FEATURE ARTICLE

Thermal Characterization and Sensor Applications of One-Dimensional Nanostructures Employing Microelectromechanical Systems

Li Shi,* Choongho Yu, and Jianhua Zhou

Department of Mechanical Engineering & Center for Nano- and Molecular Science and Technology, Texas Materials Institute, The University of Texas at Austin, Austin, Texas 78712

Received: July 15, 2005

We review the recent progress in thermal characterization and sensor applications of one-dimensional nanostructures employing microelectromechanical system (MEMS) devices. It was found by thermal measurements that the thermal conductance of a single wall carbon nanotube (SWCNT) was very close to the ballistic thermal conductance of a 1-nm-diameter SWCNT without signatures of phonon–phonon Umklapp scattering, a high thermoelectric figure of merit can potentially be obtained in bismuth telluride (Bi$_x$Te$_{1-x}$) nanowires with an optimized atomic ratio of $x$, and the thermal conductivity of metal oxide nanobelts was suppressed by increased phonon-boundary scattering. We further suggest that dielectrophoresis and other directed-assembly methods can be used for the large-scale integration of nanowires with MEMS to obtain ultrasensitive, stable, and selective sensor systems.

I. Introduction

One-dimensional (1D) nanostructures such as carbon nanotubes$^1$ and semiconductor nanowires$^2$ have received intense interest in recent years. These nanostructures have been obtained using either new “bottom-up” synthetic methods or state-of-the-art nanolithography-based patterning approaches. There have been a large number of efforts to employ these nanostructures for the fabrication of field effect transistors,$^3$ logic devices,$^7$ and field emission displays,$^{12-14}$ and thermoelectric refrigeration and power generation devices.$^{15}$ These many potential applications are accompanied by new challenges, one of which is related to the unique thermal and thermoelectric transport properties of nanotubes and nanowires. In bulk materials, thermal energy transport is facilitated by lattice vibration waves or phonons as well as charge carriers. Consequently, the thermal conductivity ($\kappa$), which is the proportionality factor between temperature gradient and heat flux, consists of a phonon contribution ($\kappa_p$) and an electron contribution ($\kappa_e$), i.e., $\kappa = \kappa_p + \kappa_e$. In metals, $\kappa_e$ is much larger than $\kappa_p$; while in insulators and semiconductors, $\kappa_p$ is much larger than $\kappa_e$. $\kappa_p$ (or $\kappa_e$) is determined by the energy dispersion and scattering processes of phonons (or electrons), both of which can be modified in nanostructures due to size and quantum confinements. It was suggested that the $\kappa_p$ of semiconductor nanowires can be largely suppressed by increased surface scattering of phonons$^{16}$ and by modification of the phonon energy dispersion.$^{17}$ The suppressed $\kappa_p$ makes it difficult for Joule heat generated locally in nanowire electronic devices to be dissipated to the substrate, leading to local hot spots that degrade the device performance and reliability.

The self-heating problem has been one of the major challenges for continuous scaling down of metal-oxide field-effect transistor (MOSFET) devices in ultra-large-scale-integrated (ULSI) circuits,$^{18}$ and will likely become one critical issue for the development of nanotube and nanowire electronic devices, especially those on flexible, low-cost polymer substrates with thermal conductivity two or more orders of magnitude lower than silicon. Thermal management is an increasingly important aspect for the further development of nanoelectronics.

One approach to address the thermal management problem relies on the development of high-thermal conductivity materials to act as heat spreaders in electronic packaging. Good-quality diamond has been known as an excellent heat conductor with a high thermal conductivity up to 3000 W/m-K at temperature 300 K, compared to the corresponding value of 400 W/m-K for copper, 150 W/m-K for silicon, 1.4 W/m-K for glass, and 0.1 W/m-K or lower for polymers. Diamond coating deposited by chemical vapor deposition (CVD) has been explored as heat spreading coating for ULSI devices,$^{18,19}$ although the difficulty and cost for the synthesis of high-quality diamond has limited its application. The discovery of carbon nanotubes (CNTs) provides a different type of high-thermal conductivity materials for thermal management applications. Unlike semiconductor nanowires, CNTs are expected to possess super-high $\kappa$ due to its unique crystalline structure, low defect concentrations, and atomically smooth surface. Various theoretical calculations have predicted that $\kappa$ of carbon nanotubes (CNTs) can surpass that of diamond$^{20,21}$ and the predictions have inspired the active development of CNT films and composites for applications as thermal interface materials for reducing the thermal interface resistance in electronic packaging. Additionally, CNT interconnect structures are also being actively pursued for next-generation ULSI devices.$^{22,23}$ If successful, CNT interconnects especially CNT via structures not only can support a large current density but they also can be used as heat spreaders to dissipate heat from local hot spots.

On the other hand, the suppressed $\kappa$ in semiconductor nanowires can be advantageous to the fabrication of energy-
Li Shi is an assistant professor in the Department of Mechanical Engineering and Texas Materials Institute at the University of Texas at Austin (UT Austin). He received his B. S. from Tsinghua University, Beijing, in 1991, his M.S. from Arizona State University, Tempe, in 1997, and his Ph.D. from the University of California at Berkeley in 2001. He was a Research Staff Member at IBM Research Division for one year before joining the faculty at UT Austin in 2002. He received the CAREER award from the National Science Foundation in 2003 and the Young Investigator Award from the Office of Naval Research in 2004. Current research undertaken by his group includes nanostructured thermoelectric materials, fundamentals of nanoscale energy transport and conversion, nanosensors, MEMS and microfluidics, and nanoscale interconnect structures for microelectronics.

