Available online at www.sciencedirect.com

SCIENCE DIRECT®

Acta Materialia 54 (2006) 1221–1225

Acta MATERIALIA

www.actamat-journals.com

Surface tension of molten silicon measured by microgravity oscillating drop method and improved sessile drop method

Hidetoshi Fujii [a,*], Taihei Matsumoto [a], Shun Izutani [a], Shoji Kiguchi [b], Kiyoshi Nogi [a]

[a] *Joining and Welding Research Institute, Osaka University, 11-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan*
[b] *Department of Mechanical Engineering, Kinki University, 3-4-1 Kowakae, Higashi-Osaka 577-8502, Japan*

Received 31 August 2005; received in revised form 16 October 2005; accepted 25 October 2005
Available online 27 December 2005

Abstract

The surface tension of molten silicon was measured using both the oscillating drop method and an improved sessile drop method. The oscillating drop method was used under microgravity conditions. The purity of the silicon sample was 9N. The atmosphere was Ar–3% H_2 gas purified using platinum asbestos and magnesium perchlorate. The result measured using the oscillating drop method agrees very well with that measured using the sessile drop method, and is expressed by the following equation: $\gamma = 733 - 0.062(T - 1687)$, where γ is the surface tension (mN/m) and T is the temperature (K). The standard deviation of the scatter of the values obtained by the oscillating drop method is less than 1% which is smaller than that obtained by the sessile drop method. In addition, the surface tension can be measured over a wider temperature range including the undercooled state using the oscillating drop method. Accordingly, a much more accurate temperature dependence is obtained.

Keywords: Surface tension; Semiconductor; Interface wetting; Crystal growth

1. Introduction

The requirement for high-quality silicon single crystals has recently been increasing, because of the need for high-performance integrated circuits (LSIs) and central processing units (CPUs) in computers and other devices. Although a computer simulation is one of the most effective methods to optimize the production of silicon for use in LSIs and CPUs, various precise thermophysical data such as surface tension, density, viscosity, and thermal conductivity of molten silicon are necessary in this case. However, there are few available data for these properties, and where they are available different values are reported by different researchers partly because silicon is a very reactive element and its surface tension is sensitive to contamination such as by oxygen [1].

In this study, the surface tension of molten silicon was measured under the same conditions using both a new oscillating drop method and the sessile drop method, which is the most commonly used for the measurement of surface tension. The oscillating drop method was carried out under microgravity conditions.

The oscillating drop method has several advantages in terms of measuring the surface tension precisely. First, the purity of the sample is maintained because the sample materials are melted without any container or substrate. Second, the accuracy of the surface tension values obtained is increased: the surface tension can be calculated using the sample mass and the frequency of the surface oscillation, not the density. The mass of the sample is measured easily and precisely while the density, which generally contains large scatter, is not. Third, because the frequency of the surface tension is simplified under microgravity conditions, the surface tension can be computed without any correction formulas. Fourth, the surface tension can be measured over a wide temperature range including the undercooled

---

[*] Corresponding author. Tel./fax: +81 6 6879 8653.
E-mail address: fujii@jwri.osaka-u.ac.jp (H. Fujii).

1359-6454/$30.00 © 2005 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.
doi:10.1016/j.actamat.2005.10.058

state, because there is no nucleation site due to the absence of any container. This advantage enables the temperature dependence to be determined much more accurately.

The sessile drop method is one of the most commonly used methods to measure surface tension. This method is carried out under terrestrial conditions in order to confirm the accuracy of results obtained from the oscillating drop method. For this purpose, the same experimental conditions were used. In this study, some improvements have also been made in order to improve the accuracy. The system is equipped with a He–Ne laser, a band-pass filter, and a high-resolution digital camera. Coupling of the laser and the band-pass filter makes the droplet profile clearer and allows the surface tension to be precisely measured.

2. Experimental

2.1. Oscillating drop method

The oscillating drop method was conducted under microgravity to obtain a spherical drop shape. The experimental apparatus is equipped with a radio frequency generator, batteries, a pyrometer, high-speed video cameras, three coils, and an infrared radiation furnace, as shown in Fig. 1. The coil system is composed of a positioning coil, heating coil, and detecting coil. The positioning coil is connected to the 12 kW radio frequency generator operating at a frequency of 400 kHz. In the same way, a 2 kW radio frequency RF current is supplied for the heating coil with a frequency of 1 MHz. The positioning coil forms a quadrupole electromagnetic field that makes the sample oblate. The heating coil forms a dipole electromagnetic field that makes the sample prolate. Accordingly, the current ratio between the positioning coil and the heating coil controls the spherical droplet shape. The detecting coil determines the position of the sample.

