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Interfacial phenomena of molten silicon: Marangoni flow and surface tension

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Temperature oscillation due to the oscillatory Marangoni flow was measured for a molten half-zone silicon column (10 mm high and 10 mm in diameter with a temperature difference of 150 K between the upper and lower solid–liquid interfaces) under microgravity by using fine thermocouples. The flow is in a hypercritical condition; that is, the Marangoni number is estimated to be over 10 000. The structure of the Marangoni instability is two-fold symmetry for the small aspect ratio (height/radius) Γ of 1 and one-fold symmetry for the melt with Γ of 2. The surface tension of molten silicon was measured by a sessile drop method in carefully controlled ambient atmospheres with various oxygen partial pressures from 4×10^{-22} to 6×10^{-19} MPa. These measurements showed that the surface tension and its temperature coefficient showed a marked dependence on oxygen partial pressure. Accordingly the effect of oxygen partial pressure on the Marangoni flow should be made clear. Moreover, Marangoni flow at the flat surface, which corresponds to the flow for the Czochralski growth system, should also be studied.

Keywords: molten silicon; microgravity; liquid column; instability; surface tension; oxygen partial pressure

1. Introduction

The crystal growth process of semiconductor silicon is controlled by a heat and mass transfer process. Within the bulk melt on Earth, buoyancy flow plays an important role, whereas at the melt surface, Marangoni flow is thought to exist and be involved in a heat and mass transfer process. For buoyancy driven flow, the flow mode has been experimentally characterized using an X-ray flow visualization technique and numerical modelling (Kakimoto *et al.* 1988). However, existence of the Marangoni

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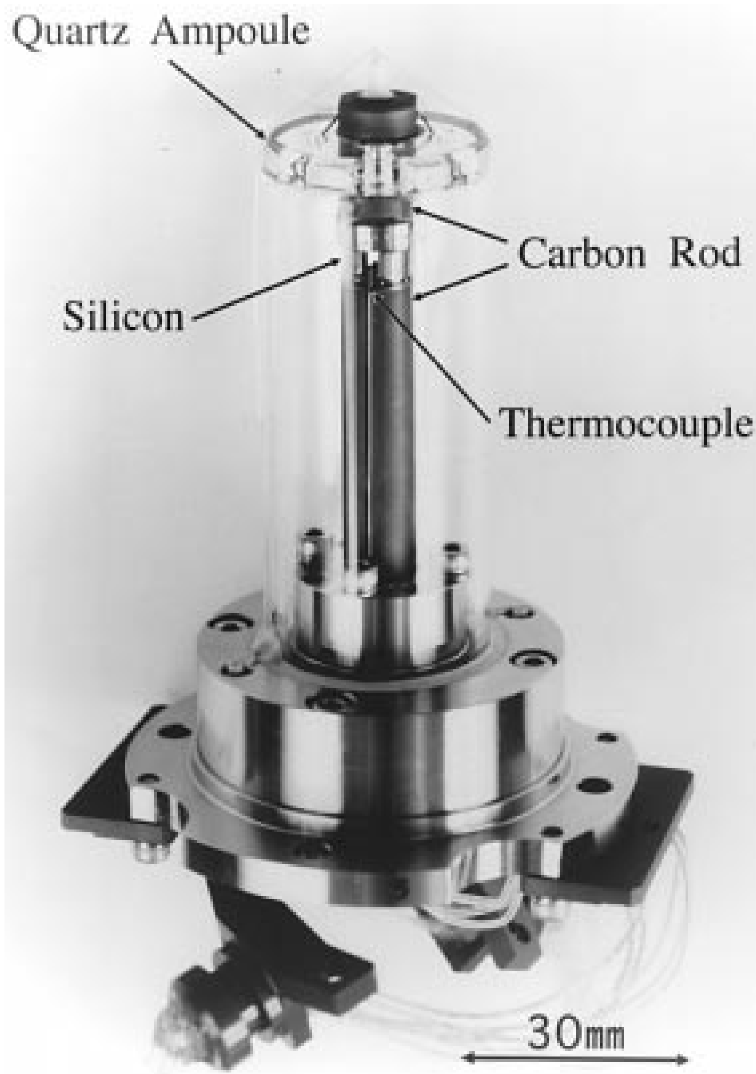


Figure 1. Ampoule containing a silicon specimen.

flow was confirmed for the first time through silicon crystal growth experiment in microgravity (Eyer *et al.* 1985). Although there have been several works reported for the Marangoni flow of other fluids with middle or high Prandtl number, e.g. silicone oil or molten salt (Schwabe *et al.* 1978; Wanschura *et al.* 1995), only limited numbers of works have been reported on fluids with low Prandlt number, Pr, fluids including molten silicon (Cröll *et al.* 1989; Levenstam & Amberg 1995; Han *et al.* 1996).

