6. SCANNING THERMAL AND THERMOELECTRIC MICROSCOPY

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1. INTRODUCTION

Thermal and thermoelectric transport in nanometer scale devices and structures has become one of the foci of current efforts in nanotechnology, due to the increasing importance of nanoscale thermal and thermoelectric transport phenomena in many applications ranging from computing to energy conversion. One important example is heat dissipation in the metal-oxide field effect transistors (MOSFETs), which have been the driving force of the semiconductor industry for the past two decades. The gate length of the MOSFET has been continuously reduced in order to achieve higher switching speed and lower manufacturing cost. This critical length has been shrunk to 85–90 nm by year 2002 and will approach 20–22 nm in year 2013 [1]. The length scale is comparable to the scattering mean free paths of electrons and phonons. As a result, nanotransistors exhibit unique electron and phonon transport phenomena that have not been observed in micron-scale devices. For example, the effective thermal conductivity of the structure is drastically reduced due to increased phonon-boundary scattering. Additionally, as nanotransistors are miniaturized, the power density is increased. These two effects combine to cause localized self-heating and elevated operating temperatures that can reduce device speed and time to failure.

Besides nanotransistors, a variety of other nanoscale devices and structures are being actively developed for electronic, optoelectronic, thermoelectric, electromechanical, and sensing applications. Examples include nanoelectronic devices based on carbon nanotubes [2], nanolasers based on ZnO$_2$ nanowire arrays [3], thermoelectric coolers
based on superlattices [4] and nanowires [5], nanosensors based on carbon nanotubes [6], Si nanowires [7], and metal oxide nanobelts [8]. The characteristic size of these low dimensional structures is in the range of 1–100 nm. The short length scale gives rise to unique thermal transport properties that cannot be observed using conventional experimental methods developed for bulk materials.

Scanning probe microscopy (SPM) techniques have enabled the direct observation of physical phenomena with high spatial resolution. A variety of novel SPM-based measurement techniques have been developed to investigate electronic, optical, thermal, mechanical, chemical, and acoustic properties in the nanoscale. Two of such techniques are the Scanning Thermal Microscopy (SThM) and Scanning Thermoelectric Microscopy (SThEM). The SThM and SThEM can measure temperature, thermal properties, thermopower, electronic band structure, carrier/dopant concentration with nanoscale spatial resolution. The ability of thermally probing nanoscale phenomena has made the SThM and SThEM a powerful tool for studying fundamental thermophysics and for characterizing micro-nano scale devices and materials. These two techniques have demonstrated applications in materials, microelectronic, energy, and pharmaceutical research and development.

A variety of SThM and SThEM methods have been explored since the invention of the scanning tunneling microscope (STM) and the atomic force microscope (AFM). This chapter introduces various SThM and SThEM instruments, and the theory and applications of these two techniques.

2. INSTRUMENTATION OF SCANNING THERMAL AND THERMOELECTRIC MICROSCOPY

2.1. Instrumentation of Scanning Thermal Microscopy

In 1986, Williams and Wickramasinghe pioneered a so-called scanning thermal profiler technique employing a STM probe with a thermocouple fabricated at the probe tip [9], as illustrated in Fig. 1. A thermocouple sensor was produced at the end of a STM probe tip by the junction of two dissimilar inner and outer conductors. An insulator separated the two conductors in all areas remote from the tip. The size of the thermocouple junction could be made to have dimensions on the order of
100 nm. When a temperature difference exists between the thermocouple junction and the end of the lead wires, a voltage could be measured at the end of the lead wires with a minimum detectable tip temperature change less than 1 mK.

Although the main purpose of the scanning thermal profiler was not for mapping temperature distribution of a surface but for regulating the tip-sample distance, it stimulated intense efforts to develop a SPM technique for thermal microscopy. Because the STM requires the sample surface to be conducting, a SThM method developed in the configuration of a STM cannot be applied readily to a dielectric sample. In many applications such as mapping the temperature distribution of a microelectronic device, the sample surface is often covered by a dielectric film. Therefore, it is desirable to develop a general SThM method that can be applied to both conducting and non-conducting samples. In 1993, Majumdar et al. [10] introduced a wire thermocouple AFM probe, as depicted in Fig. 2. In an AFM, the tip-sample spacing is regulated by the force acting on the probe tip. As such, the AFM can map the topography of both conducting and non-conducting samples. While a thermocouple is fabricated on the probe, heat transfer between the tip and the sample changes the temperature of the probe tip during tip scanning. This allows for simultaneous mapping of topography and temperature.

The heart of the SThM is the thermal probe. A variety of thermal probes have been developed following the pioneering work of Williams and Wickramasinghe and that of Majumdar et al. A comment feature of these thermal probes is a thermal sensor fabricated at the end of an AFM or STM tip. The thermal sensor can be a thermocouple, a resistor thermometer, or a Schottky diode. A thermocouple measures the temperature difference between the junction of its two constituent metals and the other (remote) ends of the two metal wires. As such, there is no fundamental limitation to miniaturize the junction in order to achieve a better spatial resolution. On the other hand, a resistance thermometer can not be miniaturized readily, because the resistance of a nanoscale resistor can be too small for sensitive electronic detection. Similar problems exist for a temperature sensor based on a metal-semiconductor Schottky diode, as the I–V characteristics of a Schottky diode is affected not only by temperature change at
the metal-semiconductor junction, but also by that of the body of the semiconductor. As a consequence, the Schottky diode sensor measures an average temperature of the junction and the body, instead of the localized temperature at the junction.