The silicon samples were of 9N purity and weighed about 0.7 g. The samples were immersed in acetone and ultrasonically cleaned three times for 3 min. The atmosphere gas was Ar–3% H_2 purified using platinum asbestos and magnesium perchlorate. Its oxygen partial pressure was estimated to be less than 10^{-14} Pa [2]. The samples were preheated in the infrared furnace to overcome the high electric resistance at room temperature. After reaching the critical temperature, an eddy current can flow on the sample surface, and the sample is electromagnetically levitated and melted by the eddy current. The temperature of the droplet was measured using a two-color pyrometer.

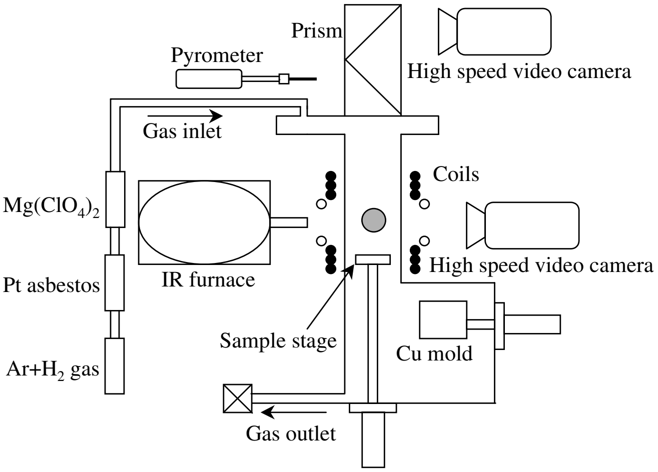


Fig. 1. Schematic of the oscillating drop method system.

A microgravity environment was achieved using the 710 m drop-shaft facility at JAMIC (Japan Microgravity Center) [3]. After the oscillation of the sample droplet decreased, the drop of the capsule was started. The gravity level then changed from 1*g* to $10^{-5}g$. The strength of the electromagnetic field was adjusted in order to control the position and the shape of the sample. The surface oscillation was recorded with two high-speed cameras from the top and the side. Two hundred frames were recorded per second. After the freefall was finished, the silicon sample was caught in a copper mold, and its mass was measured. When the change in the droplet mass was less than 0.01%, the data were used.

When the equilibrium shape is spherical, the surface tension can be calculated from the surface oscillation frequency obtained using the following equation [4]:

$$\omega_l^2 = \frac{4}{3}\pi l(l-1)(l+2)\frac{\gamma}{M} \tag{1}$$

where ω is the angular frequency of the surface oscillation, M is the droplet mass, and l is the label of the oscillation modes. In the case of $l = 2$, the frequency is called Rayleigh's frequency and is expressed by the following Rayleigh formula [4]:

$$\nu_{\mathrm{R}}^2 = \frac{8}{3\pi}\frac{\gamma}{M} \tag{2}$$

where $\omega_l = 2\pi\nu_{\mathrm{R}}$.

2.2. Improved sessile drop method

The experimental apparatus was equipped with a sample dropping device [5,6], a tantalum cylindrical heater, five concentric reflectors, a boron nitride substrate, a 10 mW He–Ne laser, a band-pass filter, a high-resolution digital camera, a B-type thermocouple (Pt–6%Rh/Pt–30%Rh), and a digital program controller, as shown in Fig. 2.

The sample was the same as that used for the oscillating drop method. The weight was 0.7 g. A BN substrate of 99% purity was used. Before the experiment, both the BN and the silicon sample were immersed in acetone and ultrasonically cleaned three times for 3 min. The substrate was then adjusted horizontally before each experiment. The silicon sample was placed in a glass tube with a spring connector on the top of the dropping device outside the chamber, as shown in Fig. 3.

