$ measured at $x \approx 0 \ \mu m$ is due to Joule heating of the GB. No Joule heating from individual wrinkles is evident. (b) Measured $A_2$ image of device tilted counter-clockwise by $\sim 30$ $^\circ$ from (a). Red arrow indicates the $x$ axis direction, and the Pd electrodes are shown with lighter contrast at the bottom-left and top-right. Wrinkles are evident as white lines across the graphene. (c) and (d) Simulated $\Delta h$ and $\Delta T$ of the device.
Table 2.2: Measured $\rho_{GB}$ from three devices in this chapter and other values reported in the literature for graphene grown by chemical vapor deposition (CVD), sorted in approximate order of increasing GB resistivity. The measurement column lists the method used to estimate $\rho_{GB}$. AC-EFM is alternating current electrostatic force microscopy. Resistive measurements are direct electrical measurements of the grain resistance, and 4-probe scanning tunneling microscopy (STM) uses a combination of 4-probe measurements and scanning tunneling spectroscopy (STS) at the GB to measure $\rho_{GB}$. The GB of Device 2 did not experience significant heating and approached the resolution of our simulations and measurements.

<table>
<thead>
<tr>
<th>Device or Study</th>
<th>$\rho_{GB}$ ($\Omega \mu m$)</th>
<th>Measurement</th>
<th>Fabrication/Grain Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Device 2 (Fig. 2.8)</td>
<td>8 ± 8</td>
<td>This Chapter</td>
<td>Electropolished Cu, APCVD, Hexagonal Grains</td>
</tr>
<tr>
<td>Device 1 (Fig. 2.7)</td>
<td>120 ± 60</td>
<td>AC-EFM</td>
<td>LPCVD, Dendritic/Flower Patchwork Grains</td>
</tr>
<tr>
<td>Device 3 (Fig. 2.9)</td>
<td>150 ± 30</td>
<td>4-Probe STM</td>
<td>Electropolished Cu, APCVD, Hexagonal Grains</td>
</tr>
<tr>
<td>Huang, 2011\cite{12}</td>
<td>&lt; 60</td>
<td>Resistive</td>
<td>LPCVD (2 Torr) Patchwork Grains</td>
</tr>
<tr>
<td>Clark, 2013\cite{13}</td>
<td>43-140</td>
<td>Resistive</td>
<td>Formed Cu Pocket, LPCVD (2 Torr), Dendritic/Flower Grains</td>
</tr>
<tr>
<td>Tsen, 2012\cite{14}</td>
<td>650 – 3,200</td>
<td>Resistive</td>
<td>APCVD, Hexagonal Grains</td>
</tr>
<tr>
<td>Yu, 2011\cite{10}</td>
<td>12,900 – 43,000</td>
<td>Resistive</td>
<td>APCVD, Hexagonal Grains</td>
</tr>
<tr>
<td>Jauregui, 2011\cite{11}</td>
<td>8,400</td>
<td>Resistive</td>
<td>APCVD, Hexagonal Grains</td>
</tr>
</tbody>
</table>

2.10 – Comparison to Grain Boundaries in Literature

Table 2.2 summarizes the GB resistivity $\rho_{GB}$ extracted from three devices in this study, compared to values reported in the literature.\cite{10-14} The full range of $\rho_{GB}$ is from ~8 to 43,000 $\Omega \mu m$ for GBs from CVD-grown graphene on Cu and transferred to SiO$_2$ substrates. By comparison, reported $\rho_{GB}$ for graphene directly grown on SiC range from 7-100 $\Omega \mu m$.\cite{13,35} Although we observe a notable 150-300% temperature increase at the GB, we estimate relatively low $\rho_{GB}$ for our devices compared to the range reported in the literature for graphene grown by CVD on Cu and transferred for measurements to SiO$_2$. Our devices were grown using similar methods to those of Clark et al.,\cite{13} and we report similar $\rho_{GB}$ as their study. Interestingly, the results summarized in Table 2.2 show no evident trend between graphene grain type and the
2.11 – Analytical Model Derivation

A two dimensional (2D) analytical model was developed to predict the temperature rise and power dissipation for the range of observed $\rho_{GB} \sim 10^{-14} \, \Omega \, \mu m$. Figure 2.10(a) shows the model geometry and associated electrostatic and thermal boundary conditions. The analytical model assumes the device is uniform in width and does not capture the non-uniform current density observed experimentally. The analytical model is a steady-state model and differs from our previously derived frequency domain FEA model used to interpret SJEM results. Solving the electrostatic component of Fig. 2.10(a) for the voltage profile $V(x)$ yields Eq. 2.6.

$$V(x) = \begin{cases} 
V_1(x < 0) = E(L + \ell + x) \\
V_2(x > 0) = E(\ell + x)
\end{cases} \quad (2.6)$$

Where $E = V_0 / (2L + \ell)$ and $\ell = \rho_{GB}/R_S$. The effective GB length $\ell$ is the length of the graphene channel with resistance equal to that of the GB.\textsuperscript{14}

The percent voltage drop and power dissipated at the GB relative to the whole device are given by $V\% = V_{GB}/V_0$ and $P\%$. The voltage drop across the GB is $V_{GB} = V_1(0)-V_2(0)$, and the voltage drop across the entire device is $V_0$. The power dissipated at any point is given by $P(x) = V(x) \times I$, where $I$ is the current. The constant (continuous) current density in the device implies $V\% = P\%$. Equation 2.7 shows a simple relation for $P\%$, $V\%$, $\ell$, and the device length $2L$.

$$P\% = V\% = 100 / (1 + 2L / \ell) \quad (2.7)$$

Equation 2.8 shows the associated temperature rise profile $T(x)$ for the device voltage profile from Equation 2.6. Equation 2.8 is derived assuming the graphene is isothermal along its width and heat flows 1D (vertical) in the substrate to the heat sink at $T_s$. 

electrical properties of GBs.\textsuperscript{10-14}
\[ \Theta(x) = \frac{\cosh(x / L_H)}{\cosh(L / L_H)} + \frac{Q_{GB} L_H}{2} \left[ \tanh(L / L_H) \cosh(x / L_H) \pm \sinh(x / L_H) \right] \]  

(2.8)

The ± sign is positive for \( x < 0 \) and negative for \( x > 0 \) and

\[ \Theta(x) = \frac{T(x) - T_s - \frac{E^2 t_s t}{\rho k_s}}{T_0 - T_s - \frac{E^2 t_s t}{\rho k_s}} \text{ and } Q_{GB} = \frac{E^2 t_s}{\rho s k} \]  

(2.9)

where \( t_s \) is the insulating substrate thickness (here 90 nm SiO\(_2\)), \( t \) is the graphene thickness, \( k_s \) is the substrate thermal conductivity, and \( k \) is the graphene thermal conductivity. The thermal healing length\(^{36} \) \( L_H = (k \times t \times t_s / k_s)^{1/2} \), which is approximately 80 nm for our geometry with 90 nm of SiO\(_2\).

Equation 2.10 yields the percent increase in GB temperature \( T_P = T_{GB} / T(L/2) \) relative to the graphene sheet. The GB temperature rise \( T_{GB} \) is divided by the temperature rise in the middle of the grain \( T(L/2) \), a point equidistant from the GB and contacts. To derive Eq. 2.10 we assume \( T_s = T_0 = 0 \) K and \( L_H \ll L \).

\[ T_P = \frac{2e^{-L/2L_H} + 0.5 Q_{GB} L_H - 1}{e^{-L/(2L_H) - 1}} \]  

(2.10)

A FEA model of the device in Figure 2.10(a) was developed to verify Equations 2.6-2.10. The FEA and analytical model yield the same results for Equations 2.6 and 2.7. The FEA and analytical model yield similar results for Equations 2.8 and 2.10. The predicted \( T(x) \) of the FEA and analytical model deviate slightly at the contacts and GB as the FEA model accounts for 2D heat spreading in the substrate. Lateral substrate heat spreading is significant within a few \( L_H \) of the GB and contacts. The analytical model does not account for lateral substrate heat spreading and overestimates \( T_{GB} \) by 20-50 % and is an upper bound of the predicted \( T_P \).
Figure 2.10: (a) Schematic for the GB analytical model, showing two graphene domains ($L = 5 \mu$m) on 90 nm SiO$_2$ with a GB at the center ($x = 0 \mu$m). The contacts are biased at $V = V_0$ (left) and $V = 0$ (right). (b) Analytically modeled voltage $V(x)$ and temperature $T(x)$ of a device with similar physical characteristics as Device 1. The figure shows the GB voltage drop $V_{GB}$ and temperature rise $T_{GB}$. (c) Predicted percent voltage drop $V_{%}$ and power dissipation $P_{%}$ at the GB and predicted percent GB temperature rise $T_{GB, %}$ relative to the graphene sheet. The effective GB length $\ell$ is the length of the graphene channel with the same resistance as the GB.$^{14}$ Lines and markers are obtained with the analytical channel and FEA models, respectively. The black triangle marker is the measured $T_{GB, %}$ of Device 1.

2.12 – Analytical Model Predictions

In order to facilitate a simpler yet physical understanding of power dissipation at GBs, we developed an analytical model to predict their temperature rise for the range of observed $\rho_{GB}$ in
all studies summarized by Table 2.2. Figure 2.10(a) shows the model geometry and associated electrostatic and thermal boundary conditions. For the analysis described below we assume graphene properties similar to Device 1 with a channel length $2L = 10 \, \mu m$. Figure 2.10(b) shows the predicted voltage $V(x)$ and temperature $T(x)$ profile of the device shown in Fig. 2.10(a). The model predicts that the small voltage drop across the GB ($V_{GB}$) causes a large localized temperature rise ($T_{GB}$) due to the highly confined Joule heating at the grain boundary. Figure 2.10(c) shows the percent voltage drop $V\% = V_{GB}/V_0$ and percent power dissipated $P\% = P_{GB}/P_0$ at the GB for the geometry shown in Figure 2.10(a), where $V_0$ and $P_0$ are the total applied voltage and power dissipation of the entire device. Current continuity along the device yields $V\% = P\%$. We estimate $V\% = P\% = 2.9\%$ for Device 1 shown in Fig. 2.7.

Figure 2.10(c) shows the predicted temperature ratio between the GB and the rest of the graphene grain, $T\% = T_{GB}/T(L/2)$, from the analytical model; here the graphene temperature is taken at $x = L/2$, the halfway point between the GB and contacts. The analytical model overestimates $T\%$ by 20-50\% compared to FEA simulations, as it does not account for the (two-dimensional) heat spreading through the substrate at the GB. The analytic model predicts $T\% \approx 300\%$ for Device 1, close to the observed value of 150-300\%. In fact, the GB dominates the temperature rise ($T\% > 200\%$) of Device 1 for any value $\rho_{GB} > 60 \, \Omega \, \mu m$, yet the associated $V\% = P\% = 1.6\%$ because the GB is a highly localized heat source versus the 10 \, \mu m long device. These results suggest that, in relatively “large” (e.g. >5 \, \mu m) interconnects with micron-size grains, GBs may not significantly affect electrical performance, but the GBs will dominate the temperature rise at such “hot spots” and therefore limit the interconnect reliability.

The measurement column of Table 2.2 lists the measurement technique used to measure the GB resistivity $\rho_{GB}$. For high $\rho_{GB} (\geq 10^3 \, \Omega \, \mu m)$ electrical (resistive) based measurements are
able to measure $\rho_{GB}$, as the GB resistance $R_{GB}$ and GB voltage drop $V_{GB}$ are large.\textsuperscript{10,11,14} For low $\rho_{GB} (\leq 10^2 \, \Omega \, \mu m)$ electrical measurements are unable to measure $\rho_{GB}$, as $V_{GB}$ and $R_{GB}$ are small,\textsuperscript{12} and only electrically based scanning tunneling microscopy (STM) measurements have been able to observe low resistivity GBs.\textsuperscript{13} Low $\rho_{GB}$ GBs do not significantly affect graphene electrical performance, particularly for longer devices (e.g. $>5 \, \mu m$).\textsuperscript{12} However, we have shown the GB temperature rise can be large for low $\rho_{GB}$ devices. The large GB temperature rise is due to highly local Joule heating at the GB. Recent work has estimated the GB influences <10 nm of the surrounding graphene,\textsuperscript{37} and even a low $V_{GB}$ will cause significant and highly localized Joule heating across such a small area. Therefore, nanometer-scale based thermometry methods, such as scanning thermal microscopy (SThM)\textsuperscript{38} and SJEM,\textsuperscript{18-20} have potential to study graphene GBs due to the large temperature rise at the GB.

In order to understand the effect of GB temperature rise on “small” (e.g. <1 $\mu m$) graphene devices and interconnects we recall recent experiments which have shown that GBs perturb the electronic wave functions for only <10 nm of the surrounding graphene.\textsuperscript{37} The electron-phonon scattering mean free path in graphene is also of the order 20-80 nm in graphene on SiO$_2$ at room temperature.\textsuperscript{33} These two length scales suggest that resistive heating only occurs within a few tens of nanometers from the GB itself. However, the length scale of heat flow (temperature decay) away from the GB heat source is the lateral thermal healing length, $L_H \approx 0.2 \, \mu m$ for common graphene on 300 nm SiO$_2$/Si substrates.\textsuperscript{30,39} Thus, the average temperature of a small (sub-micron) graphene device with even a single GB will be significantly affected by the power dissipation at the GB.

In both small and large graphene devices and interconnects with GBs, the temperature rise at such highly localized nanoscale defects could lead to premature device failure\textsuperscript{39} before the
average temperature of the graphene sheet has significantly increased. Both graphene oxidation or (top or bottom) dielectric breakdown may be more likely to occur at GBs. These scenarios are similar to CNT devices, where breakdown and highly localized temperature rise at nanoscale defects have also been studied with the SJEM technique.21

2.13 – Conclusion

In conclusion, we directly observed nanometer-scale Joule heating of CVD-grown graphene using SJEM with ~50 nm and ~0.2 K spatial and temperature resolution. We noted a small increase in temperature at some wrinkles but a large 150-300 % increase in temperature at GBs. Comparing SJEM and electrical measurements with simulations we estimate \( \rho_{GB} = 8-150 \, \Omega \mu m \) for our devices, among the lowest values reported for CVD graphene.10-14 An analytic model is developed to predict power dissipation, voltage drop, and temperature rise at GBs for the range of \( \rho_{GB} \) reported in the literature. The model predicts the GB may experience a large localized temperature increase at the GB which could lead to localized device or dielectric failure at these locations, without a significant increase of the average device temperature. Methods which measure nanometer-scale temperatures, such as SJEM and SThM have greater sensitivity to study graphene GBs. Furthermore, the large and local temperature rise at the GB may enable new research and applications for graphene GBs as nanometer-scale heat sources. Knowledge of the nanometer-scale temperature rise and Joule heating at graphene GBs is important for understanding graphene devices and their reliability.
2.14 – References


28 J. Martin, in *the COMSOL Conference*, Hannover, Germany, 4-6 November, 2008, pp. 1-7.


CHAPTER 3
NANOMETER-SCALE TEMPERATURE IMAGING FOR INDEPENDENT
OBSERVATION OF JOULE AND PELTIER EFFECTS IN PHASE CHANGE
MEMORY DEVICES

3.1 – Introduction

Nanometer-scale Joule and thermoelectric effects dominate the temperature rise and
energy consumption of electronic devices. Optical thermometry techniques are commonly used
to investigate Joule and thermoelectric effects in electronic materials, but these techniques are
diffraction limited to micrometer-scale resolution. Scanning probe microscopy (SPM) based
techniques can achieve nanometer-scale resolution, but few studies have used SPM techniques to
investigate Joule and thermoelectric effects in electronic devices. Recent work has used SPM
based thermometry techniques to measure the local thermopower of graphene and across GaAs
p-n junctions and has investigated Joule heating in Pt nanowires and plasmonic devices. However, these studies did not measure both Joule and thermoelectric effects in these devices at the nanometer-scale.

A few publications have reported the use of scanning Joule expansion microscopy
(SJEM) to investigate nanometer-scale Joule and thermoelectric effects. SJEM is a
frequency-domain thermometry technique that uses an atomic force microscopy (AFM)
cantilever to measure the local thermo-mechanical expansions of a sample. SJEM operates by
supplying a periodic voltage waveform to drive a device while the AFM measures the resulting
thermo-mechanical expansions of the surface and is capable of high spatial resolution (sub-
50 nm) and temperature resolution (~200 mK). Previous work has used the high spatial
resolution of SJEM to study Joule and Peltier effects in carbon nanotubes (CNTs),
graphene,
and phase change memory (PCM) devices. However, the coupled observation of Joule and Peltier effects yielded measurements with low sensitivity for observing nanometer-scale thermoelectric effects.

In this chapter, an SJEM technique is developed for independent observation of nanometer-scale Joule heating and thermoelectric effects, which increases the measurement sensitivity for observing thermoelectric effects at the nanometer-scale. Heating a device with a periodic and bipolar bias separates the temperature rise of the device due to Joule and thermoelectric effects at different harmonics. The separate observation of Joule and thermoelectric effects increases the sensitivity, throughput, and capabilities of the SJEM technique for observing thermoelectric effects at the nanometer-scale.

3.2 – Joule Heating and Peltier Effects

Figure 3.1(a) shows a two-terminal electronic device, where the device material has a thermopower \( S > 0 \). As current flows through the device, the temperature field near the contact interface is governed by both Joule heating (JH) and Peltier effects (PE). Figures 1(b) and (c) show the predicted temperature rise of the device due to PE and JH, and the FEA model is discussed in Section 3.3.

Figure 3.1(b) shows the device temperature rise due to Peltier heating and cooling. For a positive thermopower material the Peltier effect locally heats (cools) the junction as carriers flow into (from) the metal contact.\(^{9,10,13}\) Equation 3.1 describes heat generation due to PE as current flows from material A to B.

\[
q_{PE} = \sigma T(S_B - S_A)\nabla V
\]  

(3.1)
where the material electrical conductivity, absolute temperature, thermopower, and voltage are given by $\sigma$, $T$, $S$, and $V$.

