Study of Mutual Separation of Silicon and Quartz Using Liquid-Liquid Extraction

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The objective of this investigation was to separate silicon and silica for recycling by the liquid-liquid separation technique. In the preparation of silicon (Si) single crystal, a small amount of silicon is fixed on the surface of silica (quartz, SiO_2) crucible. The used crucible is crushed for recycling both silicon and silica in high purity from the mixed powder. Zeta-potential of silicon and silica are almost the same at pH higher than 3. Their separation by simple flotation is ruled out. However, their hydrophobic characteristics are different in several different organic solvent from the measurement of contact angle. Therefore, the liquid-liquid extraction is employed to separate silicon and silica. The result indicates that the organic solvent mixed with dodecylamine acetate could extracted the silicon powder at high purity (97-100%) with high recovery from the silica powder in the water phase.

Key Words : Silicon, Quartz, Liquid-Liquid Extraction, Contact Angle

1. Introduction

Silicon single crystal grows in silica (SiO_2) crucible by Czochralski method in electronic industry. Silicon wafer production from the single crystal has increased for producing semiconductor devices recently. After silicon crystal is removed from the silica crucible, the silica crucible is crushed for recycling both silicon and silica. In this study, the method to recovering a small amount of silicon powder and a large amount of silica (quartz) powder was conducted by grinding the silica crucible followed by liquid-liquid extraction. It was reported[1] that the technique of liquid-liquid extraction of solid was successful to separate fine minerals (less than 10 μm) with similar zeta potential in water.

2. Samples

The silicon crucible to prepare the silicon single crystal is produced by heating high purity of quartz container with the electric arc furnace. The used silica crucibles after the production of single crystal are crushed. The various amount of coated silicon spots on the silica crucible are observed as shown in Figure 1. The silicon and silica crucible were ground to minus 400 mesh (37 μm). The average particle size was approximately 6 μm. The zeta potentials of Si and SiO_2 particles were measured by the micro-electrophoresis. Figure 2 shows that zeta potentials of both Si and SiO_2 were almost the same with increasing negative charges at higher than pH 3. Therefore, Si could not be separated from SiO_2 by the flotation with conventional surfactant.

Several mg (milligram) of Silicon sample powder (average particle size 5 μm) was dispersed and conditioned for 10 min. in aqueous 1×10^{-3} M KNO_3 supporting electrolyte solution and pH was adjusted by using 1N of HCL and KOH solution.

The suspension was then charged into a 90 mm micro-electrophoresis cell of circular cross-section with internal diameter of 6 mm, equipped with a TV camera.

A potential of 110V was applied and the electrokinetic mobility was measured at both upper and lower stationary levels.

A minimum of 20 particles were timed over a distance of 50 μ (50 μm) m using hand held stopwatch. The mean value of

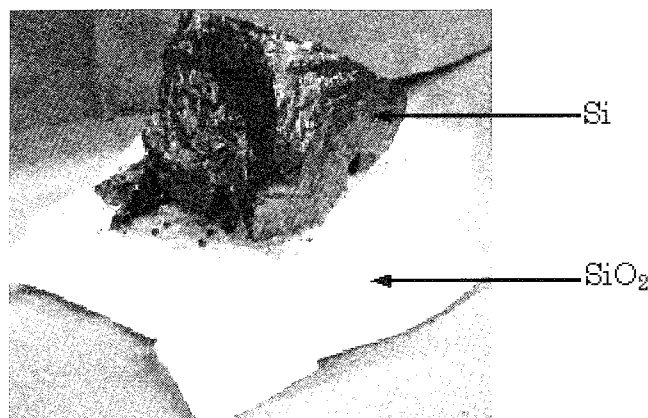
Figure 1　Lump of silicon and silica fixed on the silica crucible.

mobility time was applied to calculate the zeta potential by using Helmholz-Smoluchowski equation.

3. Experimental Procedure and Results

The principle of this study based on the attachment affinity of different particles into organic phase for separating the mixed particles. The model shown in Figure 3 has been employed to measure the contact angles of several organic solvent droplets and air bubble on the samples in water. While a large contact angle θ is observed between the solid sample surface and organic oil drop, the oil was easily expanded on the particle.

