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

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Abstract

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 fit by the following equations

$$\rho_l(T) = \rho_l(T_m) - 1.71\times10^{-4}(T - T_m) - 1.61\times10^{-7}(T - T_m)^2 \quad (\mathrm{g/cm^3})$$

$$\rho_s(T) = \rho_s(T_m) - 2.63\times10^{-5}(T - T_m) \quad (\mathrm{g/cm^3})$$

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, respectively. The error involved in the determination is estimated to be $\pm$ 0.006 (g/cm$^3$). 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.

Density data is 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 has become. more accurate in recent years because the existing techniques have improved or new techniques have been introduced. 1 n the course of developing a novel material confinement technique, we have developed a system which allows measurement of the thermophysical properties of high temperature metals and alloy s.[1] The system consists of an electrostatic leviator and non-invasive 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 alloy[3] anti 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 densit y value commonly referred to in the literature is 2.53 (g/cm$^3$)[4,5] which was measured in the 19S0s. 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. s}1owccI an anomalous density variation whose origin was not identified. In order to clarify the above discrepancies and anomaly, we decided to reinvestigate the densities of Si. After wc completed the preliminary measurement and reported the result, wc have refined the technique and have added a device to improve the accuracy of the measurement,

A spherical sample of typically 15 mg was levitated in a high vacuum environment ( ~ 1()-~ 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 video tape. 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 densit y 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. "l-he 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 completel y blocked. The temperature was measured by a three-color pyrometer whose emissivity was adjusted at Till. As is seen, the sample is substantially undercooked (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 sec because the data acquisition rate of the pyrometer is 60 times per second. The subsequent temperature rise above $T_m$ is due to an increase in the spectral emissvity upon solidification.

Figure 2 shows the density of a liquid sample, pi(T) as a function of temperature, 1'. 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 fit by the following equation:

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

where $\rho_l(T_m)$ =- **2.580.** Eq. **(1) is shown** as the curve 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. 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 arc indicated 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 non-sphericit y of the solid sample. During melting, the sample was slightly deformed becau sc 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 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 clown 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 non-sphericity 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 average. The linear fit of the data is given by

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

The density at room temperature is calculated to be 2.347 ($g/cm^3$). The coefficient of the temperature dependence agrees with the value measured with a more. rigorous method.[9].

The error involved in the density determination is determined to be ± 0.2 %, which excludes the errors in the sample temperature, and weight measurements. The liquid is rapidly evaporated during the. experiment; therefore, the weight must be estimated from the weights determined before and after the experiment. This estimation introduces the error which could be as large as ± 3 %. The error involved in the temperature measurement is expected to be minimal because the spectral emissivity of the liquid shows no temperature dependence.[10] 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 above error analysis, the confidential range of the density of the liquid at $T_m$ is determined to be 2.580 ± 0.006 ($g/cm^3$). 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 x 10-4 ($g/cm^3$ K).[5] The present measurement shows the quadratic dependence and the coefficient of the linear term at $T_m$ is approximately a half of the reported value.

Figure 5 shows the comparison of the present result with the Sasaki and Waseda results. Their density values were taken from the reports. The Sasaki and Waseda values are shown by the full circles and the open circles, respectively. The curve is the present result represented by Eq. (1). If we take into account the errors involved in the measurements, at above 1800 K, the present result and the Sasaki result agree. each other, including the temperature dependence. However, at below 1800 K, the Sasaki values show an anomalous variation especially near $T_m$. "l'his anomaly was attributed to the transient effect of a sluggish structural transition.[6] They showed 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** (g/cm$^3$). Since the cooling rate of the present measurement is much faster (- - 90 K/see at Till), the liquid in the present measurement has less time for the transition. l'bus, the downward deviation of the Sasaki values may be explained by the transient effect since their measurement is performed after holding the sample at each temperature for 30 minutes.

