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Thermophysical Property Measurements on Molten Semiconductors Using 10-s Microgravity in a Drop Shaft[1]

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The effectiveness of 10-s microgravity on thermophysical property measurements on molten materials, such as molten semiconductors, is discussed. The thermal conductivity of molten InSb was successfully measured under microgravity conditions on board the German sounding rocket TEXUS and in a drop shaft in Hokkaido, Japan. Surface tension measurements using an oscillating drop method was attempted in low gravity using a parabolic flight of the NASA KC-135 aircraft. Combined levitation and microgravity, which can provide a contamination-free and undercooled condition, is recommended as a novel approach to obtain missing thermophysical property data on undercooled melts of semiconductors.

KEY WORDS: drop shaft; levitation; microgravity; surface tension; thermal conductivity.

1. INTRODUCTION

Highly advanced computer and communication technologies, such as "multimedia," are supported by ultra-large-scale-integration (ULSI) devices which are produced using high-quality semiconductor crystals. However, as this ULSI technology advances, semiconductor crystals of greatly improved quality are required. Most semiconductor crystals are produced by a melt growth technique, where a heat and mass transfer process controls crystal

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growth. This process is understood and can be controlled through a numerical modeling, which can be carried out by simultaneously solving numerically continuity, energy, and Navier–Stokes equations, which require a knowledge of thermophysical property data. However, there is a limited amount of reliable data on thermophysical properties of molten semiconductors due to the measurement difficulties [1]. The reasons for this difficulty are as follows: molten semiconductors have high melting temperatures, high vapor pressures, and low Prandtl numbers and are corrosive, electrically conductive, and opaque to visible light.

Glazov et al. [2] were the first systematically to measure, collect, and evaluate thermophysical data on molten semiconductors. Regel et al. [3] wrote a review article on thermal conductivity. Keene [4] overviewed surface tension for molten silicon and its related systems. The authors [5] have collated thermophysical data for molten semiconductors, mentioning utilization of the microgravity environment as a new tool for studying thermophysical properties. The thermophysical properties, such as density, surface tension, viscosity, resistivity, emissivity, and thermal diffusivity, of molten silicon have been measured by Kimura et al. [6]. Also, structural analysis of molten silicon was carried out using X-ray diffraction.

This paper reports the results of thermal conductivity measurements on molten InSb under microgravity conditions and attempts to measure surface tension of molten Si in low gravity during a parabolic flight of an aircraft. Also, the significance of microgravity on thermophysical property measurements of molten semiconductors is discussed.

2. THERMAL CONDUCTIVITY OF MOLTEN InSb

Thermal conductivity of high-temperature melts is one of the most difficult thermophysical properties to measure accurately. Only 14 measurements have been reported for group-IV-element and III–V-compound semiconductors over the last 30 years. The thermal conductivity of molten InSb was successfully measured using a transient hot-wire method under microgravity on board the German sounding rocket TEXUS No. 24 and in a drop shaft at Kamisunagawa, Hokkaido, Japan.

Equation (1) shows the principle of the measurement using the transient hot-wire technique, as follows [7]:

$$\Delta T = \{Q/2\pi(\lambda_L + \lambda_s)\} \ln(t) + C \tag{1}$$

The gradient of the temperature increase $\delta(\Delta T)/\delta[\ln(t)]$ in the sensing wire is proportional to the input electric power per unit length Q and inversely proportional to the sum of the thermal conductivities of the liquid sample

