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Article

Nanocalorimeter for DTA and Mass Measurement in High Temperature Range

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The introduction of the MEMS technology into thermal sensing enables thermal analysis of minute samples. In our previous study on the cantilever type nanocalorimeter, fast DTA and mass measurement using mechanical resonance for micro- to nano-gram level samples were demonstrated. The use of the nanocalorimeter, however, was empirically limited below 400 °C. In this study, a heat-resistant MEMS calorimeter has been developed to extend the MEMS-based thermal analysis to the high temperature range. The new calorimeter is equipped with platinum thin film devices such as a resistance temperature detector (RTD), a heater and a strain gauge on a SiO_2 micro cantilever body. The characteristics of the calorimeter, performance of the DTA and the mass measurement were experimentally studied. It was shown that the annealing of the calorimeter improves the reproducibility of the devices with diminishing electrical resistance change during thermal analysis in high temperature range. In a high temperature DTA test with a micro-gram level aluminum sample, endothermic and exothermic peaks corresponding to melting and solidification were clearly observed. It was demonstrated that the heat-resistant MEMS calorimeter extended the analytical temperature range to up to 800 °C. Moreover a resonance system applicable to high temperature use was developed by introducing the strain gauge into the calorimeter. The resonance mass measurement system demonstrated a performance of nano-gram level mass measurement.

Keywords: Nanocalorimetry, MEMS, High temperature, DTA, Mass measurement

1. Introduction

With the progress of the nanotechnology, highly-sensitive, fast and multi-functional tiny sensors become available. High-speed thermal analysis and calorimetry for minute samples become possible by introducing the MEMS (Micro Electro Mechanical Systems) technology. The so-called nano-calorimetry or chip-calorimetry is expected for study and analysis of minute samples such as nano-particles, nano-structured or thin film materials. The feature of fast thermal analysis is also important for research on non-equilibrium phenomena.

Nakagawa[1)] reported a rotational phase transition of 7 pg tricosane using a cantilever of the AFM (Atomic Force Microscope) as a thermal sensor based on thermal bending. Zhang et al.[2)] showed an impressive size dependence of the melting point of indium clusters with a thin film calorimeter. Minakov et al.[3)] demonstrated a rate dependence of melting and recrystallization of the PET (Polyethylene terephthalate) by using a commercially available vacuum gauge as a chip-calorimeter. The authors group has developed a cantilever type MEMS calorimeter equipped with thin film thermal devices such as thermocouple, thermopile and heater. The cantilever type calorimeter enables the fast DTA and a resonance mass measurement of the micro- to nano-gram samples.[4)] Thermal and mass analysis of nano-gram level, so-called nano-TG, was also demonstrated.[5)]

In our previous study, the cantilever type calorimeter was designed for normal temperature range and empirically shows an upper temperature limitation of around 400 °C. The use of the MEMS calorimeter is limited to the application of polymer or low melting point materials. The nanocalorimetry did not respond to demand of analysis in high temperature range for metallic and inorganic materials. Therefore, we started developing a heat-resistant MEMS calorimeter available up to around 1000 °C with the purpose of extension of the application range of the nanocalorimetry.

In this research, the cantilever type calorimeter composed of a SiO_2 body and Pt thin film devices was made and its characteristics were experimentally studied. In a t-DTA (time differential thermal analysis) test, melting and solidification of an Al tiny sample were demonstrated. Furthermore, the resonance mass measurement method applicable to the high temperature range with 10 ng level resolution has been developed by introducing a strain gauge method instead of an optical displacement detection method. In the following part, we report the characteristics of the heat-resistant MEMS calorimeter, and performance of the high-temperature t-DTA and the resonance mass measurement.

