Chemical Behavior of Carbon in High-purity Silicon in the Dissolution and Fusion of the Matrix

Tadashi NOZAKI, Yoshihiro MAKIDE, Yoshifumi YATSURUGI,*
Yoshiyuki ENDO,* and Nobuyuki AKIYAMA*
The Institute of Physical and Chemical Research, Wako-shi, Saitama
**Komatsu Electronic Metals Co., Hiratsuka, Kanagawa*
(Received December 4, 1971)

The behavior of carbon in high-purity silicon in the dissolution and fusion of the matrix was studied by the ^{11}C-tracer technique. Silicon samples containing ^{11}C, either atomistically dispersed or mainly coagulated as SiC, were prepared. In alkali dissolution, no loss of ^{11}C was observed, and carbon originally dispersed in silicon was found to behave in a similar way to colloidal carbon under subsequent treatments. By $HF-HNO_3-KIO_4$ dissolution and succeeding $KMnO_4$ treatment, the dispersed carbon was oxidized almost quantitatively but the SiC coagulates were not completely decomposed. In alkali fusion a part of ^{11}C was lost. By fusion with $Pb_3O_4-B_2O_3$, carbon in both states was converted into CO_2. The results suggest a possible application of activation analysis to the measurement of the coagulation degree of carbon in high-purity silicon.

The behavior of a trace impurity element in the dissolution or fusion of a high-purity matrix has not yet been fully studied. We have examined the chemical behavior of carbon in semiconductor silicon in the decomposition of the matrix by means of radio-tracer technique. The results are given in this paper.

The following facts are known about carbon in silicon: (1) the solubility in solid silicon is slightly less than 3 ppm at the melting point, and carbon with a concentration above the solubility is coagulated as SiC;[1] (2) carbon is soluble up to 35 ppm in liquid silicon at the melting point, and in the solidification of carbon-saturated silicon slightly over 90% of the carbon coagulates into SiC;[1] (3) commercial semiconductor silicon usually contains from 30 ppb to 2 ppm of carbon;[1] and (4) carbon atoms dissolved in solid silicon occupy substitutionally the lattice points of the silicon crystal.[2]

As a radio-tracer, $^{11}C(\beta^+, T_{1/2}=20.3\ m)$ was used because it can be measured more easily and more precisely than ^{14}C by the scintillation counting of annihilation radiation. The excitation function and thick target yield for the $^{11}B(p,n)^{11}C$ reaction are known.[3,4] A sufficient activity of ^{11}C is easily produced by the proton bombardment of B_2O_3.

Experimental

Sample Preparation. The cyclotron at the Institute of Physical and Chemical Research was used for the proton bombardment, with the proton energy set at about 13 MeV. Three kinds of ^{11}C-containing samples were prepared by the following methods. (1) A silicon wafer doped with 50 to 100 ppm of boron was bombarded (a few μA beam, 20 min). After being left for 40 min for the ^{30}P formed by the $^{30}Si(p, n)^{30}P$ reaction to decay, the wafer was treated with a mixture of HF and HNO_3 to remove the surface contamination. (2) A B_2O_3 target was placed in a glass vessel with an aluminum foil window and bombarded with protons (about 10 μA beam, several minutes). A noticeable portion of the ^{11}C was evolved from the target as oxides and carried with a helium stream to the next room, where it was caught in a liquid-nitrogen trap after being passed through a dry-ice trap. About 50 mCi of carrier-free $^{11}CO_2$ was thus collected. A portion (about 1 g) of a semiconductor silicon rod, 1 cm in diameter and 5 cm long, sustained in an evacuated quartz tube was fused by radio-frequency heating, and the $^{11}CO_2$ was introduced into the tube. After being kept molten for a few minutes, the silicon was left to cool, and its surface layer was removed by etching. The silicon sample thus obtained contained a millicurie level of ^{11}C. (3) The process was similar to that in (2), but the silicon melt was brought into contact with a small amount of graphite powder or CO_2 gas.

