

Thermophysical Property Measurements of Molten Semiconductors in 1-g and Reduced-g Condition

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Understanding and controlling the formation kinetics of variety of crystal imperfections such as point defects, non uniform distribution of doping atoms, and impurity atoms in growing crystals are very important. Theoretical (numerical) modeling of crystal growth process is an essential step to achieving these objectives. In order to obtain reliable modeling result, input parameters, i.e. various thermophysical parameters, must be accurate. The importance of accurate thermophysical properties of semiconductors in crystal growth cannot be overly emphasized. The total hemispherical emissivity, for instance, has a dramatic impact on the thermal environment. It determines the radiative emission from the surface of the melt which determines to a large extent the profile of solidified crystal. In order to understand the convection and the turbulence in a melt, viscosity becomes an important parameter. The liquid surface tension determines the shape of the liquid-atmosphere interface near the solid-liquid-atmosphere triple point. Currently used values for these parameters are rather inaccurate, and this program intends to provide more reliable measurements of these thermophysical properties. Thus, the objective of this program is in the accurate measurements of various thermophysical properties which can be reliably used in the modeling of various crystal growth processes.

In this program, thermophysical properties of molten semiconductors, such as Si, Ge, Si-Ge, and InSb will be measured as a function of temperature using the High Temperature Electrostatic Levitator at JPL. Each material will be doped by different kinds of impurities at various doping levels. Thermophysical properties which will be measured include: density, thermal expansion coefficient, surface tension, viscosity, specific heat, hemispherical total emissivity, and perhaps electrical and thermal conductivities.

Many molten semiconductors are chemically reactive with crucibles. As a result, these dispersed impurities in the melts tend to substantially modify the properties of pure semiconductors. Sample levitation done in a vacuum clearly helps maintain the sample purity. However, in the 1-g environment, all gravity caused effects such as convection, sedimentation and buoyancy are still present in the sample. In addition, large forces needed to levitate a sample in the presence of the gravity can cause additional flows in the melt. The use of the High Temperature Electrostatic Levitator (HTESL) [1] for the present research is a recent development and little is known about the flows induced by the electrostatic forces. In this ground base program, we will define the limits of HTESL technology as various thermophysical properties of molten semiconductors are measured.

Progress

(1) Thermophysical Properties of Molten Silicon

Progress has been made in measuring thermophysical properties of molten silicon and germanium. In molten silicon, the density, the ratio between the specific heat and the spherical total emissivity, the surface tension, and the viscosity have been measured. The earlier observation of the quadratic nature[2, 3] of liquid density as a function of temperature has been confirmed, indicating a certain short range ordering that might be taking place as the

liquid undercools. Fig. 1 shows the density data of a high purity silicon and two boron doped silicon. Impurity effect could not be distinguished within this experimental error. Unlike most pure metals, the nonlinear increase of specific heat in undercooling silicon has also been repeatedly observed (see Fig. 2). Again, the formation of short range order must be responsible to such nonlinear behavior. If we use the literature value of $C_p(T_m) = 25.61$ J/mol/K, Fig. 2 allows us to determine the hemispherical total emissivity, ϵ_T , to be 0.183 which agrees closely with our earlier result of 0.18[2].

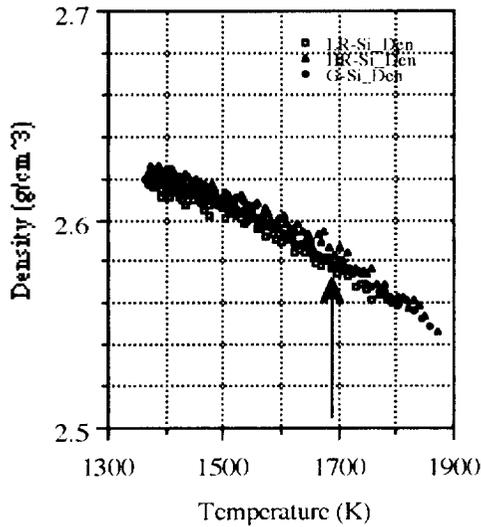


Fig. 1. Density of molten silicon.

