Membrane-based microcalorimetry for thin films and sub-milligram single-crystal

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Abstract. We report on the design, fabrication and use of micro-machined, membrane-based calorimeters for heat capacity measurements in the 20 K < T < 300 K temperature range. The membrane is made of Si₃N₄ and its thickness is as small as 250 nm. Thermometer and heater are fabricated in Pt by sputtering and optical lithography. Remarkably, the addenda of our devices are three to four orders of magnitude smaller than the most commercially performing available calorimeters. This leads to a high sensitivity, making them suitable for addressing samples in the form of thin films and sub-milligram single-crystals. Automated measurements are performed using a custom-made programme based on the quasi-adiabatic thermal relaxation method. A sample measurement is taken for a Na-Mn-O sub-milligram, and the results are reported so as to compare with the expected signal.

Keyword: Calorimetry, microcalorimeter, low temperature.

1. Introduction

Thermodynamic measurements give a great deal of information on fundamental properties, since they provide direct and quantifiable insight into, e.g., densities of state and phase transitions [1,2]. However, many interesting materials can only be obtained in the form of thin films or sub-milligram single crystals. The signal out of these samples is reduced accordingly to their size, being hence not sufficient for conventional calorimetry. Progress is growing at a pace determined by the development of the necessary experimental tools. In this respect, a primary advancement can be obtained by fabricating and using highly-sensitive calorimeters of reduced size.

The typical calorimeter has a sample holder with attached a thermometer and a heater. This as a whole is weakly linked to an external thermal bath, which provides the cooling power. The measurement technique is “simple”: a controlled heat quantity Q is provided by the heater to the sample and the holder block so the response of the system is given in terms of temperature changes ΔT. The heat capacity is thus measured as C = Q/ΔT. In practice, its realization within reduced sizes is very challenging and relatively few works have been carried out so far [3-8].

One simple technical issue that must be taken into consideration when developing any calorimeter, is that its components and surrounding elements are contributing to the measured signal. This unwanted but unavoidable heat capacity is called the “addenda”. If a high resolution is the aim, the
contribution of the addenda to the total heat capacity must be of the same order of magnitude as the sample or preferably less. Therefore the materials out of which the calorimeter is made, have to be chosen very carefully.

We show herein that micro-electro-mechanical-system (MEMS) techniques, like lithography and dry/wet etching, can be successfully employed for fabricating highly-sensitive micron-sized calorimeters. Specifically, we report on the design, fabrication and use of a membrane-based micro-calorimeters for heat capacity experiments in the 20 K < T < 300 K temperature range. The membrane is made of Si$_3$N$_4$ and its thickness is as small as 250 nm, whereas the thermometer and heater are both made of Pt. The addenda is very small (6 µJ/K at room temperature), resulting in sufficient sensitivity for detecting and measuring sub-milligram samples.

2. Principle of measurement and experimental set-up

Although the AC steady state method [9] could be used, we use the relaxation technique described by Bachmann et al. [10]. In this method, the power (P) to heat the sample is applied in the form of rectangular pulses with typical time periods of the order of seconds. After the heat is switched on (or off), the calorimeter relaxes to a new thermal equilibrium situation with a fixed temperature step, which typically amounts to $\Delta T = 3\%$. The heat capacity is then obtained by fitting the time evolution of the temperature of the calorimeter to an exponential. Our experimental set-up is schematized in figure 1. The heating is provided by a DC current source (Keithley 220), whereas the temperature in the calorimeter is monitored by a lock-in amplifier (Stanford Research 830) working in combination with an AC current source (Keithley 6221). Both heater and thermometer are measured using a four-probe configuration. The cooling is provided by inserting our devices into a Quantum Design PPMS cryostat, although they can easily implemented in any commercially available cryostat in view of the reduced size of our calorimeters (see below). All instruments are remotely controlled by a computer through GPIB connections. Automatized measurements are carried out by means of a home-made software developed using National Instruments Lab-View suite (see Section on Measurement procedure).

![Figure 1. Scheme of the experimental set-up.](image-url)
The damping of the temperature during the heating/cooling cycle is related to the heat capacity by

\[ C = K \tau_e. \]  

It should be noted that, in order to obtain the proper value of the heat capacity, it is crucial that \( \tau_e \) is much longer than the internal relaxation time, i.e., the time it takes for the thermometer to be in thermal equilibrium with the sample and addenda. This condition implies that particular care should be taken in designing the calorimeter such that the sensing part should be nearly thermally-isolated from its environment.

### 3. Design, fabrication and testing

#### 3.1. Design of the calorimeter

A special calorimeter was designed, allowing highly-sensitive specific heat measurements with the relaxation method. As detailed in the Fabrication Section, we start from a Si wafer (double-side polished with Si3N4) that offers a relatively high thermal conductivity, and forms the calorimeter frame that will be fixed to the cryostat sample-holder, e.g., a commercial sample puck of the Quantum Design PPMS. The micromachined calorimeter consists of a substrate, a heater and a thermometer. While measuring, these components contribute with their own heat capacity (i.e., addenda) which must be subtracted from the total heat capacity. In order to achieve high sensitivity, the addenda therefore has to be small, hence implying the size-shrinking of all components. The substrate, i.e., the sensing platform, is a thin membrane of Si3N4 whose size is 5x5 mm² with a thickness as small as 250 nm. Heater and thermometer are lithographically fabricated on top of the membrane. Since the Si3N4 thermal conductivity is appreciably smaller, we design the transducers to be parallel and close to each other (figure 2).