Significant efforts have been devoted to fabricate thermal probes with a thermocouple junction at the end of an AFM probe. In some early works, high thermal conductivity materials were used to make the probe. It was realized later that the thermal probe needs to be made of low thermal conductivity materials in order to thermally isolate the thermocouple junction at the end of the AFM tip. Otherwise, the temperature rise at the junction can be very different from that of the sample because of significant heat loss to the AFM cantilever. Based on a one-dimensional heat transfer model, Shi et al. addressed this issue by using low-thermal conductivity silicon dioxide ($\text{SiO}_2$) and silicon nitride ($\text{SiN}_x$) as the tip and cantilever materials [11]. It was shown by their modeling results that compared to silicon or metal probes with a similar shape, this design can improve the thermal isolation of the sensor from ambient. In addition, the thermocouple was made of Pt-Cr, Cr-Ni, or Cr-Ir to achieve low thermal conductivity and large thermopower. Furthermore, they attempted to minimize the cantilever width, metal line width and thickness, and junction size, and increased the tip height, for increasing thermal resistance of the cantilever and thermally isolating the junction.

The fabrication process of these thermal probes consisted of only wafer-stage processing steps as shown in Fig. 3, with more than 300 probes fabricated on one single wafer. First, a 0.5–1 $\mu$m thick low pressure chemical vapor deposited (LPCVD) $\text{SiN}_x$ film was grown on both sides of 100 mm diameter double-side polished silicon wafers with (100) orientation, followed by the growth of a 8-$\mu$m-thick LPCVD silicon dioxide or low temperature oxide (LTO) film. The LTO film on the backside was stripped in 5:1 buffered hydrofluoric acid (5:1 BHF) (Fig. 3(a)). The LTO on the front side of the wafers was annealed at 1000$^\circ$C for one hour. The $\text{SiN}_x$ film on the backside of the wafer was then patterned for use as a mask in a subsequent bulk micro-machining step.

The probe tips were fabricated out of the 8-$\mu$m-thick LTO film by reactive-ion-etching (RIE) and wet etching. A chrome film was sputtered on the LTO, and patterned by photoresist into squares (Fig. 3(b)). Masked by the photoresist and chrome squares, the top 5 $\mu$m-thick LTO was etched in CF$_4$ and CHF$_3$ plasma. The photoresist plus chrome masks were undercut and the precursor of a sharp-angle tip shape was defined during this etching step. After the RIE etching, the remaining LTO film was etched in BHF 5:1 until the masks were just etched free (Fig. 3(c)). Before that, the 8 $\mu$m thick LTO film at the unprotected region was etched away. The RIE plus wet etching process could reproducibly yield oxide tips with a tip radius of about 20 nm and a half angle of 10°–20°.

After the oxide tips were fabricated, a 50–100 nm-thick Pt film (or Cr film) was sputter deposited and patterned on the front sides of the wafers (Fig. 3(d)). A 250–300 nm thick LTO was then deposited to cover the tip. Photoresist with appropriate viscosity was spun on the wafer. At a certain spinning speed, surface tension prevents a sharp tip from being covered by a spin-coated photoresist, leaving the very
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Figure 3. Fabrication process of thermally-designed thermocouple AFM probes. (a) Deposit SiN\textsubscript{x} and then SiO\textsubscript{2} by LPCVD, strip SiO\textsubscript{2} and pattern SiN\textsubscript{x} at the backside of the wafer, sputter Cr; (b) pattern Cr into 10 \(\mu\)m by 10 \(\mu\)m squares; (c) etch SiO\textsubscript{2} by RIE and BHF until the Cr and photoresist mask was etched free, resulting in a SiO\textsubscript{2} tip; (d) sputter and pattern Pt on the wafer, grow SiO\textsubscript{2} on Pt by LPCVD; (e) spin photoresist on the tip, leaving the tip end uncovered, etch SiO\textsubscript{2} from the tip end; and (f) sputter and pattern Cr on the wafer, pattern SiN\textsubscript{x} on the front side of the cantilever, release the cantilever in TMAH.

The thermal time constant of the probe is an important parameter that determines limits the scanning speed of the thermal probe. This parameter was measured using a sample containing a 350 nm wide gold line. A sinusoidal current of a frequency \(f\) was passed through the gold line, resulting in a modulated temperature of the gold line at a frequency of 2\(f\). The temperature oscillation led to a 2\(f\) oscillation in the four-probe electrical resistance of the gold line, which was measured and used to calculate the 2\(f\) component in the temperature. The amplitude and phase of the 2\(f\) component of
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Figure 4. Scanning electron micrographs of a batch-fabricated probe. Left: a close up of the Pt-Cr junction at the tip end; Right: an overview of the probe.

Figure 5. Dynamic temperature response of the junction as a function of heating frequency.

the temperature at the probe tip was measured by a lock-in amplifier while the probe contacted the gold line. The result is shown in Fig. 5. The AC temperature showed a typical first order dynamic response of $T_{ac} = T_{dc} / \sqrt{1 + (2\pi f \tau)^2}$ and decreased to about $1/\sqrt{2}$ at a heating frequency of $f_0 = 18$ kHz. The time constant $\tau$, defined as $1/2\pi f_0$, was calculated to be $8.8 \mu$s.

