Ultrasonic, fast, thin-film differential scanning calorimeter

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The equipment for an ultrasonic, fast, thin-film differential scanning calorimetry [(TDSC) or nanocalorimetry] technique is described. The calorimetric cell (−0.30 cm²) operates by applying a short (≈10 ms) dc current pulse (≈10 mA) to a thin (≈50 nm) patterned metal strip, which is supported by a thin (≈50 nm) SiNₓ membrane. The calorimeter operates at high heating rates (15–200 K/ms) and is very sensitive (30 pJ/K). The design of the calorimeter, the timing/synchronization methods, as well as the choice of key components of the instrument are discussed. Comparisons are made between two dc pulsing circuits that generate the current, a battery powered system and a system based on discharge of an assembly of charged capacitors (recommended). Design concepts for the differential as well as a simplified nondifferential technique are discussed and evaluated via experiments on thin films of indium. The differential design shows an increase in sensitivity, making it suitable for small samples. The custom made electronic circuits are also described, including the design of a preamplifier with low (28×) and high (700×) gain options, which are also compared using experimental data. Noise considerations are critical for the method. Simple models which describe noise levels in the calorimetric data are given and methods for reducing noise are discussed in detail. The sources of noise in the instrument are discussed in terms of both fundamental factors such as Johnson noise of the metal strip, as well as the limiting attributes of the sensing and pulsing circuits and instrumentation. These limiting attributes include spurious signals generated by desorption of ambient gases from the sensor, ground loops, switching regulators, and missing codes in analog-to-digital converter instruments. Examples of the experimental data of heat capacity Cₚ(T) of various thin films of indium, tin, and polystyrene are presented. A complete data set of raw experimental values is included for a 20 nm sample of Sn which shows the values of current and voltage of both the sample and reference sensors, as well as the differential voltage and the final values of the heat capacity. © 2004 American Institute of Physics. [DOI: 10.1063/1.1633000]

I. INTRODUCTION

Thin-film differential scanning calorimetry [(TDSC), or nanocalorimetry] is a technique by which to probe the thermophysical properties of films with nanometer-scale thickness. TDSC has been used in investigations of the melting properties of small (down to 2 nm diameter) supported particles of In, Sn, and Al (Refs. 1–3, and references therein), microscopic monocrystals of polyethylene, and glass transition in 1–400 nm thick films of polystyrene, poly(2-vinyl pyridine), and poly(methyl methacrylate) (Ref. 5 and references therein). Similar methods have been discussed and used to study melting and crystallization in linear polyethylene. Fabrication of the microelectromechanical system (MEMS)-based sensor (calorimetro cell) and basic data processing are described elsewhere. Here we discuss in detail the equipment needed for the nanocalorimetry technique and the hardware-introduced uncertainties of this method.

II. PRINCIPLES OF OPERATION

The TDSC sensors are fabricated by a standard microlithographic process on Si wafers. The sensor consists of an extremely thin (30–400 nm thick) SiNₓ membrane supported by a Si frame, as illustrated in Fig. 1 (top plot). The lateral dimensions of the membrane are several millimeters. A thin (typically 50 nm thick) metal strip is fabricated on the top of the sensor across the membrane. The typical width of the strip is 0.5 mm. Fabrication of the TDSC sensors is discussed in detail elsewhere. Figure 1 (bottom plot) gives a brief schematic of the microfabrication process.

The sample investigated is deposited either directly onto the metal strip or onto the SiNx side beneath the strip. During operation (calorimetric scan), a pulse of current is applied through the metal strip. The strip serves both as a heater and as a thermometer. Only the part of the strip placed on the membrane far from the Si frame can be heated effectively. Metallization on the frame remains cold due to the high heat capacity of thick (typically 0.25 mm) and passive (in comparison with the membrane) Si frame. The temperature of the center (working) part of the heater on the membrane can be measured by its resistance. To do this, the voltage across the working part of heater V is monitored during the scan via patterned electrical probes (see Fig. 1). Using the value of current I through the heater, also monitored during the experiment, resistance R and temperature T as functions of time t can be calculated. The simplified circuitry used for this...
ings. In this case, all Joule heat, with power

time for dissipation of the heat from the cell to its surround-

by the heater, is consumed by an increase in the temperature

should be evaluated by a calibration procedure prior to the

a lift-off procedure.

measurement is illustrated in Fig. 2. The \( R(T) \) function

The working part of the heater, the sample on it (if any),

and the part of SiN beneath it form a calorimetric cell. Us-

ing high current, it is possible to approach adiabatic working

conditions, since the extremely fast heating rate provides no
time for dissipation of the heat from the cell to its surround-
ings. In this case, all Joule heat, with power \( P = IV \) generated

the heater, is consumed by an increase in the temperature of the cell:

\[
P(t)dt = C_p(T)dT,
\]

where \( C_p(T) \) is the total heat capacity of the cell. \( C_p(T) \)
is the sum of the heat capacity of the empty cell (addenda)

\( C_p^{\text{cell}}(T) \), which can be measured in a separate (idle) experiment,

and the heat capacity of the sample \( C_p^{\text{SMP}}(T) \).

The remarkably low thickness of the cell constituents,

i.e., the heater and the membrane, provides an extremely

small addenda, which is key to high sensitivity of the TDSC

method. However, this characteristic of the sensor in itself is

not enough to achieve the sensitivity demonstrated.\(^1\) The dif-

ferential scheme greatly improves the measurement. Two

sensors are used in this case, one with sample material on it

(the sample sensor) and the other without (the reference

sensor), as illustrated in Fig. 3. During a scan, synchronized

pulses of current from two separate supplies are applied to

the sensors. Figure 4 shows an example of typical raw ex-

perimental data. Current through the heaters \( I_S \) and \( I_R \) [Fig.

4(a)], voltage across the heaters \( V_S \) and \( V_R \) [Fig. 4(b)], and
differential voltage \( \Delta V \) [Fig. 4(e)] are monitored during the

experiment (where indices \( S \) and \( R \) are the sample and refer-

cence sensors, respectively). It has been shown,\(^9\) that the use-

ful signal, i.e., the heat capacity of the sample, is roughly

proportional to the derivative of \( \Delta V \) over time [demonstrated

in Fig. 4(e)]: \( C_p^{\text{SMP}} \approx \frac{\Delta V}{dt} \). The \( I_S \), \( I_R \), \( V_S \), and \( V_R \) data

are used to calculate the resistance of heaters \( R_S \) and \( R_R \)

[shown in Fig. 4(c)] and temperature of calorimetric cells \( T_S \)

and \( T_R \) [Fig. 4(d)]. The final output, the heat capacity of sample \( C_p^{\text{SMP}} \)
as a function of sample temperature \( T_S \) (calo-

rimetric curve), is shown in Fig. 4(f).

