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High Enrichment of ^{28}Si by Infrared Multiple Photon Decomposition of Si$_2$F$_6$

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High enrichment of ^{28}Si has been carried out using the laser isotope separation technique based on the isotopically selective infrared multiple photon decomposition of Si$_2$F$_6$. When about 2 Torr of Si$_2$F$_6$ was irradiated at a fluence of 1.0 J/cm^2 per pulse with the 10P(8) line of a TEA CO$_2$ laser at 954.55 cm^{-1}, the compound decomposed very efficiently with high isotope selectivity. The products SiF$_4$ and white solids were enriched with ^{29}Si and ^{30}Si, while the residual Si$_2$F$_6$ was enriched with ^{28}Si. The atomic fraction of ^{28}Si in residual Si$_2$F$_6$ increased with increasing decomposition of Si$_2$F$_6$; 99.9% of ^{28}Si was obtained at a consumption of 50% of initial Si$_2$F$_6$. The large-scale flow experiment yielded 99.7% ^{28}Si at a production rate of 2.5 g/h, where a mixture of 3.3 Torr Si$_2$F$_6$ and 6.6 Torr argon was irradiated with 10P(8) laser pulses at a repetition rate of 5 Hz. Merits and demerits of the present laser separation are discussed in comparison to those of conventional separation methods. Laser enrichment of ^{28}Si seems promising for economical production of large quantity of pure ^{28}Si. Various applications of silicon isotopes are briefly reviewed.

KEYWORDS: laser isotope separation, infrared multiple photon decomposition, Si$_2$F$_6$, carbon dioxide lasers, silicon 28, silicon 30

I. Introduction

It is well known that infrared multiple photon decomposition (IRMPD) sometimes shows remarkably large isotope effects under selected irradiation conditions.[1,2] Since early observations on isotope effects by Letokhov *et al.*, many efforts have been made for the application of IRMPD to practical isotope separation.[3–15] Most studies are concerned with ^{13}C separation by IRMPD of fluorohydrocarbons. Baranov has reported the production of enriched ^{12}C (atomic fraction, 99.99%; production rate, 1 g/h) by IRMPD of natural CF$_3$I using a high repetition CO$_2$ laser.[4] Fuss and his coworkers have reported the production of enriched ^{13}C (atomic purity, 50%; production rate, 65 mg/h) by IRMPD of CHClF$_2$ using a Q-switched cw CO$_2$ laser.[11–13]

Naturally occurring silicon consists of three stable isotopes: 92.23% of ^{28}Si, 4.67% of ^{29}Si, and 3.10% of ^{30}Si. Arai and his coworkers have demonstrated that the IRMPD of Si$_2$F$_6$ is highly selective on silicon isotopes in the TEA CO$_2$ laser irradiation with laser pulses in the vicinity of 950 cm^{-1}.[16–20] In addition to high isotopic selectivity, the decomposition occurs very efficiently at low fluences below 1.0 J·cm^{-2} per pulse. The efficient decomposition enables us to produce relatively large amounts of silicon isotopes using a commercially available high power TEA CO$_2$ laser. About 100 g of ^{28}Si (98–99%), ^{29}Si (12%), and ^{30}Si (20–30%) have been already provided to several research groups.[19]

Isotopically pure solid ^{28}Si is recently attracting increasing attention in solid state physics and microelectronics because of its remarkable enhancement of thermal conductivity.[21,22] In the present study the IRMPD of Si$_2$F$_6$ has been applied to the practical and high enrichment of ^{28}Si beyond 99%.

II. Experimental

1. Closed Cell

The starting material gas Si$_2$F$_6$ used here was purchased from Mitsui Chemical Company several years ago. The compound is not commercially available at present. The infrared spectroscopic analysis showed a trace of SiF$_4$ as an impurity. Therefore, Si$_2$F$_6$ was simply purified by low temperature distillation at the melting point (−95°C) of solid toluene prior to irradiation experiment, where vapor pressures of SiF$_4$ and Si$_2$F$_6$ are as follows: SiF$_4$, 760 Torr at −94.8°C; Si$_2$F$_6$, 1 Torr at −81°C and 0.12 Torr at −95°C (estimation).[23] Before handling Si$_2$F$_6$ on the vacuum line, the inner surfaces must be exposed several times to Si$_2$F$_6$, because adsorbed moisture on the surfaces rapidly reacts with Si$_2$F$_6$ to form SiF$_4$ and white solids.