A steep increase in the Sasaki values is seen near Till; however, this increase cannot be explained by the transient effect, The Sasaki values appear to become similar to the present values. A possible explanation of this anomaly is as follows: We accept their interpretation of the transient effect, i.e., the liquid goes through the structural transition to form a short range structure if it is held at temperatures below 1800 K. The structure of the liquid should resemble that of the solid, q'bus, either the diamond or graphite structure is qualified by considering the similarity between Si and C. The graphite structure may be more stable than the di amend structure at high temperat ures. However, the diamond structure becomes more stable near $T_m$ because it is the stable structure of the solid. If the diamond structure is denser (ban the graphite structure as it is true for solid C, the density of the liquid could show the steep increase near 'I'$_{nl}$ as seen in the Sasaki result. When the liquid is rapidly cooled as in the present case, it may not have enough time to form the graphi te st ruct ure but may still form the diamond structure near $T_m$ because it is the necessary path for eventual solidification. The quadratic temperature dependence of p](T) also indicates the structural transition. The density values at $T_m$ measured on cooling (Fig. 2) and heating (Fig. 3) show no difference, which implies that the diamond structure also exists in the liquid upon heating. It is conceivable that the local diamond structure exists in the liquid which is in equilibrium with the solid at Tm and the structure persistently exists even after the solid has disappeared upon the completion of melting.

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Captions

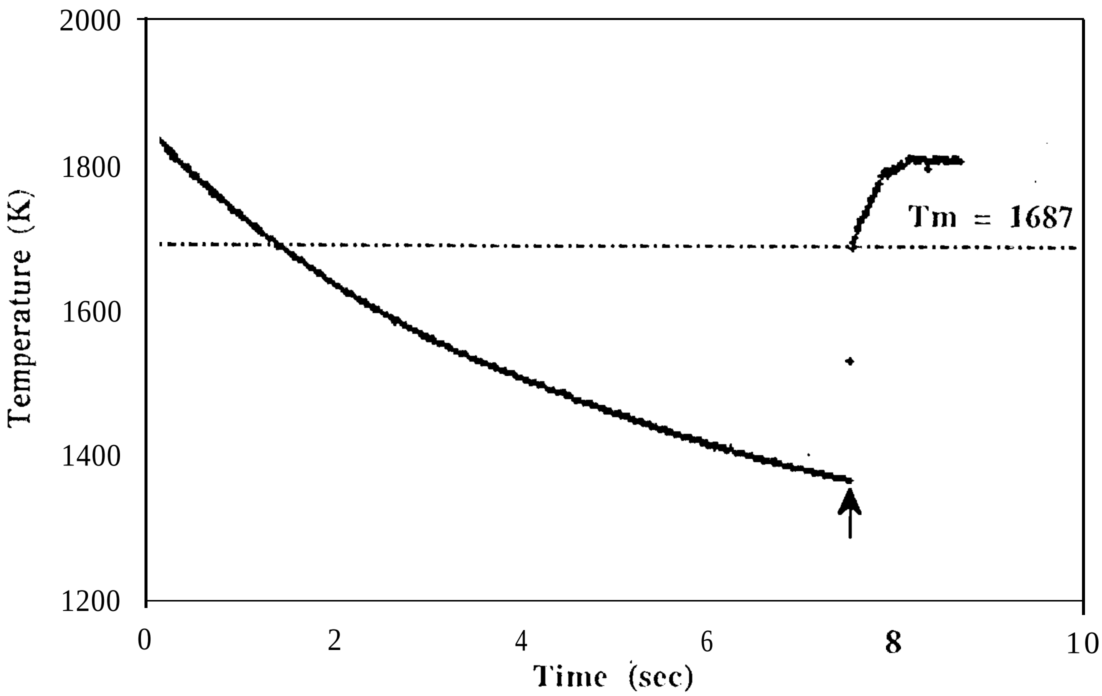
Figure 1. A typical thermogram of a sample upon cooling. The maximum undercooling level is approximately 300 K prior to the onset of crystallization indicated by the arrow.

Figure 2. 'I'he density of the liquid as a function of temperature. The curve is given by Eq. (l). The density at $T_m$ is determined to be 2.580 ($g/cm^3$).

