MICROFABRICATED WORKBENCH DESIGNED TO INVESTIGATE THERMOELECTRIC PROPERTIES OF LOW-DIMENSIONAL MATERIALS

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ABSTRACT

Microfabricated workbench has been developed to investigate thermoelectric properties of low-dimensional materials. The central area of the chip has high density of test sites for improving the probability of landing single nanowire or nanotube at desired position on the workbench when it is drop cast from solution. This obviates the extensive effort of nanomaterial manipulation required for measurement and provides a reliable platform to measure the thermal, thermoelectric, and electrical characterization across various nanomaterials. To demonstrate the efficacy of the device, the three thermal and electrical transport properties and thermoelectric figure of merit ZT of GaAs/MnAs core/shell nanowire were successfully measured using the workbench at temperatures ranging from 150 K to 300 K.

INTRODUCTION

Low-dimensional materials (LDMs), such as nanoribbons, nanowires, and nanotubes, have attracted great attention as thermoelectric materials due to their potential for having improved thermoelectric efficiency [1, 2]. However, the lack of a thermal equivalent of an “ammeter” makes the measurement of thermal and thermoelectric properties (thermal conductivity and Seebeck coefficient) in LDMs challenging. Although thermal workbenches have been reported earlier, these devices require considerable effort in terms of placement and alignment of the LDMs on the workbench or are dedicated for measurement of a single material and cannot be used for a variety of LDMs [3, 4]. In this work, we have designed and fabricated micro-workbenches with high surface density of test-sites in the central area of the chip to enhance the probability of landing a single LDM at the desired positions without any physical manipulation when drop casting from a solution containing the LDMs.

Figure 1: Mask overview of the overall workbench chip. Insets show the zoom-in of the workbenches and an oblique view SEM of the fabricated workbench showing the undercut tip areas.

The workbench consists of several closely placed thermally isolated platforms (Figure 1). Each platform has an integrated heater, thermocouple temperature sensor and platinum contact pad. The heater and thermocouple junction are placed at tip of the thermally isolated and freestanding part of the platform. The platinum pad is on top of platform and provides electrical connection to the LDM and is electrically isolated from the thermocouple and heater. 60 platform tips are located in $250\text{ }\mu\text{m} \times 250\text{ }\mu\text{m}$ central area of the workbench for improving the probability of landing a single LDM bridging two neighboring platform tips when solution containing materials is drop cast. Neighboring platform tips are $1\text{ }\mu\text{m}$ apart from each other (inset, Figure 1). Polysilicon-gold thermocouple is used for high-sensitivity temperature measurements.

FABRICATION PROCESS

The fabrication process is shown in Figure 2. First, silicon nitride ($0.3\text{ }\mu\text{m}$)/silicon oxide ($1.4\text{ }\mu\text{m}$)/silicon nitride ($0.3\text{ }\mu\text{m}$) is deposited on silicon wafer as a stress-compensated stack using low pressure chemical vapor deposition (LPCVD) and deposition of polysilicon (LPCVD, $0.4\text{ }\mu\text{m}$, boron-doped, 10^{19} cm^{-3}) is followed. The polysilicon layer is patterned to define heater and one leg of thermocouple using photolithography and reactive ion etching (RIE). And titanium (20 nm)/gold (400 nm) layer is deposited and patterned using lift-off process to complete the thermocouple structure (Figure 2(a)). Afterward, aluminium oxide (20 nm)/hafnium oxide (30 nm) is deposited using atomic layer deposition (ALD), which electrically insulates heater and thermocouple from the following titanium (30 nm)/platinum (100 nm)/nickel (150 nm) layer patterned using lift-off process (Figure 2(b)). RIE and deep reactive ion etching (DRIE) then are performed to etch the ALD layer, stress-compensated stack and silicon substrate using nickel layer and photoresist as a mask. Lastly, the silicon substrate is etched in an isotropic manner by xenon

Figure 2: Schematic diagram of fabrication process.

difluoride etching and wet etching of nickel is followed (Figure 1(c)). Placement of the LDM on workbench is achieved by drop casting from solution. And focused ion beam (FIBID) or electron beam induced deposition (EBID) of platinum is used to provide mechanical anchors and good electrical and thermal contact between the material and platinum pads of workbench (Figure 1(d)).

