Gram-Order Preparation of ^{30}Si-Enriched Silica and Silicon Powders by Means of IRMPD of Disilicon Hexafluoride

Kazunori Tanaka,* Shohei Isomura,† Hayato Kaetsu,† Yoshifumi Yatsurugi,†† Masanori Hashimoto,†† Kazuya Togashi,†† and Shigeyoshi Arai†††

Department of Industrial Chemistry, Junior College of Engineering, Shizuoka University, Johoku 3-5-1, Hamamatsu, Shizuoka 432

†The Institute of Physical and Chemical Research (RIKEN), Hirosawa 2-1, Wako, Saitama 351-01

††Komatsu Electronic Metals Co., Ltd., 2612 Shinomiya, Hiratsuka, Kanagawa 254

†††Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606

(Received August 9, 1995)

Powder silica and elemental silicon enriched with ^{30}Si were prepared at the request of nuclear physicists who had needed the isotopic samples for their research on neutron-rich nuclei. The enrichment of ^{30}Si was performed by means of the IRMPD of Si_2F_6 to SiF_4 using a CO_2 laser. The ^{30}Si-enriched SiF_4 was further converted either to silica by hydrolysis with aqueous ammonia or to silicon by $LiAlH_4$ reduction to SiH_4 followed by its thermal decomposition. As the final products we obtained 11.35 g of silica with 20.6% ^{30}Si, and 3.06 g of silicon with 17.5% ^{30}Si.

Among the recent topics in nuclear physics is the structure of extremely neutron-rich nuclei, such as ^{11}Li. The study of ^{11}Li by projectile fragmentation has suggested the existence of a large neutron halo around its nucleus.[1] This is prompting nuclear physicists to further extend their research to include other extremely neutron-rich nuclei.

Toward this end, oxygen isotopes are especially of interest because of their closed shells of protons. Extremely neutron-rich isotopes of oxygen may be produced in an ion accelerator by projectile fragmentation using ^{22}Ne or ^{30}Si as primary beams. Having already developed a technique to enrich ^{30}Si,[2,3] we were requested by one of the nuclear physicists who discovered the neutron halo to provide them with gram-order powder samples of ^{30}Si-enriched silica or silicon. In their research project, the powder samples would be fabricated into ion sources to be used in an ion accelerator for producing primary ^{30}Si beams.

The isotope-enrichment technique which we have developed gives the ^{30}Si-enriched sample as gaseous SiF_4 and white deposits, whose atomic composition is regarded as being $(SiF_2)_n$. However, the white deposits have tended to spread out so thinly over large areas on the inner walls of the reaction vessel that they could be collected only with extreme difficulty. Therefore, we had to explore a process for converting gaseous SiF_4 to silica and silicon powders with a maximized yield. The entire process for isotope enrichment and chemical conversions is described in this paper.

Isotopically Selective IRMPD of Si_2F_6

Principle. As reported before,[3] Si_2F_6 undergoes isotopically selective IRMPD (infrared multiphoton dissociation) under CO_2-laser irradiation with lines at around 950 cm^{-1}. The main reactions involved may be expressed by

$$Si_2F_6 \xrightarrow{mh\nu} SiF_4 + SiF_2 \quad (1)$$

$$nSiF_2 \longrightarrow (SiF_2)_n \quad (2)$$

Reaction (1) is the IRMPD proper, which is followed by a dark polymerization reaction (2) that yields white deposits or films of $(SiF_2)_n$.

Naturally occurring silicon consists of three stable isotopes, ^{28}Si, ^{29}Si, and ^{30}Si, whose abundances are 92.2%, 4.7%, and 3.1%, respectively. Due to the overwhelming abundance of ^{28}Si, most ^{30}Si atoms in Si_2F_6 molecules exist as $^{30}Si^{28}SiF_6$. Even if the IRMPD reaction (1) were completely selective to ^{30}Si-containing species, the maximum isotopic percentage of ^{30}Si in product SiF_4 would be limited to only as high as about 50%.

Apparatus. Although the entire apparatus for conducting the IRMPD process was essentially the same as that previously outlined,[3] several minor modifications were made for the present project. The modified apparatus is illustrated in Fig. 1. It is divided into four parts; a gas-supply system (A to C), a reaction system (D to G), a product-collection system (H to K), and a product-purification system (L to O).

