Neutron Activation Analysis of Halogens in High-Purity Silicon

By Tadashi NOZAKI, Toshi KAWASHIMA, Hideo BABA and Hidemaro ARAKI

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Extreme purification is of vital importance when silicon is used as a semiconductor material, and many papers treating many kinds of trace impurity in high-purity silicon have been published. However, neither the method of the determination nor the behavior of halogens in a given material has been studied enough. Previously, we reported[1] on the neutron activation analysis of iodine in silicon. In this paper, a method for simultaneous determination of chlorine, bromine and iodine in one sample is presented with some results.

Fusion of the neutron-irradiated silicon with potassium hydroxide containing potassium iodide as carrier was proved suitable for decomposing the sample in the determination of iodine. A similar fusion with alkali chloride, bromide and iodide as carrier should serve satisfactorily for their simultaneous determination. On such fusion under a reducing atmosphere, both chlorine and bromine in the sample will be converted into chloride and bromide respectively. Even if they were present in other forms than halide ions, they would be converted into chloride and bromide, when the basic cake is dissolved in an aqueous sulfuric acid in the presence of a large excess of iodide. Although perchlorate is not readily reduced to chloride on such a treatment, the formation of perchlorate under the given condition is least probable. Thus the carriers should work satisfactorily.

When a sulfuric acid solution containing the three halides was distilled in the presence of chromium(VI) oxide, the following three fractions of the distillate were successively obtained: (1) light brown solution containing bromine, (2) almost colorless solution containing only a small amount of halogen, (3) faintly yellow solution containing chlorine and hydrogen chloride. Addition of a sufficient quantity of oxalic acid and some water into the residual solution resulted in the reduction of the iodate to iodine. This was easily distilled, purified and converted into silver iodide for β-ray counting.

The bromine must be carefully purified. This is because after neutron irradiation of natural bromine, three radioactive nuclides of bromine are present as shown in Table I. The radiochemical purity of the bromine sample, however, can be checked precisely neither from its decay curve nor from the γ-ray spectrum. The first fraction, containing some chlorine and perhaps a trace of iodine too, was submitted, before being converted into silver bromide for counting, to a further purification, whose usefulness was checked by a tracer technique using ^{36}Cl and ^{131}I. On the

TABLE I. RADIOACTIVE NUCLIDES OF THE HALOGENS FORMED BY THE NEUTRON IRRADIATION

Nuclide	Half-life	β-Ray energy (MeV.)	γ-Ray energy (MeV.)	*Activity formed (dpm)
^{36}Cl	3×10^5y	β^-0.704 (98%)	none	negligible
^{38}Cl	37.3m	β^-4.81 (53%) 2.77 (16%) 1.11 (31%)	2.15 (31+16%) 1.60 (31%)	5.4×10^{10}
^{80m}Br	4.4h		0.049 0.037	5×10^{10}
^{80}Br	17.6m	β^-1.99 (72%) etc. β^+0.87 (3%)	0.62 (13%)	1.1×10^{12}
^{82}Br	35.9h	β^-0.444 (100%)	0.55, 1.47 eight γ-rays	9×10^7
^{128}I	25.0m	β^-2.12 (76%) etc.	0.46 (17%) others (weak)	8×10^{11}

* Just after 1 hr's irradiation of 1 g. of a natural halogen under a thermal neutron flux of 6×10^{11} n/cm^2 sec.

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[1] T. Nozaki et al., This Bulletin, 33, 320 (1960).

other hand, chlorine in the third fraction was converted into silver chloride for counting without further purification, for it involves some difficulty and is time-consuming, and there is no possible nuclide that enters the silver chloride and decays with a similar half-life emitting an energetic γ-ray. The silver chloride was proved to be radiochemically pure, as far as the distillation was carried out with care to prevent contamination with radioactive silica.

When the sample contains by far the least amount of iodine amidst the three halogens, there is another preferable process, which consists of the distillation of iodine after the treatment of the fused cake as reported previously and the separation of bromine and chlorine by the method indicated above. The two complete processes require nearly equal time, with a good yield and radiochemical purity.

Unfortunately, fluorine can not be determined by a similar technique because of the lack of a suitable radioactive nuclide formed by neutron irradiation.

Experimental

Sample.—All of the silicon samples were of transistor grade, purified by the chloride process (in U. S. A.), by the iodide process (in the Electrical Communication Laboratory) or by an unknown method (in Europe). Many other impurities in them were determined by emission spectroscopy or by neutron activation analysis with an irradiation under a higher flux and for a longer period, the results indicating their high purity. In most cases, two portions of the same sample were analyzed, each being 0.5 to 1 g.

Irradiation.—The samples enveloped in thick polyethylene sheets were irradiated in a water boiler type reactor, (Japan Research Reactor 1) for an hour under a neutron flux of about $6\times10^{11}\,n/\mathrm{cm}^2$ sec., placed side by side with the radioactivation standard of ammonium chloride, ammonium bromide and potassium iodide, and taken out swiftly through a neumatic tube.

Chemical Separation.—The irradiated samples were etched with a mixture of hydrofluoric and nitric acid, to avoid possible surface contamination pulverized, weighed and fused with potassium hydroxide (10 to 15 g.) kept just above its melting point and containing a known ammount of sodium chloride, potassium bromide and potassium iodide (each 5 to 10 mg.) as carriers. The fused cake was dissolved in sulfuric acid (2 : 3, 100 ml.) containing a small quantity of sodium sulfite (about 0.01g.). The solution was transferred into a crooked neck distillation flask (in order to protect the distillate from contamination by the radioactive silicon) and distilled after the addition of chromium-(VI) oxide (10 g.).