2. Heat-resistant cantilever type MEMS calorimeter

2.1 Concept of the heat-resistant MEMS calorimeter

The authors have studied the nanocalorimetry with the cantilever type MEMS calorimeter for the normal temperature shown in Fig.1. The normal temperature type is composed of the

SiO_2 cantilever and thin film devices of Ni and Cr. The calorimeter can be applied to three calorimetry modes, such as t-DTA with a scanning heater and thermocouple, the flux type DSC with those and thermopile, and the compensation type DSC with those and a compensation heater. The calorimeter provides high speed calorimetry for micro- to nano-gram sample of the temperature scan rate of over 10,000 K/s. The upper limitation of the nanocalorimetry is practically around 400 °C, which is far low from melting point of the used materials. The thermal stress may cause the damage of the thin film devices since thermal bending of the calorimeter was observed and breakdown of the thin film devices often happens during the high temperature scans.

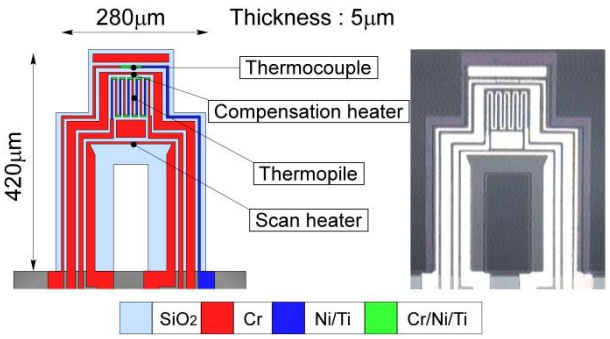

Fig.1 The cantilever type MEMS calorimeter for normal temperature range. It is applicable to the t-DTA, DSC and the resonance mass measurement.

As for the mass measurement, the calorimeter can measure mass of the sample placed at the end of the cantilever with the resolution of 10 ng level by detecting the mechanical resonance frequency of the first order with the optical method such as a laser displacement meter or a photo-interrupter. The simultaneous thermal and mass analysis, which corresponds to so-called nano-TG, was also demonstrated in the normal temperature range below 400 °C. If the resonance mass measurement method were applied to high temperature range, it would be hard to use the optical displacement monitoring method. Therefore, an alternative method for detecting the cantilever oscillation should be introduced for the heat-resistant calorimeter.

In the development of the MEMS calorimeter for high temperature range, we designed it with taking following three requirements into consideration; (1) thermal devices composed of heat-resistant materials, (2) reduction of thermal deformation and (3) self-detection of the cantilever bending. Figure 2 shows the design and fabricated calorimeter. The heat-resistant MEMS calorimeter was fabricated through the micro-fabrication process such as photolithography, sputtering, lift-off and wet-etching. The calorimeter is equipped with platinum thin film devices on the micro cantilever of 640 x 820 μm^2 rectangular-shape. Platinum was chosen as the device material because of its oxidation and corrosion resistance property and high melting point. The cantilever has a sandwich structure of the SiO_2 base of 2 μm, the Pt thin film device layer of 0.5 μm and another SiO_2 protection layer of around 1 μm. The symmetric structure with respect to the device layer is favorable to reduction of thermal stress on the thin film devices, but it reduces the sensitivity of the strain gauge at the same time. There is a tradeoff relation between the sensitivity and the thermal stress. Thus, the thickness of the current protection layer was decided to reduce the thermal stress and provide the sensitivity to some extent under the condition of the simple sandwich structure. The calorimeter has two thermal devices and one mechanical sensor. For the thermal analysis, a resistance temperature detector (RTD) and a scan heater are used. Both devices have four electrodes for precise electrical resistance measurement. A rectangular strip of Pt at the end of the cantilever is a heat spreader for making uniform temperature distribution in a sample position. The strain gauge near the bottom is newly employed for the displacement measurement instead of the external optical method. The mechanical resonance of the cantilever is maintained in the mass measurement mode by shaking the cantilever with a piezo device with positively feed backing the detected oscillation signal by the gauge.

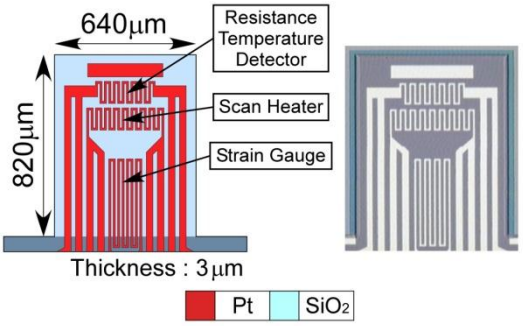

Fig.2 Design and photo of the heat-resistant MEMS calorimeter for the DTA and mass measurement.

