Heat capacity measurements of Sn nanostructures using a thin-film differential scanning calorimeter with 0.2 nJ sensitivity

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We have developed a new thin-film differential scanning calorimetry technique that has extremely high sensitivity of 0.2 nJ. By combining two calorimeters in a differential measurement configuration, we have measured the heat capacity and melting process of Sn nanostructures formed via thermal evaporation with deposition thickness down to 1 Å. The equivalent resolution of the calorimeter is 1 nanogram in mass or 0.4 Å in thickness. We have observed a decrease of up to 120 °C in the melting point of Sn nanostructures. © *1997 American Institute of Physics.* [S0003-6951(97)04301-5]

The physical properties of materials confined to reduced dimensions hold great interest in both materials science and microelectronics communities.[1] Areas of interests include nanostructures, surface reactions, surface melting, dynamics of cluster coalescence, and formation of critical-size second phase nuclei[2] in solid state reactions. Due to the ultra small geometries or the presence of nearby surfaces and interfaces, a system behaves in ways significantly different than its bulk form. For example, the melting point of small particles is size dependent, decreasing as the particle size decreases.[3–6]

Calorimetry is a powerful characterization method[7,8] because it allows for measurements of a fundamental attribute of any material process—change in energy. Unfortunately, conventional differential scanning calorimetry (DSC) techniques are difficult to apply to nanoscaled systems because the amount of energy involved is too small. Recently, however, new membrane fabrication technology[9–11] and ultrafast 10^6 °C/s heating techniques[12] have led to substantial increases in calorimetry sensitivity.[6]

In this letter, we introduce a novel thin-film differential scanning calorimetry (TDSC) technique with ~0.2 nJ sensitivity, the highest ever reported to our knowledge.[13] This is equivalent to the chemisorption energy of ~1/1000 monolayer of hydrogen on W surface.[14,15] Using TDSC, we have performed calorimetric studies on the ultrathin films of Sn deposited on Si–N substrate via thermal evaporation. In this case, the film is discontinuous and self-assembled particles are formed. TDSC is capable of measuring the melting point of these particles and has demonstrated the phenomenon of size-dependent melting point depression. Also, TDSC is capable of measuring the small changes in heat capacity C_p, allowing us to use the calorimeter as a nanobalance for measuring the quantity of materials. Furthermore, the calorimeter has the potential for experimental probing of the predicted size dependence of C_p for extremely small particles.[16]

The design of TDSC includes two adjacent thin-film heaters[10] electrically coupled in a differential mode, only one of them supporting the sample of interest. Two synchronized electrical current pulses heat each heater simultaneously up

to 300 °C at a rate of ~30 000 °C/s. The resultant difference, in the electrical response of the two heaters, relates directly to the heat capacity C_p and the change in enthalpy of sample. To our knowledge, this is the first time that differential concept has been applied to a thin-film calorimeter design.

We fabricate TDSC devices using the techniques described previously.[10,11] The planar and cross-sectional configurations of the calorimeter is shown in Fig. 1. An amorphous Si–N membrane (1000 Å in thickness) serves as a support platform for the sample and the heaters. It also ensures good thermal conduction and electrical isolation between them. Two Ni thin film stripes with identical dimensions (300 Å in thickness and 400 μm in width) form a differential heater pair: one serves as a sample heater (*s* heater) supporting sample, the other as a reference heater (*r* heater). The heaters also function as thermistors after being calibrated in a conventional tube furnace.[10,12] The mea-
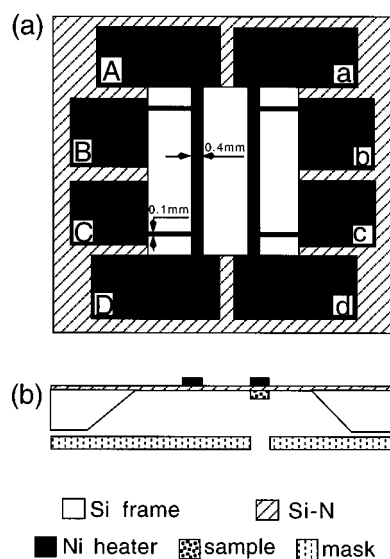

FIG. 1. (a) Planar and (b) cross-sectional view (not in scale) of the calorimeter. Two Ni thin film strips (300 Å in thickness) function as a heater pair: one as a reference heater, the other as a sample heater. A 1000-Å-thick Si–N membrane serves as sample substrate. Sample of interest is only under the sample heater for measurements.