In other word, the solid particles would move from the water phase into the organic phase and be extracted. Both surfaces of silicon (Si) and quartz (SiO$_2$) plates were well polished and washed by distilled water.

In a liquid-liquid extraction system where a solid surface is in contact with an aqueous and an oil phase, the wettability of the solid by a liquid is assessed by comparing the adhesion work of the liquid to its surface with the cohesion work of the liquid. The adhesion work of an oil $W_{a(so)w}$ is defined as the work per unit surface area required to create a solid-water interface and an oil-water interface upon destroying a solid-oil interface[2].

$$W_{a(so)w} = \gamma_{sw} + \gamma_{ow} - \gamma_{so} \qquad (1)$$

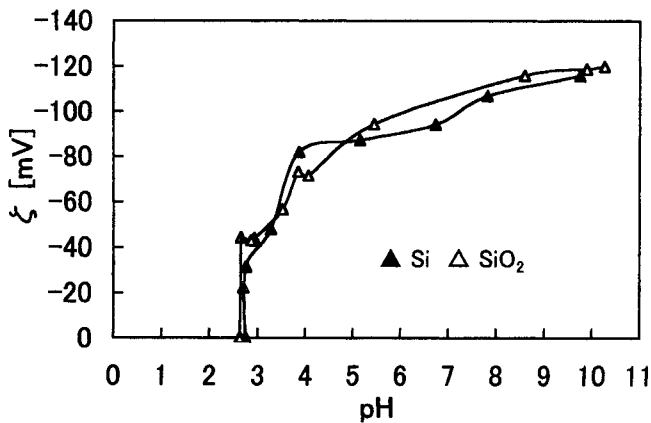Where γ_{so}, γ_{sw} and γ_{ow} are the solid/oil, solid/water and oil/
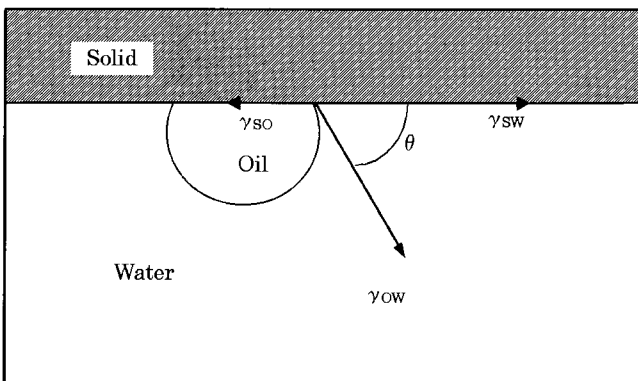
water interfacial tensions in a mutually saturated system. On the other hand, the difference between the interfacial tensions of solid/oil and solid/water interfaces is called as adhesion tension $A_{s(w-o)}$, which is defined as the work per unit area needed to withdraw a solid submerged in water into an oil pahse and remove the water entirely from the solid surface[2]. That is,

$$A_{s(w-o)} = \gamma_{so} - \gamma_{sw} \qquad (2)$$

The measured contact angles of organic droplets (n-butanol, n-pentyl acetate, isooctane) and air bubble on the silicon and quartz plate as a function of water pH are shown in Figure 4. The results demonstrate that the contact angle of organic phase on Si is much larger than that of SiO$_2$ surface. Also, the contact angle of air bubble on both Si and SiO$_2$ surfaces is smaller than that of organic droplets. The n-butanol droplet has the largest contact angle in the acidic water phase. The contact angle decreases slightly at the alkaline region. The increase of carbon chain length of the organic solvents causes the decrease of contact angle. Therefore, when the organic solvent is added in the mixed suspension of Si and SiO$_2$ particles in water with a proper agitation, there is a possibility that only the Si particles can move into organic phase and be separated from the well dispersed SiO$_2$ particles in water phase.

In addition, the interfacial tensions at the some kinds of oil/ water interfaces are shown in Figure 5[2]. As a reference, the air/ water interfacial tension value is also presented. It was found that the smallest interfacial tension was obtained at the n-butanol/water interface while the largest one at the isooctane/water interface. The results show that the value of interfacial tension was corresponded with the solubility of organic solvent in water, that is, the larger
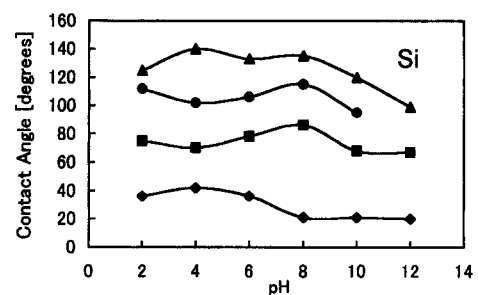
Figure 2   Zeta potentials of silicon (Si) and silica (SiO$_2$) as a function of pH.

