J Mater Sci (2007) 42:9529–9535
DOI 10.1007/s10853-007-2090-z

INTERFACE SCIENCE

Wetting and reaction between Si droplet and SiO_2 substrate

**Hideyuki Kanai · Sunao Sugihara · Hiroshi Yamaguchi · Tomonori Uchimaru ·
Naoyuki Obata · Toshiyuki Kikuchi · Fusaki Kimura · Masato Ichinokura**

Received: 4 March 2007 / Accepted: 9 August 2007 / Published online: 29 August 2007

Abstract The wetting and reaction between Si melt and SiO_2 substrate were investigated as a function of the atmosphere, temperature, and degree of vacuum. The results revealed that below 2 Torr with an Ar flow, the wetting angle is finally 90°. The Si droplet was stationary at a wetting angle of 90°. Videos indicated that the droplets moved and vibrated; Above 20 Torr, the Si droplet vibrated up and down with a frequency of approximately 2 Hz, thereby changing the wetting angle. Further, the droplet remained stationary on a substrate on which grooves with a width of 100 μm and depth of 100 μm were etched with a pitch of 1 mm. The presence of grooves or dimples on the substrates facilitated the leakage of SiO gas; as a result, the Si droplet did not vibrate. A vibration model was proposed in which the SiO gas produced at the interface between the Si droplet and the substrate according to the reaction $Si + SiO = 2SiO$ expands and leaks continuously.

Introduction

In the synthesis of single crystals of Si using the Czochralski system, it is important to investigate the wetting of liquid Si on SiO_2, as well as the reaction between them in order to reduce impurities or increase the wafer diameter. As the degree of integration in LSI increases, the requirements increase further. Although crucibles made of natural silica have been used widely, synthesized silica has recently been used to reduce impurities and suppress the formation of brown mold. Brown mold is known as the factor that reduces the operating duration of a crucible because it comes off from the crucible wall and reduces the dislocation-free-part in a Si ingot. Since the impurity levels of crucibles made of synthesized silica are less than 1/100, longer operating durations are expected. However, these crucibles pose a problem: after melting Si nuggets in a crucible, the surface of the molten Si vibrates. Therefore, the seeding and necking of Si becomes very difficult. Although the reason for this vibration has not been clarified, it is considered that the wetting and reaction between liquid Si and silica might affect the surface vibrations of molten Si [1, 2]. Fujii et al. investigated the reaction between liquid Si and SiO_2 substrates and reported that SiO gas was formed at the interface between the solid and the liquid, along with a change in the wetting angle [3].

Wetting and reaction behavior in ceramic–metal systems are of technological interest, as well as scientific interest in

---

H. Kanai (✉) · H. Yamaguchi · T. Uchimaru
Analysis Technology Group, Core Technology Center, Covalent Materials Corporation, 30 Soya, Hadano-shi 257-8566, Japan
e-mail: hideyuki_kanai@covalent.co.jp

S. Sugihara
Department of Materials Science and Ceramic Technology, Shonan Institute of Technology, 1-1-25 Tsujido Nishikaigan, Fujisawa-shi 251-8511, Japan

Present Address:
H. Yamaguchi
Center for Instrumental Analysis, College of Science & Engineering, Aoyama Gakuin University, 5-10-1 Fuchinobe, Sagamihara-shi, Kanagawa 229-8558, Japan

N. Obata · T. Kikuchi · F. Kimura
Quartz Crucibles Business Unit, Process Materials Division, Ceramics Business Group, Covalent Materials Corporation, 378 Ogunimachi Nishi-okitamagun, Yamagata 999-1351, Japan