Choongho Yu received his B.S. and M.S. degrees from Korea University and his Ph.D. degree in mechanical engineering from the University of Texas at Austin in 2004. He is currently a Postdoctoral Fellow at Lawrence Berkeley National Laboratory. His research interests include the investigation of thermoelectric materials for efficient power generation and refrigeration, thermophysical properties of low-dimensional nanostructures, and the development of molecular sensors and bio-MEMS.

Jianhua Zhou received his Ph.D. degree in mechanical engineering from the University of Texas at Austin in 2005. His research topic is in the area of thermal and thermoelectric transport in nanostructured materials. He obtained his B.S. and M.S. degrees, both in thermal engineering, from Tsinghua University in 1990 and 2000, respectively. He was a mechanical engineer at Nanjing Turbine Works from 1990 to 1997. He is currently with Applied Materials, Inc.

Efficient thermoelectric (TE) refrigeration devices for thermal management applications. TE refrigeration is achieved by the Peltier effect, whereby a current flow across thermocouple junctions can produce cooling or heating. Conversely, a temperature difference across a TE material generates a current flow and thereby electrical power, allowing for direct thermal-to-electrical energy conversion.24,25 Compared to vapor-compression refrigerators and gas-based engines, such solid-state devices are extremely attractive because they do not contain any moving parts, are environmentally benign, and allow for miniaturization. However, the coefficient of performance (COP) for TE refrigeration and the efficiency for TE power generation have been limited by the low TE figures of merit of bulk materials and are inferior to systems based on a working fluid.

The dimensionless TE figure of merit is defined as $ZT = S^2\sigma T/\kappa$, where $S$ is the Seebeck coefficient, $\sigma$ is the electrical conductivity, $\kappa$ is the thermal conductivity, and $T$ is the temperature. A $ZT$ larger than 3 is needed for a TE refrigeration unit to obtain a COP comparable to that of a vapor compression unit; while a $ZT$ larger than 6 is required to increase the efficiency of a TE generator to 20%. During the past fifty years, bismuth telluride alloys, e.g. $\text{Bi}_2\text{Sb}_2\text{Te}_3$ with a $ZT$ value approaching unity at 300 K, have remained the bulk materials with the highest $ZT$ at room temperature. Increasing the $ZT$ of bulk materials beyond this value has proved to be difficult due to two factors: (i) there is a tradeoff between $S$ and $\sigma$ as the dopant concentration is varied; and (ii) $\kappa_e$ is proportional to $\sigma$ according to the Wiedemann–Franz law.

Advances in nanostructured materials have led to new approaches to increasing the $ZT$. Theoretical calculations have suggested that $S^2\sigma$ can be increased in dimension-confined nanostructures due to a high density of states near the Fermi level,26,27 and $\kappa$ can be largely suppressed by phonon-boundary scattering28 and possibly by modification of phonon dispersion. Recently, there have been reports on the growth of thin film superlattices29,30 and nanostructured bulk alloys31 with improved $ZT$. Due to the quantum and classical size confinement effects, very high $ZT$ values have been predicted in Bi-based32 and III–V33 nanowires.

There have been efforts to experimentally verify the super-high $k$ of CNTs, suppressed $\kappa$ in semiconductor nanowires and $ZT$ enhancement in bismuth-based and III–V nanowires. The thermal conductivity of SWCNT mats and bundles was measured.34–36 The reported $k$ values are one or two orders of magnitude lower than theoretical calculations because the thermal resistance of the sample was increased by thermal contact resistance between interconnected CNTs in the sample. Measurement results of $S$ and the electrical resistance ($R_e$) of bismuth37 and bismuth antimony38 nanowire arrays deposited in anodized alumina membranes (AAMs) have been reported, but the thermal conductivity was not obtained due to thermal leakage through the AAM. Thermal conductivity measurements of 1D nanostructures are challenging due to the small sample dimension.

A so-called 3-$\omega$ method has been employed to measure the thermal conductivity of a platinum wire, a large MWCNT bundle39 and recently an individual MWCNT.40 This method relies on self-heating of a suspended wire under a sinusoidal current ($i_0\sin\omega t$) of frequency $\omega$. The sinusoidal current leads to a temperature rise modulated at the second harmonic frequency (2$\omega$). Due to the temperature-dependence of the electrical resistance ($R$) of the wire, $R$ is also modulated at the 2$\omega$ frequency. The voltage drop along the wire is $v = R(i_0\sin\omega t)$ and contains a modulated component ($v_{2\omega}$) at the 3$\omega$ frequency. The thermal conductivity of the wire is obtained with the use of a well-defined correlation between $v_{2\omega}$ and the thermal conductivity in the low-frequency regime. For using this method to measure a nanowire, however, it is important that the nanowire is metallic with a large temperature coefficient of resistance (TCR). Additionally, the contact electrical resistance needs to be eliminated so that the electrical resistance of the nanowire can be obtained. In four-probe measurements of the electrical resistance of very fine nanowires or nanotubes with the diameter on the order of 1 nm, however, the mesoscopic voltage probes are often invasive and can very well be the dominant source of scattering and hence resistance.41 Unless very weakly coupling or noninvasive voltage probes are used in the four probe measurement, the obtained four-probe resistance is not purely the intrinsic resistance of the nanostructure and cannot be used to obtain the temperature rise in the nanostructure. Moreover, electrons and phonons need to be at equilibrium during self-heating so that resistance thermometry can be employed. In SWCNTs and other nanowires under self-heating in a high electric field, electrons and phonons are not necessarily at equilibrium because the length of the nanostructure is comparable to the mean free paths for scattering between these carriers. This issue is often the case at low temperatures, where the mean free path can be long. Consequently, the 3$\omega$ self-heating method cannot be applied to obtain the temperature-dependent thermal properties of these nanostructures.