CALIBRATION OF THERMOCOUPLE

Polysilicon-gold thermocouple was made for measuring the temperature of platform tips. However, a calibration is necessary for extracting temperature rise from the thermocouple voltage. For such calibration, the workbench has a special structure where two platform tips connected to each other through a 2 μm -wide bridge consisting of stress-compensated stack/ALD/titanium/platinum layers (inset, Figure 3(a)) and was used as follows.

Seebeck coefficient at 300 K was obtained using heater, on same platform with thermocouple, as a thermistor. Initially, resistance of heater was measured with small current ($\pm 20 \mu\text{A}$) using Keithley 2400 at a temperature of 310 K. Thereafter, resistance of heater and thermocouple voltage were simultaneously measured, at an ambient temperature of 300 K, while sweeping current through the heater from 20 μA to 600 μA . Keithley 2182A nanovoltmeter was used to measure the thermocouple voltage. Figure 3(a) shows resistance of heater and thermocouple voltage as a function of heating power. By matching the resistance of the heater corresponding to that obtained at 310 K, the thermocouple voltage at 310 K was obtained. The Seebeck coefficient of thermocouple would be calculated by dividing the extracted thermocouple voltage with temperature rise of thermocouple junction. COMSOL finite element model (FEM) simulation was performed to check the temperature difference between heater and thermocouple junction. It was determined that the temperature rise

of the thermocouple junction is 24.1 % smaller than that of heater which allowed accurate calibration of the thermocouple junction from that of heater.

The Seebeck coefficient at lower temperatures was obtained using the value at 300 K. If it is supposed that Seebeck coefficient changes linearly with respect to temperature and temperature of thermocouple junction changes linearly according to heating power, thermocouple voltage can be expressed as

$$S(T + \Delta T) = S(T) + a\Delta T \quad (1)$$

$$V_{TC} = \int_0^{\Delta T} S(T + \Delta T') d\Delta T' = S(T)\Delta T + \frac{a}{2}\Delta T^2 \quad (2)$$

$$= S(T)bP_H + \frac{ab^2}{2}P_H^2$$

where S is Seebeck coefficient, T is the temperature of cryostat, ΔT is temperature rise of thermocouple junction, P_H is heating power, a is the rate of change of Seebeck coefficient with respect to temperature, and b is a ratio of temperature rise of thermocouple junction to heating power. Differentiating equation (2) gives

$$\frac{\partial V_{TC}}{\partial P_H} = S(T)b + ab^2P_H \quad (3)$$

Inset of Figure 3(b) shows the derivative of thermocouple voltage with respect to heating power as a function of heating power at the cryostat temperature of 280 K. In this case we used the heater of neighboring platform that is thermally connected, through a bridge, to the platform with thermocouple. We found that using heater and thermocouple of the same platform resulted in a noisy derivative of thermocouple voltage. Equation (1) and (3) allow us to calculate $S(280)$ using the intercept and the slope of inset of Figure 3(b) and known value of $S(300)$. The Seebeck coefficient of thermocouple was obtained using this method at temperatures ranging from 300 K down to 15 K (Figure 3(b))

Figure 3: (a) Resistance of heater and thermocouple voltage as a function of heating power at 300 K (b) Seebeck coefficient of polysilicon-gold thermocouple as a function of temperature. Inset shows derivative of thermocouple voltage with respect to heating power as a function of heating power at 280 K (V_{TC} : thermocouple voltage, P_H : heating power).

MEASURING THERMOELECTRIC PROPERTIES OF LOW-DIMENSIONAL MATERIALS

The workbench on which LDM was anchored as explained previously is placed in a vacuum cryostat with pressure below 5×10^{-6} Torr to minimize the effect of parasitic heat transport through ambient air. And a sinusoidal voltage with angular frequency ω is applied to polysilicon heater of one platform using Keithley 3390 function generator and it in turn produces 2ω temperature fluctuation. Temperature rise of heated or neighboring platform tip is obtained by measuring 2ω voltage of polysilicon-gold thermocouple using SR 830 lock-in amplifier. And 2ω voltage between two platinum pads is also measured using lock-in amplifier, which represents thermoelectric voltage induced in LDM-platinum thermoelectric circuit. The amount of heat dissipated in the heater (heating power) is calculated by measuring applied voltage and current to the heater using Keithley 2001 and Keithley 2000 multimeters.

