

Separation of Silicon and Silica by 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, SiO₂) crucible. The used crucible is crushed for recycling both silicon and silica in a 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 dodecyl ammonium acetate could extracted the silicon powder at high purity (97-100%) with high recovery from the silica powder in the water phase.

Introduction

Silicon single crystal grows in silica (SiO₂) 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 reported¹⁾ 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.

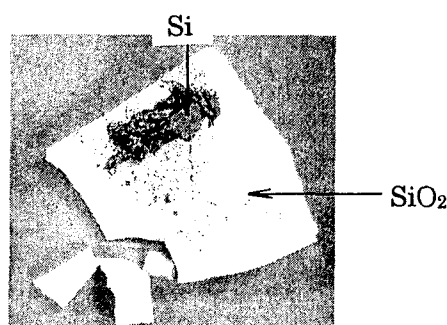


Fig.1 A small amount of Silicon fixed on the silica crucible.

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 Fig.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 SiO₂ particles were measured by the microelectrophoresis. Fig.2 shows that zeta potentials of both Si and SiO₂ were almost the same with increasing negative charges at pH higher than 3. Therefore, Si could not be separated from SiO₂ the flotation using conventional surfactant.

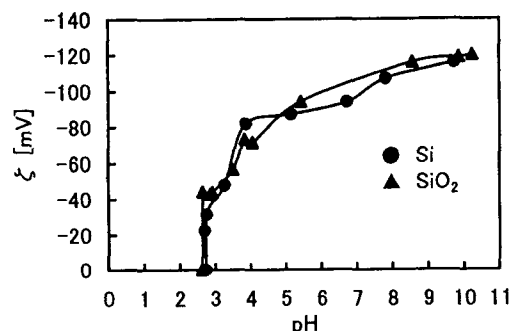


Fig.2 Zeta potentials of silicon (Si) and silica (SiO₂) as a function of pH.

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 apparatus shown in Fig.3 has been employed to measure the contact angles of several organic solvent droplets and air bubble on the samples in water. The larger the contact angle θ is observed between the solid sample surface and organic oil drop, the better the tendency for the oil to be stacked to the solid particles. 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.

The physical properties of organic solvents and water are listed in Table 1. The measured contact angles of organic droplets (n-butanol, n-pentyl acetate, iso octane) and air bubble on the silicon or quartz plate as a function of water pH are shown in Fig.4. 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. 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 2 and 3, respectively²⁾. According to Table 2, n-butanol is the easiest one to adhere to silicon surface, because of its smallest absolute value of spreading coefficient and lower adhesion tension³⁾. The lower adhesion work means that n-butanol is easier to adhere on the silicone surface. The adhesion tension of n-butanol is the lowest as compared to that of n-pentyl acetate and iso-octane. Moreover, the silicon surface shows more oleophobic affinity than quartz as comparing the numbers between Table 2 and 3.

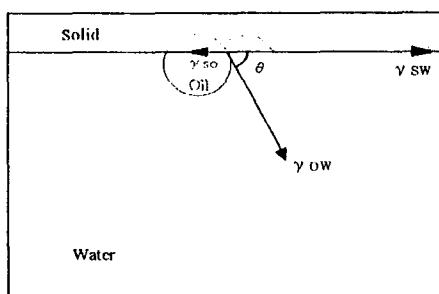
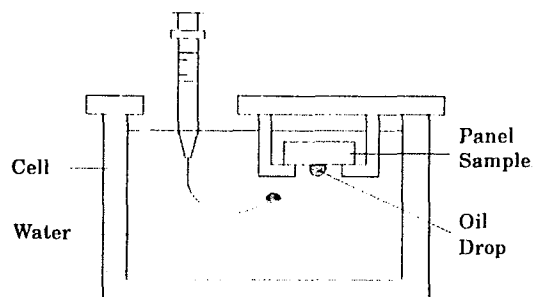


Fig.3 The apparatus for measuring contact angle of oil droplet on solid in water.

