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PURIFICATION OF SILICON THROUGH TRANSPORT REACTIONS

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PURIFICATION OF SILICON THROUGH TRANSPORT REACTIONS

[Following is the translation of an article by R. Lesser and E. Erben entitled "Ueber die Reinigung von Silicium durch Transportreaktionen" (English version above) in Zeitschrift fuer anorganische und allgemeine Chemie (Journal of Inorganic and General Chemistry), Vol. 309, No. 5-6, pages 297-303.]

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Summary

The purification of silicon by the transport reactions studied in greater detail by H. Schaefer was studied by quantitative-analytical methods. A sometimes considerable diminution of the impurity quantities could be established. The paper also describes an apparatus with which the purification of silicon can be accomplished in a simple procedure. In this process, the silicon powder is treated with iodine vapor at a certain pressure at 1150°C in a turbulence layer.

* * *

The generally high interest in pure silicon prompted us to make a more precise quantitative study of the purification effect that H. Schaefer [1-4] predicted and observed for the extremely elegant silicon transport-reaction process.

Silicon Transport by the Chloride Process

Chemical transport reactions presuppose the existence of temperature-dependent equilibria in a system. Thus, the transport of silicon in the so-called chloride process follows the formula

$$SiCl_4 + Si \underset{T_1}{\overset{T_2}{\rightleftharpoons}} 2\,SiCl_2. \qquad (1)$$

The equilibrium [illegible] to the right at higher temperatures (T_2) and to the left at lower temperatures (T_1). Here, the transport of silicon proceeds from a warmer to a colder reaction space. Of decisive significance in this process is the fact that the impurities of the original silicon are transported with it in extremely variable proportions. Preliminary calculations for the purification effect that can be expected have been carried out by Schaefer. In many cases, however, they are virtually impossible, since a number of factors that are difficult to pin down – such as the diffusion rates of the impurities in the silicon and the lack of the necessary thermodynamic bases – frequently p[illegible] only uncertain conclusions.

For this reason, we investigated the purification effect by the methods of quantitative analysis. In view of the difficulty of carrying out analyses for trace impurities in silicon, we began the work with relatively impure silicon in order to obtain that much more certainty in the analytical results. Since, however, the purification factor is to a major degree independent of the quantity of impurities in the original material, a correspondingly higher purity is obtained in the transported silicon when material of higher purity is used.

We used commercial (Merck) silicon powder of technical purity (about 98 per cent Si) as the starting material. The powder was fused under high vacuum in quartz-glass (Herasil) crucibles in order to obtain a grain size suitable for our experiments. The silicon was crushed after cooling and the desired grain-size fraction (0.5-1.0 mm) was screened out, washed several times with hydrofluoric acid, rinsed with double-distilled water, and dried at 100°. For each experiment, 10 g was placed in a quartz-glass (Heralux, Herasil, or Suprasil) tube that had been closed at one end and had an outside diameter of 27 mm and a wall thickness of 1.2-1.5 mm. At the open end, the tube had a ground-in joint by which it was connected to a high-vacuum apparatus via a T-piece. We baked the filled test-tube out for several hours at 600°C and a vacuum of 10^{-1} to 10^{-1} /sic/ Torr. The other arm of the T-piece was connected via a stopcock with a storage vessel in which silicon tetrachloride was condensed. We employed an $SiCl_4$ that is used to manufacture quartz glass of highest purity and is therefore purified with particular care. The air and HCl residues in the $SiCl_4$ storage vessel were pumped out with repeated liquid-air freezing. When the test tube had cooled to room temperature and the appropriate stopcocks had been shut and opened, we brought the $SiCl_4$ to

a temperature between 9° and 16°C and waited long enough for the corresponding partial $SiCl_4$ pressure to adjust itself through the entire apparatus. Then the test tube was melted off at a constricted point. It was then 150-200 mm long. We adjusted the temperature of the molten $SiCl_4$ or the partial $SiCl_4$ pressure before melting-off in such a way that a pressure of approximately 760 mm Hg could be expected to prevail in the tube during the transport experiments. The $SiCl_4$ and $SiCl_2$ vapor pressures can be computed for the temperatures that arise. We used a Silit tube oven, in which we placed an open Pythagoras tube, to produce the temperature gradients. Here, the reaction tube was lowered to a depth corresponding to the required temperature gradient. We shut the oven off after a transport period of 20-24 hours and removed the reaction tube after cooling.

