High Purity Isotopically Enriched ^{29}Si and ^{30}Si Single Crystals: Isotope Separation, Purification, and Growth

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We report the successful isotope separation and bulk single crystal growth of ^{29}Si and ^{30}Si stable isotopes. The isotopic enrichments of the ^{29}Si and ^{30}Si single crystals determined by mass spectrometry are 99.23% and 99.74%, respectively. Both crystals have the electrically active net-impurity concentration less than 10^{15} cm^{-3}. Thanks to the result of this work and the ^{28}Si crystals we grew previously, high quality single crystals of every stable Si isotope (^{28}Si, ^{29}Si, and ^{30}Si) have been made available for a wide variety of basic research and industrial applications. [DOI: 10.1143/JJAP.42.6248]

KEYWORDS: silicon, isotope, bulk crystal growth, Hall effect

1. Introduction

Successful growth of high quality isotopically enriched germanium[1] and diamond[2,3] crystals about a decade ago has revived the world's interest in isotope engineering of semiconductors.[4] Using germanium, a wide variety of isotope effects on phonons,[5–7] thermal conductivities,[8,9] thermal expansion coefficients,[10] and electronic band structures[11,12] have been revealed in detail.

Neutron-transmutation-doping of isotopically enriched germanium[13] has permitted carrier transport studies probing the fundamentals of ionized[14] and neutral[15] impurity scattering, variable range hopping conduction,[16] and the metal-insulator transition.[17–19] Molecular beam epitaxy of isotopically controlled germanium has enabled studies of self-diffusion[20,21] and phonons in low dimensional structures.[22–25]

Among a large collection of semiconductor materials, silicon (Si) continues to be the most important element because of its many industrial applications. Naturally available silicon (^{nat}Si) is always composed of three different isotopes in the fixed composition: ^{28}Si (92.2 at.%), ^{29}Si (4.7 at.%), and ^{30}Si (3.1 at.%). The recent successful growth of high quality ^{28}Si bulk single crystals,[26–28] has triggered the discovery of a wide variety of "new" isotope effects, including a significant narrowing of the impurity bound exciton photoluminescence[29] and impurity far-infrared absorption[30] peaks, and an absence of acceptor ground state splitting.[31] These unexpected isotope effects appear especially when the enrichment of ^{28}Si exceeds 99.98%. Some increase in the thermal conductivity at room temperature compared with that of ^{nat}Si[32–34] may be important from the industrial point of view, since it is expected to reduce the heat dissipation problem of state-of-the-art Si IC chips.[35] ^{28}Si thin films grown on ^{nat}Si substrates have contributed greatly to self-diffusion studies which provide important parameters for the development of future Si IC process simulators for the nano-scale era.[36–40] Silicon isotopes are expected to play crucial roles in the accurate determination of the Avogadro and Planck constants.[41] Finally, Si isotopes are needed in some of the most promising schemes for the realization of quantum computers.[42,43] It has been proposed that the nuclear spins of ^{29}Si embedded in the spin-free matrix of single crystalline ^{28}Si or ^{30}Si can be utilized as quantum bits (qubits) for efficient quantum computing.[43]

Previously, isotopic enrichment of Si bulk single crystals has been achieved only for the most abundant isotope, ^{28}Si.[44] However, experimental investigations to gain a better understanding of the above mentioned isotope effects desperately require high quality bulk single crystals of isotopes other than ^{28}Si, i.e., ^{29}Si and ^{30}Si. More accurate diffusion studies and the construction of Si quantum computers also require engineering using ^{29}Si and/or ^{30}Si isotopes. Because of the small natural abundance of ^{29}Si (4.7 at.%) and ^{30}Si (3.1 at.%) isotopes, enrichment of these isotopes above 99% is extremely challenging. Once they are separated by the gas centrifuge method in the form of ^{29}SiF$_4$ and ^{30}SiF$_4$, they have to be reduced chemically to polycrystalline ^{29}Si. Finally, isotopically enriched ^{29}Si and ^{30}Si single crystals are grown using the Czochralski method. The challenge during crystal growth is to avoid decreasing the original isotopic enrichment of the ^{29}Si and ^{30}Si charges, especially when the goal is to obtain an isotopic enrichment higher than 99%. There are two sources of ^{28}Si, which can be regarded as the major isotopic impurity from the point of view of ^{29}Si and ^{30}Si single crystals. One source is the ^{nat}Si seed we use for the very first single crystal growth of ^{29}Si and ^{30}Si, and the other is the quartz (^{nat}SiO$_2$) crucible used to melt the ^{29}Si and ^{30}Si charges, which has the natural isotopic abundance of 92.2% ^{28}Si. This problem can be severe in our case since the weight of ^{29}Si and ^{30}Si crystals we aim to grow is on the order of 10 grams, i.e., introduction of ~0.1 grams of ^{28}Si degrades the isotopic enrichment by 1%. The present paper describes how we have overcome these challenges and achieved high chemical purity, isotopically enriched ^{29}Si and ^{30}Si single crystals with an isotopic enrichment >99%. The dislocation density revealed by decoration etching in most parts of the both crystals is much less 10^3 cm^{-2}. The electrically active net-impurity concentration is less than 10^{15} cm^{-3}, with the dominant donors and acceptors being phosphorous and boron, respectively.

