High-speed (10^4 °C/s) scanning microcalorimetry with monolayer sensitivity (J/m^2)

S. L. Lai,[a] G. Ramanath, and L. H. Allen
Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, Illinois 61801

P. Infante
National Nanofabrication Facility, Cornell University, Ithaca, New York 14853

Z. Ma
INTEL Corporation, Hillsboro, Oregon 97124

(Received 1 May 1995; accepted for publication 20 June 1995)

We introduce a high sensitivity (1 J/m^2) scanning microcalorimeter that can be used at high heating rates (10^4 °C/s). The system is designed using ultrathin SiN membranes that serve as a low thermal mass mechanical support structure for the calorimeter. Calorimetry measurements of the system are accomplished via resistive heating techniques applied to a thin film Ni heating element that also serves as a thermometer. A current pulse through the Ni heater generates heat in the sample via Joule heating. The voltage and current characteristics of the heater were measured to obtain real-time values of the temperature and the heat delivered to the system. This technique shows potential for measuring irreversible heat of reactions for processes at interfaces and surfaces. The method is demonstrated by measuring the heat of fusion for various amounts of thermally evaporated Sn ranging from 50 to 1000 Å. © *1995 American Institute of Physics.*

Measurement of basic thermodynamic properties related to phenomena at interfaces and surfaces can facilitate our understanding of the underlying molecular processes on the nm scale, and are not only fundamental issues in materials physics,[1] but are also of technological importance. For example, thermodynamic issues of the initial stages of solid phase nucleation phenomena during silicide formation is of technological interest.[2] Other potential areas of interest include kinetics study of point defect annihilation during thermal annealing following ion implantation, as well as the studies of surface reconstruction and decomposition of adsorbed species during atomic layer epitaxy.

In the last decade, tremendous progress has been made in characterizing the structure of interfaces and surfaces, particularly with the application of transmission electron analysis techniques. However, little progress has been made in directly obtaining thermodynamic information about interfaces and thin film reactions. Most calorimetry techniques are typically not sensitive enough to perform measurements on the monolayer level due to the difficulty in measuring small amounts of heat ($\approx$1 J/m^2). In this letter, we describe a new approach to this problem by means of a novel scanning microcalorimeter designed to enable measurements of the heat capacity and the heat of fusion of Sn films with various thicknesses ranging from 45 to 1000 Å at speeds of $\approx$30 000 °C/s.

Currently, the differential scanning calorimetry (DSC) technique is the most widely used method for measuring the enthalpy of formation for (i) reaction couples, (ii) crystallization energy of amorphous materials, and (iii) the measurements of glass transition temperature.[3] However, conventional DSC is usually not sensitive enough for more detailed measurements, such as the study of the initial stages of nucleation at an interface. For example, the heat reaction of 50 Å of Ni on polycrystalline Si cannot be measured reliably by typical DSC techniques. This is because the amount of heat generated during the reaction is too small and the heat capacity of the calorimeter is too large. Consequently, special multilayer Ni/*a*-Si samples are needed to obtain a measurable signal. Several approaches to microcalorimetry are currently being developed by others in the field.[4–8] However, this work, to our knowledge, is the first to address the methodology of scanning microcalorimetry.

The ability to measure small amounts of heat depends on the relative heat capacity of the entire calorimetry system. By reducing the thermal mass of system, the sensitivity can be increased. Another basic problem in calorimetry is related to heat loss during the measurement.[9] In our system, the high heating rates of the sample during the scan is far greater than the cooling rate of the system, thus approaching near-adiabatic conditions.

By utilizing the standard thin film membrane processing technology developed at Cornell University, we combined the four components typically found in a calorimetry system, namely, the sample, the sample holder, the heater, and the thermometer, into a single multilayer thin film configuration, as shown in Fig. 1. In this initial design, the sample holder is an 1800 Å Si–N membrane that is supported at the perimeter by the Si substrate and is mechanically rugged. An 1800 Å Ni thin film stripe (with 60 Å Ti for adhesion) functions both as a resistance heater and a thermometer. The test sample is deposited on the opposite side of the membrane and has approximately the same width as that of the Ni heater. The

[a]Electronic mail: slai@uxa.cso.uiuc.edu

Downloaded¬15¬May¬2001¬to¬130.126.103.205.¬Redistribution¬subject¬to¬AIP¬license¬or¬copyright,¬see¬http://ojps.aip.org/aplo/aplcr.jsp