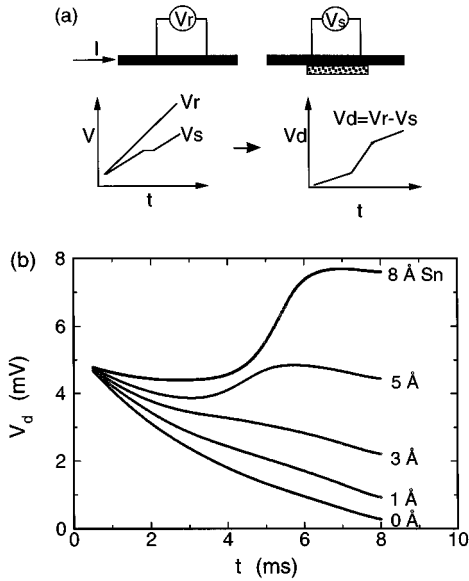[a]Electronic mail: s-lai1@students.uiuc.edu

FIG. 2. (a) Schematic illustration of the voltage responses. The differential voltage V_d directly corresponds to the presence of sample. (b) The measured differential voltages for various amount of Sn.

FIG. 3. The heat capacity of Sn samples with thickness from 0 to 5 Å. 1 Å in thickness corresponds to 2.3×10^{-9} g in mass in our measurement.

sured value for the heat capacity of the calorimeter is $\sim 6 \times 10^{-7}$ J/K at 300 K, approximately 2–3 orders of magnitude smaller than conventional DSC systems.

Our experiments include Sn samples of thickness ranging from 1 to 20 Å. We successively deposit various amounts of Sn onto the Si–N membrane side of the s heater using a shadow mask to define the sample area to be coincident with the heater. The base pressure of the thermal evaporation system is 2×10^{-8} Torr and the deposition rate is about 1 Å/s. To check the absolute temperature scale of the calorimeter *in situ*, we perform an end-of-experiment calibration by measuring the melting point of ''bulk'' Sn sample with total thickness of 190 Å.

The temperature of both heaters increases simultaneously via Joule heating when we apply identical current pulses to the heaters. With the s heater being ''loaded'' and the r heater being ''empty,'' the heating cycles of the two heater differ slightly. As a result, the voltage response of each heater during the scan differs slightly.

Figure 2(a) illustrates schematically the voltage responses. If constant currents are applied, the voltage across the r heater, V_r, increases with time in a simple fashion. This occurs because the temperature of r heater increases with time, and the resistance increases with temperature. The voltage response of the s heater, V_s, is different. Because the s-heater unit has a larger heat capacity due to the presence of sample, V_s lags behind V_r in the early stages of the scan. The duration of the flat response of V_s, as shown in Fig. 2(a), reflects the time period when the sample melts. The ''differential voltage,'' $V_d = V_r - V_s$, contains the quantitative thermal information of the sample. In practice, we measure V_d directly after amplification (gain=51) with a voltmeter to increase signal-to-noise ratio. V_r is also measured directly in experiment.

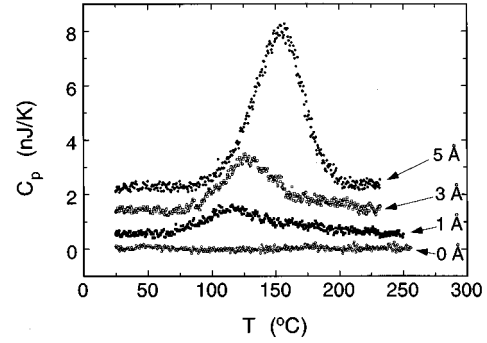Figure 2(b) shows the differential voltage V_d of the actual calorimetry measurements of Sn samples having thickness of 1, 3, 5, and 8 Å. The shape of the curves changes progressively with the amount of Sn present on the s heater. Analyses of the data will be discussed in the later section.

Figure 2(b) also shows a scan of the system having no Sn. Ideally, if the physical dimensions and microstructure of the two heaters are identical, then $V_d(t) = 0$ at any time and the curve should be completely flat. In practice, however, there are slight differences in the physical properties and dimensions between the two heaters. Such differences are exhibited in V_d from the initial scan before sample deposition intrinsically. Hence, the initial V_d is subtracted from subsequent differential voltages.

The heat Q_r consumed by the r heater can be obtained from the real-time voltage $V_r(t)$ and current $I(t)$ by integrating the power,

$$Q_r(t) = \int V_r(t) \cdot I(t) dt. \qquad (1)$$

The real-time temperature $T_r(t) = T[R(t)]$ of the heater is obtained using the resistivity vs temperature characteristics measured beforehand.[10] From the data, we have determined that the average heating rate of the calorimeter is 32 000 °C/s. Under the experimental conditions, the primary means of heat loss is conduction. A cooling rate of ~ 2000 °C/s has been measured. This indicates that the system is quasiadiabatic with most ($>94\%$) of the electrical energy consumed by the calorimeter.