Thermal Conductivity

Initially, the thermal conductivity of LDM at 300 K is extracted by matching FEM simulation to measured heating power and temperature rise of both thermocouple junctions. For FEM simulations, bulk values of thermal conductivity of gold and silicon were used and the thermal conductivity of platinum was extracted using Wiedemann-Franz law from measured electrical conductivity. The thermal conductivity of rest of the materials was obtained from reference papers [5-9]. However, FEM cannot be used at low temperatures since the temperature dependence of thermal conductivity of all materials constituting workbench is not available. For this reason, thermal conductivity of LDM at lower temperatures

Figure 4: Equivalent thermal circuit of two platforms connected to each other through LDM.

is obtained using an equivalent thermal circuit (Figure 4).

The equivalent thermal circuit was built based on the fact that the heat generated in heater will transfer to the substrate (heat sink) through LDM, and the amount of heat sinking directly to the bottom of the substrate. Another is path through LDM. Considering it, one obtains

$$P_H = P_1 + P_2 \quad (4)$$

where P_H , P_1 , and P_2 are heating power, the amount of heat flowing through LDM, and the amount of heat sinking directly to the bottom of the substrate. Temperature rise of heater of heated platform and thermocouple junction of neighboring platform can be expressed as

$$\Delta T_{H(H)} = P_1(R_{LDM} + R_N + R_C) = P_2 R_H \quad (5)$$

$$\Delta T_{N(TC)} = P_1 R_N \quad (6)$$

where $\Delta T_{H(H)}$, $\Delta T_{N(TC)}$, R_{LDM} , R_N , R_H are the temperature rise of heater of heated platform, temperature rise of thermocouple junction of neighboring platform, thermal resistance of LDM, thermal resistance from thermocouple junction of neighboring platform to bottom of substrate, thermal resistance from heater of heated platform to bottom of substrate, respectively. R_C represents sum of thermal resistance from heater to LDM and from LDM to thermocouple junction. Using equation (4) and (6), equation (5) can be reorganized to

$$R_{LDM} = \frac{P_H}{\Delta T_{N(TC)}} R_H R_N - R_H - R_N - R_C \quad (7)$$

R_H , R_N , and R_C at 300 K are extracted by FEM. However, we still need to know how these change with temperature for calculating R_{LDM} at various temperatures. In addition, temperature rise of thermocouple junction of neighboring platform produced by heat flow through substrate from heated platform needs to be subtracted from measured $\Delta T_{N(TC)}$ for accurate measurement. These could be investigated using platforms on which LDM is not anchored. The voltage was applied to heater and heating power and temperature rise of thermocouple junctions of heated and neighboring platforms was measured at various temperatures. We could then acquire temperature dependence of thermal resistance from platform tip to heat sink by dividing temperature rise of thermocouple junction by heating power. R_H and R_N should have same tendency with it even if there might be a small variation in magnitude caused by distance between heater and thermocouple junction. Considering that thermal resistance from platform tip to heat sink mainly originates from thermal resistance of suspended part of platform, it is also reasonable to assume that R_C also has same temperature dependence. And, from this measurement, we also obtained the ratio of temperature rise of thermocouple junction of neighboring platform to that of heated platform, which is used to subtract the temperature rise produced by heat transfer through substrate from measured $\Delta T_{N(TC)}$. We found that the amount of heat transferred through substrate is equivalent to that through LDM having thermal conductance of $\sim 1 \times 10^{-8}$ W/K. Therefore, if the thermal conductance of LDM is comparable to or smaller than this value, the parasitic

heat flow will reduce the accuracy of the measurement of the thermal conductivity of LDM.

Seebeck Coefficient

Seebeck coefficient of LDM can be calculated by

$$S_{LDM} - S_{Pt} = \frac{V_{TE}}{\Delta T_{H(TC)} - \Delta T_{N(TC)}} \quad (8)$$

where S_{LDM} , S_{Pt} , V_{TE} , and $\Delta T_{H(TC)}$ are Seebeck coefficient of LDM, Seebeck coefficient of platinum, and measured thermoelectric voltage, and temperature rise of thermocouple junction of heated platform, respectively. In most cases, S_{Pt} is negligibly small compared to S_{LDM} because we are interested in material which has high Seebeck coefficient. However, in case that S_{LDM} is small, S_{Pt} needs to be added to the measured Seebeck coefficient. Also, there might be a temperature difference between thermocouple junction and end of LDM if they are positioned far from each other or thermal conductance of LDM is large. Then, instead of $\Delta T_{H(TC)} - \Delta T_{N(TC)}$, we can use temperature difference between two ends of LDM calculated as