2.2. Instrumentation of Scanning Thermoelectric Microscopy

After the invention of the scanning thermal profiler, in early 1990s Williams and Wickramasinghe reported a novel method called Scanning Chemical Potential Microscopy (SCMP) for mapping the local chemical potential, essentially thermoelectric power, of a MoS$_2$ and a graphite sample [12]. In their experiment conducted in
air, an atomically sharp metal STM tip was scanned on the surface of the sample at a constant height using a unique feedback control loop. In this feedback loop, the voltage is applied to the tip through a large resistor (100 MΩ) connected in series with the tip-sample tunneling junction. In the STM mode, a constant voltage drop across the tip-sample junction was maintained by adjusting the tip height using the feedback loop. Because the sample was heated to about 30 K higher than the tip temperature held at ambient, a temperature gradient localized near the tip-sample junction was generated in the sample. This temperature difference creates a thermoelectric voltage corresponding to the local chemical potential of the sample. This thermoelectric voltage was measured intermittently between two successive STM line scans; after each STM line scan, the STM tip scanned the same line at a constant height with the feedback loop interrupted and the applied voltage reduced to zero. The obtained thermoelectric voltage map shows an atomic modulation.

In the following years, few efforts were reported on the development of thermoelectric microscopy. One notable experiment was done by Poler et al. using a setup similar to the SCMP for measuring the thermoelectric property of Guanine monolayers [13]. As they pointed out, the measured property by this technique is the thermopower (or Seebeck coefficient) of the sample. Therefore, they renamed this method as Scanning Thermopower Microscopy (STPM). Later on, Ghoshal et al. proposed to use the aforementioned thermocouple AFM probe to map the Seebeck coefficient of a sample, and named this AFM-based method as Scanning Thermoelectric Microscopy (SThEM) [14]. In this chapter, all these techniques aiming at probing surface thermoelectric properties are collectively referred as SThEM.

Very recently, Shi and Shih have further investigated the use of a SThEM method to profile Seebeck coefficient of semiconductor nanostructures including shallow p-n junctions in MOSFET devices and individual quantum well and barrier layers of superlattice thermoelectric devices [15]. Their measurement scheme is rather different from the SCPM in two aspects. First, their measurement is conducted in ultra high vacuum (UHV) because in air, heat conduction through the air gap between the STM tip and the sample dominates over that caused by electron and phonon coupling between the tip and the sample. Consequently, the temperature gradient in the sample, which is created by the colder tip, spreads over to a distance comparable to the mean free path of air molecules. This can severely limits the spatial resolution of the thermoelectric microscopy method. Second, they allowed a nanoscale elastic contact between the tip and the sample as this was found to be necessary for measuring a stable thermoelectric voltage on a semiconductor sample.

In the UHV SThEM setup, a heater wire attached to the sample holder was used to raise the sample temperature 10–30 K above ambient. The tip-sample contact was realized in the following procedure. At each point, after a tip-sample gap of about 1 nm was stabilized by feedback controlling a constant tunneling current, the control loop was disconnected by a manually-triggered relay and the STM bias was reduced to zero, as illustrated in Fig. 6. The tip and the sample were then connected to an electrometer with input impedance larger than $10^{13}$ Ω. Subsequently, the piezo-tube of the STM was used to drive the tip step by step at 0.5 Å per step toward the sample. Large fluctuation
in the measured tip-sample voltage was observed before the tip contacted the sample. The fluctuation is thought to be caused by a large and fluctuating tunneling resistance between the metal tip and the semiconductor sample. As the tip made a nano-contact with the sample, the voltage signal was found to be very stable. Further progression of the tip often caused crash. Therefore, the tip was slightly moved back and forth by up to 1 Å around the contact position to verify the stability of the measured voltage as well as to maintain an elastic contact. After the voltage measurement was made at

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure6.png}
\caption{(a) Schematic diagram of the SThEM setup. (b) Time profile of the measured voltage as the tip approached the sample. Inset: histogram of the measured voltage.}
\end{figure}
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each point, the sample was scanned to obtain a STM height image, which showed little change of image resolution. This measurement scheme is made feasible by the low drift ($\sim 10 \text{ Å/hour}$) and high vertical resolution ($\sim 0.1 \text{ Å}$) of the UHV STM.

The voltage measured between the tip and the sample during the nano-contact is caused by thermoelectric effects. As the tip contacts the sample, band bending occurs due to the formation of a Schottky junction. This leads to a built-in contact potential. Under an isothermal condition, however, the built-in potential does not contribute to the voltage measured by the electrometer. On the other hand, the contact of a colder tip and a hotter sample creates a temperature gradient in the sample concentrated near the contact (see Fig. 6). Carriers were made to drift under the temperature gradient. This leads to a thermoelectric voltage proportional to the local $S$, a spatial average in a hemispheric sample volume of a large temperature gradient, i.e.

\[
V(x, \gamma) = S(x, \gamma)(T_c - T_1)
\]

where $T_c$ and $T_1$ are the temperatures of the contact and the back side of the sample, respectively. The thermoelectric power of the metal tip and lead wires is much smaller than that of a semiconductor sample, and thus is ignored. This allows the SThEM to obtain a map of thermopower variation on the sample surface.