Typical experimental parameters are as follows. The heating rates are from 15 to 200 K/ms. The scanning tempera-
ture interval is from room temperature to 300 °C; this cor-
responds to \( 1.5–20 \) ms scan time. For the typical heat
capacity of an empty cell of \( 500–1000 \) nJ/K and resistance

FIG. 1. Top plot: Planar and cross-sectional views of a typical TDSC sensor

with a sample on it (not to scale). Bottom plot: Cross-sectional view of the

sensor at nine points during microfabrication. (a) Low stress SiN is depos-

ited on both sides of a wafer using low pressure chemical vapor deposition.

(b) Both sides of a wafer are coated with photoresist. (c) A photoresist layer

is patterned and developed. (d) A section of the SiN is etched away by

reactive ion etching. (e) The photoresist is removed and the exposed Si is

etched in an alkaline solution. (f) A photoresist layer is spun onto the front

side of the wafer. (g) The photoresist layer is patterned, the tone of the

exposure is reversed, and the photoresist layer is developed. (h) A metal

layer is deposited on the front side of the wafer. (i) The finished wafer after

a lift-off procedure.

FIG. 2. Nondifferential scheme of TDSC.

FIG. 3. Differential scheme of TDSC.
FIG. 4. (a)–(c) Raw experimental data and (f) final result for TDSC measurement of the 20 nm Sn film deposited on the sensor with Pt metallization. A current pulse of 8 ms duration starts at 1 ms. (a) Current through the heaters, (b) voltage across them, (c) heater resistance and (d) temperature for both the sample and reference sensors. Data for resistance and temperature are not valid when there is no current applied (<1 ms and >9 ms). (e) Differential voltage and its derivative over time; (f) the final \( C_p(T) \) curve of the sample.

of 50–150 Ω (for a Pt heater), the current through the heater is 10–50 mA and the voltage across it is 1–5 V. To get temperature resolution of about 1 K per reading, all electrical parameters are typically measured at a sampling rate of 100 ksamples/s (100 kHz).

III. DSC EQUIPMENT

A. Error analysis: Nondifferential mode

To analyze hardware requirements in the case of the nondifferential variant of the TDSC method, we will express errors in sample heat capacity using distributions of experimentally measured values of \( V_{IS} \) and \( V_S \) (see Fig. 2). Let us assume that the values of voltage measurement have random normally distributed deviations. We characterize these deviations in the voltage data by the root-mean-square (rms) value of deviation \( \varepsilon_V \), which we refer to as the voltage error or noise. Let \( \varepsilon_{V_{IS}} \) and \( \varepsilon_{V_S} \) be voltage errors (noise) of \( V_{IS} \) and \( V_S \), respectively. According to Eq. (1), the heat capacity of the cell is found to be

\[
C_p = \frac{P}{dT/\Delta t}.
\]

The term with the most noise, \( dT/\Delta t \), is calculated using \( R_S(t) \), which, in turn, is calculated from \( V_{IS} \) and \( V_S \). Using the relationship

\[
1 \frac{dR_S}{R_S} = \alpha \frac{dT}{dt},
\]

where \( \alpha \) is the temperature coefficient of the resistivity, and noting from the circuit in Fig. 2 that

\[
I_S = \frac{V_S}{R_S}, \quad I_{IS} = \frac{V_{IS}}{R_{IS}},
\]

the \( dT/\Delta t \) term can be expressed as

\[
\frac{dT}{dt} = \frac{1}{\alpha R_S} \frac{d[R_{IS}(V_S/V_{IS})]}{dt} = \frac{1}{\alpha V_S} \frac{dV_S}{dt} - \frac{1}{\alpha V_{IS}} \frac{dV_{IS}}{dt}.
\]

Numerically, for both \( V_{IS} \) and \( V_S \), the derivative \( dV/dt \) is expressed as \( (V_{i+1} - V_i)/\Delta t \), where \( V_i \) and \( V_{i+1} \) are consecutive data points of voltage measurements and \( \Delta t \) is the reciprocal of sampling frequency \( f_s \):

\[
\Delta t = \frac{1}{f_s}.
\]

Therefore, for the derivatives \( dV_{IS}/dt \) and \( dV_S/dt \), the errors (noise) are \( \sqrt{2} \varepsilon_{V_{IS}}/\Delta t \) and \( \sqrt{2} \varepsilon_{V_S}/\Delta t \), respectively. The error (noise) of \( dT/\Delta t \) (\( \delta_{dT/\Delta t} \)) can be expressed via the errors of two terms in Eq. (5):

\[
\varepsilon_{dT/\Delta t}^2 = \frac{2 \varepsilon_{V_S}^2}{\alpha^2 V_S^2 (\Delta t)^2} + \frac{2 \varepsilon_{V_{IS}}^2}{\alpha^2 V_{IS}^2 (\Delta t)^2} = \frac{2 \varepsilon_{V_S}^2}{\alpha^2 V_S^2 (\Delta t)^2} \left[ 1 + \left( \frac{\varepsilon_{V_{IS}}}{\varepsilon_{V_S}} \frac{R_{IS}}{R_S} \right)^2 \right]
\]

[for the last transformation we use Eq. (4)]. The fractional error of \( C_p(\delta_{C_p}) \), which is practically equal to the fractional error of the derivative \( dT/\Delta t \) (\( \delta_{dT/\Delta t} \)), can be expressed using Eq. (7):

\[
\delta_{C_p} = \delta_{dT/\Delta t} = \frac{\sqrt{2} \varepsilon_{V_S}}{\alpha V_S \Delta t} \sqrt{1 + \left( \frac{\varepsilon_{V_{IS}}}{\varepsilon_{V_S}} \frac{R_S}{R_{IS}} \right)^2}.
\]

Values \( V_S \) and \( dT/\Delta t \) are mutually dependent. Using the formula \( P = V_S^2/R_S \) and Eq. (2), we can express \( V_S \) as

\[
V_S = \sqrt{R_S C_p dT/\Delta t}.
\]

The value of temperature resolution \( r_T \) for a TDSC scan can be determined as a difference in temperature for two consecutive readings:

\[
r_T = \Delta t \frac{dT}{\Delta t}.
\]

For simplicity, we assume that the heat capacity of sample \( C_{SMP} \) is much less than the heat capacity of the cell itself: \( C_{SMP} \ll C_p \). This is also the most interesting case, because when \( C_{SMP} \) is comparable with the addenda or even larger, the signal is strong enough to be much larger than the noise in experimental output.