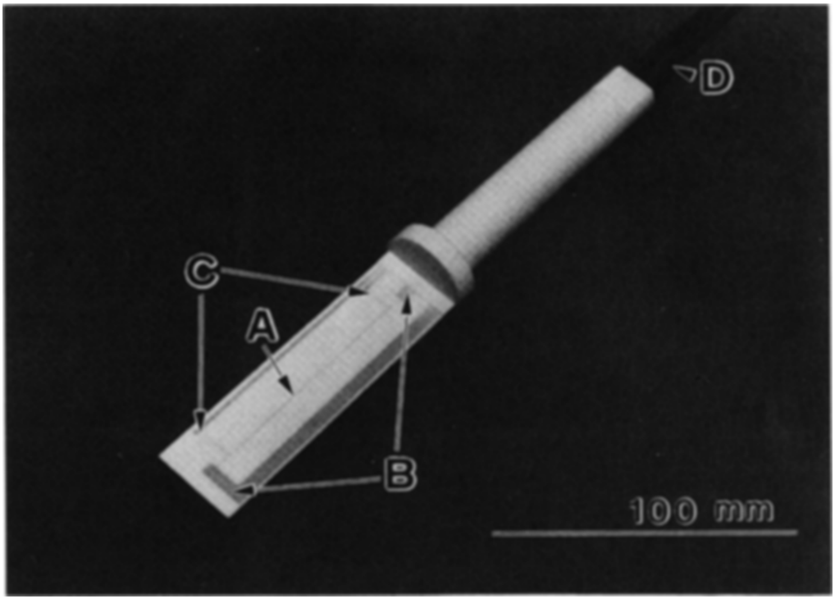

Fig. 1. Ceramic probe prepared for thermal conductivity measurement of molten InSb using transient hot-wire method. (A) Sensing wire; (B) electrodes for applying current to the wire; (C) potential electrodes for detecting voltage drop in the sensing wire; (D) platinum lead wire.

λ_L and the solid substrate λ_s. If the temperature increase in the wire is precisely measured, and the thermal conductivity of the solid substrate λ_s is given prior to the measurement, then the thermal conductivity of the liquid sample λ_L can be obtained.

To apply this technique to molten compound semiconductor InSb, we have developed a new ceramic probe using a green sheet technique, as shown in Fig. 1 [8]. A sensing wire was fabricated on the sintered alumina substrate by a printing method and coated with a thin insulation layer, so that electric leakage from the wire into the molten sample was prohibited. For measurement on board the sounding rocket and in a drop shaft, a dedicated Thermal Conductivity Measurement Facility (TCMF) was prepared, as shown in Fig. 2 [9].

Figure 3 shows thermal conductivity of molten InSb as a function of time after the start of measurement on board the TEXUS rocket and on Earth. The thermal conductivity measured on Earth appears to increase as time passes and measurements are repeated, but the data obtained under microgravity appear to be almost constant and show a good reproducibility. This means that convection was sufficiently suppressed in microgravity. A slight increase with time is explained by the temperature