Recently, we have developed a method to characterize the thermal and thermoelectric properties of individual nanotubes and nanowires with the use of microelectromechanical systems (MEMS) devices.56 We have investigated several methods for the effective assembly of 1D nanostructures with the MEMS device. The successful integration of nanowires with MEMS not only allows us to characterize nanowire properties but also enables the integration of “bottom-up” synthesized nanowires with “top-down” patterned and etched microsystems for the large-scale fabrication of functional nanowire devices. Based
on this approach, we have demonstrated highly sensitive and stable nanowire sensors.\textsuperscript{42}

The following section discusses the experimental method, our recent measurement results of thermal and thermoelectric properties of single wall (SW) CNTs, semiconductor nanowires, and metal oxide nanobelts, and the integration of metal oxide nanobelts with MEMS for sensor applications.

II. Experimental Methods

Assembly of Nanowires with MEMS. Figure 1 shows a scanning electron micrograph (SEM) of the microdevice for thermal characterization of 1D nanostructures. Reproduced with permission from ref 49. Copyright 2005 American Chemical Society.

The wafer piece covered by the solution was rocked to induce the fluid motion in a direction perpendicular to the parallel electrode pair on the membranes. Aligned by the fluid motion, nanowires often crossed the two closely spaced Pt electrodes after the solution was dried uniformly on the wafer, while no nanowires were left bridging the long SiN nanobeams that were far apart from each other. Figure 2 shows a bismuth telluride (Bi,Te\textsubscript{1-x}) nanowire trapped on the two membranes of the microdevice. Reproduced with permission from ref 53. Copyright 2005 American Institute of Physics.

Figure 1. Scanning electron microscopy (SEM) image of the MEMS device for thermal characterization of 1D nanostructures. Reproduced with permission from ref 49. Copyright 2005 American Chemical Society.

Figure 2. SEM image of a Bi,Te\textsubscript{1-x} nanowire trapped between the two suspended membranes of the microdevice. The arrows indicate four short Pt lines deposited on the nanowire by a focused ion beam (FIB) deposition method. Reproduced with permission from ref 53. Copyright 2005 American Institute of Physics.

Figure 3. SEM image showing a suspended SWCNT (indicated by the arrow) grown between the two Pt electrodes of the microdevice. Reproduced with permission from ref 49. Copyright 2005 American Chemical Society.

To increase the assembly yield, we have investigated an electric field-directed assembly method. In this method, a drop of the nanowire suspension was deposited on a diced wafer piece that contained fourteen densely packed membrane structures. The wafer piece covered by the solution was rocked to induce a fluid motion in a direction perpendicular to the parallel electrode pair on the membranes. Aligned by the fluid motion, nanowires often crossed the two closely spaced Pt electrodes after the solution was dried uniformly on the wafer, while no nanowires were left bridging the long SiN beams that were far apart from each other. Figure 2 shows a bismuth telluride (Bi,Te\textsubscript{1-x}) nanowire trapped on the two membranes of the microdevice. Reproduced with permission from ref 53. Copyright 2005 American Institute of Physics.

II. Experimental Methods

Assembly of Nanowires with MEMS. Figure 1 shows a scanning electron micrograph (SEM) of the microdevice for thermal characterization of 1D nanostructures. Reproduced with permission from ref 49. Copyright 2005 American Chemical Society.

The following section discusses the experimental method, our recent measurement results of thermal and thermoelectric properties of single wall (SW) CNTs, semiconductor nanowires, and metal oxide nanobelts, and the integration of metal oxide nanobelts with MEMS for sensor applications.

II. Experimental Methods

Assembly of Nanowires with MEMS. Figure 1 shows a scanning electron micrograph (SEM) of the microdevice for thermal characterization of 1D nanostructures. Reproduced with permission from ref 49. Copyright 2005 American Chemical Society.

The wafer piece covered by the solution was rocked to induce the fluid motion in a direction perpendicular to the parallel electrode pair on the membranes. Aligned by the fluid motion, nanowires often crossed the two closely spaced Pt electrodes after the solution was dried uniformly on the wafer, while no nanowires were left bridging the long SiN beams that were far apart from each other. Figure 2 shows a bismuth telluride (Bi,Te\textsubscript{1-x}) nanowire trapped on the two membranes of the microdevice. Reproduced with permission from ref 53. Copyright 2005 American Institute of Physics.

Figure 1. Scanning electron microscopy (SEM) image of the MEMS device for thermal characterization of 1D nanostructures. Reproduced with permission from ref 49. Copyright 2005 American Chemical Society.