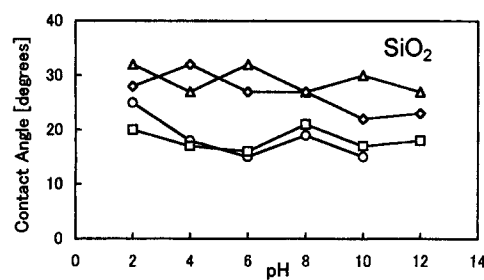(▲: n-butanol,   ●: n-pentyl acetate,   ■: Isooctane,   ◆: air bubble)

Figure 3   The model for measuring contact angle of oil droplet on solid in water.

(△: n-butanol,   ○: n-pentyl acetate,   □: Isooctane,   ◇: air bubble)

Figure 4   Contact angles of three kinds of organic droplets on the silicon and quartz surfaces as a function of pH.

Table 1   Calculated interfacial free energy for organic phase droplet and air bubble on the silicon and guartz surface in water at pH 4.

Oil or gas phase in water	Silicon (Si)					Quartz (SiO₂)				
	Contact Angle (degrees)	Adhesion Work of oil (ergs/cm³)	Cohesion Work of oil (ergs/cm³)	Spreading Coefficient of oil on solid	Adhesion Tension (dynes/cm)	Contact Angle (degrees)	Adhesion Work of oil (ergs/cm³)	Cohesion Work of oil (ergs/cm³)	Spreading Coefficient of oil on solid	Adhesion Tension (dynes/cm)
n-butanol*	140	2.7	3.0	-0.4	-1.1	29	0.2	3.0	-2.8	1.3
n-pentyl acetate**	102	18.1	30.0	-11.9	-3.1	18	0.7	30.0	-29.3	14.3
Isooctan***	70	26.9	81.6	-54.8	14.0	17	1.8	81.6	-79.8	39.0
Air bubble	46	22.2	145.6	-123.4	50.6	32	11.1	145.6	-134.5	61.7

*C₂H₅CH₂CH₂OH, **CH₃COO(CH₂)₄CH₃, ***(CH₃)₃CCH₂CH(CH₃)₂

the solubility, the smaller is the interfacial tension. On the other hand, the interfacial tensions at these oil/water interfaces were found to be independent of the solution pH over the experimental pH range at a constant temperature.

The calculated results of interfacial free energy for oil droplet and air bubble on silicon and silica surface in pH 4 of aqueous solution are summarized in Table 1[2]. According to Table 1, n-butanol is the easiest one to adhere to silicon surface, because of its smallest absolute value of spreading coefficient and lower adhesion tension[3].

The adhesion tension of n-butanol is the lowest among the three organic liquids tested. Moreover, the silicon surface shows more oleophylic affinity than quartz as in Table 1.

The oleophylic affinity tests for n-butanol on Si and SiO₂ particles in whole pH range of water have been examined. At pH 1 and 2, only Si particles can move into organic n-butanol phase (top of test tub), while SiO₂ particles are coagulated well in water phase (bottom of test tub). As water pH is higher than 4, SiO₂ particles are well dispersed in water phase and a small amount of Si particles is dispersed in water phase because the zeta-potentials of both Si and SiO₂ becomes more negative at pH is higher than 3 as shown in Figure 2. Even if the contact angle of n-butanol on Si is high at alkaline region as shown in Figure 4, the high negative zeta-potential of Si at alkaline region prevents the proper movement of Si particles into oil phase. Also the well dispersed Si O₂ in water phase in alkaline region decreases the separation speed and causes the contamination into organic phase. Moreover, Table 1 suggests the possibility that at pH4 some silica particles moves

to organic phase in n-butanol as comparing to quartz (in Table 1). In the experiment of oleophylic affinity tests for n-pentyl acetate and isooctane on Si and SiO₂ particles for various pH range of water shows the similar results[4].