In order to obtain \( C_{SP} \), the heat capacity of cell \( C_p \) should be measured twice (both with and without the sample). Then, by combining Eqs. (6) and (8)–(10) the fractional error of \( C_{SP}(\delta_{C_{SMP}}) \) can be approximated by
\[
\delta_{C_p}^{SMP} \approx \sqrt{2 \frac{\delta_{C_p} C_p}{C_p}} \\
= \frac{2 \epsilon_{V_S} \sqrt{C_p}}{\alpha r T \sqrt{R_{SMP} R_{SF}}} \sqrt{1 + \left( \frac{\epsilon_{VIS} R_S}{\epsilon_{V_S} R_{IS}} \right)^2}.
\]

Note that the heat capacities in the last equation can be easily estimated using the following formulas:

\[C_p = lw (c_{Me} \rho_{Me} h_{Me} + c_{SiN} \rho_{SiN} h_{SiN})\]

and

\[C_p^{SMP} = lw c_{SMP} \rho_{SMP} h_{SMP}^{SMP},\]

where \(c\) is specific heat capacity, \(\rho\) is the specific density, \(h\) is the thickness, \(l\) is the distance between two voltage probes, \(w\) is the width of the heater strip, and indices \(Me\), \(SiN\), and \(SMP\) denote metal of the metallization layer, \(SiN\), and the sample, respectively. Parameter \(h_{SMP}\) has a special meaning of the average sample thickness if the sample is a discontinuous film or does not cover the working part of the heater entirely.

According to Eq. (11), minimization of voltage noise \(\epsilon_V\) (both \(\epsilon_{V_S}\) and \(\epsilon_{VIS}\)) is crucial for sensitivity in a nondifferential calorimetric experiment. The value of \(\epsilon_V\) is an important metrologic characteristic which can typically be found in documentation of voltmeters [or analog-to-digital converters (ADCs)]. \(\epsilon_V\) depends on the regime of the voltmeter: the range, sampling rate, etc. A properly chosen range can sufficiently decrease measurement error. Generally, \(\epsilon_V\) is reduced by narrowing the measurement range, either by decreasing the range of amplitude, or changing from bipolar to unipolar mode. Unipolar mode can be used because both \(V_{IS}\) and \(V_S\) are unipolar.

According to Eq. (11) (the last radical term), increasing of the value of current measurement resistor \(R_{IS}\) can also improve noise characteristics. Some limitations of this method are discussed in Sec. III G3. Note that increasing \(R_{IS}\) can also lead to an increase in the range of its corresponding ADC and, subsequently, to an increase in noise \(\epsilon_{VIS}\). In a properly optimized system, the last radical term in Eq. (11) would be close to unity so a simplified expression for \(\delta_{C_p}^{SMP}\) can be used:

\[\delta_{C_p}^{SMP} \approx \frac{2 \sqrt{C_p}}{\alpha r T \sqrt{R_{SMP} R_{SF}}} \epsilon_{V_S}.\]

Figure 5 illustrates a calorimetric curve obtained by the nondifferential method. Using Eq. (11) and the experimental parameters in the caption of Fig. 5 (\(\epsilon_{VIS} = 80 \mu V\), \(\epsilon_{V_S} = 120 \mu V\), \(R_{IS} = 20 \Omega\), \(R_S = 70 \Omega\), \(\alpha = 0.0019 K^{-1}\), \(C_p = 650 nJ/K\)), \(C_p^{SMP} = 450 nJ/K\), \(f_S = 100 kHz\), \(dT/dt = 35 K/ms\), number of scans \(-100\) we can estimate that the noise of \(\Delta V\) is random and normally distributed, and characterize it by the rms value of deviations, voltage error \(\epsilon_{\Delta V}\). Similar to in Sec. III A, the error of \(d\Delta V/dt\) is \(\sqrt{2}\epsilon_{\Delta V}/\Delta t\). Since the fractional error of \(C_p^{SMP}\) \((\delta_{C_p}^{SMP})\) is close to the fractional error of \(d\Delta V/dt\), one finds that

\[\delta_{C_p}^{SMP} \approx \frac{2 V_R \epsilon_{\Delta V}}{\alpha R R_{\Delta} (d T_R/dt)^2 C_p^{SMP}}.\]

Note that an additional \(\sqrt{2}\) coefficient is added to Eq. (16) because two heat capacity measurements are required to obtain \(C_p^{SMP}\) (one with and one without the sample). \(V_R\) and \(d T_R/dt\) are mutually dependent. As in Sec. III A, combination of Eqs. (6), (9), (10), and (16) gives

For comparison with Fig. 5, the peak-to-peak value of the absolute error at room temperature (RT) can be estimated as 0.10\(\times 450 nJ/K\times 6 \approx 300 nJ/K\), which is in excellent agreement with the data presented in Fig. 5.

**B. Error analysis: Differential mode**

For analysis of noise in differential mode (see the scheme in Fig. 3), let us start with an approximate equation,

\[C_p^{SMP} \approx \frac{V_R}{\alpha R R_{\Delta} (d T_R/dt)^2} \times \frac{d \Delta V}{d t}.\]

Index \(R\) denotes the reference sensor or circuit. The derivative of differential temperature \(\Delta V\) over time \(t\) is typically the term with most noise in Eq. (15). As in Sec. III A, we assume
\[
\delta_{C_{P,\text{SMP}}} \approx \frac{2 \sqrt{C_p}}{\alpha r_T^3 C_p} \sqrt{R S f_S} \epsilon_{\Delta V}.
\]

Here we assume that \(\alpha\) and the resistance of both the sample and reference sensors are the same.

where 13 nJ/K is roughly the heat capacity of the sample close to room temperature. For comparison with Fig. 6, the peak-to-peak value of the absolute error at room temperature can be estimated to be 0.17×13 nJ/K×6≈13 nJ/K, which is in excellent agreement with the data presented in Fig. 6.

Note that, in comparison with the nondifferential measurement in Fig. 5, the differential measurement in this example gives about (300 nJ/K)/(13 nJ/K)≈20-fold improvement in the noise level. Other parameters of these two measurements are close to each other, except that of the noise characteristics of the ADC for \(\Delta V–\text{ADC}\) measurements (\(\Delta V–\text{ADC}\)), which are even worse than those of the ADCs used in the nondifferential experiment in shown in Fig. 5.