The ^{11}C atoms in the sample prepared by Method (1) can occupy a higher-energy site in the silicon crystal since it has received the nuclear recoil energy in its nascent stage. Samples obtained from (1) and (2) contain the carbon homogeneously dispersed atomistically. The sample obtained from (3) contains coagulates of SiC. The carbon content of the samples prepared by each method was as follows: Method (1), 0.5—1 ppm; Method (2), 100—500 ppb; Method (3), 10—30 ppm of the coagulated carbon together with about 3 ppm of the dispersed carbon.

Dissolution and Fusion. The silicon matrix was decomposed by the following treatments: (a) dissolution in alkaline solutions, (b) dissolution in $HF-HNO_3$ solutions, (c) fusion with NaOH and $NaOH-NaNO_3$, and (d) fusion with $Pb_3O_4-B_2O_3$. About 0.5 g of the sample was used for each treatment. In most cases the products were treated with various reagents.

(a) The sample was pulverized and added to a NaOH solution (5 mol/*l*, 25 m*l*). When the dissolution reaction subsided, the mixture was gently heated to boil. Water was occasionally added to keep the volume of the solution almost constant. The sample was also subjected to a similar treatment with a NaOH solution (5 mol/*l*) containing $NaNO_3$ (2 mol/*l*), $KMnO_4$ (0.5 mol/*l*) or CrO_3 (0.5 mol/*l*) and with a Na_2O_2 solution (2.5 mol/*l*). In the absence of $KMnO_4$ or Na_2CrO_4, the silicon was dissolved within 30 min.

(b) The sample in small plates or blocks was added to a mixture of HF (46%, 15 m*l*) and HNO_3 (60%, 15 m*l*). The silicon was dissolved in 10 min with heat evolution. The $HF-HNO_3$ mixture containing KIO_4 (3 g) was also

1) T. Nozaki, Y. Yatsurugi, and N. Akiyama, *J. Electrochem. Soc.*, **117**, 1566 (1970).
2) R. C. Newman and J. B. Willis, *J. Phys. Chem. Solid*, **26**, 373 (1964).
3) M. Furukawa, Y. Ishizaki, Y. Nakano, T. Nozaki, Y. Saji, and S. Tanaka, *J. Phys. Soc. Japan*, **15**, 2167 (1960).
4) T. Nozaki, T. Okuo, H. Akutsu, and M. Furukawa, This Bulletin, **39**, 2685 (1966).

used to accelerate dissolution.

(c) The sample was coarsely pulverized and added in small portions to NaOH (15 g) or a mixture of NaOH (10 g) and $NaNO_3$ (5 g) kept just above their melting points. Since the reaction was highly exothermic, the rate could not be controlled.

(d) A mixture of the pulverized sample, Pb_3O_4 (30 g) and B_2O_3 (6 g) was put into a Vycor-glass tube, and heated under an oxygen stream by a town gas-oxygen flame, first gently and then violently. The fusion was completed within 5 min, leaving a pale yellow glassy matter with globules of metallic lead when cooled. The oxygen stream was led to an Ascarite column after being passed through an I_2O_5–H_2SO_4–SiO_2 column in order to confirm the quantitative recovery of the ^{11}C.

For acidification of the resulting alkaline solution, HCl (1:1), H_2SO_4 (1:2) or HNO_3 (1:1) was added, in about twice the stoichiometrical amount for the neutralization of the alkali used. The cake of the alkali fusion was treated with the acids diluted further twice. In some cases, $KMnO_4$ (3 g) or CrO_3 (3 g) was added to the mixture, which was then boiled for 5 min. For collection of the suspending colloidal particles in the solution, fine powder (50 mg) of quartz or charcoal was stirred into the solution and precipitated with the particles by centrifugation. For dissolution of the precipitated hydrated silicon oxide, HF (46%, 5 m*l*) was added to the mixture.

Radioactivity Measurement. Annihilation radiation from the sample was measured by a scintillation counter with a single channel analyzer. In order to confirm the radiochemical purity of the original samples, the γ-ray spectrum and decay curve were measured; no radio-nuclide other than ^{11}C was found. Before and after each treatment, the radioactivity of the sample was measured from outside the vessel. Care was taken to keep the counting efficiency constant.