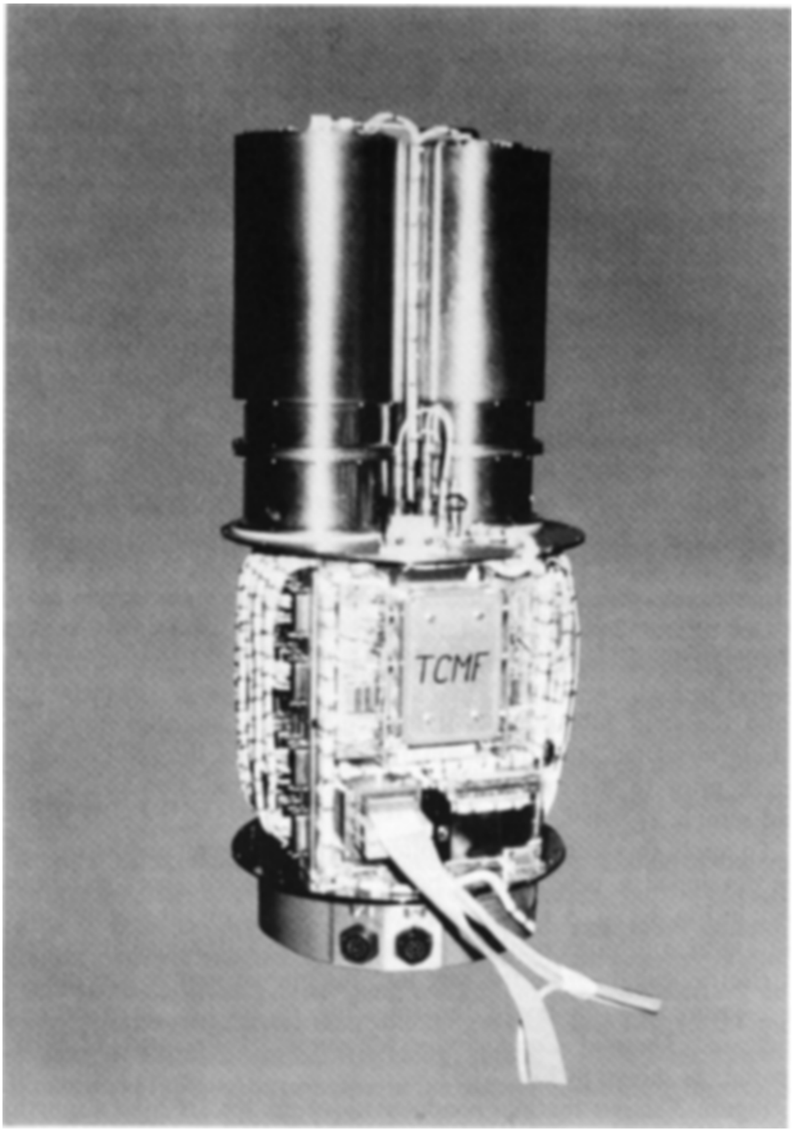

Fig. 2. Thermal conductivity measurement facility (TCMF) employed for measuring the thermal conductivity of molten InSb and molten salts on board the TEXUS rocket and in the drop shaft at Kamisunagawa, Hokkaido, Japan. Two furnaces are on the upper plate. Electronics for controlling furnaces and for measurement are below the upper plate. Batteries are below the lower plate. The height is 906 mm.

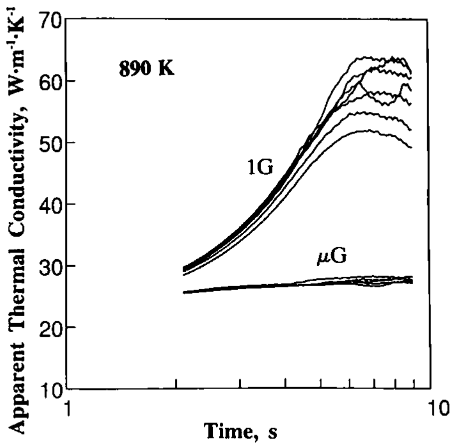

Fig. 3. Apparent thermal conductivity of molten InSb measured at 890 K under microgravity conditions on board the sounding rocket TEXUS No. 24 and on Earth: $\lambda_L + \lambda_s$.

dependence of the thermal conductivity of molten InSb and that of the alumina substrate [8].

Figure 4 shows the thermal conductivity of InSb measured under microgravity as a function of temperature [10]. Data obtained using a conventional steady-state method are also depicted [11, 12]. As shown in Fig. 4, thermal conductivity data obtained under the microgravity condition are on a single line, regardless of the method used to create microgravity: sounding rocket or drop shaft. Figure 4 also suggests that molten InSb shows metallic characteristics, while Amirkhanov and Magomedov [11] reported semiconductive characteristics of molten InSb. Estimation of thermal conductivity for molten InSb based on the Wiedemann–Franz law, i.e., contribution of free electrons to thermal conductivity, yields a value of $19 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ for the thermal conductivity at the melting point, which is in good agreement with the present data.

It should also be noted that the measurements of thermal conductivity for solid InSb showed almost the same results, regardless of the experimenters, and that this is not the case for the molten state. This means that it is difficult to measure thermal conductivity accurately on Earth and that utilizing microgravity is very effective.

Fukusako et al. [13] also tried to measure thermal conductivity of a molten salt in a microgravity, by a transient hot-wire method; a value of $0.368 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ was obtained for the thermal conductivity of molten KSCN using an improved ceramic probe.

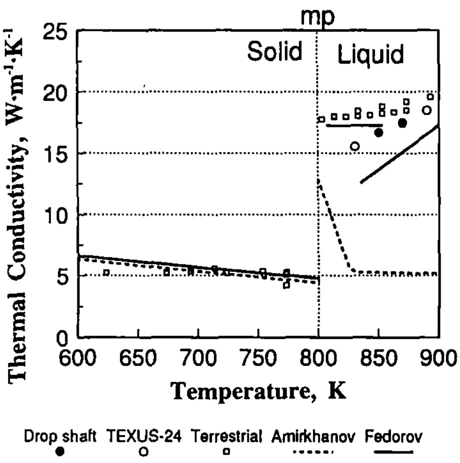

Fig. 4. Thermal conductivity of molten InSb. Data obtained under microgravity conditions are shown by open (rocket) and solid (drop shaft) circles. Squares show data obtained on Earth using the transient-hot wire method. Solid [12] and dashed [11] lines show data obtained on Earth by the conventional steady-state method. Notice that data for solid state show a good agreement regardless of experimenters, while a large scatter in the data was observed for molten state, depending on experimenters.

3. SURFACE TENSION

Surface tension is one of the important parameters in describing a surface tension-driven flow, the so-called Marangoni flow, on the surface of molten silicon. Recently, the formation of a spoke pattern was reported for a molten silicon surface [14], while the spoke pattern had previously been reported only on oxide melts. The formation of the pattern can be explained by either the Rayleigh–Bénard or the Marangom–Bénard mechanism, depending on the temperature coefficient of the surface tension of the molten silicon. The Marangoni flow of molten silicon is one of the subjects that can be studied in microgravity [15]. Many surface tension data and their temperature coefficients have been reported [4]. It was reported that the higher the surface tension at the melting point, the larger the temperature coefficient. This tendency is reported to result from surface contamination due to oxygen.

