Supplementary Material (ESI) for Lab on a Chip

ELECTRONIC SUPPLEMENTARY INFORMATION FOR

Microfabricated Thermal Modulator for Comprehensive Two-Dimensional Micro Gas Chromatography: Design, Thermal Modeling, and Preliminary Testing

S.-J. Kim, S. M. Reidy, B. P. Block, K. D. Wise, E. T. Zellers, and K. Kurabayashi

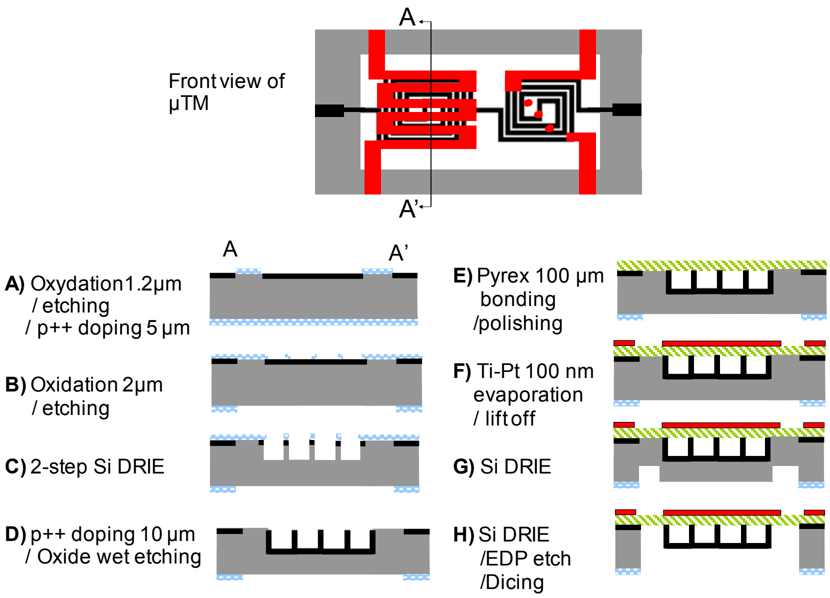

Figure S1. Fabrication process flow for the μTM . (**A**) The process was started with a silicon wafer of 4 inches in diameter and 500 μm in thickness. We thermally grew a 1.2-μm-thick oxide layer on the both sides to serve as a diffusion barrier of the boron doping. The backside was covered by photoresist and the frontside was photolithographically patterned to define the microchannels and the oxide was removed by dipping in buffered hydrofluoric acid (BHF). The exposed areas were doped with boron to a depth of 5 microns in a boron diffusion furnace. (**B**) A second thermal oxide layer was grown on both sides of the wafer as a diffusion barrier for the second boron doping. After separate patterning steps on each side of the wafer, the oxide was removed with BHF. (**C**) Microchannels (140 μm-deep and 250 μm-wide) and inlet-outlet ports (400 μm-deep and 400 μm-wide) were formed by two-step Si deep reactive etching (DRIE). (**D**) A second boron doping step was performed to protect the microchannels in the subsequent Si wet-etching process (step **H**) and the frontside oxide was removed (in BHF) in preparation for the anodic bonding process. (**E**) A glass wafer (Pyrex 7740, Sensors Prep Services, 100 μm thickness) was cleaned in sulfuric-acid solution and anodically bonded to the frontside of the wafer. (**F**) Patterned microheaters and temperature sensors (electronbeam evaporated Ti/Pt; 20 nm/100 nm) were then fabricated on the glass layer by a lift-off process in an acetone solution. (**G**) DRIE was used to define the channel areas at the backside of Si wafer. (**H**) The remaining Si around the microchannels was removed by a combination of DRIE and wet-etching with ethylene-diamine-pyrocatechol solution. Finally, the wafer was diced into individual chips.