An Ushio UGL-TEA-3C CO$_2$ laser was operated using a mixture of He, N$_2$, CO, and CO$_2$ as a lasing medium. The laser pulse has a sharp spike with a FWHM of about 0.1 μs followed by a long tail of few microseconds. The central part of the laser beam was truncated with a circular iris with a diameter of 1.5 cm. The circular beam was, without being focussed by an optical lens, introduced into the photolysis cell. The IRMPD of Si$_2$F$_6$ occurred in the optical geometry of a parallel beam. The repetition rate of pulses was mostly 0.5 Hz in the experiment using a closed photolysis cell.

The photolysis cell has a cross shape of two Pyrex glass tubes (2.0 cm inner diameter) with four NaCl windows (4.0 cm diameter, 0.40 cm thickness), which were attached

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tightly to the ends of tubes *via* rubber O-rings. The length of the cell was 10 cm in the direction of the laser irradiation, and the length was 5 cm in the direction of infrared spectral measurements. Laser fluences were simply determined from the beam cross section ($0.75 \times 0.75 \times 3.14 = 1.77$ cm^2) and observed pulse energies. The energy meter used was a Gentec ED-500. The laser fluence was changed by reducing the electrode voltage of a CO$_2$ laser.

Infrared absorption spectra of samples were measured with a JASCO FT/IR-410 infrared spectrophotometer. Si$_2$F$_6$ has large peaks at 990 and 823 cm^{-1}, and a small peak at 1,020 cm^{-1}. We could easily determine the amount of decomposition of Si$_2$F$_6$ from observed absorbances at 990 cm^{-1} before and after laser irradiation. In addition, we could observe absorption bands due to isotopic molecules of SiF$_4$ in the region of 1,010 to 1,030 cm^{-1}, although their bands overlap each other .

After laser irradiation all gases in the cell were trapped at the temperature of liquid nitrogen, and subsequently divided into two components: condensable and non-condensable components at $-95°$C. The former component was SiF$_4$ and the latter was almost exclusively Si$_2$F$_6$. Another product, white powders remained inside of the reaction cell as a non-volatile deposition at room temperature.

Isotopic compositions in SiF$_4$ were determined from peak intensities of signals for ^{28}SiF$_3^+$, ^{29}SiF$_3^+$, and ^{30}SiF$_3^+$ at $m/e = 85$, 86, and 87, respectively, in an Ulvac MSQ-400 Quadrupole Mass Analyzer. Before the determination we prepared the calibration curves of the ions showing quantitative relations between isotopic compositions and signal heights. Isotopic compositions in Si$_2$F$_6$ were determined using similar calibration curves from signals at $m/e = 151$ for ^{28,28}Si$_2$F$_5^+$, $m/e = 152$ for ^{28,29}Si$_2$F$_5^+$, and $m/e = 153$ for ^{28,30}Si$_2$F$_5^+$, because other signals for ^{29,30}Si$_2$F$_5^+$, ^{29,29}Si$_2$F$_5^+$, and ^{30,30}Si$_2$F$_5^+$ were negligibly small.

2. Open Cell

We have designed and built a flow separation apparatus for large-scale enrichment of silicon isotopes, where a Lumonics 822 or Ushio UGL-TEA-3C TEA CO$_2$ laser was used. The laser can generate a pulse with a maximum output energy of 10 J at a repetition rate of 10 Hz. However, we mostly used pulses with energies of about 5 J at a repetition rate of 5 or 10 Hz, because coating materials on the front mirror were gradually damaged at full power operation.