M. Ichinokura
Technology Development Ceramic Business Group, Covalent Materials Corporation, Nissei Bldg., 6-3 Osaki 1-chome, Shinagawa-ku, Tokyo 141-0032, Japan

the fields of composites and electronics. A lot of studies have been reported. The degree of wetting of a solid by a liquid in a solid–liquid–vapor system can be expressed by Young's equation under chemically stable and metastable equilibrium conditions [4]. Aksay et al. treated the thermodynamics of wetting in a solid–liquid–vapor system by considering the conditions that minimize the total free energy of the system [5]. They showed that an interfacial reaction resulted in the lowering of the solid–liquid interfacial tension by a contribution of the free energy of the reaction, which could result in the spreading of a liquid drop on a solid substrate. Reactions between Al and fused SiO_2 are thermodynamically favorable. Marumo and Pask reported that the wetting of fused silica by molten aluminum at temperatures of 800–1,000 °C and 3×10^{-5} Torr is dependent on the formation of a reaction zone by redox reactions [6]. It was postulated in their study that the layer adjacent to the metal drop consisted primarily of AlO stabilized by a solid solution of SiO, and that the layer adjacent to the fused silica was a spinel of AlO and Al_2O_3 stabilized by SiO. Standage and Gani studied the effect of additions of up to 2.5% of Bi and Sb on this reaction at 660–800 °C by dipping fused SiO_2 rods into molten Al and the alloys in air [7]. They detected Si and η-,(θ-,(and α-Al_2O_3, as the reaction products. Prabriputaloong and Piggot studied the same reaction in a similar manner but under a vacuum [8]. They suggested that the presence of an Al_2O_3 film on the surface of molten Al in air caused the increased dwell time of the reaction and denied the existence of the complex interfacial layers proposed by Standage and Gani [7]. Nagesh and Pask studied the wetting of silver on nickel by a sessile drop technique [9]. They reported that a NiO layer formed at the interface between silver and nickel in air; a silver droplet formed a 90° contact angle. In helium silver formed a 9° contact angle on nickel because strong adherence occurs due to attainment of thermodynamic equibrium composition in the interface zone. Ogino reported the effects of oxygen on the surface tension of liquid Co and Co–Fe alloys and the wettability of Al_2O_3 [10]. Tomsia and Pask reviewed the wetting, spreading, and reactions of sodium disilicate glass on metal in order to develop an overall understanding of the reactions and the conditions under which chemical bonding can occur at glass/metal interfaces [11]. They suggested that chemical bonding at the interface provides maximum adherence or adhesion and is dependent on saturating the interfacial zone with the substrate metal oxide that is in equilibrium with the metal.

Although a considerable number of studies have been performed on the wetting and reactions between metals and ceramics, the mechanism of the vibration of the surface of Si melt in a SiO_2 crucible has not yet been clarified. The objectives of this study are to investigate the wetting and reaction between liquid Si and SiO_2 substrates and suggest a model that explains the vibration of the Si surface.

Experimental details

The dimensions of the SiO_2 substrates were 10 mm × 10 mm × 2 mm. They were washed for 1 min with a mixed acid of HF (47%) and HNO_3 (70%). Si nuggets (Tokuyama Corporation, H grade, lot: KQ0025) were broken into small pieces of 40–60 mg in weight and then washed with HF for 1 h. Wetting was measured by the sessile drop method using a wetting measurement apparatus (Ulvac-Riko Wet-1200) equipped with an image furnace that uses a halogen lamp with a wavelength of 1.15 μm. A thermocouple was set above the Si specimen, as shown in Fig. 1, indicating that the temperature of the thermocouple is higher than the actual temperature of the Si specimen. After lowering the vacuum to below 10^{-3} Torr, an Ar gas flow was initiated to control the atmosphere for the wetting measurement. In order to obtain 20 Torr, 2 L/min of Ar gas was flowed. The specimen was heated to 1,300°C in 10 min and then further to 1,600 °C in the image furnace; it was maintained at this temperature for 5 min. The temperature was then raised in increments of 25 °C; the specimen was held at each temperature for 5 min. The change in the wetting of Si was monitored with a CCD camera throughout the measurement.

Grooves and dimples with a pitch of 1 mm were created on the SiO_2 substrates using a CO_2 laser (Keyence Co. Ltd., ML-G9370), as shown in Fig. 2. The width and depth of each groove were 100 μm. The diameter and depth of each dimple were 100 μm. After cooling the specimen that melted on the substrates, the microstructure of the interface between Si and the SiO_2 substrates was thinned using FIB (Hitachi FB2000). The specimens were then observed using a transmission electron microscope (JEOL 4000FX).