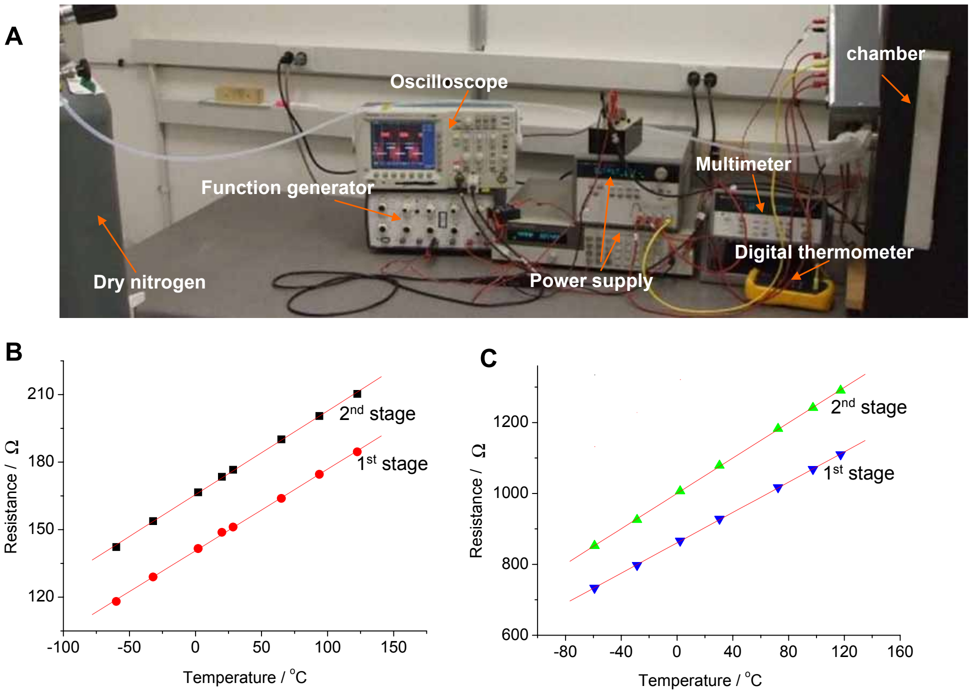

Figure S2. Experimental setup and calibration curves. (A) Experimental setup for the temperature calibration and thermal measurements. (B and C) Temperature calibration of microheaters and temperature sensors. Electrical resistances of the microheaters (B) are several times lower than those of the temperature sensors (C). Resistances (R) of the heaters and the temperature sensors are linearly proportional to the temperature (T). That is, $R = a + bT$ where a and b are constants that are determined by the linear curve fitting of each resistor.

Lumped Thermal Model

We developed a series of equations to describe the thermal response of each stage and the thermal crosstalk between the stages. To solve the ordinary differential equations, we used the ode45 solver in MATLAB (The MathWorks, www.mathworks.com). The equations were derived from a balance among the energy rates (unit: W) at three control volumes. Each control volume includes the thermal mass of the first stage, the second stage, and the rim, respectively (See Fig. 1C). The energy rates consist of the change of energy storage, conduction, convection, and radiation per unit time. We define the heat transfer as positive when the heat comes into the control volume. The resulting equations are coupled as follows:

$$\dot{E}_{1\_\mathrm{sys}} = \dot{E}_{1-\mathrm{TEC}} + \dot{E}_{1-3} + \dot{E}_{1-2} + \dot{E}_{1\_\mathrm{gen}} + \dot{E}_{1\_\mathrm{conv}} + \dot{E}_{1\_\mathrm{rad}} \quad (1)$$

$$\dot{E}_{2\_\mathrm{sys}} = \dot{E}_{2-\mathrm{TEC}} + \dot{E}_{2-3} + \dot{E}_{2-1} + \dot{E}_{2\_\mathrm{gen}} + \dot{E}_{2\_\mathrm{conv}} + \dot{E}_{2\_\mathrm{rad}} \quad (2)$$

$$\dot{E}_{3\_\mathrm{sys}} = \dot{E}_{3-\mathrm{TEC}} + \dot{E}_{3-1} + \dot{E}_{3-2} + \dot{E}_{3\_\mathrm{conv}} + \dot{E}_{3\_\mathrm{rad}} \quad (3)$$

where the numbers (1, 2, and 3) in the subscript correspond to the first stage, the second stage, and the rim, respectively. $\dot{E}_{\mathrm{i\_sys}}$ (i = 1, 2, 3) is the rate of energy storage for each thermal mass (the first stage, the second stage, and the rim) and is expressed as follows:

$$\dot{E}_{\mathrm{i\_sys}} = (\rho C_{\mathrm{p}} V)_{\mathrm{i}} \frac{dT_{\mathrm{i}}}{dt} \quad (4)$$

$$(\rho C_{\mathrm{p}} V)_{\mathrm{i}} = (\rho C_{\mathrm{p}} V)_{\mathrm{Si\_i}} + (\rho C_{\mathrm{p}} V)_{\mathrm{Pyrex\_i}} \quad (5)$$

where ρ, C_{p}, and V are the density, the specific heat capacity, and the volume of each material (Si and Pyrex), respectively. T_{i} and t are the temperature of the i$^{\mathrm{th}}$ thermal mass and time, respectively. $\dot{E}_{\mathrm{i\text{-}TEC}}$ is the conductive heattransfer between the i$^{\mathrm{th}}$ thermal mass and the thermoelectric cooler (TEC):

$$\dot{E}_{\mathrm{i\_TEC}} = \frac{k_{\mathrm{air}} A_{\mathrm{i-TEC}}}{L_{\mathrm{air}}} (T_{\mathrm{i}} - T_{\mathrm{TEC}}) \quad (6)$$

where k_{air} is the thermal conductivity of air (0.0294 W m^{-1}K^{-1}). $A_{\mathrm{i\text{-}TEC}}$, L_{air} , and T_{TEC} are the facing area of the i$^{\mathrm{th}}$ thermal mass to the TEC, the air-gap, and the TEC temperature, respectively. $\dot{E}_{\mathrm{i\text{-}j}}$ (i, j = 1, 2, 3, but i ≠ j) is the conductive heat transfer between thermal masses:

$$\dot{E}_{\mathrm{1\text{-}2}} = -\frac{k_{\mathrm{Si}} A_{\mathrm{IC}}}{L_{\mathrm{IC}}} (T_1 - T_2) - \frac{k_{\mathrm{Pyrex}} A_{\mathrm{1\text{-}2\_Memb}}}{L_{\mathrm{IC}}} (T_1 - T_2) \quad (7)$$

$$\dot{E}_{1\text{-}3} = -\frac{k_{\mathrm{Si}} A_{\mathrm{IC}}}{L_{\mathrm{IC}}}(T_1 - T_3) - \frac{k_{\mathrm{Pyrex}} A_{1\text{-}3\_\mathrm{MembIC}}}{L_{\mathrm{IC}}}(T_1 - T_3) - \frac{2k_{\mathrm{Pyrex}} A_{1\text{-}3\_\mathrm{Memb}}}{L_{1\text{-}3\_\mathrm{Memb}}}(T_1 - T_3) \tag{8}$$

$$\dot{E}_{2\text{-}1} = -\dot{E}_{1\text{-}2} \tag{9}$$

$$\dot{E}_{2\text{-}3} = -\frac{k_{\mathrm{Si}} A_{\mathrm{IC}}}{L_{\mathrm{IC}}}(T_2 - T_3) - \frac{k_{\mathrm{Pyrex}} A_{2\text{-}3\_\mathrm{MembIC}}}{L_{\mathrm{IC}}}(T_2 - T_3) - \frac{2k_{\mathrm{Pyrex}} A_{2\text{-}3\_\mathrm{Memb}}}{L_{2\text{-}3\_\mathrm{Memb}}}(T_2 - T_3) \tag{10}$$

$$\dot{E}_{3\text{-}1} = -\dot{E}_{1\text{-}3} \tag{11}$$

$$\dot{E}_{3\text{-}2} = -\dot{E}_{2\text{-}3} \tag{12}$$

where k_{Si} and k_{Pyrex} are the thermal conductivity of Si and Pyrex (130 W $m^{-1}K^{-1}$ and 1.4 W $m^{-1}K^{-1}$), respectively. A_{IC} is the cross-sectional area of the Si interconnection channel (IC), and L_{IC} is the length of the IC. $L_{1\text{-}3\_\mathrm{Memb}}$ and $L_{2\text{-}3\_\mathrm{Memb}}$ are the distances between 1-3 and 2-3, respectively. $A_{1\text{-}2\_\mathrm{Memb}}$, $A_{1\text{-}3\_\mathrm{Memb}}$, and $A_{2\text{-}3\_\mathrm{Memb}}$ are the cross-sectional areas of the Pyrex membrane between thermal mass 1and 2, 1and 3, and 2and 3; however they exclude the areas contacting the ICs. $A_{1\text{-}3\_\mathrm{MembIC}}$ and $A_{2\text{-}3\ \_\mathrm{MembIC}}$ are the cross-sectional areas of the Pyrex membrane between thermal masses 13 and 2-3, respetively, that are in contact with the ICs. $\dot{E}_{\mathrm{i\_gen}}$ is the heat generation by integrated microheaters:

$$\dot{E}_{\mathrm{i\_gen}} = V_{\mathrm{i}}^2 / R_{\mathrm{i}} \tag{13}$$

where V_{i} and R_{i} are the applied voltage and electrical resistance, respectively, at the i^{th} microheater. $\dot{E}_{\mathrm{i\_conv}}$ and $\dot{E}_{\mathrm{i\_rad}}$ are the heat transfer by convection and radiation, respectively. We assume natural convection for the $\dot{E}_{\mathrm{i\_conv}}$ term and also assume that the μTM is a small convex object in a large-cavity environment for the term $\dot{E}_{\mathrm{i\_rad}}$. They are expressed as follows:

$$\dot{E}_{\mathrm{i\_conv}} = -hA_{\mathrm{Si\_i}}(T_{\mathrm{i}} - T_{\infty}) \tag{14}$$

$$\dot{E}_{\mathrm{i\_rad}} = -\sigma_{\mathrm{SB}} \varepsilon_{\mathrm{r}} A_{\mathrm{Si\_i}}(T_{\mathrm{i}}^4 - T_{\infty}{}^4) \tag{15}$$

where h, σ_{SB}, and ε_{r} are the natural convection coefficient (10 W $m^{-2}K^{-1}$), Stephan-Boltzman constant (5.67×10^{-8} W $m^{-2}K^{-4}$) and the emissivity of the radiating Si surface (0.52), respectively. $A_{\mathrm{Si\_i}}$ and T_{∞} are the area of i^{th} thermal mass on the Si surface and ambient temperature, respectively.