The gas-supply system consists of a Si_2F_6 cylinder (A), an Ar cylinder (B), a pressure regulator (PIC-1), and mass-flow controllers (FIC-1 and FIC-2). Cylinder Si_2F_6 is admittable into the 10-L reservoir (C), and is therefrom led to the reaction vessel (F) through FIC-1. Argon can also be supplied to the

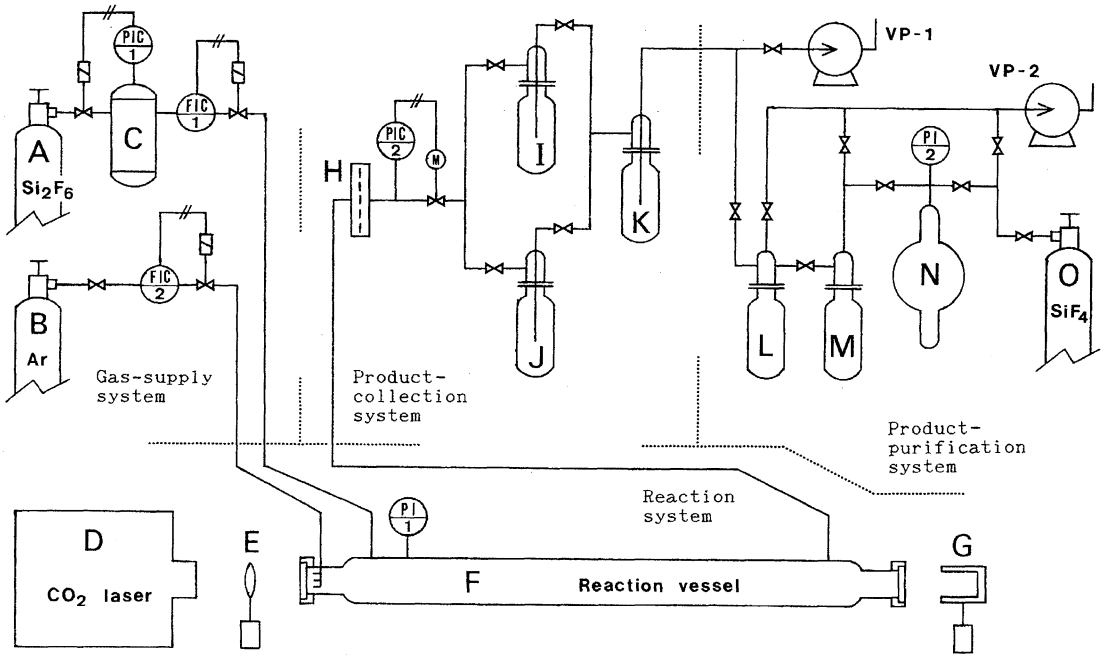

Fig. 1. Apparatus for isotopically selective IRMPD of Si_2F_6.

reaction vessel through FIC-2.

The reaction system consists of a Lumonics 822 high-power CO_2 TEA laser (D), a BaF_2 lens (E) with a focal length of 3 m, a cylindrical Pyrex-glass reaction vessel (F), and a power meter (G). The laser can generate an 8-J pulse at its full output for a repetition rate of 10 Hz. Three (D, E, G) of the above are those instruments that were employed in a previous study.[3] Although the reaction vessel has been newly constructed, it is essentially of the same design as the previous one, except for its length and the window material. The new one is 3 m long, just 1 m shorter than the previous one. Its outer diameter is 80 mm, constricted to 50 mm at both ends, where NaCl disk windows (previously KBr) are sealed. Near to the window on the laser side are two side tubes; one comes from the Si_2F_6 cylinder, and the other from the Ar cylinder. The side tube from the Ar cylinder is very close to the window, and protrudes deep into the reaction vessel, ending with a three-way manifold whose ports face the window.

The product-collection system consists of a gas filter (H), a pressure controller (PIC-2), and three cold traps (I, J, and K). The product-purification system consists of two cold traps (L and M), a volumetric bulb (N), and a storage cylinder (O).

The isotopic concentrations of silicon in product SiF_4 were determined using a Hitachi RMS-4 mass spectrometer.

Procedures. Since the IRMPD process for the purpose of $^{30}SiO_2$ production and that for ^{30}Si production were conducted separately, but by essentially the same procedures, only the latter IRMPD procedures are detailed here as the representative.