Fig. 1 Setting of Si on SiO_2 substrate; thermo-couple is located above Si

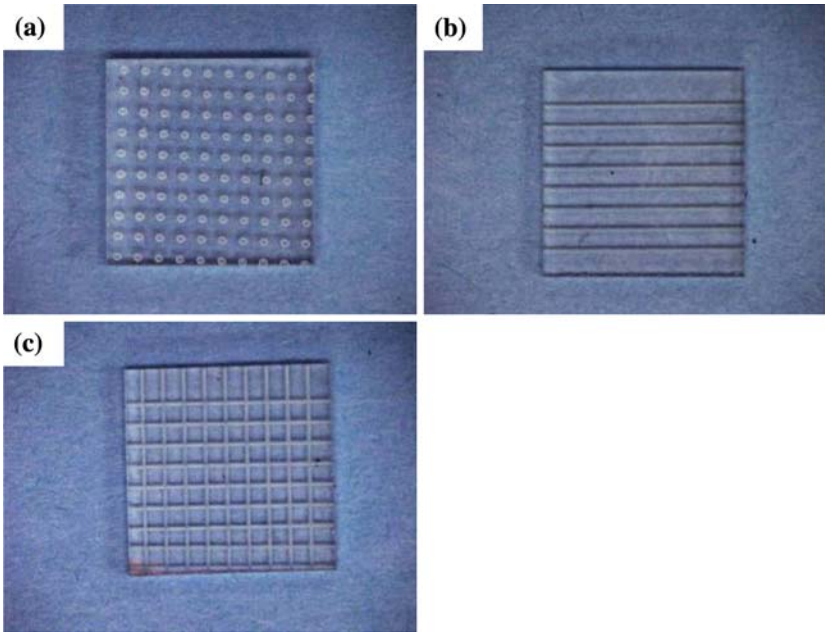

Fig. 2 Plan view of the SiO_2 substrates whose surfaces were engraved by a CO_2 laser: (**a**) dimples 100 μm in diameter and 100 μm in depth; (**b**, **c**) grooves 100 μm in width and 100 μm in depth

Results and discussion

Wetability and vibration of melted metal

After drawing a vacuum, the atmosphere reached 20 Torr with an Ar flow of 2 L/min. Silicon began melting from its upper surface around 1,350 °C, and it melted completely at 1,400 °C with a wetting angle of 150°; the wetting angle was 110° at 1,450 °C. The wetting angle varied with an increase in temperature. It was 130° at 1,500 °C and 90° at 1,550 °C. The Si droplet moved around quickly and vibrated rapidly up and down at 1,600 °C, changing the shape of the droplet, as shown in Fig. 3. The frequency of the upward and downward vibrations was in the range of 1.3–2.8 Hz. Under Ar flow and 760 Torr, the wetting angle of the Si droplet was 90° at 1,500 °C, and its vibrations were more rapid than those under 20 Torr at 1,500 °C. However, it did not vibrate when the vacuum was 2 Torr under Ar flow or lower at 1,600 °C, even though the wetting angle of Si droplet changed from 150° at 1,400°C to 90° at 1,550 °C.

Figure 4 shows the change in the surface of SiO_2 after the sessile drop experiments, as a function of the vacuum. A change in the color of the surface of the substrate can be seen in the four images in the upper row, while a change in the morphology of the surface can be seen in the four images in the lower row. As shown in images under Ar flow (760 Torr) in Fig. 4, the trace formed due to the intense movement of the Si droplet can be seen. The flatness of the surface of the substrate changed from flat to uneven. In addition, a part of the surface was colored dark yellow. By lowering the vacuum from Ar 20 Torr to 9×10^{-4} Torr, however, the surface roughness was reduced and the dark yellow almost disappeared. A trace of the rapid movement of the Si droplet can be observed by maintaining the specimen under a vacuum higher than 2 Torr. The formation of a trace of movement of Si droplet is explained by Sangiorgi and Muolo [12] and this behavior is resemble to those observed by Champion et al. [13].