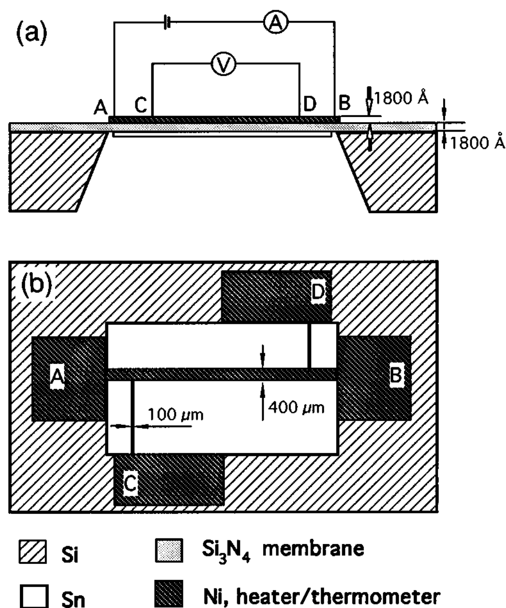

FIG. 1. Cross-sectional (a) and planar (b) view of microcalorimeter. System is based on reduced thermal mass sample holder made using a silicon nitride membrane which is only 1800 Å thick and mechanically supported at the perimeter by the Si substrate. A thin film Ni layer is deposited on the top side of the membrane and serves as both heater and thermometer. The sample of interest is deposited on the bottom side of the membrane.

membrane ensures good thermal conduction between the sample and heater, while it isolates them electrically.

The microcalorimeter was placed in an evaporator system with a base pressure of $\sim 2\times 10^{-7}$ Torr. Various amount of Sn were deposited successively and calorimetry measurements of the heat capacity and the heat of fusion of Sn thin films with varying thicknesses were performed after each evaporation without breaking vacuum. The different thicknesses of Sn and deposition rates were measured with a crystal monitor equipped inside the chamber. The deposition rate was ~5 Å/s for the first deposition, and 10–15 Å/s for the rest. The integral amount of Sn deposited was verified with a Dektak profilometer afterwards.

The calorimetry measurement is initiated by supplying a dc current pulse to the Ni heater, thus raising the temperature of the system by Joule heating, as described by Allen *et al.*[10] The voltage and current are monitored in real time during the pulse and thus the heat supplied to the near-adiabatic system is directly obtained ($P=VI$). The temperature of the system is determined by using the calibrated resistance ($R=V/I$) versus temperature characteristics of the Ni heater.

The data presented in Fig. 2(a) show the change in resistance of the heater during the heating cycle, when the total thickness of Sn deposited on the Si–N membrane was 993 Å. Resistance values are obtained from real time measurement of voltage $V(t)$ and current $I(t)$ and are normalized to the value at room temperature, 25 °C. The temperature of the heater is determined via analysis of the resistance data. The relationship between temperature and resistance was established beforehand using a conventional vacuum tube furnace and with a calibrated thermocouple, as described in detail previously.[10] With 1800 Å Si–N between the heater and Sn, the difference in temperature between the heater and sample is calculated to be less than 1 °C during the heating cycle. Figure 2(b) illustrates the real time temperature of Sn during a pulse. The flat stage of the curve is due to the melting of Sn that occurs at ≈230 °C. As the temperature reaches the melting point of Sn, additional heat is drawn from the heater; thus, the rate at which the temperature of the system increases becomes smaller. The heating rate is determined to be about 30 000 °C/s. Since the cooling rate of this system was measured to be about 1000 °C/s, it is concluded that the system approaches the adiabatic condition.

