On-line Formation of Isotopically Controlled Si Films from Fluoro-Silane

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Abstract

The formation of Si films enriched with ^{28}Si has been studied using on-line system combined with isotope separation and chemical vapor deposition (CVD) process. The isotope separation of ^{28}Si was performed with isotopic selective decomposition of hexafluorodisilane (Si_2F_6) under irradiation of CO_2 pulse laser. Si_2F_6 containing ^{29}Si and ^{30}Si was preferentially decomposed to SiF_4 and SiF_2 by laser irradiation at 952-956 cm^{-1}. ^{28}Si was enriched in the residual Si_2F_6. Si isotope concentrations in the enriched gas were measured with quadrupole mass spectrometer (QMS). The formation of Si films was conducted by microwave plasma CVD with fluoro-siline gas at substrate temperature of 523-873 K. The films were observed with scanning electron microscope (SEM) and X-ray diffraction (XRD). The isotope concentrations of Si film were measured with grow discharge mass spectrometer (GDMS). QMS analysis indicated that the average ^{28}Si concentration in the residual Si_2F_6 was 97.8%. The average yield of ^{28}Si enriched gas against to original Si_2F_6 was about 8 vol%. XRD analysis indicated that polycrystalline Si films were obtained by decomposition of fluoro-siline even at 523 K. GDMS results showed that by using ^{28}Si enriched gas, the deposited film contained ^{28}Si of 98.02%. This concentration was fairly matched with the result of QMS analysis. The yield rate of ^{28}Si enriched film was 6.75×10-6 gs^{-1}. The present result indicates the possibility of on-line formation of isotope-controlled nanostructure Si materials.

1. Introduction

Isotopically controlled silicon is expected to improve thermal properties of silicon by reduction of isotope scattering[1] and also a candidate of molar standard material[2]. Recently, the possibility of growth techniques for isotope-controlled thin semiconducting layers using liquid phase epitaxy or molecular beam epitaxy was reported[3]. These techniques make isotope-controlled nanostructure devices possible. To realize such isotopically controlled materials, the practical isotope separation process and materials formation process are required. Among several separation processes, laser isotope separation is considered as one of attractive methods to produce a large amount of isotope. CVD of siline is well established process for formation of silicon thin film.

In the present paper, the formation of Si films enriched with ^{28}Si has been studied using on-line system combined with isotope separation and CVD process. ^{28}Si enriched fluorosiline gas was prepared by infrared multi-photon decomposition of Si_2F_6 under irradiation of CO_2 pulse laser. Si films were made from ^{28}Si enriched fluoro-siline gas by using microwave plasma CVD.

2. Experimental

The infrared absorption spectra of natural Si_2F_6 and CO_2 laser emission lines are shown in Fig. 1. Since the natural abundance ratio of silicon is ^{28}Si:^{29}Si:^{30}Si = 92.23:4.67:3.10, it was considered that the strong peak at 990 cm^{-1} was due to antisymmetric stretching vibration of ^{28}Si-F bond. The previous study reported that SiF_4 has three isotope absorption peaks of ^{28}Si-F, ^{29}Si-F and ^{30}Si-F bond at 1031.54, 1022.56 and 1014.1 cm^{-1}, respectively[4]. Though the peaks of ^{29}Si-F and ^{30}Si-F bond are not obvious in Fig. 1, it was assumed from the case of SiF_4 that they appear at lower wavenumber region than 990 cm^{-1}. Since the emission lines of laser