$$\Delta T = P_1 R_{LDM} = \Delta T_{N(TC)} \frac{R_{LDM}}{R_N} \quad (9)$$

Electrical Conductivity

Electrical conductivity is measured using two platinum layers connected to each other through LDM. However, resistance of platinum layer should be subtracted from measured resistance. One method is to calculate resistance of platinum layer by using the resistivity measured with calibration structure (inset, Figure 3(a)). Another method is to electrically connect platform tip with one right next to it using FIBID and measure the resistance of the platinum structures. In addition, two probe measurements can also have errors arising from contact resistance but in the case of highly conductive LDMs this is not such a major source of inaccuracy.

Thermoelectric Properties of GaAs/MnAs Core/shell Nanowires

We investigated thermoelectric properties of Gallium Arsenide (GaAs)/Manganese Arsenide (MnAs) core/shell nanowire using the workbench. GaAs/MnAs core/shell nanowire is a suitable material for investigating magneto-thermoelectric effects, such as magneto-caloric, magneto-Seebeck, and spin-Seebeck effects, of quasi-one-dimensional system because MnAs is a ferromagnetic material whose Curie temperature is near room temperature. As a preliminary experiment for magneto-thermoelectric effects, we measured thermoelectric properties as a function of temperature. The nanowire was grown by molecular beam epitaxy and, according to TEM analysis, cross-section of nanowire is a hexagon and the longest diagonal of GaAs core and the thickness of MnAs shell are estimated to be 200 nm and 15 nm, respectively. IPA solution containing nanowires was drop cast on workbench and FIBID of

Figure 5: (a) SEM images of workbench on which GaAs/MnAs core/shell nanowire is anchored (b) Color plot of temperature distribution at 300 K (COMSOL finite element model simulation).

Figure 6: (a) Electrical conductivity of MnAs shell, Seebeck coefficient of nanowire-platinum thermoelectric circuit (b) Thermal conductivity and ZT of nanowire as a function of temperature.

platinum was used to make mechanical contact and improve electrical and thermal contact between nanowire and platinum pad. Figure 5(a) is SEM image of workbench on which single GaAs/MnAs core/shell nanowire is anchored and Figure 5(b) shows temperature distribution of the sample that is FEM simulation result.

Figure 6(a) shows temperature dependence of electrical conductivity of MnAs shell and Seebeck coefficient of nanowire-platinum thermoelectric circuit. The electrical transport (electrical conductivity and Seebeck coefficient) of nanowire are dominated by MnAs shell because GaAs core is intrinsic. Considering Seebeck coefficient of platinum is -5μ V/K [10], absolute Seebeck coefficient of MnAs shell is -16.9μ V/K at 300 K which is larger than previously reported Seebeck coefficient of bulk MnAs (-13μ V/K) [11]. It might be explained by quantum size effect on Seebeck coefficient.

Figure 6(b) shows the temperature dependence of thermal conductivity and thermoelectric figure of merit ZT of the nanowire. In contrast with electrical transport, most part of thermal transport occurs through the GaAs core because of its large cross-sectional area and dominant lattice thermal conductivity. The thermal conductivity of nanowire is 7.5 W/m-K at 300 K. It is smaller than theoretical value (20 W/m-K) of 200 nm-diameter GaAs nanowire which is recently reported [12]. It decreases with decreasing temperature whereas theoretical value has a maximum value near 100 K. These are thought to be because GaAs core has stacking faults perpendicular to the wire axis. In some regions, the nanowires undergo a transformation in crystal structure from zinc blende with a [111] growth direction to wurtzite with a [0001] growth direction [13]. It would increase phonon-boundary scattering and lead to smaller thermal conductivity than the theoretical value. Furthermore, it would make phonon-boundary scattering more dominant than Umklapp phonon-phonon scattering that results in the increasing

thermal conductivity with decreasing temperature. For calculating ZT, the Seebeck coefficient of platinum [12] was added to the measured Seebeck coefficient of nanowire-platinum thermoelectric circuit. Also, the electrical conductivity was recalculated with dimension of core and shell instead of only shell because we need electrical conductivity of core/shell nanowire instead of that of shell for obtaining ZT.

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