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Experimental study on time evolution of Marangoni flow instability in molten silicon bridge

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Temperature oscillations due to Marangoni flow instability in molten silicon half zone bridges with various aspect ratios of $As = 0.5$–2.0 were measured using six thermocouples set azimuthally 60° apart in the liquid bridge close to the cold rod. The Marangoni number was estimated to range from 3000 to 14000, based on the measured axial temperature difference. Fourier spectra of the temperature oscillations were broad and continuous; each peak was not clearly distinguished but rather appeared as a frequency band. Thus, the convection was estimated to be turbulent-like. The time evolution of the azimuthal wave number was observed by analyzing the time-dependence of the phase relationship of the temperature oscillation detected by the six thermocouples. Analyzing the mode appearance coefficient MAC as a function of the aspect ratio, the relationship between the azimuthal mode number m and the aspect ratio As was observed to be $m \cdot As \approx 2.4$; the basic structure of flow instability is sustained even under high Marangoni number. The temperature oscillation data was decomposed into that for each frequency band by using wavelet analysis. The frequencies for the $m = 1$ and $m = 3$ modes were estimated to be 0.08 to 0.2 Hz and 0.01 to 0.2 Hz, respectively.

1. Introduction

In the growth of silicon single crystals, the formation of dopant striation, i.e., the microscopic inhomogeneity of the impurity distribution in the crystals, is problematic, because it deteriorates, for example, semiconductor chip production yield. The dopant striation results from microsegregation of the impurities due to oscillatory flows in the silicon melt. One of the flows is a Marangoni flow driven by the difference in surface tension at the melt surface. Thus, investigation on the Marangoni flow instability is required. A half-zone liquid bridge, which simulates a floating-zone configuration, is generally used to investigate Marangoni flow instability. The aspect ratio, As, which represents the geometry of the liquid bridge, is defined as the ratio of height h to radius r of the liquid bridge: $As = h/r$. The Marangoni number, which represents the magnitude of the flow is defined as $Ma = -\sigma_T \Delta T h/\mu\alpha$ where σ_T, ΔT, h, μ and α are the temperature coefficient of the surface tension, the axial temperature difference of the liquid bridge, the height of the liquid bridge, the viscosity of the melt, and the thermal diffusivity of the melt, respectively. The Marangoni flow in a half-zone liquid bridge with a low Prandtl number (Pr) fluid changes from an axisymmetric steady flow to a three-dimensional (3D) steady flow, and then to a 3D periodic oscillatory flow, and finally to a 3D non-periodic oscillatory flow, as the Marangoni number increases. A 3D periodic oscillatory flow has been observed only experimentally [1]. As predicted through numerical modeling, for the liquid bridge with both high Pr fluid and low Pr fluids, a 3D flow field shows As-dependent m-fold symmetry $m \cdot As = 2.0$–2.2, m is the azimuthal wave number, i.e., the mode of the Marangoni instability) when the Marangoni number just exceeds the critical one [2–5]. Imaishi *et al.* studied numerically the critical Marangoni numbers, the azimuthal wave numbers, and the frequency for low-Pr-fluid liquid bridges with various aspect ratios ($As = 0.6$–2.2) just above the critical Marangoni number; they reported the existence of a three-fold symmetric flow field for $Pr = 0$ and time evolution of azimuthal wave number [4, 5]. However, their findings have not been confirmed experimentally because attaining a low Marangoni number has been difficult. Nakamura *et al.* experimentally observed azimuthal wave numbers of $m = 1$ and $m = 2$ in a molten silicon bridge with a Marangoni number of about 10^4 by investigating the phase relationship of the temperature oscillations measured using four thermocouples under microgravity [6]. However, as far as the azimuthal wave number detected by four thermocouples is concerned, the detectable wave number is limited to $m = 1$ and $m = 2$. Additionally, for a liquid bridge with a high Marangoni number, flow fields of various azimuthal wave numbers may appear simultaneously and/or intermittently, because multiple peaks appeared in both the Fourier spectrum of the experimental result [6] and the results of numerical simulation

[4, 5] of a non-periodic oscillatory flow. However, conventional experimental approaches have not taken into account the time-dependent behavior of the azimuthal wave number.