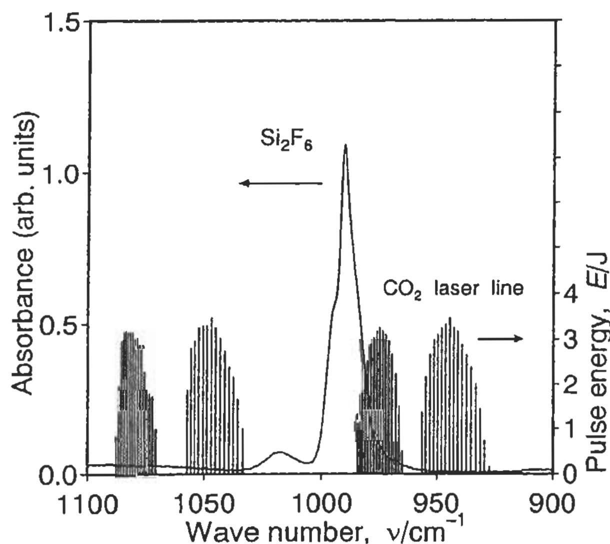


Fig.1 Infrared spectrum of Si_2F_6 and CO_2 pulse laser lines at 900-1100 cm^{-1}.

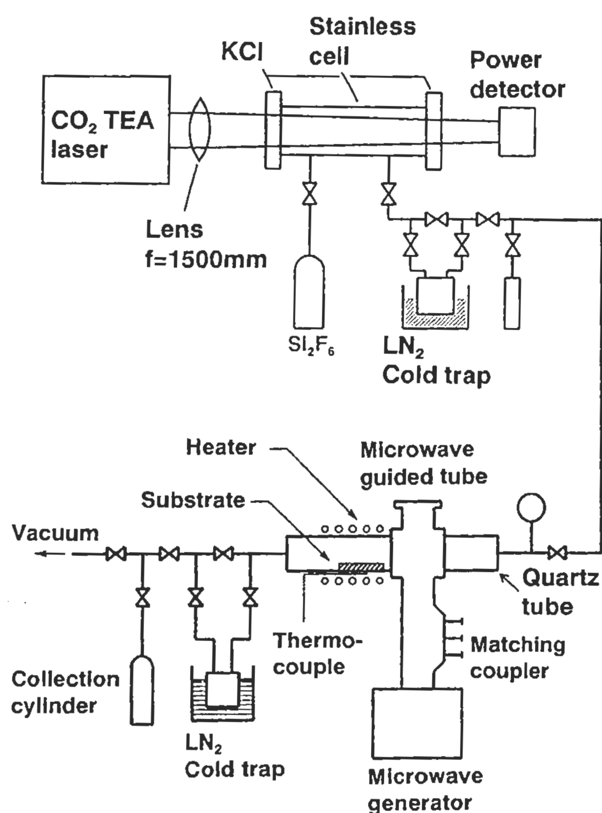


Fig.2 Schematic diagram of experimental apparatus.

exist at 930-980 cm^{-1} as seen in Fig. 1, the preferential decomposition of Si_2F_6 containing ^{29}Si and ^{30}Si is occurred as following reaction by selecting appropriate wavenumber at 930-980 cm^{-1} and ^{28}Si is enriched in undecomposed Si_2F_6 [5].

$$^{29,30}Si_2F_6(gas)+nh\nu \rightarrow {}^{29,30}SiF_4(gas)+{}^{29,30}SiF_2(solid), \quad (1)$$

where n is number of infrared photon, h the Plank constant and ν the frequency of photon.

