

Densities of Si determined by an image digitizing technique in combination with an electrostatic levitator

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We have determined the densities of Si in the liquid, $\rho_l(T)$, and solid, $\rho_s(T)$, states as a function of temperature, T , by employing an image digitizing technique and numerical calculation methods in combination with an electrostatic levitator. The obtained density data can be fitted with the following equations: $\rho_l(T) = \rho_l(T_m) - 1.71 \times 10^{-4}(T - T_m) - 1.61 \times 10^{-7}(T - T_m)^2$ (g/cm³); $\rho_s(T) = \rho_s(T_m) - 2.63 \times 10^{-5}(T - T_m)$ (g/cm³), where T_m is the melting point, 1687 K, and $\rho_l(T_m)$ and $\rho_s(T_m)$ are 2.580 and 2.311 (g/cm³), respectively. The error involved in the determination is estimated to be ± 0.006 (g/cm³). The $\rho_l(T)$ value smoothly varies through T_m and does not indicate a reported anomalous density variation. The $\rho_l(T_m)$ value is 2% larger than the literature value and the coefficient of the linear temperature dependence is approximately half of a reported value. The $\rho_s(T_m)$ value closely agrees with the literature value. © 1997 American Institute of Physics. [S0003-6951(97)03204-X]

Density data are important in the investigation of the nature and behaviors of metals and alloys. For example, the density difference between a liquid and solid at the melting point is essential in understanding melting and solidification phenomena. For this reason, density measurements have been repeatedly performed over many years and the data have become more accurate in recent years because the existing techniques have improved or new techniques have been introduced. In the course of developing a novel material confinement technique, we have developed a system which allows the measurements of the thermophysical properties of high temperature metals and alloys.¹ The system consists of an electrostatic levitator and noninvasive diagnostic devices. The capability of the system includes the measurements of the density, specific heat, hemispherical total emissivity, surface tension, and viscosity.² Advantages of the system are the elimination of contamination associated with the containers and rapid data acquisition. The system has been applied to measure the properties of several materials including a glass forming alloy³ and Si.²

Silicon is a basic material in the semiconductor industry and the crystal growth process has been continuously refined with the aid of numerical modeling to satisfy the never-ending demand for the perfect Si crystal. For modeling, the density of the liquid at melting point, $T_m = 1687$ K, is an essential parameter. A density value commonly referred to in the literature is 2.53 (g/cm³)^{4,5} which was measured in the 1950s. Recently, Sasaki, Tokizaki, Terashima, and Kimura reported a higher value, 2.556 (at 1725 K), which was measured by an improved Archimedian method.⁶ Waseda, Shinoda, Sugiyama, Takeda, Terashima, and Toguri also provided an even higher value, 2.595 (at 1725 K), which was consistent with an x-ray diffraction analysis of the radial distribution function of the liquid.⁷ The new values are significantly higher than the literature value and they seem to be more accurate according to our preliminary measurement which yielded 2.56 at T_m .² Furthermore, Sasaki *et al.* showed an anomalous density variation whose origin was not identified.⁷ In order to clarify the above discrepancies and

anomaly, we decided to reinvestigate the densities of Si. After we completed the preliminary measurement and reported the result, we have refined the technique and have added a device to improve the accuracy of the measurement.

A spherical sample of typically 15 mg (roughly 2.2 mm in diameter) was levitated in a high vacuum environment ($\sim 10^{-8}$ Torr) using the electrostatic force which counterbalanced gravity. Heating of the sample was provided by a high intensity xenon arc lamp. Cooling of the sample was achieved by natural radiative heat loss to the surroundings. The temperature of the sample was measured by a pyrometer. Also, the images of the levitated sample were stored on videotape. The density was determined from these images by employing an image digitizing technique and numerical calculation methods. The detailed description of the levitation system and the density measurement method are reported elsewhere.^{1,8} An additional device employed for the present measurement was a mechanical shutter placed in front of the xenon lamp. The device was necessary to momentarily block the high intensity light in order to obtain clear images of the sample at high temperatures.