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

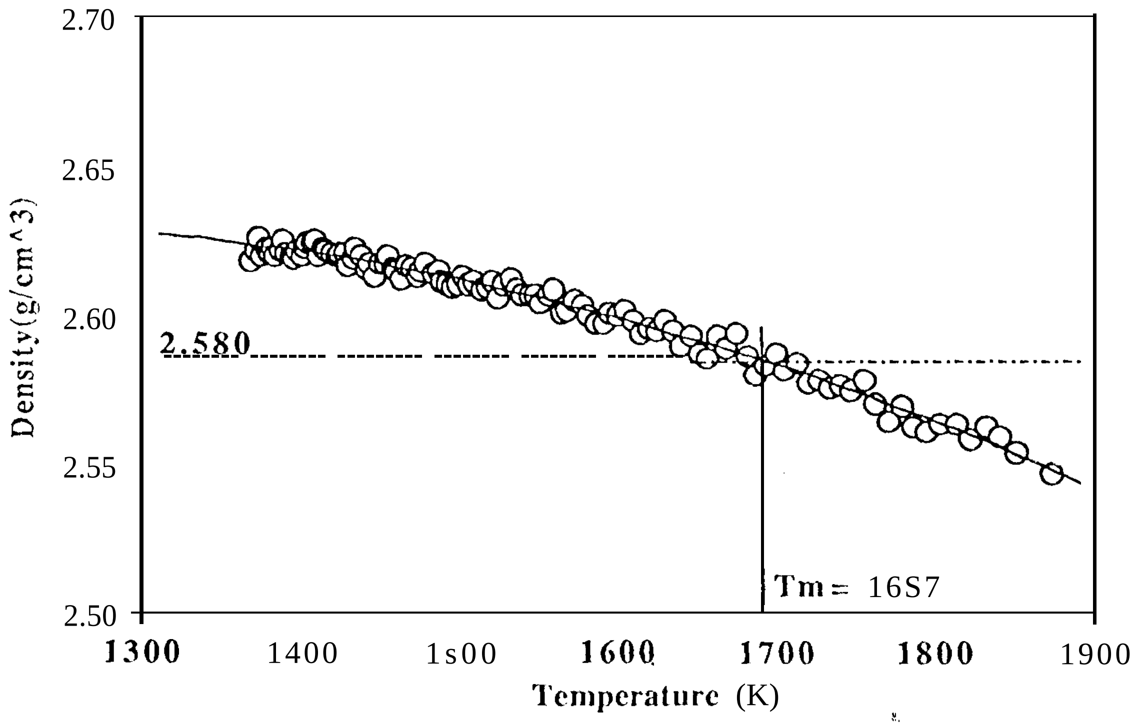
Figure 4. The density of the solid as a function of temperature, The data in Figs. 1 and 2 are also shown for easy comparison.

Figure 5. The comparison of the present result with the Sasaki (full circles) and Waseda (open circles) results. The present result is represented by Ec]. (1 ).