Figure 2. SEM image of a Bi,Te\textsubscript{1-x} nanowire trapped between the two suspended membranes of the microdevice. The arrows indicate four short Pt lines deposited on the nanowire by a focused ion beam (FIB) deposition method. Reproduced with permission from ref 53. Copyright 2005 American Institute of Physics.

Figure 3. SEM image showing a suspended SWCNT (indicated by the arrow) grown between the two Pt electrodes of the microdevice. Reproduced with permission from ref 49. Copyright 2005 American Chemical Society.

Additionally, we have used a chemical vapor deposition (CVD) method to grow individual SWCNTs bridging the two membranes of the microdevice. A solution containing catalyst made of Fe, Mo and Al\textsubscript{2}O\textsubscript{3} nanoparticles was spun on the suspended membranes, leaving catalyst particles on the membrane after the solution was dried. Alternatively, a sharp probe was used to deliver catalyst nanoparticles directly onto the two membranes. The suspended device was loaded in a 900 °C CVD tube furnace with flowing methane,\textsuperscript{47} yielding individual SWCNTs grown between two catalyst particles on the two Pt electrodes. Figure 3 shows a SWCNT grown by this method.

Thermal Conductance Measurement. The measurement device was placed in an evacuated cryostat. With a direct current (I) flowing to one of the two PRTs, Joule heat in the amount of $Q_h = IR_h$ was generated in this heating PRT with a resistance of $R_h$. Joule heat in the amount of $Q_h = 2IR_l$ was generated in the two Pt leads supplying the heating current to the PRT, where $R_l$ is the resistance of one Pt lead. Some of the heat ($Q_h$) is conducted through the sample from the heating membrane to the other membrane, which is denoted as the sensing membrane, and raised the temperature of the latter by $\Delta T_s$. In vacuum and with a small temperature rise on the heating membrane, $\Delta T_h$, heat transfer by radiation and air conduction is negligible compared to $Q_h$. The temperature distribution in each membrane is uniform, and the maximum temperature
difference in the heating (or sensing) membrane was calculated to be 1.8% (or 3.1%) of the temperature rise in the membrane.48

The total thermal conductance of the five identical supporting beams can be calculated as $G_b = \frac{Q_b + Q_l}{\Delta T_h + \Delta T_s}$, where $k_1$, $A$, and $L$ are the thermal conductivity, cross sectional area, and length of each beam, respectively. It can be shown that

$$G_b = \frac{Q_b + Q_l}{\Delta T_h + \Delta T_s}$$  \hspace{1cm} (1a)

The thermal conductance of the sample is obtained as

$$G_s = G_c \frac{\Delta T_s}{\Delta T_h - \Delta T_s}$$  \hspace{1cm} (1b)

Reduction of the Thermal Contact Resistance. The measured thermal resistance of the sample ($R_m = G_m^{-1}$) consists of the thermal resistance of the nanowire ($R_n$) and the total contact thermal resistance between the nanowire and the two membranes ($R_c$), i.e.,

$$R_m = R_n + R_c$$  \hspace{1cm} (6)

To reduce $R_c$, we used focused electron beam deposition or focused ion beam deposition to deposit a Pt layer locally on the contacts from precursor gases in a dual beam focused ion beam (FIB) tool. The deposited Pt layer is shown in Figure 4. It was found that the Pt layer deposited by focused ion beam reduces the obtained $R_m$ for about 10% for a 152-nm-diameter carbon nanofiber sample.48 To minimize the spreading of Pt and to prevent the conversion of residual precursor gas species absorbed on the sample surface into a conducting layer, we avoided imaging the sample using either the electron or ion beam right after the Pt deposition. Additionally, we avoided imaging the suspended segment of the nanowire with either ion beam or high-magnification SEM in order to prevent sample damage or contamination.

Electrical Conductance Measurement. There is often a native oxide layer on a nanowire, resulting in large electrical contact resistance between the nanowire and the Pt electrodes. This large contact resistance can be reduced by depositing a Pt line locally on top of the contact between the nanowire and the Pt electrode, using the focused electron beam or a focused ion beam deposition method. The two as-deposited Pt lines allowed for the simultaneous measurement of $S$ and $k$ of the nanowire. After the measurements of $S$ and $k$, two additional Pt lines can be deposited to connect the nanowire with the two Pt serpentine lines on the two membranes, as shown in Figure 2, so as to measure the four-probe electrical resistance ($R_{sp}$) of the nanowire. The two additional Pt lines were used as the outer electrodes for current source and drain, and the two middle Pt electrodes served as the voltage probes in the $R_{sp}$ measurement.

![Figure 4. SEM images showing a Pt layer deposited on the contact between a carbon nanofiber and a Pt electrode on the suspended device with the use of focused electron beam deposition (left) and focused ion beam deposition (right).](image)

Figure 4. SEM images showing a Pt layer deposited on the contact between a carbon nanofiber and a Pt electrode on the suspended device with the use of focused electron beam deposition (left) and focused ion beam deposition (right).