The CO_2 laser was tuned to the 10P(12) line at 951.19 cm^{-1}, and the laser beam was focused into the reaction vessel (F) by the lens (E). The molar composition of the lasing gas was $He : CO_2 : N_2 = 10 : 8 : 5$. Into the reaction vessel under laser irradiation were introduced Si_2F_6 and Ar; their partial pressures and flow rates were regulated by FIC-1 or FIC-2. The Ar stream was required to prevent the transmission of the NaCl window from degrading due to $(SiF_2)_n$ deposition.

The reaction mixture flowing out of the reaction vessel was led into either trap I or J, which were chilled down to liquid-N_2 temperature; the product SiF_4 and unreacted Si_2F_6 were together condensed there while Ar was pumped out. In order to separate SiF_4 (bp -94.8 °C) and Si_2F_6 (bp -19.1 °C), the condensation was distilled three times; first from trap I or J to trap K, then from trap K to trap L, and finally from trap L to trap M. In each distillation step the former trap was chilled to only -95 °C by a toluene slush bath, and the latter further down to liquid-N_2 temperature. The thus-purified SiF_4 product was quantified by introducing it into volumetric bulb (N) and reading the pressure with PI-2, and finally stored in the storage cylinder (O).

In this way the reaction apparatus for IRMPD (Fig. 1) was run continuously for 1 to 3 h, and a total of six runs were conducted (as shown in Table 1) under essentially identical, but somewhat different, conditions.

Results. Table 1 also summarizes the results. In the IRMPD process for the purpose of ^{30}Si-enriched silicon preparation, we produced a total of 354 mmol (10.06 g) of SiF_4 with an isotopic percentage of 17.5% for ^{30}Si. This molar quantity corresponds to a yield of 11.3% because a total of 3146 mmol of reactant Si_2F_6 was subjected to laser irradiation, and just the same molar amount of SiF_4 should be expected in complete conversions. In the IRMPD process for the purpose of ^{30}Si-enriched silica preparation, the SiF_4 product amounted to 190 mmol with 20.6% ^{30}Si.

It should be noted that in these IRMPD processes we had to compromise between excellent yield of SiF_4 and its high isotopic concentration. Even higher ^{30}Si concentrations, say

Table 1. Reaction Conditions and Performance for IRMPD Process (Eq. 1)

Run	Time	Laser operation		Gas flow			Performance			
	min	Repetition rate/Hz	Power $J\,Pulse^{-1}$	Flow rate/mmol min^{-1} Si_2F_6	Ar	Total press Torr	SiF_4 produced mmol	Isotopic concentration/% ^{28}Si	^{29}Si	^{30}Si
(For the purpose of ^{30}Si-enriched SiO_2 preparation)										
As a whole							190.0	71.8	7.6	20.6
(For the purpose of ^{30}Si-enriched Si preparation)										
1	50	8	6.0	5.2	1.95	6—9	51.5	71.4	10.8	17.8
2	98	8	4.7	5.2	1.95	6.5	36.1	76.3	7.4	16.3
3	180	5	5.2	3.3	1.62	6	66.6	76.2	8.2	15.5
4	180	5	4.9	3.3	1.62	6	68.0	75.4	8.6	16.0
5	180	5	4.1	3.3	1.62	5	93.0	71.5	9.2	19.6
6	180	6	4.1	3.3	1.62	5	38.5	71.0	9.2	19.6
As a whole							353.7	73.8	8.7	17.5

36%, could be obtained if a further sacrifice of yield was allowed under appropriate IRMPD conditions.[3]

SiF_4-to-SiO_2 Conversion

Initial Attempt Using Water. According to the literature,[4] the hydrolysis of SiF_4 proceeds in two steps:

$$SiF_4 + 2H_2O = SiO_2 + 4HF \quad (3)$$

$$SiF_4 + 2HF = H_2SiF_6 \quad (4)$$

The overall hydrolysis reaction is thus expressed by

$$3SiF_4 + 2H_2O = SiO_2 + 2H_2SiF_6 \quad (5)$$

In order to convert the ^{30}Si-enriched SiF_4 sample to silica without any trouble according to reaction (5), we rehearsed its procedure using ordinary SiF_4 as the reactant in an open reaction vessel. The stoichiometry of reaction (5) suggests a maximum molar yield of 33% for SiF_4-to-SiO_2 conversion. Actually, however, it never exceeded 15% or so, presumably because of the incompleteness of reaction (5) and of partial escape of SiF_4 from the reaction vessel.