We conducted the transport experiments with the following three temperature gradients: a) 1000 – 800°C; b) 1300 – 1100°C; c) 1400 – 1200°C.

a) The transport effect is extremely weak with the 1000 – 800°C temperature gradient. The reaction tube was perfectly clear after the experiment and showed only a thin coating weighing a few milligrams at its cooler end. The small quantity of transported silicon made analytical investigation impossible.

b) The transport effect is quite noticeable with the 1300 – 1100°C temperature gradient. About 10 per cent of the original amount had been deposited at the cooler end after an experimental period of about 24 hours. The reaction tube was somewhat clouded only at the hot end. For the most part, the transported silicon took the form of nicely crystallized needles, as can be seen from Figs. 1 and 2. The silicon was cautiously removed mechanically after the tube had been cut open and was carefully separated from the quartz fragments that tended to adhere to it. After treatment with aqua regia and double-distilled water, it was dried and used for the analytical investigations. As can be seen from the analytical results listed in Table 1, the quantity of impurities had been sharply reduced. Thus, for example, the transported silicon retains only 330 ppm of iron (about 5 per cent of the starting concentration) and 2 ppm of copper (about 2 per cent of the starting concentration). The boron content of the condensate was likewise noticeably reduced at 0.18 ppm.

c) The transport effect with the 1400 – 1200°C temperature gradient was about equal to that observed with 1300 – 1100°C. On the other hand, the reaction tubes had

Fig. 1. Reaction tube after transport experiment at 1300 → 1100°C.

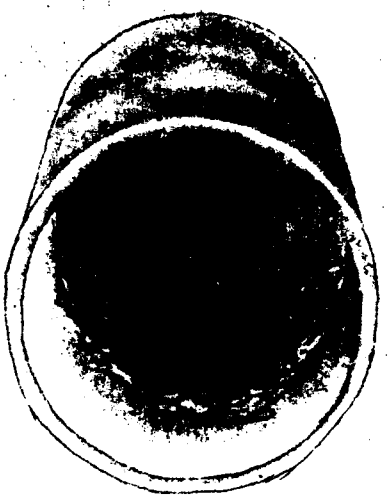

Fig. 2. Cut-open reaction tube. Appearance of transported silicon after transport experiment with 1300 → 1100°C.

been severely attacked and clouded. It became apparent when the tubes were opened that the transported silicon had condensed to form a thick wall coating, predominantly grey in color but brown to blue-grey in places.

The results of the analyses run on this transported silicon are presented in Table 1. It is seen that the purification effect is again quite noticeable. As compared to the experiments at 1300 – 1100°C, further decreases have occurred in the contents of some of the impurity elements, e.g., in the case of iron, from 5 per cent to 2 per cent, referred to the starting concentration. On the other hand, the copper content, for example, increases from 2 per cent to 22 per cent of the starting concentration. Silicon analyses gave values between 94 per cent and 98 per cent for this silicon. Since only a small fraction of the metallic impurities of the starting silicon were co-transported, the relatively low silicon content indicates a high degree of oxygen contamination. The oxygen is primarily transported from the hot to the cold zone through the SiO that forms when the silicon reacts with the quartz

TABLE 1

Results of Analysis

	Si %	Fe ppm	Al ppm	Ca ppm	Cu ppm	Bi ppm	Pb ppm	B*) ppm
(a) Si-Ausgangsprodukt	98,9	6500	2200	283	109	23	13	0,96
(b) Si-Endprodukt Chloridverfahren 1300 → 1100 °C	99,5— 99,9	330	460	202	2	< 1	2	0,18
(c) Si-Endprodukt 1400 → 1200 °C Chloridverfahren	94—98	109	90	40	24	2	2	—
(d) Si-Endprodukt Jodidverfahren	99,9	355	184	180	1	3	2	0,59

*We are deeply indebted to Herr Dr. Spenke, Siemens-Schuckert-Werke AG, Pretzfeld, for running the boron analyses.

a) Initial Si product; b) Final Si product, chloride process, 1300 → 1100°C; c) Final Si product, 1400 → 1200°C, chloride process; d) Final Si product, iodide process.

glass wall. This transport is strongly pronounced at a hot-zone temperature of 1400°C.

It proceeds from the results of our experiments that the usable working temperatures for purification of silicon occur between 1000 and 1300°C. Virtually no silicon is transported below 1000°C, and the SiO formations that occur above 1300°C result in a significant oxide content in the transported silicon. Some of the metallic-impurity contents decline appreciably in work with the chloride process, so that a silicon of quite respectable purity can be produced.

The Iodide Process

In contrast to the chloride process, two equilibria are of decisive importance in the iodide process:

$$SiJ_4 + Si \underset{T_1}{\overset{T_2}{\rightleftharpoons}} 2\,SiJ_2. \qquad (2)$$

$$Si + 2\,J \underset{T_2}{\overset{T_1}{\rightleftharpoons}} SiJ_2. \qquad (3)$$

Translator's note: J = I (iodine).

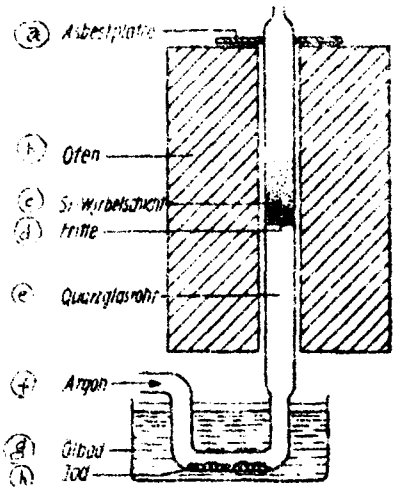

Fig. 3. Experimental arrangement for purification of silicon by iodide process. a) Asbestos plate; b) oven; c) Si turbulence layer; d) frit; e) quartz-glass tube; f) argon; g) oil bath; h) iodine.