3. THEORY OF SCANNING THERMAL AND THERMOELECTRIC MICROSCOPY

3.1. Theory of Scanning Thermal Microscopy

The sensitivity and spatial resolution of the SThM largely depend on the mechanisms of heat transfer between the thermal probe and the sample. As shown in Fig. 7, heat transfers between the probe and the sample via solid-solid conduction, conduction through the air gap between the probe and the sample, radiation, and conduction through a liquid meniscus at the tip-sample contact. Air conduction and radiation are not localized at the tip-sample contact, and thus will cause poor spatial resolution. Among these two heat transfer paths, the radiation contribution is usually negligible unless the sample temperature is very high ($> 600 \text{ K}$). On the other hand, the influence by air conduction has been found to be significant, as discussed in the following paragraph.

The relative contribution of different heat transfer mechanisms between the thermal probe and the sample was examined and quantified by Shi and Majumdar [16]. They used a thermally-designed and batch-fabricated thermal probe and several calibration samples containing thin film metal lines with different width and length. The metal lines were joule heated during the experiment and its temperature was determined by measuring its temperature-dependant electrical resistance.

The temperature rise of the thermocouple junction was measured when the tip was in contact with the joule-heated metal line. It was found that the junction temperature rise was about 53%, 46%, and 5% of that of a 50 $\mu$m, 3 $\mu$m, and 0.3 $\mu$m wide line, respectively, showing a trend of decreasing sensitivity with decreasing sample line width. This suggests that the probe was heated more by air conduction between the tip and
the larger hot area of the wider lines. This trend indicates that air conduction plays an important role in tip-sample heat transfer.

A further experiment was used to determine the relative contribution of various tip-sample heat transfer mechanisms. In the experiment, the 350 nm wide line was joule heated to 5.3 K above room temperature. The cantilever deflection and temperature rise of the sensor were recorded simultaneously when the sample was raised toward and then retracted from the batch-fabricated thermal probe. When the sample approached the tip, the cantilever deflection signal remained approximately constant before the sample contacted the tip, as shown in the deflection curve in Fig. 8. In this region, the sensor temperature rise was mostly due to air conduction between the probe and the sample, and it can be estimated that radiation contribution was negligible when both the sample and the tip were close to ambient temperature. As the tip-sample distance was reduced, the sensor temperature rise due to air conduction increased slowly. Before the sample made solid-solid contact to the tip, the adsorbed liquid layers on the tip and the sample bridged each other. Initially, this liquid bridge pulled the tip down by a van der Waals force, as being seen in the dip labeled as “jump to contact” in the deflection curve. Coincidentally, there was a small jump in the sensor temperature due to heat conduction through the liquid bridge. As the sample was raised further, both the solid-solid contact force and the sensor temperature increased gradually, until the cantilever was deflected for more than 100 nm. After this point, the sensor temperature remained almost constant as the contact force increased.

As the sample was retracted from the tip, the sensor temperature again remained almost constant until at a cantilever deflection of 100 nm, the sensor temperature rise reduced roughly linearly but at a smaller slope than that found in the approaching cycle. As the sample was lowered further, the tip was pulled down together with the
Figure 8. Cantilever deflection and temperature response of the probe as a function of sample vertical position when a 350 nm wide line was raised toward and then retracted from the tip.

sample by surface tension of the liquid bridge until after a certain point, the restoring spring force of the cantilever exceeded the surface tension and the tip “snapped out of contact” with the sample. Associated with the breaking of the liquid bridge, there was a small drop in the sensor temperature.

The above experiment shows several mechanisms. First, before the tip contacts the sample, air conduction contributed to a sensor temperature rise up to 0.03 K per K sample temperature rise, which was about 60 percent of the maximum sensor temperature rise at large contact forces. Second, conduction through a liquid meniscus was responsible for the sudden jump and drop in sensor temperature when the tip “jumped to contact” to and “snapped out of contact” from the sample, respectively. Third, solid-solid conduction resulted in the almost linear relationship between the sensor temperature rise and the contact force. This is a well understood feature for macroscopic solid-solid contacts [17]. Since the sensor temperature decreased at a slower slope during unloading (decreasing contact force), there must have been plastic deformation during loading (increasing contact force). For plastic deformation, the contact area increased with load [18], resulting in the linear increase of solid-solid contact conductance with contact force. However, since the conductance was still a function of the load during unloading, elastic recovery must have been significant.

One question remains as to why the sensor temperature saturated for cantilever deflection larger than 100 nm. To clarify this, the contact force corresponding to the 100 nm deflection need to be calculated. The spring constant of the composite
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Figure 9. Cantilever deflection and temperature response of the probe as a function of sample vertical position when the 5.8 \( \mu \)m wide line approached and then retracted from the tip.

The cantilever beam was calculated using Roark’s formulas [19] to be 0.38 ± 0.11 N/m. Therefore, the 100 nm deflection corresponds to a contact force \( F = 38 \pm 11 \text{ nN} \).

Assuming plastic deformation, this contact force resulted in a contact spot with a diameter

\[
d_c = \sqrt{\frac{4F}{\pi H}},
\]

where \( H \) is the hardness of the tip or sample, whichever is softer. Among the tip and sample materials, the hardness of Au is the lowest and is of the order of 1 GPa. This leads to \( d_c \approx 8 \text{ nm} \). The tip radius was about 50 nm. However, the details on the tip end are not clearly shown in the SEM image due to the lack of resolution. The linear increase in contact area was probably due to the roughness on the surfaces or on the sample, since it is well known that in the junction of two random rough surfaces, the contact area increases linearly with contact force [18]. As the contact force increased to about 38 nN, the contact size approached the diameter of the asperity. At this point, the contact area could not increase further with the contact force, until the asperity was completely pressed into the sample by a contact force much larger than those used in the experiment. As a result, the sensor temperature in Fig. 8 remained almost constant for a deflection larger than 100 nm.

