Purification of Silicontetraiodide by Zone-refining Process

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In spite of the superior properties of silicon as a semiconductor material, the electronic devices such as silicon transistors or power rectifiers have not been fully developed. One of the causes of this comes from the fact that the techniques of purification of this material are more difficult than those of germanium. The refining process of silicon would have to choose another direction from that of germanium especially in its chemical purification steps. Moreover, elementary silicon is so chemically active in its molten state that the zone refining can not be carried out in the same way as in the case of germanium. For these reasons, chemical purification is important to obtain a highly pure silicon.

Several methods have been presented for obtaining transistor grade silicon(1-4), but among them, the so called du Pont method is the most predominant in the industrial aspect at present. On the other hand, we expect that the silicon iodide method will be one of the promising ones for improving the purification processes. First of all, the most important problem is the methods of removing impurities in silicontetraiodide. Of course, the usual refining processes such as recrystallization, distillation and sublimation are also applicable in this case, but in addition to them, the zone-refining process, which has been proved excellent for the purification of germanium(5), may be applied to this compound. But the behavior of impurity elements in the iodide during this process has not been made clear. As some elements such as boron, phosphorus and arsenic are removed with difficulty by the zone-refining of elementary silicon(6), it is preferable to remove them from it beforehand. For this reason, we studied the behavior of a trace of boron and phosphorus in silicontetraiodide during the normal freezing and zone-melting of the material.

Recently, Rubin et al. studied the zone-melting of silicontetraiodide and they determined the segregation coefficients of several elements by spectrographic analysis(7). But as they pointed out, the concentrations of impurities at the top of the charge were too far below the limits of spectrographic detection for some elements to make clear the details of the impurity distribution through the charge.

Experimental Results

Behavior of Phosphorus in Silicontetraiodide.—*a*) *Preparation of radioactive phosphorusiodide.*—Radio isotope ^{32}P is conveniently used to trace the behavior of phosphorus during the zone melting process of silicontetraiodide. Phosphorus in silicontetraiodide will not be present in its elemental state but will exist as some iodine compounds such as diphosphorus tetraiodide or phosphorus triiodide. Radio isotope ^{32}P can easily be produced by deuteron radiation. But neither kind of phosphorus, red or yellow, can be irradiated in the cyclotron because of its high vapor pressure. In order to avoid these difficulties, it is preferable to use some phosphorus alloy. Pure copper foil with 99.96% purity and 0.2 mm. thick was vacuum-sealed with red phosphorus in a quartz tube, and was heated at 300°C for about ten hours in a furnace. During this heat treatment, the phosphorus diffused into copper and the surface of the foil turned silver white in color. This alloy was irradiated by deuteron in cyclotron to make it radioactive.

The thus activated Cu—P alloy was treated with toluene containing iodine at its boiling point for about two hours to dissolve out the activated phosphorus, and labeled phosphorusiodide could be obtained. A little portion of activated copper was accompanied with phosphorusiodide in solution forming copper iodide, but the influence of γ rays emitted from ^{64}Cu could be neglected in measuring β rays emitted from ^{32}P using a Geiger counter. Toluene solution containing radioactive phosphorusiodide was added to crystalline siliconiodide and it was dissolved completely by the addition of boiling toluene. Then it was cooled at 0°C for several hours to crystallize out

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the silicon iodide contaminated with radioactive phosphorus.

b) Measurement of phosphorus distribution by the radiochemical method. — *Segregation Experiments.* — The thus prepared silicon iodide was sealed in a quartz tube of 15 mm. diameter and 30 cm. length under reduced pressure. The content was melted by heating uniformly and cooled rapidly so that no segregation of the impurity would occur and was followed by the measurement of the initial distribution of ^{32}P. As shown in Fig. 1, the tracer was distributed uniformly throughout the rod. The content was melted again completely in a furnace which was long enough to melt it uniformly, then the quartz tube was moved down with a speed of 2.2 mm. per minute. The melted silicon iodide was solidified from the top portion outside of the furnace gradually. As a little part of the silicontetraiodide was hydrolyzed by atmospheric moisture, the melted portion of silicon iodide became somewhat turbid. But hydrolyzed products were easily segregated and transferred toward the upper part of the rod.