2.2 DTA and mass measurement system

Using the experimental setup shown in Fig.3, the characteristics of the MEMS calorimeter and t-DTA were studied. Temperature of the calorimeter is measured by the RTD. Current and voltage drop across the RTD are measured simultaneously, and resistance value of the RTD is calculated later from those values. Temperature scan is conducted by applying programmed voltage on the scan heater by a function generator. When the voltage proportional to square root of time is applied to the heater, Joule heating achieves a linear temperature scan under a constant heat conductance condition. Temperature scan at a rate below 1 Hz or of a period longer than 1 sec shows a quasi-steady state behavior under the balance of the Joule heating and heat transfer from the cantilever to ambience. Each signal is captured by an A/D board at sampling rate of 1 kHz.

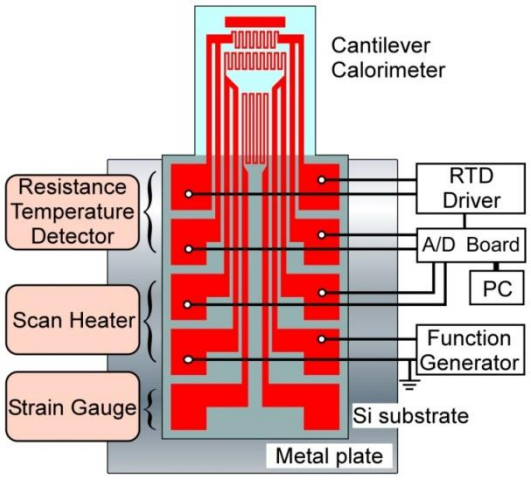

Fig.3 Experimental setup of the t-DTA

The t-DTA is conducted by two-step temperature scan without and with a sample. First, reference data is captured with an empty cantilever. Then, sample data is captured with sample-loaded state under the same scan condition. Finally, DTA data is formed by subtracting the reference data from the sample

data on a PC. The conventional thermal analysis instruments offer reference and sample pans of same thermal characteristics, and simultaneous differential measurement directly gives information of sample. Since it is difficult to fabricate two cantilevers having completely same thermal properties, the time differential thermal analysis is employed. Fortunately, the MEMS calorimeters have relatively high reproducibility in the temperature scan, because the heat transfer process is conduction dominant and time span of the analysis is so short. Therefore the t-DTA provides enough performance.

The resonance mass measurement is conducted with the setup shown in Fig.4. The strain gauge detects the oscillation of the cantilever through a bridge circuit. The oscillation wave signal is shaped and amplified through a high-pass filter and an amplifier, and then the phase of the wave is shifted so as to boost the oscillation. The feedback signal is converted to a mechanical shaking with a bending type piezo element attaching on the cantilever base. This positive feedback system automatically maintains the cantilever in resonance state. In practice, the resonance is excited by adjusting the phase of feedback signal with watching the FFT spectrum of the cantilever oscillation. For the simultaneous thermal and mass analysis, the resonance frequency is recorded through a voltage to frequency converter circuit with the thermal signals.