The point contact experiment was repeated for a 5.8 \( \mu \)m wide and 2000 \( \mu \)m long line and the result is shown in Fig. 9. While the increase of normalized sensor temperature due to solid and liquid conduction was similar in magnitude to those in Fig. 8, the normalized sensor temperature rise due to air conduction was about 0.6 K per K temperature rise on the sample, one order of magnitude higher than the corresponding one (0.03 K per K temperature rise on the sample) in Fig. 8. Therefore, it is clear that
for the 5.8-μm wide line, air conduction dominated tip-sample conduction and was responsible for the large temperature rise.

These experiments reveal that the contribution of air conduction in tip-sample heat transfer depends on the size of the heat source on the sample. For large heat sources, air conduction dominates tip-sample heat transfer. As the size of the heat source reduces, the contribution of air conduction decreases and solid-solid conduction and liquid conduction become important. For micro/nano- devices with localized submicron heated features, such as carbon nanotube circuits, air conduction contribution can be reduced to a level smaller than that from solid-solid and liquid film conduction.

To estimate the magnitude of solid-solid and liquid film conductance, Shi and Majumdar [16] developed a one-dimensional head conduction model considering various microscale heat transfer mechanisms. Using the model, they inferred from the experimental data in Fig. 8 that the thermal conductance of the liquid meniscus was $G_{lf} = 6.7 \pm 1.5$ nW/K, and solid-solid conduction varies linearly with the contact force with a contact conductance of $0.76 \pm 0.38$ W/K-N. For contact forces larger than $38 \pm 11$ nN, the solid-solid conductance saturated at $G_{ss} \approx 30$ nW/K, because the contact size between the sample and an asperity on the tip end approached the $\sim 10$ nm diameter of the asperity. For this solid-solid contact with an effective contact radius $b \approx 5$ nm, it can be shown that

$$G_{ss} = \pi k_{tp} b; \quad \frac{2}{k_{eff}} = \frac{1}{k_s} + \frac{1}{k_{tp} (\tan \theta)^2}$$

(3)

where $k_s$ and $k_{tp}$ are the thermal conductivity of the sample and the tip, respectively, and $\theta$ is the half angle of the tip. With $\theta \approx 18^\circ$, $k_s \approx 200$ W/m-K for the thin film gold metal line, $k_{tp} \approx 15$ W/m-K for the Pt-Cr film at the tip end, and $b \approx 5$ nm, it can be estimated that $G_{ss} \approx 49$ nW/K. This is approximately the saturation value of 30 nW/K estimated from the thermal model.

Due to the small contact thermal conductance at the nanoscale tip-sample contact, the temperature rise of the thin film thermocouple probe was below 0.1 K per K sample temperature rise when micro/nano- devices with submicron localized heat source were imaged. In addition, due to the influence of air conduction, the measured temperature profile by the SThM was found to deviate from the true one. This makes it necessary to correct the SThM measurement results by careful thermal modeling. Alternatively, the influence of air conduction can be eliminated by performing the SThM in vacuum.

3.2. Theory of Scanning Thermoelectric Microscopy

The critical feature of the SThEM is to generate a localized temperature gradient at the tip-sample contact. The spatial extent of this temperature gradient, which limits the spatial resolution, not only depends on the contact size or tip radius, but is also determined by the scattering length ($l$), within which local thermal equilibrium cannot be obtained. Ignoring the latter microscale heat transfer effect, one can estimate the
temperature in the sample at a distance $r$ away from the contact point to be

$$T(r) \approx T_1 - \frac{a}{r}(T_1 - T_c)$$

(4)

As $r$ is a few times larger than $a$, $T(r)$ approaches $T_1$ and the temperature gradient becomes negligible. This analysis holds only if $r \gg l$. For $r \leq l$, local thermodynamic equilibrium cannot be obtained within $r$, and the temperature gradient will have a spatial extent on the order of $l$. For example, if $l = 10$ nm, and $a = 1$ nm, according to eqn. 7, at $r = 5a = 5$ nm, $T(r)$ should have been very close to $T_1$. However, because local thermodynamic equilibrium cannot be obtained within $r = 5$ nm $< l$, it is impossible to achieve a large temperature difference between $T_c$ and $T(r = 5$ nm), and the temperature approaches $T_1$ only when $r > l$. Hence, eqn. (7) derived by ignoring the microscale heat transfer effect breaks down for a length scale of the order of $l$. At room temperature, $l$ is on the order of 1 nm for amorphous materials, and can be up to hundreds of nanometers for semiconductors. In degenerately doped semiconductors, the scattering length is found to scale with average inter-dopant distance to be a few nanometers [15]. In degenerately doped superlattice structures, $l$ is expected to be further reduced by scattering at the interfaces.

Another question in SThEM is regarding the actual temperature drop across the sample. As shown in Fig. 6, the temperature $T_c$ at the tip-sample contact is between $T_0$, the temperature of the tip holder, and $T_1$, the temperature at the backside of the sample. $T_c$ is determined by the ratio of the thermal resistance ($R_t$) of the tip to that of the sample ($R_s$), i.e.,

$$T_c = T_0 + \frac{T_1 - T_0}{1 + \frac{R_s}{R_t}}$$

(5)

Assuming spherical symmetry in the sample and the tip and ignoring microscale heat transfer effects, one can estimate $R_s$ and $R_t$ as

$$R_s \approx \left(2\pi k_s a\right)^{-1} \quad \text{and} \quad R_t \approx \left(2\pi k_t a(1 - \cos \theta)\right)^{-1}$$

(6)

where $k_s$ and $k_t$ are the thermal conductivity of the tip and the sample, respectively, and $a$ is the contact radius. Typically the tungsten STM tip has much higher thermal conductivity than a semiconductor sample. Hence, $R_s/R_t$ is large and $T_c$ is close to $T_0$.