Figure 3.1(c) shows the device temperature rise due to Joule heating. Joule heating is uniform and symmetric across the channel for a device with constant conductivity or resistivity. Joule heating also occurs at the contacts due to finite contact resistance between the channel and its contacts. Equation 3.2 describes heat generation in a device due to JH.

$$q_{JH} = \sigma(\nabla V)^2 \quad (3.2)$$

The device temperature rise is a combination of Joule and Peltier effects, and a key observation is that Peltier effects scale with voltage and Joule heating scales with the voltage squared.

**Figure 3.1**: Predicted device temperature rise $T$ due to Joule heating (JH) and Peltier effects (PE). (a) Schematic of a Ge$_2$Sb$_2$Te$_5$ (GST) device with two electrodes. The left and right electrodes are biased at $V_{DS}$ and 0 V. GST has a positive thermopower ($S_{GST} > 0$) and the electrodes have a low thermopower ($S \approx 0$). (b) Device temperature rise due to PE. The horizontal dashed line shows $T = 0$ K. (c) Device temperature rise due to JH.
As periodic current flows through the device, the temperature field near the contact interface is governed by harmonic Joule and Peltier heating. Equation 3.3 describes the sinusoidal voltage waveform applied to the device.

\[ V_{DS} = V_{0\omega} + V_{1\omega} \cos(2\pi\omega t) \]  

(3.3)

where \( V_{DS}, \omega, t, V_{0\omega}, \) and \( V_{1\omega} \) are the device bias, frequency, time, zero harmonic (DC) voltage, and first harmonic voltage amplitude (a complex number). We define a bipolar waveform as a bias with no DC component \( (V_{0\omega} = 0 \text{ V}) \) and a unipolar waveform as a bias with a single polarity \((|V_{0\omega}| = |V_{1\omega}|)\). Applying a unipolar bias to a device is the current state-of-the-art for observing nanometer-scale Joule and Peltier effects.\(^9\,\!^{10}\) Equations 3.4 and 3.5 describe Peltier and Joule heating of a device driven by a sinusoidal bias.

\[ q_{PE} = \sigma T (S_B - S_A) [\nabla V_{0\omega} + \nabla V_{1\omega} \cos(2\pi\omega t)] \]  

(3.4)

\[ q_{JH} = \sigma \left( (\nabla V_{0\omega})^2 + 0.5(\nabla V_{1\omega})^2 + 2 \nabla V_{0\omega} \nabla V_{1\omega} \cos(2\pi\omega t) + 0.5(\nabla V_{1\omega})^2 \cos(2\pi2\omega t) \right) \]  

(3.5)

Equations 3.4 and 3.5 were derived by substituting the device bias from Eq. 3.3 for the voltage \( V \) of Eqs. 3.1 and 3.2. Equations 3.4 and 3.5 describe heat generation in a device due to Joule and Peltier effects at the zero, first, and second harmonics \((0\omega, 1\omega, \text{ and } 2\omega)\). A similar relation can be derived from the equations listed in Section 3.3.

**Table 3.1:** Voltage scaling of the temperature rise \( \Delta T \) at the zero, first, and second harmonics \((0\omega, 1\omega, \text{ and } 2\omega)\) due to JH and PE effects.

<table>
<thead>
<tr>
<th>( \Delta T )</th>
<th>Unipolar Bias</th>
<th>Bipolar Bias</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 0\omega )</td>
<td>( (V_{0\omega})^2 + 0.5(V_{1\omega})^2 )</td>
<td>( V_{0\omega} )</td>
</tr>
<tr>
<td>( 1\omega )</td>
<td>( 2V_{0\omega}V_{1\omega} )</td>
<td>( V_{1\omega} )</td>
</tr>
<tr>
<td>( 2\omega )</td>
<td>( 0.5(V_{1\omega})^2 )</td>
<td>( 0 )</td>
</tr>
</tbody>
</table>

Table 3.1 shows the voltage scaling of Joule and Peltier effects at the zero, first, and second harmonics due to bipolar and unipolar biases. Applying a unipolar bias causes JH to
occur at all three harmonics and PE to occur at the zero and first harmonics. Unipolar heating causes JH to be present at the same harmonics as PE. Applying a bipolar bias causes JH to occur at the zero and second harmonics and PE to occur only at the first harmonic. Applying a bipolar bias allows for independent observation of Joule and Peltier effects as the temperature rise due to Joule heating is at a different harmonic than the temperature rise due to Peltier effects.

3.3 – Frequency Domain Thermoelectric Model

The frequency domain thermoelectric transport equations are derived as follows. Equations 3.6 and 3.7 show the modified Poisson and heat diffusion equations to account for thermoelectric transport.\(^\text{14,15}\)

\[
\nabla \sigma(SVT + \nabla V) = 0 \tag{3.6}
\]

\[
\rho_d c_p \frac{\partial T}{\partial t} = \nabla(k + \sigma S^2 T)VT + \nabla(\sigma ST)VV + \sigma(S \nabla TVV + [VV]^2) \tag{3.7}
\]

The density, heat capacity, thermal conductivity, electrical conductivity, thermopower, temperature, and voltage are given by \(\rho_d\), \(c_p\), \(k\), \(\sigma\), \(S\), \(T\), and \(V\). Equations 3.6 and 3.7 are coupled and must be solved simultaneously. Equation 3.3 shows the applied sinusoidal bias which generates the temperature oscillations shown in Eq. 3.8.

\[
T = T_{0\omega} + T_{1\omega} \cos(2\pi\omega t) + T_{2\omega} \cos(2\pi 2\omega t) \tag{3.8}
\]

The subscripts 0\(\omega\), 1\(\omega\), and 2\(\omega\) denote the amplitude of \(V\) and \(T\) at the zero, first, and second harmonics. The device is biased at a frequency \(\omega = 43\) kHz. The first and second harmonic components are complex numbers, and the first and second harmonic peak-to-peak temperature rises are defined \(\Delta T_{1\omega} = 2|T_{1\omega}|\) and \(\Delta T_{2\omega} = 2|T_{2\omega}|\). Driving the device with a bias at 0\(\omega\) (DC) and 1\(\omega\) bias causes a 0\(\omega\), 1\(\omega\), and 2\(\omega\) temperature rise as Joule heating scales with \(V^2\). The Fourier
transform of Eqs. 3.3, and 3.6-3.8 yields Eq. 3.9 the frequency domain thermoelectric transport equation.

\[
\begin{bmatrix}
4(k + \sigma S^2 T_{0\omega}) & 2\sigma S^2 T_{1\omega} & 2\sigma S^2 T_{2\omega} & 4\sigma S T_{0\omega} & 2\sigma S T_{1\omega} \\
2\sigma S^2 T_{1\omega} & 2k + \sigma S^2 (2T_{0\omega} + T_{2\omega}) & \sigma S^2 T_{1\omega} & 2\sigma S T_{1\omega} & \sigma S (2T_{0\omega} + T_{2\omega}) \\
2\sigma S^2 T_{2\omega} & \sigma S^2 T_{1\omega} & 2(k + \sigma S^2 T_{0\omega}) & 2\sigma S T_{2\omega} & \sigma S T_{1\omega} \\
\sigma S & 0 & 0 & \sigma & 0 \\
0 & \sigma S & 0 & 0 & \sigma \\
\end{bmatrix}
\begin{bmatrix}
T_{0\omega} \\
T_{1\omega} \\
T_{2\omega} \\
V_{0\omega} \\
V_{1\omega} \\
\end{bmatrix}
= \begin{bmatrix}
2\sigma \left\{ S(2\nabla T_{0\omega} \nabla V_{0\omega} + \nabla T_{1\omega} \nabla V_{1\omega}) + 2(\nabla V_{0\omega})^2 + (\nabla V_{1\omega})^2 \right\} \\
\sigma \left\{ S(2\nabla T_{0\omega} \nabla V_{1\omega} + 2\nabla T_{1\omega} \nabla V_{0\omega} + \nabla T_{2\omega} \nabla V_{1\omega}) + 4\nabla V_{1\omega} \nabla V_{0\omega} \right\} - i4\pi \rho_a c T_{1\omega} \omega \\
\sigma \left\{ S(\nabla T_{1\omega} \nabla V_{1\omega} + 2\nabla T_{2\omega} \nabla V_{0\omega}) + (\nabla V_{1\omega})^2 \right\} - i4\pi \rho_a c T_{2\omega} 2\omega \\
0 \\
0 \\
\end{bmatrix}
\tag{3.9}
\]

The terms on the left hand side of Eq. 3.9 are the transport terms. The terms on the right hand side without frequency dependence are generation terms, and the terms with frequency dependence describe periodic heat diffusion. The model is coupled with a thermo-mechanical model for comparison with scanning Joule expansion microscopy (SJEM) measurements.

Equation 3.9 was implemented in a finite element analysis (FEA) model of a device, shown in Figure 3.1(a), to predict Joule and thermoelectric device behavior. The model is similar to 2D phase change memory (PCM) device models used in previous SJEM measurements.10,12

The model is bounded by the electrode bias as shown, a heat sink of $T_{0\omega} = 300$ K along the bottom surface, and free surfaces along the top. All other surfaces are insulated and constrained. Joule and Peltier effects are generated in the Ge$_2$Sb$_2$Te$_5$ (GST) device from its high resistivity $\rho_{GST} = 2.5 \times 10^{-4}$ $\Omega$ m and large thermopower $S_{GST} = 250$ $\mu$V K$^{-1}$. The device was modeled as a 22 nm thin GST device with a 4 $\mu$m channel length. Joule heating also occurs at the contacts due to finite interface resistivity ($\rho_C = 2 \times 10^{-9}$ $\Omega$ m$^2$) between the GST and metal.
Figure 3.2: Predicted harmonic temperature rise due to unipolar and bipolar biases for different values of $S_{GST}$. (a,b) The temperature rise at the zero harmonic $\Delta T_{0\omega}$. (c,d) The peak-to-peak temperature rise at the first harmonic $\Delta T_{1\omega}$. (e,f) The phase of the temperature rise at the first harmonic $\Theta_{1\omega}$. (g,h) The peak-to-peak temperature rise at the second harmonic $\Delta T_{2\omega}$. The solid red and dashed blue lines show $\Delta T$ due to carrier flow to the right and left. The large symmetric $\Delta T$ of the channel is due to JH, and the change in $\Delta T$ with carrier flow at the contacts is due to PE. Vertical dashed lines show the channel edge.

3.4 – Predicted Frequency Domain Heating

Figure 3.2 shows the predicted device temperature rise at each harmonic due to unipolar and bipolar biases for different values of device thermopower. The zero, first, and second harmonic temperature rises are given by $\Delta T_{0\omega}$, $\Delta T_{1\omega}$, and $\Delta T_{2\omega}$, and the phase of the first harmonic temperature rise is given by $\Theta_{1\omega}$. SJEM cannot measure the non-periodic $\Delta T_{0\omega}$. Also, the maximum voltage applied by the unipolar and bipolar biases are equal, such that the
temperature rise of the device due to unipolar and bipolar biases were equal. Therefore, $V_{0\omega}$ and $V_{1\omega}$ under unipolar bias were simulated as one-half of $V_{1\omega}$ under bipolar bias.

Figures 3.2(a) and (b) show the predicted $\Delta T_{0\omega}$ due to unipolar and bipolar biases. Joule heating is evident for both unipolar and bipolar biases as the large and symmetric temperature rise across the channel. Figure 3.2(a) shows that $\Delta T_{0\omega}$ changes at the contacts with carrier flow direction, indicating local Peltier heating and cooling.\(^9\,10\,13\) Also, the simulated $V_{1\omega}$ is larger under bipolar bias than unipolar bias which causes a larger predicted $\Delta T_{0\omega}$ for the bipolar bias than the unipolar bias.

Figures 3.2(c-f) show the predicted peak-to-peak first harmonic temperature rise $\Delta T_{1\omega}$ and phase $\Theta_{1\omega}$ due to unipolar and bipolar biases. Figure 3.2(c) shows Joule heating, as the large temperature rise across the channel, and Peltier effects, as the change in temperature at the contacts with carrier flow direction. Applying a unipolar bias causes both Joule and Peltier effects to be observed in $\Delta T_{1\omega}$. Figure 3.2(d) shows two positive spikes in $\Delta T_{1\omega}$ at the contacts, which is due to Peltier heating and cooling of the contacts. The predicted $\Delta T_{1\omega}$ is positive for both Peltier heating and cooling as $\Delta T_{1\omega}$ shows only the magnitude of the first harmonic temperature rise. Figure 3.2(f) shows the predicted $\Theta_{1\omega}$ changes 180 ° between the contacts indicating the contacts oppositely experience heating and cooling. The 180 ° shift in $\Theta_{1\omega}$ is further evidence of Peltier heating and cooling of the contacts.\(^9\,10\,13\) The combination of the observed spikes in $\Delta T_{1\omega}$ and 180 ° shifts in $\Theta_{1\omega}$ indicate the bipolar heated device is experiencing Peltier effects. Figs. 3.2(d) and (f) show only the Peltier effect is observed in the first harmonic temperature rise when applying a bipolar bias.\(^12\) Figure 3.2(c) shows that increasing the device thermopower increases the change in temperature at the contacts with carrier flow direction, and Fig. 3.2(d) shows that increasing the device thermopower increases the magnitude of the spikes.
at the contacts. The changes in Figs. 3.2(c) and (d) at the contacts with increasing thermopower are due to increasing Peltier effects, and fitting FEA predictions to SJEM measurements at the contacts can predict both Peltier effects in the device and the device thermopower.\textsuperscript{9,10,12}

Figures 3.2(g) and (h) show the predicted peak-to-peak second harmonic temperature rise $\Delta T_{2\omega}$ due to unipolar and bipolar biases. Joule heating is evident for both unipolar and bipolar biases as the large and symmetric temperature rise across the channel. The simulated $V_{1\omega}$ is larger under bipolar bias than unipolar bias which causes a larger predicted $\Delta T_{2\omega}$ for the bipolar bias than the unipolar bias. Figs. 3.2(g) and (h) show a slight change in $\Delta T_{2\omega}$ with thermopower which is due to the Seebeck effect. The Seebeck effect induces a thermoelectric voltage across a device due to a temperature difference at its junctions with dissimilar thermopower materials. The induced voltage slightly changes the power dissipation of the device. The changes are typically too small to be observed experimentally. In general, Figure 3.2 shows the predicted harmonic temperature rise of a device due to Joule and Peltier effects and shows that a bipolar bias separates the temperature rise of the device due to Joule and Peltier effects at two different harmonics.

\section*{3.5 – Application to Phase Change Memory Devices}

This chapter will now discuss how fitting FEA predictions to SJEM measurements can predict the thermopower of PCM devices, where both Joule and Peltier effects are important.\textsuperscript{16} SJEM measurements using both unipolar and bipolar bias investigated JH and PE in lateral GST devices. The measurements demonstrate that applying a bipolar bias enables independent observation of Joule and Peltier effects in PCM devices and improves the precision of predicting device thermopower.
Figure 3.3: (a) Schematic of lateral GST devices and scanning Joule expansion microscopy (SJEM) measurements. (b-e) Measured and predicted $\Delta h_{1\omega}$ and $\Delta h_{2\omega}$ due to unipolar and bipolar biases. Symbols and solid lines show measurements and predictions. The solid red line and red circles and the dashed blue line and blue triangles show $\Delta h$ with carrier flow to the right and left. (f) The coefficient of determination $R^2$ for FEA fitting of SJEM measurements to predict $S_{GST}$. The bipolar measurement provides significantly improved estimate for $S_{GST}$.

Figure 3.3(a) shows a schematic of the lateral GST devices and the SJEM technique. The devices are similar to the model shown in Fig. 3.1(a), and the geometry and properties of the FEA model were adjusted to match the measured device. Lateral GST devices consisted of 60-110 nm of PMMA, 60 nm of Au, 10 nm TiW, 22 nm GST, and 300 nm SiO$_2$ on a Si substrate. The device shown in Fig. 3.3 was annealed at 150 °C for 10 min and has a channel length of 3.6 μm. The measurements shown in Fig. 3.3 are an average of 32 line scans, and the GST properties were found by fitting the FEA model to each line scan. The first and second harmonic peak-to-
peak surface expansions $\Delta h_{1\omega}$ and $\Delta h_{2\omega}$ were measured using SJEM and are proportional to $\Delta T_{1\omega}$ and $\Delta T_{2\omega}$.

Figures 3.3(b) and (c) show the measured and predicted first harmonic surface expansion due to unipolar and bipolar biases. Figure 3.3(b) shows PE cause $\sim 18$ pm change in $\Delta h_{1\omega}$ at the contacts with change in bias polarity. The PE is difficult to observe because the $\Delta h_{1\omega}$ due to JH is relatively large. Figure 3.3(c) shows $\sim 18$ pm tall spikes in $\Delta h_{1\omega}$ at the contacts due to PE. The magnitude of the observed PE is the same in Figs. 3.3(b) and (c). However, the $V_{1\omega}$ under unipolar bias was equal to one-half of $V_{1\omega}$ under bipolar bias, and Peltier effects at $1\omega$ scale with $V_{1\omega}$, as shown in Table 3.1. The PE is resolved with two measurements using unipolar heating, while only a single measurement is required using bipolar heating. Since each unipolar heating measurement observes half the PE, the combination of two unipolar measurements yields the same result as a single bipolar measurement.

Figures 3.3(d) and (e) show the measured and predicted second harmonic surface expansion due to unipolar and bipolar biases. Fitting measurements and predictions for $\Delta h_{2\omega}$ yields the GST resistivity $\rho_{GST} = 2.6 \times 10^{-4}$ Ω m and GST-TiW contact resistivity $\rho_{C} = 2 \times 10^{-9}$ Ω m. The device was biased at $V_{DS} = 2.5$, 3.6, and 4.3 V and all bias conditions were used to fit measurements and predictions. The measurements and predictions are similar for all biases, and only $V_{DS} = 4.3$ V is shown in Figs. 3.3(b-e) for clarity.