To see whether the flow field maintains the basic structure of m-fold symmetry even in a high Marangoni number region, in the present study we have investigated the time-dependent behavior of the azimuthal wave number by analyzing the phase relationship of temperature oscillations obtained using six thermocouples, and we have analyzed the appearance ratio of the azimuthal wave number as a function of the aspect ratio. We employed wavelet analysis using the spline-4 function, so as to extract the frequency band corresponding to azimuthal wave numbers of $m = 1$ and $m = 3$.

2. Experimental setup

2.1. Preparation of liquid bridge

As shown in Fig. 1, the sample cartridge consisted of a silicon sample supported by upper and lower carbon rods in a quartz ampoule. The sample was heated in a mono-ellipsoidal mirror furnace to form a molten silicon bridge with a radius of 5 mm. Bridge height h was 2.5, 3.0, 3.5, 4.0, 5.0, 7.0 and 10.0 mm, with a corresponding aspect ratio of 0.5, 0.6, 0.7, 0.8, 1.0, 1.4 and 2.0. By locating the focus point of a halogen lamp on the upper carbon rod, we obtained a unidirectional temperature gradient; the temperature on the upper side of the silicon bridge was higher than that on the lower side, so that buoyancy flow was suppressed to a great extent, although the flow experiment was conducted under normal gravity conditions. The nonuniformity of the temperature distribution in the azimuthal direction was vanishingly small. Six thermocouples were set azimuthally 60° apart along the periphery of the liquid bridge 1 mm aside the lower rod, so as to detect the azimuthal wave number $m = 1$, 2 and 3. The thermocouples consisted of a ϕ0.1-mm Pt-Pt13%Rh R-type wires and a quartz-glass sheath with inner and outer diameters of 0.7 and 1.0 mm, respectively. The head of the quartz-glass sheath was coated with carbon so as to obtain good wettability with molten silicon. The sampling rate was 10 Hz. The same measurement system was used to measure the axial temperature difference so that the Marangoni number could be estimated. Argon gas of 6N purity was flowed at a rate of 2 l/min around the liquid bridge.

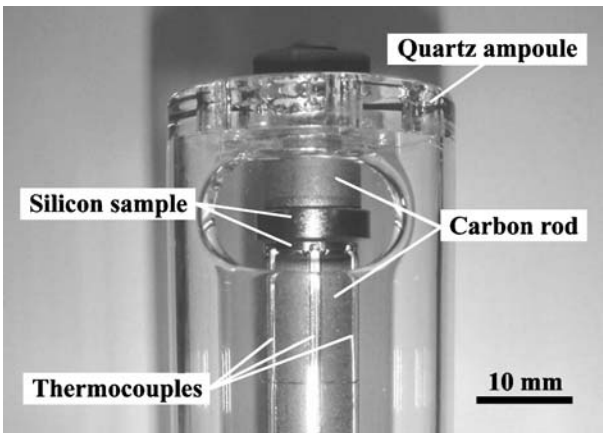


Figure 1 Sample configuration. Two pieces silicon solid samples are melted to from a liquid bridge.

2.2. Determination of mode wave number

Heating a molten silicon bridge by infrared from a halogen lamp in a mirror furnace causes formation of a low temperature field inside the bridge. This low temperature field is deformed into one with m-fold symmetry due to flow instability and this field fluctuates azimuthally. If a thermocouple is set at a fixed point within a liquid bridge, the temperature signal fluctuates at the same frequency as that of the non-axisymmetric low-temperature field, because the cold-temperature region moves back and forth with respect to the thermocouple. If multiple thermocouples are installed azimuthally in the liquid bridge (see Fig. 1), and if the phase relationship of the measured temperature oscillation among them is analyzed, the azimuthal wave number of the flow instability and its frequency can be obtained at the same time [6]. In the present experiment, six thermocouples were set in the silicon melt. The temperature oscillation data were analyzed, assuming that even under high Marangoni number conditions the thermal field retains a basic structure, such as m-fold symmetry, that can be explicitly observed under low Marangoni number conditions.