The third important issue for the SThEM is the Schottky barrier formed due to the contact of a metal tip and a semiconductor sample. As a result, carriers are depleted from the contact point. Assuming spherical symmetry in the sample and $w \gg a$, where $w$ is the depletion width, one can estimate that

$$w \approx \left(\frac{3a \varepsilon \varepsilon_0 |\phi|}{Ne}\right)^{1/3}$$

(7)

With $a = 1$ nm, $\phi = 0.5$ V, $N = 10^{19}$ cm$^{-3}$, $\varepsilon = 16$, one finds $w = 5$ nm. This number is just slightly larger than the inter-dopant distance. In the derivation of
Eqn. 7, a continuous distribution of dopants has been assumed. This continuum assumption shall break down when \( w \) is shorter than the dopant-dopant distance. Nevertheless, it can be expected the depletion width is in the range of 5–10 nm. This depletion zone can have a different \( S \) from the bulk value, and affect the SThEM measurement. However, it was found that the measured \( S \) values by SThEM were very close to the bulk values [15]. This observation was attributed to a smaller radius \((w)\) of the depletion zone than the spatial extent \((l)\) of the hemispheric region with a large temperature gradient. As such, the bulk-like region where \( w < r < l \) contributes to most of the measured thermoelectric voltage of the SThEM.

4. APPLICATIONS OF SCANNING THERMAL AND THERMOELECTRIC MICROSCOPY IN NANOTECHNOLOGY

4.1. Thermal Imaging of Carbon Nanotube Electronics

Carbon nanotubes (CNs) are made of graphitic cylinders. One distinguishes between multi-wall carbon (MW) CNs consisting of a series of coaxial graphite cylinders, and single-wall (SW) CNs that are one atom thick, usually with a small number (20–40) of carbon atoms along the circumference and several micron long along the cylinder axis.

At room temperatures, electrons near the Fermi level in a metallic SWCN can have a long mean free path on the order of microns [20]. For a metallic SWCN a few microns long, electron flows from one end of the tube to the other end without scattering with phonons, electrons, defects, and boundary. This situation is referred as ballistic electron transport. Semiconducting SWCNs have recently been observed to behave like ballistic conductors [21], while both ballistic [22] and diffusive [23] transport behaviors have been reported by MWCNs.

Experiments also found that metallic CNs can sustain high electric fields on the order of 100 kV/cm and high current densities up to \( 10^9 \) A/cm\(^2\) [23, 24], two orders of magnitude higher than a normal metal such as copper. This excellent current carrying capacity of CNs may have potential applications for micro/nano electronics.

The potential electronic applications of CNs require a detail understanding of their electrical as well as thermal transport properties. Despite of various studies on electron transport, there remain several unanswered questions regarding heat dissipation in current carrying CNs. First, it is unclear whether heat dissipation occurs in the bulk of the CNs or at the contacts. For a SWCN at low electric fields, for example, heat dissipation is not expected to occur in the bulk. On the other hand, compared to the low field transport property, the electron-phonon scattering mechanism can be different at high fields for metallic SWCN. As shown by Yao et al. [24], for metallic SWCNs current saturates at about 25 \( \mu \)A at applied voltage exceeding a few volts. They proposed that the current saturation is due to electron scattering with optical phonons at high electric field. For MWCNs and semiconducting SWCNs, heat dissipation in the bulk is likely to occur if they are diffusive. However, there lack of direct experimental evidences to justify these predictions.
Shi et al. have used the SThM technique to measure temperature distribution in current-carrying CNs and to investigate heat dissipation in the nanostructures [25, 26]. They have observed temperature profiles supporting ballistic (diffusive) transport in SWCNs and MWCNs. The measurement result on a MWCN is discussed below.