Figure 1 presents a schematic diagram of a flow separation apparatus, which is essentially the same as one published previously except small changes.[19] The regulating valve for the automatic pressure control was moved from the position behind the cell to the position behind the trap. The valve was frequently choked with a white powder at the previous position. The main part of a flow irradiation cell was a Pyrex cylindrical tube with a diameter of 8 cm with a BaF$_2$ window (5.0 cm diameter, 0.5 cm thickness) at both tube ends. Although isotopically selective IRMPD occurred in the optical geometry of the parallel beam, we focussed the beam by the lens with a long focal length of about 200 cm. The weak convergence seems to compensate for the reduction of the fluence as the beam passes through Si$_2$F$_6$. The diameter of the lens was large enough for the passage of the whole beam area without any loss. The total length of the cell was 400 cm and the total volume of the cell was 13.7 *l*. The entrance window for the laser was always blown with a stream of argon gas to prevent solid deposition on the window. The flow rates of Si$_2$F$_6$ and argon, and the pressure inside of the cell were automatically regulated with flow and pressure controllers. The product SiF$_4$ and residual Si$_2$F$_6$ were collected by the trap cooled with liquid nitrogen. Afterward, SiF$_4$ and Si$_2$F$_6$ were separated from one another by low temperature distillation at $-95°$C. Amounts of SiF$_4$ and Si$_2$F$_6$ were determined from their pressures in the glass bulb with a known volume. Iso-

PIC: Pressure controller,   FIC: Mass-flow controller,   PI: Pressure meter,   VP: Vacuum pump,
C: Pressure buffer,   G: Power meter,   N: Volumetric bulb
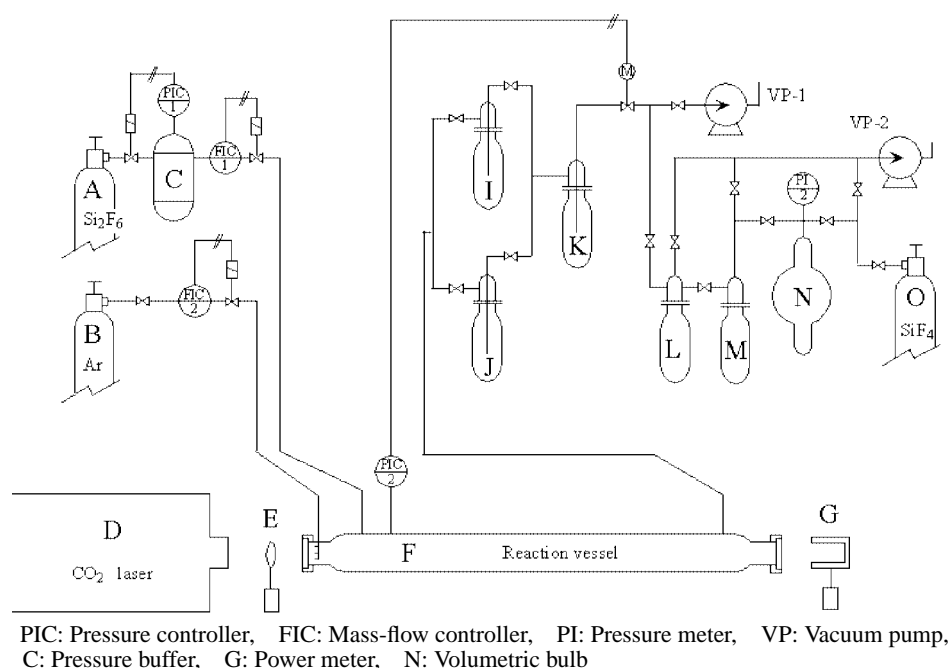
Fig. 1   Apparatus for flow experiment

topic compositions of both fluorosilanes were determined using a mass spectrometer. If necessary, infrared spectra of the fluorosilanes were also measured.

III. Results and Discussion

1. Laser Isotope Separation

Silicon compounds having an Si–F bond in molecules generally have an intense absorption band due to Si–F stretching vibration in the infrared region of 950 to 1,050 cm^{-1}, where a CO_2 laser has many emission lines. First of all, we have examined silicon isotope effects on IRMPD of SiF_4, SiF_3Cl, SiF_2Cl_2, SiF_3Br, SiF_3CH_3, and Si_2F_6 using a TEA CO_2 laser. Of these compounds examined, hexafluorodisilane has been found to undergo highly selective IRMPD in the irradiation with laser pulses at wavenumbers around 950 cm^{-1}.[16–20]