Combining $Q_r(t)$ and $T_r(t)$ yields the heat consumption as a function of temperature, namely $Q_r(T)$. The heat consumption function $Q_s(T)$ for the s heater is obtained following the same procedure, using $V_s(T) = V_r(t) - V_d(t)$. The heat exchange between the heater and sample is then

$$\Delta Q(T) = Q_s(T) - Q_r(T) \qquad (2)$$

and the heat capacity of sample is

$$C_p = \frac{d\Delta Q(T)}{dT}. \qquad (3)$$

The measured $C_p(T)$ in Fig. 3 represents changes in the heat capacity of the sample and shows the development of a distinguishable peak that is attributed to the melting of Sn. In each $C_p(T)$ curve, the baseline value of C_p is the heat capacity of the sample prior to melting, while the peak reveals
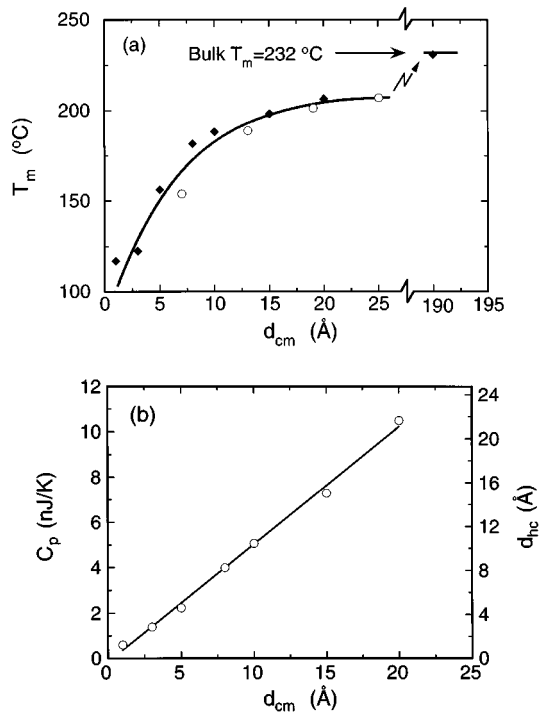
FIG. 4. (a) Melting point as a function of the deposition thickness for Sn. Results from both this experiment (♦) and Ref. 6 (○) are presented. (b) Heat capacity of Sn sample as a function of deposition thickness d_{cm} measured by crystal monitor. The right axis represents the scaled thickness d_{hc} from the bulk heat capacity of Sn (0.227 J/K g).

the melting process: the position of the peak indicates the melting point, the area under the peak corresponds to the heat of fusion.

With the TDSC technique, we can now easily observe the material properties of nanostructures, in particular the melting process. In Fig. 3, the position of the C_p peak is the average melting point T_m of the nanostructures. Figure 4(a) illustrates the shift in T_m as the deposition thickness varies. T_m decreases from 231 °C for the 190 Å sample (bulk value =232 °C) to ~120 °C for 1 Å sample. This phenemenon is size-dependent melting point depression.[3–6] As discussed earlier, small amounts of Sn deposited on an inert substrate form self-assembled particles. Our previous measurements of Sn particle size with transmission electron microscopy (TEM) and scanning electron microscopy (SEM) techniques have shown that the average particle diameter is about 160 Å when the deposition thickness is 16 Å, the minimum thickness at which the measurements have been carried out.[16] The generally accepted model for the melting point depression phenomenon is that each particle consists of a solid core surrounded by a thin liquid shell.[17] Using the TDSC technique we are now able to probe nanometer-sized systems directly.[6]

Our TDSC device is extremely sensitive. Analysis of the noise fluctuations of the data reveals the device has 0.20 nJ/K resolution. Figure 4(b) is a plot of the change in the baseline C_p (left axis) with the thickness measured by the crystal monitor, d_{cm}. The right axis scales the Sn thickness with the bulk value of heat capacity (0.227 J/K g). From this analysis, the calorimeter has a resolution of 0.4 Å or 1 nanogram in terms of the amount of Sn. This is the highest sensitivity of any scanning calorimeter to our knowledge. It allows the calorimeter to be used as a nanobalance capable of measuring the quantity of material on nanogram scale, by means of measuring the heat capacity C_p associated with the material.

The size of the C_p peak directly relates to the amount of energy for melting. As is the case for T_m, the normalized heat of fusion ΔH_m also shows a size-dependent depression. It decreases from 62 J/g for the 190 Å sample (bulk value =58.9 J/g) to 17 J/g for the 1 Å sample. The energy resolution of our TDSC is determined to be 0.2 nJ.

In summary, we have developed a new thin-film differential scanning calorimetry technique that has extremely high sensitivity. For the first time, our thin-film calorimeter design incorporates the differential measurement concept. Using the TDSC technique, we have measured the heat capacity and melting process of Sn samples of nanogram in mass and demonstrated that the energy resolution of this novel calorimeter is about 0.2 nJ. A decrease of up to 120 °C in the melting point of Sn has been measured using our novel calorimeter.

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