THERMOPHYSICAL PROPERTIES OF MOLTEN SILICON
MEASURED BY THE JPL HIGH TEMPERATURE ELECTROSTATIC LEVITATOR

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ABSTRACT

Five thermophysical properties of molten silicon measured by the High Temperature Electrostatic Levitator (HTESL) at JPL are presented. The properties measured are the density, the constant pressure specific heat capacity, the hemispherical total emissivity, the surface tension and the viscosity. Over the temperature range investigated (1350 ~ 1850K), the measured liquid density showed a quadratic nature expressed by

\[ \rho(T) = 2.58 - 1.59 \times 10^{-4} (T - T_m) - 1.15 \times 10^{-7} (T - T_m)^2 \text{ gr/cm}^3 \]

with \( T_m = 1687 \text{ K} \). The volume expansion with respect to the melting point could be expressed by

\[ \frac{V(T)}{V_m} = 1 + 6.18 \times 10^{-5} (T - T_m) + 4.72 \times 10^{-8} (T - T_m)^2. \]

The hemispherical total emissivity of molten silicon at the melting temperature was determined to be 0.18, and the resulting constant pressure specific heat was as shown in Fig. 5. The surface tension and the viscosity could be expressed respectively by

\[ \sigma(T) = 765 - 0.016 (T - T_m) \text{ mN/m}, \]

and

\[ \eta(T) = 0.75 - 1.22 \times 10^{-3} (T - T_m) \text{ mPa·s}. \]
I. INTRODUCTION

Reliable thermophysical properties of molten silicon are essential for accurate predictions of crystal growth processes which are intended to grow larger and higher quality silicon crystals. Thus, it has been a continuing challenge to try to measure more accurate values of these properties as our understanding for the physical and chemical processes involved in various measurement techniques grow and as more reliable techniques are developed. In the past several years, there have been several coordinated programs both in the United States and in Japan, all of which have the common objective of producing more accurate properties of molten silicon using various techniques. Most of the participating investigators used conventional techniques after substantial improvements. However, most of these investigators used some form of crucibles to contain their molten samples, risking possible chemical and physical reaction between the melt and the crucibles. Our group at Jet Propulsion Laboratory, as one of the participants of a coordinated program, attempted to measure the properties of molten silicon using the high temperature electrostatic levitator (HTESL)[1], a levitator that was recently developed at JPL. While the competing techniques have produced some remarkable examples of molten silicon properties, the superior method of the HTESL can be seen by examining the various attributes that make it so unique.

One of the defining aspects of the HTESL (which distinguishes it from the crucible-dependent methods) is that it can levitate a silicon melt in a high vacuum while maintaining the purity of the sample. This creates unparalleled results as the HTESL is able to achieve further states of purification in its melts as various volatile impurities evaporate off the samples. In addition, such a well isolated melt tends to undergo deeply undercooled states prior to solidification, allowing us to investigate their properties. Additional characteristics of the HTESL which made the present work possible are: (i) its quiescent sample positioning and open sample views allowed accurate pointing of various non-contact diagnostic instruments such as pyrometers or imaging camera etc., (ii) purely radiative cooling that could be achieved
when the heating beam was blocked allowed accurate measurement of the ratio between the heat capacity and the hemispherical total emissivity, (iii) nearly spherical levitated drop shape helped measuring accurate measurements of the mass density and the surface tension.

In this paper, we report six thermophysical properties of molten silicon that were recently measured using the HTESL. These properties include density, volume expansion coefficient, constant pressure heat capacity, hemispherical total emissivity, surface tension and viscosity. Whenever possible, our results will be discussed in comparison with those of other investigators in the programs including those of our earlier works[2, 3]. For example, while the JPL group measured the surface tension in the ordinary gravitational environment (1-g environment) using the HTESL, Professor Nogi's group in Osaka University measured the same property using an electromagnetic levitator in a reduced gravity environment (~10^{-5} g) which was provided as their system freely fell through the 10-second drop-shaft in Hokkaido, Japan. Also, while Professor Yusuru Sato's group at Tohoku University measured the viscosity using the oscillating viscometer, Professor Kasuhiro Mukai's group in Kyushu Institute of Technology used the sessile drop technique to measure the density of molten silicon. Although all of the above investigators used different methods, all the sample materials they used had to come from a same pure silicon crystal grown by Sumitomo Metal Industries, Ltd. for this program.