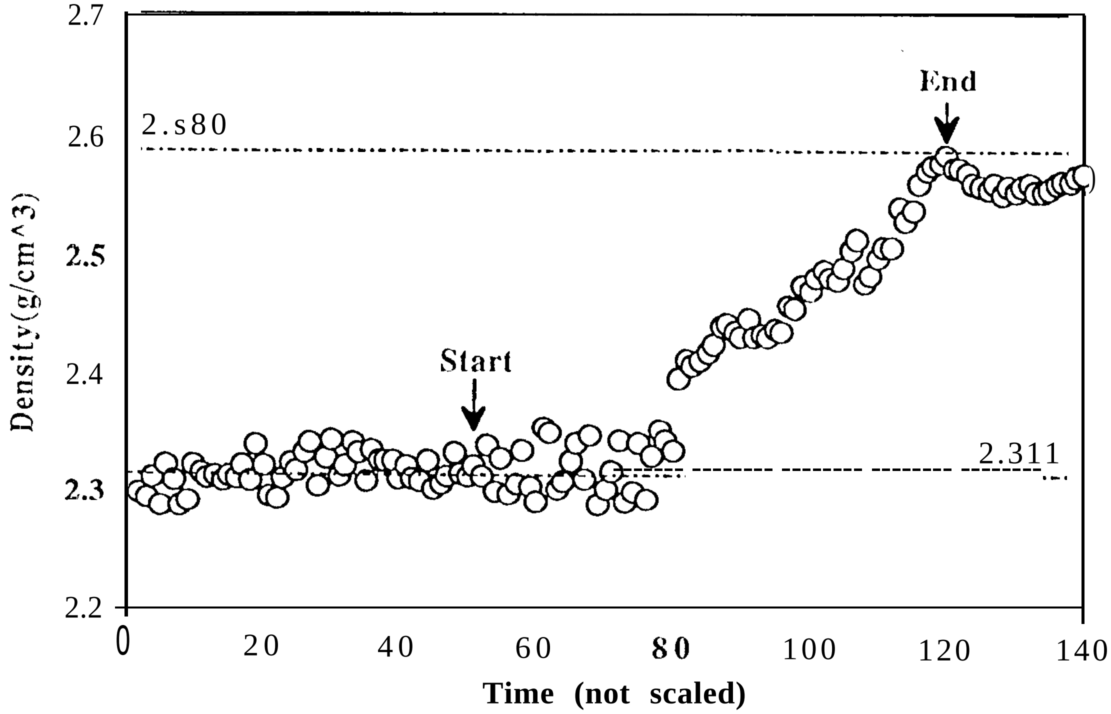
2000
1800
1600
1400
1200
Temperature (K)
Tm = 1687
0
2
4
6
8
10
Time (sec)


Fig. 1


2.70
2.65
2.60
2.55
2.50
2.580
Tm = 16S7
1300
1400
1s00
1600
1700
1800
1900
Temperature (K)
Density(g/cm^3)