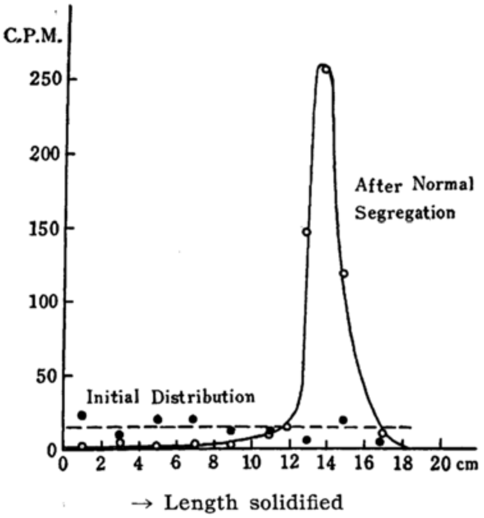

Fig. 1. Distribution of phosphorus after normal freezing.

The distribution of phosphorus after normal segregation could be found by measuring the radioactivity of β-rays emitted from ^{32}P at every 10 mm. length of the rod using a sealing device. The results are shown by curve 2 in Fig. 1 by plotting the counting rate against the distances from the top of the rod.

This method was convenient to carry out the experiment of segregation or zone melting processes, because repetition using the same sample was possible. But the selfabsorption by silicontetraiodide and the absorption by quartz wall made the counting rate less, and when the iodide changed its phase, liquid to solid and vice versa, local strong strength sometimes broke the quartz tube.

These troubles could be avoided by using a quartz boat instead of a tube as shown in Fig. 2. In this case, dried argon gas was introduced gently from the top of the boat to carry the evaporated iodide toward the end of the boat. After normal segregation or zone refining processes, the rod of silicon iodide was taken off from the boat and cut into about ten segments, and each

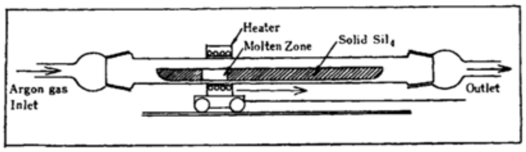

Fig. 2. Zone melting of silicontetraiodide.

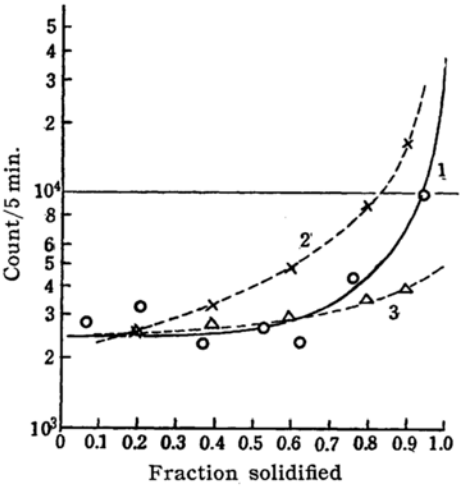

Fig. 3. Distribution of phosphorus in silicontetraiodide after normal segregation.

1. Experimental Result
2. Calculated $k=0.1$
3. 〃 $k=0.8$

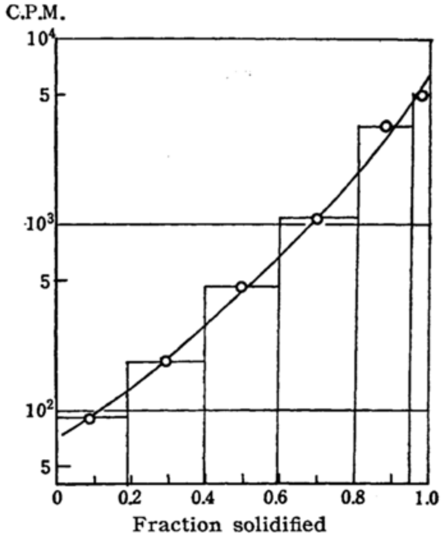

Fig. 4. Distribution of phosphorus after three passes of molten zone.

of them was weighed quickly avoiding the hydrolysis by the atmospheric moisture. Then they were hydrolyzed in a quartz evaporating dish by adding distilled water and dried up on a hot plate. The radioactivity of the samples thus obtained was measured by a Geiger counter.

The results are shown in Fig. 3. Curve 1 indicates the distribution of phosphorus after normal segregation with a velocity of 2.5 mm./min., and Fig. 4 shows the result of zone refining of three passes with a velocity of 0.83 mm./min. In both cases the counts of one gram of hydrolyzed products per five minutes were plotted against a solidified fraction of the iodide bar.

Behavior of Boron in Silicontetraiodide.—*Determination of boron by colorimetric method using curcumin.*—As it is impossible to trace the behavior of boron by using its radioisotope because of its short half life, there is no way but chemical analysis for this purpose. The colorimetric method using curcumin seemed to be the most satisfactory.

Several reports have been published on the determination of boron by this method[8-11]. But some of them have poor reproducibility, because coloring conditions, such as the concentration of the reagents, the time of treating, the evaporation temperature and the dissolving method of formed curcumin-boron complex, affect the results significantly.