2. Isotope Separation, Purification, and Single Crystal Growth

With current technology, an isotope separation of silicon with a high level of enrichment is achieved most effectively by gas centrifugation. Other methods such as magnetic mass separation, ion exchange, and laser technology exist but they have not succeeded in the large quantity separation of Si isotopes. The centrifugation technology is based on the separation of the gas components in a very strong centrifugal field (the centrifugal acceleration more than $5 \times 10^6 \mathrm{m/s^2}$ in the rotor of the centrifuge. For the centrifugal separation of Si, SiF_4 is preferentially used because only one isotope of fluorine exists, namely ^{19}F, and SiF_4 has sufficient vapor pressure at room temperature.[45] The relative change of isotope concentration after one cycle of centrifugation is about 0.1, therefore a cascade of centrifuges is usually used. The higher the isotopic enrichment goal, the more centrifuges must be used in the cascade. We use a cascade with about 100 centrifuges. Centrifugation separates the lighter isotope from the heavier one. Because Si has three isotopes, several stages are needed to separate ^{29}Si.[46,47] In the first stage $^{28}SiF_4$ is separated from the mixture of $^{29}SiF_4$ and $^{30}SiF_4$. Then in the next cascade of centrifuges, $^{29}SiF_4$ is separated from $^{30}SiF_4$. Therefore the production of ^{29}Si and ^{30}Si is more expensive and the separated quantities of ^{29}Si and ^{30}Si are much smaller than for ^{28}Si.

The transformation of isotopically enriched $^{29}SiF_4$ and $^{30}SiF_4$ into polycrystalline ^{29}Si and ^{30}Si was carried out in a two-stage process as described in Ref. 43. In the first stage, silane ($^{29}SiH_4$ and $^{30}SiH_4$) was produced by the chemical reaction $CaH_2 + SiF_4 \rightarrow SiH_4 + CaF$. The silane gas was then purified by low-temperature rectification and then transformed into elementary ^{29}Si or ^{30}Si by pyrolysis: $SiH_4 \rightarrow Si + 2H_2$. Finally, ^{29}Si and ^{30}Si polycrystals were deposited on a hot Mo wire. The resulting product was a granular material with a grain size between 0.3 and 0.5 mm. 19.5 grams of ^{29}Si and 13 grams of ^{30}Si polycrystalline materials were prepared in this manner. Special measures have been taken to minimize isotopic dilution during chemical transformation. Table I shows the isotopic composition of the isotopically enriched ^{29}Si and ^{30}Si charges on passing from SiF_4 to single crystals.

Single crystals were grown from the ^{29}Si and ^{30}Si granular charges by the Czochralski technique using quartz crucibles.