The nature of the demonstrated advantage of the differential method becomes clear if we compare expressions for fractional errors in nondifferential \(\left(\delta_{C_{P,\text{SMP}}}^{\text{nondif}}\right)\) and differential \(\left(\delta_{C_{P,\text{SMP}}}^{\text{dif}}\right)\) methods [see Eqs. (14) and (17)]:

\[
\frac{\delta_{C_{P,\text{SMP}}}^{\text{nondif}}}{\delta_{C_{P,\text{SMP}}}^{\text{dif}}} = \frac{\epsilon_{V_S}}{\epsilon_{\Delta V}}.
\]

For small samples, the measured differential signal \(\Delta V\) is close to zero. Consequently, the \(\Delta V–\text{ADC}\) range of measurement can be effectively reduced, which causes a large reduction in the noise level \(\epsilon_{\Delta V}\) (see the note above choosing the range of measurement in Sec. III.A). In most cases, the simplest method for reducing the \(\Delta V–\text{ADC}\) range is using a preamplifier with an absolute value of gain \(|g|>1\) and negligible noise. In this case, the effective noise of \(\Delta V–\text{ADC}\) would be smaller than the specified value by factor of \(|g|\). That is, a preamplifier with gain \(g=–28\) makes \(\delta_{C_{P,\text{SMP}}}\) for a differential measurement (in the example above) much smaller than for a nondifferential one.

However, it should be noted that decreasing the noise of \(\Delta V–\text{ADC}\) by using preamplifiers with large gain has limitations. Since, in practice, \(\Delta V\) is not exactly zero even for infinitesimal samples, using large gains would lead to over-range conditions. Additionally, some types of noise in the TDSC assembly (i.e., noise of the current supply, thermal noise of the sensors, internal noise of the preamplifier) scale with the gain of the preamplifier and become a dominant factor at large enough gains. These issues are discussed in detail in Secs. III.E–III.G.

A related problem is the choice between differential and nondifferential modes of operation for the given sample. For samples with heat capacities much smaller than the addenda \((C_{P,\text{SMP}} ≪ C_{P,\text{cell}})\), differential mode usually is the only choice. However, when \(C_{P,\text{SMP}}\) is comparable with \(C_{P,\text{cell}}\) or larger (for simplicity, average thicknesses of the sample and the working part of sensor can be compared instead of heat capacities), the signal will be large enough to make using the nondifferential mode feasible. In this case of a strong signal, the gain of the preamplifier should be small enough to prevent over-range conditions. However, with a decrease in gain, the difference in sensitivity between two modes vanishes, and a technically more simple nondifferential mode can be more favorable.

**C. Error analysis: Additional considerations**

The following considerations are applicable both for nondifferential and differential modes of TDSC.

Noise \(\delta_{C_{P,\text{SMP}}}\) can also be effectively reduced at the expense of the temperature resolution, \(r_T^\prime\): \(\delta_{C_{P,\text{SMP}}} \propto r_T^\prime\) [see Eqs. (11) and (17)]. It is worth noting that simple box averaging (smoothing) of the \(C_P(T)\) curve is not effective, because any improvement in noise would be proportional only to \(r_T^\prime\). A more detailed discussion can be found elsewhere.9

Averaging of more than one scans is an effective and practical way to reduce the noise. Generally, \(\delta_{C_{P,\text{SMP}}}\)
D. ADCs used in TDSC: Additional considerations

Most ADCs, which can serve as $\Delta V$–ADCs, can work also as ADCs for $V_{IS}$, $V_{IR}$, $V_{S}$, and $V_{R}$ measurements. However, TDSC optimization makes different demands for $\Delta V$–ADC and ADCs for nondifferential (ND-ADCs) parameters.

Good dc characteristics are more important for ND-ADCs. Calorimetric cell temperature $T$ is the most sensitive parameter for errors such as significant offset, gain error, and integral nonlinearity. Using Eqs. (3) and (4), the error of $T(\varepsilon_T)$ is found to be

$$
\varepsilon_T = \frac{1}{\alpha} \sqrt{\delta_{VIS}^2 + \delta_{V_S}^2},
$$

where $\delta_{VIS}$ and $\delta_{V_S}$ are fractional errors of $V_S$ and $V_{IS}$. Due to small values of $\alpha$, $\varepsilon_T$ is sensitive to $\delta_{VIS}$ and $\delta_{V_S}$. For example, $\delta_{VIS} = \delta_{V_S} = 0.1\%$ (accuracy of $0.1\%$ is not a bad value for ADCs with $100$ kHz sampling frequency) and $\alpha = 0.0019 \; \text{K}^{-1}$ (from the examples discussed above) give $\varepsilon_T \approx 0.7 \; \text{K}$, which cannot be tolerated in some precise experiments.

In contrast, $\Delta V$ measurements are resistant to dc errors such as offset and gain error. Since $C_P$ is proportional to the $\Delta V$ derivative [Eq. (15)], the offset has no importance. Gain error would proportionally magnify the $C_P$ value; since error in the absolute $C_P$ value of a few percent is typically acceptable, gain error is not very important either.

The ac characteristics are very important for both ND-ADCs and $\Delta V$–ADC, but the latter is typically more sensitive. Frequency-domain specifications such as total harmonic distortion (THD), the spurious-free dynamic range (SFDR), or the signal-to-noise and distortion (SINAD) ratio characterize the presence of spurious signals on the $C_P(T)$ curve. An example of an extreme type of spurious signal, the missing codes effect, is shown in Fig. 7. It should be noted that spurious signals significantly increase when the signal amplitude approaches the ADC range limit.

We conclude that an ADC optimized for accurate dc and low-frequency ac measurements is more suitable as a ND-ADC, whereas an ADC optimized for precision ac-signal analysis or high-quality audio applications is more appropriate as the $\Delta V$–ADC. ADCs with nominal resolution not less than 16-bit and frequency band not less than from 0 to 25 kHz (which corresponds to 50 kHz and more of sampling and output frequency) are recommended. Low input impedance of the ADC provides shunting of the circuitry and decreases the accuracy of temperature measurements. We recommend input impedance greater than 1 M$\Omega$. Note that only ADCs with true differential inputs can be used; those with pseudodifferential, single-ended or inputs polarized by any means require an additional preamplifier with differential inputs (an example is shown in Fig. 8). Inasmuch as a preamplifier is typically used for $\Delta V$–ADC, this requirement for $\Delta V$–ADC is not important.
E. Differential mode: Acquisition of differential voltage data

