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Nano-DTA and nano-DSC with cantilever-type calorimeter

Osamu Nakabeppu[a,*], Kohei Deno[b,1]

[a] Meiji University, School of Science and Technology, Department of Mechanical Engineering, Higashimita 1-1-1, Tama-ku, Kawasaki 214-8571, Japan
[b] Tokyo Institute of Technology, Graduate School of Science and Engineering, Department of Mechanical Sciences and Engineering, Japan

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ABSTRACT

Differential thermal analysis (DTA) and differential scanning calorimetry (DSC) of the minute samples in the range of microgram to nanogram were studied using original cantilever-type calorimeters. The micro-fabricated calorimeter with a heater and thermal sensors was able to perform a fast temperature scan at above 1000 K/s and a high-resolution heat measurement. The DTA of minuscule metal samples demonstrated some advances such as the thermal analysis of a 20 ng level indium and observation of a strange phase transition of a binary alloy. The power compensation type DSC using a thermal feedback system was also performed. Thermal information of a microgram level sample was observed as splitting into the DSC and DTA signals because of a mismatch between the sample and the calorimeter. Although there remains some room for improvement in terms of the heat flow detection, the behavior of the compensation system in the DSC was theoretically understood through a lumped model. Those experiments also produced some findings, such as a fin effect with sample loading, a measurable weight range, a calibration of the calorimeter and a product design concept. The development of the nano-DTA and nano-DSC will enable breakthroughs for the fast calorimetry of the microscopic size samples.

1. Introduction

New distinguished methods have been developed by introducing the nanotechnology or micro-electro-mechanical systems (MEMS) technology into the research fields of the thermal analysis and calorimetry. Performance of the temperature and heat measurements has been drastically improved by the MEMS technology. Micro thermal sensors, such as thin-film thermocouple or resistors on diaphragm, bridge, and cantilever structures, have the features of both high thermal resistance and low thermal capacity, and enable the measurement of trace amounts of heat with a high temporal resolution. Furthermore, integration of the devices and sensors in a tiny body allows advanced functions in thermal measurement and control such as self-calibration, improved sensitivity, and a thermal feedback control function. Along with such progress in the nanotechnology, a novel thermal analysis method, so-called "nanocalorimetry" or "chip calorimetry," has emerged with expectations of a rapid progress in the thermal analysis and calorimetry.

Significant pioneering studies have been reported since the end of the 20th century. Differential thermal analysis (DTA) of indium clusters on a thin-film calorimeter, which is composed of two thin metal strips on a thin membrane, have shown interesting results by continuous temperature scanning at an exceedingly high rate, namely the discrete melting point of the indium clusters corresponding to its size [1].

Thermal observation of a catalytic reaction using a thermal-bending-type tiny bimorph cantilever probe has also been reported [2]. The reaction of oxygen and hydrogen on a Pt layer of the cantilever in a vacuum chamber was observed as periodic exothermic reactions at the microwatt level with period of several tens of seconds.

Furthermore, observations of the rotating phase transition of an extremely small polymer specimen were also reported. With a micro-mechanical calorimetry using the thermal bending of an atomic force microscope (AFM) cantilever probe, it was demonstrated that the phase transition of Tricosane down to 7 pg can be observed in continuous heating and cooling operations [3]. Conventional commercial thermal analyzers or calorimeters typically need a several milligram samples for a reliable analysis. This study shows that the MEMS technology can provide significant opportunities for the thermal analysis and calorimetry of the small samples ranging from milligram to micro, nano, and even picogram levels.

There are many rate-related processes in the phase transition and state change of the polymer materials. Thus, very fast temperature scan rates can reveal hidden behaviors. For example, the

* Corresponding author.
E-mail address: onakabep@meiji.ac.jp (O. Nakabeppu).
[1] Present affiliation: Canon Inc.

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Nomenclature

T	Temperature [°C or K]
ΔT	Temperature difference [K]
P	Heating rate or heat flow [W]
Q	Heat [J]
G	Thermal conductance [W/K]
G_Q	Feedback gain
H	Enthalpy [J]
τ	Time constant [s]
m	Mass [kg]
f	Frequency [Hz]
t	Time [s]
t_P	Period of temperature scan [s]
L	Latent heat [J/kg]
C	Heat capacity [J/(kg K)]
E	Voltage [V]
α	Coefficient
β	Coefficient

Subscript

s	Sample
r	Reference
h	Heater
∞	Ambient value

melting and reorganization process of polyethylene terephtalate (PET) shows a rate dependence in a fast heating process up to the order of 10,000 K/s [4,5].

