Time-dependent simulations of a membrane-based nanocalorimeter

S Tagliati, J Pipping and A Rydh
Department of Physics, Stockholm University, AlbaNova University Center, SE – 106 91 Stockholm, Sweden
E-mail: Stella.Tagliati@fysik.su.se

Abstract. We present time-dependent numerical simulations of the thermal and electrical response of a membrane-based nanocalorimeter designed for general studies of heat capacity and latent heat of milligram to sub-microgram samples. The investigated device is based on free-standing, 150 nm thick silicon nitride membranes onto which thin film heaters and temperature sensors are fabricated. This design makes the thermal link small enough to allow both relaxation and ac steady-state methods to be used interchangeably. We compare simulations of the two-dimensional thermal behavior of the nanocalorimeter with the results of experiments. The simulations take current distribution, heat generation and heat flow into consideration, and shed light on the frequency dependent contribution of the membrane heat capacity in ac steady-state experiments. The simulations also illustrate where energy is stored, thus assisting further improvement of the device design.

1. Introduction

Caloric measurements play an important role in understanding the fundamental properties of newly discovered materials. Ac steady state [1] and thermal relaxation calorimetry [2] are widely used techniques for measuring heat capacity of small samples such as single crystals and thin films. While ac calorimetry gives high resolution, thermal relaxation has higher absolute accuracy. The two methods can be combined if the time constant for relaxation is low enough to be well defined and if the internal thermal connection between thermometer, heater and sample is good. We are developing a nanocalorimeter where these conditions are satisfied by using free-standing membranes and stacking thin film heaters and thermometer on top of each other with an additional thermalization layer. The current geometry of the device is shown in Fig 1a. In the center of a silicon nitride membrane, a pile of heaters and thermometer is fabricated, electrically insulated by AlO$_x$. The sample is placed on a 110 \times 110 \mu m^2 central area. To obtain both good resolution and absolute accuracy from the device, several issues need to be well understood: how the background heat capacity depends on frequency, if decoupling between sample and platform occurs, if there are any systematic errors, and how uniform the temperature of the sample area is. Analyzing AC steady state experiments is, however, not trivial. Numerical simulations represent a useful tool in this respect, to better understand the thermal and electric properties of the device. Here we present time-dependent simulations to investigate the frequency dependence of the temperature oscillations at ac steady state. Such frequency dependence acts as a fingerprint of any device. The simulations show that good absolute accuracy can be obtained provided that the heater power is appropriately defined.
Figure 1. (a) Photolithographic layout used for numerical simulations of the nanocalorimeter. Heaters and thermometers are fabricated onto $1 \times 1 \text{ mm}^2$ silicon nitride membranes pre-etched in a silicon frame. Titanium is used for ac and offset heaters. A square GeAu thermometer [3, 4] is connected to the frame by internal Au leads and external Ti leads. The heater meanders and thermometer are superimposed in the central $110 \times 110 \mu \text{m}^2$ area and electrically insulated by AlO$_x$ layers. A metallic thermalization layer (not shown) is also covering the central area; it acts to distribute heat and improve the thermal contact with the sample. (b) Mesh of the membrane area used in the simulations.

In the relaxation method a known amount of power $P$ is dissipated into the heater to raise the sample temperature an amount $\Delta T$ above the frame temperature. At time $t = 0$, $P$ is set to zero and $T(t) = T_{\text{base}} + \Delta T e^{-t/\tau_{\text{ext}}}$ is measured. The ac method uses an ac current through the heater which produces a temperature response $T(t) = T_{\text{base}} + \Delta T + T_{\text{ac}} \exp(i2\omega_h t)$, where $\omega_h$ is the angular frequency of the heater current. In the simplest model, the amplitude of the temperature modulation is related to the heat capacity through [5]

$$T_{\text{ac}} = \Delta T / \sqrt{1 + (2\omega_h \tau_{\text{ext}})^2}$$

(1)

For both methods $\tau_{\text{ext}} = C/k$ where $k = P/\Delta T$ and $C = C_S + C_M$ is the sum of the sample and membrane heat capacities. Equation (1) usually describes well the frequency dependence as long as the sample is not too small and the internal thermal conductivity is good enough, corresponding to a short internal time constant $\tau_{\text{int}} << \tau_{\text{ext}}$. This condition corresponds to a temperature decay depending on a single time constant in the relaxation method [6], and to a good coupling between sample, thermometer and heater in the ac method.