Since the various mode wave numbers are supposed to appear at the fixed aspect ratio, we attempted to analyze the mode appearance coefficient MAC ϕ_m as a function of aspect ratio. We defined the MAC as the appearance time for each wave number normalized by the total observation time. The MAC was calculated as follows; for temperature oscillation data obtained by six thermocouples, the Fourier series expansion was obtained azimuthally up to $m = 3$, as shown in Equation 1. The MAC ϕ_m was obtained as a mean square of weight factors $a_{\mathrm{m,j}}$ and $b_{\mathrm{m,j}}$, as shown in Equation 2.

$$T(\theta, i) = a_{0,\mathrm{i}} + \sum_{m=1}^{3} a_{\mathrm{m,i}} \cos(m\theta) + b_{\mathrm{m,i}} \sin(m\theta) \quad (1)$$

$$\phi_m = \frac{1}{N} \sum_{i=1}^{N} \left\{ a_{\mathrm{m,i}}^2 + b_{\mathrm{m,i}}^2 \right\} \quad (2)$$

Note that the $m = 4$ and higher cannot be distinguished using this method, as long as six thermocouples are used.

3. Results and discussions

3.1. Estimation of Marangoni number

Estimating the Marangoni number requires measuring temperature differences and temperature coefficient of the surface tension. The mean values of the temperature differences between the upper and lower ends of the molten silicon bridge surface was about 72, 79, 92 and 105 K, corresponding to aspect ratio of 0.6, 1.0, 1.4, or 2.0, respectively. The temperature difference increased linearly with the aspect ratio. However, since wetting of the sheaths by the molten silicon was neither

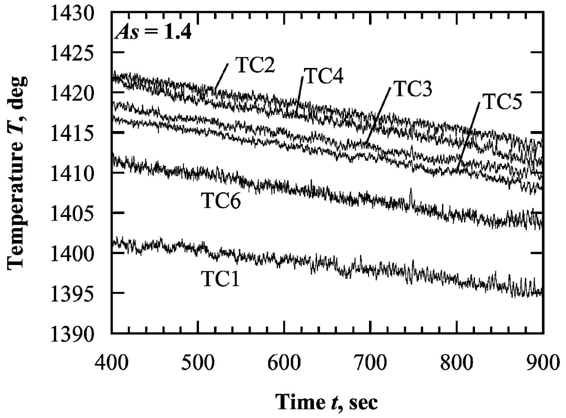


Figure 2 Time history of the temperature oscillation measured using six thermocouples. Note that oscillation data were analyzed; absolute value of temperature contains error.

sufficient nor equal among the sheaths (see 3.2), this resulted in a measurement error of about 10 K; therefore, the estimated error in the Marangoni number was about 10–20 %. Mukai *et al.* showed that surface tension and its temperature coefficient of molten silicon depend on the oxygen partial pressure of the atmosphere surrounding the surface [7]. We observed the formation of a piece of oxide film at the melt surface adjacent to the lower bottom. This suggests that the oxygen partial pressure at the melt surface was almost that for saturation at the melting point ($Po_2^{\text{surface}} = 1 \times 10^{-14}$ Pa); consequently, the temperature coefficient of the surface tension was estimated to be -0.36 $\times$ 10^{-3}N·m^{-1}·K^{-1} [8, 9]. Thus, the Marangoni numbers were estimated to be 3×10^3, 5×10^3, 9×10^3 and 1.4×10^4, corresponding to the aspect ratio of 0.6, 1.0, 1.4, or 2.0, respectively. Thermal diffusivity α and viscosity μ of the molten silicon were 2.12×10^{-5} m^2·s^{-1} and 7.0×10^{-4}Pa·s, respectively. These Marangoni numbers were much higher than the second critical Marangoni number ($Ma_{c2} = 200$), where the flow changes from stationary to oscillatory.