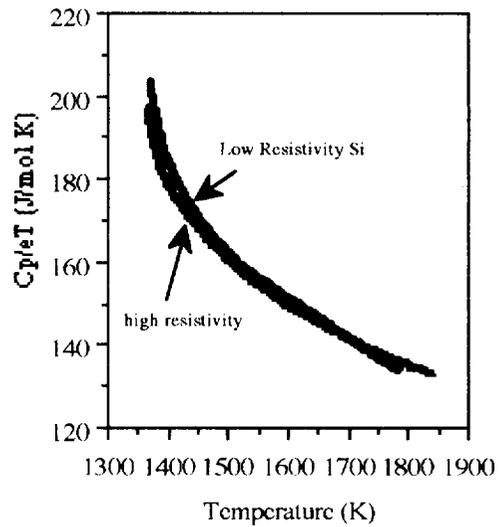


Fig. 2. C_p/ϵ_T vs. temperature of molten Si.

Fig. 3 and Fig. 4 are the surface tension and the viscosity data of a pure silicon and they are compared with the data by Sasaki et al.[4]. However, the sample rotation which set in during the sample heating process could not be controlled. Since the drop resonance frequency should depend on the rotation rate[5, 6], it was important to develop a sample rotation control capability to ensure the rotation frequency falls within an acceptable range.

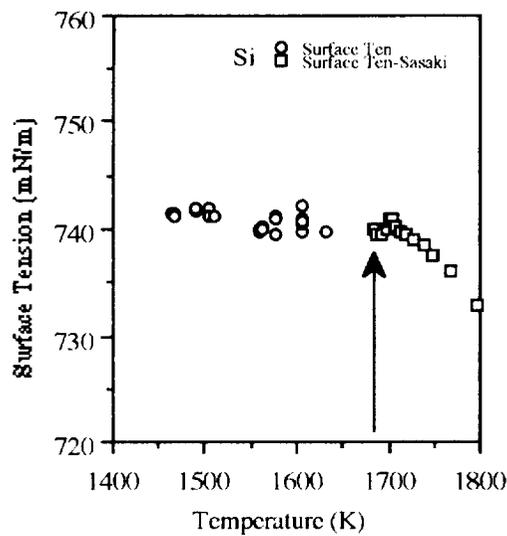


Fig. 3. Surface tension of molten silicon.

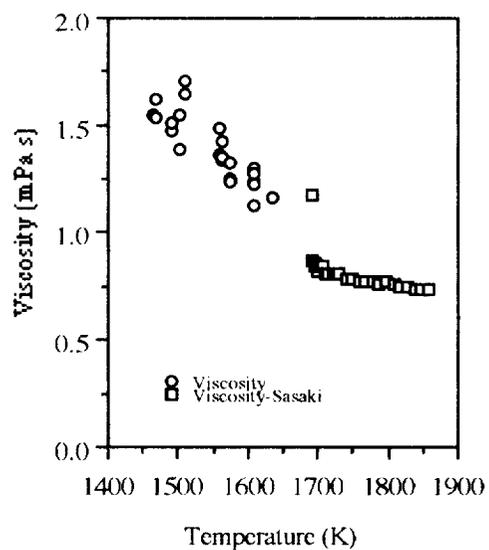


Fig. 4. Viscosity of molten silicon.

(2) Effect of Drop Rotation on Oscillation Frequency

The capability of systematically controlling rotational state of levitated samples is very important in containerless materials processing. When we want to measure surface tension through drop oscillation, we like to have a non-rotating drops. On the other hand, we like to have the drop rotating if we want to have a sample uniformly heated by a directional heating source. In general, in the absence of rotation control, levitated samples ended up showing different degrees of rotation. According to Busse's analysis[5], surface tension measurement by drop oscillation can be severely influenced by the rotational state of the drop. We had to develop a drop rotation control method to increase the accuracy of our surface tension and viscosity data.

As a result the rotation control method that was adapted to the HTESL was developed. A rotating magnetic field of appropriate frequency and strength was applied to the levitated sample in order to induce required torque. Drop oscillation was induced and frequency was measured at a preset rotational state. Fig. 5 shows the experimental data so obtained at several different rotation frequency and they were compared with the Busse's theoretical prediction[5]. From this figure, if the drop was rotating at the rate of 30 Hz, measured oscillation frequency would be about 10 % higher than that of non-rotating drop. This may translate to approximately 5 % error in measured surface tension. Fig. 6 show the effect of rotation on the damping time constant. At the present time there is no theory which can explain this quantitatively. Anyhow, this result suggests that the decay time constant is dependent to the rotational state of the drop, producing an additional source of error in the final viscosity values.