The initial ΔV-signal is amplified using a custommade, low-noise preamplifier with differential input and asymmetrical output. Then, the amplified signal is digitized by a precision ΔV−ADC. The principal circuitry of the preamplifier is demonstrated in Fig. 8. The preamplifier is designed using the classical scheme for an instrumentation amplifier.10 The preamplifier is based on Linear Technology LT1028AC operational amplifiers with ultralow voltage and current spectral noise densities: $e_{\text{Vamp}} = 0.85$ nV/√Hz and $e_{\text{opamp}} = 1.0$ pA/√Hz, respectively (typical values, input referred, measured at 1 kHz frequency and ambient temperature of 25°C), and good high-speed characteristics (typical gain−bandwidth GBW product value of $f_{\text{GBW}} = 75$ MHz).11 The total input referred voltage noise density $e_V$ of the preamplifier can be expressed as

$$e_V = \sqrt{2}e_{\text{Vamp}} + 2(e_{\text{opamp}}R_{\Delta V})^2 + e_{\text{VT}}^2,$$

where the spectral density of thermal (Johnson) noise $e_{\text{VT}}$ is given by

$$e_{\text{VT}} = \sqrt{4kTR_{\Delta V}},$$

where $k$ is the Boltzmann constant ($1.38 \times 10^{-23}$ J/K) and $R_{\Delta V}$ is the resistance of the source of the ΔV signal. Typical values of $T = 300$ K and $R_{\Delta V} = 200$ Ω (for Pt metallization) give $e_{\text{VT}} = 1.8$ nV/√Hz, which is significantly larger than $e_{\text{opamp}}R_{\Delta V} = 0.2$ nV/√Hz and $e_{\text{Vamp}}$. So, in this case, the value of $e_V = 2.2$ nV/√Hz is determined largely by $e_{\text{VT}}$. Modifications of the sensor design can considerably reduce the value of $R_{\Delta V}$. Replacing Pt metallization by a Au one decreases $R_{\Delta V}$ about fivefold; shortening the heater and increasing the thickness of the metallization will also reduce $R_{\Delta V}$. In this case the contribution of the $e_{\text{Vamp}}$ term will grow and, at some point, can be the major type of noise. Using $n$ operational amplifiers ($n > 1$) in parallel can solve this problem. The effective voltage noise density $e_V$ of such design will be reduced by a factor of $\sqrt{n}$. Current noise $e_I$ will be increased by the same factor, but it will not increase the total noise because in Eq. (20) the term with the $e_I$ value contains a reduced $R_{\Delta V}$ coefficient.

The gain of preamplifier $g$ is a subject for special consideration. The output signal of the preamplifier is measured by an ΔV−ADC, which is characterized by input referred voltage noise density $e_{\text{VADC}}$. The ΔV−ADC adds additional noise to the value measured unless the gain of the preamplifier is so high that $e_V \times |g| \gg e_{\text{VADC}}$. On the other hand, the gain of the preamplifier is limited by the amplitude of the ΔV signal: after amplification this signal should not exceed the full scale input range of the ΔV−ADC device. For example as shown in Fig. 4, the amplitude of the signal is ~80 mV, and for the typical input range of ±10 V the gain should not exceed 120.

To keep the signal in the input range of the ADC without sacrificing signal-to-noise characteristics, several methods have been used. Using the ADCs with ultrahigh resolution gives the best results. An alternative is using a preamplifier with regulated gain. In this case, the low gain values can be used for massive samples with a high ΔV signal (when there is no increase in noise seen in the strong signal), while the high gain values can be useful for small samples. However, even in small sample and idle experiments, the ΔV signal can be high enough so as to limit the possible gain value due to nonideal matching of the sample and reference sensors. Figure 9 demonstrates a typical ΔV signal for the idle experiment. Although the ΔV signal shown in Fig. 9 is relatively small (~10 mV) because both sensors are match well, the gain would be limited to 1000 (10 V/10 mV) for a typical ΔV−ADC input range of ±10 V. If we cared to measure the transient process at the beginning of the scan shown in Fig. 9 (at 1 ms), it would require gain less than 500 (10 V/20 mV).

To reject the strong ΔV signal caused by the difference in sensors, a special method can be used. As schematically illustrated in Fig. 10(a), a low gain preamplifier with gain $g_1$ is used to acquire data (low-gain baseline) from the first idle experiment. Then, in the additional idle experiment and during the experiment with the sample, the baseline is repeated by a function generator [a digital-to-analog converter (DAC)], and is subtracted from the signal by an additional operational amplifier. The result of the subtraction is additionally amplified (with gain $g_2$) and filtered. The total gain for the signal, measured by ΔV−ADC, is equal to $g_1g_2$.

![Figure 9](image-url) **FIG. 9.** Typical ΔV(t) dependence in an idle experiment. This measurement was made before the measurements shown in Fig. 4.

![Figure 10](image-url) **FIG. 10.** (a) Block diagram of baseline signal subtraction for the high-gain ($g_1 \times g_2$) method. The dashed line is used to acquire data in the first idle experiment. Then, in the second idle experiment and the experiment with the sample, the baseline accumulated is subtracted from the signal and the result is additionally amplified. (b) Block diagram of the regular (low-gain) method.
(high-gain measurement). The additional idle experiment gives the baseline for the high-gain measurement. The sequence of data acquisition is illustrated in Fig. 11. The standard data acquisition circuitry is shown in Fig. 10(b) for comparison. Technically, repeatable generation of a low noise signal is easier than digitizing a signal with the same signal-to-noise ratio. For this scheme, illustrated in Fig. 10, we use a 12-bit Hewlett-Packard 33120A 15 MHz function/arbitrary wave form generator with a Hewlett-Packard HP3458A voltmeter as the ADC. An example of improvement in the data achieved by this method is shown in Fig. 12. Curve (1) obtained using high-gain measurement [Fig. 10(a)], is significantly less noisy than curve (2) obtained by low-gain measurement [Fig. 10(b)]. Note that the decreased noise level in the high-gain curve (1) allows us to resolve the fine structure of the melting peak (shown in Fig. 12 between 1.5 and 3 ms) of deposited indium clusters.

F. Differential mode: Current source

The differential mode of TDSC sets special requirements on the noise level of the current source that feeds the heater of the sensor. To get the best results, the voltage noise in the heater \( e_{VH} \) caused by noise of the current through the heater \( e_{IH} \), should be much less than the thermal noise in the heater \( e_{VTH} \). Here \( e_{VH} \), \( e_{IH} \), and \( e_{VTH} \) are spectral noise densities, \( e_{VH} = R_S e_{IH} \), and \( e_{VTH} = \sqrt{4kT R_S R_A} \). Typical values of \( T = 300 \) K and \( R_A = 70 \Omega \) (for Pt metallization) give \( e_{VTH} = 1.1 \text{ nV}/\sqrt{\text{Hz}} \), so \( e_{IH} \) should be much less than 16 pA/\( \sqrt{\text{Hz}} \). In order to achieve this level of current noise, no active regulators of the current are used in the current source, as can be seen in Figs. 2 and 3. For typical values of \( V_{SUP} = 20 \) V and \( R_A = 1 \) k\( \Omega \), \( e_{IH} = \sqrt{4kT/(R_A^2 R_S)} = 3.9 \) pA/\( \sqrt{\text{Hz}} \). It is recommended that one use high quality components for the current source. We typically use low-noise stable wire-wound resistors (for example, Vishay Dale RS-2B), and logic level N-channel enhancement-mode metal–oxide–semiconductor field-effect transistors (MOSFETs) with low resistance in the open state as switches (for example, the Fairchild Semiconductor RF1K490088, with resistance at open state \( R_{DS(\text{on})} = 0.06 \) \( \Omega \), or the RFP30N06LE, with \( R_{DS(\text{on})} = 0.047 \) \( \Omega \)).

