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Effect of gas evolution at solid-liquid interface on contact angle between liquid Si and SiO_2

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The contact angle between liquid Si and SiO_2 was measured with the sessile drop method at 1723 K. The contact angle changed very unusually due to the evolution of SiO gas at the solid/liquid interface. It was found that the real contact angle between liquid Si and SiO_2 is about 80° or less at 1723 K though the apparent contact angle of 95° was observed for a long time during the experiment. The difference in the contact angle can be explained with a model of a composite material. Although the real contact angle is more important in a physical point of view, the apparent contact angle should be adopted in some cases such as simulation works. © *1999 Kluwer Academic Publishers*

1. Introduction

The wettability of SiO_2 by liquid Si is one of the most important thermophysical values in the semi-conductor industry. As the degree of integration of LSI is increasing, the optimization of the producing condition of Si single crystals is strongly required to produce wafers with higher quality and larger diameter. A computer simulation is one of the most effective methods for the optimization. However, the results of the simulation are very dependent on the adopted thermophysical values and there are few reliable data for them. The contact angle between liquid Si and SiO_2 is the one of the most important thermophysical values for the simulation because a SiO_2 crucible is used in the Czochralski method.

It is well known that Si reacts with SiO_2 very quickly producing a gas phase of SiO at elevated temperature. When the wetting in such a system is measured, the formed gas is expected to affect the apparent contact angle. For example, in liquid Al/Al_2O_3 system, the Al_2O_3 substrate is eroded and the apparent contact angle decreases with time while the real contact angle is constant. In the system, Al reacts with Al_2O_3 producing a gas phase of Al_2O [1, 2].

In this study, the effect of the evolution of gas phases on wetting is also investigated in detail using the liquid Si/SiO_2 system and a method is suggested of the evaluation of the wetting in such a system.

2. Experimental

The sessile drop method was used to measure the contact angle. The Si samples used were non-doped materials and 9N pure. The Si samples had about 150 mm^3 volume each and were preheated by immersion in 20% hydrofluoric acid to remove the oxide film on the surface, then in water and acetone. Since only a few impurities in substrates can also affect the wetting [3, 4], high purity SiO_2 samples were used. Table 1 gives the chemical composition of the SiO_2 samples. The plates had dimensions of 20(l) × 20(w) × 5(t) mm.

The sample was heated using a tantalum cylindrical heater and five concentric molybdenum reflectors. The contact angle was measured at 1723 K (1450 °C) in a vacuum of less than 1×10^{-5} Torr (1.3×10^{-3} Pa). It was also measured in an Ar atmosphere as a reference experiment. In both environments, the formation of SiO, a gas phase, was dominant in the reactions near the sample surface and therefore the partial pressure of SiO and oxygen around the sample surface were estimated to be less than 1.6×10^{-3} and 4.3×10^{-14} Pa, respectively [5]. The temperature was measured using an R type thermocouple (Pt/Pt13%Rh) located closed to the sample. The temperature was calibrated using the melting points of pure Au and Si.

The sessile drop was photographed with a 35 mm camera with bellows and macro lenses. The coordinates of twenty points on the outline of the droplet were measured on projections of the monochrome negatives (magnification 20×) and the contact angles were calculated using the Laplace equation.

3. Experimental results and discussion

3.1. Unusual change in contact angle

The wetting phenomenon of SiO_2 by liquid Si was very complicated. The Si droplet vibrated intensively

TABLE I Chemical composition of SiO_2 (ppm)