There are two types of Marangoni flow; one occurs in a liquid column and corresponds to floating zone crystal growth, and the other occurs at a flat surface and corresponds to Czochralski crystal growth using a crucible. Research on the Marangoni flow of molten silicon has been carried out only for the liquid column configuration.

Temperature coefficient of molten silicon is a driving force for the Marangoni flow. However, surface tension and its temperature coefficient for molten silicon were suggested to be sensitive to the amount of adsorbed oxygen on the melt surface

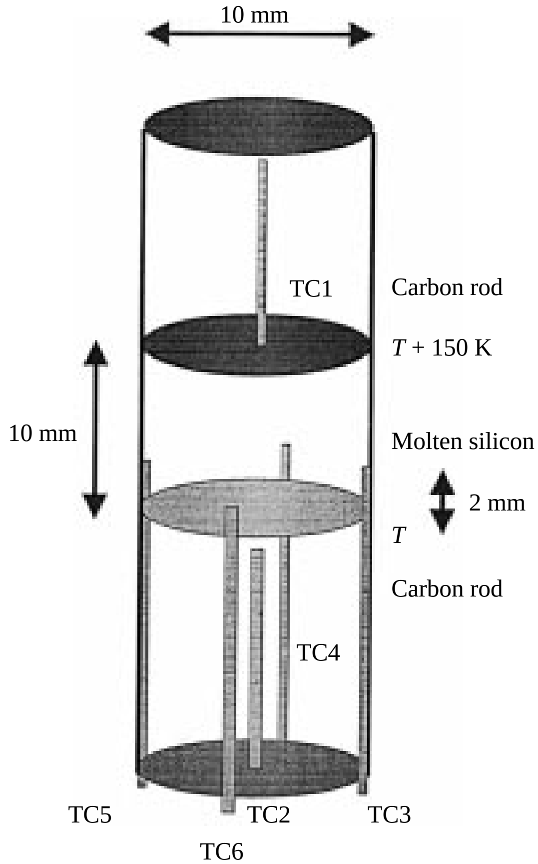


Figure 2. A sketch of the silicon specimen.

(Keene 1987). The oxygen concentration in silicon crystals is higher in the melt contained by a silica crucible, i.e. in the Czochralski case, and lower in the melt for the floating zone configuration. However, precise measurements of surface tension and its temperature dependence for molten silicon in ambient atmosphere with defined oxygen partial pressure has not yet been reported.

In the present work, we have tried to examine experimentally the Marangoni flow of molten silicon in microgravity and also on Earth. There are several approaches to Marangoni flow research, i.e. measurement of a temperature field, observation of a flow field, surface oscillation observation, crystal growth, computational simulation and so on. Among these we have employed temperature oscillation measurements and computational simulations in the present work. The effect of the oxygen partial pressure of ambient atmosphere on the temperature coefficient of the surface tension of molten silicon and on the Marangoni flow is also discussed.

2. Experiment

Figures 1 and 2 show the configuration of the present experiment. A silicon specimen 10 mm high and 10 mm in diameter was sustained between the upper and lower carbon rods within a silica glass ampoule. A molten silicon column was formed under microgravity conditions on board the NASDA (National Space Development Agency