The bromine distilled out in the first few minutes. The colored distillate was caught in an aqueous sodium sulfite (25 ml. of 10 g./l. solution) containing sodium chloride and potassium iodide (each a few mg.), oxidized by adding concentrated phosphoric acid (10 ml.) and potassium permanganate (20 ml. of 10 g./l. solution), and the bromine was extracted with carbon tetrachloride (20 ml.), back-extracted with hydroxylamine (0.1 g.) in nitric acid (1 : 100, 20 ml.) and converted into silver bromide.

A tracer study to prove the usefulness of this purification was carried out preliminarily by the use of ^{36}Cl and ^{131}I. On oxidation with permanganate, no detectable ^{36}Cl (less than 1/5,000) entered the organic phase, but a trace of iodine did when the treatment was performed with less care. However, the iodine was removed completely (to less than 1/5,000) by back-extraction, for a solution of hydroxylamine in dilute nitric acid reduces molecular bromine to bromide and oxidizes iodide to iodine.

The distillation was continued, and after several minutes from the disappearence of the bromine color when a faint color of chlorine became recognizable by a careful observation, the distillate was introduced into an aqueous sodium sulfite (10 g./l. 25 ml.). When the color of chlorine in the distillate disappeared, the chloride was converted into silver chloride without further purification. It was somewhat preferable to carry out the distillation of bromine with a smaller amount (1 g.) of chromium(VI) oxide and to add a larger amount (10 g.) before the distillation of chlorine.

When the determination of iodine was necessary, it was attained by adding a sufficient quantity (more than 30 g.) of oxalic acid and some water (30 ml.) into the residual solution, distilling the liberated iodine and converting it into silver iodide after the purification as mentioned previously[1].

Each silver halide was filtered off with a glass filter (No. 3), washed with nitric acid (1 : 100, 50 ml.), water, ethanol and ether, and submitted to counting and weighing. The time required for the chemical process was less than an hour for bromine, about one hour for chlorine and 1.2 hr. for iodine, with a yield exceeding 50%.

Radioactivation Standard.—Each of the irradiated bromide and iodide was dissolved in water containing a known amount of the same halide as carrier, and converted into silver bromide and iodide after being purified by the oxidation, extraction and back-extraction. On the other hand, silver chloride was precipitated without purification.

Counting. — A simple G-M counter of an end window type was used in all cases. For chlorine, a scintillation counter with a large sodium iodide crystal (4″×4″) and a single channel analyzer was also used (the region between 1.8 MeV. and 3.5 MeV.). More precise determination could be done by the latter, but the efficiency of the former was somewhat higher. The decay curve of the chlorine measured by a G-M counter agreed well with that of the standard sample and the theoretical curve. The agreement of the decay curve of the bromine and iodine with that of the corresponding standard was complete. For lowering the detection limit, use of a 2π counter was also examined, and its efficiency was found to be about five times higher than that of the G-M counter with the sample kept as near as possible.

Results and Discussion

Some of the results are shown in Tables II and III. It is natural that a silicon purified by the chloride method contains a trace of chlorine and that purified by the iodide method contains iodine. On the other hand, it should be an interesting fact that most of the high-purity silicons contain two other halogens too, indicating a tendency that the less the concentration of a halogen becomes, the greater the persistency with which it remains in the silicon. Silicon powder obtained by the thermal decomposition of silicon tetraiodide usually contained several ppm of iodine. The iodine content could be lowered down to about 0.3 ppm by a simple technique (i. e. fusion under an argon flow or segregation). Table III indicates the segregation of iodine in a single crystal of silicon about 7 cm. long prepared by pulling it from the melt at a rate of 1 cm. per min. Here, it is also shown tha the iodine content decreased fairly rapidly down to 0.3 to 0.2 ppm. However, a high-purity silicon prepared by the iodide process and purified by 30 times' zone refining still contained nearly the same amount of iodine. On the other hand, a determination showed that heating in a hydrogen atmosphere seems to be effective to reduce the iodine as low as several hundredths ppm.

TABLE II. HALOGEN CONTENT OF HIGH-PURITY SILICONS

Method of purification	Halogen content (ppm)		
	Cl	Br	I
Chloride method	2.2	0.18	0.15
Iodide method	0.2	0.05	0.38
(Unknown)	<0.15	<0.02	0.17

TABLE III. SEGREGATION OF IODINE

Location (centimeter from the tail)	0.3	1.6	2.9	4.8	6.2
Iodine content (ppm)	1.5	0.94	0.83	0.32	0.22

As the result, a trace of any of the three halogens remains in a high-purity silicon quite persistently after many physical purifications, and the persistency increases with the decrease of its concentration. The authors are wishing to elucidate this reason.

When it is assumed that an activity of 150 cpm at the initiation of counting is essential for precise identification of the nuclide, the detection limit is 1.5×10^{-7} g., 1.5×10^{-8} g. and 3.0×10^{-8} g. for chlorine, bromine and iodine respectively by the use of a G-M counter and under the conditions described above. Use of a 2π counter could lower the limit down to one-fifth of the above values.

Summary

A trace quantity of chlorine, bromine and iodine was determined simultaneously by neutron activation analysis. By careful distillation of a solution containing the alkali-fused silicon, chromium(VI) oxide and sulfuric acid, bromine and chlorine were distilled out separately, leaving iodine in the residual solution, which was then distilled out after adding oxalic acid.

Most kinds of high-purity silicon contained more than 0.1 ppm of a halogen, which was used in the course of its purification process, and also two other halogens, though of a smaller quantity.

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The Electrical Communication Laboratory
Musashino, Tokyo