Since the original silicon contained a high-level activity of ^{11}C, the sample was placed at least 30 cm apart from the scintillator, thus making the counting efficiency almost insensitive to a small variation in the sample position. When the sample lost most of its ^{11}C activity, it was placed close to the scintillator, and the efficiency was calibrated by a resin-covered ^{22}Na standard source inserted in the center of a non-radioactive replica of the sample. In order to stop the positrons completely and to make the self-absorption constant, the silicon sample before the dissolution or fusion was sandwiched between polystyrene or iron plates with such a thickness as to give almost the same absorption as the self-absorption in the sample after the treatment. The effect of volume change caused by the addition of acid was corrected by insertion of a polystyrene plate beneath the sample in the measurement before the addition.

Results and Discussion

The results for the silicon sample containing only the atomistically dispersed carbon are given in Fig. 1. No significant difference in the behavior of ^{11}C was observed between the samples prepared by Methods (1) and (2).

In the alkali dissolution, no loss of ^{11}C was observed and the behavior of ^{11}C was not affected by the addition of $NaNO_3$ or Na_2O_2. In the presence of $KMnO_4$ or K_2CrO_4 the dissolution did not proceed smoothly, probably because the silicon surface was covered with oxides of manganese or chromium. We see from

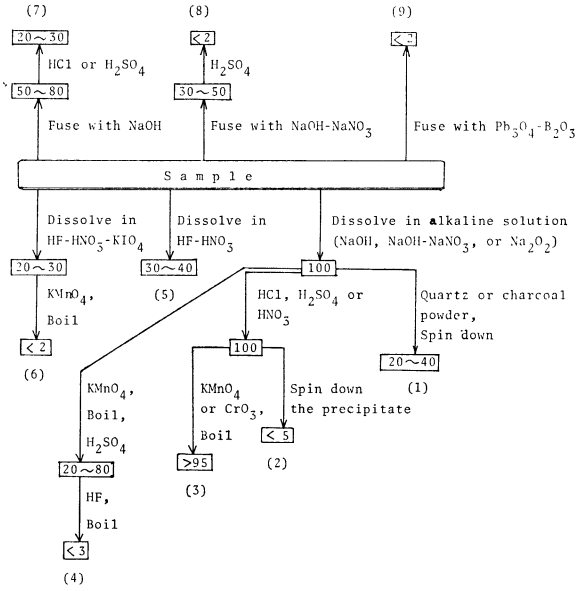

Fig. 1. Behavior of homogeneously dispersed carbon. Fraction of ^{11}C remaining in the reaction mixture (%). Figures in the parentheses are the treatment number in the text.

Treatments 1, 2, and 3 (Fig. 1) that the carbon in the alkaline solution was not dissolved as carbonate or any other soluble compound but turned into colloidal particles. The solution contained Na_2CO_3 in a quantity sufficient for a carrier of $^{11}CO_3^{2-}$. In order to examine whether CO_2 was evolved quantitatively by acidification of the solution, a solution containing $Na_2{}^{11}CO_3$ and Na_4SiO_4 was prepared and acidified; the evolution was almost quantitative, although a small fraction (less than 10%) of ^{11}C sometimes remained even after the solution was boiled. The results of Treatments 2 and 3 suggest that the carbon was held in the precipitate of hydrated silicon oxide formed by the acidification of the alkaline silicate solution. In Treatment 4 (Fig. 1), the fraction of ^{11}C remaining after the addition of H_2SO_4 varied remarkably depending mainly on the stirring efficiency and other conditions at the moment of addition. When the boiling in Treatment 4 before the acidification was prolonged, no noticeable difference in the remaining fraction of ^{11}C was found. It can thus be deduced that the oxidation of carbon by $KMnO_4$ was slow in the alkaline solution but made fast by the acidification, after which, however, hydrated silicon oxide soon precipitated embracing the carbon and thus preventing oxidation. When HF was added, the silicon oxide was dissolved and the carbon was rapidly oxidized. Treatment 6 (Fig. 1) also shows the effectiveness of the $KMnO_4$ oxidation in acid solution. The inefficiency of the oxidation in the alkaline solution might be due to the covering of the carbon suspension with hydroxides or carbonates of impurity elements in the reagents.

After the alkali fusion (Treatments 7 and 8, Fig. 1) the fraction of the ^{11}C remaining is found to depend markedly on the vigorousness of the fusion reaction—the more vigorous the reaction, the less the fraction remaining. The effect of $NaNO_3$ as oxidizing agent

was clearly observed in the alkali fusion.