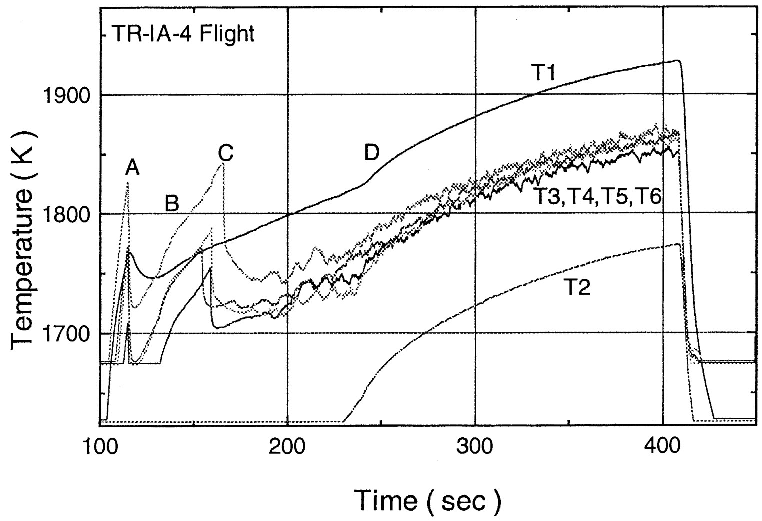


Figure 3. Temperature fluctuation in microgravity. Lamp power was changed from 1300 to 900 W at point A, where temperature detected by one thermocouples out of six reached 1823 K. Melting started at point B. Around point C temperature ($T3-T6$) decreased because the thermocouples touched the silicon melt. At point D a liquid column was formed completely.

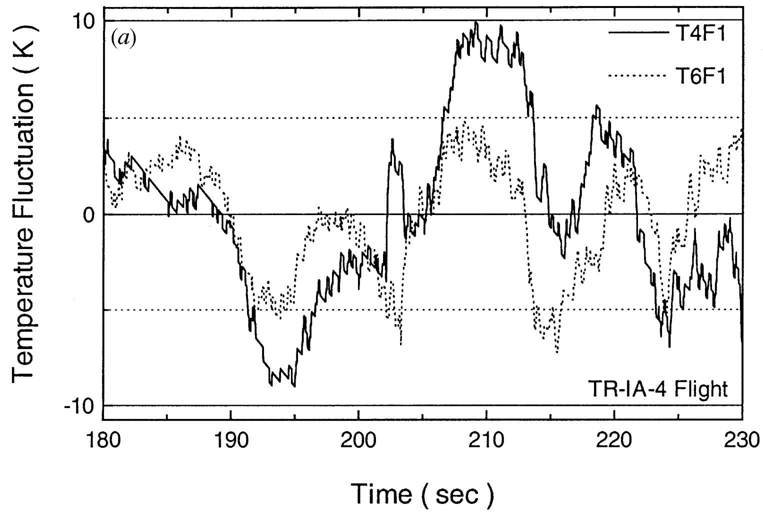
of Japan) sounding rocket TR-I-A #4 using a mirror furnace (Hibiya *et al.* 1996), where only Marangoni flow can be observed by eliminating the effect of buoyancy. A temperature difference of 150 K was maintained between the upper and lower rods. As shown in figure 2, four fine thermocouples separated by 90° along the azimuthal direction were attached to the melt surface in order to detect temperature oscillation due to the Marangoni instability (the sampling frequency was 40 Hz). Two thermocouples were set within carbon rods close to the solid–liquid interface to monitor the temperature difference between the upper and lower interfaces. Argon gas of 6N-purity was flowed through an ampoule at a rate of $2\ell\ \text{min}^{-1}$ to prohibit condensation of silicon oxide on the ampoule inner wall. The detailed experimental procedure is reported elsewhere (Nakamura *et al.* 1998).

3. Results and discussion

(*a*) *Structure of the Maranogni instability*

Figure 3 shows temperature data obtained in microgravity and temperature oscillations due to instability of the Marangoni flow of the silicon melt column. As clearly seen in figures 4*a*, *b*, temperature oscillation during column formation (C-D in figure 3) shows a marked difference from that after column formation (after D). Spectral analysis showed that observed frequencies were 0.1 Hz for column formation and 0.15 Hz after column formation, while power spectrum density after column formation was too low for finding a particular frequency, as shown in figure 5. This means that flow is in a hypercritical condition, i.e. far away from a transition from a stationary to an oscillatory flow.