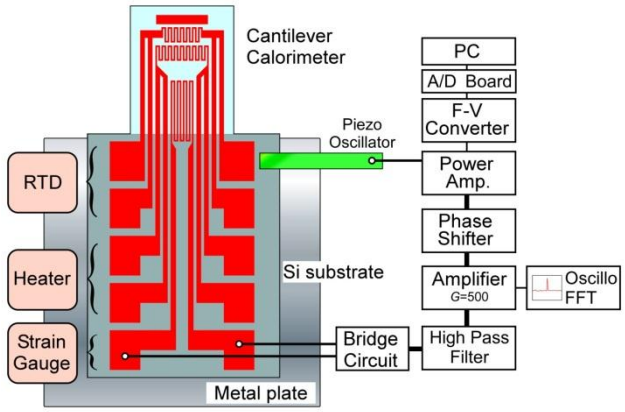

Fig.4 Auto resonance system with the strain gauge

2.3 Specifications of the calorimeter

Specifications in thermal and mechanical characteristics are tabulated in Table 1. The thermal response of the heat-resistant MEMS calorimeter under the atmospheric condition was investigated by applying triangle wave heating at frequency of 0.1~100 Hz and detecting temperature oscillation by the RTD. Fig.5 shows the board diagram of the temperature amplitude for the triangle-wave heating of 14 mW maximum power at each frequency. At the range of 0.1~1 Hz, constant temperature response of about 94 K was obtained. It shows the thermal conductance G from the cantilever to the ambient is 151 μW/K. With the increase in the heating frequency, temperature amplitude gradually reduces and cut-off frequency f_c and time constant τ are estimated to be 12 Hz and 13 ms, respectively. From these values, effective heat capacity of 2.0 μJ/K was derived. With the assumption of maximum temperature raise of 600 K and the measured time constant, maximum scan rate was estimated to be 45,240 K/s. The calorimeter shows good thermal response and enables extremely fast temperature scan of 10^4 K/s order. The temperature coefficient α of the RTD was measured through a melting test of tiny indium sample on the calorimeter during a temperature scan below 1 Hz. By comparing the RTD output at the melting with standard melting point of indium, the α was decided to 1.81 x 10^{-3} K^{-1}. This value is smaller than the temperature coefficient of bulk platinum. One of the reasons may be an effect of a buffer layer of Cr between the Pt thin film and the SiO_2 base.

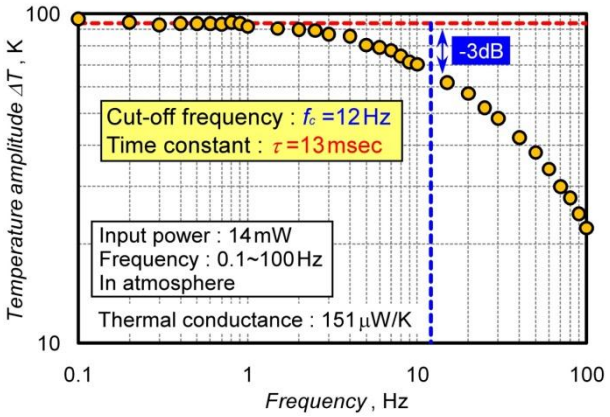

Fig.5 Thermal response of the heat-resistant MEMS calorimeter

Table 1 Specifications of the heat-resistant MEMS calorimeter

Thermal time constant	τ [msec]	13
Heat capacity of the cantilever	C_p [μJ/K]	2.0
Thermal conductance to ambient	G [μW/K]	151
Maximum scan rate (@ΔT = 600 °C)	ϕ [K/sec]	45,240
Temp. coefficient of the RTD (R.T.~ 250 °C)	α [1/K]	1.81 x 10^{-3}
Resonance frequency (in air)	f_R [kHz]	4.7
Effective mass of the cantilever	M^* [μg]	1.46
Spring constant	k [N/m]	1.27

Mechanical properties were decided through a resonance mass measurement test. In the linear vibration theory, the resonance frequency of the first order of the rectangular shaped cantilever is expressed by the following equation.

$$f_R = \frac{1}{2\pi}\sqrt{\frac{Ewt^3}{4l^3(m_s + 0.24lwt\rho)}} = \frac{1}{2\pi}\sqrt{\frac{k}{m_s + M^*}} \quad (1)$$

Where, E is Young's modulus, ρ is density, w, t, l are width, thickness and length of the cantilever. M^* and m_s represent the effective mass of the cantilever and concentrated mass of sample at the end of the cantilever, respectively. The k is effective spring constant of the cantilever. Eq. (1) indicates that resonance frequency is inverse proportion to the square root of the effective mass of $m_s + M^*$. In order to decide the M^* and k, the resonance frequency of the calorimeter with known mass samples is measured. Detail will be described in the section of mass measurement. Typical results are included in the Table 1.