The first challenge is to carry out the Czochralski growth with a very small amount of the charge. In this case high, radial temperature gradients are required to avoid the freezing of the melt near the crucible wall. Such growth conditions are very difficult to realize either with resistance heating or low frequency induction heating (normally used for Czochralski growth) because of the deep penetration of the electromagnetic field into the graphite succeptor. In order to overcome this challenge, a floating zone furnace with 3 MHz frequencies has been converted to the Czochralski puller for the growth of very small amount of ^{29}Si and ^{30}Si. The second challenge, as stated above, is the lack of isotopically enriched Si seeds for the growth of the single crystal. Direct contact of ^{nat}Si seeds with mono-isotopic ^{29}Si and ^{30}Si melt leads to degradation of the isotopic purity. We have tapered the shape of the $\langle 100 \rangle$ ^{nat}Si seeds for the growth of ^{29}Si so that the amount of seed melting can be minimized when they are dipped into the ^{29}Si melt. For the ^{30}Si, we used a part of the ^{30}Si that we had grown previously as a seed to avoid isotopic contamination, as we will show later. The third challenge is to avoid isotopic contamination from the direct contact of the mono-isotopic ^{29}Si and ^{30}Si melts with the $^{nat}SiO_2$ crucible. In order to overcome this problem, we have coated the quartz crucible with 100–150 μm $^{29}SiO_2$ and $^{30}SiO_2$ layers for the growth of the ^{29}Si and ^{30}Si single crystals. All growth processes were carried out under Ar pressure of about 1100 mbar and constant gas flow of $600 \mathrm{Nl\,h^{-1}}$. More than 99% of the melt volume was crystallized during the growth (solidification fraction $g > 0.99$).

3. Characterization

Figure 1 shows the isotopically enriched ^{29}Si and ^{30}Si single crystals. Isotopic analysis was performed at IChPS using laser-ionization mass-spectrometry (LIMS).[48,49] The isotopic compositions of the isotopically enriched $^{29}SiF_4$ and $^{30}SiF_4$ gas, ^{29}Si and ^{30}Si granular materials (before Cz growth), and of their single crystals (after Cz growth) are shown in Table I. We have achieved an isotopic enrichment of well over 99% for both crystals. Table I also shows that our strategy of using a tapered shape ^{nat}Si seed and coating the crucible with $^{29}SiO_2$ has worked very well, since the degradation of the enrichment of ^{29}Si is only 0.2% before and after the growth. For the growth of the ^{30}Si single crystal, the degradation is zero within our experimental error because we have used the isotopically enriched ^{30}Si seed that we

Table I.   Isotopic composition of the separated SiF_4 granulate (before crystal growth), and single crystals (after growth) as determined by laser ionization mass-spectrometry (LIMS) as described in Ref. 44.

Content of Si isotopes, at%	Natural Si	Isotopically enriched ^{29}Si			Isotopically enriched ^{30}Si		
		$^{29}SiF_4$	Granulate (before growth)	Crystal (after growth)	$^{30}SiF_4$	Granulate (before growth)	Crystal (after growth)
^{28}Si	92.23	0,377 ±0,072	0.303 ± 0.013	0.563 ± 0.017	0.074 ±0.046	0.087 ± 0.009	0.072 ± 0.01
^{29}Si	4.67	99,576 ±0,105	99.487 ± 0.045	99.225 ± 0.023	0.097 ±0.054	0.179 ± 0.052	0.186 ± 0.011
^{30}Si	3.10	0,047 ±0,018	0.211 ± 0.012	0.212 ± 0.015	99,829 ±0.060	99.735 ± 0.053	99.742 ± 0.015
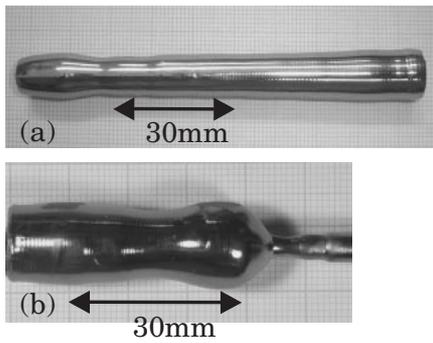
Fig. 1. Photographs of isotopically pure (a) ^{29}Si and (b) ^{30}Si single crystals.

Fig. 3. Temperature dependence of the free electron mobility in the ^{29}Si (●) and ^{30}Si (○) single crystals.