Figure 2 presents an infrared absorption spectrum observed for natural Si_2F_6 and intensities of 10P and 10R lines of a CO_2 TEA laser. The band with the peak at 990 cm^{-1} is certainly ascribed to the $^{28}SiF_3$ anti-symmetric stretching vibration mode of $^{28,28}Si_2F_6$.[24,25] The same figure also shows peak wavelengths estimated for $^{29,29}Si_2F_6$ (A at 981 cm^{-1}) and $^{30,30}Si_2F_6$ (B at 973 cm^{-1}). Heicklen and Knight have reported that $^{28}SiF_4$, $^{29}SiF_4$, and $^{30}SiF_4$ have respective absorption peaks at 1,031.8, 1,022.9, and 1,014.4 cm^{-1}.[26] We assumed the same isotopic shifts as SiF_4 in Fig. 2. Our theoretical calculations predict that frequencies of anti-symmetric SiF_3 stretching vibration modes are 992.3 cm^{-1} for $^{28,28}Si_2F_6$, 983.9 cm^{-1} for $^{29,29}Si_2F_6$, and 976.0 cm^{-1} for $^{30,30}Si_2F_6$.

The spectrum of Si_2F_6 in Fig. 2 corresponds to one photon absorption process which is different from the so-called multiple photon absorption process. Lyman and his coworkers have reported that the multiple photon absorption spectrum for natural Si_2F_6 has a peak at 977.5 cm^{-1}, which shifts to a lower energy side by 12.5 cm^{-1} as compared to the peak at 990 cm^{-1} in the one photon absorption spectrum. Their spectrum has been measured at an average fluence of 0.28 J/cm^2 using a free electron laser.[27] We consider that there may be considerable isotopic shifts among multiple photon absorption spectra for molecules containing $^{28}SiF_3$, $^{29}SiF_3$, and $^{30}SiF_3$. The shifts must be responsible for the isotopic selec-

tivity in the IRMPD of Si_2F_6. However, multiple photon absorption spectra have not been measured directly for isotopic Si_2F_6 molecules other than $^{28,28}Si_2F_6$.

The final product SiF_4 and white solids were enriched with ^{29}Si and ^{30}Si in the isotope selective IRMPD of Si_2F_6, while residual Si_2F_6 was enriched with ^{28}Si. Our previous studies have demonstrated that the irradiation of natural Si_2F_6 with the 10P(12) line at 951.19 cm^{-1} gives the highest selectivity of ^{30}Si.[16,17] When 2 Torr of Si_2F_6 was irradiated with pulses at a fluence of 0.25 J/cm^2 per pulse, the SiF_4 produced was found to contain 46% of ^{28}Si, 8% of ^{29}Si, and 46% of ^{30}Si. Since the enrichment of ^{30}Si is mainly caused by the selective IRMPD of $^{28,30}Si_2F_6$, it is almost impossible to obtain ^{30}Si with isotopic purities higher than 50%.

The initial step of the IRMPD of Si_2F_6 is the monomolecular decomposition of a vibrationally excited Si_2F_6 molecule into SiF_4 and SiF_2 as shown in Reaction (1), where n stands for the number of absorbed photons by Si_2F_6:

$$Si_2F_6 + nh\nu \rightarrow SiF_4 + SiF_2. \tag{1}$$
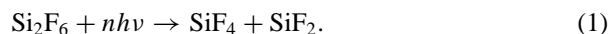
Subsequently, SiF_2 radicals aggregate to form white solids, as shown in Reaction (2), where m stands for the number of radicals in aggregation:

$$mSiF_2 \rightarrow (SiF_2)_m. \tag{2}$$

The pyrolysis studies of Si_2F_6 show that the decomposition requires an activation energy of 206 or 193.5 kJ/mol, which corresponds to 18 or 17 photons at 950 cm^{-1}.[28,29] This fact means that the Si_2F_6 molecule must absorb at least 17 or more laser photons prior to decomposition.

The relations between decomposition yields or isotopic selectivities and laser fluence have been examined extensively in the previous paper.[17] The observed results show that the minimum fluence required for IRMPD is as low as 0.2 J/cm^2 at wavenumbers around 950 cm^{-1}. Since the Ushio CO_2 laser can generate the pulse beam of the 10P(12) line with higher fluences than 1 J/cm^2, the IRMPD occurs very efficiently within the large volume along the parallel beam. As the result, one can attain large yields of silicon isotopes in the IRMPD of this compound.