Another important aspect of the design is that both current sources (for the sample and reference sensors) should be precisely ac and dc decoupled, both from each other and from laboratory power lines. The whole system should be grounded at one point (typically the middle of the connection between the low-potential probes of sensors, as shown in Fig. 3). Neglecting these requirements creates ground loops and introduces significant spurious signals. This effect is illustrated in Fig. 13, where the initial signal (curve 1) and the signal after decoupling of the current source from power lines (curve 2) are shown. Note that spurious signals caused by ground loops typically appear as periodic signals with frequency of ac power and its second harmonic (60 and 120 Hz, respectively, in the U.S.).

Decoupling the current sources can be done in different ways. We have used two different types of current source in order to decouple the sources from each other and from the laboratory power lines. The first is based on the use of (off-the-shelf) 9 V batteries and the second is based on use of high quality capacitors. We have found that the capacitor system is better due to its long-term stability as well as its excellent scan-to-scan reproducibility. Details of each type of

![FIG. 11. \( \Delta V \) data acquired in the baseline subtraction method. (1) Initial \( \Delta V \) signal in the low-gain (\( g_1 = -28 \)) measurement (the first idle experiment). (2) High-gain (\( g_1/g_2 = 704 \)) baseline acquired in the second idle experiment. (3) \( \Delta V \) data acquired in the experiment with the sample (0.4 nm thick indium deposit). All curves are averages of 100 scans from room temperature up to about 300 °C.](image1)

![FIG. 12. (1) \( d(\Delta V)/dt \) signal obtained in high-gain \( g_1/g_2 = 704 \) and (2) low-gain \( g_1 = -28 \) measurement. Sample: 0.4 nm thick indium deposit. Curve (1) is shifted vertically for clarity. Both curves are averages of 100 scans from room temperature up to about 300 °C.](image2)

![FIG. 13. (1) Spurious signals in the \( \Delta V \) signal. For comparison (2) the same curve for decoupled current sources is presented. Both curves represent a single scan with no current through the sensors.](image3)
current source are now discussed. The most simple one is using batteries as a power supply. Figure 14 schematically illustrates this. The disadvantage of this method is that the discharge characteristics of batteries are not stable from scan to scan. Additionally, the voltage of the supplies should be monitored during the experiment to prevent failure caused by the limited electrical capacity of batteries. We have found that stability characteristics strongly depend on the type of battery used. We typically use Duracell 9 V PC1604 batteries with an alkaline Zn–MnO₂ electrochemical system, made in the U.S., and Ultralife 9 V U9VL batteries with a Li–MnO₂ system, made in the U.S. Each current supply typically contains two batteries connected serially.

A more advanced current source exploits capacitors as a power storage medium instead of batteries. A capacitor-based battery replacement for the current supply is shown in Fig. 15. The capacitors are recharged before each scan by a dc power supply, fed by laboratory ac power lines. During the scan, the capacitors are disconnected from the dc power supply. Typically, discharge of the capacitors during the scan is less than 1%. For example, for 20 V of initial voltage, a typical assembly with 5000 μF of total capacity stores 20 V×5000 μF=0.1 C of charge; the typical scan shown in Fig. 4 consumes about 18 mA×8 ms~0.14 mC. We typically use high-stability, high-frequency wet tantalum capacitors (for example, the Vishay Sprague 135D and M39006). Good ac decoupling can be achieved by minimizing parasitic electric capacitance between the current supply and all ac-fed, dc power supplies. Switches, which connect energy-accumulating capacitors and dc power supplies, should have negligible capacitance across an open connection. Electromechanical relays usually meet this requirement.

Since accumulating data from many scans is our usual practice, the repeatability of scans is important. Repeatability of the voltage across the energy-storing capacitors before each scan can be improved by using additional relays to charge the capacitor, as shown in Fig. 15. After being discharged in a scan, the capacitors are first recharged through a regular relay with high current capacity and a current-limiting resistor. After some time interval, a mercury wet relay makes an additional connection between the capacitor and the dc power supply. Mercury contacts provide negligible contact resistance even for small charge currents at the end of the charging procedure, and thus ensure repeatability of the voltage on the capacitor. Additionally, the dc power supply for charging the main energy-accumulating capacitor should be stable. We typically use a Hewlett-Packard E3632A dc power supply with output voltage stability of ±0.02% ±1 mV.

G. Differential mode: Additional considerations

1. Heating rates: Hardware limitations

As mentioned above, the typical heating rates are between 15 and 200 K/ms. Experimentally, the heating rates are controlled either by adjusting the value of the resistor in the heater circuit (see Figs. 2, 3, and 14) or (more rarely) by adjusting the voltage of the current supply. The range of the heating rate is limited by two main factors. As the heating rate is lowered, heat loss to the surroundings increases and the system departs from the ideal adiabatic condition. In addition, at lower rates, the overall uniformity of the temperature deteriorates, especially at the edges of the cell. Although we can partially compensate for the heat loss,9 correction for the temperature nonuniformity requires additional investigation. Consequently, to achieve adiabatic conditions with the present cell design, the heating rate should be significantly larger than the passive cooling rate of the cell, which is typically 1–2 K/ms in the 100–200 °C temperature range.

The upper limit of the heating rate is set by transient processes mostly at the start of a scan [for example, see Figs. 4(e), 9, 11, 12, 18]. These processes typically take a few tenths of a millisecond. To reduce transient processes, all of the equipment that is connected directly to the sensors (e.g., the current supply and ADCs), should be in close proximity and linked by short connecting wires.

Interestingly, the temperature lag effect typically is not a limiting factor for the upper value of the heating rates in the TDSC technique. The lag between the temperature of the thermometer and the average temperature of the sample is inherent for dynamic methods and is a common problem in conventional DSC. Nevertheless, for typical samples used in TDSC measurements, the thickness does not exceed several hundred nanometers and the temperature gradient across

FIG. 14. Battery-based current source.