![Figure 5. Thermal conductance ($G$) of the SWCNT as a function of the temperature ($T$). Filled circles are the measurement results. The solid, dotted, and dashed lines are the ballistic thermal conductance of a 1-nm-, 2-nm, and 3-nm-diameter SWCNT, respectively, calculated by Mingo and Brodio. Reproduced with permission from ref 49. Copyright 2005 American Chemical Society.](image)

Figure 5. Thermal conductance ($G$) of the SWCNT as a function of the temperature ($T$). Filled circles are the measurement results. The solid, dotted, and dashed lines are the ballistic thermal conductance of a 1-nm-, 2-nm, and 3-nm-diameter SWCNT, respectively, calculated by Mingo and Brodio. Reproduced with permission from ref 49. Copyright 2005 American Chemical Society.
scattered after it exits the SWCNT and enters the opposite contact in order for the phonon flow to adopt the different temperature of the contact. Hence, the ballistic thermal conductance is essentially the maximum contact thermal conductance between the SWCNT and the two thermal reservoirs.

The calculated ballistic thermal conductance consists of only the contribution from phonons, i.e., \( G_\text{p} \). It has been calculated that the electron contribution (\( G_\text{e} \)) is negligible compared to \( G_\text{p} \) at moderate temperatures.\(^{51}\) In the temperature range between 110 and 300 K, the measured thermal conductance of the SWCNT consists of mainly the phonon contribution.

Mingo and Brodio\(^{50}\) noted that the measured \( G \) of an individual MWCNT\(^{52}\) was close to 40% of the ballistic thermal conductance of graphite for \( T < 300 \) K. Here, the measured \( G \) of the SWCNT is also proportional to the ballistic thermal conductance for SWCNTs in the temperature range between 100 K and 300 K. Phonons can be reflected when entering the two contacts from the CNT, lowering the thermal conductance of the CNT to a fraction of the ballistic thermal conductance. Additionally, local defects in the suspended CNT can reduce the phonon transmission coefficient, lowering \( G \) to a fraction of the ballistic thermal conductance. The \( G \) reduction due to these effects is approximately temperature-independent to the first order, and the resulting \( G \) vs \( T \) curve is proportional to the ballistic thermal conductance. On the other hand, the phonon—phonon Umklapp scattering process can reduce \( G \) from the ballistic thermal conductance, and a larger reduction is expected at higher temperatures, making the \( G \) vs \( T \) curve deviate from the trend of the ballistic thermal conductance. Since the measured \( G \) vs \( T \) curve is proportional to the ballistic thermal conductance at \( T < 300 \) K for both the SWCNT and the MWCNT, we conclude that Umklapp process was insignificant in both samples at \( T < 300 \) K.

The thermal conductivity of the SWCNT was calculated for the case that the diameter was 1, 2, and 3 nm, according to \( \kappa = G/LA \), where \( L \) is the length of the suspended segment of the SWCNT between the two membranes and \( A \) is the cross-sectional area, which is not a well-defined quantity for a SWCNT. We followed ref 50 to calculate \( A = \pi d \delta \), where \( \delta = 0.335 \) nm is the layer separation in graphite. The obtained \( \kappa \) in Figure 7 is on the same order of magnitude as the measurement results of an individual MWCNT,\(^{52}\) which is also shown in the figure. More accurate measurement of the thermal conductivity can be obtained if a through-hole is etched in the substrate of the microdevice to allow for accurate TEM measurement of the diameter of the SWCNT.

IV. Thermoelectric Properties of Bi\(_x\)Te\(_{1-x}\) Nanowires

We have measured the thermoelectric properties of two batches of bismuth telluride (Bi\(_x\)Te\(_{1-x}\)) nanowires with different atomic ratio or \( x \).\(^{53,54}\) The Bi\(_{1-x}\)Te\(_x\) nanowires were deposited in the nanopores of anodized alumina membranes (AAMs) with the use of an electrochemical deposition method.\(^{55}\) The growth direction of the nanowire was \( (11\overline{2}0) \), perpendicular to the c-axis. During the deposition, the Bi to Te atomic ratio in the electrolytes was 2 to 3 for the first batch and 1 to 1 for the second batch. High-resolution transmission electron microscopy (HRTEM) measurements of the nanowires revealed that these nanowires were single crystalline, and the native surface oxidation layer was about 2–10 nm thick. The chemical composition of one nanowire from the first batch and four nanowires from the second batch were obtained with the use of an energy dispersive spectrometer (EDS) of the HRTEM. The Bi-to-Te ratio of the nanowire from the first batch was 46% to 54%. The average EDS-obtained atomic fraction of the four nanowires from the second batch is 54% of Bi and 46% of Te with a standard deviation of 4.2%.

We have measured different properties of the four samples listed in Table 1 from the two different batches. Among these samples, sample 1 consists of two nanowires whereas all other samples consist of only one nanowire.

For sample 1 from the first batch, the obtained \( S \) in Figure 8 was positive, indicating that the nanowire was p-type. For this
120 K. On the other hand, all the four-probe resistance were linear, suggesting that the Schottky contact resistance was T were observed for sample 2 at 230 K, as shown in Figure 10. Linear two-probe 360 K, but show nonlinear behavior of a Schottky contact at T were rather linear in the temperature range between 240 and 356 x Bi 0.46 Te 0.54 crystal, 25 which has an atomic 4, four Pt electrodes were patterned on the nanowire segments Pt spreading was minimized during the Pt deposition. For sample 3, the nanowire was deposited on an oxidized silicon wafer, 4, four Pt electrodes were patterned on the nanowire by FIB and four Pt electrodes were patterned on top of the nanowire. Figure 9. SEM image of a bismuth telluride nanowire deposited on a substrate with four Pt contacts patterned on top of the nanowire. sample, the value of 260 µV/K at T = 300 K was 60% higher than that for bulk Bi0.46Te0.54 crystal, 25 which has an atomic ratio similar to that of the first batch, and 15% higher than that of Bi3Te3, which was found to have the largest S for p-type Bi1Te1−x, bulk crystals. 25 For sample 4 from the second batch, S was negative, suggesting electron-like majority carriers. As a comparison, bulk Bi1Te1−x single crystals are p-type for x > 0.37, n-type for x < 0.37, and bulk Bi0.485Te0.515 is highly p-doped. 25, 56 A different crystal phase might have developed for the second batch of nanowires with x ≈ 0.54, leading to the negative S.