The atmospheric gas was also the same as that used for the oscillating drop method. The sample was heated at a

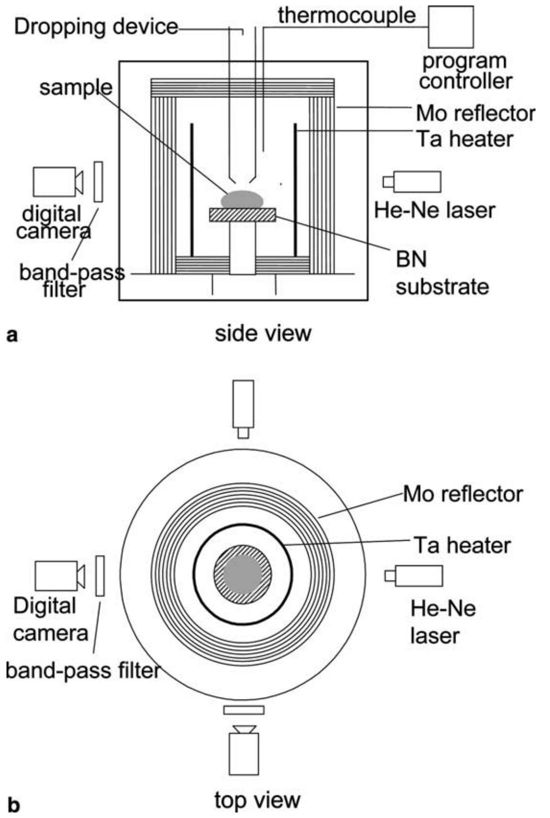
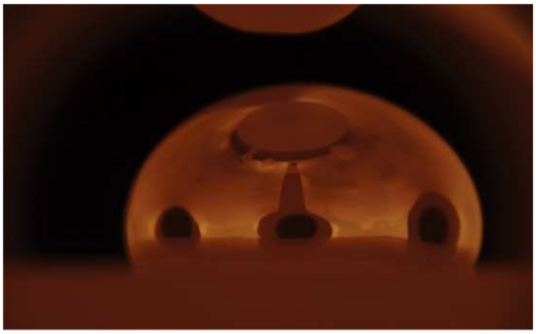


Fig. 2. Schematic of the improved sessile drop method system.

rate of 10 K/min. After reaching the measurement temperature, the sample was inserted into the bottom of the alumina dropping tube and held for 60 s for it to melt, as shown in Fig. 3. Molten silicon was then forced from a small $\phi1$ hole at the bottom of the alumina dropping tube and dropped onto the BN substrate by a small difference between the chamber and the alumina tube. As soon as the molten silicon came into contact with the BN substrate, photographs were taken of the drop profile. The coordinates of the droplet profile were determined from the



a Irradiation of Si and heater

b with laser and band pass filter

Fig. 4. Effect of laser and band-pass filter on droplet appearance: (a) without laser and band-pass filter, (b) with laser and band-pass filter.

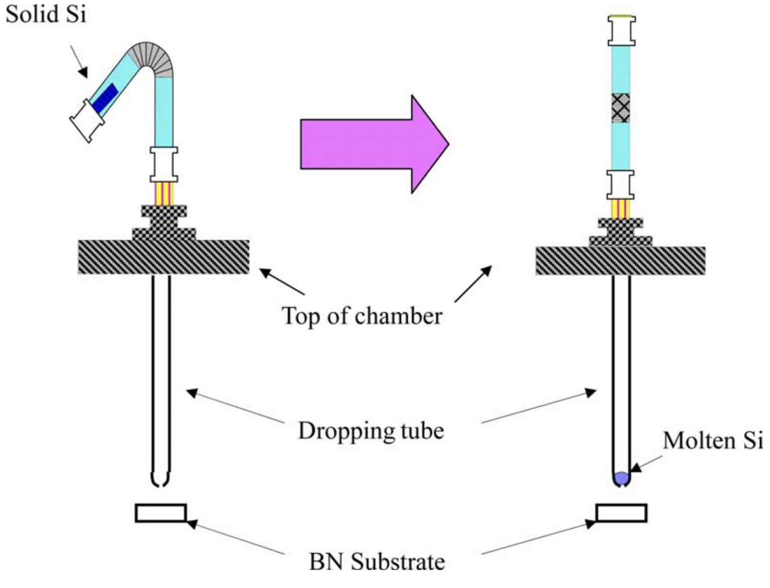


Fig. 3. Dropping device of the improved sessile drop method. The silicon sample was first placed in a glass tube outside the chamber. After reaching the measurement temperature, the sample was inserted into the bottom of the alumina dropping tube and molten silicon was then forced from a small $\phi1$ hole at the bottom of the alumina dropping tube.

images. The photographs obtained were analyzed using a computer with automatic image processing programs, in which the surface tension could be calculated; this eliminated any operator subjectivity.