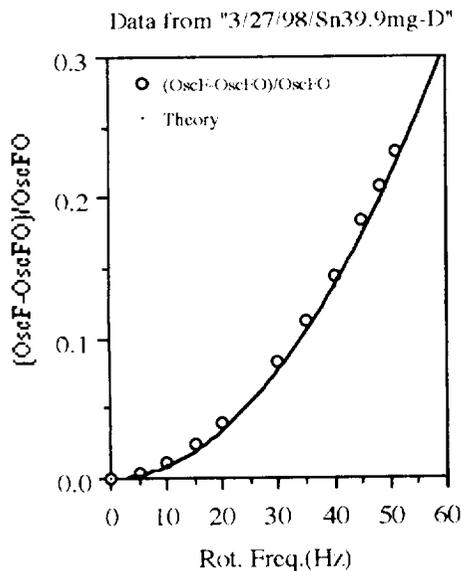


Fig. 5. Sample oscillation vs. rotation.

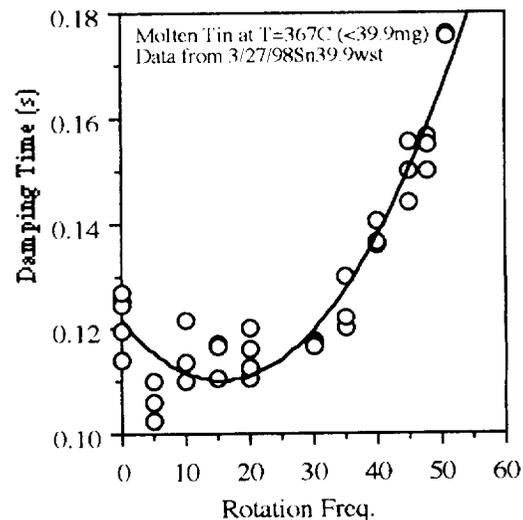


Fig. 6. Damping constant vs. rotation.

(3) Thermophysical Properties of Molten Germanium[7]

Pure germanium was melted and the density, the ratio of heat capacity to hemispherical total emissivity, the surface tension, and the viscosity were measured. Although the drop temperature was raised to ~ 200 K above the melting temperature, germanium undercooled less than 100 K. Probably it was necessary to desolve remaining impurity particles by further superheating the sample. Temperature dependence of the electrical resistivity of molten germanium was measured using the newly developed non-contact method for electrical

resistivity[8]. This method was based on the fact that electrical conductivity of the rotor in an induction motor was proportional to the torque when all other parameters remained fixed. From the measured resistivity, the thermal conductivity of germanium was determined using the Wiedemann-Franz-Lorenz relationship. Considering the fact that thermal conductivity is one of the transport properties of liquids which is susceptible to gravity induced flows, this indirect approach to thermal conductivity from electrical conductivity measurement may have an important implication in terms of increased accuracy of thermal conductivity in 1-g environment.

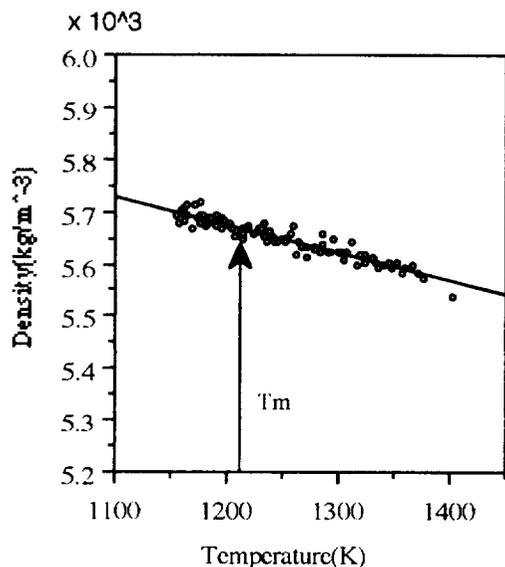


Fig. 7. Density of molten Ge vs temperature.