Comparing figures 4*a*, *b*, the phase relationship among temperature signals detected by the four thermocouples (see figure 2) is different during and after column formation. During the column formation period, temperature measured by the thermocouples opposite each other (T4F1 detected by TC4 and T6F1 detected by TC6)



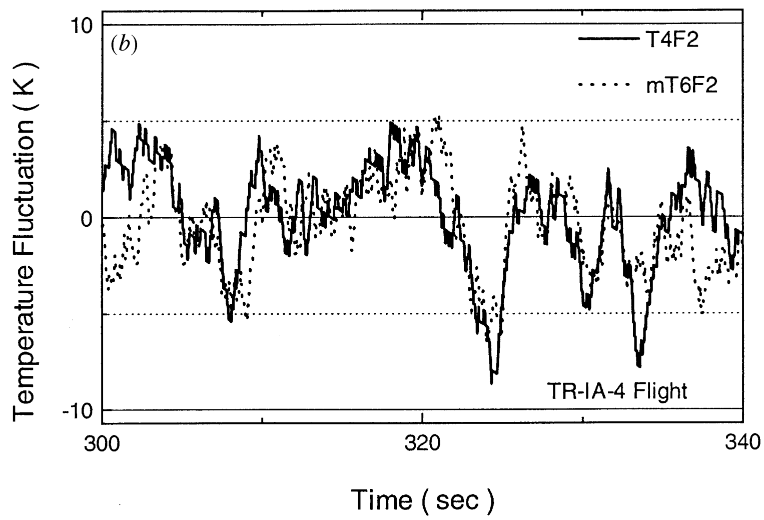


Figure 4. (*a*) Temperature fluctuation data during the column formation. T4F1 and T6F1 were obtained from the temperature data (see figure 3) by subtracting the average temperature increase. T4F1 and T6F1 correspond to the thermocouples TC4 and TC6, respectively. (*b*) Temperature fluctuation data after the column formation. The data were obtained by the same method as in (*a*). mT6F2 represents the inverse sign of T6F2.

fluctuates in the same phase as shown in figure 4*a*, while temperature fluctuation is the antiphase relation between thermocouples separated by 90°. After the column formation, temperature fluctuation data measured by the thermocouples set opposite each other show an antiphase relationship, as shown in figure 4*b*. Note that in figure 4*b* temperature fluctuation data mT6F2 represents the inverse of T6F2.

The above mentioned phase relationship of the temperature fluctuation can suggest the existence and motion of a non-axisymmetric temperature field within a liquid column. A cold temperature region is formed in the liquid column, because the liquid column is heated by radiation from the lamp. When the antiphase relationship is detected by the thermocouples set opposite each other, the existence of a one-fold symmetrical temperature field is plausible. The cold temperature region is

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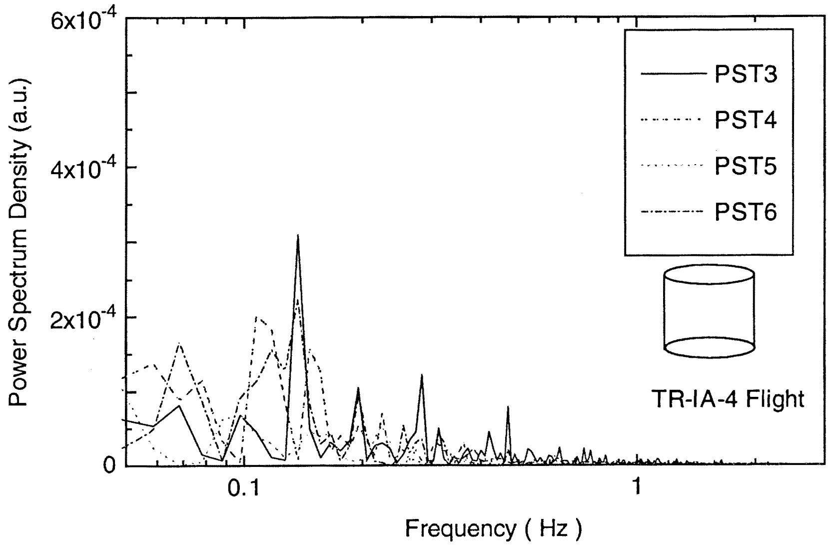

Figure 5. Power spectrum density obtained after column formation. PST3 was calculated using the temperature fluctuation data detected by thermocouple TC3.

