Neutron Activation Analysis of Iodine in Silicon

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The determination of trace impurities in silicon is of great importance in the research and industry of the semiconductor material. The neutron activation analysis has played an important role in this field, being used for many kinds of impurity and even in routine work[1]. Among the numerous reports, however, none, as far as listed in the "*Analytical Abstracts* (Society for Analyt. Chem. England)" up to Vol. 6 No. 3 (March, 1959) has dealt with halogens in silicon, though the semiconductor material has been purified through one of its halogen compounds. The present authors determined iodine in silicon purified by the iodide or the chloride method.

Natural iodine consists entirely of ^{127}I, which is activated by thermal neutrons into ^{128}I [σ=6 barn, $T_{1/2}$=25 min., β 2.12 (76%), etc., γ 0.45 (17%) etc.]. When more than a few p.p.m. of iodine is present with outany other appreciable amount of impurity that emits γ-rays or positrons, the γ-ray spectrometry with a multi-channel pulse-height analyzer provides an easy method for quantitative analysis[2]. But when the iodine content is lower, chemical separation becomes necessary, because the photo-peak of ^{128}I is masked by the "Bremsung" of β-rays from ^{31}Si ($T_{1/2}$=2.62 hr., $E_{\max}$=1.48 MeV.).

The separation method must be checked carefully, because iodine has many oxidation states, which involve complicated behavior of isotopic exchange, and because, molecular iodine as well as hydrogen iodide is volatile. The treatment of silicon with a mixture of hydrofluoric and nitric acid, a suitable process for many cases, cannot be used here. On the other hand, there is an advantageous rule that any kind of iodine oxide, at least in an ordinary concentration, reacts instantaneously and stoichiometrically with an excess of iodide in an acid solution to give molecular iodine. Fusion of the silicon with potassium hydroxide containing potassium iodide as the carrier, followed by treatment with sulfuric acid, and oxidation with sodium nitrite to molecular iodine, provides a method of chemical separation, the last being distilled and converted into silver iodide. Its usefulness was checked by the use of ^{131}I produced carrier free in silicon by the neutron irradiation of tellurium diffused in the silicon.

Experimental

Sample.—About 1 g. portion of metallic silicon, prepared by the thermal decomposition of silicon tetraiodide or by the reduction of silicon tetrachloride with zinc was used for each analysis. Details concerning each of the samples are described later.

Irradiation.—The sample and reference standard were put side by side in a poly ethylene capsule and irradiated in JRR-1 (Japan Research Reactor 1) under a thermal neutron flux of about 6×10^{11}n/cm^2·sec. The activity of ^{128}I reaches about 80% of its saturation by one hour irradiation.

Self-shielding Effect. — Thermal neutrons for which the absorption cross section of natural silicon is only 0.13±0.03 barns, traverse one centimeter in this material, thereby decreasing the flux by only less than 1%. Thus with an ordinary quantity of the sample, the self-shielding effect can legitimately be neglected.

Chemical Separation of Iodine.—The irradiated silicon was immediately powdered in a special mortar made of iron. A weighed amount (about 0.8 g.) of the silicon powder was slowly added to potassium hydroxide (about 10 g.) which is maintained just above its melting point, and contained a known quantity (several milligrams) of potassium iodide as the carrier. When the vigorous reaction with the evolution of hydrogen became feeble, the mixture was carefully heated to complete the reaction rapidly. The fused matter was treated with 100 ml. of 5 N sulfuric acid containing a few milligram of sodium chloride and potassium bromide as a hold-back carrier. A solution of sodium nitrite was added to the product, and the liberated iodine distilled into a dilute solution of sodium sulfite. This distillate was treated again with sulfuric acid and sodium nitrite, and the molecular iodine was extracted with xylene, washed with dilute sul-

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[1] B. A. Thompson et al., *Anal. Chem.*, **30**, 1023 (1958).

[2] T. Ichimiya et al., *Radioisotopes* (Jap. R. I. Association), 7, 281 (1958).

[3] For example, A. C. Wahl, "Radioactivity Applied to Chemistry", John Wiley & Sons, Inc., New York (1951), p. 32.

furic acid and water, and extracted back into an aqueous solution containing a small excess of sodium sulfite, from which silver iodide was precipitated by the addition of acetic acid, silver nitrate and nitric acid. The precipitate was filtered off through a glass filter (No. 3), washed with a very dilute nitric acid, water, ethanol and ether. The entire process required an hour, or, properly operated, slightly less, with a chemical yield of 50 to 70%.

Radioactivation Standard.—A weighed crop of potassium iodide in a polyethylene envelope was irradiated together with the silicon, and dissolved into a solution containing a known amount of inactive potassium iodide. A part of this solution was oxidized as above, and the molecular iodine extracted with xylene, washed with an aqueous potassium hydrogen sulfate and water, and similarly converted into silver iodide.

Counting.—A simple G-M counter with an end window tube served very conveniently, when the iodine content was more than 0.01 μg., while a 2π counter of gas flow type was used for less iodine. By the use of the latter, whose counting efficiency is several times higher than the former, 3/4 or more of the total disintegration could be detected by virtue of the back-scattering of the β-rays, when the sample was placed on such a heavy metal plate as tin, with negligible loss due to self-absorption. The activity was measured at short time intervals for about 150 min.