Applying a bipolar bias significantly improves the precision of device thermopower measurements compared to measurements using a unipolar bias. Figure 3.3(f) shows the error for fitting FEA predictions to SJEM measurements to predict the GST thermopower $S_{GST}$ for unipolar and bipolar based measurements. The coefficient of determination $R^2$ is the error between predictions and measurements for predicting $\rho_{GST}$, $\rho_{C}$, and $S_{GST}$. Figure 3.3(b) shows the
Peltier effect causes a difference in $\Delta h_{1\omega}$ with carrier flow direction. Fitting FEA predictions to SJEM measurements of the difference in $\Delta h_{1\omega}$ with carrier flow direction predicts $S_{GST} = 240 \pm 26 \, \mu V \, K^{-1}$. Fitting the measured and predicted $\Delta h_{1\omega}$ using the bipolar technique predicts $S_{GST} = 250 \pm 10 \, \mu V \, K^{-1}$. The $S_{GST}$ predicted using a bipolar bias has a smaller deviation than the $S_{GST}$ predicted using a unipolar bias. The average measured uncertainty of $\Delta h_{1\omega}$ for measurements using unipolar and bipolar biases are $\sim 8$ and $\sim 2$ pm. The measurement uncertainty of the unipolar measurements is larger than that of the bipolar measurements for observing Peltier effects, which increases the predicted uncertainty of thermopower measurements when using a unipolar bias.

Observing Peltier effects using a unipolar bias requires two measurements which increases the measured uncertainty. A single SJEM measurement had an average uncertainty of $\sim 2-3$ pm. Using a unipolar bias requires two measurements to observe Peltier effects which doubles the variance (the square of the uncertainty) from a single measurement and the drift between the two measurements further increases the average uncertainty. The uncertainty therefore increased from $\sim 2-3$ pm for a single SJEM measurement to $\sim 7-8$ pm when observing Peltier effects using a unipolar bias. Using a bipolar bias requires a single measurement to observe Peltier effects and the measured uncertainty is the same as a single SJEM measurement.

Measurements using a bipolar bias to independently observe JH and PE have several advantages over measurements using a unipolar bias. Measurements using a bipolar bias have lower measured uncertainty for observing PE than measurements using a unipolar bias, which increases the precision of thermopower measurements and allows for observation of thermoelectric effects in low thermopower devices. Bipolar heating also enables lateral mapping of devices with heterogeneous Joule and thermoelectric effects, since the thermoelectric effects
can be resolved with a single measurement; unipolar measurements require two precisely aligned measurements to resolve nanometer-scale thermoelectric effects. Finally, measurements using a bipolar bias can be performed twice as fast as a unipolar measurement.

3.6 – Sensitivity of Bipolar Thermopower Measurements

This chapter now investigates the measurement sensitivity of the bipolar bias technique by observing thermoelectric effects in devices with lower thermopowers. Figures 3.4(a-c) show the measured and predicted $\Delta h_{1\omega}$ for three GST devices with different properties. Figure 3.4(a) shows the measured and predicted $\Delta h_{1\omega}$ from the device shown in Fig. 3.3. Figures 3.4(b) and (c) show devices with channel lengths of 4.2 and 2.9 μm which were annealed at temperatures of 200 and 250 °C for 10 min. Figure 3.4(d) shows the error for fitting FEA predictions to SJEM measurements to predict $S_{GST}$ for the three devices. Figure 3.4(d) shows that measurements using a bipolar bias enable precise prediction of material thermopower from $30 \pm 3$ to $250 \pm 10 \mu V K^{-1}$. The predicted uncertainty of $S_{GST}$ increases with increasing GST thermopower for the following reason. The measured percent uncertainty of $\Delta h_{1\omega}$, the measured uncertainty of $\Delta h_{1\omega}$ divided by the measured $\Delta h_{1\omega}$, was similar for each device. The observed $\Delta h_{1\omega}$ is due to local Peltier heating and cooling, and the PE is proportional to the GST thermopower. Therefore, the measured percent uncertainty of $\Delta h_{1\omega}$ causes a proportional percent uncertainty in the predicted GST thermopower. Figure 4(c) shows good agreement between measurements and predictions and indicates that measurements using a bipolar bias enable accurate prediction of the material thermopower down to $\sim 30 \mu V K^{-1}$, the lowest thermopower device available.
Figure 3.4: Measured and predicted $\Delta h_{1\omega}$ from a bipolar bias for three GST devices with predicted $S_{GST} = 250 \pm 10$ (a), $110 \pm 5$ (b), and $30 \pm 3$ (c). (d) The error of the predicted $S_{GST}$ from FEA fitting to SJEM measurements for the three devices. Fitting FEA predictions to SJEM measurements for bipolar heating enables precise prediction of material thermopower from 30 to 250 $\mu$V K$^{-1}$. The additional measured $\Delta h_{1\omega}$ peaks shown in the channel of 4(b) and (c) are due to PE between GST phases.$^{12}$

3.7 – Conclusion

In conclusion, a technique for independent observation of nanometer-scale Joule and thermoelectric effects was developed using AFM based measurements of nanometer-scale temperature fields. The temperature rise of a device is governed by both Joule and thermoelectric effects, and heating a device with a periodic and bipolar bias separates the temperature rise due to Joule and thermoelectric effects at different harmonics. An AFM based thermometry
technique known as SJEM can simultaneously observe both the Joule and Peltier harmonic temperature rise of the device, such that Joule and Peltier effects can be independently observed. The independent observation of nanometer-scale Joule and thermoelectric effects improves the sensitivity and precision of nanometer-scale thermoelectric measurements. Coupling predictions and measurements of the temperature rise of PCM devices enables precise prediction of device thermopower from $30 \pm 3$ to $250 \pm 10 \, \mu V \, K^{-1}$. Furthermore, the derived harmonic relations for Joule and thermoelectric effects are applicable to other thermometry techniques; facilitating new studies of nanometer-scale Joule and thermoelectric heating, vital to the design of efficient electronics.
3.8 – References


CHAPTER 4

DIRECT OBSERVATION OF NANOMETER-SCALE JOULE AND PELTIER EFFECTS IN PHASE CHANGE MEMORY DEVICES

4.1 – Introduction

Phase change memory\(^1\) (PCM) is a non-volatile memory technology with potential for fast (sub-nanosecond)\(^2\) and low power (femtojoule)\(^3,4\) operation. PCM has potential to replace DRAM and Flash memory in future electronics.\(^5\) Data in chalcogenide-based PCM, such as Ge\(_2\)Sb\(_2\)Te\(_5\) (GST), are stored by the large ratio (>10\(^3\)) in electrical resistance between amorphous and crystalline states of the material. Reversible switching between phases is typically driven by Joule heating; however, Peltier,\(^6\) Seebeck,\(^7\) and Thomson\(^8\) effects have been observed to contribute to phase change.\(^9\) Previous studies have shown the thermopower for bulk and thin film face-centered cubic (fcc) GST is large (200-400 \(\mu\)V/K).\(^7,10,11\) Electrical contacts and thermal interfaces to GST are also important for heat generation and thermal confinement of GST devices.\(^12-15\) Recent work has indirectly and separately measured the role of interfaces\(^12\) and thermoelectric effects\(^6,8\) in GST devices. These are essential, because electrical and thermal interfaces could reduce PCM programming power\(^12,13\) by 20-30\%, and thermoelectric effects may reduce power consumption\(^9\) an additional 20-40\% depending on the thermopower of thin GST films. However, direct observations of Joule, Peltier, and current crowding (interface) effects at the nanometer-scale in a PCM device are still lacking.

In this chapter, we measured the nanometer-scale temperature distributions in lateral PCM devices using scanning Joule expansion microscopy (SJEM),\(^16-19\) which is an atomic force

microscopy (AFM) based thermometry technique. The measurement’s spatial and temperature resolutions were sub-50 nm and ~0.2 K. Joule heating dominated the temperature rise of the GST, while the temperature rise at the TiW contacts consisted of Joule, Peltier, and current crowding effects. Transfer length method (TLM) measurements on devices with varying lengths yielded GST electrical resistivity ($3.7 \pm 0.5 \times 10^{-4} \, \Omega \, \text{m}$) in the fcc phase, and GST-TiW electrical contact resistivity ($2.0 \pm 1.3 \times 10^{-8} \, \Omega \, \text{m}^2$). Comparing SJEM measurements to a finite element analysis (FEA) model, uncovered the thermopower ($350 \pm 150 \, \mu \text{V} \, \text{K}^{-1}$) of a 25 nm thick film of fcc-GST.

4.2 – GST Device Fabrication

Figure 4.1(a) shows the lateral GST test devices. GST (25 nm) was deposited on 300 nm thermal SiO$_2$ with a highly p-doped Si substrate. For electrical contact, 100 nm TiW (10/90 % weight) was patterned by photolithography and deposited by sputtering. Devices were encapsulated by electron-beam evaporation of 10 nm SiO$_2$. Fabrication was completed by spin coating 60 nm of poly(methyl methacrylate) (PMMA) on the samples. The PMMA protects the devices from oxidation, and amplifies thermo-mechanical expansions of the PCM device during operation, as needed for the SJEM technique. Before starting the SJEM measurements we crystallized the GST into predominately fcc phase by baking the entire device on a hot plate at 200 °C for 5 minutes.

Figure 4.1(a) also shows a schematic of the SJEM experiment. A sinusoidal waveform at 28 kHz with peak voltage $V$ was applied to resistively heat the device. The associated thermo-mechanical expansions of the sample were measured by the AFM cantilever, laser, and photodiode. A lock-in amplifier at the heating frequency $\omega_H$ with a low-pass filter bandwidth of
3-27 Hz recorded the peak-to-peak surface expansion $\Delta h$. The spatial resolution was $\sim50$ nm and temperature resolution was $\sim0.2$ K based on previous reports$^{16,19}$ and similar sample geometries.$^{18}$ The spatial resolution is further discussed in Section 4.5. SJEM can directly resolve current crowding and Peltier effects due to current flow between the GST and TiW as the current transfer length $L_T = 1.2 \pm 0.5 \, \mu m$, calculated below, between the GST-TiW is greater than the spatial resolution.

![Diagram](image)

**Figure 4.1:** (a) Schematic of phase change memory (PCM) device and scanning Joule expansion microscopy (SJEM) experiment. Lateral test devices consisted of 60 nm PMMA, 10 nm SiO$_2$, 100 nm TiW, 25 nm GST, and 300 nm SiO$_2$ on a Si substrate, from top to bottom. GST was crystallized into the face-centered cubic (fcc) phase by baking at 200 $^\circ$C for 5 min.$^{20}$ SJEM operates by supplying a periodic voltage waveform to resistively heat the GST device, while atomic force microscopy (AFM) measures the resulting peak surface thermo-mechanical expansion $\Delta h$. (b) Measured $\Delta h$ overlaid on topography for a device. The peak-to-peak GST temperature rise $\Delta T$ is proportional to $\Delta h$.$^{17,18}$
Figure 4.1(b) shows the surface expansion $\Delta h$ overlaid on the topography of a device. The GST peak temperature rise $\Delta T$ is proportional to $\Delta h$ and is related by FEA modeling.\textsuperscript{17,18} The device was biased with $V = \pm 8.9$ V at 28 kHz, and $\Delta h$ was recorded at $\omega = 56$ kHz, as Joule heating occurs at twice the applied frequency for a bipolar sine wave. Further increasing $\omega$ decreases $\Delta h$ as the thermal diffusion length decreases, which decreases the amount of material which thermo-mechanically expands.\textsuperscript{19} At the micrometer-scale $\Delta h$ is uniform across the device indicating uniform lateral heating, electric field, and resistivity distribution. Figure 1(b) also reveals some rough TiW contact edges from the lift-off process, which were avoided during measurements to limit measurement artifacts.

![X-ray diffraction (XRD) measurements of the GST films after the 5 min. anneal at 200 °C. Red dashed vertical lines are the predicted peak locations for fcc GST. The peak at ~33° is from the underlying Si.](image)

**Figure 4.2:** X-ray diffraction (XRD) measurements of the 25-nm thick GST film after the 5 min. anneal at 200 °C. Red dashed vertical lines are the predicted peak locations for fcc GST. The peak at ~33° is from the underlying Si.

Figure 4.2 shows X-ray diffraction (XRD) measurements of the GST films after the anneal. The peaks present at the (111), (200), and (220) labels indicate the film is in the fcc state. Slight shifts in the XRD peak locations are due to strain or small changes in stoichiometry. The relative intensities of the fcc peaks change due to the preferred direction of growth. The calculated ~8 nm grain size is smaller than 15-20 nm in previous work.\textsuperscript{22} Smaller grains yield shallow and broad peaks in the XRD measurements compared to previous work.\textsuperscript{7,20,22} The low
peak intensity can indicate the presence of the amorphous phase. However, the anneal conditions and measured resistivity is within the range of fcc films ($10^{-4} - 10^{-3} \ \Omega \ \text{m}$)\textsuperscript{1,3,23} indicating the film is predominantly fcc.\textsuperscript{7,20}

**Figure 4.3.** Transfer length method (TLM) measurements of 55 GST devices. A linear fit to two-terminal measurements of device resistance $R_{DS}$ yields the GST sheet resistance $R_{\square} = 15 \pm 2 \ \text{kΩ/□}$ and twice the GST-TiW contact resistance $2R_{C_{\text{W}}} = 35 \pm 11 \ \text{kΩ} \ \text{µm}$. The linear fit and standard deviation are shown by the solid red and dash-dot blue lines. The inset shows a top-view of the device geometry with GST channel length $L = 1.5$ to $10 \ \text{µm}$ and a fixed width $W = 245 \ \text{µm} \ (W \gg L)$.

### 4.3 – Transfer Length Method Measurements

Before analyzing the SJEM measurements, we obtained device and contact resistance information. Device resistance $R_{DS}$ was measured with two-terminal measurements and the channel length $L$ was measured using a combination of atomic force microscopy (AFM) and optical microscopy. The measured resistance $R$ is a series combination of $R_{DS}$ and a series resistance $R_{\text{Series}}$. The series resistance includes resistance from the leads, TiW contact pads, and TiW-probe interface. As shown in Table 4.1, the TiW resistivity is large and therefore contributes significantly to $R_{\text{Series}}$. Contacting the probes several times to the same TiW contact pad yielded $R_{\text{Series}} = 60 \pm 13 \ \Omega$, with $R_{\text{Series}} > 80 \ \Omega$ for a few measurements. Variation in device
probe location adjusts $R_{\text{Series}}$ and $R$ substantially and would increase the uncertainty of the TLM measurements. The average $R_{\text{Series}}$ was subtracted from $R$ to yield $R_{\text{DS}}$ for the TLM measurements. An optical microscope (3,500x magnification) measured $L$ for each device at different points along the channel. Four devices were measured by both AFM and the optical microscope. AFM measurements were within ~100 nm of optical measurements. The optical measurements showed $L$ deviated ~200 nm across the channel width.

Figure 4.3 shows TLM measurements of the device resistance $R_{\text{DS}}$ of 55 GST devices with lengths $L = 1.5$ to $10 \mu \text{m}$ and fixed width $W = 245 \mu \text{m}$ (see Fig. 4.3 inset). The slope and y-axis intercept of a linear fit to measurements yields the sheet resistance $R_\square = 15 \pm 2 \Omega/\square$ and twice the GST-TiW contact resistance per width $2R_CW = 35 \pm 11 \Omega \mu \text{m}$. Therefore, the GST resistivity $\rho_{\text{GST}} = 3.7 \pm 0.5 \times 10^{-4} \Omega \text{m}$ for the fcc phase, similar to previous studies.$^{23,24}$ The GST-TiW electrical interface resistivity $\rho_C$ and current transfer length $L_T$ are calculated from:

$$R_C \cdot W = \left( \frac{\rho_C}{L_T} \right) \coth \left( \frac{L_C}{L_T} \right) \quad (4.1)$$

$$L_T = \sqrt{\frac{\rho_C}{R_C}} \quad (4.2)$$

Equations 4.1 and 4.2 yield $\rho_C = 2.0 \pm 1.3 \times 10^{-8} \Omega \text{m}^2$ and $L_T = 1.2 \pm 0.5 \mu \text{m}$, where the TiW contact length was $L_C >> L_T$. The contact resistance is larger than in a previous study for TiW with fcc GST$^{26}$ ($\sim 10^{-9} \Omega \text{m}^2$), which is attributed to the relatively lower quality of the sputtered TiW in this work, and lower thermal budget of our devices.

4.4 – Finite Element Analysis Model Equations

The thermo-mechanical expansion $\Delta h$ and corresponding temperature rise $\Delta T$ were predicted from a two-dimensional (2D) FEA model of the devices, used to interpret the SJEM measurements. A 2D model is appropriate as $W \gg L$ for our devices. Equations 4.3 and 4.4 show
the modified heat diffusion and Poisson equations to account for thermoelectric transport.\textsuperscript{27,28}

The Fourier transform of the equations were coupled to a thermo-mechanical model and yielded the frequency response of the predicted $\Delta h$ and $\Delta T$.

\[
\rho_d c_p \frac{\partial T}{\partial t} = \nabla (k + \sigma S^2 T) \nabla T + \nabla (\sigma ST) \nabla V + \sigma \left( SVT \nabla V + \left[ \nabla V \right]^2 \right) 
\]

(4.3)

\[
\nabla \sigma (SVT + \nabla V) = 0 
\]

(4.4)

The density, heat capacity, thermal conductivity, electrical conductivity, thermopower, temperature, and voltage are given by $\rho_d$, $c_p$, $k$, $\sigma$, $S$, $T$, and $V$. Equations 4.5 and 4.6 show the expected voltage and thermal waveforms.

\[
V = V_{0\omega} + V_{1\omega} \cos(2\pi\omega t) 
\]

(4.5)

\[
T = T_{0\omega} + T_{1\omega} \cos(2\pi\omega t) + T_{2\omega} \cos(2\pi 2\omega t) 
\]

(4.6)

The subscripts denote the amplitude of $V$ and $T$ at the zero, first, and second harmonics.