3. DTA test of micro-gram metal samples

3.1 DTA in normal temperature range

Figure 6 shows a result of a fast t-DTA of tiny indium sample with the heat-resistant MEMS calorimeter. A temperature scan

was carried out from room temperature to 250 °C in a second. The fast temperature scan of over 470 K/s enables to observe endothermic and exothermic peaks corresponding to melting and solidification of the indium sample. The RTD was calibrated using the detected melting peak of indium. The latent heat L is obtained from the product of the peak area S and thermal conductance of the cantilever G.

$$L = G \cdot S \tag{2}$$

The latent heat of melting and solidification was calculated as L_m = 49.6 μJ and L_s = 45.5 μJ from the Eq. (2). From a standard heat of fusion of indium, the measured heat is equivalent to 1.6~1.8 μg. The calorimeter demonstrated fast t-DTA for micro-gram level sample.

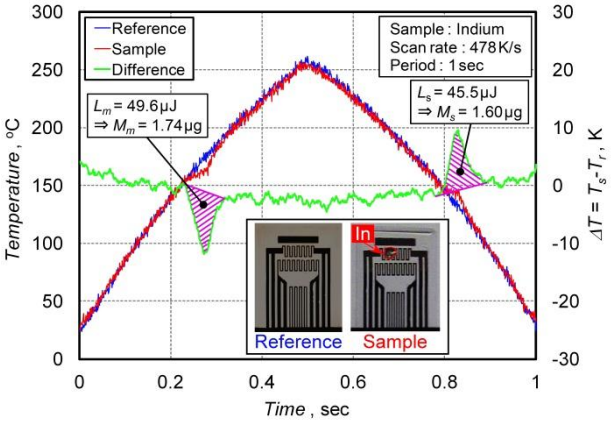

Fig.6 Fast t-DTA of micro-gram level indium sample with the heat-resistant MEMS calorimeter

3.2 Characteristics of the RTD in high temperature range

During a temperature scan test in high temperature range up to around 700 °C, we found that the resistance of the thin film thermal devices increased after each temperature scan. Such a phenomenon was not observed in the DTA in the normal temperature range below 250 °C. Since the low reproducibility in temperature scan is critical for the t-DTA, we examined high temperature characteristics of the RTD in series temperature scans ranging from room temperature to around 700 °C. The heating was conducted by applying a periodic voltage wave with the form of square root of time on the heater. Although the maximum voltage of the wave was kept constant, heating rate reduced gradually because of the increase in resistance of the heater. Tiny zinc and indium samples were loaded on the cantilever to identify the temperature using the melting point.

Electrical resistance of the RTD in a total of 101 times of the temperature scan is plotted in Fig.7. At the first scan, it can be seen that resistance of the RTD elevates after the scan with respect to the initial level. The resistance elevation per scan gradually reduces with repeating the temperature scan. At the 101st scan, the resistance elevation after the scan becomes very little. The trend of the resistance after the each scan shows the first order decay feature, and is extrapolated to convergence value of about 291 Ω within 1000 sec. The resistance of the scan heater also increased with the high temperature scan. Thus, the maximum temperature reduced with scan number. For example, the maximum temperature of 714 °C at the first scan decreased to 602 °C at the 101st scan. The resistance trend during the high temperature scans showed that the annealing up to required temperature reduced the drift of the resistance in adequately small level within relatively short duration and improves the reproducibility of the Pt thin film devices. Although the reason or mechanism of the resistance change has not been clarified yet, the annealing can be effective for the high temperature thermal analysis with the MEMS calorimeter.