2. Numerical simulations

Numerical simulations were performed with Comsol Multiphysics using the heat transfer module to describe heat flow and the AC/DC module for electrical properties. Since the in-plane dimensions are more than three orders of magnitude larger than the final stack thickness, we simulated the process by a pseudo-3D model described by the heat equation [7]

$$C_{2D} \frac{\partial T}{\partial t} - \nabla \cdot (\kappa_{2D} \nabla T) = \dot{P} d + h_a(T_a - T) + h_b(T_b - T)$$

(2)

Here, $C_{2D} = \rho C d$ where $\rho$ (g/cm$^3$) is the density, $C$ (J/gK) is the specific heat and $d$ is the layer thickness, $\kappa_{2D} = \kappa d$, where $\kappa$ (W/cmK) is the thermal conductivity, $\dot{P}$ (W/cm$^3$) is the resistive heating power density; $h_{a,b}$ (W/cm$^2$K) is the heat transfer coefficient between layers, and $T_{a,b}$ are
The temperatures of neighboring layers above and below the given layer. Radiative heat transfer was neglected. The heat transfer coefficient terms in Eq. (2) were used to approximate the thermal conduction perpendicular to the layers. The temperature differences between the layers were, however, found to be negligible for the studied frequency range. The parameters needed for the simulations are $C_0$, $k$, and $\rho$ for each layer and the resistivity for the layers (heater and thermometer) whose electrical behavior is involved. The resistivity of the Ti heaters was adjusted so that the numerical results agreed with the measured electric response. Values of specific heat and thermal conductivities were estimated from the literature [8, 9] and Wiedemann-Franz law. To make the external time constant coincide with experiments, the membrane specific heat had to be adjusted by 10%. The temperature offset was found to agree well with experiments using the estimated values of thermal conductivities. The simulations presented and the experiments carried out for comparison were performed at a base temperature $T_0 = 50$ K.

3. Results and discussion

When using the ac steady state technique a key characterization of the system is the frequency dependence at constant temperature. Figure 2a shows the temperature modulation of the thermometer as a function of heater frequency at constant ac power. It is clearly seen that the simulations describe the experimental data well over the entire frequency range. However, both curves start to deviate from the simple expression of Eq. (1) at about 30 Hz. This behavior can be attributed to a frequency dependence of the area of the membrane that is actively participating in the temperature oscillations. Temperature oscillations are dampened out on a thermal length scale $L = \sqrt{2D/\omega}$ where $D = \kappa/\rho C$ is the thermal diffusivity [10, 11]. With increasing frequency the effective area that is temperature modulated shrinks and at high frequency only the central area is left. When sample layers are added onto the thermalization layer the relative contribution from addenda heat capacity becomes gradually smaller and the frequency dependence approaches the $1/f$ behavior of Eq. (1). For $C_S \geq 2C_M$, the deviations are already hard to discern. If the frequency becomes high enough, experiments will again start to deviate from the $1/f$ behavior [12]. Such deviations may appear somewhat similar to the
Figure 3. Energy oscillation contours for the empty device at different frequencies. The shaded area corresponds to oscillations $\varepsilon_{ac} > 0.03\varepsilon_{ac,max}$. In panel d, the effect of dissipation in the heater current leads is obvious. (a) $f = 0.01$ Hz (b) $f = 25$ Hz (c) $f = 100$ Hz (d) $f = 1000$ Hz.

frequency-dependent membrane contribution, but arise when internal relaxation time between sample and platform can no longer be neglected. In the current simulations this is not seen because the sample is a thin film that is well thermally anchored to the thermalization layer. At very high frequency the thermal conductance of the AlO$_x$ layers will put a final, upper limit to the available device frequency. This limit is, however, well outside any experimentally interesting range.