FIG. 15. Capacitor-based replacement for the battery-based current supply shown in Fig. 14.
the sample–membrane–heater “sandwich” is negligible. The lag in temperature can be estimated using the following heat transfer considerations. An insulated thick plate with thickness \( h \) is suddenly exposed to constant heat input \( q \) on the front side of the plate. Above Fourier number \( F_{0} = \sigma r / \rho c h^{2} \), the drop in temperature \( \Delta T \) across the plate is constant, \( \Delta T = qh / 2\sigma \), where \( \sigma \) is the thermal conductivity of the plate.\(^{17}\) Noting that \( q = \rho c h dT / dt \) and using the characteristic thermal diffusion (TD) time \( \tau_{TD} = h^{2} \rho c / \sigma \), one can express \( \Delta T = (\tau_{TD} / 2)(dT / dt) \) and \( F_{0} = t / \tau_{TD} \). One of the worst cases of samples, investigated by the TDSC method, was a 400 nm thick polystyrene film.\(^{5}\) Using \( \rho = 1.043 \text{ g/cm}^{3}, \ \sigma = 1.223 \text{ J g}^{-1} \text{ K}^{-1} \), and \( c = 0.105 \text{ W m}^{-1} \text{ K}^{-1} \), the \( \tau_{TD} = 2 \mu s \). This means that, after about 1 \( \mu s \), the difference in temperature across the sample is about 0.2 K even at the highest heating rate of 200 K/ms used. Note that, using typical ADCs with a 100 ksample/s sampling rate, there is 2 K resolution at the same heating rate, which is much larger than the absence of the thermal lag effect in a 5 nm thick discontinuous In film. The shift of the melting peak is comparable to the temperature resolution of the measurement (the distance between experimental points).

2. Real-time control and time reproducibility

The TDSC equipment in differential mode requires synchronization between events such as the start and finish of current pulses through the sensors, the timing of charge capacitors, and the triggering of measurement devices. Good synchronization and repeatability of all time intervals are achieved by using a simple, microcontroller-based control device, e.g., a pattern generator (PG), as illustrated in Fig. 17. The PG acquires the time schedule for the experiment from the computer and then controls the measurement process in real time. Clocking of the PG is based on a standard quartz resonator, which provides excellent frequency stability (±50 ppm maximum for the currently used 8 MHz HC-49U crystal\(^{19}\)).

Good synchronization of current pulses also requires fast MOSFET switches and their control circuitry. Ac and dc decoupling of the MOSFET control circuitry from the PG output is achieved by a high speed optocoupler (see Fig. 14). We typically use Hewlett-Packard HCPL-2400 optocouplers\(^{20}\) with a 40 MBd typical data rate. The MOSFET driver should generate high current pulses to speed up switching of the MOSFET transistor, but should not consume significant current from the power supply, which has a limited capacity for stored energy. We typically use complementary MOS (CMOS) drivers with high output currents (six Schmitt-trigger inverters, SN74ACT14N\(^{21}\), with ±24 mA output current for each element and 1.5 mA maximal supply current).

Since the typical time interval between consecutive scans is 1 s, the operation time \( t_{o} \) of all electromechanical relays in the system should be much less than 1 s. We use miniature relays with a few milliseconds operation time \( t_{o} \) [Tyco V23026,\(^{22}\) \( t_{o} = 2 \text{ ms} \), SRC Devices LQ52,\(^{23}\) \( t_{o} = 6 \text{ ms} \)]. The maximum value of \( t_{o} \) for the mercury wet relays\(^{24}\) is 1.75 ms.

![FIG. 17. Real-time control system.](Image 531x246)

![FIG. 18. Illustration of the sensitivity of the differential voltage [referred to the output (RTO) of the preamplifier] to changes in values of adjustable resistors \( R_{AS} \) and \( R_{AE} \) (see Fig. 3). The preamplifier gain is equal to 704. Each curve is an average of 100 scans from room temperature up to about 300 °C. Sample: 2 nm thick indium film (the step in each curve shows melting of the indium particles).](Image 526x620)
3. Heater circuit adjustment

There is some degree of freedom in adjustment of the sensor’s heater circuitry. Generally, the first step in a typical experiment is to establish a nominal heating rate. This is easily accomplished by coarse adjustment of the trimming resistors, $R_{AR}$ and $R_{AS}$ (see Fig. 2). If the instrument is to be used in differential mode, which has the potential for high sensitivity, the response of both heaters must be carefully matched on a very fine scale. This can be accomplished by adjusting resistor $R_{AS}$ and thus fine-tuning the ratio $R_{AS}/R_{AR}$. Even small changes in this ratio will produce significant changes in the $\Delta V(t)$ signal, as shown in Fig. 18.

Adjusting the circuitry to obtain a flat $\Delta V(t)$ (as horizontal as possible, like the second curve from the top in Fig. 18) suppresses noise. There are several possible reasons for this effect. During data processing, the noisy terms contained in the $d(\Delta V)/dt$ factor are weighted less than other, less noisy terms. From a hardware point of view, a $\Delta V(t)$ signal that spans a small range collects fewer spurious signals. Full scale signals are generally more affected by integral nonlinearity in an ADC transfer function. Moreover, an ADC transfer function may exhibit more errors upon an increase in $d(\Delta V)/dt$. Additionally, making the $\Delta V(t)$ signal flatter sometimes allows us to reduce the range of the ADC, which often gives an advantage in decreasing the noise level.

Adjustments in the trimming resistors in order to obtain a flat $\Delta V(t)$ are recommended for the idle experiment in all cases. However, care should be taken if adjustments are performed in subsequent experiments with the sample. Only adjustment of the sample circuitry (e.g., of $R_{AS}$) is allowed. It is imperative that the reference circuitry (e.g., $R_{AR}$) remains the same for both the idle and subsequent experiments, in order to use corrections derived from the idle experiment. Additionally, after adjustment of $R_{AS}$ in the experiment with the sample, no simplified methods of calculation can be used.

It is important to be able to reproducibly set and reset the resistance in the heater circuit many times over the course of the experiment. An idle experiment typically includes many scans with different heating rates and, consequently, different settings for the adjustable resistors. In subsequent experiments with the samples, these resistor values, at least for the reference part of circuit, should be precisely reset to the original values. Because of this, the use of a precision resistor decade as an adjustable resistor is strongly recommended. Trimming of the adjustable resistors can be made either manually or (preferably) electronically. In the latter case, effective ac and dc decoupling of the decade from the control device (see the discussion in Sec. III E) should be made. We control the decades by electromechanical relays (typically by the Tyco V23026).22

There are concerns about choosing the resistance value of current measurement resistors $R_{IS}$ and $R_{IR}$ (Fig. 3). As mentioned in Sec. III A, increasing the $R_{IS}$ and $R_{IR}$ values suppresses noise, but there are limits to these resistances.