SiO_2	Al	Fe	Na	K	Cu	B
> 99.9 mass %	0.1	0.05	0.05	0.05	<0.01	<0.01

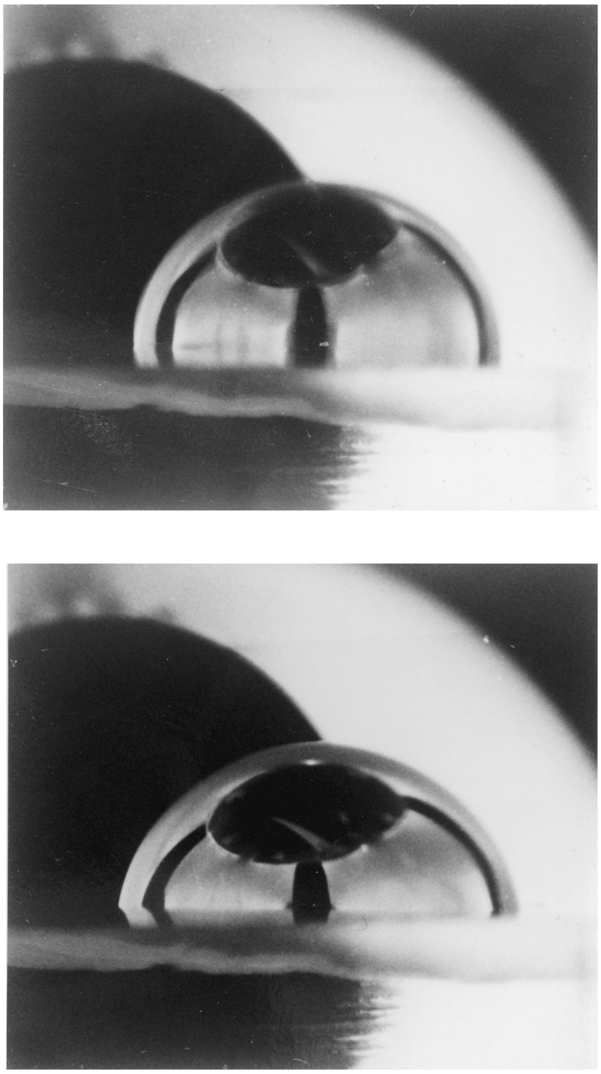

Figure 1 Appearance of vibrating droplet in the periodic period.

on the SiO_2 substrate and it sometimes jumped up off the SiO_2 substrate. Fig. 1 shows typical appearances of a vibrating droplet. Their apparent contact angles are very different. The change in the contact angle during an experiment is shown schematically in Fig. 2. The change consists of stationary periods and periodic periods. For the initial about 200 seconds in the experiments, a stationary period is maintained. The contact angle in this period is about 95°. Then, there is a periodic period where the contact angle changes from about 110° to about 80° with a very high frequency of about 1 Hz. After the periodic changes occurred several times or several tens of times, another stationary period started again. The contact angle in the stationary period was about 95° again.

This unusual changes are caused by the evolution of SiO gas at the solid-liquid interface.

$$Si(l) + SiO_2(s) \rightarrow 2SiO(g) \uparrow \qquad (1)$$

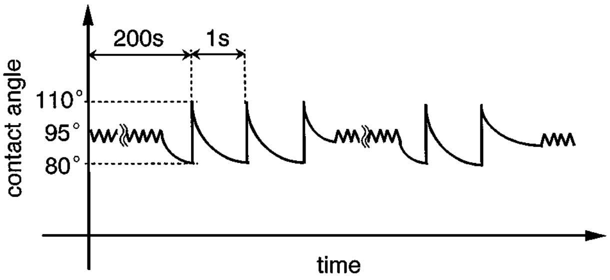

Figure 2 Schematic diagram of change in contact angle between Si and SiO_2.

The SiO_2 substrate was eroded due to the reaction, as shown in Fig. 3. There is a series of rings, which indicates the movement of the droplet during the experiment. The quantity of SiO gas produced can be estimated from the decrease in mass of the sample when it is assumed that all the decrease in mass was caused by the evolution of SiO gas. About 5.0×10^{-3} mol of SiO was formed per hour, that is, about 0.20 ml of SiO was formed per second under the atmospheric pressure.

When an atmospheric gas is used instead of the vacuum condition, the rate of the evolution of gas phases is expected to be reduced. Accordingly, Ar atmosphere was also used in this study. However, there was not a big difference in the change of contact angle as well as in the movement of the droplet.