Simulations are an excellent tool to understand possible systematic errors in the experimentally determined heat capacities. By fitting the model expression of Eq. (1) to the simulated data of Fig. 2b, we found that the obtained sample heat capacities deviated by about 15% from the expected values. The explanation for this deviation is that the heater power is underestimated if the heater voltage is measured in a four-probe configuration such as the one illustrated in Fig. 1a. The simulations show that there is an additional 20% heater power in the heater current leads outside the central meander that partially contributes to the heating. By using a power adjusted for this effect, the model is found to well describe the simulated curves, as seen in Fig. 2b. We thus added 75% of the power of the heater current leads to the measured heater power before calculating $\tau_{ext}$ from $C, P$ and $\Delta T$.

The effects of frequency-dependent membrane addendum and unwanted heating in heater current leads are clearly illustrated by studying energy oscillations, i.e., $\varepsilon_{ac} = C_{2D}T_{ac}$, where $C_{2D}$ is the composite heat capacity per surface area including all layers and sample. In Fig. 3, contours of such energy oscillations are shown for different frequencies. The shaded area illustrates where the main part of the energy oscillations occur. It is clearly seen that the active area shrinks with increasing frequency. To obtain a more quantitative understanding of the empty device energy distribution, the energy was integrated over the central $110 \times 110 \text{ m}^2$ area and compared with the energy integrated over the total area and over the area defined by the largest AlO$_x$ layer. It is found that about 87% of the energy oscillations are located outside the central area at low frequencies, decreasing to 61% at $f = 1000$ Hz. The fraction of energy oscillations outside the AlO$_x$ layer at the same high frequency is 21%, consistent with the contribution from dissipated power in the heater current leads outside the central area. The energy oscillations generated by the heater meander are thus rather well confined to the AlO$_x$ area at high frequencies, and separated from the energy oscillations in the heater leads, as seen in Fig. 3d. It should be noted that the central temperature oscillations will be dampened in the presence of a sample, while the oscillations of the leads will remain almost unchanged. Since these oscillations do not reach the thermometer sensor they are not a direct problem, but they represent a possible source of noise. Together with the uncertainty caused by the leads dissipation, it is thus clear that more focus should be spent on designing heater current leads with less dissipation in relation to the heater meander.

In Fig. 4 the temperature and energy profiles for the case of constant heating, as appropriate
Figure 4. (a) Isothermal contour plot for the empty device at constant heater power (before relaxation). (b) Corresponding contours of constant energy $\varepsilon = C_2D\Delta T$. The energy shade scale is linear from white ($\varepsilon = 0$) to black (highest value of $\varepsilon$).

for relaxation experiments, are shown. From the isothermal contour plot it is clear that the temperature uniformity is good within the sample area. The high conduction of the internal Au leads of the thermometer, however, causes the adjacent membrane areas to heat unnecessarily. Making the Au leads shorter would decrease this area and thus lower the over-all membrane addendum as well as increase the relaxation time constant when the temperature gradient becomes more uniform. The corresponding energy contour plot of Fig. 4 illustrates the contribution of different membrane areas to the heat capacity addendum in a relaxation measurement. Integrating the energy $\varepsilon$ over the entire membrane and dividing the result by $\Delta T$ gives a heat capacity $22.5$ nJ/K, which should be compared to the value $C_M = 17.4$ nJ/K obtained from the simulations of Fig. 2b. The difference between the values can be reasonably understood taking the distribution of heat into consideration.

To conclude, we have found that a nanocalorimeter with good absolute accuracy and a well-behaved response for ac steady-state measurements can be obtained by introducing minor changes in the device design.

Acknowledgments
Support from the Knut and Alice Wallenberg Foundation, the Swedish Research Council and the SU-core facility in nanotechnology is acknowledged. We thank V M Krasnov for suggestions in connection with the development of the fabrication process.

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