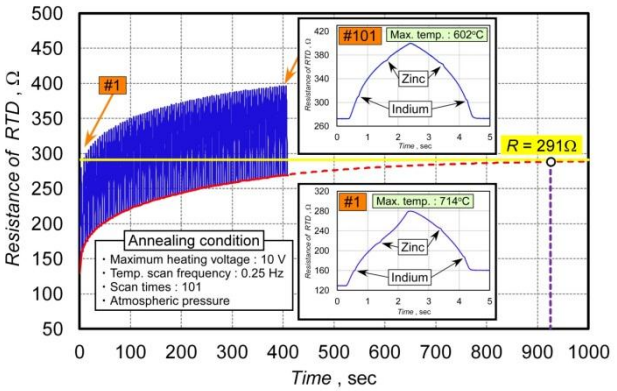

Fig.7 Electrical resistance change of the RTD in a series temperature scan of 101 times

After the series scan experiment, we extracted a relation between the resistance and known temperatures; room temperature, melting point of the zinc and that of indium. The calibration curve of the RTD resistance R against the temperature difference from room temperature ΔT can be expressed by the following quadratic equation, not by the linear equation.

$$R = 272.25 \times \left(1 + 1.07 \times 10^{-3} \Delta T - 4.51 \times 10^{-7} \Delta T^2\right) \tag{3}$$

Although, the temperature coefficient of the RTD was derived from the linear relationship in the normal temperature range as above mentioned, the precise calibration of the RTD with a polynomial equation is required for the high temperature thermal analysis. Using the above calibration equation, the resistance data at the 101st scan was converted to temperature data, and then the melting and solidification peaks are extracted by assuming base line using the temperature data nearby each peak as shown in Fig.8. It shows that the phase change of 2 μg level metal sample can be measured with an acceptable accuracy level by the high temperature scan up to 600 °C. For high temperature use of the MEMS calorimeter, the annealing and the calibration of the RTD in the wide temperature range are required.

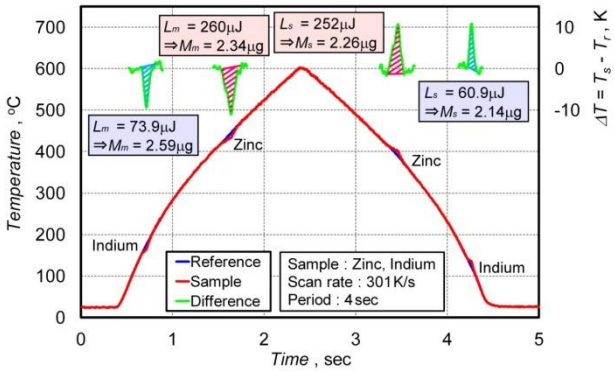

Fig.8 High temperature thermal analysis after the annealing

3.3 DTA in high temperature range

High temperature t-DTA was conducted with a micro-gram level aluminum sample with another annealed calorimeter. The calorimeter was annealed in advance by the consecutive temperature scans with gradually increasing the highest temperature from 500 to 800 °C until the resistance drift reduced adequately. Here, tiny pieces of zinc and indium for the temperature calibration were loaded before the annealing.

After the annealing treatment, reference data was taken by scanning the calorimeter with the zinc and indium pieces. Then, a tiny aluminum sample was loaded on the cantilever and sample data was taken under the same condition as the reference.

The t-DTA of the tiny aluminum sample was performed by the temperature scan ranging from room temperature to 840 °C in a four seconds period as shown in Fig.9. The calibration of the RTD was done by the three melting points and room temperature. Melting and solidification peaks of the aluminum sample are clearly observed with a high reproducibility.