3.2. Time evolution of wave number and mode appearance coefficient

Fig. 2 shows the temperature oscillations for a liquid bridge with $As = 1.4$. There is a discrepancy in the background temperature (about 10–20 K) among the thermocouples. Judging from video pictures from a CCD camera, this was probably due to a difference of the wetting behavior of the molten silicon on the thermocouple sheaths; this would be due to the dissolution of coated carbon into the silicon melt, and a sheath made of SiO_2 directly touching the silicon melt. Thus, we extracted only the temperature fluctuation from the background and analyzed this. From the synchronized temperature oscillation data obtained by six thermocouples, we obtained information on temperature fluctuation T, time t, and space (azimuth θ). We normalized the amplitudes of the temperature oscillations by the mean value of absolute temperature. The T-θ relationship at each moment was interpolated using a cubic spline function and plotted in a circular format, so that the azimuthal wave number and its motion can be visualized, as shown in Fig. 3. Fig. 3a shows an example of a snapshot for an azimuthal wave number 3 for a liquid bridge with $As = 0.8$. Fig. 3b shows all information of temperature T, time t and azimuth θ. Note that Fig. 3a corresponds to $t = 6.8$ s in Fig. 3b. As shown in Fig. 3, the wave number was time-dependent; the wave number besides $m = 3$ was observed. However, in this method, the spatial resolution with respect to azimuth is limited by he number of thermocouples; i.e., with only six thermocouples, an azimuthal wave number of 4 or more cannot be observed.

Fig. 4 shows the result of mode appearance coefficient (MAC). As shown in Fig. 4, the $m = 1$, $m = 2$ and $m = 3$ modes appeared, regardless of the aspect ratio. In Fig. 4, values are normalized by the strongest appearance coefficient. The existence of the $m = 3$ mode was experimentally confirmed for the first time for a molten silicon bridge. The $m = 1$ mode looks to preferentially appear at the aspect ratio of $As = 2.0$, and the $m = 3$ mode at $As = 0.8$. For the $m = 1$ mode, the onefold symmetric temperature field does not oscillate but rotates [10]. Rotation mode was found through computational modeling for the liquid bridge of molten tin with an aspect ratio of $As = 2.0$ [5]. The $m = 2$ mode at $As = 1.0$ and 1.4 looks correct, whereas the $m = 2$ peaking at $As = 0.5$ and 0.6 can be surmised from that of $m = 4$, because six thermocouples can identify $m = 4$ as $m = 2$. Through this observation, the following relationship looks valid, i.e., $m \cdot As \approx 2.4$. Furthermore, the preferential aspect ratio for each wave

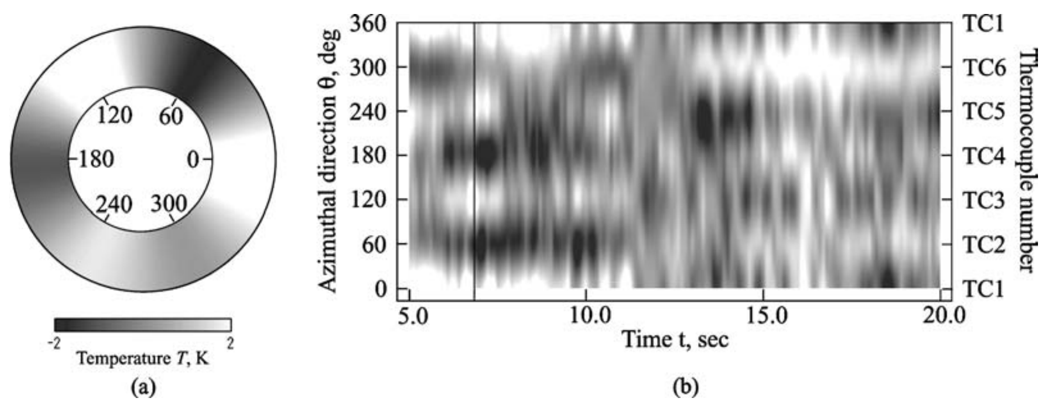


Figure 3 (a)Example for a snap-shot of azimuthal wave number $m = 3$ for a liquid bridge with an aspect ratio of $As = 0.8$. (b) The time evolution of the azimuthal wave number. The mode changes as observation time passes.