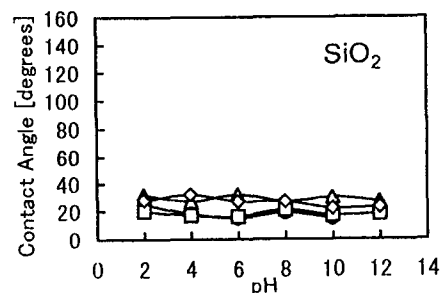
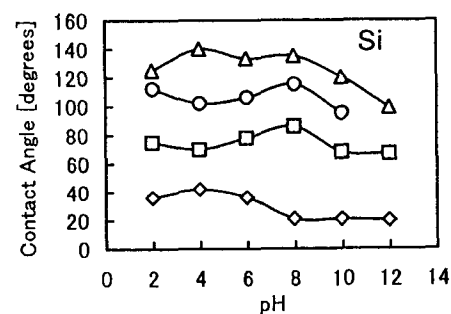


Fig.4 Contact angles of three kinds of organic droplets on the silicon and quartz surfaces as a function of pH.

Table 1. Physical properties of organic solvent and water.

Solvent	Sp.gr (g/cm ³)	Viscosity At 20°C (cp)	Surface Tension (dyne/cm)	Solubility(wt%) O in W W in O (20°C)	
n-butanol	0.810	2.950	24.6	7.8	20.00
Iso-octane	0.692	0.504	18.8	0.00	0.005
n-pentyl acetate	0.875	0.924	25.7	0.17	1.15
Water	0.998	1.002	72.8		

Table 2. Calculated interfacial free energy for organic phase droplet and air bubble on the silicon surface in water at pH4.

Oil or gas phase in water	Interfacial Tension(20°C) (dynes/cm)	Contact Angle (degrees)	Adhesion Work of oil (ergs/cm ²)	Cohesion Work of oil (ergs/cm ²)	Spreading Coefficient of oil on solid	Adhesion Tension (dynes/cm)
n-butanol	1.5	140	2.7	3.0	-0.4	-1.1
n-pentyl acetate	15.0	102	18.1	30.0	-11.9	-3.1
Isooctan	40.8	70	26.9	81.6	-54.8	14.0
Air bubble	72.8	46	22.2	145.6	-123.4	50.6

Table 3. Calculated interfacial free energy for organic phase droplet and air bubble on the quartz surface in water at pH4.

Oil or gas phase in water	Interfacial Tension(20°C) (dynes/cm)	Contact Angle (degrees)	Adhesion Work of oil (ergs/cm ²)	Cohesion Work of oil (ergs/cm ²)	Spreading Coefficient of oil on solid	Adhesion Tension (dynes/cm)
n-butanol	1.5	29	0.2	3.0	-2.8	1.3
n-pentyl acetate	15.0	18	0.7	30.0	-29.3	14.3
Isooctan	40.8	17	1.8	81.6	-79.8	39.0
Air bubble	72.8	32	11.1	145.6	-134.5	61.7

The oleophobic affinity tests for n-butanol on Si and SiO₂ particles in whole pH range of water are shown in Fig.5. 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 dispersed well 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 Fig.2. Even if

the contact angle of n-butanol on Si is high at alkaline region as shown in Fig.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 SiO₂ in water phase in alkaline region decreases the separation speed and causes the contamination into organic phase. Moreover, Table 3 suggests the possibility that some silica particles at pH 4 moves to organic phase in n-butanol as comparing to Table 2. In the experiment of oleophobic affinity tests for n-pentyl acetate and

iso-octan on Si and SiO₂ particles for various pH range of water shows the similar results.

The 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 Fig.6. As DAA concentration is higher than 150 ppm, the silica particle surface charge at pH1 is positive as estimated in Fig.2. It will adsorb DAA as a double layer and disperses well in water. Thus, the contact angle on silica surface may be reduced at pH1²⁾. Therefore, the silica particles are well dispersed and remain in aqueous phase.