The isotopic selectivity does not change appreciably up to 8 Torr, although it decreases rapidly with increasing pressure beyond 8 Torr. On the other hand, the yield of decomposition of Si_2F_6 decreases almost exponentially with an increase in pressure. We always filled the photolysis cell with 2 Torr of Si_2F_6 in the present experiment using a closed cell.

Table 1 tabulates the composition of isotopic molecules in natural Si_2F_6. If the isotopic selectivity in IRMPD is perfect, the atomic purity of ^{28}Si should reach 100% at a consumption of 14.94% of initial Si_2F_6, while the product should have 47.96% of ^{28}Si, 31.26% of ^{29}Si, and 20.78% of ^{30}Si. **Figure 3** presents the relation between isotopic purity of ^{28}Si in the residual Si_2F_6 and consumption of Si_2F_6 in the irradiation of 2 Torr Si_2F_6 with 10P(8) laser pulses at 954.55 cm^{-1}, where the laser fluence was 1.0 J/cm^2 per pulse in a parallel beam geometry. The 10P(8) laser line has been shown to give the highest selectivity in the enrichment of ^{28}Si.[16,17] The purity of ^{28}Si increases with increasing decomposition of Si_2F_6 and reaches 99.9% at a consumption of 50%. Therefore, the irra-
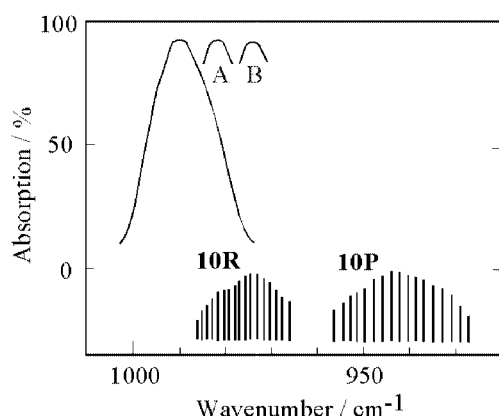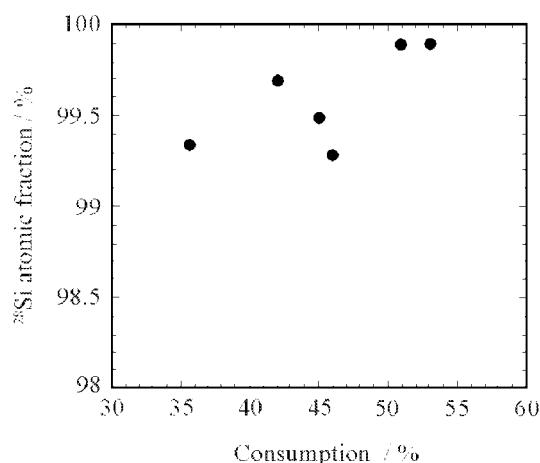

Fig. 2 Infrared absorption spectrum of $^{28,28}Si_2F_6$, and absorption peaks estimated for $^{29,29}Si_2F_6$ (A) and $^{30,30}Si_2F_6$ (B), together with intensities of 10P and 10R lines of a CO_2 TEA laser

Table 1 Isotopic composition of Si_2F_6

Isotopic molecule	Abundance (%)
$^{28,28}Si_2F_6$	85.06
$^{28,29}Si_2F_6$	8.61
$^{28,30}Si_2F_6$	5.72
$^{29,29}Si_2F_6$	0.22
$^{29,30}Si_2F_6$	0.29
$^{30,30}Si_2F_6$	0.10

Fig. 3 Relation between ^{28}Si atomic fraction in residual Si_2F_6 and consumption of Si_2F_6

Two Torr of natural Si_2F_6 was irradiated with laser pulses at $954.55\,cm^{-1}$. The laser fluence was $1\,J/cm^2$.

diation of Si_2F_6 with 10P(8) laser pulses causes the IRMPD of $^{28,28}Si_2F_6$ to some extent, although the amount of the decomposition per pulse is less than those of Si_2F_6 molecules containing ^{29}Si and ^{30}Si.