2. EXPERIMENTAL PROCEDURES

The high temperature electrostatic levitator (HTESL) levitates a sample ~3 mm in diameter between a pair of parallel disk electrodes that are spaced about 10 mm as schematically shown in Fig. 1. The bottom electrode was surrounded by four side electrodes for the purpose of position stability in the horizontal directions. To induce resonant oscillations on a sample an AC high voltage amplifier was connected to the bottom electrode to generate an oscillating electric field at the sample position. This electrode assembly was housed by a stainless steel chamber that was typically evacuated to ~10^{-8} Torr before sample heating began. Fig. 2 shows
a schematic diagram of the HTESL. The sample was heated by a focused 1 kW xenon arc lamp which was capable of raising the sample temperature to ~2300 K. To measure the temperature of the levitated sample, a non-contact single color pyrometer (custom made) operating at 750 nm (filter width: ~10 nm) was used. The pyrometer incorporated a photomultiplier tube along with a log ratio amplifier for higher sensitivity. Since the wavelength chosen for the pyrometer overlapped with the spectrum of the xenon arc lamp, the temperature measurement could be done only when the lamp was totally blocked. The sample temperature was then calibrated at the melting point of the sample by adjusting the emissivity of the pyrometer. When data taking was required in the presence of arc-lamp radiation, an alternate pyrometer which operated at 4 μm was used. Detailed description of the HTESL was given in an earlier publication [1].

Pure silicon (named as 'G-silicon') cubes were cut from a large crystal that was grown by Sumitomo Metal Industries, Ltd. using floating zone method and the Japan Space Utilization Promotion Center (JSUP) distributed them to all investigators which included us. Major impurity contents of these samples were 1.91 x 10^{16} atoms/cm^3 of carbon and 23 ± 3 ppm of oxygen, and their electrical resistivity was 1.58 KΩ-cm. These cubes were further cut into smaller cubes, and they were ground roughly into spheres before they were cleaned (by immersion in 5% HF at room temperature for 5 minutes, rinsed in distilled water, and finally rinsed in anhydrous ethanol).

Since the levitation forces in HTESL does not affect the sample temperature and a sample that is levitated in it is isolated in a high vacuum, the cooling process when the heating source is blocked will be described by the radiative heat transfer equation

\[
\frac{m}{M} C_p \frac{dT}{dt} = -\varepsilon_T A \sigma_{SB} (T^4 - T_a^4)
\]

(1)

where \( m \) is the sample mass, \( M \) the atomic weight, \( C_p \) the molar heat capacity at constant pressure, \( T_a \) and \( T \) are respectively the ambient and sample temperatures, \( \varepsilon_T \) the hemispherical total emissivity, \( A \) the surface area of the sample, and \( \sigma_{SB} \) the Stefan-Boltzmann constant.
(5.6705x10^{-8} \text{ W.m}^{-2}.\text{K}^{-4}). The fact that the measurement of $c_p/e_T$ is possible from this equation by measuring a cooling curve is one of the important merits of the HTESL. The density measurement of a molten silicon was carried out by taking video images of the sample simultaneously with the temperature measurement during a cooling process. Afterward, the video images so obtained were analyzed for the density measurement correlating them with the temperature.

3. MASS DENSITY MEASUREMENT

The basic process for the density measurements was consisted of (i) digitization of recorded video image, (ii) edge detection, (iii) calculation of the area (therefore the volume of the sample) through a linear spherical harmonic fit, and (iv) calibration of the data with respect to a reference sphere for absolute dimension of the sample. The density is then obtained using the sample mass which was measured immediately following the experiment. A detailed description of the density measurement method used in this experiment can be found in an earlier publication [4].

Figure 3 shows the result of our density measurements of molten silicon over a 500K span. As we have observed in our two earlier works[2, 3], the density results over the temperature range $1350 \text{ K} < T < 1850 \text{ K}$ again showed a quadratic nature which could be fit by the following equation:

$$\rho(T) = 2.58 - 1.59 \times 10^{-4} (T - T_m) - 1.15 \times 10^{-7} (T - T_m)^2 \text{ g/cm}^3. \quad (2)$$

