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New design of a microcalorimeter for measuring absolute heat capacity from 300 to 550 K

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ABSTRACT

We report development of a new type of a microcalorimeter based on an amorphous membrane composed of Si:N and SiO_2 layers, which holds an isothermal Au film of a disc shape and concentric Pt leads as a heater and a thermal sensor. Two-dimensional thermal simulation was used to confirm that the layout of the isothermal platform and metallic leads result in nearly perfect isothermal conditions at temperatures from 20 to 600 K. Moreover, by placing the insulating SiO_2 layer between the isothermal film and metallic leads, we could locate all electrical and thermal components in the top side of the membrane, allowing the micro-fabrication easy and cost-effective. The micro-fabrication method produces a total of 49 devices in a four inch Si wafer and can be also applied in a larger wafer size. Heat capacity value of the isothermal platform was found to be as small as ~6 μJ K^{-1} at room temperature. Upon applying the lumped-τ_2 model in the measurement scheme, we found that specific heat of an Al_2O_3 single crystal (NIST standard, ~0.2 mg) was consistent with the literature value within ~3% at temperatures between 300 and 550 K. Our results show that the circular layout of the isothermal platform with better heat confinement is useful for increasing the accuracy of measured heat capacity if the other parameters such as thickness and thermal conductivity of each layer in the membrane are fixed.

1. Introduction

Heat capacity (C_p) is one of the most fundamental probes for studying the basic properties of solids such as magnetic, structural and electronic phase transitions [1–5]. Since many emergent materials of interest including oxide single crystals, polymers and bio-materials often exist in a small volume, C_p measurements of those small samples become quite challenging due to relatively large addenda heat capacity, C_{add}, of a calorimeter platform. The C_{add} value of a commercially available calorimeter is typically as high as 1–10 mJ K^{-1} at room temperature. Therefore, if C_p of a sample (C_{sample}) is not much larger than C_{add}, it is difficult to measure C_p accurately. In order to overcome this limitation, it is important to reduce C_{add}.

Over the past three decades, numerous efforts have been made to fabricate novel micro or nanocalorimeters with greatly reduced C_{add} [6–13]. In particular, it has been well established that a calorimeter platform made of amorphous Si:N (*a*-Si:N) membrane is useful for achieving extremely small C_{add} down to a few nJ K^{-1} [9–12]. For this reason, the microcalorimeter made of the Si:N membrane is being progressively used to measure various small samples with enhanced sensitivity. A few examples include thin nanofilms [11,12,14–17], nanoparticles [18], nanopolymers [13, 19–21], micro-organic materials [22], carbon nanotubes [23,24] and micro-bio materials [25]. However, it is noted that most of those micro or nanocalorimeters have adopted the resistive heater having a simple line or serpentine lines, which can often produce temperature gradient within the sample platform [9,11,17,24,26,27]. Therefore, in order to achieve the isothermal condition on the sample platform, a thick metallic layer with high thermal conduction or a thin membrane layer has been tried, which consequently leads to a larger C_{add} or a fragile membrane, respectively. Moreover, circular heater lines have been also tried, which can possibly result in more homogeneous heat distribution within the membrane platform [28,29].

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We have previously developed several types of microcalorimeters based on the *a*-Si:N membrane, i.e., Type I-III, which consist of basically meander-shaped heater/sensor leads on the sample platform [30,31]. Type I and II microcalorimeters, however, produced rather large errors in the C_p data as high as 15–20% from 20 to 300 K. Those errors were mainly coming from an imperfect isothermal condition in the sample platform. Moreover, the Type III microcalorimeter with well separated and relatively thin heater/sensor leads has exhibited reduced measurement errors down to 10% from 20 to 300 K. In spite of these results, C_{add} values were rather large at room temperature (~20 μJ K^{-1}), and the measurement error systematically increased at higher temperatures to reach as high as 10–15% [32]. In order to enhance the accuracy of measured C_p and to reduce temperature gradient within the sample platform, it has become necessary to modify geometry of a resistive heater and a thermal sensor.

In this paper, we report a new Type IV microcalorimeter with much reduced errors above 300 K. Based on computer simulations of two dimensional (2D) thermal profile and micro-fabrication, we found that a sample platform composed of concentric Pt leads as a heater and a thermal sensor, and an isothermal Au film of a disc shape had better heat confinement, thus producing a better isothermal condition. Moreover, we had both of the isothermal platform and heater/sensor leads located in one side of the membrane by use of an amorphous SiO_2 (*a*-SiO_2) insulation layer so that the micro-fabrication became easy and cost-effective. As a result, the Type IV microcalorimeter provided accurate C_p value within 3% of the standard data at temperatures from 300 to 550 K when we use for measurements the lumped-τ_2 model, in which the effect of the radiation at high temperatures can be considered effectively.