Fig. 4 shows the change in the state of the droplet during the experiment. When the substrate is rough enough, the produced SiO gas can be released from the gaps between the liquid Si and the valleys of the roughness of the substrate. However, the mountains (pointed parts) are more easily eroded because the curvatures of the points are larger and hence the points are more surface-active. Consequently, the surface of the substrate becomes flatter and flatter with time. About 200 seconds after the initial contact of Si with SiO_2, the surface of the substrate was not rough enough for the gas to be released. In this case, a large amount of the gas is released intermittently and the apparent contact angle increases to 110° because of the impact of the gas release. The droplet sometimes jump up off the substrate for the gas to be released. When the droplet is located on the flat surface, the periodic period is maintained. However, the droplet sometimes changes its position, as shown in Fig. 3. In this case, the change in contact angle enters the stationary period again.

3.2. Equilibrium contact angle

The initial value of the contact angle between liquid Si and solid SiO_2 was about 95°. The period where the value is observed is much longer than any other period. The value is close to the previously reported values [6–8], as shown in Table 2. However, it seems that the value does not correspond to the real contact angle of this system.

In the periodic period, the contact angle changes from about 110° to about 80° in a very short period. The larger value of 110° is an unstable value caused by the impact occurring when the accumulated gas is released. Thus, the contact angle is approaching to the equilibrium contact angle in the periodic period. Because the

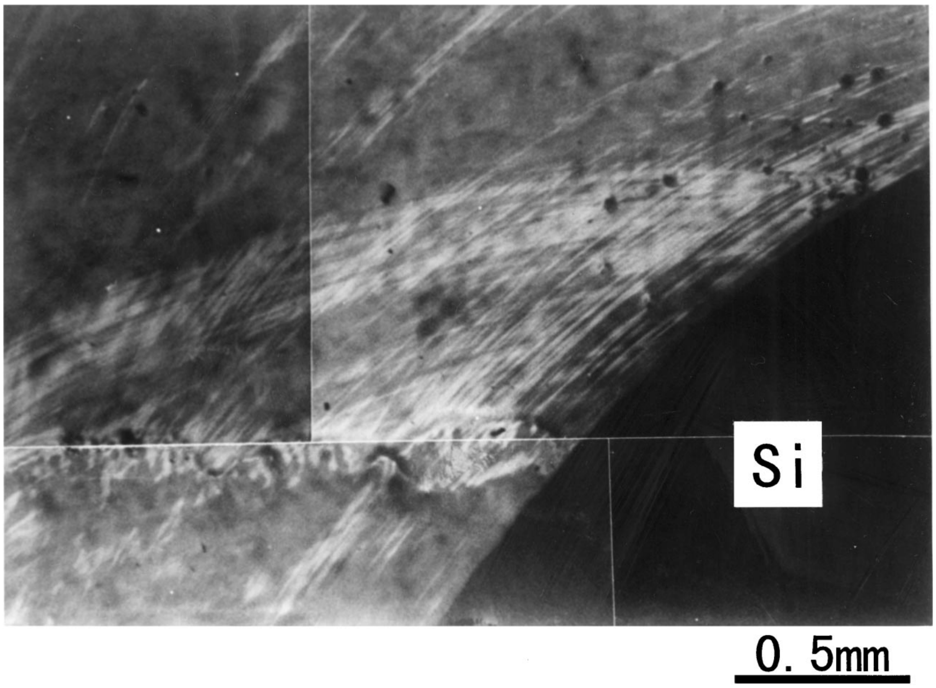

Figure 3 Trace of Corrosion of SiO_2 substrate.

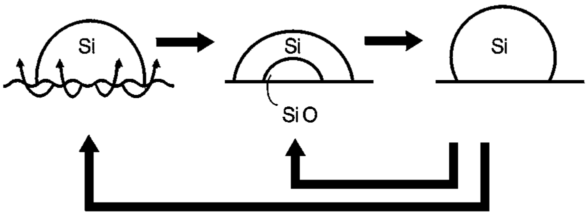

Figure 4 Change in state of SiO gas and droplet.

contact angle decreased to about 80° continuously, the equilibrium value should be equal to or less than 80°, not equal to 95°. In this period, the three phase line may be pushed forward due to the accumulated gas at the solid/liquid interface, and the contact angle can hence be an advancing contact angle. An advancing contact angle is generally larger than the equilibrium contact angle. When the solid surface is completely flat, the advancing contact angle is equal to the equilibrium contact angle. As mentioned before, because the change in the contact angle in this period occurs on a flat solid surface, the difference between the equilibrium contact angle and the advancing contact angle should be very small [9, 10]. Therefore, it can be concluded that the equilibrium contact angle of the liquid Si/SiO_2 system is equal to or less than 80°, and that the value of 95° is not the real contact angle.