The R4p of three samples has been measured. For samples 2 and 3, the nanowire was deposited on an oxidized silicon wafer, and four Pt electrodes were patterned on the nanowire by FIB deposition, as shown in Figure 9. There was no electrical leakage between two Pt electrodes after a 100 nm wide cut was made by FIB on the nanowire between the two electrodes, suggesting Pt spreading was minimized during the Pt deposition. For sample 4, four Pt electrodes were patterned on the nanowire segments laid on the suspended microdevice using focused ion beam (FIB) deposition, similar to Figure 2.

The two-probe current-voltage (I−V) curves for sample 1 were rather linear in the temperature range between 240 and 360 K, but show nonlinear behavior of a Schottky contact at T < 230 K, as shown in Figure 10. Linear two-probe I−V curves were observed for sample 2 at T ≥ 4 K and for sample 3 at T > 120 K. On the other hand, all the four-probe I−V curves were linear, suggesting that the Schottky contact resistance was eliminated in the four-probe measurement. The two-probe resistance (R2p) of sample 1 was calculated from the linear I−V curves and is shown in Figure 11 together with the R3p and R4p of sample 2 and sample 3 from the same batch.

The σ values calculated from R4p are shown in Figure 12 together with the reported room-temperature σ for bulk Bi0.46− Te0.54 and Bi0.485Te0.515 crystals. The room-temperature σ of sample 2 and sample 3, both from the first batch, were within 10% difference from those reported for bulk Bi0.46−Te0.54 and the Bridgman-type Bi0.46−Te0.54 single crystals. 56 While it has been found that the bulk σ decreases approximately linearly with increasing temperature as a result of increased electron−phonon scattering, 56 the σ of the nanowires shows a very weak temperature dependence. For sample 2, the decrease of σ with increasing temperature was somewhat similar to but at a much smaller slope than the bulk behavior. While the smaller slope can be attributed to a surface-scattering dominated electron mean free path that is insensitive to the temperature, the room-temperature σ was not reduced by enhanced surface scattering.

The behavior of sample 3 is somewhat similar to that of a semiconductor, for which an increase of the carrier concentration can lead to an increased σ with increased temperature. Additionally, the presence of local defects or conduction barriers in the nanowire can lead to the increased σ with temperature.

The σ of sample 4 from the second batch was almost independent of temperature. The room-temperature value was within 10% difference from those for bulk Bi0.485Te0.515 and Bridgman-type Bi0.51Te0.49 single crystals. 56

The κ of the three samples from the first batch were not obtained, and only the G of sample 1 was obtained. The κ of sample 4 from the second batch has been measured, and the measurement results are shown in Figure 13 together with the obtained G of sample 1 from the first batch.

For bulk Bi2Te3, the thermal conductivity peaks at a temperature below 75 K and decreases from 75 K to a minimum at about 270 K due to the Umklapp phonon−phonon scattering. 57 Additionally, the electron and phonon contributions to the thermal conductivity of bulk Bi2Te3 are approximately 46% and 54%, respectively, at 300 K. 25
In fact, for this nanowire from the second batch, the room-temperature value at 350 K was increased from 0.4 to 0.485 for the bulk crystals. The shift of the maximum for sample 4 was about 40% lower than those reported in ref 56 of bulk Bi$_{0.485}$Te$_{0.515}$ crystals, while the phonon wavelength ($\lambda$) on the order of 1 nm. For a surface roughness ($\sigma$) on the order of 1 nm, the scattering cross section is proportional to $(\sigma \lambda)^2$, where $\lambda$ is the wavelength and is much smaller for electrons than for phonons. Thus, one expects that the surface roughness may reduce $\kappa_p$ to a much larger extent than the reduction in $\sigma$. Because the chemical composition of the nanowire is different from that of the bulk crystal used for comparison, however, it is possible that an increase of $x$ from $x = 0.485$ for the bulk crystal to $x = 0.54$ for the nanowire possibly leads to an increase in $\sigma$ and a reduction in $\kappa_p$, although $\sigma$ was found to be reduced more than $\kappa_p$ when $x$ was increased from 0.4 to 0.485 for the bulk crystals. In fact, for this nanowire from the second batch, the ZT shown in Figure 15 was rather low due to the low $S$ value at this chemical composition.

For Bi$_{x}$Te$_{1-x}$ nanowires from the first batch with $x \approx 0.46$, we found that the $S$ was 15%–60% higher than and $\sigma$ was within 10% difference from the corresponding bulk values. We also observed signatures of increased phonon-boundary scattering that should reduce the lattice thermal conductivity. These evidences suggest that high ZT can potentially be obtained in Bi$_{x}$Te$_{1-x}$ nanowires with an optimized atomic ratio.