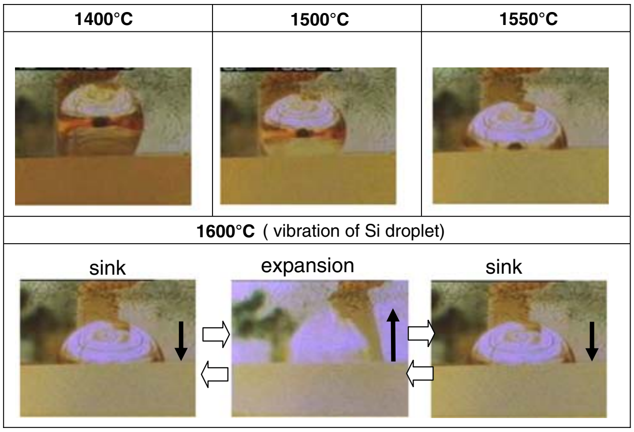

Fig. 3 Change in shape of Si droplet on SiO_2 substrate with increase in temperature under 20 Torr with Ar flow of 2 L/min. Silicon droplet vibrated up and down, changing its shape by sinking and expanding at 1,600 °C

A balance among the three types of interfacial energies—γsl (solid/liquid), γsv (solid/vapor), and(γlv (liquid/vapor)—determines the wetting, and the balance continues until the nonequivalent state becomes stable [14, 15]. The value γ_{sl} becomes smaller than γ_{sv} if a stable oxide is present at the surface of the molten metal or at the interface between the molten metal and the substrate [16]. This

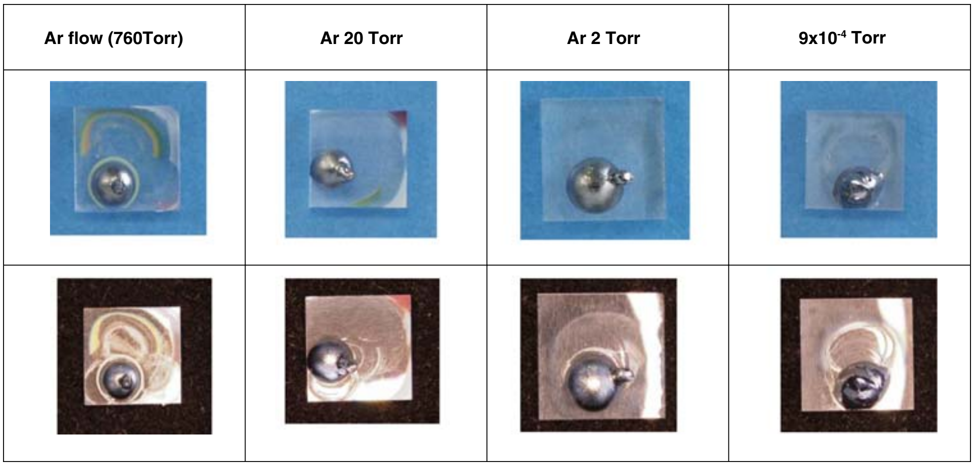

Fig. 4 Si droplet on SiO_2 substrate, as a function of vacuum after cooling (temperature was 1,500 °C): changes in color of the surface of SiO_2 substrates (upper photos) and change in their surface roughness (lower photos) can be seen

results in good wetting with an acute angle. As reported by Nagesh et al., the oxide indicated a lower surface energy of 400 mJ m^{-2} on nickel oxide, as compared to that on nickel (2203 mJ m^{-2}) [9]. Although a stable oxide reduces the surface energy in general, hereafter the value of γ_{sv} is getting greater, thermodynamically unstable oxide decomposes easily and the surface energy γ_{sl} increases, resulting in poor wettability. On the other hand, Ag and Cu are good wetting examples in which stable oxides forms on their surfaces andγ_{sl} becomes smaller than γ_{sv} [17–19]. Sugihara et al. reported that wetting under a vacuum is better than that in a N_2 or Ar atmosphere, based on the results of an experiment on the relation between the atmosphere and the wetting of Ag and Cu on a $BaTiO_3$ substrate [20]. This result indicates an electron exchange between Ag metal and Ti^{3+} or Ti^{4+} ions since the oxide formed on the Ag surface is unstable [21].

It is clear that the Po_2 of the atmosphere in wetting experiments is reflected in the wetting behavior. However, the more important factor is whether the oxides at the interfaces or the oxide substrate are thermodynamically stable.