The 10 mW He–Ne laser was used as a backlight to observe the droplet. The diameter of the laser beam was 2 mm, and was expanded to 20 mm. The band-pass filter was positioned between the digital camera and the chamber to remove the irradiation of the droplet itself and the heater. The filter could absorb all wavelengths other than the laser wavelength of 632 nm. As a result, a very clear droplet shape can be observed, as shown in Fig. 4. The droplet images were obtained using the digital camera. The camera has a high resolution of 2000 × 1312 pixels and 256 gray levels. In addition, a large charge-coupled device (CCD) size of 15.6 × 23.7 mm in the camera was used to decrease the error from the lens curvature. The temperature controlled by the digital program controller was measured by the thermocouple. The thermocouple was positioned close to the sample. The temperature was calibrated using the melting points of some pure metals.

3. Results and discussion

The results of the surface tension measurements using the oscillating drop method are shown in Fig. 5. The calculated surface tension of silicon is expressed as follows:

$$\gamma = 733 - 0.062(T - 1687) \tag{3}$$

where γ is the surface tension (mN/m) and T is temperature (K). The surface tension was measured over a wide temperature range (1357–1890 K). This range includes an undercooled state (up to 330 K below the melting point). The standard deviation of the data scatter were 7 K, which was less than 1% of the surface tension values: much smaller than the values measured by conventional methods [7–11].

The results obtained using the sessile drop method are also shown in Fig. 5. These values were measured only from 1700 to 1809 K. The temperature range was restricted due to droplet solidification, reaction with the substrate, and the heater durability. The standard deviation of the scatter was less than 3%. The results of the sessile drop method agree with those of the oscillating drop method.

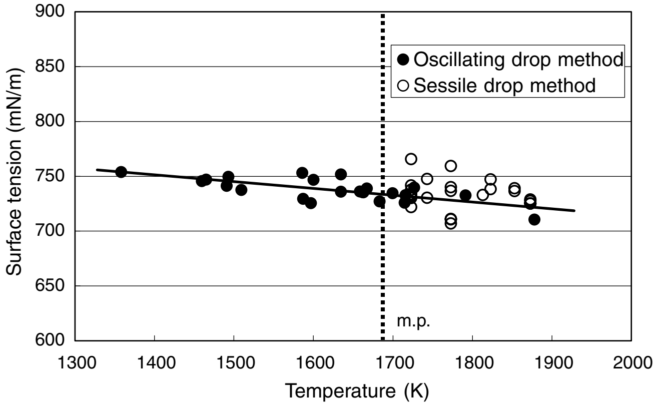


Fig. 5. Surface tension of molten silicon measured using the oscillating drop method and sessile drop method.

The oscillating drop method has several advantages. The surface tension can be calculated using only the surface oscillation frequency and the mass, not using the density. This leads to a smaller scatter, because the volume of the sample, namely the conversion to the real scale, is unnecessary. When a size is measured from the recorded-image data, as in the conventional methods, the determination of the interface is a significant problem that may cause a large error in the values of surface tension.

In addition, the sample is levitated and does not come into contact with any crucibles or substrates, and consequently the sample is free of contamination. Also, because there is no nucleation site, a wide undercooled range (330 K below the melting point) was available, which led the expanded measurement temperature range. Thus, the surface tension and particularly its temperature dependence measured using the oscillating drop method are more reliable. This accurate temperature dependence is very useful for precisely estimating the degree of the Marangoni convection. This is almost always true, particularly for high-melting materials or very reactive materials.

The sessile drop method used in this study is also improved in several respects. A band-pass filter was used to eliminate the irradiation wavelengths from the sample and the heater. Only the wavelength of the laser can pass through the filter. This produces a clearer sample contour which leads to a decrease in the reading errors. The high-resolution digital camera was used in order to analyze the droplet profile digitally. In addition, the large CCD size in the camera decreased the error from the lens curvature. In this study, the droplet was photographed in two directions to confirm the symmetry of the droplet. When the surface tension values obtained from the two directions were different by over 30 mN/m, the data were rejected.

The temperature range was restricted between 1700 and 1809 K for the sessile drop method due to droplet solidification, reaction with the substrate, and the heater durability. Accordingly, if there are no data from the oscillating drop method, it seems that another temperature dependence is easily misled from Fig. 5. The main contamination source is generally the substrate. The BN substrate is suitable for silicon, because the contact angle is large and the reaction is small [12]. Especially, boron barely affects the surface tension [13].