The frequency of the applied bias $\omega = 28$ kHz for all experiments. The predicted peak voltage applied to the device $V_{DS} = \text{sign}(V_{0\omega})(|V_{0\omega}| + |V_{1\omega}|)$ is applied to the non-grounded TiW edge in the model. The peak temperature rise of the GST $\Delta T = 2|T_{1\omega}|$. The Fourier transform of Eqs. 4.3 and 4.4 with Eqs. 4.5 and 4.6 yields Eq. 4.7.

\[
\begin{bmatrix}
4(k + \sigma S^2 T_{0\omega}) & 2\sigma S^2 T_{1\omega} & 2\sigma S^2 T_{2\omega} & 4\sigma ST_{0\omega} & 2\sigma ST_{1\omega} \\
2\sigma S^2 T_{1\omega} & 2k + \sigma S^2(2T_{0\omega} + T_{2\omega}) & \sigma S^2 T_{1\omega} & 2\sigma ST_{1\omega} & \sigma S(2T_{0\omega} + T_{2\omega}) \\
2\sigma S^2 T_{2\omega} & \sigma S^2 T_{1\omega} & 2(k + \sigma S^2 T_{0\omega}) & 2\sigma ST_{2\omega} & \sigma ST_{1\omega} \\
\sigma S & 0 & 0 & \sigma & 0 \\
0 & \sigma S & 0 & 0 & \sigma 
\end{bmatrix} 
\begin{bmatrix}
T_{0\omega} \\
T_{1\omega} \\
T_{2\omega} \\
V_{0\omega} \\
V_{1\omega} 
\end{bmatrix} 
= 
\begin{bmatrix}
2\sigma \left\{ S(2\nabla T_{0\omega} \nabla V_{0\omega} + \nabla T_{1\omega} \nabla V_{1\omega}) + 2(\nabla V_{0\omega})^2 + (\nabla V_{1\omega})^2 \right\} \\
\sigma \left\{ S(2\nabla T_{0\omega} \nabla V_{1\omega} + 2\nabla T_{1\omega} \nabla V_{0\omega} + \nabla T_{2\omega} \nabla V_{1\omega}) + 4\nabla V_{1\omega} \nabla V_{0\omega} \right\} - i4\pi \rho_d \mu T_{1\omega} \omega \\
\vdots \\
\sigma \left\{ S(\nabla T_{1\omega} \nabla V_{1\omega} + 2\nabla T_{2\omega} \nabla V_{0\omega}) + (\nabla V_{1\omega})^2 \right\} - i4\pi \rho_d \mu T_{2\omega} \omega \\
0 \\
0 
\end{bmatrix} 
\]

(4.7)
Equation 4.7 was coded into the PDE physics and coupled with thermo-mechanical physics in COMSOL. Transforming and solving the equations in the frequency domain reduced computation time and convergence issues. Interface resistance and dissipation were implemented in COMSOL using home-built code.

The peak measured voltage $V$ and predicted device voltage $V_{DS}$ are related by:

$$V_{DS} = (V \times R_{DS}) / R$$

The measured resistance $R = R_{Series} + R_{DS}$. The simulation predicts the device resistance $R_{DS}$ for the modeled devices based on $\rho_{GST}$, $\rho_C$, and $L$. Varying $\rho_{GST}$ and $\rho_C$ changes the predicted $\Delta h$ as the predicted device power dissipation changes. The best fit between measured and predicted $\Delta h$ determined $\rho_{GST}$ and $\rho_C$ which also predicted $R_{DS}$ and $V_{DS}$. For $L = 7$ and 1.5 µm devices, $R = 433$ and 198 Ω, $R_{DS} = 550$ and 279 Ω. The predicted $R_{DS}$ is larger than $R$, as the model simulates the probes are 200 µm from the GST channel, when actual probes were within ~100-150 µm of the channel. The overestimation of the TiW contact length adds ~50-100 Ω to $R_{DS}$.

Figure 4.4: Schematic of model geometry. The model geometry is similar to experiments, with the Si domain modeled as shown. All of the boundaries are electrically and thermally insulated and mechanically constrained unless otherwise noted. The 10 nm SiO$_2$ capping layer was not modeled as it did not affect predictions.
4.5 – Finite Element Analysis Model Geometry

Figure 4.4 shows a schematic of the FEA model with boundary conditions. All surfaces were electrically insulated, thermally insulated, or mechanically constrained except those discussed below. The two TiW edges were fixed at $V_{DS}$ and ground, respectively. The bottom edge was fixed at $T_{0\omega} = 300$ K and $T_{1\omega} = T_{2\omega} = 0$ K. The edges along the top were not mechanically constrained. Varying electrical and thermal boundary conditions on the sides from insulating to grounds and heat sinks did not affect predictions.

The domain size is ~5 times the Si thermal diffusion length $L_{PD} = \left[\frac{k}{\rho \cdot c_p \cdot \omega}\right]^{1/2}$. The heating frequency $\omega = 28$ kHz for unipolar sine waves and $2\omega = 56$ kHz for bipolar sine waves, as in Fig. 1(b). The material properties of Si are listed in Table 4.1 and $L_{PD} \approx 40$ µm for $\omega = 28$ kHz. Thermo-mechanical expansion of Si accounts for ~32 and ~56 % of the predicted $\Delta h$ for the $L = 1.5$ and 7 µm devices. Thermo-mechanical expansion of PMMA accounts for ~63 and ~41 % of the predicted $\Delta h$ for the $L = 1.5$ and 7 µm devices. Therefore, the GST, TiW, and SiO$_2$ are ~5 % of the predicted $\Delta h$. We estimate the spatial resolution of SJEM for the GST devices to be similar to our previous work with graphene$^{18}$ due to similar sample geometry and the small contribution of GST to lateral thermal conductance and thermo-mechanical expansion. Decreasing the domain $<L_{PD}$ decreases the temperature rise and thermo-mechanical expansion of the Si, which decreases the predicted $\Delta h$. The device temperature can also decrease due to increased substrate conductance. However, a large thermal resistance between the device and Si substrate can reduce the Si temperature rise and thermo-mechanical expansion to negligible values as shown by our previous work with carbon nanotubes (CNTs)$^{19}$.

Figure 4.4 shows the modeled geometry. A PMMA thickness of 60 nm was measured on the TiW using an AFM to measure the topography of a scratch through the PMMA on the
The TiW contacts were measured to be 80 and 100 nm thick with and without the PMMA by AFM. Therefore, the PMMA thickness was 80 nm in the channel. The PMMA geometry was replicated in the simulation. The measured and modeled PMMA surfaces are similar except within 200 nm of the TiW edge. The measured PMMA has a smooth profile over the TiW edge, instead of the discontinuous profile modeled. The model predicted a dip in $\Delta h$ near the TiW edge, which was not observed in measurements. The discrepancy between predictions and measurements for the dip is attributed to the change in heat flow and thermo-mechanical expansion with the two different PMMA geometries. Therefore, predictions within 200 nm of the edge were ignored.

Table 4.1: Electro-thermo-physical properties of materials used in the simulation. From left to right the listed properties are the thermal conductivity, density, heat capacity, electrical resistivity, thermopower, coefficient of thermal expansion, Poisson’s ration, and elastic modulus.

<table>
<thead>
<tr>
<th>Material</th>
<th>$k$ W m$^{-1}$ K$^{-1}$</th>
<th>$\rho_d$ kg m$^{-3}$</th>
<th>$c_p$ J kg$^{-1}$ K$^{-1}$</th>
<th>$\rho$ $\Omega$ m</th>
<th>$S$ $\mu$V K$^{-1}$</th>
<th>$\alpha_{CTE}$ K$^{-1}$ ×10$^6$</th>
<th>$\nu_p$</th>
<th>$E$ GPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>GST</td>
<td>0.5$^{22}$</td>
<td>6,300$^{22}$</td>
<td>200$^{22}$</td>
<td></td>
<td></td>
<td>17$^{29}$</td>
<td>0.3$^{29}$</td>
<td>36$^{29}$</td>
</tr>
<tr>
<td>TiW</td>
<td>5</td>
<td>16,000</td>
<td>160</td>
<td>1.3×10$^{-5}$</td>
<td>1</td>
<td>5$^{24}$</td>
<td>0.28$^{24}$</td>
<td>410$^{24}$</td>
</tr>
<tr>
<td>PMMA</td>
<td>0.18$^{18}$</td>
<td>1,200$^{30}$</td>
<td>1,500$^{30}$</td>
<td></td>
<td>-</td>
<td>50$^{19}$</td>
<td>0.35$^{19}$</td>
<td>3$^{19}$</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>1.4$^{18}$</td>
<td>2,220$^{31}$</td>
<td>745$^{31}$</td>
<td></td>
<td>-</td>
<td>0.5$^{19}$</td>
<td>0.17$^{19}$</td>
<td>64$^{19}$</td>
</tr>
<tr>
<td>Si</td>
<td>80$^{32}$</td>
<td>2,330$^{31}$</td>
<td>712$^{31}$</td>
<td></td>
<td>-</td>
<td>2.6$^{19}$</td>
<td>0.28$^{19}$</td>
<td>165$^{19}$</td>
</tr>
</tbody>
</table>

Table 4.1 lists the material properties used in the simulation. The electrical resistivity $\rho$ and thermopower $S$ for PMMA, SiO$_2$ (insulator), and Si (substrate) were not included in simulation. The GST-TiW and GST-SiO$_2$ thermal interface conductance $G_{CON} = 4\times10^7$ W m$^{-2}$ K$^{-1}$, similar to previous studies.$^3$ Varying the GST-TiW $G_{CON} = 10^{7-9}$ W m$^{-2}$ K$^{-1}$ had little effect on predictions. Typical values of $G_{CON}$ for the Si-SiO$_2$, TiW-SiO$_2$, SiO$_2$-PMMA and GST-SiO$_2$ interfaces had little effect on predictions and were neglected. The 10 nm SiO$_2$ capping layer had
no effect on predictions and was not modeled. The TiW thermopower was assumed small compared to $S_{GST}$.

Figure 4.5: Effect of model properties on predicted (a) $\Delta h$ and (b) $\Delta T$ for $V = +3.2$ V for the $L = 1.5$ µm device, Device 1. The solid black line is from Fig. 4.6 with properties from Table 4.1. The red solid line, blue dashed line, green dash-dot line, and magenta dotted line vary $\rho_C = 3 \times 10^{-10}$ Ω m$^2$, $S_{GST} = 1$ mV K$^{-1}$, $k_{TiW} = 1$ W m$^{-1}$ K$^{-1}$ and $S_{TiW} = S_{GST}$ from Fig. 3. The black arrow indicates the direction of hole current flow.

Figure 4.5 shows the effect of varying the material properties on the predicted $\Delta h$ and $\Delta T$ for the $L = 1.5$ µm device for $V = +3.2$ V. Decreasing $\rho_C = 3 \times 10^{-10}$ Ω m$^2$ significantly decreases $\Delta h$ and $\Delta T$ in the contacts due to less power dissipation at the GST-TiW interface. Decreasing the TiW thermal conductivity $k_{TiW} = 1$ W m$^{-1}$ K$^{-1}$ decreases heat spreading into the contacts. Therefore, $\Delta h$ and $\Delta T$ decrease quickly as $|x|$ increases in the contacts. Increasing $S_{GST} = 1$ mV
K⁻¹ increases Peltier heating and cooling of the left and right contacts. The spike in Δh and ΔT at the left contact is due to a hot spot which develops at the GST-TiW interface due to increased heat generation from increased $S_{GST}$ or decreased heat spreading due to decreased $k_{TiW}$. A larger $\rho_C$ will also form a hot spot at the GST-TiW interface due to increased heat generation. Setting the TiW thermopower $S_{TiW} = S_{GST}$ eliminates Peltier effects in our simulation as there is no difference in thermopower at the GST-TiW interface. We do not observe Thomson heating in our devices, as the negative Thomson coefficient of fcc GST\(^9\) would heat the GST near the TiW in a manner opposite to our SJEM measurements.

### 4.6 – TiW Thermal Conductivity

Van der Pauw measurements were used to evaluate the sputtered TiW film (1 cm\(^2\) sample, 100 nm thickness, 10/90 % wt, annealed at 200 °C similar to GST devices) and found an electrical resistivity $\rho_{TiW} = 1.3\times10^{-5}$ Ω m. Using this value, the Wiedemann-Franz law predicts an estimated electron thermal conductivity $k_{el} \approx 0.6$ W m\(^{-1}\) K\(^{-1}\) at room temperature. The phonon thermal conductivity $k_{ph}$ can be estimated from kinetic theory as:

$$k_{ph} = \frac{1}{3} C_{ph} v \lambda$$  \hspace{1cm} (4.9)

Where $C_{ph}$, $v$, and $\lambda$ are the phonon heat capacity, phonon velocity, and phonon mean free path.

The Debye model is used in Eq. 4.10 to approximate $C_{ph}$.

$$C_{ph} = 9 n_a k_B \left( \frac{T}{T_D} \right)^3 \int_0^{T_D/T} \frac{x^4 e^x dx}{(e^x-1)^2}$$  \hspace{1cm} (4.10)

Where $n_a$, $k_B$ and $T$ are the atom number density, Boltzmann constant, and temperature. Assuming a lattice constant $a \approx 3.1$ Å, approximately the lattice spacing of Ti and W, and a body-centered cubic (bcc) structure for TiW\(^{33}\) we calculate $n_a \approx 4\times10^{24}$ kg\(^{-1}\) and the density $\rho_d$.
along with the heat capacity are listed in Table 4.1. The Debye temperature $T_D \sim 400$ K is found as:

$$T_D = \frac{\hbar v}{k_B} \left(6\pi^2 n_a\right)^{1/3} \tag{4.11}$$

where $\hbar$ is the reduced Planck’s constant and the speed of sound in W is used to estimate $v \approx 3.2 \times 10^3$ m s$^{-1}$. Varying $v = 2-5 \times 10^3$ m s$^{-1}$ and $a = 2.8-3.2$ Å adjusts $k_{ph}$ by at most 50%. The largest uncertainty of $k_{ph}$ is due to the estimation of the phonon mean free path $\lambda$. Based on the relatively high $\rho_{TiW}$ of our films, we estimate $\lambda \sim 1-2$ nm, as there is likely a large amount of disorder in the TiW which scatters both electrons and phonons. X-ray diffraction (XRD) measurements indicate the grain size is $\sim 3$ nm. Finally, the combined TiW thermal conductivity is $k_{TiW} = k_{el} + k_{ph} \approx 5$ W m$^{-1}$ K$^{-1}$. Figures 4.6(a) and 4.8(a) show that predictions based on $k_{TiW} \approx 5$ W m$^{-1}$ K$^{-1}$ agree well with our SJEM measurements.

4.7 – Device 1 Analysis

Figure 4.6(a) shows the measured and predicted $\Delta h$ for a $L = 1.5$ µm device, Device 1. A unipolar sine wave directed current flow (holes in p-type GST) across the device for $V = \pm 1.6$, $\pm 2.4$, and $\pm 3.2$ V. Measurements are an average of 32 scans with deviation smaller than the markers.

We observe heat generation at the GST-TiW interface due to current crowding and Peltier effects. Current crowding is independent of carrier flow direction and occurs at the GST-TiW interface due to a finite interface resistivity, $\rho_C$, between the GST channel and TiW contacts. On the other hand, the Peltier effect$^{34}$ is dependent on the direction of current flow through the GST-TiW junction and heats (cools) the junction as carriers flow into (out of) the contact due to the difference in GST and TiW thermopower. The TiW-GST interface properties
were found by fitting the predicted and measured $\Delta h$. A $\rho_{GST} = 1.7 \times 10^{-4} \ \Omega \cdot m$ and $\rho_C = 3 \times 10^{-9} \ \Omega \cdot m^2$ predicts $\Delta h$ and $R_{DS}$ which match measurements. Both $\rho_C$ and $\rho_{GST}$ are close to values obtained from TLM measurements summarized in Fig. 4.3. We estimated the thermopower of GST in the fcc phase $S_{GST} \approx 350 \pm 150 \ \mu V \ K^{-1}$, by comparing measurements of the Peltier effect at the contacts in Fig. 4.6 with the FEA model.

![Figure 4.6](image)

**Figure 4.6:** (a) Measured and predicted $\Delta h$ and (b) predicted $\Delta T$ for $V = \pm 1.6$, $\pm 2.4$, and $\pm 3.2 \ \text{V}$ for the $L = 1.5 \ \mu \text{m}$ device, Device 1. The edges of the GST-TiW contacts are marked by black vertical dashed lines. (a) Symbols show measured $\Delta h$ and lines show the predicted $\Delta h$. Current (hole) flow left and right are shown in red circles and solid lines, and blue triangles and dashed lines, respectively. The arrows indicate the hole flow direction with color and every second measurement is shown for clarity. (b) Predicted GST temperature rise $\Delta T$ for hole flow to the left (red solid line) and right (blue dashed line) is due to Peltier effects at the contacts. The black dashed lines and arrows are similar to (a).
Figure 4.7: (a) Measured and predicted $\Delta h_{\text{Peltier}}$ at the GST-TiW interface for the $L = 1.5 \, \mu m$ device, Device 1. Three bias conditions are shown $|V| = 1.6$, 2.4, and 3.2 V in green dash-dot line and crosses; blue dashed line and triangles; and red solid line and dots. The GST thermopower $S_{\text{GST}} = 250$, 500, and 500 $\mu V \, K^{-1}$ for $|V| = 1.6$, 2.4, and 3.2 V. Bars located in the top-left show the standard deviation of the measurements over 32 scans. Measurements are shown by markers and predictions are shown as solid lines. (b) The coefficient of determination $R^2$ for predictions from both contacts. The three bias conditions are shown similar to (a). The average $R^2$ is shown as a black solid line. Negative $R^2$ indicates the measurement average is a better fit than predictions.

Figure 4.6(b) shows the predicted $\Delta T$ and reveals the roles of Joule, Peltier, and current crowding effects of the PCM test device. Joule heating dominates power dissipation in the GST as expected, showing $\Delta T$ which scales with $V^2$. The majority of heat generation at the contacts is due to the finite $\rho_C$ and associated current crowding effect. A small temperature “spike” occurs at $|x| = 0.75 \, \mu m$ for hole flow from the GST into the contact. The small hot spot forms due to heat
generation at the contact, from current crowding and/or Peltier heating, combined with the low thermal conductance of the surrounding materials. Peltier heating and cooling is observed as the change in ΔT with hole flow direction. At |V| = 1.6 and 3.2 V the difference in ΔT with carrier flow at the channel edge is ~1.5 and 3 K (~63 and ~32 % of the channel ΔT). The temperature resolution of 0.2-0.4 K, increasing with increasing bias, was determined by the predicted uncertainty in ΔT from the deviation of the measured Δh.