Surface tension measurement of molten silicon was carried out by an oscillating drop method using electromagnetic levitation in a pure (6N) argon gas atmosphere on earth [16]. The working equation for this method is described by formulating the oscillation of liquid droplets, as follows [17, 18],

$$\nu_R^2 = (\pi/3)\, l(l-1)(l+2)\, \gamma/M \tag{2}$$

where ν_R, l, γ, and M are the Rayleigh frequency of oscillation, mode of oscillation ($l=2$), surface tension, and specimen mass, respectively. However, when this method is applied on Earth, correction is necessary due to gravitational and magnetic forces, as follows [19]:,

$$\nu_R^2 = \tfrac{1}{5} \sum_{m=-2}^{2} \nu_{2,m}^2 - \bar{\nu}_t^2\, [1.9 - \tfrac{1}{2}(Z_0/R)^2] \tag{3}$$

$$Z_0 = \frac{g}{8\pi^2 \bar{\nu}_t^2} \tag{4}$$

$$\bar{\nu}_t^2 = \tfrac{1}{3} \sum_{m=-1}^{1} \nu_{1,m}^2 \tag{5}$$

For the split $l=2$ mode oscillation, an average frequency of $\nu_{2,m}$ should be used. For the $l=1$ mode (translational mode for droplet mass center), the effects of magnetic and gravitational forces should be corrected, as shown in the second term of the right-hand side of Eq. (3), where $\nu_{1,m}$ is the frequency of the $l=1$ mode oscillation. R and g are the radius of the droplet and gravitational acceleration, respectively.

A value of $783.5 \times 10^{-3}\ \mathrm{N \cdot m^{-1}}$ for the surface tension of silicon at its melting point was obtained (see Fig. 5). It should be noted that surface tension was successfully measured even in an undercooled condition of 300 K and that the largest temperature coefficient ever reported was observed: $-0.65 \times 10^{-3}\ \mathrm{N \cdot m^{-1} \cdot K^{-1}}$. The fact that a high surface tension at the melting point and the highest temperature coefficient were observed means that the obtained values correspond to those for pure silicon, because doped impurities of Sb and O evaporated upon melting and a B-doping level of 4×10^{18} atoms $\cdot$ $\mathrm{cm^{-3}}$ for the present specimens does not affect the surface tension [20].

Surface tension measurement by an oscillating drop method was attempted using the development model of an electromagnetic containerless processing facility, TEMPUS [21], during a parabolic flight of the NASA KC-135 aircraft [22]. Although oscillation of molten silicon droplets was successfully observed as shown in Fig. 6, collecting a sufficient amount of oscillation data for calculating surface tension was very difficult due to turbulence during the present parabolic flight.

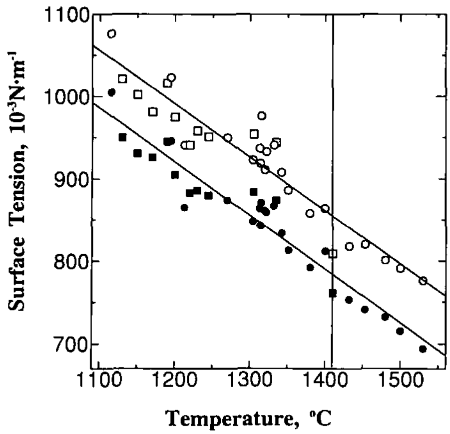

Fig. 5. Surface tension of molten silicon. Solid and open symbols show surface tensions with and without correction, respectively; see Eqs. (2) and (3). Squares and circles correspond to Sb- and B-doped specimens, respectively.