V. Thermal Conductivity of Metal Oxide Nanowires

We have employed the microdevice to measure the thermal conductivity of 53-nm-thick, 204-nm-wide, and 64-nm-thick, 108-nm-wide SnO$_2$ nanobelts in the temperature range of 80–350 K. As shown in Figure 16, the obtained $\kappa$ values were found to be substantially lower than the bulk values. To understand the origins of the reduced $\kappa$, we have compared the measurement results with a full dispersion transmission function calculation. In the calculation, the phonon dispersion relation was obtained for the rutile structure. Matthiessen’s rule was used to obtain the frequency-dependent relaxation time of phonons as $\tau_e^{-1} = \tau_U^{-1} + \tau_i^{-1}$. Here, $\tau_U^{-1}$, $\tau_i^{-1}$ are the Umklapp, boundary, and impurity scattering rates, respectively. A phenomenological expression for the Umklapp scattering rate has been used: $\tau_U^{-1} = Be^{-\omega^2 T}$, where $B$ and $b$ are two fitting parameters and $\omega$ is the phonon frequency. The boundary and impurity scattering rates can be written as $\tau_b^{-1} = v/FL$ and $\tau_i^{-1} = A\sigma^2$. Here, $v$ is the phonon group velocity, $L$ is the thickness for the nanobelt, $F$ is a parameter representing specularity of phonon reflection at the boundaries, the $FL$ product is referred as the effective thickness of the sample, and $A$ is a parameter arising from Rayleigh scattering of phonons by atomic scale impurities.

After obtaining the fitting parameters from the measurement data obtained for bulk crystals, the thermal conductivity of
nanowires was calculated for different effective thickness $F_L$, with other parameters kept as the same as the bulk values. The solid lines of Figure 16 are two sets of calculated $\kappa$ in the (101) direction as a function of temperature. One can see that the measurement data of the 64-nm-thick and 53-nm-thick $\text{SnO}_2$ nanobelt agree rather well with the calculation results with $F_L = 64$ and 39 nm, respectively. This suggests that an increased phonon-boundary rate alone can well account for the significantly suppressed $\kappa$ of the nanobelts. Increased phonon-boundary scattering alone can also account for another measurement result of the suppressed $\kappa$ of silicon nanowires, except for a 22-nm-diameter Si nanowire, the smallest one of the samples, where other phonon confinement effects may have also play a role.

VI. Integration of Nanowires with Microdevices for Sensor Systems

In addition to providing an ideal system for investigating phonon transport in dimension-confined systems, the single-crystal metal oxide nanobelts are very attractive for sensor applications. Metal oxide sensors are commonly used for the detection of inflammable and toxic gas species. The sensing mechanism is based on resistivity change upon surface reduction—oxidation (redox) reactions with gas species. Because only the surface layer is affected by the reaction, the sensitivity of a metal oxide sensor increases for decreasing thickness, motivating the development of thin film metal oxide sensors. However, one common problem with polycrystalline thin film metal oxide sensors is grain boundary poisoning that limits the repeatability and long-term stability. Because the nanobelts are as thin as 10 nm, which approaches the electrostatic screening length, almost the entire thickness is affected by redox reactions with gas species, leading to high sensitivity.

Metal oxide sensors require a high operating temperature to enhance redox reactions so as to achieve the optimum sensitivity. This requirement has motivated us to integrate nanobelts with thermally isolated suspended micro-heater devices that can reduce the power consumption so that battery-operated miniaturized sensor arrays can be obtained. More importantly, a major challenge for the development of sensor technologies based on nanobelts or other “bottom-up” synthesized nanostructures is the large-scale manufacturing of well-organized nanostructure sensor arrays. To address this challenge, we have investigated the assembly of nanobelts with the “top-down” fabricated MEMS device that was developed for thermal characterization of nanowires. We found that positive DEP can be used for the assembly of nanobelts with the MEMS device at a high yield.

The two membranes of the microdevice were supported by long, low-thermal conductivity silicon nitride (SiN$_x$) beams and were thermally isolated from the substrate. The temperature of the membrane can be increased and monitored with the use of the PRT serpentine patterned on the membrane. With only 3.8 mW power consumption in the Pt RT, the membrane temperature can be raised to 500 °C.

We have tested the device shown in Figure 17 that had one nanobelt trapped between the two Pt electrodes. We used a FIB method to deposit a thin Pt coating on the nanobelt so as to improve the electrical contact. The sensor was mounted in a small flow-through chamber and tested with $\text{NO}_2$ and dimethyl methyl phosphonate (DMMP) gases diluted in air. Figure 18 shows the response of the nanobelt sensor to 0.2, 0.5, 0.9, 1.7, and 10 ppm $\text{NO}_2$ balanced with air when the nanobelt temperature was 200 °C. The voltage applied to the nanobelt was 2 V. Without the contact treatment, on the other hand, the bunch of nanobelts in the flow-through chamber was purged with room air. The recovery was much faster than that of the bunch of nanobelts tested in an earlier work. It took less than three minutes, which could be the time required for completely purging $\text{NO}_2$ out of the flow-through chamber, for the single nanobelt sensor to be refreshed. On the other hand, the bunch of nanobelts in the earlier work was not completely refreshed 40 min after the $\text{NO}_2$ gas was shut off.