Next, dodecylamine acetate (DAA) was added in the aqueous phase to improve the silica recovery at pH1. The effect of DAA concentration on the recovery of silica is shown in Figure 6. As DAA concentration is higher than 150 mg/l, the silica particle sur-
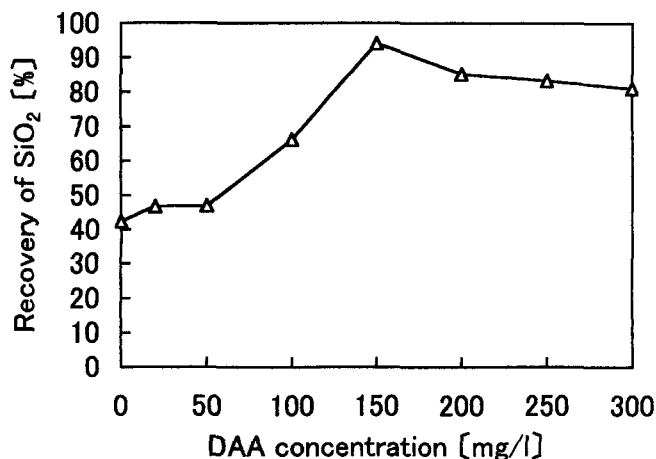
Figure 6   Effects of DAA concentration at pH1 of aqueous phase on the recovery of SiO₂ into water phase for the n-butanol by liquid-liquid extractin.
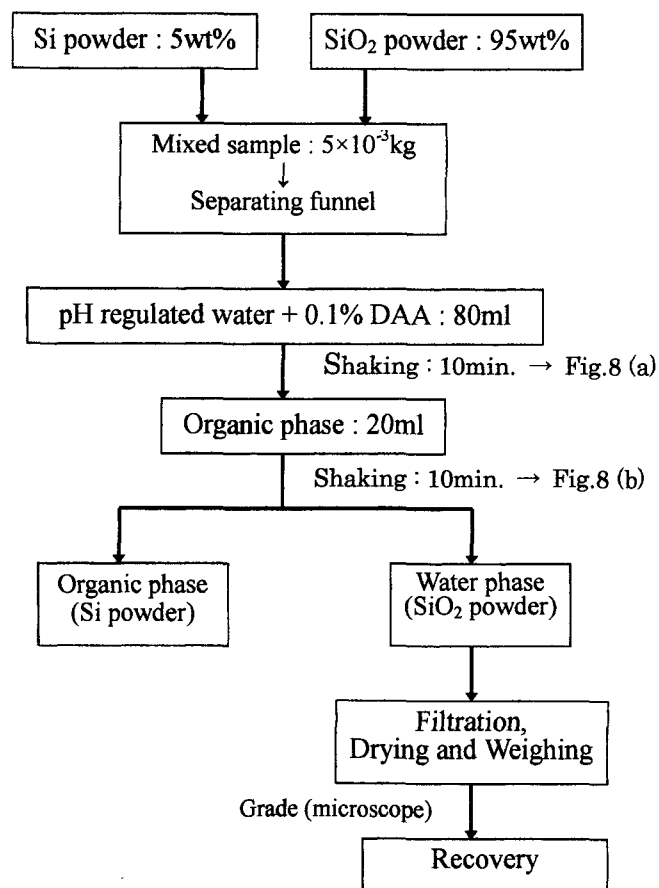
Figure 7   The flow sheet of liquid-liquid extraction for the separation of Si and SiO₂ mixed particles.

Figure 5   Oil/water interfacial tensions as a function of pH at 298 K[2].

face charge at pH1 is positive as estimated in Fig. 2. It will adsorb DAA as a double layer and well disperses in water. Thus, the contact angle on silica surface may be reduced at pH1[2]. Therefore, the silica particles are well dispersed and remain in aqueous phase. It is difficult to clearly explain the mechanism of a double layer adsorption on the surface of SiO_2 particles. However it can be said that the recovery of SiO_2 particles is lower when DAA concentration in water is going down as it is considered that the mono-layer is formed on the surface of SiO_2. On the other hand, a large amount of the DAA concentration of constant recoveries are obtained.