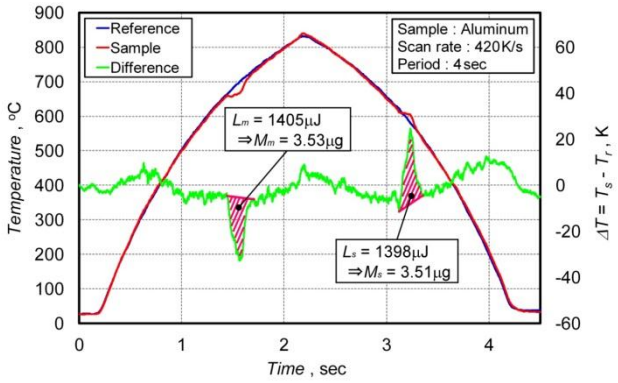

Fig.9 High temperature time-DTA of aluminum sample

During the scan in the high temperature range, small light emission was observed. After the t-DTA experiment, the heated cantilever was observed under an optical microscope. Since the heater was already broken, power was applied to the RTD. Figure 10 shows the red glow state of the heated thin film. The red glow region spreads from the center of serpentine part to outside with increase of power. If the radiation from the calorimeter became a dominant heat transfer mechanism, steep slope change in the temperature scan curve would appear because of an increase in the heat conductance. From the temperature scan data in the Fig.9, the thermal conductance, which is defined by the ratio of heating rate to temperature rise, shows a gradual increase with temperature. The effect of the radiation below the current maximum temperature may be small. The increase of the thermal conductance seems to be mainly caused by the increase of the heat transfer coefficient of natural convection in the surrounding air.

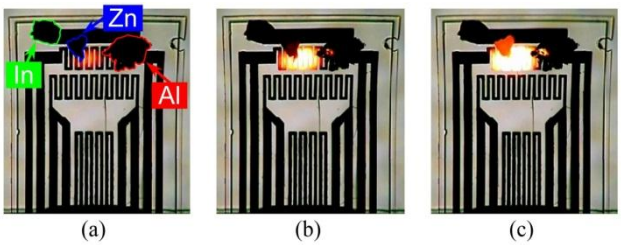

Fig.10 A red glow of the heat-resistant MEMS calorimeter

4. Resonance mass measurement with the heat-resistant MEMS calorimeter

4.1 Calibration of mass measurement

As above mentioned in the chapter 2, the effective mass M^* and spring constant k were decided through the calibration using the known mass samples. The resonance frequencies were measured step by step using the auto resonance system for an empty state, a one particle loaded state and a two particles loaded state. Here, the spherical particles of known density (Sepabeads, SP20SS, Mitsubishi Chemical Co.) were used as the calibration weight. The mass of the particle was calculated from its diameter measured under a microscope.

From the practical point of view, the resonance frequency f_R may be written by the following expression.

$$f_R = \frac{1}{2\pi}\left(\frac{k}{m_s + M^*}\right)^n \qquad (4)$$

In the calibration process, there are two options in deciding the properties of the cantilever and the characteristics of the resonance. One option is the way where the dependence n is fixed to -1/2 as the theory and M^* and k are decided from the experimental data. The other is that the M^* is calculated from the CAD designed values and the dependence n and k are derived from the experiment. Calibration curves with the both way are plotted in Fig.11 and the derived variables are tabulated in Table 2. Fortunately, there is no practical difference between the two calibration curves. However, it is better to adopt the former way of the fixed dependence of -1/2, since there must be some error in the fabrication and it is difficult to know the precise mass of the cantilever in advance.

After the calibration process a small indium piece was loaded and the resonance frequency was measured. The resonance frequency was converted to the mass of the piece and the effective mass of the calorimeter by using the calibration curve as shown in Fig.11. Those two calibration curves provide the mass of about 1.9 μg with 1.8 % difference. It shows that the fabrication, the calibration process and the excitation of resonance were conducted with adequate accuracy.

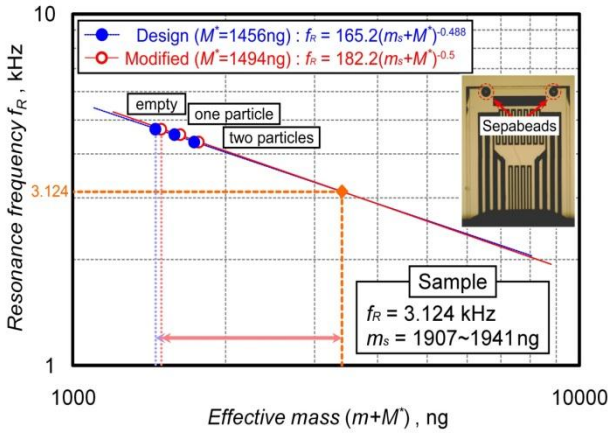

Fig.11 Calibration curve between the effective mass and the resonance frequency

Table 2 Fitting of the variables in the mechanical resonance

Priority	M^* [μg]	k [N/m]	n [-]
n	1.494	1.30	-0.5 (theory)
M^*	1.456 (design)	1.27	-0.488

4.2 Nano-gram level mass monitoring test

Performance evaluation of the simultaneous thermal and mass analysis with the heat-resistant MEMS calorimeter has not been conducted yet. So far a mass monitoring test with volatile organic substance was conducted to find the resolution.