Analog common inputs of all ADCs (or preamplifiers) should be connected to the ground terminal, shown in Fig. 3, to prevent excessive noise. Increasing $R_{IS}$ and $R_{IR}$ increases $V_{IS}$ and $V_{IR}$ values. The top inputs of the $V_{IS}$ and $V_{IR}$ volt-

FIG. 19. Spectral components of high frequency noise in the $\Delta V$ signal (FFT plot). Components (1)–(3) and (5)–(7) are caused by the CRT monitor, and (4) is caused by the on-line UPS.

meters (as they appear in Fig. 3) have the highest common-mode potential (voltage between analog common and given inputs). Typically, the common-mode potential should not exceed 12–15 V (even if the voltage between signal inputs is within the voltmeter range limits). Exceeding the common-mode potential can cause faulty measurements, parasitic current through the input to the analog ground and, ultimately, permanent ADC failure. Even within the range specified by the manufacturer, measurements close to the limit of the common-mode potential can introduce additional spurious signals. As a rule of thumb, the voltage between the analog ground and any ADC (or preamplifier) input should be kept below 10 V all the time.

Additionally, large $R_{IS}$ and $R_{IR}$ reduce the ability to manipulate the heating rate by adjusting $R_{AS}$ and $R_{AR}$.

The voltage of the current supply is set to the highest possible level in order to minimize noise and changes in current during the scan, and is rarely adjusted.

4. Grounding considerations

As shown above, ground loops created by coupled current supplies introduce intolerable noise in the $\Delta V$ data. This clearly demonstrates that proper grounding, as well as shielding, is a critical part of TDSC equipment design. Common terminals of the analog part of all ADCs (and preamplifiers) should be connected to one point, which is typically the middle of the connection between low-potential probes of sensors, as shown in Fig. 3. All ground connections should be made with short, thick, copper, insulated wires. All signal connectors should be as short as possible and should have a grounded shield. Shielded twisted pairs are recommended. The vacuum chamber for TDSC should be metallic or surrounded by metal, and all metal parts should be grounded.

5. Additional noise sources

Noisy equipment in or near the laboratory can cause serious problems. Vacuum chambers are typically equipped with voltage regulators for different purposes (for example, resistive heating for in situ deposition). These usually use solid-state regulators and are noisy. Generally, all impulse
power devices are inherently noisy. For instance, by switching an on-line uninterruptable power supply (UPS) to bypass mode and replacing regular cathode ray tube (CRT) computer monitors by liquid crystal displays (LCDs) we can reduce the noise significantly. Figure 19 demonstrates a typical fast Fourier transform (FFT) plot for the $\Delta V$ signal acquired by the setup equipped with a UPS and CRT monitor. Spectral components of the high frequency noise are caused by the CRT monitor [components (1)–(3) and (5)–(7)] and by the UPS [component (4)] shown in Fig. 19. Nevertheless, we have found that modern switching-mode low-power supplies (such as computer power supplies) do not introduce noticeable noise.

6. Vacuum-dependent spurious signals

Adsortion and desorption of contaminants (e.g., adsorbed gases) in poor vacuum can generate significant spurious signals for small sample experiments, as illustrated in Fig. 20. Preheating the sensors by an additional scan immediately before measurement usually reduces this problem. Nevertheless, in some cases, preheating the sensor with the sample is not possible. This could be the case if the sample were prepared a by special treatment, and the experiment probes the state of the sample right after this treatment. Probing the heat capacity of a freshly annealed polymer film is one example. The preheating scan would destroy the state of the film. In such cases, improving vacuum conditions is recommended. Additionally, preheating/pulsing the reference sensor is useful.

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\[ R_{IS} \] resistance of the current measurement resistor in the sample cell circuit (\( \Omega \))
\[ R_{IR} \] resistance of the current measurement resistor in the reference cell circuit (\( \Omega \))
\[ R_{DS(on)} \] resistance of the MOSFET switch in the open state (\( \Omega \))
\[ R_{\Delta V} \] resistance of the source of \( \Delta V \) (\( \Omega \))
\[ r_T \] temperature resolution (K)
\[ T \] temperature (K, °C)
\[ \Delta T \] drop in temperature across the plate (K)
\[ t \] time (s)
\[ t_o \] relay operation time (s)
\[ V \] voltage (V)
\[ V_s \] voltage across the sample cell heater (V)
\[ V_R \] voltage across the reference cell heater (V)
\[ V_i, V_{i+1} \] consecutive results of voltage measurement (V)
\[ V_{IS} \] voltage across the current measurement resistor in the sample cell circuit (V)
\[ V_{SUP} \] voltage of power supply (V)
\[ w \] width of the heater strip (m)
\[ \alpha \] temperature coefficient of resistivity (K\(^{-1}\))
\[ \alpha_R \] temperature coefficient of resistivity of the reference cell heater (K\(^{-1}\))
\[ \Delta t \] time between two consecutive measurements (samples) (s)
\[ \Delta V \] differential voltage (V)
\[ \delta_{C_B} \] fractional error of \( C_B \)
\[ \delta_{C_{SMAP}} \] fractional error of \( C_{SMAP} \) obtained by the differential method
\[ \delta_{C_{SMAP}^{de}} \] fractional error of \( C_{SMAP} \) obtained by the differential method
\[ \delta_{C_{SMAP}^{non-de}} \] fractional error of \( C_{SMAP} \) obtained by the non differential method
\[ \delta_{dTD/dt} \] fractional error of \( dT/dt \)
\[ \delta_{VS} \] fractional error of \( V_s \)
\[ \delta_{VIS} \] fractional error of \( V_{IS} \)
\[ e_{dTD/dt} \] rms error (noise) of \( dT/dt \) (K/s)
\[ e_T \] rms error (noise) of \( T \) (K)
\[ e_V \] rms voltage error (noise) (V)
\[ e_{VS} \] rms error (noise) of \( V_s \) (V)
\[ e_{VIS} \] rms error (noise) of \( V_{IS} \) (V)
\[ e_{\Delta V} \] rms error (noise) of \( \Delta V \) (V)
\[ \sigma \] thermal conductivity (W m\(^{-1}\) K\(^{-1}\))
\[ \rho \] specific density (kg/m\(^3\))
\[ \rho_{Me} \] specific density of the metallization (kg/m\(^3\))
\[ \rho_{SiN} \] specific density of the SiN\(_i\) membrane (kg/m\(^3\))

\[ \rho_{SMAP} \] specific density of the sample kg/m\(^3\)
\[ \tau_{TD} \] characteristic thermal diffusion time (s)

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