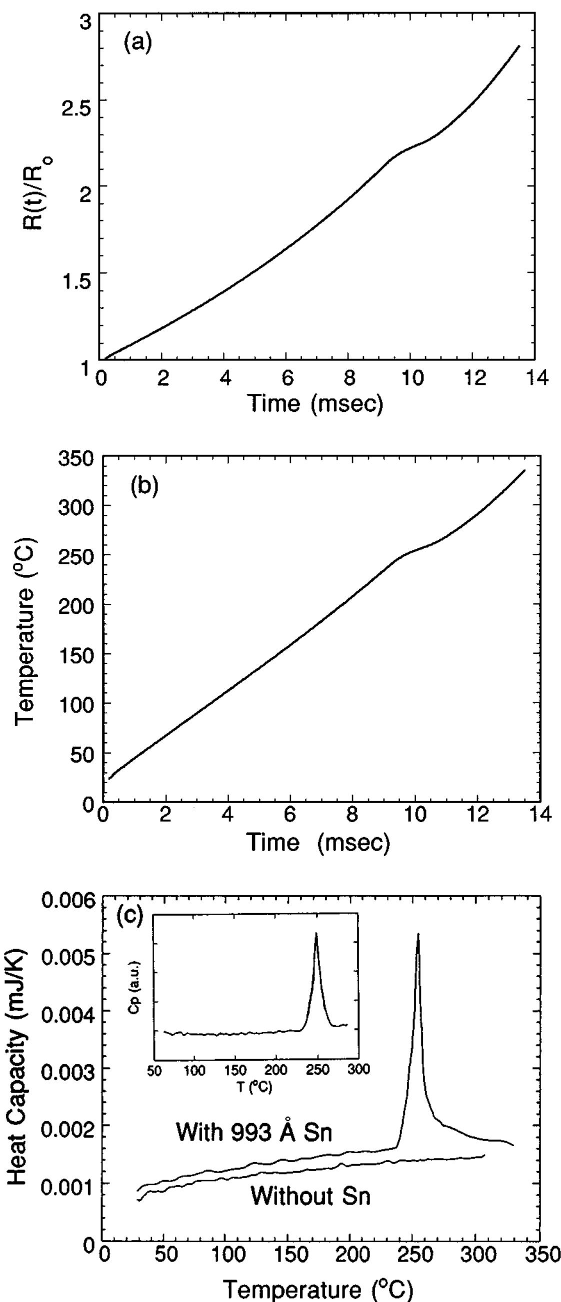

FIG. 2. Calorimetry measurement of a 993 Å thick Sn sample. (a) Real time resistance normalized to $R_0(T=25\ °C)$; (b) temperature of sample determined using calibrated resistance vs temperature characteristics; (c) heat capacity of the system with and without Sn on the bottom side of the Si–N membrane.

The heat capacity of the system can be directly obtained from the data using the following expression:

Downloaded¬15¬May¬2001¬to¬130.126.103.205.¬Redistribution¬subject¬to¬AIP¬license¬or¬copyright,¬see¬http://ojps.aip.org/aplo/aplcr.jsp

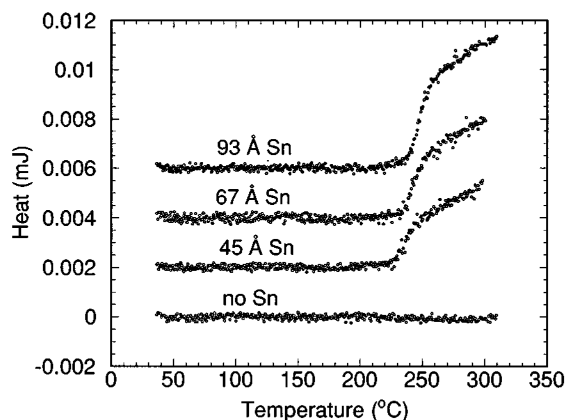

FIG. 3. Example showing the amount of heat associated with the melting process for 0, 45, 67, and 93 Å of Sn. The heat attributed to the heat capacity of the entire system prior to the melting of Sn is subtracted from the total heat measured. Note each curve is offset for clarity.

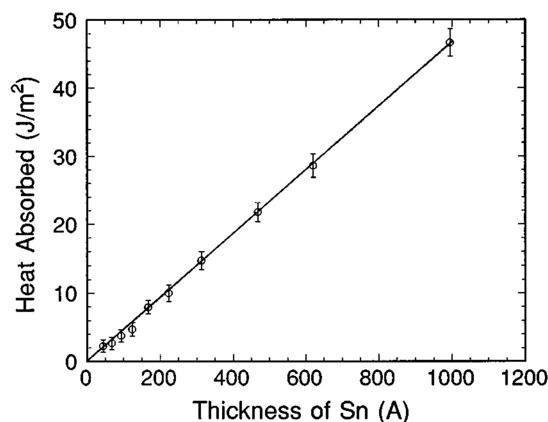

FIG. 4. Heat of fusion of Sn as a function of amount of Sn deposited. The values are converted according to the area of Sn stripes.

$$C_p = \frac{dQ/dt}{dT/dt} = \frac{V(t)I(t)}{dT/dt} . \quad (1)$$

C_p is plotted as a function of temperature in Fig. 2(c). The baseline value shown in the curve represents the heat capacity of the whole system. The sharp peak (≈230 °C) is due to the melting of Sn. From this experiment the heat of fusion is obtained by integrating the area under the peak and measured to be 65 J/g, which is within ≈10% of the value found in the literature.[11] Also shown in Fig. 2(c) is the heat capacity of the system prior to Sn deposition. The difference in the heat capacities between the systems with and without Sn is attributed to the added heat capacity of the deposited Sn. This difference can be used to determine the effective thickness of Sn. Also shown in the inset is the result of an earlier measurement by Allen.[12] In that experiment, a free-standing Ni foil (6 μm in thickness) acted as heater and Sn was used as sample to measure the heat capacity. Between Sn and Ni, a LiF layer was deposited as isolator.