Figure 1 shows a typical thermogram of a sample on cooling when the heating source is completely blocked. The sample temperature was determined by measuring the emitted energies at three spectra wavelengths (700, 750, and 800 nm). The spectra emissivities of the liquid sample at these wavelengths were determined at T_m and assumed to be constants in the present temperature range. Strictly speaking, the temperatures in Fig. 1 closely represent the true sample temperatures only when the emissivity is constant within the measured range. As is seen, the sample is substantially undercooled (approximately -300 K) prior to the onset (indicated by the arrow) of crystallization. Due to recalescence, the sample temperature almost instantaneously rises to T_m (dot and dash line). Only one temperature is registered during recalescence, which indicates that the recalescence time is approximately 1/30 s because the data acquisition rate of the pyrometer is 60 times per second. The subsequent temperature rise above T_m is caused by an increase in the spec-

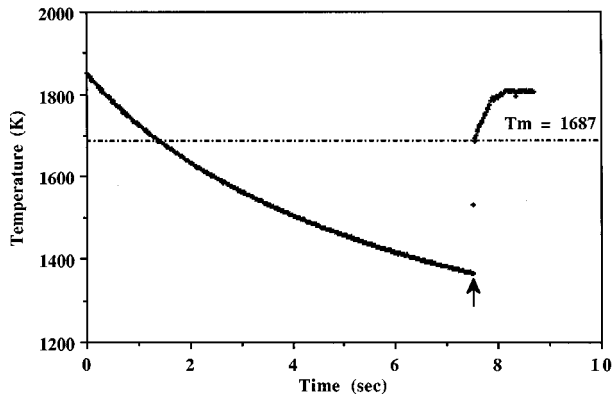


FIG. 1. A typical thermogram of a sample upon cooling. The maximum undercooling level is approximately 300 K prior to the onset of crystallization indicated by the arrow.

tral emissivity of the solidifying sample. Therefore, the apparent temperature increase does not represent the true sample temperature rise.

Figure 2 shows the density of a liquid sample, $\rho_l(T)$ as a function of decreasing temperature, T . The density is determined from the images taken during the cooling process whose thermogram is shown in Fig. 1. Unlike pure metals whose densities show a linear temperature dependence, $\rho_l(T)$ shows a quadratic dependence which can be fitted by the following equation:

$$\rho_l(T) = \rho_l(T_m) - 1.71 \times 10^{-4}(T - T_m) - 1.61 \times 10^{-7}(T - T_m)^2 (\text{g/cm}^3), \quad (1)$$

where $\rho_l(T_m) = 2.580$. Equation (1) is shown as the solid line in the figure.

Figure 3 shows the densities of the solid and liquid, which were determined while a levitated sample went through the melting process on increasing temperature. For this measurement, a nearly spherical solid sample was initially heated up near T_m . The sample was then gradually heated further by increasing the intensity of the xenon lamp until it was melted and superheated. The shutter was employed to obtain the clear images of the sample during the process. Approximate start and end of melting are indicated

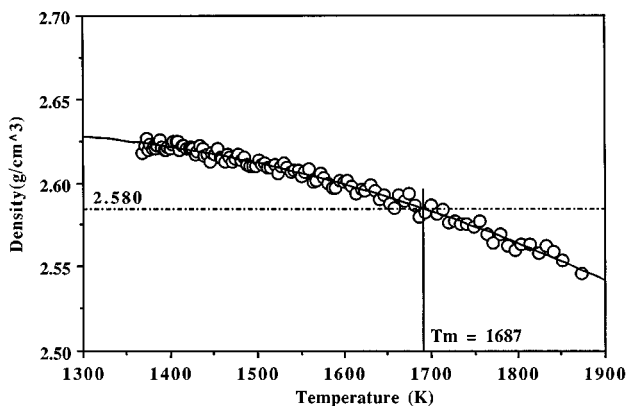


FIG. 2. The density of the liquid as a function of decreasing temperature. The solid line is given by Eq. (1). The density at T_m is determined to be 2.580 (g/cm^3).