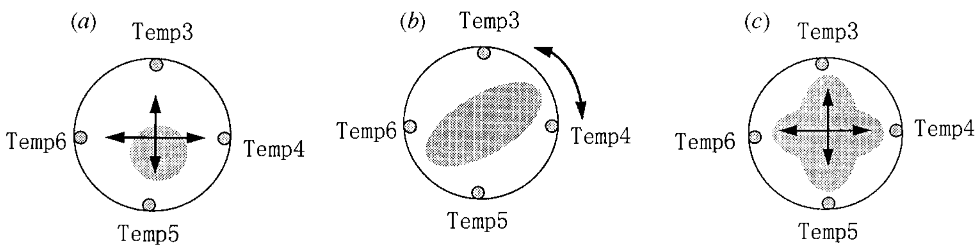

Figure 6. Proposed model of non-axisymmetric distribution of temperature in a molten silicon column: (*a*) one-fold symmetrical distribution: (*b*) and (*c*) two-fold symmetrical distribution. Temperature in a shadowed region is lower than in a surrounding region.

expected to move randomly, as shown in figure 6*a*. The antiphase relationship of the temperature fluctuation between the neighbouring thermocouples (separated by 90°) suggests the existence of a two-fold symmetrical temperature field. The structures of these temperature fields are shown in figures 6*b*, *c*: rotation and/or pulsation.

Wanshura *et al.* suggest that the structure of these instabilities depends on the aspect ratio of the liquid column Γ. The wave number of the Maranogni instability for liquid column m is written as $m = 2/\Gamma$ (Wanschura *et al.* 1995). This idea can explain the present experimental results: that is, $m = 2$ for the column formation period (short column) and $m = 1$ after column formation (long column). The measured frequency corresponds to that of azimuthal oscillation of the instability structure.

Numerical simulation for occurrence of the instability in the molten silicon in the present configuration is not finished, while the simulation for the liquid with a Prandtl number Pr of 1.0 in a similar configuration to the present one suggests that instabilities with $m = 1, 2$ can take place depending on the column aspect ratio. Figure 7 shows velocity and temperature fields of a liquid column with a Prandtl number of 1.02, aspect ratio of 1.33 and Marangoni number Ma of 3330 (Imaishi & Yasuhiro 1997). A cross section is shown at a melt height $Z = 0.855\Gamma$. As shown in figure 7, instability with a wave number $m = 2$ takes place for a short column. The

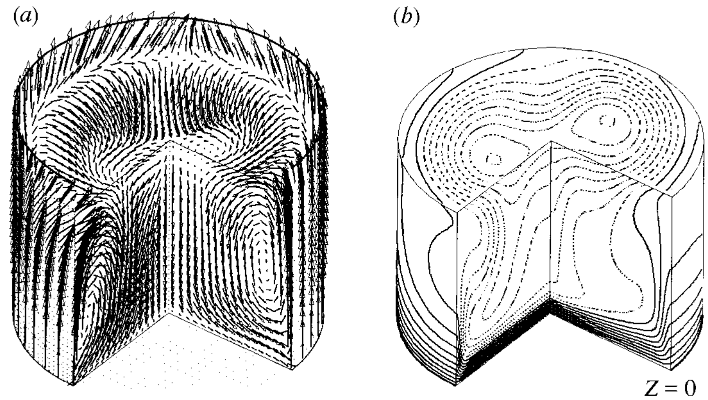

Figure 7. Velocity (*a*) and temperature (*b*) fields of a liquid column with Prandtl number Pr = 1.02, aspect ratio $\Gamma = 1.33$ and Marangoni number $Ma = 3330$, which shows instability with wave number of $m = 2$. Cross section is shown at height $Z = 0.855$.

simulation results support the present experimental result of temperature fluctuation measurements.