In comparison, the silicon density results of our first work using the same HTESL[2] were

$$\rho(T) = 2.56 - 1.69 \times 10^{-4} (T - T_m) - 1.75 \times 10^{-7} (T - T_m)^2 \text{ g/cm}^3, \quad (3)$$

while the results from our second work[3] could be expressed by
\[
\rho(T) = 2.58 - 1.71 \times 10^{-4} (T - T_m) - 1.61 \times 10^{-7} (T - T_m)^2 \text{ g/cm}^3, \quad (4)
\]

respectively, where \( T_m = 1687 \) K. All of the sample materials used were pure silicon although they were from different origins. All three results consistently showed quadratic temperature dependence, and they agreed within 1% at the melting point. Again, we have not observed any abrupt rise of density near the melting temperature as was reported by Sasaki et.al. [5]. These investigators used an improved Archimedian method to avoid the effect of surface tension. The linear fit to their most reliable data above and away from the melting point was expressed by

\[
\rho(T) = 2.575 - 2.12 \times 10^{-4} (T - T_m) \text{ g/cm}^3, \quad (5)
\]

showing a very close agreement at \( T_m \) with our two recent results given by Eq. (2) and (4). Recently, Niu et al.[6] also measured the density using sessile drop technique (boron nitride as the crucible). However, their result 2.52 g/cm at the melting point is smaller than ours by 2.3%. Our value for \( \left( \frac{\partial \rho}{\partial T} \right)_p = - 1.59 \times 10^{-4} \text{ g/cm}^3/\text{K} \) at \( T_m \) is about 25% smaller than their result. The volume expansion which was derived from Eq. (2) can be expressed by

\[
\frac{V(T)}{V_m} = 1 + 6.18 \times 10^{-5} (T - T_m) + 4.72 \times 10^{-8} (T - T_m)^2, \quad (6)
\]

and this is also shown in Fig. 3 along with the density.

4. SPECIFIC HEAT AND HEMISPHERICAL TOTAL EMISSIVITY

One of the important capabilities of HTESL is that it allows accurate determination of \( c_p/\varepsilon_T \) from a temperature vs. time profile which can be obtained during a radiative cooling process. A typical radiative cooling profile of a silicon melt is shown in Fig. 4. The melt started cooling from 160 K above the melting temperature and it undercooled as much as 300 K before
a recakescence took place. Upon the recakescence the sample temperature rose sharply to an isotherm state. Unlike many pure metals, Fig. 4 does not show a constant radiance over the isotherm region. This is due to changing spectral emissivity over the region. The output of a single color pyrometer operating at 750 nm was calibrated taking the temperature immediately following the recakescence as its melting temperature ($T_m = 1687$ K). A rearrangement of Eq. (1) for the ratio between $c_p$ and $\varepsilon_T$ gives

$$\frac{C_p}{\varepsilon_T} = \frac{\lambda M \sigma_{SB}(T^4 - T_0^4)}{m \frac{dT}{dt}}.$$

Since $T$ and $dT/dt$ can be obtained from Fig. 4, and the surface area $A$ can be extracted from the density data, $C_p/\varepsilon_T$ can be readily obtained. The result so obtained for a molten silicon is shown in Fig. 5. This result is nearly identical at the melting point with our previous result[2], and the overall agreement over 400K range was within 2%.

From Fig. 5, if either $C_p(T)$ or $\varepsilon_T(T)$ is known, the other can be determined. When a literature value $C_p(T_m) = 25.61$ Joule/mole/K[7] was used as the specific heat at the melting point, the corresponding hemispherical total emissivity $\varepsilon_T(T_m)$ that could be determined from Fig. 5 was 0.18. There are no literature values available to compare this result with other than our own[2] which was obtained using the HTESL. Again, the present value $\varepsilon_T(T_m) = 0.18$ is identical with our earlier result.

Now, if we can assume that $\varepsilon_T(T) = 0.18$ holds over the liquidus temperature range of the present interest, and we can determine $C_p(T)$ from Fig. 5 by simply multiplying $\varepsilon_T(T) = 0.18$ to it. $C_p(T)$ so obtained is also shown in Fig. 5 along with $C_p/\varepsilon_T$. Again, the non-linear temperature dependency of $C_p(T)$ is consistent with our earlier result[2].
5. SURFACE TENSION AND VISCOSITY

Good stability of sample position and nearly spherical sample shape helped inducing a pure $P_{2,0}(\cos \theta)$ mode, and it greatly simplified the data analysis for the surface tension and the viscosity. To excite a

The resonant oscillation of a levitated silicon drop was induced by applying a low-level ac electric field to the bottom electrode as shown in Fig. 1 and searching for the resonance frequency. When a resonance was found, the mode of the oscillation was confirmed to be a $P_{2,0}(\cos \theta)$ mode. Then, the intensity and the duration of the field had to be adjusted so that the amplitude of the oscillating drop did not exceed ~10% of the drop radius. Changing amplitude of oscillation drop was detected using a photodetector. A typical transient drop oscillation that was detected following the termination of the excitation filed is shown in Fig. 6. Such signals were digitized and stored in a computer together with the corresponding temperature information for later analysis. For the present experiment, the sample temperature had to be maintained at a predetermined value during the data taking before it was changed to another temperature. A pyrometer operated at 4 μm had to be used to avoid interference by the xenon lamp.