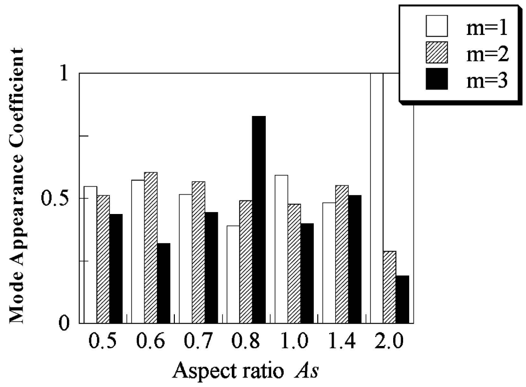


Figure 4 Mode appearance coefficient for molten silicon bridges as a function of the aspect ratio. Calculation methods are shown in Section 3.1.

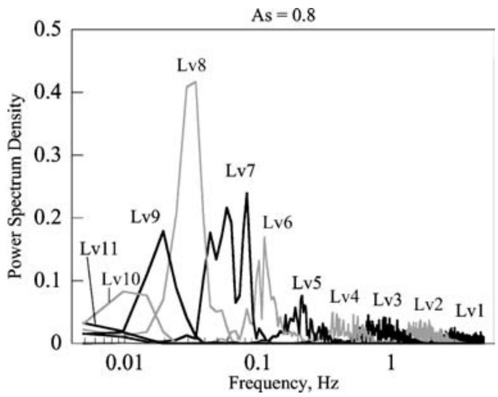
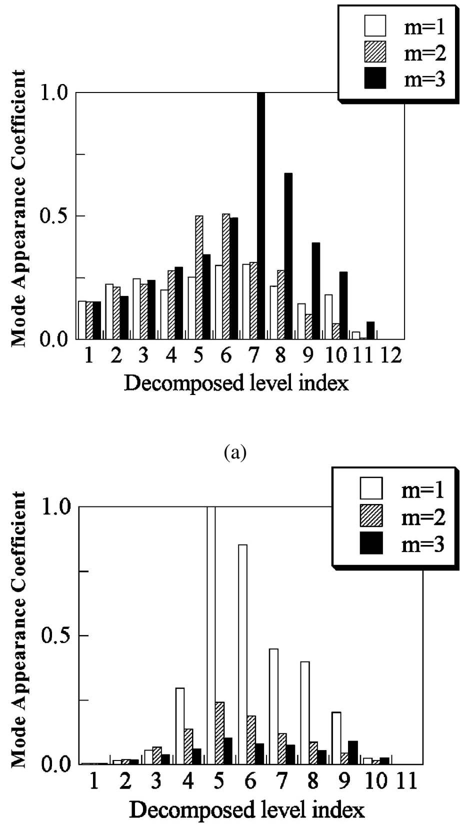


Figure 5 Fourier spectra of the decomposed oscillations for the liquid bridge with an aspect ratio of $As = 0.8$. Lv shows decomposed level index.

number looks to shift slightly toward the higher aspect ratio than that expected by Wanshura *et al.* i.e., $m \cdot As = 2.0$. This is probably due to effect of high Marangoni number. In conclusion, it is suggested that even under the high Marangoni number conditions, such as 10^3–10^4, the instability structure sustains the basic structure which was defined at the low Marangoni number condition. Although from this method the azimuthal wave number can be inferred, instability mode, such as twist and/or rotation, cannot be estimated directly. Detailed study based on $T - t - \theta$ analysis would be required using a liquid bridge with rather low Marangoni numbers.