The faster recovery observed in the nanobelt was attributed to the absence of grain boundaries or interfaces along the isolated nanobelt of a single-crystal structure. In fact, we found that the Pt coating deposited on the nanobelt by the FIB method was critical for eliminating the sensor poisoning effect. Without this contact treatment, it was observed that even a sensor consisting of just a single nanobelt could be poisoned, i.e., the current could not recover fully after the $\text{NO}_2$ gas was shut off. With the contact treatment, on the other hand, this poisoning effect was completely eliminated, suggesting that the single-crystal nanobelt itself was not poisoned but a poor contact between the nanobelt and the Pt electrode could still be poisoned. This finding suggests that the slow recovery observed in the...
bunch of nanobelts tested in the earlier work was due to poisoning either at the poor contacts between the nanobelts and the electrodes or at the interfaces between connecting nanobelts in the bunch of nanobelts. The elimination of such poisoning is essential for obtaining high sensor stability and repeatability.

We have also tested another as-assembled nanobelt sensor consisting of a single nanobelt with diluted DMMP gas obtained from a permeation tube containing a liquid phase of DMMP. Figure 19 shows the sensor response to DMMP gas balanced with air when the device was Joule-heated to 500 °C. The current through the nanobelt increased for about 5% and 3%, respectively, in respond to the 78 and 53 ppb DMMP diluted in air. This sensitivity can potentially be enhanced to sub-ppb levels by doping the nanobelt with CaO, a catalytic additive for increasing the sensitivity of metal oxide sensors for DMMP detection. Most importantly, in contrast with thin film metal oxide sensors for DMMP detection, the as-assembled nanobelt sensor did not show any poisoning effect upon exposure to DMMP and the current recovered quickly as DMMP was shut off.

VII. Concluding Remarks and Future Directions

These experiments employing MEMS devices show that CNTs have super-high thermal conductivity with potential applications as heat spreaders in electronic packaging applications, that the thermal conductivity of semiconductor and metal oxide nanowires are suppressed due to phonon-boundary scattering, and that high thermoelectric figure of merit can potentially be obtained in bismuth telluride and other semiconductor nanowires. It was found in our measurements that the thermal and thermoelectric properties of individual nanowires and nanotubes are largely influenced by the crystal structure including crystalline quality, chemical composition, and surface roughness. In the experiments reviewed in this article, the physical properties and crystal structure were not obtained on the same nanostructures and the correlation between the crystal structure and thermoelectric properties could not be established. We have a current effort to improve the MEMS device in order to characterize the structure and properties of the same individual nanostructure. In the new design, a through hole is etched in the substrate of the suspended device to allow for transmission electron microscopy (TEM) and energy dispersion spectroscopy (EDS) measurements of the nanostructure. The obtained crystalline quality, surface roughness, and chemical composition can be correlated with the obtained thermal and thermoelectric properties. Additionally, micro Raman spectroscopy or Raleigh scattering measurements can also be employed to characterize the nanostructure assembled on the microdevice. These measurements will potentially provide a comprehensive set of structure and property data on the same nanostructure, which will be invaluable for improving our understanding of the effects of nanostructures on charge and phonon transports.

Furthermore, a method has been developed elsewhere for measuring the mechanical properties such as elastic modulus of individual CNT. This mechanical measurement method can potentially be integrated with the microdevice that we developed for thermal measurements. The integration can be obtained with the addition of a microactuator to control the lateral movement of one of the two SiN membranes, so that the thermal property can be measured as a function of stress in the nanowire. The obtained results can be highly useful, because the thermal and thermoelectric properties depend on stress in the materials. In fact, high ZT has been observed in bulk crystals under a compressive stress, and the charge transport property in CNTs has been known to be sensitive to bending.

In the direction of the large-scale integration of nanowires for sensor systems, the recent development of controlled nanowire assembly and growth methods can enable wafer-scale fabrication of micromachined sensor arrays containing multiple layers of different surface-functionalized nanowire sensor elements with different catalytic additives for ultrasensitive and stable detection of chemical species and biomolecules. It has been reported that the Langmuir–Blodgett (L–B) method can allow for the large-scale assembly of aligned nanowire monolayers. Similar to a metal oxide thin film deposited using a physical vapor deposition (PVD) method, the L–B nanowire monolayer can be patterned using conventional photolithography and etching. Multiple metal oxide nanowire films can be sequentially deposited using the room-temperature L–B method and patterned using photolithography. The room-temperature L–B deposition eliminates mass diffusion between adjacent layers of metal oxides, a major problem in the fabrication of thin film metal oxide sensor arrays using high-temperature PVD of multiple metal oxide films. This method will likely allow for the fabrication of selective gas sensor arrays consisting of functionalized metal oxide nanobelts integrated with a MEMS platform that consists of a microchromatography column and preconcentrator for gas separation and preconcentration. Alternatively, the selectivity can also be obtained with the use of a pattern recognition approach, where an array of sensors made of different metal oxides with different catalytic additives generates a distinct response pattern for a gas species or mixture.

Acknowledgment. This work is supported in part by the Chemical and Transport Division of National Science Foundation, Office of Naval Research (Program Manager: Dr. M. E. Gross), and National Aeronautic and Space Administration through a subcontract from Eloret Corporation. The authors thank C. G. Jin, P. Kim, D. Li, X. G. Li, A. Majumdar, N. Mingo, Z. L. Wang, Z. Yao, and Q. Ye for collaboration in this research.

References and Notes

(2) Lieber, C. M. RSB Bull. 2003, 28, 486.