Since the surface charge on a levitated drop modifies the apparent surface tension, one should use the Rayleigh's expression for charged drop oscillation frequency $\omega_{2e}$ to determine the surface tension $\sigma(T)[8],$

$$\sigma = \frac{r_o^3 \rho}{8} \left( \frac{\omega_{2e}^2}{8 \pi^2 r_o^4 \rho \epsilon_o} \right). \quad (8)$$

where $r_o$ is the radius of the drop when it assumes a spherical shape, $\rho$ is the density of the drop, and $\epsilon_o$ is the permittivity of vacuum. The drop surface charge $Q_s$ can be determined by the force balance equation for levitation between the gravitational and the electric forces. Finally, the effect of non-uniform surface charge distribution to the surface tension had to be corrected using the theoretical analysis by J. Feng et al.[9]. Such non-uniform charge
distribution is expected as a strong electrostatic field is applied to a charge carrying sample to balance the gravitational force. A detailed description of the technique of measuring surface tension using a HTESL will be published elsewhere[10].

The surface tension data of the G-silicon so obtained are shown in Fig. 7 along with the results recently reported data by Fujii et al.[11] and by Kimura et al.[12]. The linear fit to our data was given by

\[ \sigma(T) = 765 - 0.016 (T - T_m) \text{ mN/m} \]  

over 1580 < T < 1750 K. Our surface tension 765 mN/m at the melting temperature is approximately 40 mN/m (5.3%) larger than 725 mN/m reported by Fujii et al. and 24 mN/m (3.2%) larger than the data by Kimura et al. Fujii et al. used containerless method in a reduced gravity condition while Kimura et al. used the ring method in 1-g condition. Our result also agrees favorably with 783.5 mN/m obtained by Pryzborowski et al. in 1-g condition using an electromagnetic levitator[13]. However, 823 mN/m reported by Niu et al.[6] who used sessile drop technique is substantially higher than all the other results. Comparing our data with those obtained by Fujii et al. are particularly interesting since: (i) both silicon samples originated from the same G-silicon crystal, (ii) we used an electrostatic levitator while they used an electromagnetic levitator, and (iii) while our measurements were done in the gravitational environment, their experiment was conducted under a reduced gravity condition which was obtained as their levitator was freely falling in the 10-second drop-shaft (in Hokkaido, Japan). However, ~5% difference between these two sets of data cannot be explained at this time. As for the temperature dependence of surface tension, \( d\sigma/dT \), our result -0.016 mN/m/K agrees reasonably with those of Fujii et al. and Kimura et al.. However, it is much smaller than -0.48 and -0.65 mN/m/K that were respectively reported by Nui et al. and by Pryzborowski et. al..
The viscosity of the sample was extracted from the decay time constant of the signal. According to Lamb[14], the damping constant $\tau_2$ of a freely decaying $P_{2,0}(\cos\theta)$ mode signal is related to the viscosity $\eta$ of the liquid by

$$\frac{1}{\tau_2} = \frac{5\eta}{\rho r_0^2}.$$  \hspace{1cm} (10)

where $\rho$ and $r_0$ are as defined earlier. A detailed description of the technique of measuring viscosity using a HTESL will be published elsewhere[10].

The viscosity data obtained by substituting measured decay time constants $\tau_2$ into Eq. (10) are shown in Fig. 8. Also shown in the figure are the two reference data recently reported by Kimura et al.[12] and by Sato et al.[15]. The solid dots are the exponential fit to our data. Our data show scatter that is approximately $\pm 0.1$ mPa·s which corresponds $\pm 10\%$ uncertainty in our viscosity data. We believe that this scatter was caused by small perturbation injected by the position controlling electrostatic forces during the period of free oscillation mode. While the oscillation frequency is hardly sensitive to such perturbation forces, the damping constant is very sensitive to such forces particularly in low viscosity liquids. More work is needed to reduce such perturbation.