Model for vibration

In order to investigate whether an oxide layer exists at the interface between Si and SiO_2, TEM analysis was carried out. Figure 5 shows bright-field images of the interface between a Si droplet and a SiO_2 substrate cooled down from 1,600 °C under 20 Torr with an Ar flow. As revealed in Fig. 5a, the interface is wavy, indicating the same strong vibrations of the droplet, as shown in Fig. 4. However, the secondary phase cannot be located at this interface, as seen in the high-magnification micrographs (Fig. 5b). In addition, EDS analyses suggested that no reaction phase or secondary phase was present on either side of the interface, as shown in Fig. 5a. It can thus be inferred that an oxide film is neither formed at the interface between the Si droplet and the substrate nor on the surface of the Si

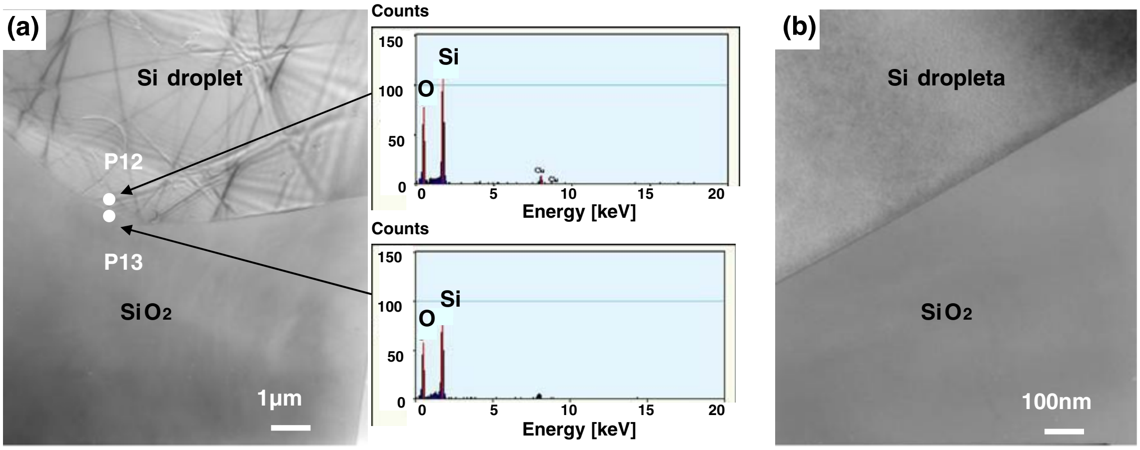

Fig. 5 TEM micrographs of cross-section of the interface between Si droplet and SiO_2 substrate, revealing wavy interface (**a**) and no secondary phase (**b**). P12 and P13 are 10 nm away from the interface

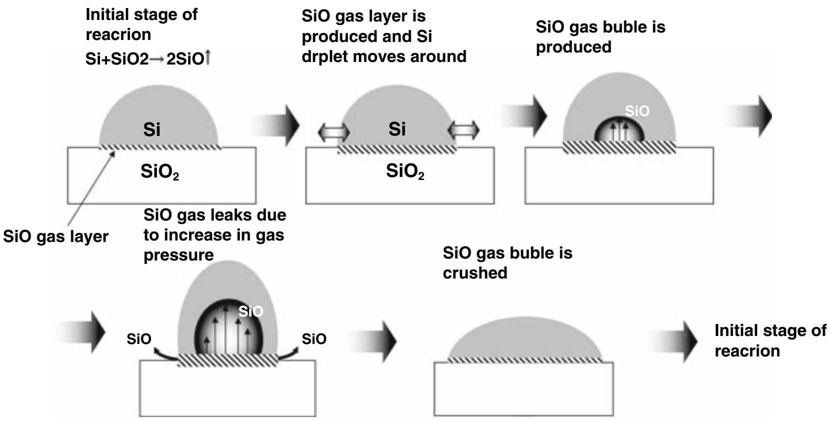

Fig. 6 Schematic explanation of vibration of Si droplet on SiO_2 substrate

droplet. Figure 6 shows a model for the vibration of the Si droplet. First, Si melts completely and then SiO gas is produced at the interface between the Si droplet and SiO_2 substrate according to the following reaction:

$$Si + SiO_2 \rightarrow 2SiO \quad (1)$$

The existence of a SiO gas layer at the interface enables the droplet to move around.