Figure 10 shows the AFM topographic image of a sample containing a 7-nm diameter MWCN on 1-μm-thick SiO₂ of a Si wafer. Four 30-nm-thick Au/Cr lines were patterned on top of the MWCN by electron beam lithography and lift off technique. Electrostatic force microscopy (EFM) was used to determine various electrical resistances in the device. A 100 mV AC voltage was applied at contact 2 with contact 3 grounded and contacts 1 and 4 floating. The frequency of the voltage was set to the
resonant frequency of the EFM cantilever probe, which is a conducting AFM probe. Because of the electrostatic force between the sample and the probe, the cantilever was made to oscillate at its resonant frequency and the oscillation amplitude is proportional to the voltage of the sample in close proximity to the probe tip [22]. The sample voltage can be measured from the oscillation amplitude. The obtained EFM image was shown in Fig. 10(b). The voltage profile shown in Fig. 10(c) indicates that voltage decayed almost linearly along the MWCN and there were large voltage drops near the two contacts. The two terminal resistance measured with a bias of 100 mV between contacts 2 and 3 was 52 KΩ. From the EFM data, it was estimated that the electrical resistance was about 26 KΩ in the tube, and 16 and 10 KΩ at contacts 2 and 3, respectively. The segment of the tube between contacts 2 and 3 was 2.6 μm long. Therefore, the resistance in the tube was about 10 KΩ/μm. The linear voltage drop along the tube and the resistance value confirm the results from previous EFM study [22] that MWCNs behave as a diffusive conductor with a well-defined resistance about 10 KΩ/μm. In addition, for this device, the tube-contact interface were not clean, resulting in the much larger contact resistance than that found in the MWCN sample used in the previous EFM experiment. SThM was further used to verify that the MWCN sample was diffusive and dissipative. A voltage of 0.7 V was applied at contact 4 with contact 1 grounded and contacts 2 and 3 floating. This resulted in a current of 9.3 μA. The corresponding thermal image and temperature profile were shown in Figs. 10(d) and 10(e). It is clear that the temperature at the middle was higher than those close to contacts 2 and 3 and the overall curvature of the profile is negative. This indicates that heat indeed was dissipated in the bulk of the tube. It should be noted that on top of the metal covering the tube, the probe measured a much lower temperature than that when the probe was directly on top of the tube. It is possible that the temperature on top of the 30 nm thick metal had decreased significantly although the temperature could be high in the tube underneath the metal.

4.2. Thermal Imaging of ULSI Devices and Interconnects

SThM has been employed to map temperature distribution on top and cross sectional surfaces of MOSFETs and ULSI interconnects. Kwon et al. employed the batch-fabricated SThM probes to map temperature distribution on the cross sectional surface of an operating MOSFET with a gate length of 5 μm [27]. The thermal images clearly show a hot spot near the drain side. This is believed to be caused by the pinch-off effect near the drain, which results in a discontinuous channel and significant heat dissipation there. Efforts are currently underway to measure temperature distribution on the cross sectional surface of nanotransistors with a gate length shorter than 100 nm. Shi et al. have used the SThM to study localized heating in different VLSI submicrometer W-plug via structures provided by Texas Instruments, Inc. The via samples consisted of two levels of 0.6 μm thick Al-Cu metallization that were separated by a layer of 0.9 μm thick SiO₂ and connected through one or more W-plug vias. There was a 0.1 μm TiN layer on the top and bottom of each metal line. The samples were coated with a standard passivation layer of 1 μm thick SiO₂ followed by a capping layer of
0.3 μm thick Si₃N₄, as shown in Fig. 11. The topography, cross section, and SThM-measured temperature distribution of one via structure are also shown in Fig. 11 for a current of 40.5 mA. For this sample, the two metal lines were 3 μm wide and were connected by three 0.4 μm diameter vias. The temperature rise in the vias was determined from the change in electrical resistance using a temperature coefficient of resistance (TCR) of 1.01 × 10⁻³ K⁻¹ obtained from an earlier work [28]. The via temperature was measured by the resistive thermometry as a function of current. For a current of 40.5 mA, the temperature rise in the via was 30 K. During scanning, the maximum temperature rise in the junction was found to be 15 K when the probe was directly on top of the vias. The high temperature region spread to the current flow direction.

4.3. Shallow Junction Profiling

Homo- and hetero- junctions constitute the fundamental building blocks of electronic, optoelectronic, and thermoelectric devices. Characterization of the dopant/carrier distribution and the electronic structures of semiconductor junctions is thus an important task. For example, profiling shallow p-n junctions in MOSFETs has been a prominent characterization issue that has challenged the semiconductor industry for many years. Simulation and characterization of dopant implantation, diffusion and activation is currently one of the highest-priority tasks among the research needs for extending CMOS, to its ultimate limit at or beyond the 22-nm node. In order to understand how different processing parameters and device structures will affect the dopant/carrier profiles and the electronic structures, accurate characterization data must be obtained.
6. Scanning Thermal and Thermoelectric Microscopy

Figure 12. (A) STM image of a GaAs p-n junction array (filled state with sample bias of $-2$ V). The bright strips are p-doped with Be to $1.1 \times 10^{19}$ cm$^{-3}$, and the dark strips are n-doped with Si to $9 \times 10^{18}$ cm$^{-3}$. Scale bar: 100 nm. (B) Measured thermoelectric voltage (circles) and calculated $S$ profile (dash line) across the p-n junction as a function of distance ($x$) from the metallurgical junction. The two measurement profiles (open and solid circles) were obtained at two different $y$ locations with $T_1 - T_0 = 20$ K. The $x$ position is obtained from STM images of a scan size of 30 $\times$ 30 nm.

using 2D dopant/carrier profiling tools with a 2 nm spatial resolution and 4% accuracy, as specified by the 2001 International Technology Roadmap for Semiconductors. A number of 2D dopant/carrier profiling methods have been investigated. However, the roadmap requirements have not been satisfied and 2D dopant/carrier profiling has remained essentially unsolved [29].