![Design of the calorimeter.](image)

We use Pt for fabricating the transducers as well as the leads and pads. The choice of one material only for all electrical components facilitates the fabrication process. The Pt patterning that connects...
the pads with the transducers, represents the “heat link” between calorimeter and thermal bath. Its design, therefore, directly influences the characteristic time $\tau_e$ of the measurement.

### 3.2. Microcalorimeter construction

The processing steps to fabricate our calorimeters are detailed in figure 3. We start from a 300 $\mu$m-thick Si wafer double-coated with Si$_3$N$_4$. In order to selectively remove the Si$_3$N$_4$, we pattern the top side with a square photoresist mask of 5x5 mm$^2$ (figure 3a). The Si$_3$N$_4$ is completely removed by Reactive Ion Etching (RIE) in a composition of 9CF$_4$:1O$_2$ for four minutes (figure 3b). The region covered by Si$_3$N$_4$ is then used as protection for Si etching in a hot KOH solution (30 wt.% of water). The temperature of the solution is kept stable at 80$^\circ$C, providing an etching rate of $\sim 1.2$ $\mu$m/min. The complete removal of the Si leads to the suspended Si$_3$N$_4$ membrane inside a Si frame (figure 3c). Because the Si$_3$N$_4$ membrane is very thin ($\sim 250$ nm), care must be taken in order not to break it when the Si on the borders is etched completely.

Upon completing the fabrication of the membrane, we pattern on the back side a photoresist mask for all electrical components, i.e. heater, thermometer, leads and pads (figure 3d). Hence we sputter a Ti / Pt film (3 nm / 50 nm), whose thickness is calibrated by profilometry measurements (figure 3e). The heater and thermometers are finally obtained after a lift-off process (figure 3f).

A problem we are faced with refers to the low thermal conductivity of the Si$_3$N$_4$. In order to guarantee a good thermalization between heater and thermometer, we deposit a thin copper film by shadow mask on the top side. Alternatively, we add a small amount of thermal grease, e.g. Apiezon N.

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**Figure 3.** a) Si wafer covered by photoresist mask; b) reactive ion etching of Si$_3$N$_4$; c) Si$_3$N$_4$ membrane after wet etching of Si; d) photo resist mask for heater and thermometer; e) Pt deposition; f) lift-off to remove photoresist; g) completed device; h) device with sample.

### 3.3. Measurement procedure

In order to measure the heat capacity as a function of temperature, we install our calorimeter in a sample puck of the Quantum Design PPMS system. The electronics is then set-up as depicted in figure 1. Fully automated measurements are performed using a custom-made programme based on the quasi-adiabatic thermal relaxation method. Figure 4 shows a representative screen capture taken during the running of a measurement.
In a typical measurement, we start by setting the system temperature (corresponding to the initial temperature of the measurement) in the “PPMS parameters” panel (figure 4). Following the stabilization of the system temperature, we check for the temperature in the membrane and wait till we obtain a stable reading. A heat pulse is then provided to the calorimeter according to the parameters that we set in the “Measurement settings” panel (figure 4). The programme automatically looks for that pulse which properly provides the desired $\Delta T$ (typically we work with 3% $\Delta T$ steps). When this step is accomplished, we start collecting experimental data. In figure 4 top-right panel, one can notice an example temperature relaxation, which follows the characteristic exponential decay. Finally the software performs the fits, and calculates, saves and plots the resulting heat capacity. Before switching to the next temperature, measurements may be repeated to minimize the noise.

3.4. Characterization and example measurement

The resistance of Pt is known to linearly decrease with temperature down to 20 K, below which it levels off. This value limits the low-temperature applicability of our Pt thermometers. The heat capacity of the present design empty calorimeter is depicted in figure 5, together with that of an empty commercial PPMS calorimeter based on a sapphire platform.
PPMS calorimeter for comparison. To measure the addenda depicted in figure 5, we have thermalized heater and thermometer together by adding a 200 nm-thick copper film on the back side of the membrane. Remarkably, one can notice that the addenda of our device are up to three-four orders of magnitude smaller than that of the commercial apparatus. The addenda of this work amounts to 6 µJ/K at room temperature and decreases to 0.5 µJ/K at the lowest temperature. The reason for the broad bump observed around 60 K (figure 5) is unknown yet.

Figure 6. Experimental heat capacity of Na-Mn-O, as collected with a membrane-based calorimeter and a standard PPMS calorimeter.

As a test measurement, we have collected the heat capacity of a m ≈ 200 µg poly-crystal of the double perovskite compound Na-Mn-O [11,12], see figure 3h for a photograph of the mounted sample on the Si3N4 membrane. Figure 6 shows the excellent agreement of our data with that measured with a standard (PPMS) calorimeter on a massive (m = 50 mg) equivalent sample. Concerning the three observed features, the peak at 176 K is associated with a structural phase transition, whereas the ones at 125 K and 90 K are due to antiferromagnetic ordering of two different magnetic sublattices, respectively [11, 12].

4. Conclusions

Employing MEMS techniques, we successfully fabricated calorimeters based on a Si3N4 membrane having thickness as small as 250 nm. Thin-film heater and thermometer, both made of Pt, are lithographically implemented on the membrane. We experimentally demonstrate that the reduced size of all components leads to a heat capacity of the empty calorimeter that is three-four orders of magnitude smaller than conventional calorimetry. This results in an increased sensitivity making our devices particularly valuable for addressing studies in microgram samples, like thin films and single crystals.

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