SiO gas accumulates inside the Si droplet with increasing temperatures. Then, a SiO gas bubble is formed and it expands. Although the SiO gas bubble expands upward, it leaks from the edge of the droplet and the expanded droplet dents when the SiO gas pressure in the droplet exceeds the Ar gas pressure. Repetition of this process causes the movement and vibration of the Si droplet.

Fig. 7 Si droplet on BN substrate after cooling: Si droplet did not move at all under 20 Torr with Ar flow of 2 L/min and the BN substrate was not colored, as revealed in Fig. 4

In order to investigate whether the vibration occurs due to the expansion and leakage of the SiO gas produced by reaction (1), the same experiment was carried out under an Ar atmosphere of 20 Torr using a BN substrate. The melted Si did not vibrate at all nor move around. Figure 7 shows a Si droplet on the BN substrate after cooling, indicating no trace of movement. Thus, the Si droplet vibrates and moves around on the SiO_2 substrate due to the formation, accumulation, and release of SiO gas by reaction (1). Sugihara et al. described the wetting between molten metal and nonoxides from the viewpoint of electron movement between the melted metal and substrate [22]. According to their result, oxide substrates exhibit better wetting characteristics than nitride substrates since their covalent bonds are stronger than the ionic bonds due to the electron movement at the interface between the ceramic substrate and metal deposited on it. In addition, Sugihara reported that AlN substrates exhibited poorer wetting than oxide substrates [15].

When vacuum was 2 Torr or less, the Si droplet was stationary at a wetting angle of 90° at 1,550 °C and it did not vibrate at 1,600 °C. This result might indicate that an oxide film was formed on the surface of the Si droplet. Therefore, Si droplet changed the wetting angle from 150° to 90° and the reaction (1) causing vibration of Si droplet was restrained by the formation of oxide film. When the vacuum was 20 Torr or greater, however, an oxide film was not formed, as discussed above. Therefore, Si droplet vibrated. The wetting angle of the Si droplet finally became

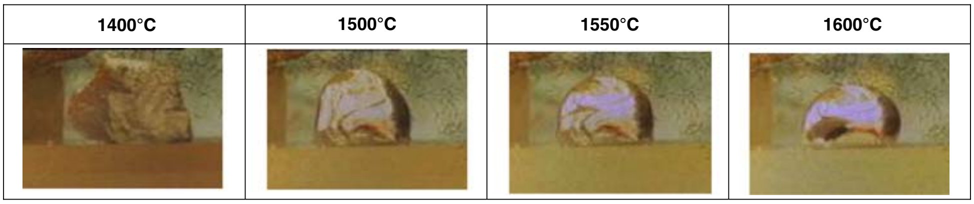

Fig. 8 Change in wetting angle of Si droplet on SiO_2 substrate having 100-μm-wide, 100-μm-deep grooves under an Ar atmosphere at 20 Torr

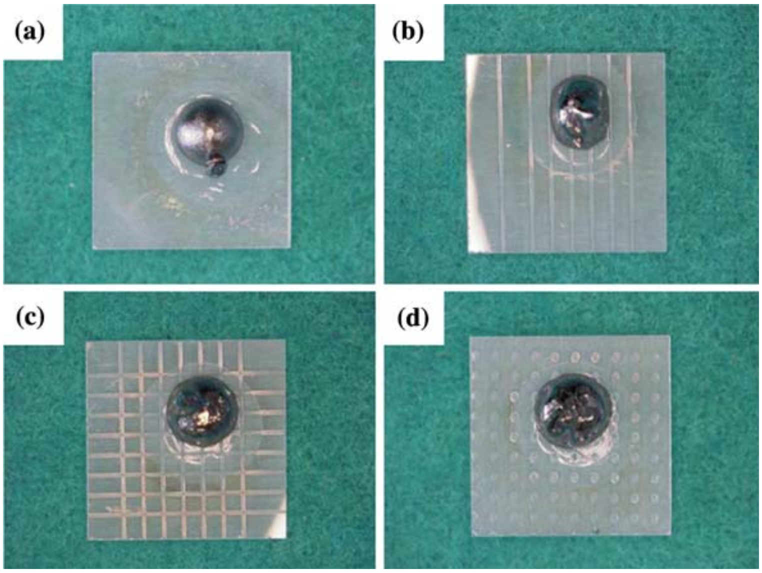

Fig. 9 Si droplets on SiO_2 substrates after cooling: Notice that the surfaces of the substrates are different: (**a**) reference (smooth surface), (**b**) line grooves, (**c**) mesh grooves, (**d**) dimples