Final Success by Using Aqueous Ammonia. (i) Apparatus. We thought that the SiO_2 yield might be enhanced somewhat closer to 33% by using a closed reaction vessel and by neutralizing intermediate HF and acidic product H_2SiF_6 with an appropriate base. We thus designed a closed-glass reaction vessel, as shown in Fig. 2. It is a ca. 2-L bulb with two necks; the large one at the top and the small one at a side. The large one is connected to a stopcock, which is then attached to a funnel, each through a ground joint. The side neck permits the bulb to be pumped out.

(ii) Procedures and Results. A test reaction was carried out as follows. After evacuation of the bulb, 0.043 mol of ordinary SiF_4 was admitted into it, giving rise to a pressure of 500 Torr (1 Torr=133.3 Pa). While the bulb was cooled in a water-ice bath, about 200 ml of 5% ammonia contained in the funnel was added dropwise to yield white floculous SiO_2. The precipitate was filtered off, washed with water, dried overnight in an electrical oven at 80 °C, and weighed 2.82 g. This is an unexpected remarkable result, suggesting the practically complete SiF_4-to-SiO_2 conversion, because the corresponding theoretical weight is 2.73 g.

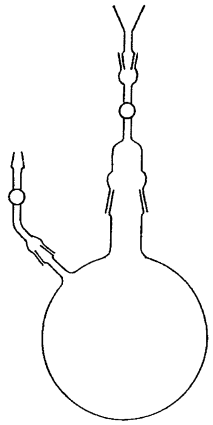

Fig. 2. Apparatus for SiF_4-to-SiO_2 conversion.

Thus, the whole ^{30}Si-enriched SiF_4 sample prepared for silica preparation was treated by this method; we obtained 11.35 g of SiO_2 containing 20.6% ^{30}Si.[5]

(iii) Remarks. The complete conversion to SiO_2 using aqueous ammonia might presumably be expressed by

$$SiF_4 + 4NH_3 + 2H_2O = SiO_2 + 4NH_4F \quad (6)$$

While still not well understood, this remarkable result deserves some comment. It is known that the hydrolysis of silicon tetrahalides is suppressed by the addition of acids.[6] This is probably due to a retardation of water coordination to the central silicon of SiF_4. The reverse is expected for base addition, which might facilitate the coordination of water molecules or hydroxyl ions; the coordination structure then undergoes decomposition.

SiF_4-to-SiH_4-to-Si Conversions

From SiF_4 to SiH_4. According to Finholt et al.,[7] $LiAlH_4$ is an excellent reducing agent for the preparation of some hydrides. Among good examples presented by them is the reduction of $SiCl_4$ to SiH_4 in ether:

$$LiAlH_4 + SiCl_4 = LiCl + AlCl_3 + SiH_4 \quad (7)$$

We thought that SiF_4 would also be smoothly reduced to monosilane by $LiAlH_4$.

(i) Apparatus. The vacuum apparatus for $LiAlH_4$ reduction has been made chiefly of Pyrex glass, as shown in Fig. 3. Trap A is used for trapping the ^{30}Si-enriched SiF_4 sample coming through valve V from stainless-steel cylinder O. Trap B (60 mm in o.d., 230 mm long from the bottom to the joints of the side arms) serves as the reaction vessel; one of the side arms is fitted with a small flask (B_{S1}) with a bent neck, and the other with a reflux condenser (B_{S2}). In order to enable shaking by hand, trap B is connected by rubber tubings to the rest of the vacuum line. The other part (C to H) is mainly used for purification, quantitation, and the storage of product silane.

(ii) Procedures and Results. About one fourth of the total 354-mmol ^{30}Si-enriched SiF_4 sample was admitted from the cylinder to the vacuum line, and frozen in trap A by chilling it with liquid N_2. Into reaction vessel B was placed $LiAlH_4$ (10 g). Side flask B_{S1} was charged with diethyl ether (150 ml), which had previously been freed from minute traces of water by allowing the reagent to stand overnight with Molecular Sieve 3A. About one half of this diethyl ether was transferred to the bottom of reaction vessel B by rotating the flask around the ground joint. The reaction vessel was then chilled using ethyl alcohol as a refrigerant (−30 to −40 °C). Petroleum ether slush (ca. −120 °C) was used to chill reflux condenser B_{S2} and trap C, and liquid nitrogen was employed for trap D. By opening valve V, near-atmospheric He was introduced as a carrier, which passed through a train of traps (A, B, C, and D), and was finally vented through an Hg bubbler (E).