In the large-scale experiment using an open cell we produced 99.7% ^{28}Si at the rate of 0.042 mole/h (2.5 g of ^{28}Si/h), as tabulated in **Table 2**, where the laser was tuned to the 10P(8) line at $954.55\,cm^{-1}$, the repetition rate of pulses was 5 Hz, and the laser output was 22.2 W. If one year is defined as $8\,h \times 200\,d$ in operation, the total amount of ^{28}Si is 4 kg/yr using only one TEA CO_2 laser, which is, although powerful, commonly employed in laser chemistry. It is quite possible to increase the productivity by optimization of experimental factors and by improvement of laser power or repetition rate. On the other hand we produced 0.014 mole SiF_4/h (atomic fraction of ^{30}Si, 33%), where the laser was tuned to the 10P(12)

line at $951.22\,cm^{-1}$ and the repetition rate was 10 Hz. The results are also included in Table 2.

2. Other Separation Methods

Although silicon isotopes have been produced on a milligram scale by electromagnetic separation, the method cannot provide practical amounts of isotopes in materials science or industries. In the low temperature distillation of SiF_4 the observed separation factor seems too low to be applied to practical separation of silicon isotopes.[30] Separation by chemical exchange is still at the preliminary stage of the study. The ultracentrifuge of SiF_4, which has provided highly pure ^{28}Si to research groups in Japan and Germany for their solid state physics studies, may compete with laser separation in future.[22,31]

In conventional separation methods high enrichment is finally accomplished through the cascade of a huge number of unitary separation processes. It is impossible to design a cascade of separation processes in photochemical methods. Fortunately, high enrichment of ^{28}Si is attained only in one irradiation process. Prolonged laser irradiation or repetition of irradiation processes probably makes it possible to produce ^{28}Si with higher purities than 99.9%. Although Si_2F_6 is not commercially available, the compound can be easily obtained in the fluorination of Si_2Cl_6 with SbF_3.[29] The preparation of Si_2Cl_6 has been described in Inorganic Synthesis; the most satisfactory is the chlorination of calcium-silicon alloy.[32] The cost of Si_2F_6 may be lowered considerably depending on the amount of production.

3. Application of Silicon Isotopes

We have already provided enriched ^{28}Si (98–99%) and ^{30}Si (20–30%) in chemical forms of SiO_2 and solid Si to several research groups in Japan. The white powder of SiO_2 was produced from the hydrolysis of SiF_4 in aqueous solutions of ammonia, where the SiF_4 was enriched with ^{30}Si in the present laser method. SiO_2 with a ^{28}Si-purity of 99% was produced from the hydrolysis of ^{28}Si-enriched Si_2F_6. Solid silicon enriched with ^{30}Si was produced in the following way:[20] SiF_4 enriched with ^{30}Si was reduced with $LiAlH_4$ in diethylether to form SiH_4. Thermal decomposition of the SiH_4 yielded solid Si enriched with ^{30}Si. We consider that solid Si enriched with ^{28}Si may be produced from Si_2F_6 in the same way as SiF_4, after Si_2F_6 is isotopically purified in the present laser method. **Table 3** tabulates various applications of silicon isotopes.[21,22,31,33–38]

Table 2 Production rates of silicon isotopes in large-scale separation

Laser line	Pulse condition	Isotope	Feed rate of natural Si_2F_6	Pressure	Production rate
10P(8) $954.55\,cm^{-1}$	4.5 J/pulse 5 Hz	^{28}Si 99.7%	0.072 mole/h	Si_2F_6 3.3 Torr Ar 6.6 Torr	0.042 mole/h unreacted Si_2F_6 2.4 g(Si)/h
10P(12) $951.19\,cm^{-1}$	3.3 J/pulse 10 Hz	^{30}Si 33.0%	0.20 mole/h	Si_2F_6 2.3 Torr Ar 1.8 Torr	0.014 mole/h SiF_4 0.4 g(Si)/h

Table 3 Various application of silicon isotopes[21, 22, 31, 33–38]