Lyoo et al. have employed the STHEM method for measuring the local $S$ at a number of locations across GaAs p-n junctions. One set of measurement data are shown in Fig. 12. One can observe an abrupt inversion of the polarity of the measured thermoelectric voltage within a distance of 2 nm from the junction. The measured thermoelectric voltage at each point of the p-n junction is due to the diffusion of local carriers under a temperature gradient, and is coupled to the local carrier concentration. For an n-type nondegenerate semiconductor, the local thermopower is [30]

$$S = \frac{1}{-eT} \left( E_c - E_F + \frac{3}{2} k_B T \right) = -\frac{k_B}{e} \left( \ln \frac{N_c}{n} + \frac{3}{2} \right) < 0$$

(8)
For a p-type nondegenerate semiconductor,

\[
S = \frac{1}{eT} \left( E_F - E_V + \frac{3}{2} k_B T \right) = \frac{k_B T}{e} \left( \ln \frac{N_c}{N_v} + \frac{3}{2} \right) > 0
\]  

(9)

where \( E_C(E_V) \) is the conduction (valence) band edge, \( E_F \) is the Fermi level, \( n(p) \) is the electron (hole) concentration, \( N_c(N_v) \) is the effective density of states of electrons (holes), \( k_B \) is the Boltzman constant, \( e \) is the electron charge, and \( T \) is the temperature. These equations illustrate that the magnitude and sign of \( S \) depend on carrier concentration and type, respectively. The dependence of \( S \) on the carrier type has been routinely used for determining the dopant type using the hot probe method in characterization laboratories. In fact, connecting a hot probe to a semiconductor and measuring the sign of the generated thermoelectric voltage is a textbook example for determining dopant types.

Using Eqns. 8 and 9 and those for degenerate semiconductors, Lyeo et al. have calculated the thermopower profile from the dopant profile obtained by SIMS. As shown in Fig. 12, the calculated thermopower profile exhibits the same trend as the measured thermoelectric voltage profile. They have further calculated the band structure and carrier profile from the STPM measurement results, as shown in Fig. 13. The calculation procedure is as following. First, they calibrated the STPM measurement using a sample with known dopant concentration and thermopower. The calibration allows them to convert the measured thermoelectric voltage to thermopower. The band structure and carrier concentration were then obtained using Eqns. 8 and 9 as well as those for degenerate semiconductors.

As a comparison, they also calculated the band structure and carrier concentration from the SIMS dopant profile. The band structure was obtained using the depletion approximation, and was used to calculate the carrier profile according to the Fermi-Dirac statistics. As shown in Figs. 13, the results from the SIMS and STPM exhibit good agreements with each other, except at the edges of the depletion region. Lyeo et al. have conducted a detailed study and concluded that the discrepancy shown in Fig. 13 was due to the break down of a continuum assumption at a length scale comparable to the dopant–dopant distance (~5 nm) and the inaccuracy of the depletion approximation, both invoked for the calculation based on the SIMS profiles.

Nevertheless, their work demonstrates that by nanoscale profiling of \( S \), the SThEM can be used to map out band structure and carrier concentration with nanometer spatial resolution. Furthermore, the carrier concentration is a reasonable good measure of the activated dopant density, when the dopant density varies over a scale comparable to the Debye length (13 nm at a concentration of \( 10^{17} \text{ cm}^{-3} \) and 0.4 nm at \( 10^{20} \text{ cm}^{-3} \)) [31].

As a 2D dopant/carrier profiling tool, the SThEM technique has two distinct features. First, for other dopant profiling techniques such as SCM and STM, the voltage applied to the tip creates an electric field penetrating into the sample. This electric field further causes band bending in the sample and shift the apparent junction location. It has been observed that the electronic junction locations obtained by SCM and STM
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Figure 13. Carrier profile across the p-n junction shown in Fig. 12. Solid and dotted lines are electron and hole concentrations, respectively, calculated based on the energy band diagram obtained from the SIMS dopant profile using the depletion approximation. Solid and open circles are electron and hole concentrations, respectively, calculated from the measured S profile. To convert the measured thermoelectric voltage to the S profile, we calibrated the SThEM measurement using a sample with known S. Inset: Energy diagram of the p-n junction (Lines: calculated from the SIMS dopant profile using the depletion approximation. Circles: calculated from the measured S profile)

depend strongly on the tip voltage [32], and can shift 2–20 nm from that obtained from the SThEM. In SThEM, no voltage is applied at the tip during thermopower measurement. Thus, the unwanted effects of tip voltage-induced band bending and junction shifting are absent in SThEM, allowing SThEM to locate the actual electronic junction. Furthermore, the abrupt inversion of thermoelectric power across the electronic junction allows one to use SThEM to locate the electronic junction with a precision and resolution better than 2 nm.

5. SUMMARY AND FUTURE ASPECTS

The Scanning Thermal and Thermoelectric Microscopy methods discussed in the preceding sections have allowed the direct observations of thermal and thermoelectric transport phenomena in the nanometer scale. Several applications including mapping temperature distribution on nano and molecular electronics, and shallow junction profiling have been demonstrated. A variety of other applications have also been demonstrated using these techniques. For example, the SThM has the capability of mapping thermal conductivity and diffusivity of a polymer sample with sub micron spatial
resolution. This unique feature has been used to image polymer blends and found applications in drug research and development [33–36]. The ability of SThEM in mapping Seebeck coefficient with nanometer scale spatial resolution can be applied to probe the superior thermoelectric properties of low dimensional thermoelectric materials, including quantum well, wire, and dot superlattices that will potentially revolutionize the energy conversion process.

Currently, new techniques are being invented for improving the spatial resolution or accuracy of these two techniques. For example, recent developments in near field optical techniques for nano-thermometry have stimulated much interest in this direction. In addition, the possibility of using tunneling [39] or nano-contact thermometry to improve [37–38] the spatial resolution of the SThM is being investigated. The success of these new methods will allow the SThM and SThEM to become highly-powerful microscopic tools for nanotechnology research and development.

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