Fig. 2. Temperature dependence of the free electron concentration in the ^{29}Si (●) and ^{30}Si (○) single crystals. Solid curves are the best fits as described in the text.
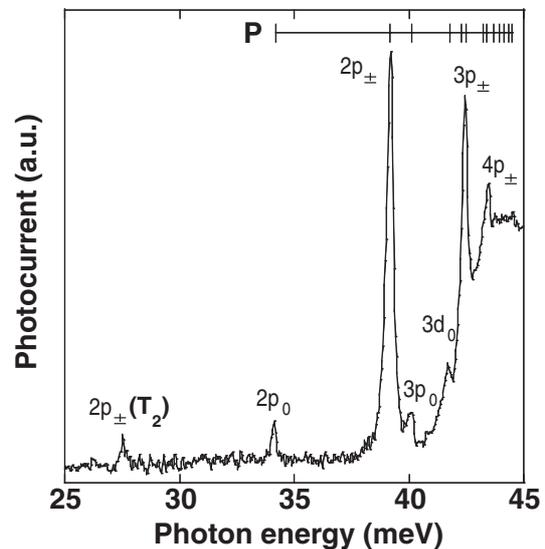
Fig. 4. PTI spectrum of the ^{29}Si single crystal.

prepared previously.

Both crystals are entirely n-type, and the typical free electron concentrations as a function of temperature are shown in Fig. 2 for a sample sliced from the middle of the ingots. Both curves are fitted with the standard free carrier statistics:[50]

$$\frac{n(n + N_A)}{N_D - N_A - n} = \frac{1}{\beta} N_C \exp\left(-\frac{E_D}{kT}\right) \qquad (1)$$

where n is the free electron concentration, $\beta = 2$ is the degeneracy factor of the conduction band, $N_C = 6.18 \times 10^{15} T^{3/2}$ cm^{-3} is the effective density of states in the conduction band, $E_D = 0.045$ eV is the ionisation energy of phosphorus (P) in Si for the case of ^{29}Si and ^{30}Si crystals. We use N_D and N_A, which are the concentrations of donors and acceptors, respectively, as fitting parameters to draw the best fit (solid curves) in Fig. 2. From these excellent fits, we confirm that the majority of donors are phosphorus in both crystals. The concentration of the donor phosphorus (N_D) and acceptors (N_A) in both crystals found from the curve fitting are; $N_D = 1.77 \times 10^{15}$ cm^{-3} and $N_A = 9.95 \times 10^{14}$ cm^{-3} in the ^{29}Si crystal and $N_D = 5.12 \times 10^{14}$ cm^{-3} and $N_A = 2.23 \times 10^{14}$ cm^{-3} in the ^{30}Si crystal. The mobility is also well behaved, as shown in Fig. 3. In order to confirm that the majority impurity is phosphorus, we have performed photo-

thermal ionisation spectroscopy (PTIS).[51] Figure 4 shows the PTI spectra of the ^{29}Si single crystal obtained at $T = 16$ K. Every line observed corresponds to one of the excitations from the ground to an excited state of an electron bound to phosphorus in Si, i.e., the presence of P is confirmed. If we repeat the same measurement with light whose energy is above the band gap of silicon, we observe a series of dips corresponding to boron acceptors, i.e., boron is the dominant compensating acceptor center. We have observed essentially the same spectrum with ^{30}Si, confirming the presence of phosphorus and boron. For the ^{30}Si crystal, the concentration data given above show fair correlations with preliminary results of low-temperature (4.2 K) FTIR spectroscopy ($N_P = 1.3 \times 10^{14}$ cm^{-3}, $N_B = 8.4 \times 10^{13}$ cm^{-3}) and PL spectroscopy ($N_P = 7 \times 10^{14}$ cm^{-3}, $N_B = 4 \times 10^{14}$ cm^{-3}). The spectroscopic measurement of the P and B concentrations in ^{29}Si sample is also underway. The carbon and oxygen concentrations in both crystals were probed by infrared absorption spectroscopy at $T = 300$ and 77 K. The oxygen and carbon concentrations in the ^{29}Si crystal as determined by FTIR absorption and mass spectrometry are 3.1 ×

10^{17} cm^{-3} and 5.1×10^{16} cm^{-3}, respectively. In ^{30}Si crystal the oxygen and carbon concentrations were 5×10^{16} cm^{-3} and 8×10^{16} cm^{-3}.

4. Conclusions

We have been able to grow isotopically enriched ^{29}Si and ^{30}Si single crystals of high chemical purity for the first time. We believe that the availability of these isotopes of Si in such a pure form will permit important progress in a variety of basic and applied research areas.

Acknowledgment

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