2. Experimentals

2.1. Thermal simulation

To apply thermal simulation by use of COMSOL Multiphysics™, the two types of microcalorimeters were prepared. Fig. 1 shows a structure of Type III and of newly designed Type IV microcalorimeters used in the simulation. The cross-sectional and planar views of Type III are shown in Fig. 1(a) and (b), respectively, which consists of the Au isothermal layer located in the center of the *a*-Si:N membrane (1000 nm thick). Meander-shaped Au heater/sensor leads (50 nm thick) are located on the left and right sides of the Au isothermal layer, respectively. The width of Au heater/sensor leads is 20 μm and the distance between each

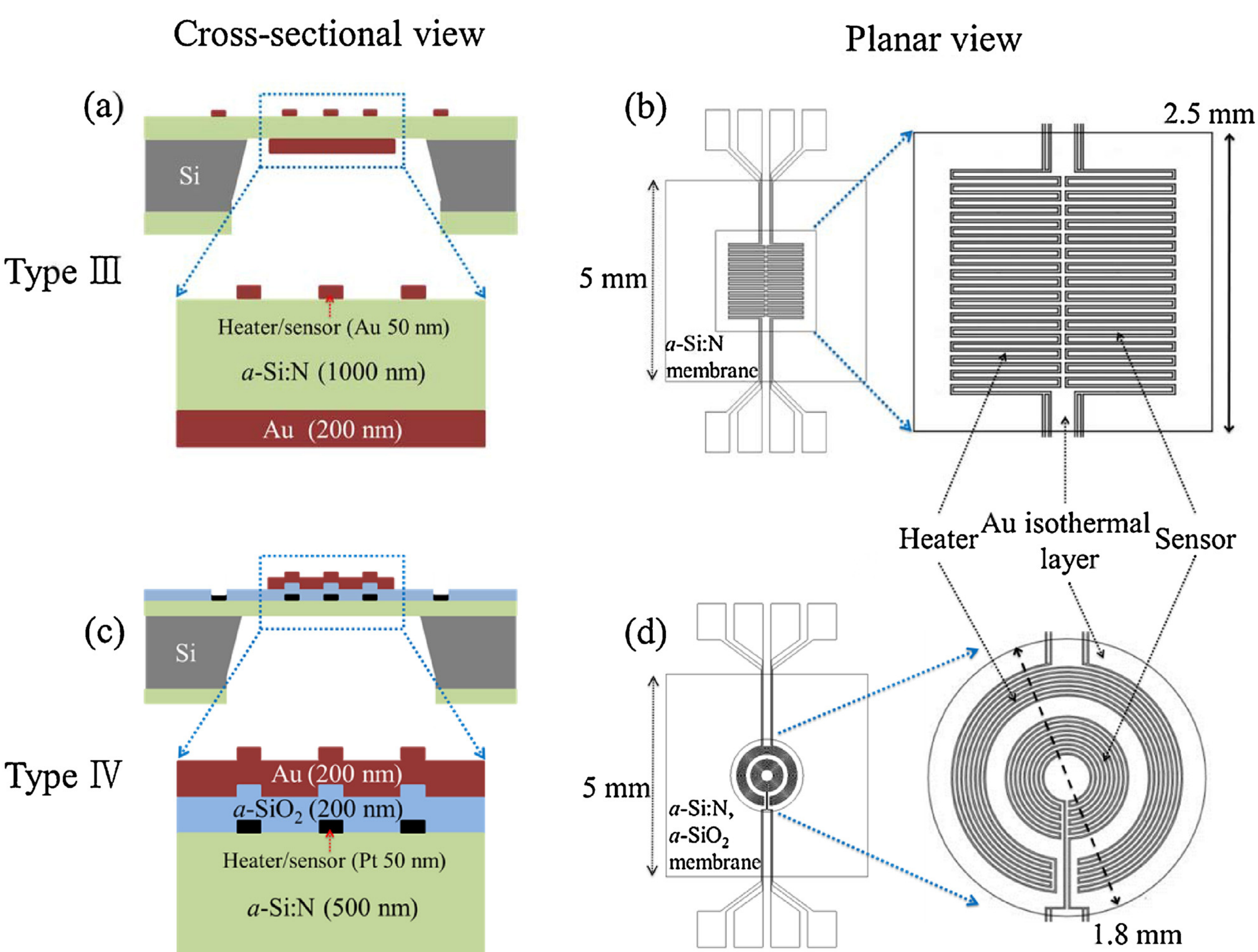

Fig. 1. Schematic drawings showing (a) cross-sectional and (b) planar layouts of our previous microcalorimeter (Type III, reproduced from Ref. [31]), and (c) cross-sectional and (d) planar layouts of the new microcalorimeter fabricated in this work (Type IV). In (a) and (b), the *a*-Si:N membrane is supported by the Si frame (10 × 10 mm^2) while the Au isothermal layer is located in the backside of the *a*-Si:N membrane. In (c) and (d), the membrane area is composed of *a*-Si:N and *a*-SiO_2 layers while the Au isothermal layer of a disc shape and Pt heater/sensor leads of a concentric shape are located in the center of the membrane. The area of the Au isothermal region is reduced in Type IV microcalorimeter.