Suggested Flowsheet:

The flow sheet of liquid-liquid extraction for the separation of Si and SiO_2 mixed particles is shown in Figure 7. Silicon powder of 5 wt% and silica powder of 95 wt% are artificially mixed and put into a separating funnel that pH is regulated, the surfactant DAA is added and water is added to 6.25% solids. The organic solvent at 20% is then added in the suspension and shaken for 10 minutes. After standing for a while, most of silicon particles move into the organic phase, while silica particles remain and disperse in water phase. For example, Figure 8 shows the Si particles in the
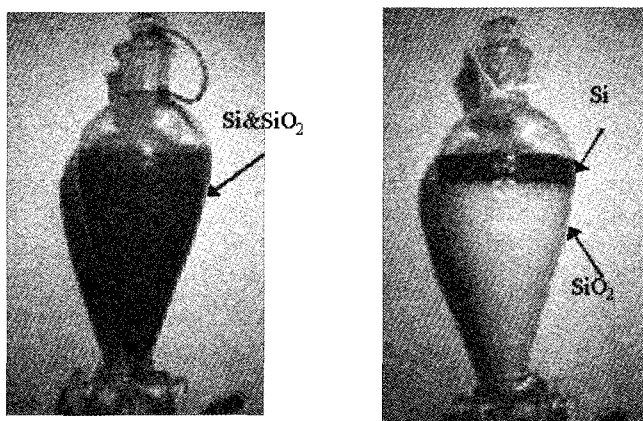

Figure 8   Pictures of the mixed particles of Si and SiO_2 in separating funnel after shaking for 10 minutes (a) without using organic phase and (b) using n-butanol phase in water phase.
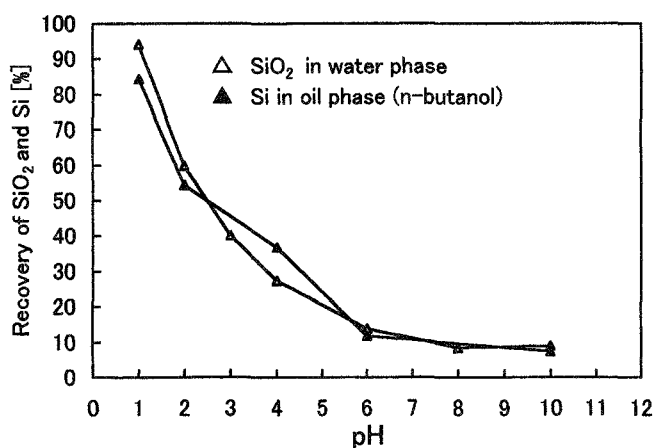

Figure 9   Recovery of Si in n-butanol phase and SiO_2 in water phase containing 150 mg/l of DAA as a function of pH.

n-butanol phase and the SiO_2 particles in the water phase of a separating funnel. The each fraction is collected separately and the particles are filtrated, dried and weighted. The separation results are measured by counting the particle numbers under the optical microscope. As results, the 100% grade has been obtained at pH1 by using n-butanol. The recoveries of Si in n-butanol phase and Si O_2 in water phase containing 150 mg/l of DAA as a function of pH are shown in Figure 9. At lower pH region, the higher recovery of Si and SiO_2 is obtained.

4.   Conclusion

The recycle for Si (single crystal sticked on the silica crucible) and SiO_2 (silica crucible) was investigated. After the used silica crucible was crushed and ground, Si and SiO_2 mixed powders were separated by using liquid-liquid extraction. The zeta-potentials of silicon and quartz are almost the same with negative charge at pH higher than 3. Based on the wetting characteristics of the solid surface during the liquid-liquid extraction process, the contact angles of the oil dropped into the pure water on the silicon and quartz surface were measured at various pH range. The maximum contact angle was obtained when the n-butanol was used at acidic pH range. A confirmative flow sheet was conducted for the liquid-liquid extraction to recover the quartz from the silicon by mixing 5 wt% silicon and 95 wt% quartz at the selected pH, using dodecylamine acetate (DAA) as a surfactant along with the organic solvent.

The optimal purity of quartz can be obtained by using 150 mg/l of DAA in water phase at pH1 and n-butanol as an organic separating phase. As a result, the recovery of the pure quartz was 95.6% and the grade was 100%.

References:

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