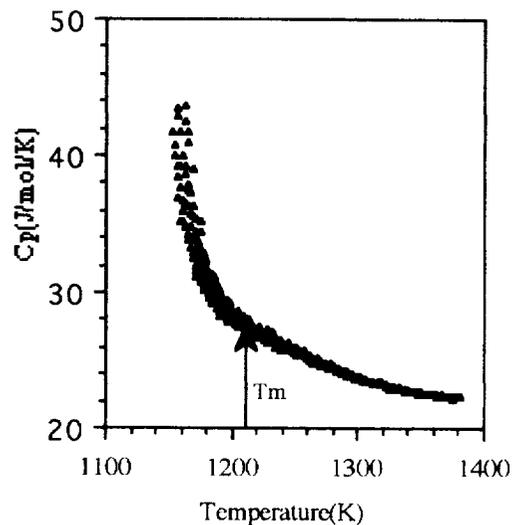


Fig. 8. Cp of molten Ge vs. temperature.

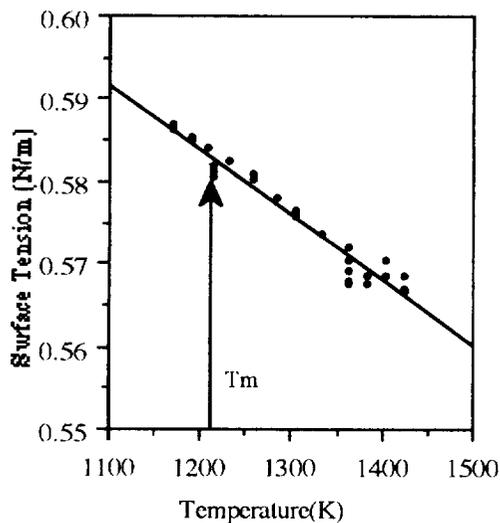


Fig. 9. Surface tension of molten Ge.

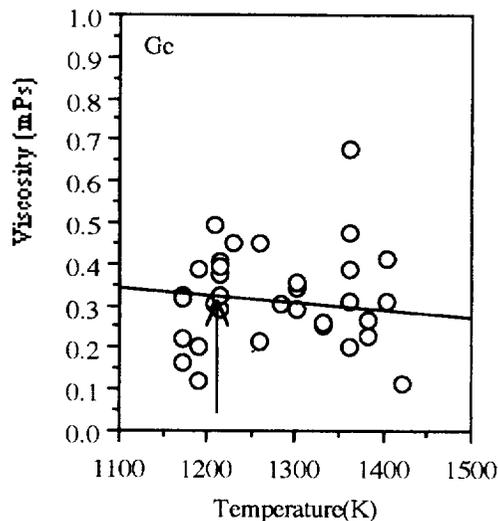


Fig. 10. Viscosity of molten germanium.

The measured liquid germanium density could be expressed by $\rho_{\text{liq.}} = 5.67 \times 10^3 - 0.542 (T - T_m)$ Kg m⁻³ with $T_m = 1211.3$ K, the volume expansion coefficient by $\alpha = 0.9656 \times 10^{-4}$ K⁻¹, and the hemispherical total emissivity at the melting temperature by $\epsilon_{T,\text{liq.}}(T_m) = 0.17$. Assuming constant $\epsilon_{T,\text{liq.}}(T) = 0.17$ in the liquid range which have been investigated, the constant pressure specific heat was evaluated as a function of temperature (Fig. 10). The surface tension could be expressed by $\sigma(T) = 583 - 0.08 (T - T_m)$ mN m⁻¹ and the temperature dependence of electrical resistivity of molten germanium, when $r_{\text{liq.}}(T_m) = 60 \mu\Omega\text{cm}$ was used as a reference point, could be expressed by $r_{c,\text{liq.}}(T) = 60 + 1.18 \times 10^{-2} \cdot (T - 1211.3) \mu\Omega \cdot \text{cm}$ (Fig. 11). The thermal conductivity which is determined by the resistivity data according to the Wiedemann-Franz-Lorenz law is given by $\kappa_{\text{liq.}}(T) = 49.43 + 2.90 \times 10^{-2} (T - T_m)$ W/m/K (Fig. 12).