90° even though the oxide film was not formed. The reason is not clear but it is supposed that SiO gas layer formed between Si droplet and the SiO_2 substrate due to the reaction (1) reduced the interface energy. That is, γgl (SiO gas layer/Si doplet) should be smaller than γsl (SiO_2 substrate/Si doplet).

Improvement of vibration

As shown in Fig. 4, the Si droplet moved around on a SiO_2 substrate with a smooth surface. In this section, the movement of a Si droplet on substrates with different surfaces under an Ar atmosphere of 20 Torr is described. The surface was processed by a CO_2 laser to form 100-μm-wide, 100-μm-deep grooves. Figure 8 reveals the behavior of a Si droplet for increasing temperatures. Si began melting from its surface and melted completely at 1,450 °C. The Si droplet remained stationary between two grooves and neither moved around nor vibrated after melting. Figure 9 shows the droplet on substrates with different surfaces after cooling. In the case of mesh patterns or dimple patterns on the surface of the substrate, the Si droplet did not move around but stayed between the grooves or dimples when increasing the temperature. Figure 10 shows bright-field images of the interface between the Si droplet and the SiO_2 substrate on which it did not vibrate. As shown in Fig. 10a, the interface is flatter and smoother than that of the substrate not subjected to the laser process (Fig. 5). A secondary phase cannot be observed at the interface, and EDS analyses suggested that no reaction phase existed on either side of the interface. The Si droplet did not vibrate even though SiO gas was produced by reaction (1). If the substrate has grooves or

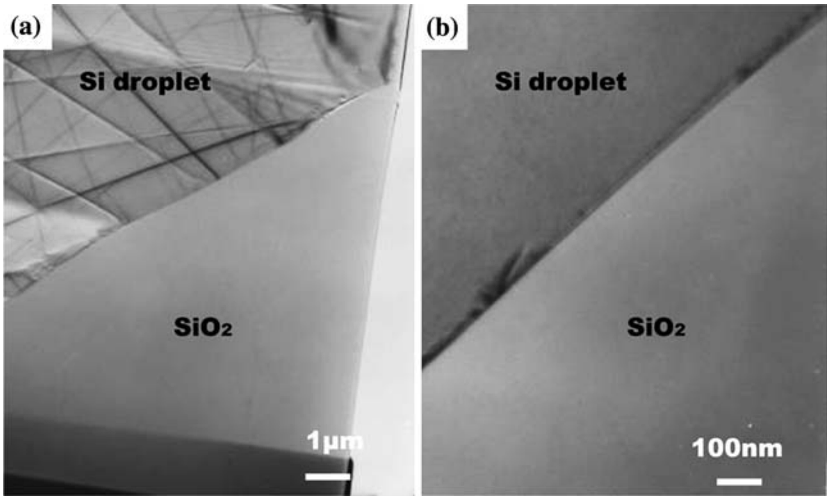

Fig. 10 TEM micrographs of cross-section of interface between Si droplet and SiO_2 substrate with mesh grooves: (**a**) and (**b**) show the same area but under different magnifications