Check on the Chemical Process.—The chemical process was checked by the use of silicon containing ^{131}I, which was prepared by the irradiation of silicon doped with tellurium. The following reactions take place,

$$^{130}\mathrm{Te}\ (n,\ \gamma)\ ^{131}\mathrm{Te} \xrightarrow[25\ \mathrm{min.}]{\beta^-,\ \gamma} {}^{131}\mathrm{I} \xrightarrow[8.06\ \mathrm{d.}]{\beta^-,\ \gamma}$$

$$^{131}\mathrm{Xe}\ (\text{stable})$$

$$\text{or,}\quad ^{130}\mathrm{Te}\ (n,\ \gamma)\ ^{131m}\mathrm{Te} \xrightarrow[30\ \mathrm{hr.}]{} {}^{131}\mathrm{Te} \longrightarrow$$

$$^{131}\mathrm{I} \longrightarrow {}^{131}\mathrm{Xe}.$$

^{131}I emits various γ-rays, among which that of 0.364 MeV. is predominant, and with the irradiated tellurium the area covered by this photo-peak in the γ-ray spectrum decayed with the half-life of ^{131}I, while other peaks of lower energies due to other radioactive nuclides of tellurium (mostly of metastable state) survived longer. It would be reasonable to assume that the two radioisotopes, ^{128}I and ^{131}I, formed in the silicon, pass the so-called hot atom state and behave similarly throughout the chemical process.

Very pure silicon and a small quantity of metallic tellurium in an evacuated silica ampoule were heated over 1000°C for many hours, to cause the latter to diffuse into the former. The ampoule was kept in the reactor for a week. After several days, the silicon was washed with aqua regia and slightly etched with a mixture of hydrofluoric and nitric acids to remove surface contamination. The activity in the silicon was counted with a scintillation counter with a well-type crystal and a single channel analyzer (the region between 0.32 and 0.41 MeV.). The silicon without tellurium contained but negligible activity. After the same chemical process described above, the activity of ^{131}I in the silver iodide was measured under the same condition. The chemical yield being taken into account, the separation method was proved satisfactory within a standard error due to counting, which amounted to 3% in this case.

Results

The results are shown in the table, where I in the column of sample denotes that the silicons were purified by the iodide process, and Cl by the chloride process. The iodide process has been carried out in the Electrical Communication Laboratory in order to obtain semiconductor grade silicon. This method consists of converting a raw silicon into silicon tetraiodide, of purifying the iodide by various techniques, and of thermal decomposition of the iodide with continuous evacuation. The samples I–1 were silicons just after this stage. I–2 was obtained by keeping molten I–1 containing 4.5 p. p. m. of iodine in a silica vessel for an hour under an argon gas flow. I–3 were taken out of the tail of a single crystal made by the cooling method from I–1 containing 1.3 p. p. m. of iodine. The tail end of the crystal contained much more iodine (2.0 p. p. m.) than a part several millimeters above it (0.32 p. p. m.). These silicons were usually of type N. Floating zone refining has also been applied to obtain a material of higher quality. The samples denoted by Cl were silicons of transistor grade prepared by the chloride process in a certain foreign country, and this silicon is now widely used as the transistor material.

Sample	Number of different samples assayed	Iodine content (p. p. m.)
I–1	3	1.3, 4.5, 4.5
I–2	1	0.35
I–3	2	2.0, 0.32
Cl	2	0.005, 0.05

Discussion

After the chemical process, the decay curve of the silver iodide is usually straight on a semilog plot in accordance with the theoretical half-life. However, when the iodine content is lower than 0.01 μg. and the distillation is carried out carelessly, the separated silver iodide is contaminated with radioactive silica. Without the distillation, the precipitate of silver iodide is by no means free from silica (about 10 μg. of silicon); without the extraction, about 1 μg. of silicon enters the precipitate.

When 0.002 μg. of iodine is present in silicon, it gives an activity of about 100 cpm to the 2π counter after the chemical treatments, and is enough for quantitative analysis and the measurement of the decay curve. If a reactor with a higher neutron flux were available, less iodine could be determined; however, the problem of decontamination from radioactive silicon would become more important. In such a case, repetition of the distillation would be necessary.

Determination of segregation constant of iodine and analysis of chlorine and bromine, with a slight modification of the method, in silicon are now under planning.

Summary

A trace quantity of iodine in silicon was determined by the neutron activation analysis. A chemical separation process, which involves potassium hydroxide fusion with potassium iodide as a carrier, was proved satisfactory by the use of ^{131}I produced by the neutron irradiation of tellurium diffused in silicon. By this method, the iodine was converted into silver iodide ready for counting and weighing within an hour, with a yield exceeding 50%. When it is assumed that a counting rate of 100 cpm is enough for accurate detection of activities, the limit of detection is 0.002 μg. of iodine with a neutron flux of 6×10^{11} n/cm^2 sec. and by the use of a 2π counter.

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