TABLE II Comparison of contact angles of SiO_2/Si system

Researcher	Temperature (K)	Atmosphere	Contact angle (deg)
Li [6]	1703	Ar	92
Sangiorgi [7]	1723	Ar	87
Kalmicov [8]	1753	Ar	90
This study	1723	Ar	96
(Stationary period)	1723	10^{-5} Torr	95
This study	1723	Ar	<80
(Periodic period)	1723	10^{-5} Torr	<80

3.3. Apparent contact angle

Why or how can the value of 95° be observed in the stationary period? The period where the value is observed is much longer than any other period.

This phenomenon can be explained when the substrate is regarded as a composite of solid SiO_2 and a gas phase. The contact angle, θ_C, of a composite consisting of material A and material B is expressed with the following equation [11].

$$\cos\theta_C = F_A \cos\theta_A + F_B \cos\theta_B \qquad (2)$$

where, F_A and F_B are the ratios of A phase and B phase at the three phase line [12]. θ_A and θ_B are the contact angle for the pure A phase material and the pure B phase material. When B phase is a gas phase, the above equation can be changed as follows.

$$\cos\theta_C = F_A \cos\theta_A - F_B \qquad (3)$$

The equation is called Cassie's equation. When 95° is substituted into θ_C and 80° is substituted into θ_A, F_A and F_B is calculated to be 0.78 and 0.22 respectively. Consequently, the substrate can be regarded as a composite material including about 20% SiO gas phase. Thus, it has been clear that the apparent contact angle does not always represent the real contact angle in reactive systems where a large amount of gas is evolved. In a physical point of view, the apparent contact angle is less important than the real contact angle. In some cases such as a simulation of a production process, however, the apparent contact angle should be adopted instead of the real contact angle.

4. Summary

The contact angle between liquid Si and SiO_2 was measured at 1723 K and the following points have been found.

(1) When a large amount of gas phase is produced by interfacial reactions in a system, the evolution of the gas phase can affect the apparent contact angle and hence the apparent contact angle is not always equal to the real contact angle.

(2) The real contact angle between liquid Si and solid SiO_2 is about 80° or less at 1723 K.

(3) The apparent contact angle which is observed for a longer time than any other value is about 95° at 1723 K. The substrate can be regarded as a composite material including about 20% gas phase.

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References

1. R. D. CARNAHAN, T. L. JOHNSTON and C. H. LI, *J. Amer. Ceram. Soc.* **41** (1958) 343.
2. J. A. CHAMPION, B. J. KEENE and J. M. SILLWOOD, *J. Mater. Sci.* **4** (1969) 39.
3. H. FUJII and H. NAKAE, *ISIJ Int.* **30** (1990) 1114.
4. H. FUJII and H. NAKAE and K. OKADA, *Metall. Trans.* **24A** (1993) 1391.
5. Z. NIU, K. MUKAI, Y. SHIRAISHI, T. HIBIYA, K. KAKIMOTO and M. KOYAMA, *J. Jpn. Crystal Growth* **23** (1996) 374.
6. J. G. LI and H. HAUSNER, *Mater. Lett.* **14** (1992) 329.
7. R. SANGIORGI, M. L. MUOLO, D. CHATAIN and N. EUSTATHOPOULOS, *J. Amer. Ceram. Soc.* **71** (1988) 742.
8. P. NIKOLOPOULOS and G. ONDRACEK, "The Interfacial Energy between Oxides and Liquid Metals" (Verbundwerkstoffe, 1980) p. 391.
9. N. EUSTATHOPOULOS and B. DREVET, *J. Phys. III* **4** (1994) 1865.
10. V. DE JONGHE, D. CHATAIN, I. RIVOLLET and N. EUSTATHOPOULOS, *J. Chim. Phys.* **87** (1990) 1623.
11. A. B. D. CASSIE, *Discussions Faracay Soc.* **3** (1948) 11.
12. H. FUJII, H. NAKAE and K. OKADA, *Acta Metall. Mater.* **41** (10) (1993) 2963.

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