In order to start SiF_4 reduction, the liquid-N_2 bath chilling trap A was replaced by an isopentane-slush bath (−159 °C with a SiF_4 vapor pressure of 1 Torr). The resulting SiF_4 vapor was transferred by He carrier to reaction vessel B, where the He–SiF_4 mixture bubbled in the $LiAlH_4$–diethyl ether suspension and thereby SiF_4 was reduced to SiH_4. During the reaction, the flow rate of the He carrier was adjusted to ca. 10 ml min^{-1}, and the reaction vessel was maintained in the chilled ethanol bath. The supply rate or concentration of SiF_4 in the SiF_4–He mixture was controlled coarsely by changing the trap-A refrigerant successively from isopentane slush to petroleum ether slush, then to ethanol slush, and finely (from time to time) by adding to these refrigerants a small amount of liquid nitrogen. Most of the diethyl ether leaving reaction vessel B was returned back by means of reflux condenser B_{S2}, although some escaped and was collected in trap C. Due partially to this solvent loss, the reaction suspension in B gradually became more viscous with the progress of the reaction. In order to smoothen $LiAlH_4$ reduction in this highly viscous suspension, it was necessary to shake reaction vessel B quite often. Also, near to the end of the reaction, more diethyl ether was supplied from flask B_{S1} at appropriate time intervals to lower the viscosity. More than 1 h was needed for completing the reduction of the whole ^{30}Si-enriched SiF_4 sample. Product silane was collected as white powders in trap D immersed in liquid N_2.

For purification, the silane was vacuum-distilled by warming trap D to a temperature of petroleum ether slush (−120 °C) and chilling the finger of bulb F to the liquid-N_2 temperature. Similar distillation was repeated between the cold finger of bulb F and that of volumetric bulb G. The ^{30}Si-enriched SiH_4 thus condensed in the finger of volumetric bulb G was then warmed to room temperature, and the resulting vapor was expanded to mercury manometer PI-1 for quantitation, and was finally stored in small cylinder H.

A series of the above procedures for SiF_4-to-SiH_4 conversion was repeated one more time using a similar amount of the ^{30}Si-enriched SiF_4 sample. We thus obtained a total of 208 mmol of ^{30}Si-enriched SiH_4 from 211 mmol of ^{30}Si-enriched SiF_4, giving rise to a conversion yield of 99%. The rest of the ^{30}Si-enriched SiF_4 sample, i.e., 143 mmol, was saved for other purposes.

From SiH_4 to Si. (i) Apparatus. This process, i.e.,

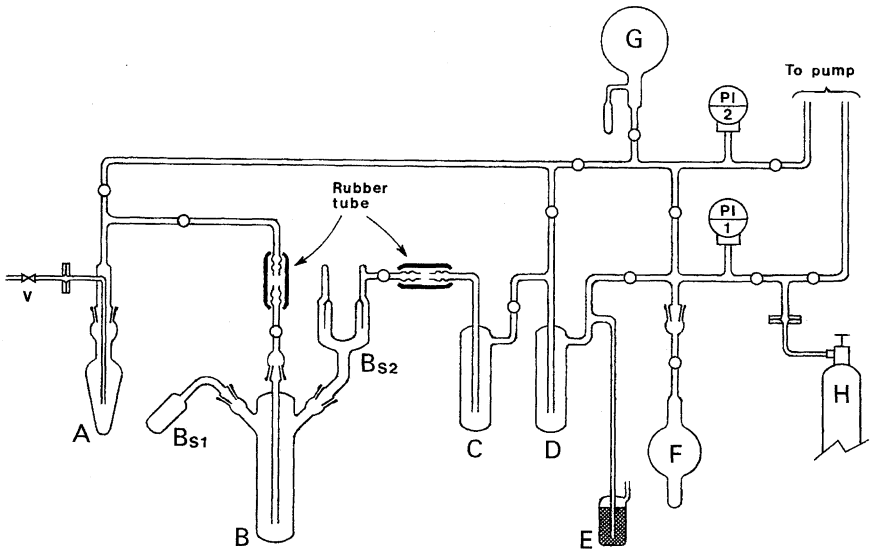

Fig. 3. Apparatus for SiF_4-to-SiH_4 conversion.