Figure 4.7 shows the fitting of predictions to measurements to determine the GST thermopower, $S_{GST}$. The difference in Δh for hole flow left and right (due to Peltier heating and cooling of the contacts) is denoted $\Delta h_{Peltier} = \Delta h(j+) - \Delta h(j-)$, where $j+$ and $j-$ denote hole flow left and right. Figure 4.7(a) shows the measured and predicted $\Delta h_{Peltier}$ at the GST-TiW interface for |V| = 1.6, 2.4, and 3.2 V. In Fig. 4.7(a) the GST thermopower $S_{GST} = 250, 500, \text{ and } 500 \mu\text{V K}^{-1}$ for |V| = 1.6, 2.4, and 3.2 V, corresponding to the best fits from Fig. 4.7(b). Figure 4.7(b) shows the coefficient of determination $R^2$ for predictions at both contacts for each bias condition. The average $R^2$ curve has a maximum $R^2 = 0.65$ which predicts $S_{GST} \approx 350 \pm 150 \mu\text{V K}^{-1}$ for fcc phase GST, similar to previous studies.\textsuperscript{7,10,11} The uncertainty in $S_{GST}$ was estimated from a 0.1 decrease below the maximum $R^2$.

4.8 – Device 2 Analysis

Figure 4.8 shows SJEM measurements and FEA predictions for a $L = 7 \ \mu\text{m}$ device, Device 2. Figure 4.8(a) shows the measured and predicted surface expansion $\Delta h$, and Fig. 4.8(b) shows the predicted device temperature rise $\Delta T$. The analysis is similar to Device 1 of Section 4.7 and duplicate details are omitted here. The device was resistively heated by applying a unipolar sine wave with $V = \pm 3.6, \pm 6.3, \text{ and } \pm 8.9 \ \text{V at } 28 \ \text{kHz. Measurements are an average of 64 scans}$. 

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with standard deviations smaller than the symbol size for $|V| = 3.6$ and 6.3 V, and approximate twice the symbol size for $|V| = 8.9$ V. For the device in Fig. 4.8, $\rho_{GST} = 2.0 \times 10^{-4}$ Ω m, and $S_{GST} = 400 \pm 150$ μV K$^{-1}$. We attribute the dissimilar measured $\Delta h$ at the left and right contacts to dissimilar $\rho_C$ and heat dissipation at the contacts, likely due to non-uniform adherence between the TiW and GST. We found $\rho_C = 3$ and $13 \times 10^{-9}$ Ω m$^2$ for the right and left contacts, respectively. We are unable to discern if other devices exhibited non-uniform $\rho_C$ as the TLM measurement is an average of the 55 tested devices.

![Figure 4.8: (a) Measured and predicted $\Delta h$ and (b) predicted $\Delta T$ for $V = \pm 3.6$, $\pm 6.3$, and $\pm 8.9$ V for the $L = 7$ μm device, Device 2. The edges of the GST-TiW contacts are marked by black vertical dashed lines. (a) Symbols show the measured $\Delta h$ and lines show the predicted $\Delta h$. Current (hole) flow to the left and right is shown in red circles and solid lines, and blue triangles and dashed lines, respectively. The arrows indicate the hole flow direction with color and every fifth measurement is shown for clarity. (b) Predicted GST temperature rise $\Delta T$ for hole flow to the left (red solid line) and right (blue dashed line).](image-url)
Figure 4.9: (a) Measured and predicted $\Delta h_{Peltier}$ at the GST-TiW interface of the left contact, with $S_{GST} = 400 \, \mu V \, K^{-1}$ for the $L = 7 \, \mu m$ device, Device 2. Three bias magnitudes are shown $|V| = 3.6, 6.3, \text{ and } 8.9 \, V$ in green dash-dot line and crosses; blue dashed line and triangles; and red solid line and dots. Measurements are shown by markers and predictions are shown as solid lines. Bars in the top-left are the standard deviations of the measurement averaged over 64 scans. The Peltier effect causes the observed difference in heat generation with carrier flow. (b) The coefficient of determination $R^2$ for predictions from both contacts, with three bias conditions similar to (a). The average $R^2$ is a black solid line.

Joule heating and Peltier effects are evident in Fig. 4.8(b). Peltier heating and cooling is observed as the change in $\Delta T$ with hole flow direction. At $|V| = 3.6$ and $8.9 \, V$ the difference in $\Delta T$ with carrier flow at the GST-TiW edge is $\sim 2.1$ and $\sim 5.6 \, K$, respectively ($\sim 60\%$ and $\sim 26\%$ of the channel $\Delta T$). The temperature resolution of $0.2$–$0.7 \, K$, increasing with increasing bias, was determined by the predicted uncertainty in $\Delta T$ from the deviation of the measured $\Delta h$. 

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Figure 4.9 shows the fitting of the predicted GST thermopower $S_{GST}$ to measurements. The average $R^2$ curve has a maximum $R^2 = 0.82$ which predicts $S_{GST} = 400 \pm 150 \, \mu V \, K^{-1}$. A similar value for $S_{GST}$ is predicted using the mean absolute percent error (MAPE) between measurements and predictions, described below. The difference in $S_{GST}$ between the $L = 1.5$ and 7 µm devices is due to uncertainty in the measurement.

Figure 4.10: The mean absolute percent error (MAPE) for predicted $\Delta h_{Peltier}$ for the $L = 7$ µm device, Device 2. Shown are $|V| = 6.3$ and 8.9 V in blue dashed and red solid lines.

Figure 4.10 shows the mean absolute percent error (MAPE) of the predicted $\Delta h_{Peltier}$ to measurements. The MAPE is calculated at both contacts for $|V| = 6.3$ and 8.9 V for the $L = 7$ µm device, Device 2. The predicted $S_{GST} = 450$ and 400 µV K$^{-1}$ for $|V| = 6.3$ and 8.9 V. Figure 4.10 can be compared to Fig. 4.9 to determine $S_{GST}$. The MAPE and $R^2$ are two methods for determining the error in the predicted and measured $\Delta h_{Peltier}$. The MAPE for $|V| = 3.6$ V and the $L = 1.5$ µm device are >100% and are not shown.

4.9 – Conclusion

In conclusion, we observed Joule, Peltier, and current crowding effects in a fcc phase GST device using SJEM with ~50 nm spatial and ~0.2 K temperature resolution. The sheet and
contact resistance of GST and GST-TiW were measured by TLM, and also confirmed by FEA simulation fitting against the SJEM data. Joule heating dominated power dissipation in the GST channel, while power dissipation at the GST-TiW contacts was a combination of Peltier and current crowding effects. Comparing measurements and modeling predictions, we obtained $S_{GST} = 350 \pm 150 \, \mu V \, K^{-1}$ for a 25 nm thick film of fcc phase GST. The large measured thermopower of GST could reduce the energy consumption by $>50\%$ in highly scaled PCM devices due to Peltier heating, compared to scenarios which only utilize Joule heating. \(^9\) PCM energy consumption can be further reduced by optimizing the GST-contact interface \(^{13}\) and interface thermopower. \(^6\) Such knowledge of nanometer-scale Joule, thermoelectric, and interface effects in GST devices should enable improvements in energy efficient designs of future PCM technology.
4.10 – References


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CHAPTER 5
HETEROGENOUS NANOMETER-SCALE JOULE AND PELTIER EFFECTS IN SUB-25 NM THIN PHASE CHANGE MEMORY DEVICES

5.1 – Introduction

Phase change memory\(^1\) (PCM) is a non-volatile memory technology with potential for fast (sub-nanosecond)\(^2\) and low power (femtojoule)\(^3,4\) operation. PCM has potential to replace DRAM and Flash memory in future electronics.\(^5\) Data in chalcogenide based PCM, such as Ge\(_2\)Sb\(_2\)Te\(_5\) (GST), are stored by the large ratio (>10\(^3\)) in electrical resistance between amorphous and crystalline states of the material. Reversible switching between phases is typically driven by Joule heating; however, Peltier,\(^6\) Seebeck,\(^7\) and Thomson\(^8\) effects have been observed to contribute to phase change.\(^9\) Previous studies have shown the thermopower for bulk and thin film face-centered cubic (fcc) GST is large (200-400 µV K\(^{-1}\)).\(^7,10-13\) Higher temperature annealing forms hexagonal close-packed (hcp) GST\(^14\) which reduces the GST thermopower (15-50 µV K\(^{-1}\)).\(^7,10,11,13\) Few studies have examined the effect of amorphous, fcc, and hcp phases on electrical\(^15,16\) or thermoelectric\(^7,12\) properties of thin GST films, which are important for device scaling. Electrical contacts and thermal interfaces to GST are also important for heat generation and thermal confinement of GST devices.\(^17-20\) Recent work has measured the role of interfaces\(^17\) and thermoelectric effects\(^6,8,12\) in GST devices. These studies are essential, since electrical and thermal interfaces could reduce PCM programming power\(^17,18\) by 20-30%, and thermoelectric effects may reduce power consumption\(^9\) an additional 20-40% depending on the thermopower of thin GST films. However, little is known of electrical properties, interface resistances, thermopower, and heat generation in sub-25 nm thin GST films.
In this chapter, we measured the nanometer-scale temperature distribution and properties of lateral PCM devices with 11 and 22 nm thin GST. Transfer length method (TLM) measurements on devices with varying channel lengths yielded the GST electrical resistivity $\rho_{GST}$ and GST-TiW contact resistivity $\rho_C$ for each sample. Effective media theory (EMT)\textsuperscript{7,21} calculations yielded the crystal fraction of amorphous, fcc, and hcp GST for the 11 and 22 nm thin GST samples annealed at 150, 200, and 250 °C. Nanometer-scale thermometry with sub-50 nm spatial and ~0.2 K temperature resolution was accomplished by scanning Joule expansion microscopy (SJEM),\textsuperscript{12,22-25} an atomic force microscopy (AFM) based technique. The SJEM technique is modified for independent and direct observation of Joule and Peltier effects. We observe uniform heating for mixed amorphous and fcc GST thin films, and laterally heterogeneous Joule and thermoelectric effects in mixed fcc and hcp GST thin films. Increasing the annealing temperature increases the hcp GST crystal fraction and the heterogeneous Joule heating and Peltier heating and cooling between fcc and hcp GST. We develop a two and three dimensional (2D and 3D) finite element analysis (FEA) model to understand SJEM results. The 3D FEA model predicts the observed heterogeneous heating and estimates the hcp GST grain size. Comparing SJEM measurements with the 2D FEA model predicts $\rho_{GST}$ and $\rho_C$, which are in good agreement with values obtained from TLM measurements. SJEM measurements and modeling also yield the first measurements of the thermopower of sub-25 nm thin GST films.
Figure 5.1: (a) Schematic of lateral phase change memory (PCM) device and scanning Joule expansion microscopy (SJEM). PCM devices consisted of 60-200 nm of PMMA, 30-60 nm of Au, 10 nm TiW, 11-22 nm GST, and 300 nm SiO$_2$ on a Si substrate, from top to bottom. The device channel length and GST thickness are shown by $L$ and $t_{GST}$. SJEM operates by supplying a periodic voltage waveform to resistively heat the device while the AFM measures the resulting peak-to-peak surface thermo-mechanical expansion $\Delta h$. (b) Measured $\Delta h$ overlaid on topography for device with channel length 7.5 $\mu$m, GST thickness 22 nm, and anneal temperature 250 °C. The peak-to-peak temperature rise $\Delta T$ is proportional to the measured $\Delta h$.\textsuperscript{12,22,25} The measured thermo-mechanical expansion is non-uniform indicating heterogeneous lateral GST structure.

5.2 – Device Fabrication

Figure 5.1(a) shows the lateral GST device. A 300 nm SiO$_2$/Si wafer was diced into $\sim$1.5 $\times$ 1.5 cm$^2$ samples, and GST with thickness $t_{GST} = 11$ or 22 nm was sputtered onto the samples at 5 mT in an Ar environment at a rate of 2.5 nm min$^{-1}$. The samples were annealed at a temperature $T_A = 150$, 200, or 250 °C for 10 min in a N$_2$ environment, with a heating and cooling
rate of ~30 °C min⁻¹. The sample resistance $R_{\text{Sample}}$ was measured in-situ of the anneal using TiW contacts which were patterned and sputtered at the sample corners before the GST deposition. After annealing, lateral GST devices with channel length $L = 2$ to 12 μm were fabricated by photolithography patterning and sputtering of 10 nm TiW (10/90 % weight) and 30-60 nm Au. The Au reduces the electrode sheet resistance. Fabrication was completed by spin coating 60-200 nm of poly(methyl methacrylate) (PMMA) on the samples. The PMMA serves a dual purpose: it protects the devices from oxidation, and amplifies thermo-mechanical expansions of the PCM device during operation. Figure 5.1(b) shows the PMMA topography of a typical device.

Figure 5.2: In-situ annealing sample resistance $R_{\text{Sample}}$ with temperature $T$. The GST samples were 11 nm thin and annealed at temperatures $T_A = 150$, 200, and 250 °C shown in dash-dot red, dotted blue, and solid black lines. Samples were annealed in N₂ environment at $T_A$ for 10 min with 30 °C min⁻¹ heating and cooling rate.

Figure 5.2 shows in-situ annealing $R_{\text{Sample}}$ measurements for the 11 nm thin GST samples annealed at 150, 200, and 250 °C. The measurements are two probe resistance measurements across the ~1.5 × 1.5 cm² samples. The large change in $R_{\text{Sample}}$ at ~160 °C indicates the majority of GST quickly transforms from amorphous to fcc GST. Although the sample annealed at 150 °C was below the transition temperature, the measured ~10⁴ Ω change in room temperature
resistance indicates the sample is predominately fcc phase GST. Samples annealed at higher temperatures have $>10^4 \, \Omega$ change in resistance, indicating the presence of hcp GST.\textsuperscript{13}

### 5.3 – Scanning Joule Expansion Microscopy

Figure 5.1(a) shows a schematic of the SJEM experiment. A sinusoidal waveform at frequency $\omega = 43 \, \text{kHz}$ and bias amplitude $V$ drives the device and generates resistive heating within the device. The resulting thermo-mechanical expansions of the sample were measured by the AFM cantilever, laser, and photodiode. A lock-in amplifier at the first or second harmonic, $1\omega$ or $2\omega$, with a low-pass filter bandwidth of 3-27 Hz recorded the peak-to-peak (twice the amplitude) surface expansion $\Delta h$. The spatial resolution was ~50 nm and temperature resolution was ~0.2 K based on previous reports.\textsuperscript{12,22} SJEM can resolve current crowding and Peltier effects due to current flow between the GST and TiW as the current transfer length $L_T = 0.4-1.2 \, \mu\text{m}$ between the GST-TiW (the distance over which $1/e$ of the current is transferred between the two materials) is greater than the spatial resolution.\textsuperscript{12}

Figure 5.1(b) shows the measured surface expansion $\Delta h$ overlaid on the topography of a 7.5 $\mu\text{m}$ channel length and 22 nm thin GST device annealed at 250 °C. The device is biased with amplitude $V_{DS} = 8.9 \, \text{V}$. Subtracting the voltage drop across the electrodes and probes from $V$ yields the device bias amplitude $V_{DS}$. The GST peak-to-peak temperature rise $\Delta T$ is proportional to $\Delta h$ and is related using FEA modeling.\textsuperscript{12,22,25} The measured $\Delta h$ is non-uniform across the device, indicating heterogeneous lateral heating, electric field, and resistivity distribution due to presence of mixed fcc and hcp GST.
Figure 5.3: Transfer length method (TLM) measurements of all samples. The GST thickness $t_{\text{GST}}$ and annealing temperature $T_A$ are labeled on each plot. The black dots are measurements. The solid red and dash-dot blue lines are the simple linear regression best fit and deviation. The slope of the fit is the sheet resistance $R_{\square}$ in kΩ/□ and the $y$-axis intercept is twice the contact resistance per width $2R_C \times W$ in kΩ μm.
### 5.4 – Measured GST Properties

Before analyzing SJEM measurements, we obtained device and contact resistance information from TLM measurements for each sample. The lateral GST devices have a device width $W = 245$ μm and source-drain spacing $L = 2\text{–}12$ μm. The sheet and contact resistance of each sample was calculated from simple linear regression of the measured resistance of more than 10 devices per sample. The GST resistivity, GST-TiW contact resistivity, and current transfer length were calculated from the sheet and contact resistance,\textsuperscript{12,22,28} described below.

Figure 5.3 shows transfer length method (TLM) measurements of all samples. The lateral GST devices have a device width $W = 245$ μm and a channel length (source-drain spacing) $L = 2\text{–}12$ μm. The calculation of GST resistivity $\rho_{GST}$ and GST-TiW contact resistivity $\rho_{C}$ from TLM measurements\textsuperscript{12,22} is discussed below for the 11 nm thin GST sample annealed at 150 °C, shown in Fig. 5.3(a). Simple linear regression of device resistance $R_{DS}$ yields the sheet resistance $R_{\Box} = 37 \pm 2$ kΩ/□ ($\rho_{GST} = 4.1 \pm 0.2\times10^{-4}$ Ω m) and twice the contact resistance per width $2R_{C}\times W = 42 \pm 15$ kΩ μm with a coefficient of determination $R^2 = 0.97$ for the fit. The current transfer length $L_{T}$ and $\rho_{C}$ are calculated from:\textsuperscript{28}

\begin{equation}
R_{C}\times W = (\rho_{C}/L_{T})\coth(L_{C}/L_{T})
\end{equation}

\begin{equation}
L_{T} = \sqrt{\rho_{C}/R_{\Box}}.
\end{equation}

Equations 5.1 and 5.2 yield $\rho_{C} = 1.2 \pm 0.9\times10^{-8}$ Ω m$^2$ and $L_{T} = 570 \pm 210$ nm for the 11 nm thin GST sample annealed at 150 °C. We note $L_{T}$ is much smaller than the TiW contact length $L_{CON}$\textsuperscript{12}. Some of the devices for the 11 nm thin GST sample annealed at 150 °C had partially destroyed channels, and $W$ was measured optically for each device on this sample. All other samples had intact channels.
Figure 5.4: (a) Calculated GST resistivity $\rho_{\text{GST}}$ and GST-TiW contact resistivity $\rho_{\text{C}}$ with annealing temperature $T_A$ from transfer length method (TLM) measurements. Red and blue lines show $\rho_{\text{GST}}$ and $\rho_{\text{C}}$. (b) Calculated crystal fraction $x_f$ from effective media theory (EMT)\textsuperscript{21} of amorphous, fcc, and hcp phase GST ($x_{\text{amr}}$, $x_{\text{fcc}}$, and $x_{\text{hcp}}$) are shown in black, red, and blue lines. The figure shows dotted lines with triangle markers and solid lines with circle markers for 11 and 22 nm thin GST.