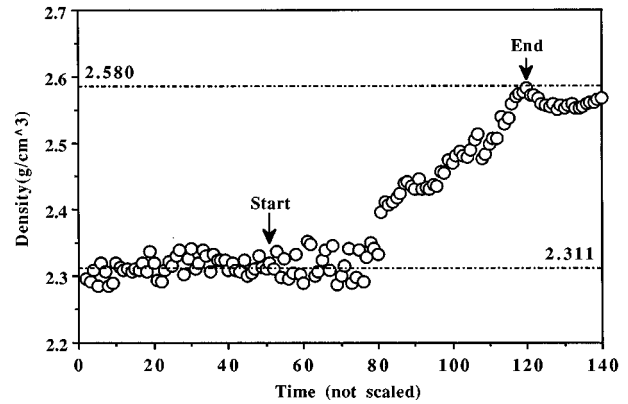


FIG. 3. The densities of the solid and liquid at T_m , which are determined while the sample goes through melting process on increasing temperature. The approximate start and end of melting are indicated by the arrows.

by the arrows. During melting, the sample temperature stayed at T_m . The density of the solid, $\rho_s(T_m) = 2.311$ (g/cm^3) was determined by taking the average of the data near T_m . This value agrees with an often quoted value, 2.31, in the literature. The large scattering of the data is due to nonsphericity of the solid sample. During melting, the sample was slightly deformed because the two phases tended to separate owing to the density difference. This deformation caused the scattering of the data during melting. The density reaches the maximum at the end of melting. Once melting is completed, the temperature starts rising, which is seen as the decrease in the density. The density increase toward the end of the time is due to the temperature decrease after reaching the maximum.

Figure 4 shows the density of the solid, $\rho_s(T)$, as a function of decreasing temperature. For this measurement, a solid sample was heated up near T_m and then cooled by radiative heat loss to the surroundings. The temperature was measured by a single-color pyrometer which was capable of measuring the temperature down to 550 K. In Fig. 4, the density of the solid is combined with the densities in Figs. 2 and 3 for comparison. The large scattering of the data is mainly due to the nonsphericity of the sample. Since the sample was randomly rotated, the accurate determination of the density was possible by collecting a large number of data and taking an

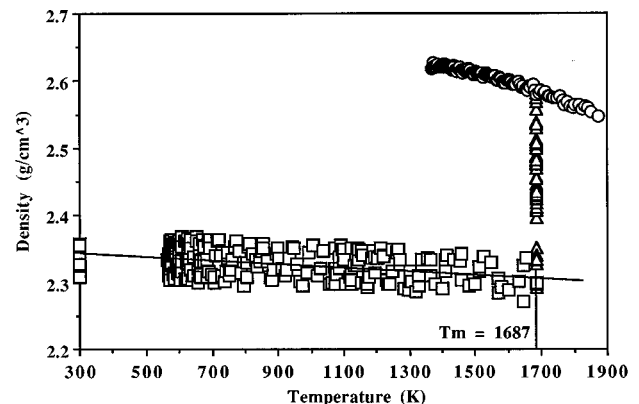


FIG. 4. The density of the solid as a function of decreasing temperature. The data in Figs. 1 and 2 are also shown for easy comparison.

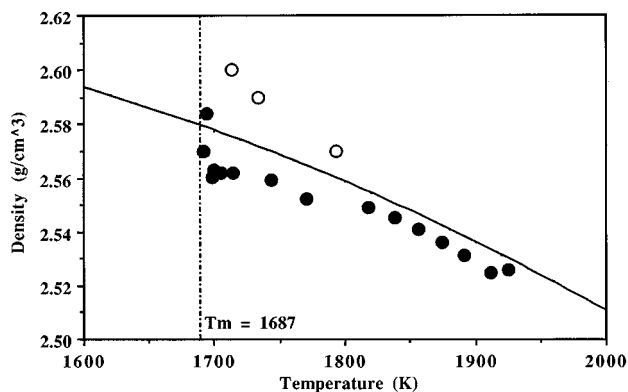


FIG. 5. The comparison of the present result with the Sasaki (full circles) and Waseda (open circles) results. The present result is represented by the solid line calculated from Eq. (1).