(*b*) *Oxygen partial pressure dependence of surface tension and its temperature coefficient*

As mentioned in § 3 *a* the Marangoni flow of the molten silicon column shows instability and the power spectrum density of the oscillation is very weak. This means that the flow is in a hypercritical condition. This is supported by a calculated Marangoni number, which is much higher than the critical Marangoni number of about 100 (Cröll *et al.* 1989), as follows:

$$Ma = (|\partial\gamma/\partial T|\Delta T L)/(\mu\kappa). \tag{3.1}$$

Here, $\partial\gamma/\partial T$ is the temperature coefficient of surface tension for molten silicon, ΔT is the temperature difference between the upper and lower interfaces of the column, L is the column height, μ and κ are the viscosity ($\mu = 7 \times 10^{-4}\,\mathrm{kg\,m^{-1}\,s^{-1}}$) and thermal diffusivity ($\kappa = 2.12 \times 10^{-5}\,\mathrm{m^2\,s^{-1}}$) of the molten silicon, respectively. The Marangoni number ranges from 5000 to 20 000 depending on $\partial\gamma/\partial T$. According to Keene, surface tension and its temperature coefficient of molten silicon depend on the magnitude of surface contamination by adsorbed oxygen (figure 8) (Keene 1987). We measured surface tension and its temperature coefficient using a sessile drop method in ambient atmospheres with various oxygen partial pressures (Niu *et al.* 1998). A substrate made of BN was used for the following reasons: this is less reactive with molten silicon and a large contact angle can be obtained so that good measurement accuracy for surface tension is assured. An electromagnetic levitation technique was also employed for surface tension measurement (Przyborowski *et al.* 1995).

Figure 9 shows surface tension of molten silicon as a function of temperature for various oxygen partial pressures of the ambient atmosphere from 4.8×10^{-22} to 1×10^{-19} MPa. It is noteworthy that surface tension and its temperature coefficient show marked dependence on oxygen partial pressure. From this figure it is understood that surface tension and its temperature coefficient measured by a levitation technique in a 6N-argon gas atmosphere ($\gamma = 783.5 \times 10^{-3}\,\mathrm{N\,m^{-1}}$ and $\partial\gamma/\partial T = -0.65 \times 10^{-3}\,\mathrm{N\,m^{-1}\,K^{-1}}$) correspond to those measured in an oxygen partial pressure of *ca.* 10^{-21} MPa. If we plot surface tension as a function of logarithmic ambient oxygen

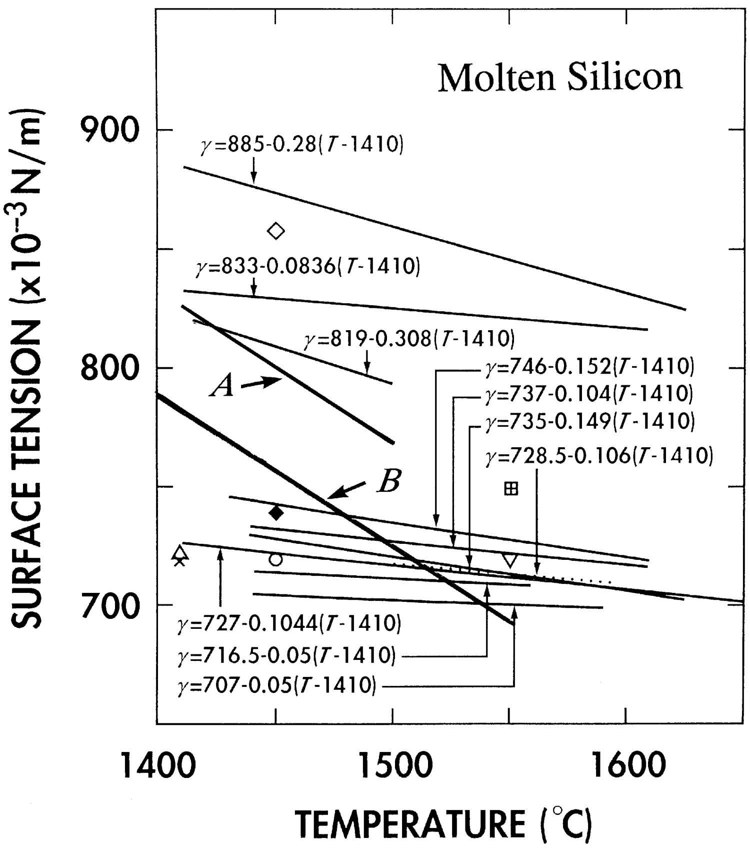

Figure 8. Reported surface tension of molten silicon reviewed by Keene (1987). Newly obtained data by the authors are also included: (A) by the sessile drop method at $P_{O_2} = 4.8 \times 10^{-22}$ MPa (Niu *et al.* 1998) and (B) by the levitation method in 6N argon atmosphere (Przyborowski *et al.* 1995).