Figure 5.4(a) shows the GST resistivity and GST-TiW contact resistivity from TLM measurements on all the samples. The measured GST resistivity $\rho_{\text{GST}}$ continuously decreases with increasing annealing temperature. The measured GST-TiW contact resistivity $\rho_{\text{C}}$ also decreases with annealing temperature until $T_A = 250$ °C. The contact resistance for the samples annealed at 250 °C is a few ohms, near our TLM measurement resolution, and we are unable to determine if $\rho_{\text{C}}$ is lower than the values shown in Fig. 5.4(a) from TLM measurements. The measured contact resistance of the 22 nm thin GST sample annealed at 200 °C is also near the measurement resolution.
5.5 – Effective Media Theory

Effective media theory (EMT)\textsuperscript{21} predicts the effective properties of a multiple phase mixture assuming each phase is randomly distributed as spheres in an uniform effective medium.\textsuperscript{21} We describe the assumption that each sample is a binary phase mixture below. Equation 5.3 relates the crystal fraction $x_f$ and conductivity $\sigma$ of a binary mixture composed of A and B phases.\textsuperscript{21}

$$x_A \frac{\sigma_A - \sigma_E}{\sigma_A + 2\sigma_E} + x_B \frac{\sigma_B - \sigma_E}{\sigma_B + 2\sigma_E} = 0 \quad (5.3)$$

The subscripts denote the material phase, and the effective mixture conductivity is given by $\sigma_E$. TLM measurements yielded the effective resistivity of each sample. The crystal fraction is calculated using Eq. 5.3, using the measured $\rho_{GST}$, and assuming the resistivity of amorphous, fcc, and hcp GST are $\rho_{amr} = 1 \ \Omega \ m$, $\rho_{fcc} = 2 \times 10^{-4} \ \Omega \ m$, and $\rho_{hcp} = 3.3 \times 10^{-6} \ \Omega \ m$, similar to published values.\textsuperscript{4,13} Equation 5.3 can also calculate the effective thermal conductivity of a binary mixture.

EMT was applied to calculate the crystal fraction $x_f$ of the GST phases\textsuperscript{7} of each sample. The in-situ annealing resistance measurements show a large ($\sim 10^3$-10$^4 \ \Omega$) change in sample resistance at $\sim 160 \ ^{\circ}C$ indicating the majority of GST quickly changes from amorphous to fcc GST.\textsuperscript{26,27} The sample resistance continuously decreases with increased annealing temperature indicating a gradual transition from fcc to hcp GST.\textsuperscript{14} Samples annealed above 160 °C have little amorphous phase present and are assumed to be a binary mixture of fcc and hcp GST. Samples annealed below 160 °C have significant amorphous phase and are assumed to be a binary mixture of amorphous and fcc GST. The application of EMT is further described below.

Figure 5.4(b) shows the calculated crystal fraction for amorphous, fcc, and hcp GST for each sample. The crystal fraction of amorphous, fcc, and hcp GST are given by $x_{amr}$, $x_{fcc}$, and
The majority of samples are dominated by fcc GST; except the two samples annealed at 250 °C have a significant fraction of hcp GST. We are unable to explain the observed trends in the calculated crystal fraction with GST thickness. Previous work has shown the amorphous to fcc phase transition temperature does not significantly change with film thickness and the fcc to hcp transition temperature decreases with decreasing film thickness. Therefore, we expect similar $x_f$ for samples annealed at 150 °C and higher $x_{hcp}$ for the thinner samples annealed at higher temperatures, contrary to our observations. Interfaces dominate the growth kinetics of thin film GST, and further work is required to understand the growth of thin GST films on SiO$_2$.

**5.6 – Finite Element Analysis Model**

Two and three dimensional (2D and 3D) frequency domain thermoelectric-mechanical finite element analysis (FEA) models were developed to predict GST device behavior. Fitting the 2D model to SJEM measurements predicted device properties, temperature rise $\Delta T$, and surface thermo-mechanical expansion $\Delta h$. The 3D FEA model was used to explain heterogeneous device heating. The derivation of FEA models for similar devices has been previously described.

We developed 2D and 3D FEA models with modified electrode properties, large thermal interface conductances, and accounting for non-uniform channel power dissipation. The model is similar to a previous FEA model. We set the electrode resistivity to zero for the model. Therefore, the predicted resistance of the FEA model was equal to the predicted device resistance as the model did not predict the additional electrode resistance. The density, heat capacity, coefficient of thermo-mechanical expansion, Poisson’s ratio, and elastic modulus of the Au/TiW electrodes were 1,900 kg m$^{-3}$, 129 J kg$^{-1}$ K$^{-1}$, 12×10$^{-6}$ K$^{-1}$, 0.42, and 80 GPa. The measured resistivity of our Au/TiW contacts was used with the Wiedemann-Franz law to calculate the thermal conductivity of our electrodes to be 60 W m$^{-1}$ K$^{-1}$. The thermal interface
conductance of all interfaces was set to $10^{10}$ W m$^{-2}$ K$^{-1}$ which improved the agreement between measurements and predictions. The predicted device surface expansion of the 2D FEA model was adjusted by ±10 % to account for changes in power dissipation across the 245 μm wide channel due to variations in channel length and phase distribution.

Figure 5.5: Schematic of two dimensional (2D) model geometry with boundary conditions. The frequency domain zero and first harmonic device bias are given by $V_{DS,0\omega}$ and $V_{DS,1\omega}$, where $V_{DS,1\omega}$ is a complex number. The frequency domain zero, first, and second harmonic temperature rise are given by $T_{0\omega}$, $T_{1\omega}$, and $T_{2\omega}$, where $T_{1\omega}$ and $T_{2\omega}$ are complex numbers.

Figure 5.5 shows a schematic of the 2D FEA model. The model geometry was similar to experiments with 60-200 nm of PMMA, 40-70 nm of Au/TiW, 11-22 nm GST, 300 nm SiO$_2$, and 200 μm Si, from top to bottom. The model is 400 μm wide. The large domain was chosen to be larger than the Si thermal diffusion length for the bias frequency $\omega = 43$ kHz. The device is biased at the contacts and has a heat sink at the bottom. The top surfaces are not mechanically constrained. All other surfaces are electrically and thermally insulated, and mechanically constrained.

A 3D FEA model was developed to predict the behavior of mixed fcc and hcp GST devices. The 3D model accounts for heat spreading into the substrate and the heterogeneous lateral fcc and hcp GST distribution. The model is similar to the 2D model except the Si domain
is 100 μm long in the $x$ and $z$ directions, and the model is 10 μm wide in the $y$ direction. Figure 5.1(b) shows the axes orientations. The small model width does not significantly affect the predicted $\Delta T$ and $\Delta h$ as the majority of heat transfer occurs in the $x$ and $z$ directions. The model has the same constraints as the 2D model. The faces normal to the $y$ direction are electrically and thermally insulated and free to move in the $z$ direction.

The applied voltage amplitude $V$ and device voltage amplitude $V_{DS}$ are related by $V_{DS} = (V \times R_{DS})/R$. The measured resistance is given by $R = R_{Series} + R_{DS}$, where $R_{DS}$ is the device resistance and $R_{Series}$ is the parasitic series resistance. Devices used for TLM measurements were also used for SJEM measurements, and the TLM measured $R_{DS}$ was used to calculate $V_{DS}$ for fitting FEA predictions to SJEM measurements. We subtracted a small (~5-10 Ω) parasitic resistance, due to the probes and contact pads, from the TLM measured resistance to obtain $R_{DS}$. The parasitic resistance was measured by contacting probes across the same contact pad. A home-built atomic force microscopy (AFM) probe station electrically contacted devices for SJEM measurements. The AFM probe station made poor contact with devices due to the PMMA coating and scratching of the soft contacts. The AFM probe station had ~10-30 Ω of parasitic series resistance. The $R_{DS}$ predicted from FEA fitting of SJEM measurements was in good agreement with TLM measurements for all devices.

5.7 – Independent Joule and Thermoelectric Measurements

A two dimensional (2D) FEA model of the devices was used to predict the peak-to-peak thermo-mechanical surface expansion $\Delta h$ and corresponding GST temperature rise $\Delta T$, used to interpret the SJEM measurements. A 2D model is appropriate for our devices, since $W \gg L$. The model simulates Joule and thermoelectric effects in the GST devices and the corresponding
device thermo-mechanical expansions. To simulate SJEM measurements, the heat diffusion and Poisson equations were modified to account for thermoelectric transport\textsuperscript{29,30} and were coupled with a thermo-mechanical model. The Fourier transform of the equations yielded the frequency response of the predicted $\Delta h$ and $\Delta T$.\textsuperscript{12}

Figure 5.6: Diagram of independent SJEM observations of Joule and Peltier effects. (a) Schematic of device with two electrodes on a positive thermopower ($S > 0$) channel, similar to the lateral GST devices. The left and right electrodes are biased at $V_{DS}$ and ground (GND) and have $S = 0$. (b) Time domain diagram of $V_{DS}(t)$ and the device temperature rise $T$. Top image shows $V_{DS}$ in time $t$ for a bipolar waveform, and the bottom image shows $T$ in red solid and blue dashed lines corresponding to $V_{DS}$ for the red circle and blue triangle in the top image. (c) The resultant frequency domain first and second harmonic temperature rise $\Delta T_{1\omega}$ and $\Delta T_{2\omega}$ in dashed and solid black lines. Joule and Peltier effects are proportional to $\Delta T_{2\omega}$ and $\Delta T_{1\omega}$. The vertical dashed black lines indicate the channel edges.

Figure 5.6 shows a modified version of the SJEM technique used for independent observations of Joule and Peltier effects in the lateral GST devices. Figure 5.6(a) shows a
schematic of a device similar to the lateral GST devices. For the device in Fig. 5.6(a), hole flow into (from) the contacts locally heats (cools) the device.\textsuperscript{12,22,31} The schematic shows both time and frequency domain diagrams of the technique. We distinguish the time dependent device bias $V_{DS}(t)$ from the frequency domain zero and first harmonic device bias by $V_{DS,0\omega}$ and $V_{DS,1\omega}$, where $V_{DS,1\omega}$ is a complex number. We distinguish the time dependent temperature rise $T$ from the zero, first, and second harmonic temperature rise by $T_{0\omega}$, $T_{1\omega}$, and $T_{2\omega}$, where $T_{1\omega}$ and $T_{2\omega}$ are complex numbers. The first and second harmonic peak-to-peak temperature rise are given by $\Delta T_{1\omega} = 2|T_{1\omega}|$ and $\Delta T_{2\omega} = 2|T_{2\omega}|$. For SJEM measurements the peak-to-peak device temperature rise $\Delta T$ is proportional to the measured peak-to-peak sample surface thermo-mechanical expansion $\Delta h$.

Figures 5.6(b) and (c) show a diagram of the temperature rise of the device in Figure 5.6(a) due to Joule and Peltier effects. Figure 5.6(b) shows the temperature distribution for a bipolar waveform, defined as $V_{DS}(t) = V_{DS,1\omega}\sin(\omega t)$ where time is given by $t$. Joule heating is evident as the large temperature rise across the device and is independent of the carrier flow direction. The Peltier effect is evident at the contacts as the small change in $T$ with carrier flow direction.\textsuperscript{12,22} Joule heating is proportional to $V_{DS}^2$ and Peltier effects are proportional to $V_{DS}$. Joule heating occurs at the zero and second harmonic $2\omega$, and Peltier effects occur at the first harmonic $1\omega$ for a device subject to a bipolar waveform. Therefore, $\Delta T_{2\omega}$ is due to Joule heating, and $\Delta T_{1\omega}$ is due to Peltier effects. Figure 5.6(c) shows the frequency domain $\Delta T_{1\omega}$ and $\Delta T_{2\omega}$ from Fig. 5.6(b). Joule heating is evident in Fig. 5.6(c) as the large $\Delta T_{2\omega}$ across the channel. Peltier effects are evident as the small $\Delta T_{1\omega}$ at the contacts. We conclude that independent measurements of Joule and Peltier effects are possible using SJEM, by biasing a thermoelectric device with a bipolar waveform and observing $\Delta T_{2\omega}$ and $\Delta T_{1\omega}$. We note $T_{1\omega}$ experiences a $180^\circ$
phase shift between the contacts as Peltier heating or cooling of the contacts depends on the bias polarity, or carrier flow direction.\textsuperscript{12,22}

**5.8 – Uniform GST Properties**

Figure 5.7 shows the measured and predicted $\Delta h$ for 2.2 $\mu$m channel length and 22 nm thin GST device annealed at 200 °C. The device is biased with amplitude $V_{DS} = 0.9$, 1.2, and 1.5 V. The measured $\Delta h$ was uniform in the $y$-direction indicating uniform lateral heating, electric field, and resistivity distribution. Comparison of measurements and predictions of the temperature distribution in the device yields the GST properties.\textsuperscript{12} Measurements are an average of 18 line scans with deviation smaller than the markers.

Figure 5.7 shows $\Delta h$ measurements and predictions of Joule heating, current crowding, and Peltier effects. Figure 5.7(a) shows the measured and predicted $\Delta h_{2\omega}$, due to Joule heating. Joule heating occurs in the GST channel and at the GST-TiW contacts due to finite $\rho_{GST}$ and $\rho_C$.\textsuperscript{12,22} Fitting the measured and predicted $\Delta h_{2\omega}$ predicts $\rho_{GST} = 4.8 \pm 0.3 \times 10^{-5}$ $\Omega$ m and $\rho_C = 1.1 \pm 0.3 \times 10^{-11}$ $\Omega$ m$^2$ for the 2.2 $\mu$m channel length and 22 nm thin GST device annealed at 200 °C, similar to TLM measurements. Figure 5.7(b) shows the predicted $\Delta T_{2\omega}$ from Fig. 5.7(a). The predicted $\Delta T_{2\omega}$ is larger than our previous measurements for thin GST films.\textsuperscript{12} Figure 5.7(c) shows the measured and predicted $\Delta h_{1\omega}$, due to Peltier effects. Peltier heating and cooling occurs at the GST-TiW contact due to their difference in thermopower.\textsuperscript{12,22,31} Fitting the measured and predicted $\Delta h_{1\omega}$ yields $S_{GST} = 110 \pm 10$ $\mu$V K$^{-1}$ for the device with a calculated composition of 69 $\pm$ 1 % fcc and 31 $\pm$ 1 % hcp GST. Fitting measurements and predictions for $\rho_{GST}$, $\rho_C$, and $S_{GST}$ yields a coefficient of determination $R^2 = 0.68$ between FEA predictions and SJEM measurements. The fitting error was determined by fitting each measured line scan to FEA.
predictions. A small spike in $\Delta h_{1\omega}$ is observed at $x = 0 \ \mu m$, due to the presence of a small grain of hcp GST in the predominately fcc GST sample. The difference in $S_{GST}$ between fcc and hcp GST causes local Peltier effects in the channel, explored further below, and was not included in 2D FEA simulations. Figure 5.7(d) shows the predicted $\Delta T_{1\omega}$ from Fig. 5.7(c). At the contact, Peltier heating and cooling cause a 1.6 and 3 K change in temperature, $\Delta T_{1\omega}$, compared to the Joule heating induced temperature rise, $\Delta T_{2\omega}$, of 7 and 18 K for $V_{DS} = 0.9$ and 1.5 V. Peltier effects were ~23 and ~17 % of the contact temperature change for $V_{DS} = 0.9$ and 1.5 V.

**Figure 5.7**: Measured and predicted $\Delta h$ and $\Delta T$ for a 2.2 $\mu m$ channel length and 22 nm thin GST device annealed at 200 °C for $V_{DS} = 0.9$, 1.2, and 1.5 V. (a) Measured and predicted second harmonic surface expansions $\Delta h_{2\omega}$ due to Joule heating. Black circles and solid black lines show measurements and predictions. (b) Predicted $\Delta T_{2\omega}$ from fitting measurements and predictions in (a). The model predicts $\rho_{GST} = 4.8 \pm 0.3 \times 10^{-5}$ $\Omega$ m and $\rho_{C} = 1.1 \pm 0.3 \times 10^{-11}$ $\Omega$ m$^2$. (c) Measured and predicted first harmonic surface expansions $\Delta h_{1\omega}$ due to Peltier effects. Black circles and solid black lines show measurements and predictions. (d) Predicted $\Delta T_{1\omega}$ from fitting measurements and predictions in (a). The model predicts $S_{GST} = 110 \pm 10$ $\mu V$ K$^{-1}$.
5.9 – Measured Heterogeneous Joule and Thermoelectric Effects

Figure 5.8 shows the measured heterogeneous $\Delta h$ for three 11 nm thin GST devices with channel lengths 2.5, 3.2, and 2.5 μm annealed at 150, 200, and 250 °C. Figures 5.8(a-c) show the measured $\Delta h_{2\omega,\text{Norm}}$ which is the measured $\Delta h_{2\omega}$ normalized by the average channel $\Delta h_{2\omega}$. The measured $\Delta h_{2\omega,\text{Norm}}$ is an indicator of local GST Joule heating. Figures 5.8(d-f) show the measured $\Delta h_{1\omega,\text{Norm}}$ which is the measured $\Delta h_{1\omega}$ normalized by the average contact $\Delta h_{1\omega}$. Figures 5.8(g-i) show the measured $\Delta h_{1\omega}$ phase $\Theta_{1\omega}$. The measured $\Delta h_{1\omega,\text{Norm}}$ and $\Theta_{1\omega}$ are indicators of local GST Peltier effects.