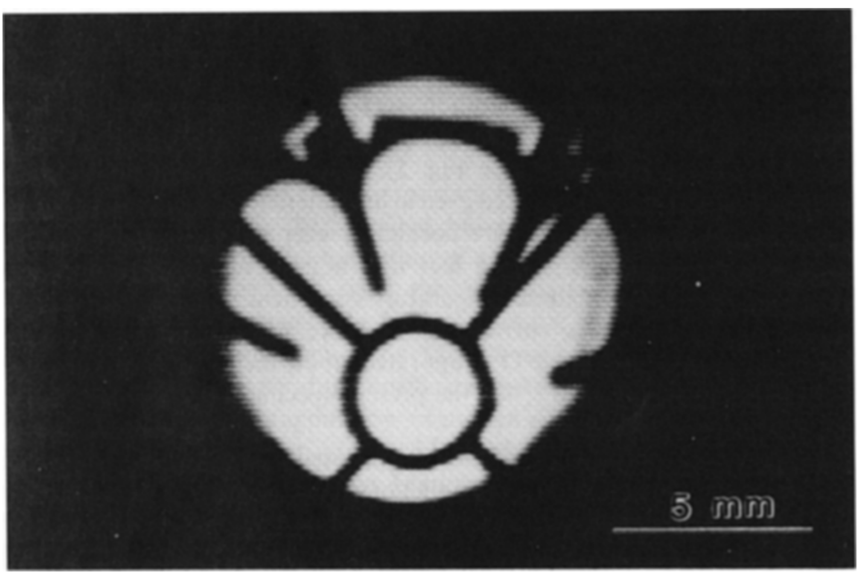

Fig. 6. Top view of the oscillating of a molten silicon droplet observed during parabolic flight of the NASA KC-135 aircraft. The cursor (ring shaped) and top of cage (arm shaped) are also shown.

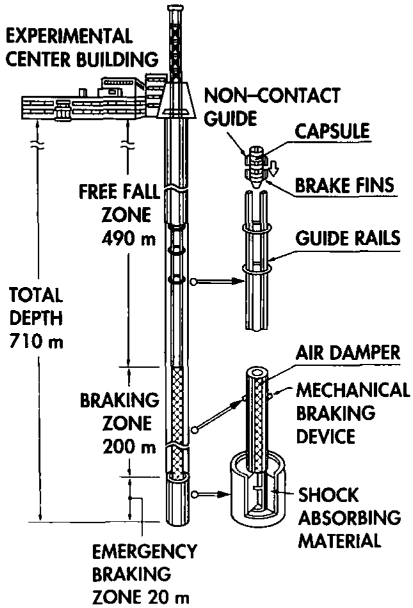

Fig. 7. Drop shaft in Kamisunagawa, Hokkaido, Japan, which assures 10-s microgravity of less then $10^{-4}\,g_0$.

It was concluded through this experiment that utilization of free fall at a drop shaft at Kamisunagawa, Hokkaido, Japan—which can supply 10 s high-quality microgravity of less than $10^{-4}\,g_0$ (Fig. 7)—would be one of the best solutions for repeated measurement of surface tension; a long-term microgravity, such as a space shuttle flight, can also provide an opportunity to measure surface tension of molten materials more accurately [23].

Niu et al. [24] measured surface tension of molten silicon by a sessile drop method using a BN substrate under carefully controlled oxygen partial pressure and quantitatively reported a marked oxygen partial pressure dependence of surface tension and its temperature coefficient. The result shows a good agreement with that obtained using an oscillating drop method. Combining levitation and an oxygen partial pressure control technique might supply more accurate knowledge of the surface tension of molten silicon.

4. DISCUSSION AND PERSPECTIVE

As described above, the microgravity environment has been demonstrated to be a new tool to measure accurately thermophysical properties of molten materials. A current topic of thermophysical property studies on molten semiconductors is the existence of an anomaly of the properties just above the melting point [6]. For example, very fast flow would exist beneath the growing crystal and the temperature distribution within a crucible would be quite different from the expected one, if an anomalous increase in density of molten silicon really existed just above the melting point and showed a volumetric expansion coefficient value of 1×10^{-3} K^{-1}. Thus, the anomalous phenomena should be confirmed using various measurement techniques, if they really exist. However, existence of the anomaly is reported to be in a limited temperature region, i.e., 15 K above the melting point, and the measurement accuracy has almost the same order as that of reported anomalous increase in properties. To see the phenomena more clearly, extension of the measurement temperature is required toward a lower temperature region including an undercooled one. However, as long as a conventional technique is applied, the following problems still remain: measurement can be done only above the melting point due to utilization of a crucible which results in solidification as soon as the temperature is lowered to below the melting point and also causes contamination of the specimen. Due to this, most thermophysical property data for molten materials in the undercooked region have been missing. Therefore, the combination of levitation technique and microgravity can provide a solution to this problem.

An appropriate microgravity platform should be selected, depending on the thermophysical properties to be measured. Most thermophysical properties related to heat transport phenomena and surface tension can be measured using the 10-s microgravity in the drop shaft. The density can also be measured if a spherical shape is obtained and its diameter is measured accurately. Specific heat data for molten semiconductors in the undercooled region are also missing. Many questions still remain to be answered, which suggest that systematic thermophysical studies need to be undertaken.

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