3.3. Analysis of frequency

The frequency f should be understood as an important characteristics of the flow instability in the course of the Marangoni flow study, as well as the Marangoni number Ma and the mode wave number m. However, in the present study, it is difficult to determine uniquely the relationship between the wave number and frequency, because the flow is turbulent-like and various wave mode numbers appear irregularly and the Fourier spectrum of the temperature oscillation has multiple peaks, although numerical modeling under the small Marangoni number condition shows a single frequency for each instability mode [4, 5]. We attempted to compare the Fourier spectrum of temperature oscillation with MAC of that decomposed into components of narrow frequency bands by wavelet analysis. Wavelet decomposition is a kind of band-pass filtering. A major characteristics of this method is both to decompose and to reconstruct frequency distribution data without loosing any part of the original data. We used a spline-4 function as a mother wavelet. Because the Nyquist frequency of our experiment was 5 Hz, for a frequency of level j, the decomposed oscillation ranges approximately from 5×2^{-j} Hz to $5 \times 2^{-j+1}$ Hz. Fig. 5 shows, for example, the Fourier spectrum of the decomposed oscillations for the liquid bridge with $As = 0.8$, and the oscillations of levels 6, 7, 8 and 9 are recognized as the main components; they ranged from 0.01 to 0.2 Hz. Fig. 6a shows MAC for the oscillation for the liquid bridge with $As = 0.8$ at each level; this was obtained the same way as that



(b)

Figure 6 (a) Mode appearance coefficient for a molten silicon bridge with an aspect ratio of as a function of decomposed index level for an aspect ratio $As = 0.8$ (a) and $As = 2.0$ (b).

used for Fig. 4. From Fig. 6a, it is clear that the high appearance ratios of $m = 3$ at level 6, 7, 8 and 9 would be main factors of the high appearance ratio of $m = 3$ in Fig. 4 (at $As = 0.8$). For $As = 2.0$, similarly the high appearance ratio of $m = 1$ at level 5, 6 and 7 would contribute to formation of the wave number of $m = 1$ in Fig. 4 and its frequency would range from 0.08 to 0.2 Hz (see Fig. 6b).

Using the phase-shift interferometry, frequency analysis of the surface oscillation of molten silicon was attempted for a liquid bridge with the same aspect ratios and the almost same Marangoni number as that for the present study [11]. Two frequency bands were observed. Each band did not show a single frequency but had a range with a central frequency. They showed time dependent behavior. This suggests that flow has turbulent-like characteristics. Although it is difficult to identify frequency for each instability mode uniquely, instability structure can be observed more easily, if we use a liquid bridge with a smaller Marangoni number, so that we can bridge the Marangoni flow studies between that at higher Marangoni numbers (experimental) and that at smaller Marangoni numbers (numerical).

4. Summary

We measured the temperature oscillations in molten silicon bridges with various aspect ratios ($As = 0.5$–2.0) under the high Marangoni number conditions such as $Ma = 3000$–14000 using six thermocouples spaced equally apart in the azimuthal direction, so as to observe the relationship among the aspect ratio, wave number and frequency of the oscillating non-axisymmetric thermal field due to Marangoni flow instability. The Fourier spectrum showed multiple peaks for a high Marangoni number and suggests the existence of multiple modes. Time analysis of non-axisymmetric behavior of thermal fields ($T - t - \theta$ plot) shows time evolution of flow instability structure. The $m = 3$ mode was experimentally observed at $As = 0.8$. The relationship between the azimuthal wave number and the aspect ratio, $m \cdot As \approx 2.4$, which is valid for the small Marangoni number case, was observed even under the high Marangoni number condition, through analyzing the mode appearance coefficient (MAC). This means that the thermal field, even under a high Marangoni number condition, retains the basic structure, although a complex flow field is formed due to the emergence of small vortices. The temperature oscillation data were decomposed into components of various frequency bands using wavelet analysis. Comparing the relationship between the MAC and the Fourier spectrum of decomposed oscillation, the frequencies for the $m = 1$ and $m = 3$ modes were estimated to be 0.08 to 0.2 Hz and 0.01 to 0.2 Hz, respectively.

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