Fig. 6 shows a comparison between the measured and previously reported values of silicon surface tension. The present values agree well with many previous results. However, these values cannot simply be compared with each other because the surface tension of molten silicon is very sensitive to contaminants such as oxygen. The details of the experimental conditions cannot always be obtained from the literature.

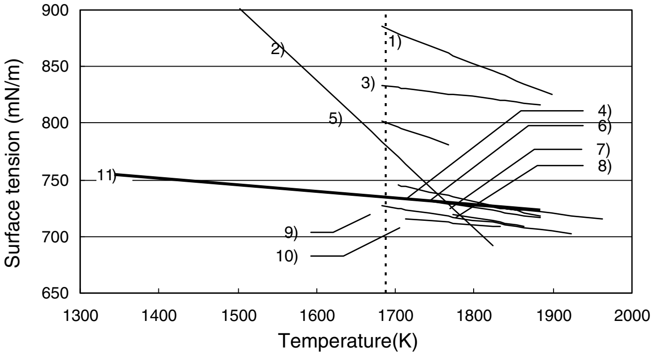


Fig. 6. Comparison between measured values and previously reported values of silicon surface tension: (1) Ref. [7], (2) Ref. [14], (3) Ref. [15], (4) Ref. [10], (5) Ref. [16], (6) Ref. [17], (7) Ref. [18], (8) Ref. [19], (9) Ref. [20], (10) Ref. [21], (11) this work.

4. Conclusion

The surface tension was measured by the oscillating drop method and the improved sessile drop method. The former method was used under conditions of microgravity. The results obtained from the oscillating drop method agree with those obtained from the sessile drop method. The temperature dependence of the surface tension can be expressed as follows:

$$\gamma = 733 - 0.062(T - 1687)$$

where γ is the surface tension (mN/m) and T is the temperature (K). The temperature ranges for the two methods were 1357–1890 and 1700–1809 K, respectively. The standard deviation of the scatter is less than 1% for the oscillating drop method and 3% for the sessile drop method. Thus, the surface tension and particularly its temperature dependence measured using the oscillating drop method are more reliable than those measured using the sessile drop method. The accurate temperature dependence is very useful for precisely estimating the degree of the Marangoni convection. This is almost always true, particularly for high-melting materials or very reactive materials.

Acknowledgements

The authors greatly appreciate the support from the Japan Space Forum (JSF), the New Energy and Industrial Technology Development Organization (NEDO), and the Japan Space Utilization Center (JSUP).

References

[1] Niu Z, Mukai K, Shiraishi Y, Hibiya T, Kakimoto T, Koyama M. J Jpn Cryst Growth 1996;23:374.
[2] Fujii H, Matsumoto T, Nogi K. Acta Mater 2000;48:2933.
[3] JAMIC users' guide, 6, 1996.
[4] Rayleigh Lord. Proc R Soc Lond 1879;29:71.
[5] Nogi K, Ogino K. Can Inst Mine Metall 1983;22:19.
[6] Fujii H, Nakae H, Okada K. Acta Metall 1993;41:2963.
[7] Hardy SC. J Cryst Growth 1984;69:456.
[8] Lukin S, Zhuchkov VI, Vatoli NA. J Less Common Metals 1979;69:399.
[9] Langen M, Hibiya T, Eguchi M, Egry IJ. Cryst Growth 1998;186:550.
[10] Huang X, Togawa S, Chung SI, Terashima K, Kimura SJ. Cryst Growth 1995;156:52.
[11] Egry I, Lohoefer G, Jacobs G. Phys Rev Lett 1995;75:4043.
[12] Mukai K, Yuan Z. Mater Trans JIM 2000;41:338.
[13] Mukai K, Yuan Z. Mater Trans JIM 2000;41:331.
[14] Przyborowski M, Hibiya T, Eguchi M, Egry I. J Cryst Growth 1995;151:60.
[15] Rhim W, Ohsakka K. J Cryst Growth 2000;208:313.
[16] Kawasaki N, Watanabe K, Nagasaka Y. High Temp High Press 1998;91:30.
[17] Naidich YuV, Perevertailio VM, Obshchak LP. Russ J Phys Chem 1975;49:917.
[18] Levin ES, Gel' PV, Baum BA. Russ J Phys Chem 1966;40:455.
[19] Keck PH, Horn WV. Phys Rev 1953;512:91.
[20] Lukin SV, Zhuchkov VI, Vatolin NA. J Less Common Metals 1979;67:399.
[21] Popel' SI, Shergen L, Tsarevskii BV. Russ J Phys Chem 1970;44.