Either by the dissolution in $HF–HNO_3–KIO_4$ and subsequent $KMnO_4$ treatment or by the $Pb_3O_4–B_2O_3$ fusion, the dispersed carbon was oxidized almost quantitatively. Thus either procedure could be used for the separation of ^{11}C in the activation analysis of carbon in silicon by means of the $^{12}C(^3He,\alpha)^{11}C$ reaction. A procedure for the activation analysis using Treatment 6 was given in detail.[5] In order to facilitate the complete oxidation of the carbon, however, it is recommended to use a larger quantity (10 g) of $KMnO_4$ than that given previously (1 g).[5] Treatment 9 (Fig. 1) was developed and has been used by Engelmann and co-workers.[6] From our experience in this treatment, a part of the carbon was likely to be incorporated in lead drops formed from Pb_3O_4 not being oxidized easily unless oxidation was completed rapidly. In our determination, we pulverize the sample, mix it with $Pb_3O_4–B_2O_3$ powder, and heat the mixture in a Vycor-glass tube with a town gas-oxygen flame.

The behavior of the coagulated carbon in the above two treatments are shown in Fig. 2. The sample contained also dispersed carbon. The entire carbon was decomposed by $Pb_3O_4–B_2O_3$ fusion. In the dissolution with $HF–HNO_3–KIO_4$ followed by treatment with $KMnO_4$, the decomposition of the coagulated carbon was incomplete. It is certain that the more

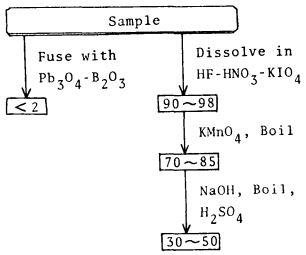

Fig. 2. Behavior of coagulated carbon.
Fraction of ^{11}C remaining in the reaction mixture (%).

perfect the crystal structure of the SiC coagulates, the less complete the decomposition into CO_2. In the activation analysis of carbon by the $^{12}C(^3He,\alpha)^{11}C$ reaction, a part of the ^{11}C formed in the coagulates is driven out of them by the nuclear recoil effect and converted into $^{11}CO_2$ by means of the $HF–HNO_3–KIO_4–KMnO_4$ treatment. Thus in this case, the fraction of ^{11}C converted depends also on the grain size of the coagulates.

TABLE 1. SENSIBILITY OF THE THREE METHODS FOR THE DIFFERENT PHYSICAL STATES OF CARBON IN SILICON

Method		Homogeneously dispersed carbon	Coagulated carbon
Activation analysis	$Pb_3O_4–B_2O_3$ fusion (or nondestructive)	+	+
	$HF–HNO_3–KIO_4–KMnO_4$ dissolution	+	±
Infrared spectrophotometry		+	−

The three methods for the determination of carbon in semiconductor silicon are given in Table 1. The nondestructive activation analysis (the first method) can be applied only to carbon-doped silicon. The fraction of the coagulated carbon determined as carbon by the second method is dependent on the state of the coagulates, namely, the grain size and the perfectness of the crystal structure. We have obtained the calibration curve for infrared spectrophotometry (the third method) using various semiconductor silicon samples analyzed for carbon by the activation analysis.

Therefore, by the use of all the three methods or two of them, it is now possible to get information on the physical state of carbon in silicon, though high accuracy is often needed in the determinations. Actually, when silicon samples of relatively high carbon contents were kept at 1300°C for many hours, the infrared-active carbon contents decreased gradually without any significant change in the results obtained by the second method.

We would like to express our thanks to members of the Cyclotron Operation Group of the Institute of Physical and Chemical Research for their help in the bombardment.

5) T. Nozaki, Y. Yatsurugi, and N. Akiyama, *J. Radioanal. Chem.*, **4**, 87 (1970).

6) Ch. Engelmann, J. Gosset, M. Loeuillet, A. Marschal, P. Ossart, and M. Boissier, "Modern Trends in Activation Analysis," Vol. 2, ed. by J. R. DeVoe, U. S. Dept. of Commerce, Washington D. C. (1969), p. 819.