partial pressure (see figure 10), the gradient corresponds to the excess amount of oxygen atoms adsorbed on the molten silicon surface (Γ_O) according to the Gibbs adsorption isotherm

$$\Gamma_O = -2(1/RT)(\partial\gamma/\partial \ln P_{O_2}). \tag{3.2}$$

Here, R and T are the gas constant and temperature, respectively. The excess amount of oxygen on the silicon melt surface at full coverage, Γ_O, was evaluated to be 2.1×10^{-6} mole m^{-2} at 1693 K and at P_{O_2} of 1×10^{-21}–5×10^{-20} MPa. This means that one out of every ten atoms is oxygen and suggests that the oxygen concentration is extremely high at the surface, while the bulk concentration of oxygen was calculated to be *ca.* 0.001 mass% (8.5×10^{17} atoms cm^{-3} $\approx$ 18 ppm), based on the equilibrium constant for the following chemical reaction between an oxygen molecule in a gas phase and an oxygen atom in molten silicon (Hirata & Hoshikawa 1990):

$$\tfrac{1}{2}O_2(g) = \underline{O}(l). \tag{3.3}$$

The temperature coefficient of molten silicon is plotted as a function of oxygen partial pressure of the ambient atmosphere (figure 11). A larger absolute value of temperature coefficient was obtained than that previously reported (compare with the data in figure 8).

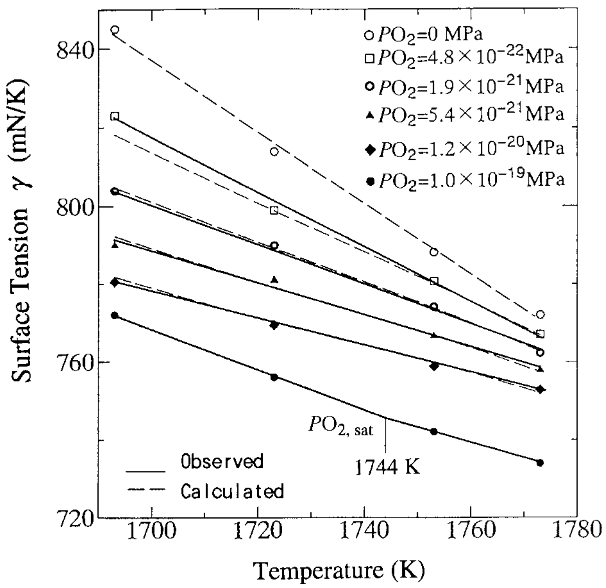

Figure 9. Surface tension of molten silicon as a function of temperature for various oxygen partial pressures of ambient atmosphere from 4.8×10^{-22} to 1×10^{-19} MPa.

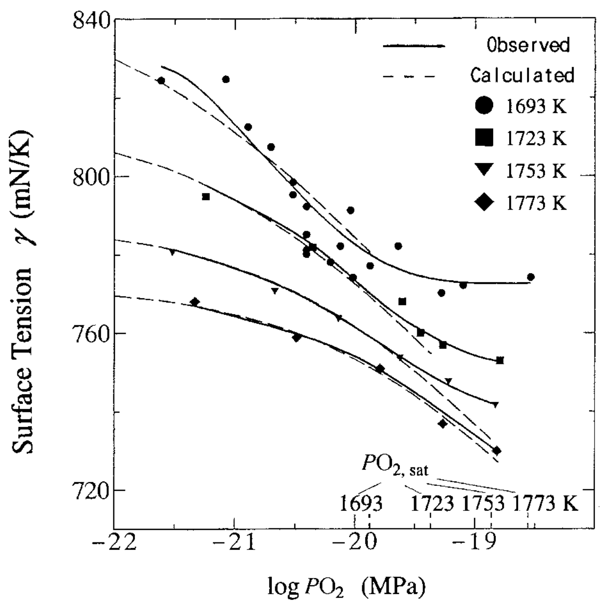

Figure 10. Surface tension of molten silicon as a function of logarithmic oxygen partial pressure of ambient atmosphere P_{O_2}.