thermal decomposition of SiH_4, was kinetically studied by Hogness et al.[8] using a simple, cylindrical reaction vessel. However, we constructed a rather sophisticated apparatus for the sake of safety as well as for the sake of easy and efficient collection of product silicon. An essential part of the apparatus is shown in Fig. 4. As can be seen from the top illustration, the whole apparatus can be flushed with either Ar or N_2 before handling SiH_4. The exhaust gas from the reaction vessel is passed through a liquid-N_2 trap and a bubbler of aqueous NaOH, and then vented. (***Caution!*** *The national safety regulation enacted after this experiment requires more stringent safeguards in handling silanes.*)

The reaction vessel shown in the middle illustration is made of quartz except for the metal cap. The main tube A (80 mm o.d., 76 mm i.d., 760 mm in length) is partly constricted in the right end, which is connected to a metal bellows. The left end is fitted with a metal cap, as shown in the bottom illustration. Both the right and left connections were designed so as to completely prevent any possible gas leakage. Into the main tube is placed an inner tube B (74 mm o.d., 70 mm i.d., 500 mm long), which is sandwiched between two quartz plates (C and D). Plate C has an access tube for the reactant mixture, and plate D is perforated. This arrangement inside the main tube renders the product silicon deposit mainly upon the inner walls of the inner quartz tube, and, hence, lightens our labor of scraping and collecting the product silicon. (***Caution!*** *The quartz tube can easily crack when subjected to silicon deposition on its surface.*) Surrounding the reaction vessel is an infrared furnace (type P810C-P, Shinku Riko). Quartz plates (C and D) also serve to prevent the metal cap and the metal bellows from being overheated by this furnace.

The bottom illustration details a part of the metal cap. It is constructed from stainless-steel and aluminum parts. In order to ensure leak tightness, Viton O-rings are also used as shown. The Teflon® seal is put as buffer between the quartz reaction tube (A) and end cap (N).

(ii) Procedures and Results. The Typical procedures were as follows. After the whole apparatus was first repeatedly flushed with argon or nitrogen, the reaction vessel was evacuated. During evacuation the infrared furnace was switched on to allow the reaction vessel to be heated to 600