In the test, *l*-menthol was deposited onto the cantilever and sublimation process from the cantilever was recorded as resonance frequency change. The *l*-menthol is a colorless columnar crystalline substance and sublimates at room temperature. The test was conducted with a following procedure. The *l*-menthol was melted in a tiny crucible. The deposition of the *l*-menthol vapor on the calorimeter occurred when the crucible was set beneath the calorimeter, and yielded enough amounts within a few seconds. After the crucible was moved away from the calorimeter, sublimation of the deposited *l*-menthol was observed as the resonance frequency change. Figure 12 shows a typical result of the deposition and sublimation processes. Maximum amount of the deposition is estimated to be 80 ng and the gradual increase of the frequency after the steep drop indicates the sublimation. The resonance frequency returns to the initial level within about 25 seconds.

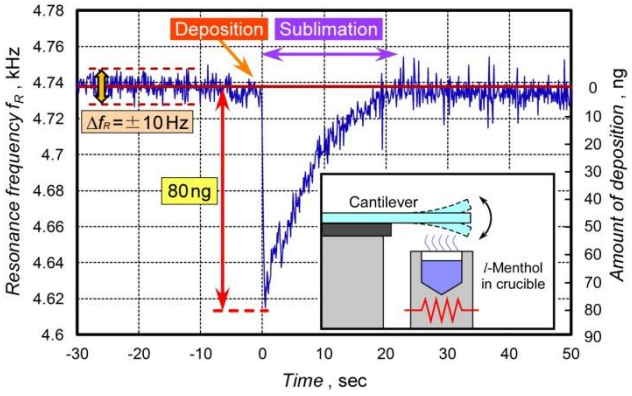

Fig.12 Mass monitoring during deposition and sublimation process of *l*-menthol

From the Eq. (1) of the resonance frequency, the resolution of the mass measurement Δm is proportional to a ratio of standard variation to the resonance frequency $\Delta f_R/f_R$ as described by the following equation.

$$\Delta m = -2\frac{\Delta f_R}{f_R} M^* \qquad (5)$$

From Fig.12, the amount of a fluctuation in the resonance frequency is estimated to be ±10 Hz. From Eq. (5), the resolution turns out to be ±6 ng. It shows that the calorimeter can perform the nano-gram level mass measurement.

5. Conclusion

The cantilever type heat-resistant MEMS calorimeter was fabricated and tested for the t-DTA in the high temperature range and the resonance mass measurement of micro- to nano-gram samples. The calorimeter is equipped with the RTD, heater and strain gauge of Pt thin film on the SiO_2 body for the high temperature use. The specifications of the calorimeter in thermal and mechanical characteristics show the performance in high-speed temperature scan rate of over 10,000 K/s and the mechanical resonance frequency of about 5 kHz. It was revealed that the annealing of the calorimeter is necessary to get the reproducible electrical resistance characteristics of the devices to the high temperature scan.

The high temperature DTA test with the annealed calorimeter showed that melting and solidification of micro-gram level aluminum were clearly observed by temperature scan over 800 °C. The upper limitation in the temperature scan range of the MEMS calorimeter was substantially extended. The resonance mass measurement system available for the high temperature operation was developed by introducing the strain gauge in the calorimeter. The system demonstrated the mass measurement performance with 6 ng resolution in the test of the deposition on and sublimation from the calorimeter of the volatile substance. The possibility in the high temperature thermo-mass analysis for the micro- to nano-gram samples was demonstrated.

Acknowledgements

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