Both Kimura et al. and Sato et al. used the oscillating cub method. Each group reported several sets of viscosity data which were crucible dependent. Kimura et al. believed that such differences were caused by the difference in wetting properties between the crucibles and silicon melt. The data by Kimura et al. shown in Fig. 8 were obtained using a SiC coated graphite crucible and showed the highest viscosity, while Sato et al. obtained their highest values when a graphite crucible was used. While Kimura et al. observed rapidly increasing viscosity near the melting point, Sato et al. have not observed such anomaly. Aside such anomaly, near the melting point our result is about $0.1$ mPa·s smaller than Kimura's while it is about $0.1$ mPa·s larger than Sato's.
6. DISCUSSIONS

We used the HTESL at JPL and measured six thermophysical properties of molten silicon, which included the density, volume expansion, hemispherical total emissivity, constant pressure heat capacity, surface tension and viscosity, over a 400 K temperature range around its melting point. The temperature range includes the undercooled state of molten silicon as much as \(-300\)K.

The density data agreed closely with other two sets of data that were previously measured with the HTESL. All these data consistently showed quadratic nature over a 500K temperature span. We again confirmed the quadratic nature of the density as a function of temperature. We have not observed any anomalous behavior of density near the melting temperature as reported by Kimura et al[12] who used an improved Archimedian method. If such density anomaly was as a result of a process that was much slower than our cooling time, we were not expected to observe it. Nevertheless, their data away from the melting point agreed well with ours.

The present data for \(C_{pl}/\epsilon_T\) were basically identical to our previous result[2]. When a literature value for \(C_p(T_m)\) was used, the resulting \(\epsilon_T(T_m)\) was identical with our earlier result. Accurate measurement of \(C_{pl}/\epsilon_T\) for molten silicon is probably the main contribution of this work toward the determination of specific heat. In order to determine \(C_{pl}\) rigorously from the \(C_{pl}/\epsilon_T\) data as shown in Fig. 5, a non contact method of independently measuring \(\epsilon_T\) have to be developed. The investigators participating in the recent coordinated programs measured neither \(C_{pl}\) nor \(\epsilon_T\) to which our results could be compared.

In the surface tension and viscosity measurement process we observed that the viscosity was susceptible to the perturbation forces injected by the electrostatic levitation forces while the surface tension was not. Also, we observed that both surface tension and viscosity could depend on the rotational state of a drop[16]. Therefore, a special care was given in the process of measuring the surface tension and the viscosity presented in this paper to ensure that no significant rotation was present during the measurements.
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REFERENCES


FIGURE CAPTIONS

Fig. 1. Schematic side view of the electrode assembly, showing a sample levitated between the top and the bottom electrode. The bottom electrode is surrounded by four side electrodes for the purpose of the position control in the horizontal directions. An AC high voltage amplifier connected to the bottom electrode provides an oscillating electric field at the sample position to excite the sample oscillations.

Fig. 2. Schematic diagram of the high Temperature electrostatic levitator at JPL: a) He-Ne position sensing laser, b) Position sensing detector, c) Focusing lens, d) Focusing reflector, e) Side positioning electrode, f) Top/bottom electrode, g) Sample h) Back light diffuser, i) Fiber optical back light, j) He-Ne blocking filter, k) Long distance microscope, l) CCD camera, m) Pyrometer, n) Xenon heating lamp.

Fig. 3 The density and the volume expansion of the molten silicon as a function of temperature.

Fig. 4. A typical radiative cooling process of molten silicon showing more than 300 K of undercooling.

Fig. 5. $C_p/E_T$ and $C_p$ of the molten silicon as a function of temperature. $C_p/E_T$ was derived from Fig. 3 using the equation (1). $C_p$ was obtained from $C_p/E_T$ by multiplying $E_T = 0.18$.

Fig. 6. A typical signal from a freely oscillating silicon drop that followed the termination of the electric field pulse.

Fig. 7. Surface tension of the molten silicon is shown in comparison with the results obtained by Fujii et al. and by Kimura et al. as a function of temperature.

Fig. 8. Viscosity of molten silicon is shown along with other results obtained by Kimura et al. and by Sato et al.. The exponential fit to our data is shown with solid dots.
To HV amplifier

Top electrode

Sample

Side electrodes (4)

Bottom electrode

AC HV amplifier