The authors also showed a calorimetric study with the cantilever-type nanocalorimeters [6,7]. The calorimeters were developed with the same technique used in making a scanning thermal microscope (SThM) cantilever probe [8,9]. With the calorimeter, the DTA and DSC of tiny metal samples were tried. A mass measurement method in the range of microgram to nanogram was also demonstrated using a mechanical resonance of the cantilever-type calorimeter [7]. It is applicable to nano-thermogravimetry (TG) with coupling the temperature scanning.

A combination of a combinatorial method and nanocalorimetry was also reported. It allows the high-throughput thermal analysis of thin-film compound of different composition by depositing the sample on a two dimensional array of nanocalorimeters with composition gradient and then conducting the fast calorimetry with each calorimeter [10,11].

In this paper, characteristics of the nano-DTA and nano-DSC with the original cantilever-type calorimeters are reported. In the following sections, we discuss the calorimeters and their specifications, the DTA experiments with twin calorimeters or a single calorimeter, the experiment and theoretical analysis on the power compensation (pc-) DSC, and some practical findings on the nanocalorimetry. Topics of the resonance mass measurement or the nano-TG will be reported in our forthcoming paper.

2. Cantilever-type nanocalorimeters

Two types of cantilever calorimeters were made by the basic microfabrication process (Fig. 1): the DTA type and the DSC type. The cantilever body of both types is made of SiO_2, which is a 2-μm-thick thermal oxidation layer on a Si substrate. Metal lines of Ni and Cr were fabricated by the lift-off method and then covered with a protective layer of 1-μm-thick deposited SiO_2. The cantilevers were isolated from the Si substrate by a wet etching process.

The dimensions of the DTA-type calorimeter are 230 μm long, 270 μm wide and 3 μm thick. Four devices are arranged on the cantilever between the end and the base: a heat spreader for maintaining a uniform temperature in a crosswise direction, a straight line heater for the temperature scan, a thin-film Ni–Cr thermocouple for measuring temperature, and a serpentine-shaped thermopile for monitoring the heat flow along the calorimeter. The typical line width of the heater and sensors is 6 μm.

Performing the DTA requires the twin calorimeters with identical characteristics to reduce the common mode noise and disturbances. Thus, the twin calorimeters were made within 1 mm region on the same Si chip through the same fabrication process. However, they often showed some differences each other in the specifications such as the heat capacity, the thermal conductance, and the sensitivity of the thermocouple. It may be caused by some inevitable unevenness in the deposition rate and etching rate in the process. Thus, we used two differential methods in the DTA experiments: the simultaneous differential method with the twin calorimeters of identical characteristics, and the time-differential method where the reference and the sample data are taken in sequence using the same single calorimeter, referred to as the time-DTA.

The DSC calorimeter was designed for the power compensation type. It was equipped with four devices: the thermocouple, a

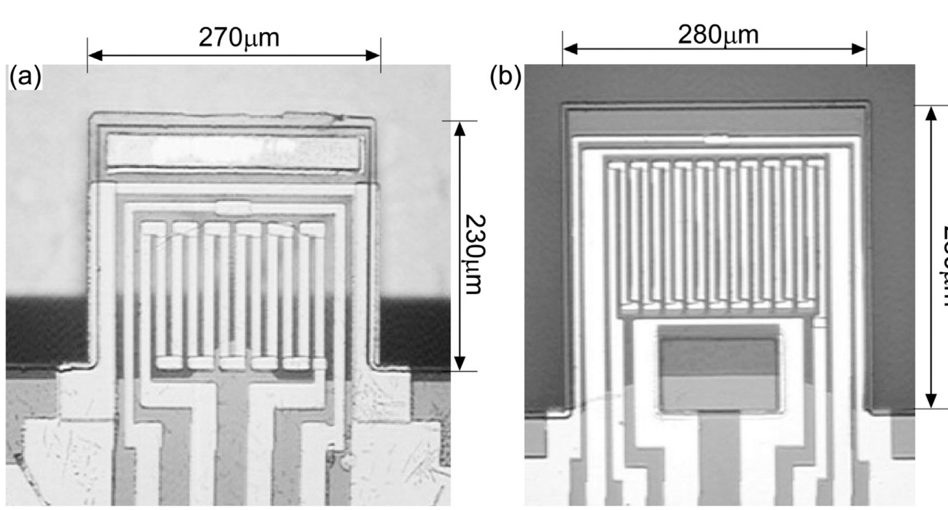

Fig. 1. Cantilever-type nanocalorimeters. The DTA type (a) includes heat spreader, heater, thermocouple and thermopile from the end to bottom. The DSC type (b) has thermocouple, compensation heater, thermopile and scan heater.