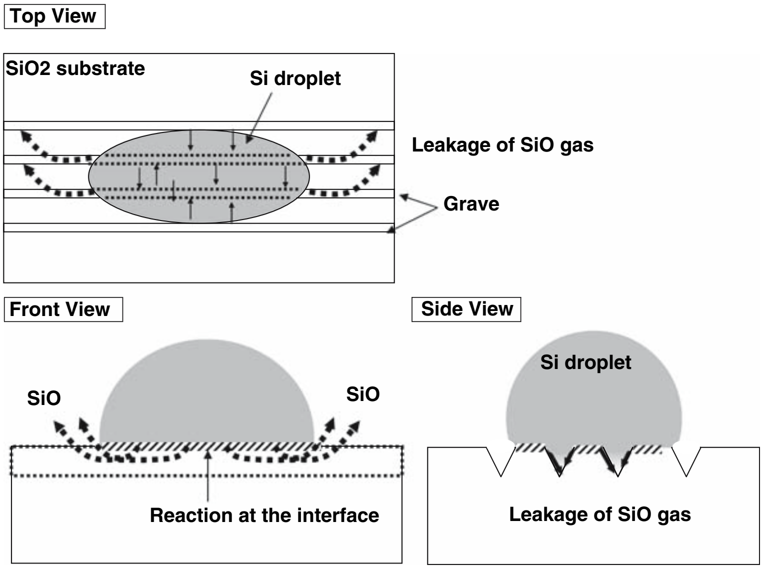

Fig. 11 Schematic explanation of suppression of vibration of Si droplet

dimples on its surface, the SiO gas produced leaks through them and is not retained inside the droplet, as shown in Fig. 11. Therefore, the droplet does not vibrate. In addition, the movement in the horizontal direction is restricted by the surface tension at the edges of the grooves and dimples.

Conclusions

The wetting and reaction between Si melt and SiO_2 substrate were investigated, as a function of the atmosphere, temperature, and degree of vacuum, and the behavior of Si droplet was monitored by a CCD-camera. The model proposed in this paper can explain the vibration of a Si droplet that causes the surface of molten Si to vibrate in a crucible during the Czochralski process for the production of single Si crystals. The formation of SiO gas due to the reaction between the Si droplet and the SiO_2 substrate causes the droplet to expand. The droplet becomes dented due to leakage at its edges when the SiO gas pressure exceeds the limit of the internal gas pressure. Due to the repetition of this process, the Si droplet moves and vibrates. In order to prevent such vibrations, it is imperative that the liberated SiO gas be allowed to escape by fabricating leakage paths, such as grooves and dimples.

References

1. Niu Z, Mukai K, Shiraishi Y, Hibiya T, Kakimoto K, Koyama M (1996) J Jpn Crystal Growth 23(5):374
2. Mukai K et al (2000) Mater Trans JIM 41(5):639
3. Fujii H, Yamamoto M, Hara S, Nogi K (1999) J Mater Sci 34:3165
4. Sugihara S, Okazaki K (1992) Materia Japan 31(3):197
5. Aksay IA, Hoge CE, Pask JA (1974) J Phys Chem 78(12):1178
6. Marumo C, Pask JA (1977) J Mater Sci 12:223
7. Standage AE, Gani MS (1967) J Am Ceram Soc 50(2):101
8. Prabriputaloong K, Piggott MR (1973) J Am Ceram Soc 56(4):184
9. Nagesh VK, Pask JA (1983) J Mater Sci 18:2665
10. Ogino K et al (1982) J Jpn Inst Metal 46(10):957
11. Tomsia AP, Pask JA (1986) Dent Mater 2:10
12. Sangiorgi R, Muolo ML, Ceramic developments (1988) In: Sorrel CC, Ben-Nissan B (eds) Mater Sci Forum 34–36:427
13. Champion JA et al (1969) J Mater Sci 4:39
14. Pask JA (1987) Ceramic Bull 66(11):1587
15. Sugihara S, Hirose Y (1994) J Ceram Soc Jpn 102(3):217
16. Levi G, Kaplan WD (2002) Acta Mater 50:75
17. Taimatsu H et al (1985) J Jpn Inst Mater 49(7):523
18. Sugihara S, Okazaki K (1993) J Mater Sci 28:2455
19. Sugihara S (1990) J Jpn Soc Powder Powder Metall 37(7):1052
20. Sugihara S, Okazaki K, Terashima Y, Kisamori K (1991) Jpn J Appl Phys 30(9B):2413
21. Sugihara S et al (1998) J Korean Phys Soc 32(2):S1119
22. Sugihara S, Yamamoto M, Isobe T, Yutoh Y (2003) Adv Quant Chem 42:465