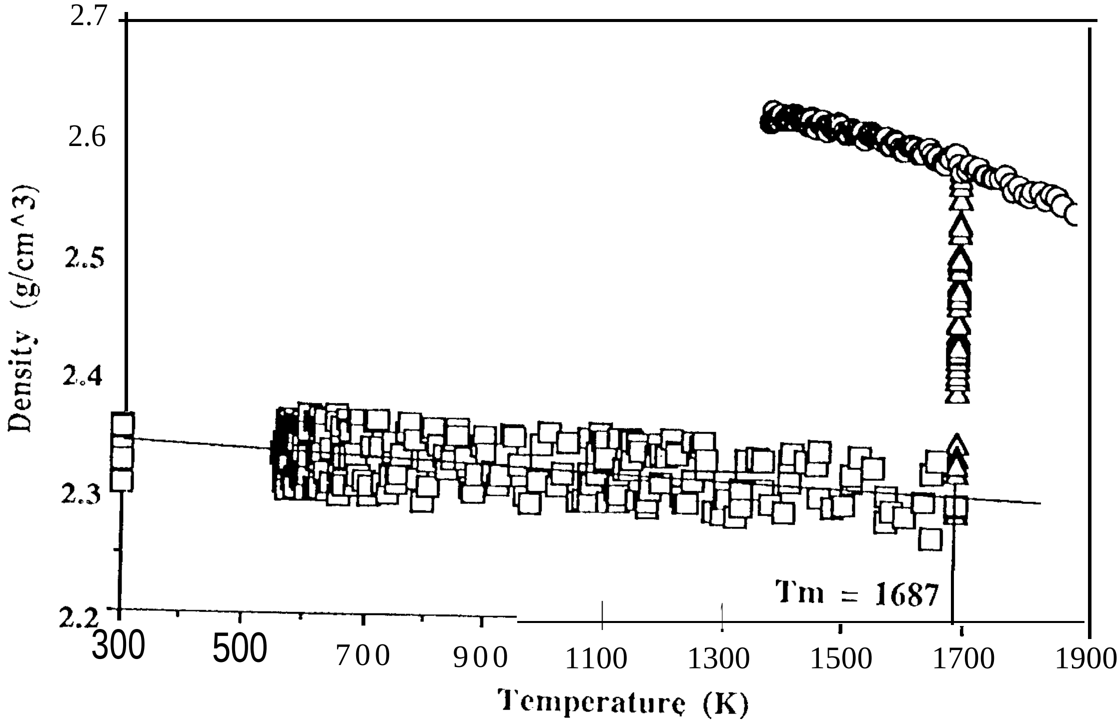
/f) 2

(8 7) -



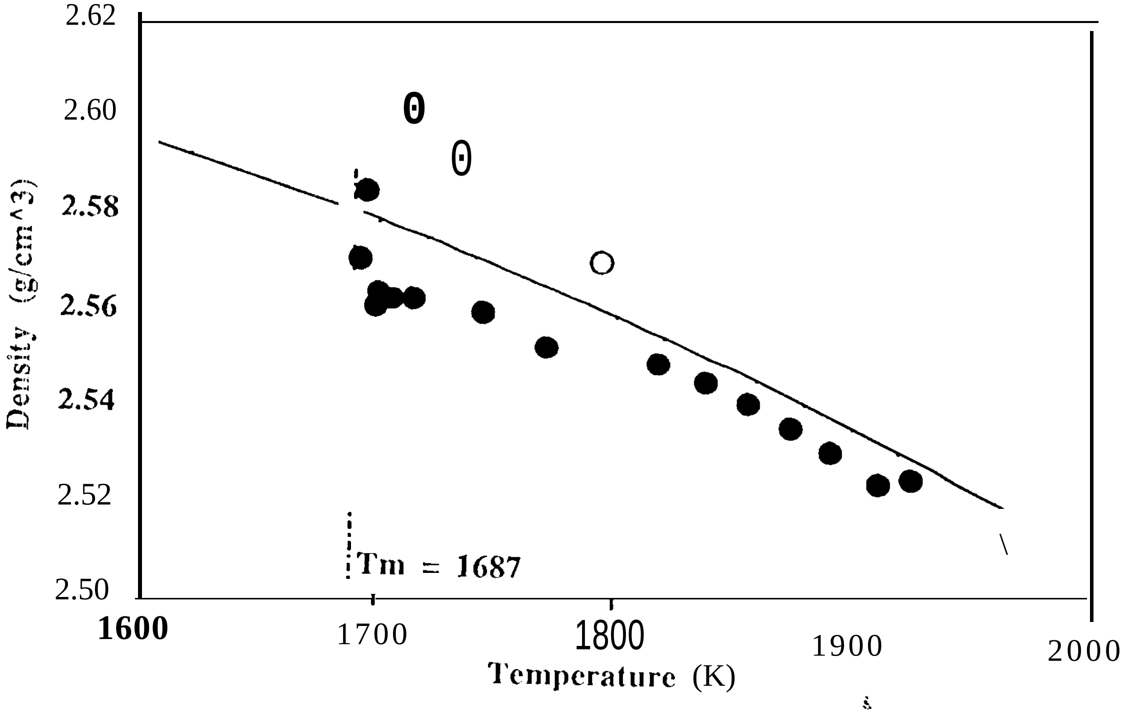
End
2.s80
Start
2.311
2.7
2.6
2.5
2.4
2.3
2.2
Density(g/cm^3)
0
20
40
60
80
100
120
140
Time (not scaled)


Fig. 3



2.7
2.6
2.5
2.4
2.3
2.2
Density (g/cm^3)
Tm = 1687
300
500
700
900
1100
1300
1500
1700
1900
Temperature (K)


Fig. 4



2.62
2.60
2.58
2.56
2.54
2.52
2.50
Density (g/cm^3)
Tm = 1687
1600
1700
1800
1900
2000
Temperature (K)


Fig. 5