Reagents.—*a*) *Curcumin-oxalic acid solution.*—Dissolve 5.0 mg. of crystalline curcumin and 0.5 g. of recrystallized oxalic acid in 50 ml. of redistilled ethanol. This solution was prepared freshly immediately before use and kept cold.

b) *Boron standard solution.*—Dissolve 0.1430 g. of boric acid (extra pure grade) in 500 ml. of redistilled water. Dilute 5.0 ml. portion of this stock solution to 500 ml. (the boron content will be 0.5 γ per ml.).

Standard Reference Curves.—Taking zero to 5.0 ml. of the standard boron solution in quartz evaporating dishes, 1 ml. of hydrochloric acid (1 : 1) and 2 ml. of curcumin oxalic acid solution were added, then they were diluted with distilled water to make the total volume 8 ml. These evaporating dishes were floated on a water bath which was kept at 55±2°C until the contents were dried up. The evaporation could be accelerated by the aid of a gentle air flow on the liquid surface. Ten ml. of ethanol was added to each dish to dissolve the residue, and the solution was transferred to an absorption measurement cell of 10 mm. length. The absorbancy at 540 mμ was measured using a spectrophotometer.

As shown in Fig. 5, curcumin solution itself has absorption maximum at 430 mμ, while boron complex has its maximum at 540 mμ. The curcumin-boron complex is rather stable and no detectable change was observed after several hours as shown in this figure. Beer's law plot is shown in Fig. 6. It was necessary to make blank tests on each sample in order to minimanize the fluctuation of the results.

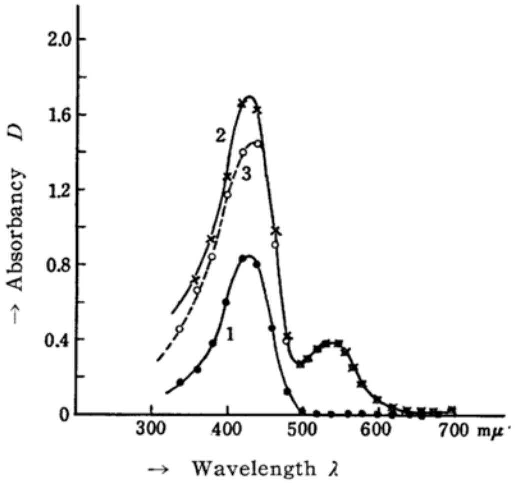

Fig. 5. Light absorption curves of curcumin-oxalic acid solution and curcumin-boron complex.

1. Curcumin solution
2. Curcumin-boron complex (initial absorption)
3. Curcumin-boron complex (after 17 hr.)

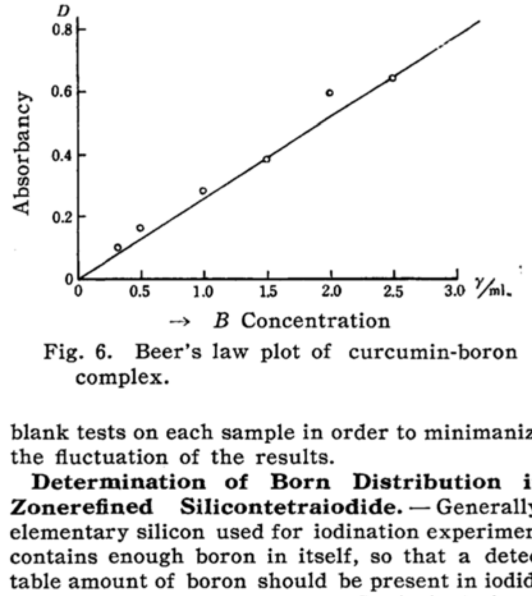

Fig. 6. Beer's law plot of curcumin-boron complex.

Determination of Born Distribution in Zonerefined Silicontetraiodide. — Generally, elementary silicon used for iodination experiment contains enough boron in itself, so that a detectable amount of boron should be present in iodide without adding any on purpose. So the hydrolyzed product used for activity measurement of ^{32}P could be used for the determination of boron. About 10 ml. of distilled water was added to the sample and it was heated gently in a quartz evaporating dish to extract the boron into solution as boric acid. Then it was filtered and the precipitate of silicon dioxide on filter paper was washed several times with warm water to remove the boron compound completely. The filtrate was evaporated by heating in a quartz evaporating dish to about 5 ml. Using this solution, boron was determined as described above.