Application	Isotopes required
High thermal conductivity silicon wafer	^{28}Si
Phonon mediated elementary particle detector	^{28}Si
Silicon based nuclear spin quantum computer	^{28}Si
Silicon self diffusion coefficient measurement	^{28}Si, ^{30}Si
Determination of size distribution of silicon clusters	^{28}Si
Precise determination of Avogadro number	^{28}Si, ^{29}Si, ^{30}Si
Effects of various silicon fertilizers on botanical growth	^{28}Si, ^{29}Si, ^{30}Si
^{29}Si doping into GaAs crystal	^{29}Si
Nuclear reactions of ^{30}Si with high energy particles	^{30}Si
Neutron transmutation doping	^{30}Si
Nuclear magnetic resonance studies	^{29}Si
Geochemical studies	^{28}Si, ^{29}Si, ^{30}Si
Ceramics studies	^{28}Si, ^{29}Si, ^{30}Si

IV. Concluding Remarks

The infrared multiple photon decomposition of Si$_2$F$_6$ was isotopically selective in the irradiation with CO$_2$ laser pulses at wavenumbers in the vicinity of 950 cm^{-1}. Decomposition occurred efficiently at fluences below 1 J/cm^2 per pulse and therefore in a large photolysis volume along the parallel laser beam. The products SiF$_4$ and white solids were enriched with ^{29}Si and ^{30}Si, while the residual Si$_2$F$_6$ was enriched with ^{28}Si. When 2 Torr of Si$_2$F$_6$ was irradiated with 10P(8) line pulses at 954.55 cm^{-1} and at a laser fluence of 1.0 J/cm^2, the atomic purity of ^{28}Si in residual Si$_2$F$_6$ reached 99.9% at a consumption of 50% of initial Si$_2$F$_6$. In the flow experiment using a high power TEA CO$_2$ laser we were able to demonstrate the production of 99.7% ^{28}Si at the rate of 2.5 g/h, which corresponds to a productivity of 4 kg/yr. Silicon-30 (atomic purity of ^{30}Si, 30%) was produced at the rate of 0.5 g/h. Silicon isotopes are attracting increasing attention in many fields of science and technology. Especially, highly pure ^{28}Si is apparently useful as a material with high thermal conductivity in microelectronics.