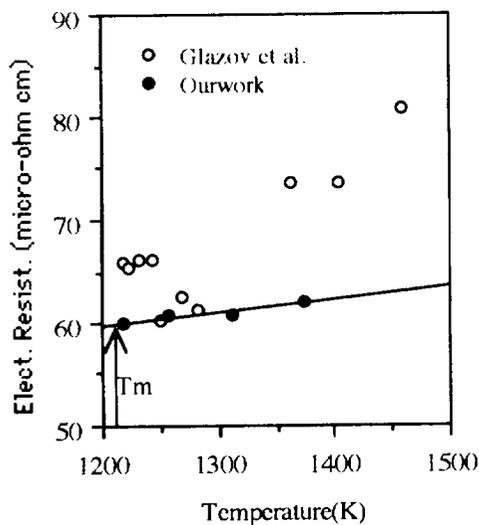


Fig. 11. Elect. resistivity of molten Ge.

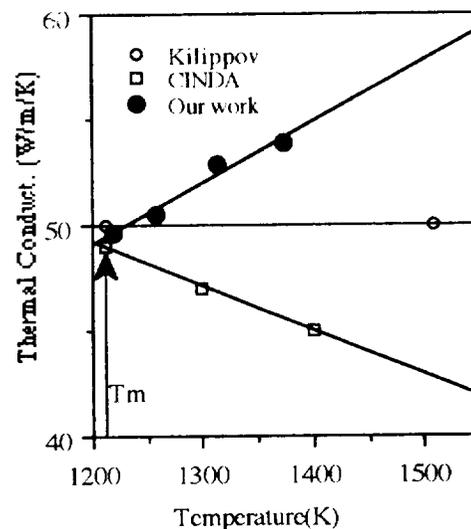


Fig. 12. Thermal conductivity of Ge.

(4) A Comment about the Viscosity Measurements

The viscosity measurement method relies on the measurement of the damping time constant of a freely oscillating drop. On the other hand, levitation of a melt in a 1-g environment requires application of a strong controlled electrostatic field to counter the weight. Any interference of a free decay process by the levitation control force can modify the decay process, and the decay constant is modified by it. The lower the viscosity is the more susceptible the decay constant will be to the external perturbation. Evidences for the range of viscosity measurable in 1-g by the JPL HTESSL are being accumulated. Above their melting temperatures, both molten silicon and germanium showed viscosities that were less than 1 mPs. Examining the scatter amplitude of these data, ~ 1 mPs seems to be just about the limit.

Such susceptibility to external noise is relatively more pronounced as the viscosity of the melt decreases. In the present case, the most dominant perturbing force was coming from the levitation force which corrected the sample position 480 times per second. The viscosity data we obtained scattered between 0.13 mPs and 0.7 mPs. In contrast, Glazov et al.[9] reported 0.78 mPs for germanium and 1.1 mPs for silicon at the respective melting points.

(5) Upgrading of the JPL HTESL

The knowledge on spectral emissivity of a sample material at the wavelength of pyrometer is important to determine the true temperature of the sample. Without this capability, a known reference temperature is essential, and a further assumption on constant spectral emissivity over a temperature region of interest has to be made. In an environment where such a reference point does not exist, temperature information of a given alloy becomes quite uncertain. For this reason, we have purchased and integrated in the JPL HTESL a commercial instrument which measures the spectral emissivity that will help determine the true temperature. Also installed was a 100 W YAG laser which would allow the sample temperature measured even during sample heating cycle. This high power laser will be able to heat a sample higher than 2000 C. This upgrading process required construction of an almost whole new HTESL system.

Spectral emissivity measurement, laser heating and sample rotation capabilities are the three important additions in the HTESL. In summary, the new facility can measure the following properties:

- (1) true temperature by measuring spectral emissivity;
- (2) density (or the volume expansion coefficient);
- (3) the ratio between the specific heat and the hemispherical total emissivity;
- (4) surface tension of liquids within a wide viscosity range;
- (5) viscosity;
- (6) electrical conductivity;
- (7) thermal conductivity determined from the measured electrical conductivity using the Wiedemann-Franz-Lorenz Law.

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