Curve 1 in Fig. 7 shows the distribution of

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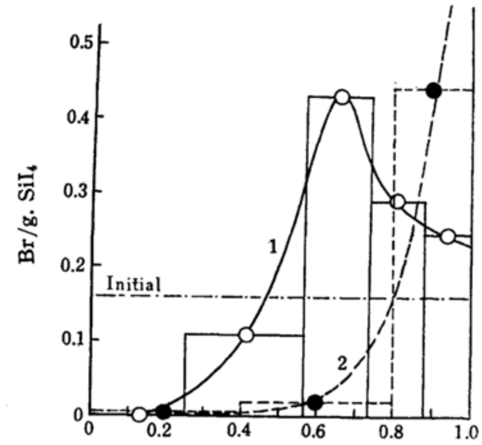

Fig. 7. Distribution of boron after zone refining with different moving speed.
1. Six passes (2.4 mm./min.)
2. Three passes (0.83 mm./min.)

boron after six passes of single zone with a moving speed of 2.4 mm. per min., and curve 2 shows that of three passes with a speed of 0.83 mm./min. In both cases the width of the molten zone was about 20 mm.

Consideration of the Results

Several studies have been reported on the segregation effect of the binary solution of metals. The zone purification method was developed from this principle by Pfann, and the behavior of impurity elements in semiconducting materials has been made clear by many workers. It is well known that the distribution of impurity concentration throughout the ingot after normal segregation is expressed by the equation[5)]

$$C=kC_0(1-g)^{k-1} \qquad (1)$$

In this equation, g represents the solidified fraction, C_0 the initial concentration, C the impurity concentration at a point g, and k the distribution constant defined by the ratio of impurity concentration in solid to that in liquid. In the case of segregation of phosphorus in silicontetraiodide this equation may be also applicable. Let k be equal to 0.1 and 0.8, the distributions of phosphorus throughout the iodide bar are represented by curve 2 and 3 respectively in Fig. 3. Comparing these curves with experimental results, it can be said that the results can not be represented by the above equation, but it consists of two different k values. As colloidal silicon dioxide produced by the hydrolysis of tetraiodide has a tendency to adsorb phosphorus as well as some other trace impurities, it is reasonable to consider that a part of phosphorus will be adsorbed by the colloidal silicon dioxide and segregated together. For the reason given above, the beginning portion of the curve shows a large k value corresponding to the distribution constant of phosphorus itself, and the end portion of the curve shows a small k value which corresponds to that of the hydrolyzed product. In this case, the segregation equation can be written as

$$C=C_0\{k_1(1-g)^{k_1-1}+k_2(1-g)^{k_2-1}\} \qquad (2)$$

Curve 1 and 2 in Fig. 8 show the distribution of solute assuming $k=0.1$ and $k=0.8$ respectively. Curve 3 shows the result of calculation from Eq. 2 using $k_1=0.1$ and $k_2=0.8$. C_0 is unity in each case. The resultant curve 3 shows good correspondence with experimental results.

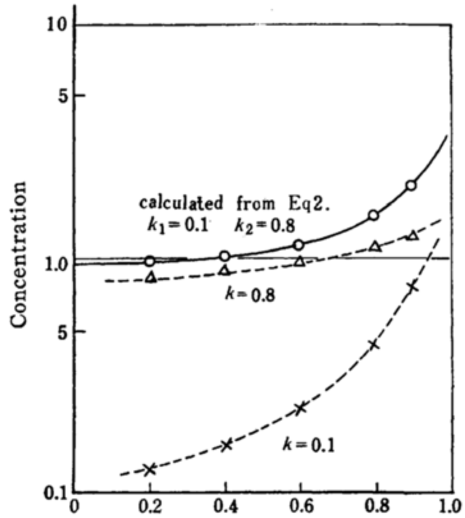

Fig. 8. Resultant distribution calculated from Eq. 2. $k_1=0.1$ $k_2=0.8$

The results of the zone refining process showed a promising effect to remove phosphorus after three passes of single zone, for instance, the concentration could be decreased one tenth of the initial amount at the top portion and the ratio of concentration of phosphorus at the end and the top parts of the bar reached three powers of ten.

As for boron, the results were not so distinct as in the cace of phosphorus, but better refining efficiency could be expected by this process than in the case of its elementary state.

Summary

The behavior of phosphorus and boron as impurity elements in silicon tetraiodide was studied during the normal segregation and zone melting processes. Both of them can be removed efficiently by this process, and it is considered that the colloidal hydrolyzed product suspended in silicon tetraiodide plays a predominant role for segregation because of its high adsorptivity to these elements. The distribution curve of radioactive phosphorus seems to show the influence of this material.

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