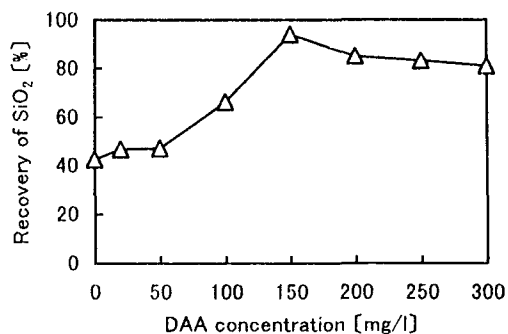


Fig.6 Effects of DAA concentration at pH1 of aqueous phase on the recovery of SiO₂ into water phase for the n-butanol by liquid-liquid extraction.

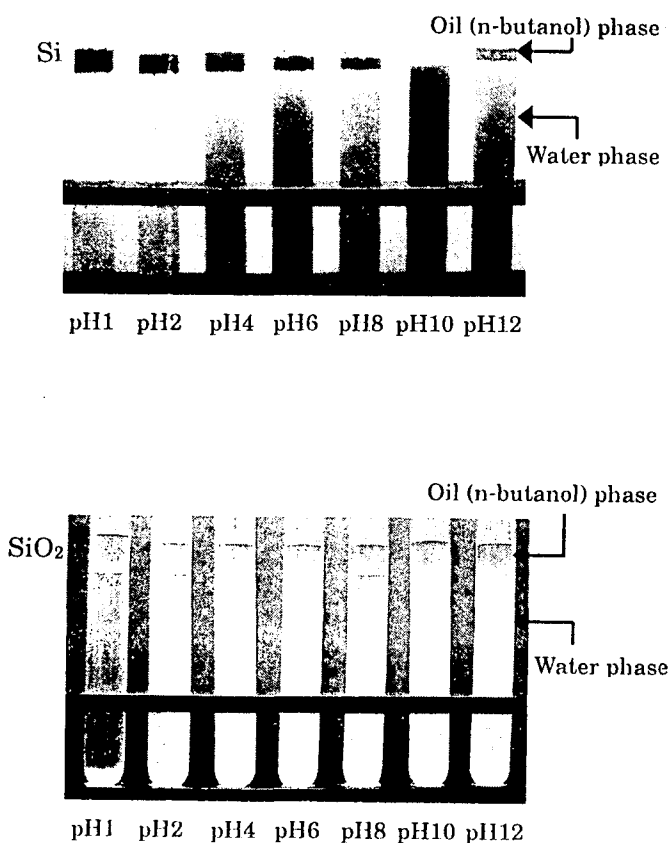


Fig.5 Oleophobic affinity test of Si and SiO₂ for n-butanol in various pH range of water.

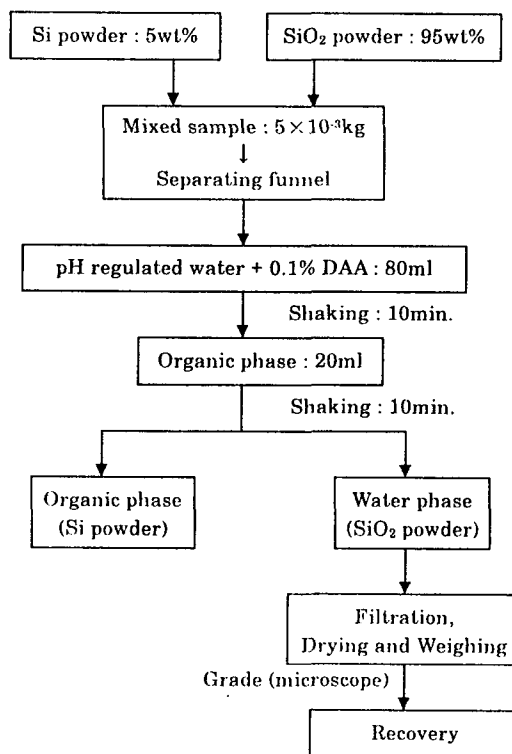
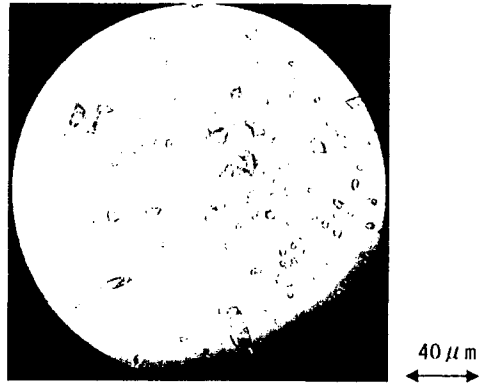