**Figure 5.8:** Measured $\Delta h$ for 11 nm thin GST devices. The devices had channel lengths of 2.5, 3.2, and 2.5 μm and were annealed at temperatures $T_A = 150$, 200, and 250 °C. (a-c) Measured $\Delta h_{2\omega,\text{Norm}}$ which is the measured $\Delta h_{2\omega}$ normalized by the average channel $\Delta h_{2\omega}$, due to Joule heating. (d-f) Measured $\Delta h_{1\omega,\text{Norm}}$ which is the measured $\Delta h_{1\omega}$ normalized by the average contact $\Delta h_{1\omega}$, due to Peltier effects. (g-i) Measured $\Delta h_{1\omega}$ phase $\Theta_{1\omega}$. A 180 ° shift in $\Theta_{1\omega}$ distinguishes regions which experience Peltier heating from regions which experience Peltier cooling, depending on bias polarity. Scale bar is shown in (a) and dashed black lines indicate the edges of the channel.
Figures 5.8(a-c) show the measured $\Delta h_{2\omega,\text{Norm}}$ for the three devices. The measured $\Delta h_{2\omega,\text{Norm}}$ is proportional to $\Delta T_{2\omega}$ and an indicator of local GST Joule heating. Figures 5.8(a-c) show increasing heterogeneity of $\Delta h_{2\omega,\text{Norm}}$ with increasing annealing temperature. We attribute the heterogeneous lateral Joule heating of our devices to the presence of large grains (>100 nm) of hcp GST in a matrix of fcc GST. The presence of hcp grains in a matrix of fcc GST would create a heterogeneous lateral structure and resistivity distribution causing heterogeneous lateral Joule heating. We note the calculated crystalline fraction of hcp GST increases with increasing annealing temperature. The device in Fig. 5.8(a) has a low hcp phase crystal fraction and experiences uniform Joule heating, and the device in Fig. 5.8(c) is composed of 48 ± 6 % hcp GST and experiences large heterogeneous lateral Joule heating. The measured $\Delta h_{2\omega,\text{Norm}}$ deviates ~45 % across the channel in Fig. 5.8(c), or the Joule heating induced temperature rise varies ±45 % across the channel. We further describe heterogeneous lateral Joule heating, including a similar but smaller trend for the 22 nm thin GST samples, below.

Figures 5.8(d-f) show the measured $\Delta h_{1\omega,\text{Norm}}$ for the three devices. The measured $\Delta h_{1\omega,\text{Norm}}$ is proportional to $\Delta T_{1\omega}$ and indicates local Peltier effects due to lateral changes in material thermopower. Figure 5.8(d) shows $\Delta h_{1\omega,\text{Norm}}$ for a device with low hcp phase crystal fraction experiences uniform Peltier effects at the contacts and no Peltier effects in the channel indicating the device has laterally uniform thermopower. Figures 5.8(e) and (f) show $\Delta h_{1\omega,\text{Norm}}$ for two devices with significant hcp GST crystal fraction and show significant $\Delta h_{1\omega,\text{Norm}}$ measured in the channel. The presence of both fcc and hcp GST in the channel causes local Peltier heating and cooling due to the large difference in fcc and hcp GST thermopower (150-300 $\mu$V K$^{-1}$). Large spikes are evident in $\Delta h_{1\omega,\text{Norm}}$ for these two devices in the channel and at the contacts. The heterogeneous resistivity distribution forms preferential current pathways,
locally increasing the current density and locally enhancing thermoelectric effects. However, the average $\Delta h_{1\omega}$ is the largest in Fig. 5.8(d) due to the large difference in amorphous-fcc GST and TiW thermopower (200-400 $\mu$V K$^{-1}$). Figure 5.8(e) shows the measurement resolves $\sim$100 nm structure in $\Delta h_{1\omega}$, confirming the measurement spatial resolution.

Figures 5.8(g-i) show the measured $\Theta_{1\omega}$ for the three devices. SJEM measures the amplitude $\Delta h_{1\omega}$ and phase $\Theta_{1\omega}$ of the surface thermo-mechanical expansion at $1\omega$ due to Peltier effects. The measured $\Delta h_{1\omega}$ indicates the local magnitude of Peltier heating and cooling. The measured $\Theta_{1\omega}$ indicates if the sample experiences local Peltier heating or cooling with bias polarity. A 180 ° shift in $\Theta_{1\omega}$ is observed between Peltier heated and cooled locations. Figure 5.8(d) shows measurable $\Delta h_{1\omega}$ at the contacts indicating Peltier effects at the contacts. Figure 5.8(g) shows a 180 ° shift in $\Theta_{1\omega}$ between the contacts indicating one contact experiences Peltier heating while the other contact experiences Peltier cooling. Therefore, Peltier heating and cooling can be discerned by combination of measureable $\Delta h_{1\omega}$ and 180 ° shifts in $\Theta_{1\omega}$. The devices in Figs. 5.8(h) and (i) show similar behavior to Fig. 5.8(g), but additional peaks in $\Delta h_{1\omega}$ and 180 ° shifts in $\Theta_{1\omega}$ are observed in the channel corresponding to intra-GST Peltier heating and cooling, due to the presence of fcc and hcp GST.

We hypothesize why uniform lateral heating is observed in amorphous-fcc GST devices and heterogeneous lateral heating is observed in fcc-hcp GST devices. We attribute the difference in heating due to the different growth mechanisms of fcc and hcp GST which develop different thin film GST structure. Previous work has shown fcc GST grows from amorphous GST as small grains ($< 10$ nm) or 20-30 nm diameter columns at a GST-SiO$_2$ surface. Previous work has also shown fcc GST grows as a uniform lateral plane from amorphous GST at a free GST surface. Our samples have both a GST-SiO$_2$ and free GST surface. The growth of a
uniform lateral plane of fcc GST would result in uniform heating for amorphous-fcc samples. The growth of small sub-50 nm grains of fcc GST in a matrix of amorphous GST would also result in uniform sample heating as the many small grains are below our measurement resolution. Previous work has shown fcc GST gradually transforms into hcp GST with increasing annealing temperature.\textsuperscript{14} We observe heterogeneous lateral heating of our fcc-hcp GST devices indicating the hcp grain size increases to a size greater than our measurement spatial resolution. The observation of Peltier heating and cooling in the GST channel indicates intra-GST Peltier effects due to the presence of the two different phases with different thermopowers. We conclude the uniform lateral heating of amorphous-fcc GST devices is due to the planar or small grain size growth of fcc GST, and the heterogeneous lateral heating of fcc-hcp GST devices is due to the gradual growth of large hcp grains from fcc GST.

Figure 5.9 shows the normalized deviation of the measured channel second harmonic expansion $\sigma(\Delta h_{2\omega})$ for all devices. We calculate $\sigma(\Delta h_{2\omega})$ by normalizing the measured deviation of $\Delta h_{2\omega}$ across the channel with the average channel $\Delta h_{2\omega}$. The normalized deviation is a relative measure of lateral heterogeneous device Joule heating. Figure 5.9 shows $\sigma(\Delta h_{2\omega})$ increases with increasing annealing temperature. The increase in lateral heterogeneous heating with increased annealing temperature is due to increasing hcp GST crystal fraction. Figure 5.9 also shows $\sigma(\Delta h_{2\omega})$ increases with decreasing GST thickness. The increase in lateral GST heterogeneous heating with decreasing GST thickness is not well understood, and further work investigating the growth and structure of thin GST films is required to explain the trend.\textsuperscript{7,26,27} We also observe the measured $\sigma(\Delta h_{2\omega})$ typically increases with decreasing channel length for devices with significant hcp GST crystal fraction. Decreasing channel lengths can approach the hcp grain size and creates
highly preferential current pathways, or shorts, across the device through the hcp grains. We measured similar channel length devices on each sample.

![Figure 5.9](image)

**Figure 5.9:** Normalized deviation of $\Delta h_{2\omega}$ across the device channel $\sigma(\Delta h_{2\omega})$; calculated by dividing the deviation of $\Delta h_{2\omega}$ across the channel with the average channel $\Delta h_{2\omega}$. The measured $\sigma(\Delta h_{2\omega})$ indicates the amount of heterogeneous device Joule heating. The dashed red line with triangles and solid blue line with circle markers show $t_{GST} = 11$ and $22$ nm. Error bars show measurement deviation, with some error bars smaller than the markers.

### 5.10 – Predicted Heterogeneous Joule and Thermoelectric Effects

Figure 5.10 shows the measured and predicted surface thermo-mechanical expansion for two 22 nm thick GST devices. The measured device has a 7.5 μm channel length and was annealed at 250 °C. The simulated device has a channel length of 8 μm. We do not expect a match between measurements and predictions as the phase distribution of the measured device is unknown. The development of the three dimensional (3D) FEA model was previously described in Section 5.6.

Figure 5.10(a) shows the simulated phase distribution of the GST channel. Cylinders of 400 nm diameter and thickness equal to $t_{GST}$ of hcp GST were randomly placed in a matrix of fcc GST. Additional hcp GST was added at certain locations to reduce meshing and computation
intensity. The measured and simulated devices are composed of 70 ± 3 % and 67 % hcp GST. The simulated fcc and hcp GST properties were $\rho_{GST} = 2\times10^{-4}$ and $3.3\times10^{-5}$ and $S_{GST} = 200$ and 15 $\mu$V K$^{-1}$.

Figure 5.10: Measurements (b, d, and f) and predictions (c, e, and g) of $\Delta h$ for a 22 nm thin GST device. The measured device has a 7.5 $\mu$m channel length and was annealed at 250 °C. The simulated device has an 8 $\mu$m channel length. We do not expect a match between measurements and predictions as the measurement phase distribution is unknown. (a) Schematic of model phase distribution with fcc and hcp GST shown in gray and red. (b,c) Measured and predicted heterogeneous $\Delta h_{2w}$ due to Joule heating of preferential current pathways through mixed fcc and hcp GST. (d,e) Measured and predicted $\Delta h_{1w}$ due to local Peltier effects between fcc and hcp GST and at the GST-TiW contact. (f,g) Measured and predicted $\Theta_{1w}$. The 180 ° shifts in $\Theta_{1w}$ is consistent with Peltier heating and cooling, depending on bias polarity. The dotted vertical black lines indicate the channel edge, and the scale bar is shown in (a).
Figures 5.10(b-g) show the measured and predicted heterogeneous $\Delta h$ for the two devices. Figures 5.10(b) and (c) show measured and simulated heterogeneous $\Delta h_{2\omega}$, indicating non-uniform lateral Joule heating and resistivity distribution. The heterogeneous lateral resistivity distribution is due to the presence of large and randomly mixed fcc and hcp GST grains in the device. Figures 5.10(d-g) show measured and simulated spikes in $\Delta h_{1\omega}$ and 180° shifts in $\theta_{1\omega}$ indicating local Peltier effects. The Peltier effects observed at the GST-TiW contact is due to the difference in thermopower between the GST and TiW. The Peltier effects observed in the GST channel is due to the difference in thermopower between fcc and hcp GST. The simulation only considers Joule and Peltier effects in a lateral GST device due to a random mixture of large hcp and fcc GST grains, and the simulation predicts the measured heterogeneous heating behavior well. Therefore, we attribute the measured heterogeneous Joule and Peltier effects in our devices to the presence of large fcc and hcp GST grains in the thin films.

We estimate the hcp GST grain size from Figures 5.10(a), (d), and (e). The same method is used to calculate the average hcp GST grain length $l_{hcp}$ from Figs. 5.10(d) and (e). The accuracy of the method is verified by comparing the calculated $l_{hcp}$ from Fig. 5.10(e) to the calculated $l_{hcp}$ from the phase distribution shown in Fig. 5.10(a) for the simulation. We calculate $l_{hcp} = 0.8 \mu m$ for the simulation from Fig. 5.10(a) by dividing the volume of hcp GST by the number of hcp grains and assuming the hcp GST is composed of uniform diameter cylinders with thickness equal to $t_{GST}$. We summarize the calculation of $l_{hcp}$ using Figs. 5.10(d) and (e) below, and the following paragraph fully describes the calculation. Figures 5.10(d) and (e) are used to calculate $l_{hcp}$ by estimating the average distance between $\Delta h_{1\omega}$ peaks, corresponding to changes in GST phase. We calculate $l_{hcp} = 1.1 \mu m$ for the device shown in Fig. 5.10(e), close to the $l_{hcp} = 0.8 \mu m$ from Fig. 5.10(a). We expect our method of calculating $l_{hcp}$ from peaks in $\Delta h_{1\omega}$
to overestimate \( l_{hcp} \) as not every fcc-hcp interface experiences significant Peltier effects. Therefore, the distance between \( \Delta h_{1\omega} \) peaks will be larger than the average grain sizes. We calculate \( l_{hcp} = 0.7 \, \mu m \) for the device shown in Fig. 5.10(c) which is a 22 nm thick GST sample annealed at 250 °C.

The hcp GST grain size is estimated from the measured and predicted Peltier effects shown in Figures 5.10(d) and (e). The data of Figs. 5.10(d) and (e) were mapped to a rectangular grid of points with 50 nm spacing between points. We removed all points with values less than 1.5 times the average \( \Delta h_{1\omega} \). We then performed the following calculation at each point. For a given point, we calculated the distance to the nearest data point in 10 ° increments. We discarded distance measurements between adjacent points indicating they were from the same \( \Delta h_{1\omega} \) peak. Figures 5.10(d) and (e) show many of the \( \Delta h_{1\omega} \) peaks are >100 nm wide and would compose many adjacent points of our grid. All the calculated distances for all the points were averaged together to find the mean distance between \( \Delta h_{1\omega} \) peaks. The mean distance between \( \Delta h_{1\omega} \) peaks is the average distance between fcc and hcp phases. The average fcc and hcp grain sizes determine the average distance between fcc and hcp phases, and the relative size of fcc and hcp grains can be estimated from the fcc and hcp crystal fractions. We estimated the average hcp grain size \( l_{hcp} \) by multiplying the calculated average distance between fcc and hcp phases by \( 2 \times \lambda_{hcp} \). We expect to overestimate \( l_{hcp} \) using this method as discussed above.

5.11 – Effective Thin Film GST Properties

Figure 5.11 shows the measured and predicted \( \Delta h \) for a 3.2 \( \mu m \) channel length and 11 nm thin GST device annealed at 200 °C. The measured \( \Delta h \) was heterogeneous in the \( y \)-direction due to the non-uniform fcc and hcp phase distribution, discussed above. Matching 2D FEA
predictions and SJEM measurements for laterally heterogeneously heated devices predicts the effective device properties at the measurement location. For the device in Fig. 5.11, FEA fitting of SJEM measurements predicts the effective GST properties. Measurements are an average of 18 line scans with deviations smaller than the markers.

Figure 5.11: Measured and predicted $\Delta h$ for the 3.2 μm channel length and 11 nm thin GST device annealed at 200 °C. (a) Measured and predicted $\Delta h_{2\omega}$ for $V_{DS} = 1.5$, 2.2, and 2.6 V. Black circles and solid black lines show measurements and predictions. The model predicts the effective channel $\rho_{GST} = 5.5 \pm 0.4 \times 10^{-5}$ Ω m and $\rho_{C} = 3.3 \pm 0.5 \times 10^{-10}$ Ω m², similar to TLM measurements. (b) Measured and predicted $\Delta h_{1\omega}$ at $V_{DS} = 2.6$ V. Black circles and solid black lines show measurements and predictions. The model predicts $S_{GST} = 72 \pm 10$ μV K⁻¹ for the device. Additional measured $\Delta h_{1\omega}$ peaks in the channel center are due to Peltier effects between fcc and hcp GST, which were not included in the 2D model. The measured $\Delta h$ was non-uniform in the $y$-direction, and the dotted vertical black lines indicate the channel edge.
Figure 5.11(a) shows the measured and predicted $\Delta h_{2\omega}$ for the device at $V_{DS} = 1.5$, 2.2, and 2.6 V. Fitting the measured and predicted $\Delta h_{2\omega}$ predicts $\rho_{GST} = 5.5 \pm 0.4 \times 10^{-5}$ $\Omega$ m and $\rho_{C} = 3.3 \pm 0.5 \times 10^{-10}$ $\Omega$ m$^2$, similar to TLM measurements. We discuss the discrepancy between the measured and predicted $\Delta h_{2\omega}$ at the contacts due to error in simulating the thick PMMA coating of this device below.

Figure 5.11(b) shows the measured and predicted $\Delta h_{1\omega}$ for the device at $V_{DS} = 2.6$ V. The other biases are not shown for clarity, although all bias conditions are used when fitting measurements and predictions. Fitting the measured and predicted $\Delta h_{1\omega}$ predicts $S_{GST} = 72 \pm 10 \mu$V K$^{-1}$ for the device with a calculated composition of 72 $\pm$ 1 % fcc and 28 $\pm$ 0.01 % hcp GST. Fitting measurements and predictions for $\rho_{GST}$, $\rho_{C}$, and $S_{GST}$ yields $R^2 = 0.65$. Figure 5.11(b) shows additional measured $\Delta h_{1\omega}$ peaks in the channel due to Peltier effects between fcc and hcp GST. The location of the $\Delta h_{1\omega}$ peaks correspond to measured changes in $\Delta h_{2\omega}$, or local Joule heating. The local change in Joule heating accompanied by Peltier effects indicates current is flowing between fcc and hcp GST with different resistivities and thermopowers. Heterogeneous heating of GST was not included in the 2D FEA model.

Thick layers of PMMA (>100 nm) caused a discrepancy between FEA predictions and SJEM measurements of $\Delta h$ at the contacts. The measured PMMA coating is 10-20 nm thinner at the contact edge and gradually increases over a ~1 $\mu$m distance to the measured thickness. Figure 5.5 shows the model assumes a flat and uniform PMMA profile at the contacts. Therefore, the model has a thicker PMMA coating at the contact edge and over predicts $\Delta h$ at the contact edge by ~10 %. The predicted GST-TiW contact resistivity from FEA fitting of SJEM measurements typically has >10 % error and is not significantly affected by the over prediction of $\Delta h$. However, the predicted GST thermopower from FEA fitting of SJEM measurements is over estimated by
~10% due to the over prediction of $\Delta h$ at the contacts. Therefore, we decrease $S_{GST}$ by 10% for thick PMMA devices.