The equilibrium (2) corresponds to that of the chloride process, while equilibrium (3) does not arise in the chloride process under normal working conditions, because $SiCl_2$ has a considerably larger energy of formation than SiI_2.

Reaction (2) is endothermic, i.e., the higher the temperature, the greater the displacement of equilibrium toward the right. Reaction (3) is, on the other hand, exothermic, so that the equilibrium goes farther to the left at higher temperatures. Now since both reactions are further accompanied by a change in the number of moles present and are therefore pressure-dependent, we can account for the following phenomenon, which is known as transport reversal: if we place the silicon and a relatively large quantity of SiI_4 in a quartz-glass tube, seal it, and produce a temperature gradient from 1150 to 950°C, the silicon in the hot zone migrates toward the colder zone, as in the chloride process, because equilibrium (2) predominates due to the high iodide pressure. Now if we lower the iodide pressure down to a critical value, the migration ceases, because now the transport in the direction of the hot zone in accordance with Eq. (3) is in process and the transport after Eq. (2) is offset. As the pressure is lowered further, the transport direction is actually reversed and the

silicon in the cooler zone now migrates toward the hot zone. The critical pressure – that at which transport reversal occurs – is about 65 Torr SiI_4 with this temperature gradient.

We started with the following experimental arrangement (Fig. 3) to make practical use of the transport-reversal effect in a simple manner.

We placed silicon having a grain size of 0.1 mm in a vertical quartz-glass tube with a fused-in large-pored frit. We used the same silicon as in the chloride process. Then we passed argon through the tube at a flow rate sufficient to keep the silicon on the frit in flowing motion. The argon first passed through an iodine-filled vessel and became saturated with iodine vapor in the process. Next, the flow zone was heated to 1150°C and the temperature of the iodine supply vessel adjusted in such a way that the SiI_4-pressure in the flow zone would be about 50 Torr.

Because the iodine pressure is too low, the silicon cannot be transported away from the flow zone in accordance with Eq. (2), since this zone is simultaneously the hottest point of the entire system. Nor can it be carried away in accordance with Eq. (3), since it is already at the hottest point. Consequently, no transport occurs, but only slow recrystallization of the silicon through the gaseous phase, which is accompanied by extensive removal of impurities.

The yield after an experimental period of 20 hours is nearly 90 per cent. A loss does occur, primarily because slight abrasion of the silicon takes place in the flow zone, producing fine particles that are carried out of the zone by the argon. Furthermore, some silicon invariably escapes as the iodide in accordance with the equilibria. The quartz-glass tube was attacked to some degree by erosion of the silicon powder during the experiments and clouded by the recrystallization. It was replaced after 100 working hours.

The use of a flow zone or turbulence layer provides a guarantee that the iodine will work unhindered and quite uniformly on all zones of the silicon powder. The results of quantitative analysis of samples that had been treated for 20 hours in each case are presented in Table 1. Again we observe a very sharp decline in some of the impurity contents, e.g., to 5 per cent of the quantity present in the original silicon in the case of iron and to 1 per cent in the case of copper. Even the boron content declined markedly. It is possible to reduce the impurities significantly more sharply by the use of longer experiment times. Moreover, the use of purer initial products under the same experimental conditions will naturally result in purer end products, so that it is possible to produce semiconductor-quality silicon with

good yields when all of the possibilities offered by the iodide process are completely exhausted.

Analytical Procedures

Analysis of the starting and transported silicon was carried out as follows:

a) For the silicon determination, the substance was dissolved in dilute potassium hydroxide solution and the silicic acid precipitated with hydrochloric acid and volatilized by the familiar hydrofluoric-acid procedure.

b) The iron and aluminum contents were determined gravimetrically and photometrically. For this purpose, the specimen was treated with hydrofluoric acid and nitric acid and the residue evaporated with sulfuric acid and absorbed in acidified double-distilled water. For the gravimetric determination, we co-precipitated the iron and aluminum in hydroxide form and weighed out the sum of the oxides. From this, we next determined the iron colorimetrically as the ferrocyanide and thus obtained the aluminum content indirectly. When small quantities were present, the iron and aluminum were determined directly by photometric means, the iron as the cyanide and the aluminum with eriochromcyanin [5].

c) For the calcium determination, the specimen was treated, as described above, with hydrofluoric, hydrochloric and sulfuric acids and the residue taken up with water and the calcium precipitated as the oxalate from a solution that had been weakly acidified with acetic acid. The oxalate was filtered and calcined. We absorbed the calcining residue with a small amount of hot water and determined the calcium complexometrically.

d) We determined the copper, bismuth, and lead with dithizon [6] after removal of the silicon by the procedure described above.

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