Figure 2 shows the schematic diagram of experimental apparatus. Si_2F_6 with purity better than 99% was produced by fluorination of Si_2Cl_6 with ZnF_2. Si_2F_6 was introduced into 2000 mm long, 54.6 mm inner diameter stainless steel cell with KCl windows at both ends. The flow rate and pressure of gas were set at 1.67-167 mm^3s^{-1} and 3.34-789 Pa, respectively. The beam of CO_2 pulse laser was slightly focused by ZnSe lens and thrown at the cell. The wavenumber and energy of laser were set at 929.022-983.284 cm^{-1} and 0.5-3.12 J, respectively. The irradiation was performed with a repetition of 10 Hz at room temperature. Si_2F_6 was decomposed to form SiF_4 and SiF_2 by laser irradiation. Both product SiF_4 and residual Si_2F_6 were captured with liquid nitrogen cold trap and then separated into each component by low temperature distillation. After separation, the measurements of isotope concentration were performed with off-line QMS by the sampling of gas. In the plasma CVD, to investigate optimum condition of film formation, natural abundance SiF_4 was used as a source gas prior to use of isotope enriched fluoro-siline gas. H_2 and Ar gas were also used as plasma assist and scavenging gas, respectively. The quartz plates of $12\times12\times1$ mm^3 were used as film deposition substrates. The substrate was placed inside of the quartz reaction tube so that the substrate does not contact plasma. Substrate temperature was kept at 523-873K. Microwave of 2.45 GHz, 8.4×10^{-4} Wm^{-2} was applied to quartz reaction tube. After the deposition, the films were observed and identified with SEM, XRD. In the case of using ^{28}Si enriched source gas, undecomposed fluoro-siline gas was collected at liquid nitrogen trap and reused as a source gas. The isotope concentrations of film were measured by using GDMS.

3. Results and discussion

3.1 Isotope enrichment of ^{28}Si

Figure 3 shows the relation between the concentrations of silicon isotope in the residual Si_2F_6 and the irradiation wavenumber of laser. Since ^{29}Si and ^{30}Si were eliminated from Si_2F_6 as a result of preferential decomposition of Si_2F_6 to SiF_4 and SiF_2 at 940-955 cm^{-1} [5], ^{28}Si was concentrated in residual Si_2F_6. When the laser

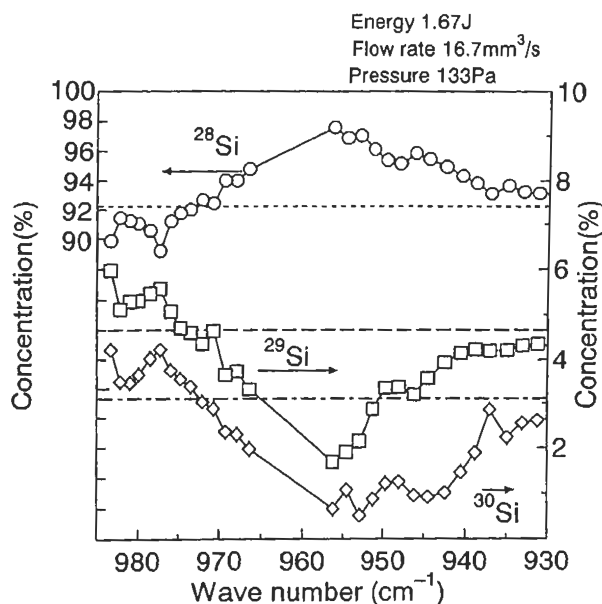


Fig.3 Concentrations of Si isotope in the residual Si_2F_6 as a function of wavenumber.

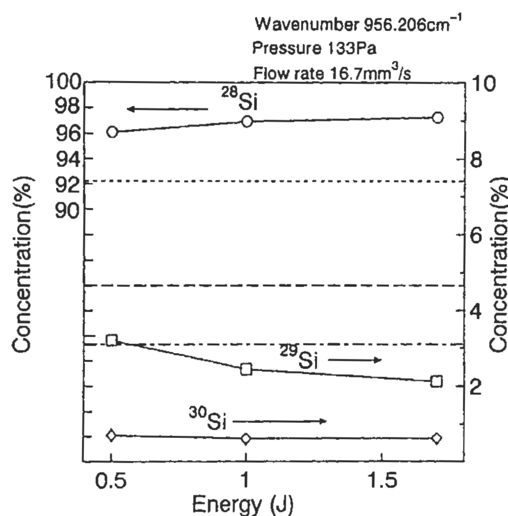


Fig.4 Energy dependence of Si isotope concentrations in the residual Si_2F_6.