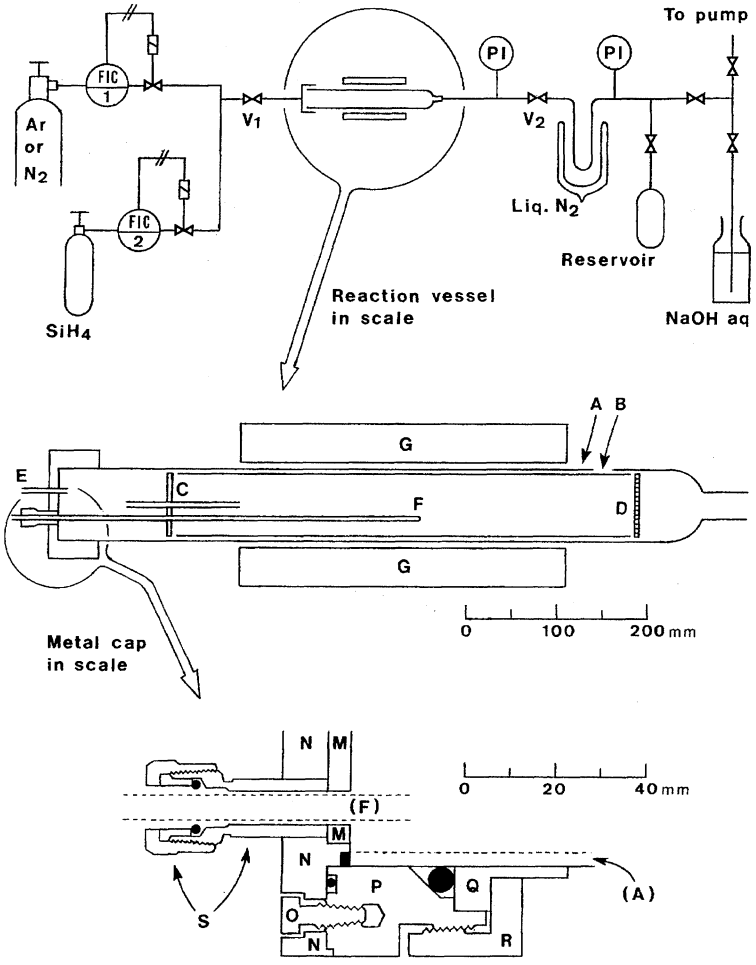

Fig. 4. Apparatus for SiH_4-to-Si conversion. (A) Main tube, (B) Inner tube, (C) Plate with a gas delivery tube, (D) Perforated plate, (E) Gas inlet tube, (F) Thermocouple sheath, (G) Infrared furnace, (M) Inner plate [SUS 304], (N) End cap [SUS 304], (O) Bolt [SUS 304], (P) O-ring coupler [Al], (Q) Cuff [Al], (R) Box nut [Al], (S) Cajon Ultra-Torr Adapter [SUS 316], (Solid circle) Viton O-ring, (Solid rectangle) Teflon® ring.

°C; evacuation was further continued for half an hour at that temperature. Valve V_2 was closed, and ^{30}Si-enriched SiH_4 was introduced into the reaction vessel at a flow rate of ca. 20 ml min^{-1} until a pressure of 380 Torr was attained (ca. 31 mmol or 740 cm^3 at 1 atm and 20 °C). Valve V_1 was immediately closed, and about 10 min thereafter a sudden production of white smoke was observed, accompanied by silicon deposition on the inner quartz tube. (***Caution!*** *The sudden smoking-deposition reaction was so exothermic that the reaction temperature would easily have reached or exceeded even 800 °C if the power supply to the infrared furnace had not been reduced properly without delay.*) In order to complete silane decomposition, the reaction vessel was allowed to stand at 600 °C for 3 to 4 h. The silicon deposits were inhomogeneous in appearance and texture, varying from place to place; brown films, small lumps, powders, and the like. After reaction the residual gas in the reaction vessel was slowly pumped out through the liquid-nitrogen trap, which was carefully inspected for unreacted silane. No condensations were observed, indicating complete decomposition of the silane. The inner tube was withdrawn, and the silicon deposits on its surface were scraped off. Scrapings from other parts of the reaction vessel were also collected together.

The above-mentioned entire procedure for SiH_4-to-Si conversion was repeated 5 more times using a combined total of 194 mmol of ^{30}Si-enriched SiH_4. The whole collection of Si scrapings weighed 3.06 g; this weight corresponds to 0.108 mol on the basis of atomic weight of Si 28.41 for the ^{30}Si-enriched sample (^{30}Si-atomic concn=17.5%, ^{29}Si-atomic concn=8.7%, Table 1), and gives a yield of 55.6% for the SiH_4-to-Si process.[9)]

(iii) Remarks. The rather low yield (55.6%) was perhaps entirely due to the difficulty and incompleteness of collecting the silicon deposits by scraping. Some of the silicon deposits were so strongly adhered to the quartz walls that we had to give up to collet them. Otherwise, we would have scraped the surface layers of the quartz walls, together with the silicon deposits, giving rise to an isotopic dilution of ^{30}Si.

References

1) K. Kobayashi, O. Yamakawa, K. Omata, K. Sugimoto, T. Shimoda, N. Takahashi, and I. Tanihata, *Phys. Rev. Lett.*, **60**, 2599 (1988).

2) M. Kamioka, Y. Ishikawa, H. Kaetsu, S. Isomura, and S. Arai, *J. Phys. Chem.*, **90**, 5727 (1986).

3) S. Arai, H. Kaetsu, and S. Isomura, *Appl. Phys.*, **B53**, 199 (1991).

4) T. Chitani, "Muki Kagaku," (Inorganic Chemistry), Sangyo Tosho, Tokyo (1959), p. 499.

5) Since no significant isotopic separation is expected during SiF_4-to-SiO_2 conversion, we regard the ^{30}Si-isotopic concentration measured with reactant SiF_4 as being retained in the final product SiO_2.

6) T. Moeller, "Inorganic Chemistry," John Wiley and Sons, New York (1952), p. 679.

7) A. E. Finholt, A. C. Bond, Jr., and H. I. Schlesinger, *J. Am. Chem. Soc.*, **69**, 1199 (1947).

8) T. R. Hogness, T. L. Wilson, and W. C. Johnson, *J. Am. Chem. Soc.*, **58**, 108 (1936).

9) Since no significant isotopic separation is expected during SiF_4-to-SiH_4-to-Si conversions, we regard the ^{30}Si-isotopic concentration measured with reactant SiF_4 as being retained in the final product, elemental Si.