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Membrane-based calorimetry for studies of sub-microgram samples

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Abstract. We have developed a membrane-based microcalorimeter for general measurements of heat capacity and latent heat using a combination of ac steady-state and relaxation methods. The differential calorimeter is designed for sub-microgram samples studied over a wide range of temperatures and magnetic fields. The device is based on free-standing silicon nitride membranes of 150 nm thickness onto which thin film heaters and temperature sensors are fabricated. While production-line fabrication may benefit from back-etching as a final step, it is often easier to start with pre-etched membranes in a research laboratory. With selected nano-fabrication methods this is possible. Due to a robust heater and very low thermal conductance of the final calorimeter, the sample can be heated to more than 100 K above base temperature. This enables instantaneous calibration, and makes the device capable of being used for ultra-fast temperature control, relaxation studies, and measurements that combine good absolute accuracy, high resolution, and information on latent heat.

1. Introduction
Calorimetry is a method well suited for studies of mesoscopic samples [1, 2, 3]. In addition to probing thermal properties arising from mesoscopic effects, the use of small samples generally brings several advantages, such as good homogeneity and high availability. Using sub-milligram samples, however, makes it difficult to realize adiabatic conditions. For this reason, measurement of small heat capacities are generally performed by an ac steady state method [4]. While ac calorimetry gives higher resolution, relaxation methods [5, 6] have higher absolute accuracy and can probe latent heat. Several groups have fabricated membrane-based micro-calorimeters of various design [1, 7, 8, 9, 10]. Here we describe the development of a differential microcalorimeter based on silicon-nitride membranes with thin film heaters and a resistive bridge thermometer. Thanks to the use of membranes and thin films, the system shows exceptional low thermal conductance. As a consequence, the relaxation time constant between the caloric cell and thermal bath is long enough for relaxation methods to be of practical use and complement the ac calorimetry.

2. Experimental method
The processing steps of the calorimeter cell are shown in figure 1a. In total six layers are deposited onto dual Si₃N₄ membranes using photolithography, electron beam evaporation and subsequent lift-off. The use of a differential scheme, where one membrane acts as reference...
Figure 1. (a) Onto a silicon frame with pre-etched Si$_3$N$_4$ membranes (0), heaters (1), temperature sensor (3), insulation (2, 4) and thermalization (5) layers, and bonding pads (6) are fabricated using lift off. (b) Temperature sensor layer made up of four resistance thermometers (meanders) in bridge configuration. (c) Schematic of the temperature sensor circuitry. The on-cell bridge is combined with a parallel, room-temperature balance reference.

and the other hosts the sample, improves absolute accuracy as well as resolution. The thin membranes provide the thermal isolation needed to obtain pseudo-adiabatic conditions while contributing a minimum of background specific heat (addenda). Estimated values of the heat capacity and thermal conductance of the lift-off layers are given in table 1.

The heater is a resistive meander patterned at the center of the membrane on an area of $110 \times 110$ $\mu$m$^2$. With suitable currents, it delivers dc and ac power to raise and modulate the sample temperature. The resistance thermometers layer, figure 1b, is used to measure the temperature increase of sample and reference ($T_{\text{offs}}$) through $R_S$ and $R_R$, and the base temperature ($T_{\text{base}}$) of the silicon frame (thermal bath) through $R_1$ and $R_2$. A small temperature oscillation of the sample can be detected with high resolution by measuring the potential difference $U_{\text{ac}} = V_S - V_{S,\text{ref}}$, where $V_{S,\text{ref}}$ is an adjustable voltage potential, see figure 1c. The reference potential is set to give $U_{\text{ac}} = 0$ when the sample is unheated. A thermocouple is often used as temperature sensor [11], but the resistance thermometer presents some advantages: it requires only thin layers and thus reduces the heat capacity addendum, and it is easy to impedance-match with amplifiers.

Table 1. Estimated room temperature values of the heat capacity of the central $110 \times 110$ $\mu$m$^2$ area ($C_{\text{center}}$), active heat capacity ($C_{\text{active}}$), and thermal conductance $k$. The active heat capacity corresponds to the effective area that is temperature modulated at low frequencies, taken as 1/10th of the $1 \times 1$ mm$^2$ membrane area. Layers are numbered according to figure 1a.

| Layer       | Material | Thickness (nm) | $C_{\text{center}}$ (nJ/K) | $C_{\text{active}}$ (nJ/K) | $k$ (W/K) |
|-------------|----------|----------------|----------------------------|---------------------------|-----------|
| 0. Membrane | Si$_3$N$_4$ | 150            | 3.1                        | 26                        | $8 \times 10^{-7}$ |
| 1. Heater   | Ti       | 45             | 0.7                        | 4.7                       | $5 \times 10^{-7}$ |
| 2. Insulation | AlO$_x$ | 45             | 1.5                        | 5.1                       | $27^*$ |
| 3. Sensor | Ti       | 55             | 0.9                        | 2.9                       | $3 \times 10^{-7}$ |
| 4. Insulation | AlO$_x$ | 70             | 2.6                        | 8.5                       | $17^*$ |
| 5. Thermalization | Al       | 20             | 0.6                        | 0.6                       | $144^*$ |
| **Total**  |          | 150 – 385      | 9.4                        | 48                        | $1.6 \times 10^{-6}$ |

*Thermal link between layers
Figure 2. (a) Thermometer and heater resistance as a function of temperature. The variation between curves is related to the widths of the meanders. (b) Resistances as a function of $R_1$.