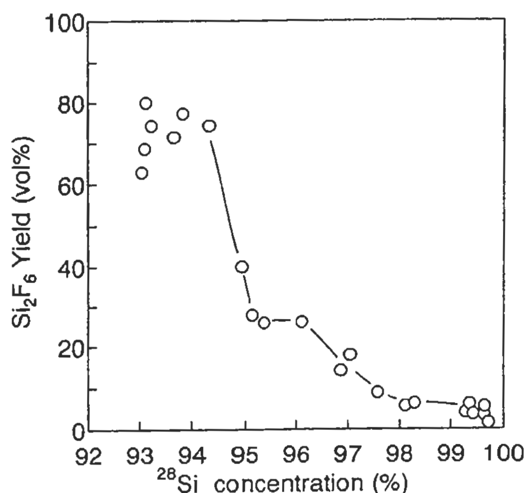


Fig.5 Relation between Si_2F_6 yield and ^{28}Si concentration.

line was selected at 956.205 cm^{-1}, the concentration of ^{28}Si increased up to 97.6%. On the other side, since the laser lines are close to the absorption peak of ^{28}Si-F bond at 975-980 cm^{-1}, the decomposition of Si_2F_6 including ^{28}Si was preferentially occurred. The residual Si_2F_6 contained 6% of ^{29}Si and 4.3% of ^{30}Si by the irradiation at 983.305 cm^{-1}. Figure 4 shows the energy dependence of silicon isotope concentration in the residual Si_2F_6 at 956.205 cm^{-1} which is optimum wavenumber for enrichment of ^{28}Si as seen in fig. 3. The concentration of ^{28}Si increased with the increasing of laser energy. Since higher energy than 1.67 J could not be obtained at 956.205 cm^{-1} by the limitation of laser apparatus, more enrichment wasn't conducted. Figure 5 shows the relation between isotope enriched Si_2F_6 yield against original Si_2F_6 and ^{28}Si concentration in the once gas through process. The yield decreased rapidly with increasing of ^{28}Si concentration. After optimizing separation conditions, the maximum concentration of 99.72% was obtained though the yield was only 1.5 vol%. As seen in fig. 5, if the ^{28}Si concentration of 99% is enough, the yield of 5% is easily obtained by this process. From the above results, the mass production of Si_2F_6 gas enriched with ^{28}Si was performed under the optimum condition of laser wavenumber and energy. QMS analysis indicated that the final concentration of ^{28}Si in the stored Si_2F_6 gas was 97.8%. This isotope-enriched gas of 1737 cm^3 was obtained with the average yield of 8 vol% against original Si_2F_6.

3.2 Formation of Si films by plasma CVD

To determine the optimum conditions of Si film formation, natural abundance SiF_4 was used as a source gas at first. The gas flow rates of SiF_4, H_2, and Ar were set at 33.3, 1000, and 333 mm^3s^{-1}, respectively. The total pressure was kept at 133 Pa. Figure 6 shows the surface morphology of deposited films at various substrate temperatures. As seen in fig. 6, the growth of grain size and its network structure was promoted with increasing the temperature. The reason of small grain size in fig. 6(d) was considered that the film structure was changed into more dense by heat effect. The growth rate of film thickness was also measured from the cross section view of film by SEM. The growth rate was 6.9×10^{-10} ms^{-1} and it was independent from substrate temperature. Figure 7 shows the X-ray diffraction patterns of Si films at various substrate temperatures. Sharp peaks corresponding to Si crystalline plane were detected at each temperature. XRD analysis indicated that polycrystalline Si films were obtained by decomposition of fluoro-siline using plasma CVD at relatively low temperature of 523K. Figure 8 shows the Si film yield rate and collection efficiency as a function of SiF_4 flow rate in the once gas through process. Though the Si collection efficiency decreased with increasing the SiF_4