Acknowledgment

References

1) R. V. Ambartzmian, V. S. Letokhov, E. A. Ryabov, N. V. Chekalin, *Sov. Phys. JETP Lett.*, **20**, 273 (1974).
2) V. S. Letokhov, *Nonlinear Laser Chemistry*, Springer Ser. Opt. Vol. 4, Springer-Verlag, Berlin, (1983).
3) A. V. Evseev, V. S. Letokhov, A. A. Puretzky, *Appl. Phys.*, **B36**, 93 (1985).
4) V. Yu. Baranov, *IEEE J. Quantum Electron.*, **QE-19**, 1577 (1983).
5) M. Gauthier, C. G. Cureton, P. A. Hackett, C. Willis, *Appl. Phys.*, **B28**, 43 (1982).
6) A. Outhouse, P. Lawrence, M. Gauthier, P. A. Hackett, *Appl. Phys.*, **B36**, 63 (1985).
7) S. Arai, K. Sugita, P. H. Ma, Y. Ishikawa, H. Kaetsu, S. Isomura, *Chem. Phys. Lett.*, **151**, 516 (1988).
8) S. Arai, K. Sugita, P. H. Ma, Y. Ishikawa, H. Kaetsu, S. Isomura, *Appl. Phys.*, **B48**, 427 (1989).
9) K. Sugita, P. H. Ma, Y. Ishikawa, S. Arai, *Appl. Phys.*, **B52**, 266 (1991).
10) K. Sugita, Y. Miyamoto, S. Arai, S. Kuribayashi, T. Majima, S. Yamamoto, *J. Phys. Chem. A*, **104**, 2587 (2000).
11) W. Fuss, J. Göthel, M. Ivanenko, W. E. Schmid, P. Hering, K. L. Kompa, K. Witte, *Isotopenpraxis Enviro. Health Stud.*, **30**, 199 (1994).
12) W. Fuss, J. Gothel, M. M. Ivanenko, K. L. Kompa, W. E. Schmid, K. Witte, *Z. Phys.*, **D29**, 291 (1994).
13) J. Gothel, M. Ivanenko, P. Hering, W. Fuss, K. L. Kompa, *Appl. Phys.*, **B62**, 329 (1993).
14) P. Parthasarathy, S. K. Sarkar, N. V. Iyer, K. V. S. Rama Rao, J. P. Mittal, *Appl. Phys.*, **B56**, 321 (1993).
15) A. Batra, S. K. Sarkar, V. Parthasarathy, *J. Photochem. Photobiol. A*, **83**, 193 (1994).
16) M. Kamioka, S. Arai, Y. Ishikawa, S. Isomura, N. Takamiya, *Chem. Phys. Lett.*, **119**, 357 (1985).
17) M. Kamioka, Y. Ishikawa, H. Kaetsu, S. Isomura, S. Arai, *J. Phys. Chem.*, **90**, 5727 (1986).
18) S. Arai, M. Kawai, H. Morimoto, K. Tanaka, H. Seyama, M. Soma, *Appl. Phys.*, **B47**, 243 (1988).
19) S. Arai, H. Kaetsu, S. Isomura, *Appl. Phys.*, **B53**, 199 (1991).
20) K. Tanaka, S. Isomura, H. Kaetsu, Y. Yatsurugi, M. Hashimoto, K. Togashi, S. Arai, *Bull. Chem. Soc. Jpn.*, **69**, 493 (1996).
21) W. S. Capinski, H. J. Maris, E. Bauser, I. Silier, M. Asen-Palmer, T. Ruf, M. Cardona, E. Gmelin, *Appl. Phys. Lett.*, **71**, 2109 (1997).
22) T. Ruf, R. W. Henn, M. Asen-Palmer, E. Gmelin, M. Cardona, H.-J. Pohl, G. G. Devyatych, P. G. Sennikov, *Solid State Commun.*, **115**, 243 (2000).
23) D. R. Stull, *Ind. Eng.*, **39**, 517 (1947).
24) F. Hofler, S. Waldhor, E. Hengge, *Spectrochim. Acta*, **28A**, 29 (1972).
25) V. E. Sahini, R. Grigorovici, A. Butucelea, *Rev. Roumaine Chim.*, **23**, 643 (1978).
26) J. Heicklen, V. Knight, *Spectrochim. Acta*, **20**, 295 (1964).
27) J. L. Lyman, B. E. Newnam, T. Noda, H. Suzuki, *J. Phys. Chem. A*, **103**, 4227 (1999).

28) M. Bowery, J. H. Purnell, *Proc. R. Soc. London Ser. A*, **321**, 341 (1971).

29) S. K. Bains, P. N. Noble, R. Walsh, *J. Chem. Soc., Faraday Trans.*, **82**, 837 (1986).

30) T. R. Mills, *Sep. Sci. Technol.*, **25**, 335 (1990).

31) K. Takyu, K. M. Itoh, K. Oka, N. Saito, V. I. Ozhogin, *Jpn. J. Appl. Phys.*, **38**, L341 (1999).

32) Editor-in-chief H. S. Booth, *Inorganic Syntheses*, McGraw-Hill 1939, New York, Vol. 1, p. 42 (1935).

33) E. E. Haller, *J. Appl. Phys.*, **77**, 2857 (1995).

34) M. Asen-Palmer, K. Bartkowski, E. Gmelin, M. Cardona, A. P. Zhernov, A. V. Inyushkin, A. Taldenkov, V. I. Ozhogin, K. M. Itoh, E. E. Haller, *Phys. Rev. B*, **56**, 9431 (1997).

35) H. Bracht, E. E. Haller, R. Clark-Phelps, *Phys. Rev. Lett.*, **81**, 393 (1998).

36) B. E. Kane, *Nature*, **393**, 133 (1998).

37) P. Becker, H. Bettin, P. De Bievre, C. Holm, U. Kutgens, F. Spieweck, J. Stumpel, S. Valkiers, W. Zulehner, *IEEE Trans. Instrum. Meas.*, **44**, 522 (1995).

38) B. A. Young, B. Cabrela, A. T. Lee, *Phys. Rev. Lett.*, **64**, 2795 (1990).