average. The linear fit of the data is given by

$$\rho_s(T) = \rho_s(T_m) - 2.63 \times 10^{-5} (T - T_m) (\text{g/cm}^3). \quad (2)$$

The density at room temperature is determined to be $2.347 \text{ (g/cm}^3\text{)}$. The coefficient of the temperature dependence closely agrees with the value measured with a more rigorous method.⁹

The error involved in the liquid density determination with the present technique is determined to be $\pm 0.2\%$, which excludes the additional errors in the sample temperature and weight measurements. A liquid is usually held at a high temperature for tens of seconds before a data acquisition on cooling is performed. This is necessary to establish an equilibrium initial temperature. During this holding and the proceeded slow heating, a rapid evaporation of the liquid occurs; therefore, the weight just before the cooling process must be estimated from the weights determined before and after the experiment. This estimation introduces the error which could change $\rho_l(T_m)$ by as much as $\pm 3\%$ when the data acquisition is repeated several times. However, this error does not affect the temperature dependence terms of Eq. (1) because evaporation during the data acquisition on cooling (which lasts only ~ 8 s) is negligible. The error involved in the temperature measurement is expected to be minimal because our assumption of the spectral emissivities of the liquid to be constants is supported by a study which shows that the spectra emissivity of liquid Si has no temperature dependence.^{10,11} These additional errors may exist in the density shown in Fig. 2, but do not in the density shown in Fig. 3 because both the temperature and weight are precisely known for the density measurement at T_m . By taking into account the above error analysis, the confidential range of the density of the liquid at T_m is determined to be $2.580 \pm 0.006 \text{ (g/cm}^3\text{)}$. This value is higher than the literature value and close to the Sasaki and Waseda values. Another discrepancy from the literature value is the temperature dependence of the density. The reported linear dependence coefficient is $-3.5 \times 10^{-4} \text{ (g/cm}^3 \text{ K)}$.⁵ The present measurement shows the quadratic dependence and the coefficient of the linear term at T_m is approximately half of the reported value.

Figure 5 shows the comparison of the present result with the Sasaki and Waseda results.^{6,7} If we take into account the

errors involved in the measurements, at above 1800 K, the present result and the Sasaki result agree with each other, including the temperature dependence. However, at below 1800 K, the Sasaki values exhibit an anomalous variation, first, the downward deviation from the present result and then a steep increase near T_m approaching the present result. They demonstrated that when a liquid was brought down to a lower temperature from a higher temperature, an initial density was small but it gradually increased over several hours and settled at a final density. The difference between the initial and final densities was as large as $0.005 \text{ (g/cm}^3\text{)}$. They attributed this anomaly to the transient effect of a sluggish structural transition.⁶ Since the rapid evaporation rate of liquid Si prevented us from performing a similar measurement, we could not confirm this anomaly.

We observed that the density of liquid Si showed the quadratic temperature dependence. This is different from metals which generally show linear dependencies. It is known that some binary semiconductor compounds partially retain their solid semiconductor structures above their melting points, which are clearly indicated by the isotherms of their viscosities and electrical conductivities of the liquids.⁴ These semiconductor structures, however, are gradually dissociated as the liquid temperature increases and the metallic structure dominates at higher temperatures. Although it is not obvious from the viscosity and electrical conductivity data,⁴ the quadratic temperature dependence of the density may allow us to speculate a similar structural transition in liquid Si. If this speculation is true, the density of the liquid should show a linear temperature dependence at a higher superheating level where the metallic structure (sixfold coordination) dominates. On the other hand, at a deeper undercooling level, the semiconductor structure (fourfold coordination) may dominate; then, the density should show a linear dependence with a different coefficient. We are working on an improvement of our system to extend the superheating and undercooling levels so that we may be able to confirm the above speculation.

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