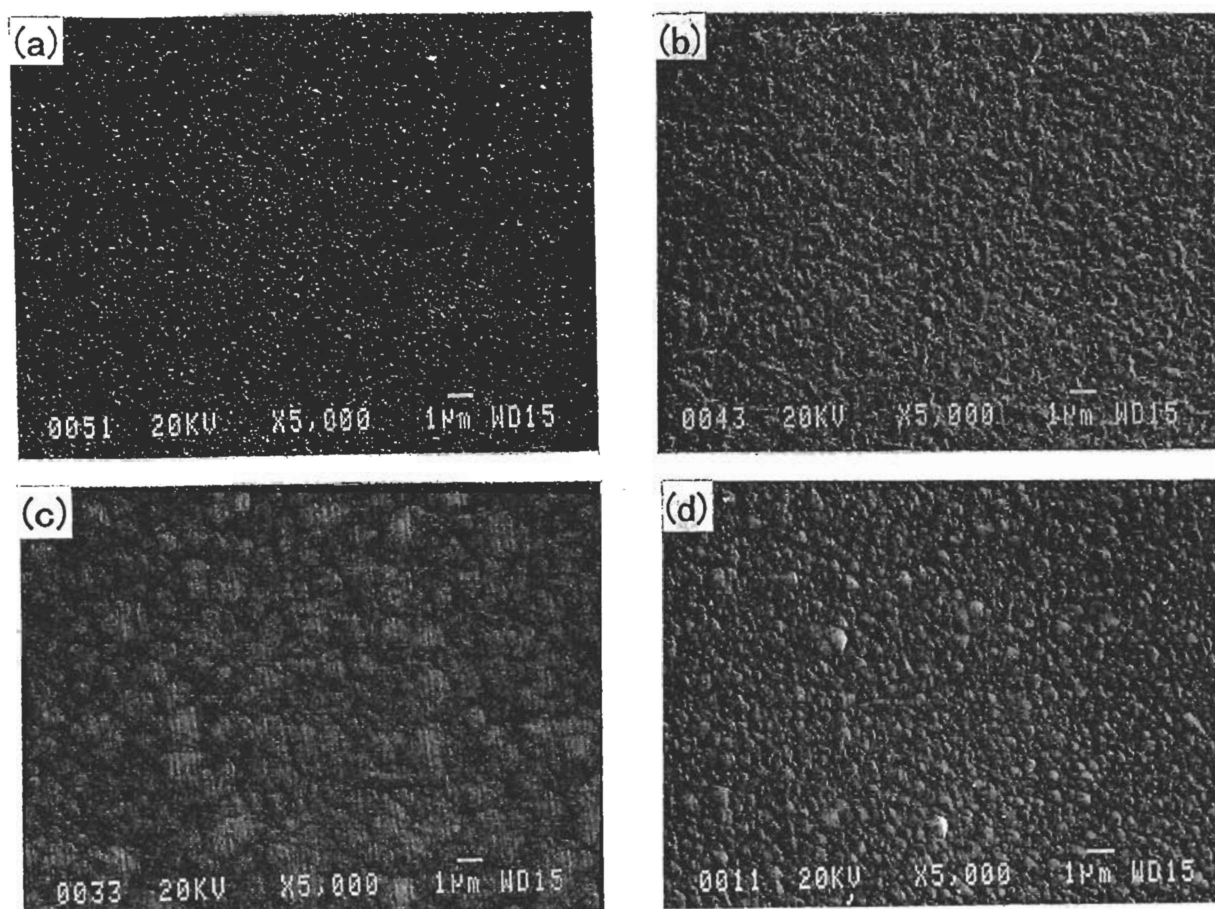
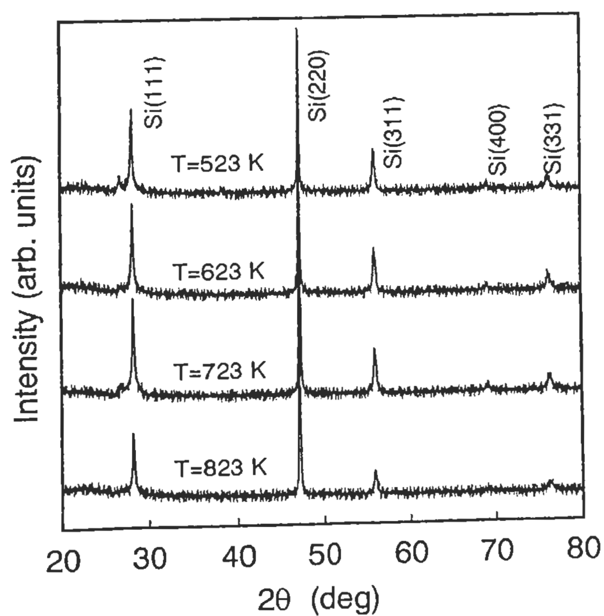