Another useful method for obtaining heat of fusion for samples with small amounts of Sn involves the measurement of the total heat. In this method the heat as a function of time $Q(t)$ is obtained by directly integrating the power delivered to the system, as given by the following expression:

$$Q(t) = \int P(t)dt. \quad (2)$$

Since the temperature of the system at any time t is known from the resistance data, dependence of the total heat as a function of temperature, $Q(T)$ can be readily obtained.

Figure 3 shows the results of experiments of various amounts (0, 45, 67, and 93 Å) of Sn. In order to easily show the amount of heat associated with the melting process, the heat attributed to the average heat capacity of the system is subtracted from the total heat measured. As can be seen from the data, this system is clearly sensitive to an equivalent of monolayer sensitivity (1 J/m^2). The measured value of the heat of fusion of the 45 Å Sn sample is within 30% of the bulk value. The measured heat of fusion for various thicknesses of Sn is plotted in Fig. 4. From the literature references, the value of ΔH is 59.0 J/g; our measurement shows that the average value of ΔH is 64 J/g.

In Fig. 3, note the increasing slope in the $Q(T)$ curve after the abrupt change where the melting has occurred. This is because the Sn sample is slightly wider than the Ni heater due to lateral misalignment between the shadow mask and the Ni heater during evaporation. The Sn adjacent to the heater continues to melt on the edges as the heater warms the surrounding regions laterally adjacent to the heater.

In summary, a novel scanning microcalorimeter with monolayer sensitivity has been devised. The sensitivity of the system was demonstrated by measuring the heat of fusion of small amounts of Sn. With this system, measurements can be made at speeds of about 30 000 °C/s, enabling experiments to be performed under near-adiabatic conditions.

We gratefully acknowledge Dr. L. Hess and Dr. D. Nelson of National Science Foundation for the financial support (SGER DMR 94-19604). We would like to thank Professor Gert Ehrlich and Professor David Cahill, University of Illinois at Urbana-Champaign, for stimulating discussions. Thanks are also due to L. Rathbun and L. Keim, Cornell University, and J. Ziegler, University of Illinois at Urbana-Champaign, for their technical assistance in fabricating the films and designing electronic devices.

[1] K. N. Tu, J. W. Mayer, and L. C. Feldman, in *Electronic Thin Film Science for Electrical Engineers and Materials Scientists* (Macmillan, New York, 1992).
[2] Z. Ma and L. H. Allen, Phys. Rev. B **49**, 13501 (1994).
[3] F. Spaepen and C. V. Thompson, Appl. Surf. Sci. **38**, 1 (1989).
[4] S. Randzio and W. Zielenkiewicz, Phys. Chem. **XXIV**, 323 (1976).
[5] C. E. Borroni-Bird and D. A. King, Rev. Sci. Instrum. **62**, 2177 (1991).
[6] A. Stuck, C. E. Wartnaby, Y. Y. Yeo, and D. A. King, Phys. Rev. Lett. **74**, 578 (1995).
[7] D. W. Denlinger, E. N. Abarra, K. Allen, P. W. Rooney, M. T. Messer, S. K. Watson, and F. Hellman, Rev. Sci. Instrum. **65**, 946 (1994).
[8] R. E. Cavicchi, G. E. Poirier, J. S. Suehle, M. Caitan, S. Semancik, and D. R. F. Burgess, J. Vac. Sci. Technol. A **12**, 2549 (1994).
[9] J. M. E. Harper, Ph.D. thesis, Stanford University (1975).
[10] L. H. Allen, G. Ramanath, S. L. Lai, and Z. Ma, Appl. Phys. Lett. **64**, 417 (1994).
[11] *American Institute of Physics Handbook*, 3rd ed. (McGraw-Hill, New York, 1972).
[12] L. H. Allen (personal communication). Previous measurements were made on a free-standing Ni foil 6 μm in thickness, supplied by Alfa Company. This experiment was designed in April 1994.

Downloaded¬15¬May¬2001¬to¬130.126.103.205.¬Redistribution¬subject¬to¬AIP¬license¬or¬copyright,¬see¬http://ojps.aip.org/aplo/aplcr.jsp