As mentioned above the role of oxygen on surface tension and its temperature coefficient have been thoroughly clarified. However, unanswered questions still remain. Although the melt oxygen concentration for specimens which were employed for surface tension measurement by the sessile drop method and showed temperature coefficients of $-0.4 \sim -0.8 \times 10^{-3}\,\mathrm{N\,m^{-1}\,K^{-1}}$ was estimated to be in the order of 0.001 mass% (5×10^{17} atoms $\mathrm{cm^{-3}} \approx 10$ ppm) based on thermodynamical calcula-

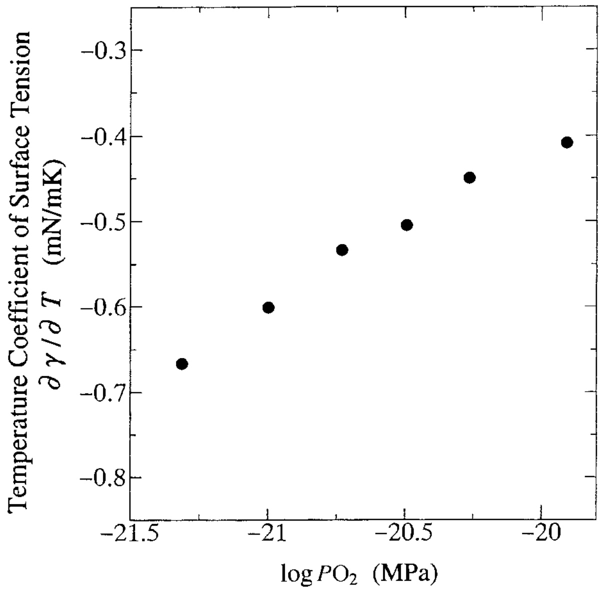

Figure 11. Temperature coefficient of surface tension of molten silicon as a function of oxygen partial pressure of ambient atmosphere P_{O_2}.

tion, SIMS (secondary ion mass spectroscopy) analysis showed oxygen concentration of less than 2×10^{16} atoms cm^{-3}, i.e. the detection limit of the SIMS analysis for oxygen. The measured oxygen concentration was lower than that thermodynamically calculated. This is also the case for the specimens used for surface tension measurements by the levitation method. On the contrary, a silicon specimen employed for temperature oscillation experiment in microgravity showed oxygen concentration of 7×10^{17} atoms cm^{-3} (SIMS analysis). The origin of oxygen incorporation in the present experiment is the dissolution of the silica sheath of the thermocouples. An absolute value of temperature coefficient one order of magnitude smaller than that measured in the present work has been reported ($-0.05\ mN\ m^{-1}\ K^{-1}$) (Popel' *et al.* 1970) and was attributed to oxygen contamination (Keene 1987). Therefore, we cannot yet appropriately estimate the temperature coefficient of surface tension for the specimen in the microgravity experiment.

(*c*) *Future works*

Through the present work, it was made clear, as shown in figure 11, that the temperature coefficient of surface tension for molten silicon is sensitive to the oxygen partial pressure of the ambient atmosphere. This suggests that the Marangoni flow should also be sensitive to the oxygen partial pressure of ambient atmosphere, i.e. melt oxygen concentration and adsorbed oxygen on the melt surface. Therefore, we deduce that the mode of the Marangoni flow of molten silicon is quite different between that for Czochralski-growth and that for floating-zone-growth systems. For the Czochralski case, oxygen concentration is assumed to be high around the silica crucible wall which supplies oxygen, while it is very low for the floating-zone case.

The Marangoni flow in the liquid column corresponds to the floating-zone system, whereas the Marangoni flow on the flat surface corresponds to that in the Czochralski case. Although the Marangoni flow for the liquid column has been made clear to some

Figure 12. Network pattern observed at the surface of molten silicon (Yamagishi & Fusegawa 1990).

extent, nothing has been explained for that in the Czochralski case. Therefore, a study on the Marangoni flow for the flat surface melt should be promoted. As shown in figure 12, the network structure or the spoke pattern observed on the melt surface could be related to the Marangoni–Bénard instability (Yamagishi & Fusegawa 1990; Yi *et al.* 1994).

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