Fig.6 Surface morphology of deposited films on quartz substrate at 523 K(a), 623 K(b), 723 K(c), 823 K(d).



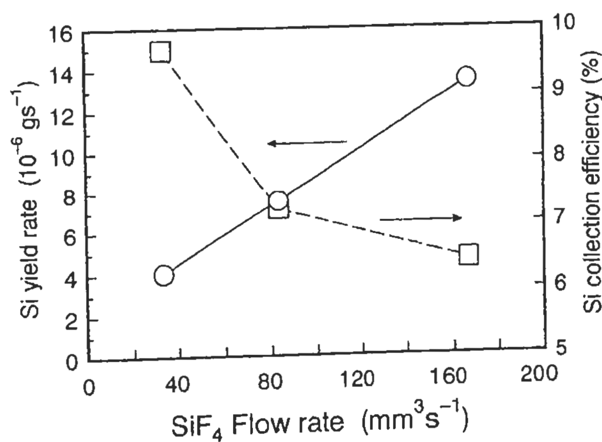


Fig.7 X-ray diffraction patterns of Si films at various substrate temperature.

Fig.8 Silicon film yield rate and collection efficiency as a function of SiF_4 flow rate.

flow rate, the film yield rate increased linearly. In the CVD process, undecomposed fluoro-siline gas is collected at liquid nitrogen trap and reused as a source gas. This result indicated the possibility that the high Si film yield rate due to increment of source gas flow rate is compatible with the high Si collection efficiency due to repetition of CVD process.

Finally the Si isotope enriched film was made from ^{28}Si concentrated Si_2F_6 gas. The deposition was performed under the same condition with natural SiF_4 at temperature of 673 K. The Si isotope ratio of deposited film was determined by using GDMS and compared to the result of QMS measurement of isotope enriched gas. From GDMS measurement, it was shown that the deposited film contained ^{28}Si of 98.02%. This concentration fairly coincided with the value of QMS analysis. Totally, 1.54 mg of ^{28}Si enriched film was obtained with the yield rate of $6.75\times10^{-6}gs^{-1}$.

4. Conclusion

On-line formation of isotopically controlled Si film was performed by combination of laser isotope separation and plasma CVD. The effects of wavenumber and energy of CO_2 laser on the enrichment of ^{28}Si were examined. In the plasma CVD by using fluoro-siline, the effect of substrate temperature and flow rate of source gas was examined. The followings were concluded:

1. High enrichment of ^{28}Si in the residual Si_2F_6 was observed by laser irradiation at 952-956 cm^{-1}.
2. The average concentration of ^{28}Si in the residual Si_2F_6 gas was 97.8%. This isotope enriched gas was obtained with the average yield rate of about 8 vol%.
3. The polycrystalline Si films were obtained by decomposition of fluoro-siline using plasma CVD at 523-873K.
4. The film formed from Si enriched source gas contained ^{28}Si of 98.02%. This film was obtained with the average yield rate of 6.75×10^{-6} gs^{-1}.
5. The present results indicate the possibility of on-line formation of isotope-controlled nanostructure Si materials.

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