In the standard measurement mode a known ac current flows through the heater. A fairly large dc current is fed through the resistance bridge with a small ac modulation used to measure $R_S$ and $R_1$ with high precision for determination of $T_{offs}$ and $T_{base}$. The amplitude of the sample temperature oscillation, picked up in $U_{ac}$ at the second harmonic of the heater current, is given by $T_{ac}^S = U_{ac}/(I_{dc}^S \cdot dR_s/dT)$. The current $I_S$ through the sample branch of the bridge is obtained as $I_{ac}^S = I_{WB}^S/(1 + \gamma \cdot (U_2/U_1)^{ac/dc})$ where $\gamma$ is the ratio of $R_1$ and $R_2$ measured at room temperature. To practically enable all measurements simultaneously, a set of time- and phase synchronized lock-in amplifiers based on a field-programmable gate array (FPGA) was used.

3. Results and discussion

During the photolithography it is hard to achieve the exact same width of all six meanders (heaters and resistance thermometers). For this reason, each meander resistance shows a slightly different slope as a function of temperature, see figure 2a. Meanwhile, all the resistances show a good, linear behavior if plotted as function of $R_1$, as illustrated in figure 2b. This makes calibration easy. After determining $R_1(T)$, the other resistances need to be measured only at two separate temperatures. For Ti as used here, the sensitivities $d \ln R/dT$ vary from $3 \cdot 10^{-3}$ K$^{-1}$ at room temperature to a maximum of $5 \cdot 10^{-3}$ K$^{-1}$ around 100 K before vanishing at 20 K.

The temperature offset between sample and thermal bath is shown in figure 3a. Thanks to the robustness of the heaters, the sample can be heated to more than 100 K above base temperature. From measurements of $T_{offs}(P)$, the thermal link $k$ between sample and bath can be obtained.

Figure 3. (a) $T_{offs}$ versus power at $T_{base} = 68$ K. The non-linearity of the curve is due to temperature dependence of $k$. (b) Relaxation of sample (83 ng YBa$_2$Cu$_3$O$_{7-\delta}$ crystal) and reference (empty) after the heater power is turned off, measured at $T_{base} = 110$ K.
as \( k = 1/(dT_{\text{offs}}/dP) \). The time constant \( \tau_{\text{ext}} = C/k \) represents the characteristic time required for the system to relax after the heater power has been turned off. The time dependence of the relaxation, shown in figure 3b is expected to follow \( T(t) = T_{\text{base}} + \Delta T \cdot \exp(-t/\tau_{\text{ext}}) \). Using this equation to fit the experimental curves for both sample and reference side gives \( \tau_{\text{ext}}^S = 4.5 \cdot 10^{-2} \text{ s} \) and \( \tau_{\text{ext}}^R = 1.36 \cdot 10^{-2} \text{ s} \). Combining these results with the already determined \( k \) finally results in \( C_S = 60 \text{ nJ/K} \) and \( C_R = 18 \text{ nJ/K} \) for the particular sample and temperature of figure 3.

While the relaxation method is useful for measuring the absolute value of the heat capacity, it is not so sensitive to small changes in \( C \) that are instead preferably detected using the ac steady state method. The amplitude of the temperature modulation is here related to the heat capacity through \( T_{\text{ac}} = T_{\text{offs}}/\sqrt{1 + (2\omega_h \cdot \tau_{\text{ext}})^2} \) where \( \omega_h \) is the frequency of the heater current. Figure 4 shows a frequency scan of the experimental \( T_{\text{ac}} \) for sample and reference and the corresponding best fits to this expression. The difference between experimental and theoretical curves on the reference side can be explained as a frequency dependent part of the heat capacity. The temperature oscillation of the thermal link (membrane) is dampened out on a thermal length scale \( L = \sqrt{2D/\omega} \) where \( D \) is the thermal diffusivity [12]. On the sample side, the deviations from the theoretical behavior above about 50 Hz occur when the internal relaxation between sample and membrane can no longer be neglected. From the experimental data in figure 4 the internal time constant can be estimated to be \( 1.1 \cdot 10^{-3} \text{ s} \).

![Figure 4](image)

Figure 4. Temperature oscillation amplitude for sample and reference as a function of heater current frequency. The experimental curves were measured at \( T_{\text{base}} = 68 \text{ K} \). The theoretical curves were obtained using \( \tau_{\text{ext}}^S = 3.6 \cdot 10^{-2} \text{ s} \) and \( \tau_{\text{ext}}^R = 0.70 \cdot 10^{-2} \text{ s} \). At low frequencies, the reference heat capacity corresponds to \( C_{\text{active}} \), but at high frequencies only \( C_{\text{center}} \) is left.

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