We observe an increase in the measured $\Delta h$ heterogeneity as the GST thickness decreases. Figures 5.7 and 5.11 show the measured $\Delta h$ of two devices with similar channel lengths and annealing temperatures but different GST thickness. The thinner device in Fig. 5.11 experiences increased lateral heterogeneous heating. We observe an increase in lateral heterogeneous heating for all the 11 nm thin devices compared to similar 22 nm thin devices. Further study into the growth mechanisms of thin film GST\textsuperscript{7,26,27} is required to understand the GST structure which causes the increased lateral heterogeneous heating with decreasing GST thickness.

Figure 5.12(a) shows the predicted GST resistivity and GST-TiW contact resistivity from fitting FEA predictions to SJEM measurements of $\Delta h_{2\omega}$ for all the measured devices. A minimum of 3 devices were measured per sample. The predicted $\rho_{GST}$ in Fig. 5.12(a) is similar to the TLM measurements shown in Fig. 5.4(b). However, FEA fitting of SJEM measurements predicts lower $\rho_c$ values than TLM measurements. The contact resistance of the 11 nm thin GST devices annealed at 250 ºC and the 22 nm thin GST devices annealed at 200 and 250 ºC were near the TLM measurement resolution. Therefore, TLM measurements yielded inaccurate measurements of $\rho_c$ for these samples. However, we observed noticeable contact heating in our $\Delta h_{2\omega}$ measurements for similar devices, allowing the FEA model to predict $\rho_c$ for these devices. Figure 5.12(a) shows FEA fitting of SJEM measurements predicts lower $\rho_c$ values for these samples than TLM measurements. FEA fitting of SJEM measurements is unable to predict $\rho_c < 2\times10^{-11} \ \Omega \ \mu m^2$ as no significant contact heating was observed for these devices. Adjusting the device geometry can increase the $\rho_c$ resolution of TLM or FEA fitting of SJEM measurements.
Figure 5.12: Predicted GST resistivity $\rho_{\text{GST}}$, GST-TiW contact resistivity $\rho_C$, and GST thermopower $S_{\text{GST}}$ from FEA fitting of SJEM measurements. Dotted lines with triangle markers and solid lines with circle markers show 11 and 22 nm thin GST. (a) Red and blue lines show $\rho_{\text{GST}}$ and $\rho_C$. (b) Red and black lines show the predicted $S_{\text{GST}}$ from FEA fitting of SJEM measurements and $S_{\text{GST}}$ calculated from EMT. Error bars in (a) and (b) show the calculated standard of deviation with some deviations smaller than the markers.

Figure 5.12(b) shows the predicted GST thermopower from fitting FEA predictions to SJEM measurements of $\Delta h_{\text{M}}$ for all the measured devices. The GST thermopower continuously decreases with increasing annealing temperature as amorphous, fcc, and hcp GST have decreasing thermopowers. Effective media theory (EMT) was applied to calculate $S_{\text{GST}}$ from the calculated GST crystal fractions shown in Fig. 5.4(b), described below. We calculate slightly lower $S_{\text{GST}}$ when applying EMT than the predicted $S_{\text{GST}}$ from FEA fitting of SJEM measurements. A large discrepancy is observed between the two methods for the 11 nm thin GST sample annealed at 150 °C and is also discussed below. The agreement between EMT
calculations and FEA fitting of SJEM measurements indicates EMT can accurately describe the behavior of thin film GST, and the electrical and thermoelectric properties of 11-22 nm thin GST films behave like a uniform and random mixture of bulk GST phases.\textsuperscript{21,33}

5.12 – Effective Media Theory Thermopower Calculation

EMT was applied to calculate the thermopower\textsuperscript{7,33} of the samples. Equation 5.4 relates the thermal conductivity $k$ and thermopower $S$ of a binary mixture of A and B phases.

$$
\frac{k_E}{S_E} = \frac{1}{4} \left\{ (3x_A - 1) \frac{k_A}{S_A} + (3x_B - 1) \frac{k_B}{S_B} + \left[ (3x_A - 1) \frac{k_A}{S_A} + (3x_B - 1) \frac{k_B}{S_B} \right]^2 + 8 \frac{k_A}{S_A} \frac{k_B}{S_B} \right\}^{1/2}
$$

(5.4)

The subscripts denote the material phase, and the effective mixture thermal conductivity and thermopower are given by $k_E$ and $S_E$. The effective thermopower is calculated using Eq. 5.4, the calculated crystal fractions, and assuming the thermal conductivity and thermopower of amorphous, fcc, and hcp GST are $k_{amr} = 0.2$ W m\textsuperscript{-1} K\textsuperscript{-1} and $S_{amr} = 400$ μV K\textsuperscript{-1}, $k_{fcc} = 0.6$ W m\textsuperscript{-1} K\textsuperscript{-1} and $S_{fcc} = 200$ μV K\textsuperscript{-1}, and $k_{hcp} = 1.7$ W m\textsuperscript{-1} K\textsuperscript{-1} and $S_{hcp} = 15$ μV K\textsuperscript{-1}, similar to published values.\textsuperscript{7,13,14} Equation 5.3 was used to calculate the effective thermal conductivity for each sample.

Three factors may explain the discrepancy between the thermopower calculated applying EMT and the thermopower predicted by FEA fitting of SJEM measurements for the 11 nm thin GST sample annealed at 150 °C. (1) Amorphous GST thermopower is larger than the value used in our EMT calculations. Increasing the amorphous GST thermopower in our calculations would improve the fit between the EMT calculated and FEA predicted thermopower for the 11 nm thin GST sample annealed at 150 °C. However, increasing the amorphous GST thermopower in our calculations would also worsen the fit between the EMT calculated and FEA predicted
thermopower for the 22 nm thin GST sample annealed at 150 °C. (2) Amorphous GST thermopower increases as the GST thickness decreases to 11 nm. Therefore, only the EMT calculated thermopower of the 11 nm thin sample annealed at 150 °C would increase. However, the mean free path of carriers in amorphous GST is less than a few nanometers, and amorphous GST thermopower should be similar to bulk values for GST films thicker than 10 nm. Previous work has shown no dependence of amorphous GST thermopower with GST film thickness down to 25 nm. (3) Thermoelectric transport for the 11 nm thin GST sample annealed at 150 °C is dominated by amorphous GST. The FEA predicted GST thermopower for this sample is close to amorphous GST thermopower, indicating the amorphous phase may dominate thermoelectric effects in such thin GST films. However, we would also expect amorphous GST to dominate the measured GST resistivity for the same sample. Further work is required to explain the discrepancy between the thermopower calculated applying EMT and the thermopower predicted by FEA fitting of SJEM measurements for the 11 nm thin GST sample annealed at 150 °C.

5.13 – Conclusion

In conclusion, we measured the nanometer-scale temperature distribution and properties of lateral PCM devices with 11 and 22 nm thin GST, after annealing at 150, 200, and 250 °C. A modified SJEM technique enabled independent measurements of heterogeneous Joule and Peltier effects in thin GST films with sub-50 nm spatial and ~0.2 K temperature resolution. The GST resistivity, GST-TiW contact resistivity, and crystal fraction of each phase were estimated from TLM measurements and EMT calculations. We observe uniform heating for mixed amorphous and fcc GST and heterogeneous Joule and Peltier effects in mixed fcc and hcp GST thin films. A 3D FEA model predicts the observed heterogeneous Joule heating and Peltier effects...
effects between fcc and hcp GST and estimates the hcp grain size. Increasing the annealing temperature increases the hcp crystal fraction, increasing heterogeneous Joule and Peltier effects. Comparing SJEM measurements with a 2D FEA model predicts $\rho_{GST}$, $\rho_C$ and $S_{GST}$ of the sub-25 nm thin GST films. The estimated $S_{GST}$ matches well with calculations using EMT. The large measured thermopower of GST for the low annealing temperature ($T_A = 150 \, ^\circ C$) could reduce the energy consumption by >50 % in highly scaled PCM devices due to Peltier heating, compared to scenarios which only utilize Joule heating.\textsuperscript{9} However, higher annealing temperatures increase hcp GST crystalline fraction, which decreases GST thermopower and the predicted reduction in PCM energy consumption. Knowledge of nanometer-scale Joule, thermoelectric, and interface effects in GST devices should enable improvements in energy efficient designs of future PCM technology.
5.14 – References


30 J. Martin, in *the COMSOL Conference*, Hannover, Germany, 4-6 November, 2008, pp. 1-7.


CHAPTER 6
CONCLUSION

This dissertation develops and implements a nanometer-scale thermometry technique to investigate nanometer-scale thermal transport in graphene and phase change memory (PCM) based electronics. Although previous work has investigated heat generation in graphene and PCM devices, there has been little work which has investigated nanometer-scale heat generation in these materials. Measurements of nanometer-scale heat generation in graphene and PCM devices are important as grain structure, interfaces, and thermoelectric effects can dominate device performance at this small scale, and applications of both technologies require scaling to nanometer size. In this work, a nanometer-scale thermometry technique was used to measure the role of grain boundaries and wrinkles in heat generation of chemical vapor deposition (CVD) grown graphene devices. This dissertation also improved the capabilities of nanometer-scale thermometry by developing a technique for independent and direct observations of nanometer-scale Joule and thermoelectric effects. The technique was demonstrated by investigating nanometer-scale Joule and thermoelectric effects in PCM devices. The results presented here develop techniques for improved nanometer-scale thermometry and develop current knowledge of nanometer-scale thermal transport.

6.1 – Research Summary

Nanometer-scale thermometry of CVD graphene using scanning Joule expansion microscopy (SJEM) observed a small temperature rise at select graphene wrinkles and a large temperature rise at graphene grain boundaries (GBs). Comparing measurements with simulations predicted the GB resistivity and temperature rise. An analytic model was developed to predict
the power dissipation, voltage drop, and temperature rise of a GB as a function of GB resistivity. The model predicts a large temperature rise at the GB, but the GB may not significantly affect graphene electrical performance. Understanding Joule heating and the associated temperature rise at GBs can mitigate polycrystalline graphene device failure and is important for designing future graphene electronics.

A new thermometry technique enabled independent and direct observation of nanometer-scale Joule and Peltier effects. The difference in voltage dependence causes Joule and thermoelectric effects to decouple to different harmonics when a device is driven by a bipolar bias. A finite element analysis (FEA) model using frequency domain thermoelectric equations was developed to explain the decoupling of Joule and thermoelectric effects. The technique was demonstrated on PCM devices using scanning Joule expansion microscopy (SJEM), which showed the several advantages of the new technique. Comparing measurements and predictions for the new technique enabled precise thermopower measurements over a large range of PCM device thermopowers. The development of this technique will enable new studies of Joule and thermoelectric heat generation in electronics, vital to the design of efficient electronic devices.

Nanometer-scale thermometry of face-center cubic (fcc) phase GST using SJEM revealed Joule, Peltier, and current crowding effects. The sheet and contact resistance of GST and GST-TiW were measured by transfer length method (TLM) measurements and also confirmed by fitting FEA predictions against SJEM measurements. Joule heating dominated power dissipation in the GST channel, while power dissipation at the GST-TiW contacts was a combination of Peltier and current crowding effects. Comparing modeling predictions and measurements predicted the thermopower for fcc phase GST. The large measured thermopower of fcc GST could reduce the energy consumption of highly scaled PCM devices due to Peltier heating.
Further study of nanometer-scale GST heating investigated the properties of mixed phases in GST thin films. A modified SJEM technique enabled independent and direct measurements of heterogeneous Joule and Peltier effects in GST. The GST resistivity, GST-TiW contact resistivity, and crystal fraction of each phase were estimated from TLM measurements and calculations using effective media theory (EMT). We observed uniform heating for mixed amorphous-fcc phase GST and heterogeneous Joule and Peltier effects in mixed fcc and hexagonal close-packed (hcp) phase GST thin films. The heterogeneous heating increased with hcp crystalline fraction. A FEA model predicted the heterogeneous Joule and Peltier effects between fcc and hcp phases and was used to estimate the hcp grain size. Comparing SJEM measurements with a FEA model predicted the GST resistivity, GST-TiW contact resistivity, and GST thermopower of the mixed phase GST thin films. The predicted GST thermopower matches calculations using EMT. Understanding nanometer-scale Joule and thermoelectric effects in GST devices will enable energy efficient design of future PCM technology. Furthermore, nanometer-scale thermometry measurements can reveal Joule and thermoelectric heating due to defects, interfaces, and grain structure of electronic materials, important for developing future electronics and increasing current knowledge of nanometer-scale thermal transport.

6.2 – Future Research Directions

The work described in this dissertation enables future research into nanometer-scale thermometry and thermal transport of new electronic devices. Nanometer-scale thermometry can be improved by increasing SJEM lateral resolution and measurement throughput. New electronic devices utilizing carbon nanotube networks (CNNs) and 2D transition metal dichalcogenides (TMDCs) can enable new electronic applications. However, little is known of nanometer-scale
thermal transport in CNNs and 2D TMDCs. Optimal future work will utilize new nanometer-scale thermometry techniques to investigate and characterize new phenomenon in electronic devices.

Initial studies using SJEM predicted the lateral resolution of SJEM was limited by the atomic force microscopy (AFM) cantilever tip radius. State-of-the-art AFM cantilevers have ~1 nm tip radius, but current SJEM lateral resolution is still limited to 10-50 nm by heat diffusion in the sample. Decreasing lateral heat diffusion in the sample would increase SJEM lateral resolution. Heat diffusion decreases with decreasing material thermal diffusivity and increasing heating frequency. However, decreasing heat diffusion also decreases the total thermo-mechanical expansion of the sample and therefore the SJEM signal. The SJEM signal can also decrease due to the material’s thermo-mechanical expansion dynamics at high frequencies. However, the SJEM signal can be increased by coupling SJEM measurements with the AFM cantilever resonance. The ideal substrate for SJEM measurements would encapsulate the device in a material with low thermal diffusivity and high a coefficient of thermal expansion (CTE). The low thermal diffusivity would limit lateral heat diffusion and increase SJEM resolution. The large CTE would increase sample thermo-mechanical expansion and increase SJEM signal. Future SJEM work could also utilize thermally anisotropic materials, with relatively large vertical and low lateral thermal diffusivity. The low lateral thermal diffusivity would limit lateral heat diffusion and increase SJEM lateral resolution. The high vertical thermal diffusivity would increase vertical heat flow and the vertical sample thermo-mechanical expansion, thus increasing the SJEM signal. Ultra-high resolution SJEM thermometry can be achieved by operating at high frequencies and by utilizing materials with low thermal diffusivities and high CTEs.
Nanometer-scale thermometry throughput can be improved by using multi-frequency SJEM measurements. The advantage of multi-frequency SJEM measurements is divided between linear and non-linear thermal transport. Temperature oscillations at different frequencies do not interact for devices described by linear thermal transport equations. Therefore, driving a device with biases at multiple frequencies causes independent temperature oscillations in the sample at each frequency. The SJEM technique can measure the resultant surface thermo-mechanical expansion due to all of the temperature oscillations, and a lock-in amplifier at each oscillation frequency can record the sample thermo-mechanical expansions at each frequency. Therefore, a single SJEM measurement can independently and simultaneously record the surface expansion for each bias frequency, and the measurement throughput can be increased by the number of bias frequencies. Choosing the correct frequencies enables multi-frequency SJEM to measure sample thermal diffusivity and Joule heating of complex device geometries in a single measurement with nanometer-scale resolution. Multi-frequency SJEM can simultaneously investigate Joule heating of a device with multiple current pathways, if each current pathway is biased at different frequencies. Devices described by non-linear thermal transport equations couple temperature oscillations at different frequencies. This dissertation examined the coupling of first and second harmonic temperature oscillations due to Joule and thermoelectric effects. Further investigation will show if multi-frequency SJEM can observe other non-linear thermal transport effects.

Scaling PCM to the sub-10 nm scale requires comprehension of the properties and structure of ultra-thin GST films. Little is known of the physical properties of sub-10 nm thin GST films, and recent work has shown GST films do not exhibit stable phase change below ~5 nm. The growth and structure of crystalline phases in ultra-thin GST is also not well known and is likely dominated by interfaces. The influence of GST grain size, boundary scattering,
and confinement on GST properties and heating is also not understood. Nanometer-scale thermometry of ultra-thin GST devices can improve current comprehension of ultra-thin GST electrical, thermal, and thermoelectric properties, and the measurements can reveal the nanometer-scale grain structure of ultra-thin GST films. Knowledge of ultra-thin GST film properties and structure is required to design energy efficient and highly-scaled PCM devices.

Carbon nanotube (CNT) networks (CNNs) are a promising new carbon nanomaterial for future flexible electronics, but the presence of CNT-CNT junctions can degrade CNN performance. Previous work has investigated the electrical resistance of individual CNT-CNT junctions, but thermal transport across CNT-CNT junctions is currently not well understood. Recent work has shown the CNT-CNT thermal boundary resistance is large and substantially increases the local CNT temperature. SJEM can measure CNT temperature with nanometer-scale lateral resolution, and individual CNT-CNT junctions can be isolated by fabricating CNT cross-bar structures. SJEM measurements of a CNT cross-bar device would observe the large and local temperature rise at the CNT-CNT junction due to the additional CNT-CNT thermal interface resistance at the junction. Comparison of measurements and simulations would predict the CNT-CNT thermal interface resistance. Knowledge of CNT-CNT thermal interface resistance would aid in the implementation of future CNN devices and improve fundamental comprehension of thermal transport.

Nanometer-scale thermal transport is not well understood in new 2D transition metal dichalcogenide (TMDC) based electronic devices. TMDCs have potential to enable new transistors, optoelectronics, and flexible electronics. Electrical transport between 2D TMDCs and metal contacts exhibit ohmic, rectifying, and tunneling behavior, and little is known of 2D TMDC thermopower which could dominate the nanometer-scale temperature rise at the contacts.
Recent work has measured an anomalously large thermopower for monolayer MoS$_2$\textsuperscript{16,16}. Nanometer-scale heat generation in the channel of 2D TMDC devices is also not well understood. Nanometer-scale thermometry has unique opportunities to improve current comprehension of thermal transport in 2D TMDCs and to study Joule, thermoelectric, rectifying, and tunneling effects in 2D materials. Knowledge of nanometer-scale heat generation and transport in 2D TMDCs, CNNs, graphene, and PCM will enable large contributions to the comprehension of nanometer-scale thermal transport in future electronics.
6.3 – References