Fig.7 The flow sheet of liquid-liquid extraction for the separation of Si and SiO₂ mixed particles.

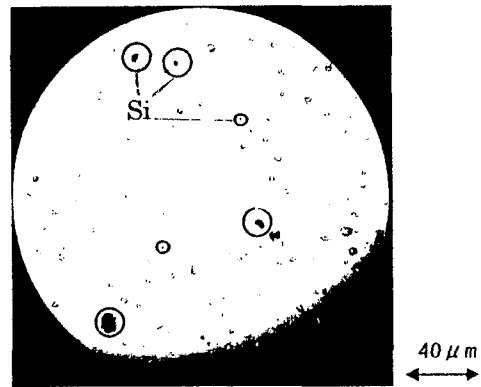
Suggested Flowsheet:

The flow sheet of liquid-liquid extraction for the separation of Si and SiO₂ mixed particles is shown in Fig.7. Silicon powder in 5wt% and silica powder in 95wt% 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, Fig. 8 shows the Si particles in the n-butanol phase and the SiO₂ 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.

The separated particles are shown in Fig.9. The 100% grade has been obtained at pH1 by using n-butanol and 97% grade at pH2. The recoveries of Si in n-butanol phase and SiO₂ in water phase containing 150mg/l of DAA as a function of pH are shown in Fig.10. At lower pH region, the higher recovery of Si and SiO₂ are obtained. Especially at pH 1 the grade and recovery are largest as shown in Fig. 8 and 9.



n-butanol, pH1, DAA150mg/l
SiO₂ : grade 100%



n-butanol, pH2, DAA150mg/l
SiO₂ : grade 97%

Fig.9 The photographs of separated particles in water phase containing 150mg/l DAA at pH1 and pH2 by the separation using the n-butanol as organic phase.

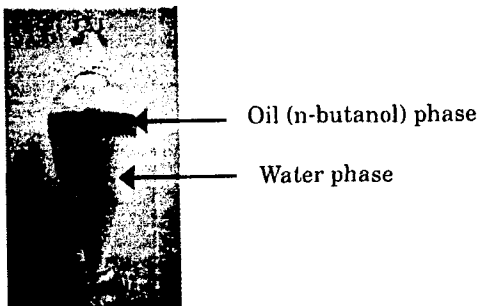


Fig.8. Si particles in n-butanol phase and SiO₂ particles in water phase of the separating funnel.

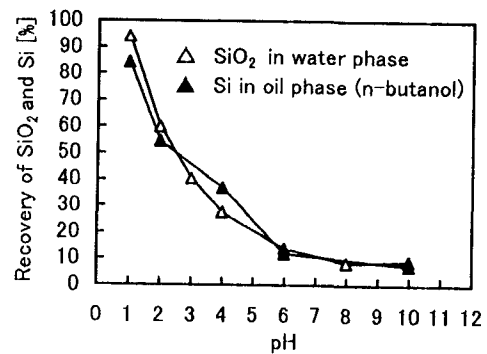


Fig.10 Recovery of Si in n-butanol phase and SiO₂ in water phase containing 150mg/l of DAA as a function of PH.

Conclusion

The recycle for Si (single crystal stucked on the silica crucible) and SiO₂ (silica crucible) was investigated. After the used silica crucible was crushed and ground, Si and SiO₂ 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 silicon in 5wt% and quartz in 95wt% 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 ppm 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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