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Express Letter

Growth and Characterization of the Isotopically Enriched ^{28}Si Bulk Single Crystal

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We report on the successful growth of an isotopically enriched ^{28}Si bulk single crystal of the size ∼4 mm in diameter and ∼50 mm in length. The isotopic enrichement of ^{28}Si (99.924 at%), ^{29}Si (0.073 at%), and ^{30}Si (0.003 at%) has been determined by secondary-ion-mass spectroscopy (SIMS). The crystal is entirely p-type with the room temperature free-hole concentration $\sim 5 \times 10^{17}$ cm^{-3}. The majority impurity is found to be aluminum which can be removed easily in the future zone purification process.

KEYWORDS: Si, bulk crystal, isotope, floating-zone growth, LSI substrate

Along with the substantial progress in semiconductor science and technology, control of the isotopic composition of semiconductor materials (“Isotope Engineering”) has attracted much attention especially in the past decade.[1,2] Many physical properties including the phonon frequency, phonon life time, lattice constant, thermal conductivity, specific heat, electron-phonon interaction, electron- and nuclear-spin resonance, spin dependent photoluminescence, and nuclear reaction via neutron-transmutation-doping are known to depend on the isotopic composition of the semiconductor crystals.[1,2]

Most of elements which constitute semiconductor crystals are composed of a multiple number of stable isotopes with the fixed abundance given by nature. Silicon (Si), one of the most important semiconductor elements, is composed of three different isotopes: ^{28}Si (92.2 at%), ^{29}Si (4.7 at%), and ^{30}Si (3.1 at%). The present work reports on the separation of ^{28}Si stable isotopes by the gas centrifuge technique[3] and subsequent growth of an isotopically enriched bulk ^{28}Si crystal using the floating-zone method.

Altering the isotopic composition is equivalent to changing the mass distribution of the lattice sites that constitute the crystal. This gives a dramatic effect on the lattice vibrational properties, especially on the thermal conductivity of the crystal. With the advancement of Si power electronics and LSI devices, effective dissipation of heat through Si substrates on which circuits are fabricated has become very important. More than 50 years ago, Pomeranchuk has predicted theoretically the possibility of increasing the thermal conductivity by isotopic enrichment.[4] Such an isotope effect was confirmed experimentally on isotopically enriched ^{74}Ge by Geballe and Hull.[5] They have shown 300% increase in the thermal conductivity at $T \approx 20$ K by going from Ge of the natural isotopic abundance to ^{74}Ge of the 95.8% enrichment.[5] More recently dramatic increase in the thermal conductivity (larger than 40%) was measured between diamond thin films of the natural isotopic abundance (98.9% ^{12}C) and of the ^{12}C enrichment 99.9%.[6] Systematic studies of the thermal conductivity as a function of temperature and isotopic composition of bulk Ge crystals was performed by a group including two of the present authors (KMI and VIO).[7] They have determined successfully the values of numerical coefficients[7] that had not been known in the standard conductivity models.[8–10] Based on these models with appropriately scaled coefficients for Si, more than 40% increase in the room temperature conductivity in isotopically enriched Si was predicted. More recently, an evidence for more than 50% increase in the room temperature conductivity was shown experimentally with liquid-phase-epitaxially (LPE) grown ^{28}Si thin films of the enrichment 99.7%.[11] ^{28}Si thin films grown on natural Si substrates are commercially available now for the LSI application requiring improved heat dissipation.[12] In contrast to the advancement of the Si isotope engineering in “thin films”, growth of isotopically enriched “bulk” Si of semiconductor-grade has not been realized. There has been one report on the growth of isotopically enriched ^{28}Si bulk crystal,[13] but the crystal contained large concentration of boron impurities which is extremely hard to remove by further zone purification, i.e., it could not be used neither for applications nor for many of the basic studies that required semiconductor-grade Si. It is clear that the semiconductor-grade bulk crystals of improved thermal conductivity are useful for the fabrication of large-volume power devices and LSI circuits. The bulk is needed also for the accurate determination of the thermal conductivity of Si as a function of isotopic composition, since the thermal conductivity obtained with thin films are measured usually in the transient-mode,i.e., the absolute and truly thermal equilibrium values of conductivity are difficult to obtain. Thus the bulk crystal grown in this work is of great importance for both applications and basic studies.

The isotope engineering of bulk Si is believed to play an important role also in the development of *spintronic devices* in which spins of electrons are controlled to add new functions to the conventional electronic devices.[14,15] Recently, very elegant and realistic quantum computer construction scheme was proposed by Kane.[16] His idea makes use of interactions between nuclear spins and electron spins of phosphorus donors in Si. In this device, the relaxation of the phosphorus nuclear spins via interaction with ^{29}Si nuclear spins needs to be surpressed.[16] Therefore, the development of isotopically enriched ^{28}Si and/or ^{30}Si crystals that are depleted of ^{29}Si stable isotopes with the nuclear spin 1/2 is important. The crystal grown in the present work will be used in the near future for various spin-related basic studies.

Finally but not the least, there are serious demands for

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chemically pure, isotopically enriched Si single crystals in the field of metrology. Si crystals of natural isotopic composition is widely used for the accurate determination of the Avogadro constant because of its unsurpassed chemical purity and crystalline perfection.[17,18] However, the measurement has become so accurate that the standard uncertainty is limited by the small concentration of defects and variation of the lattice mass and constant due to existence of the three stable isotopes in Si. In order to reduce the uncertainty, Wacker-Chemitronic Company in Germany has grown a 99.02% ^{28}Si single crystal for Physikalisch-Technische Bundesanstalt.[13] Unfortunately, the crystal was found to contain the residual boron concentration of $1.55 \times 10^{18}\,\mathrm{cm}^{-3}$, clearly too high to be called semiconductor-grade, and the enrichment 99.02% was found to be too low for the improvement of the standard uncertainty.[13] The crystal reported in the present paper has a factor of two smaller impurity concentration and the better isotopic enrichment. It can be used in the future as a seed crystal for the large diameter bulk ^{28}Si growth for metrological standards.

Growth of isotopically enriched Si requires isotopically separated starting materials in elemental form in large enough quantity. In the Si separation process, volatile, chemically reactive silicon tetrafloride (SiF_4) was used as a working gas. SiF_4 enriched with ^{28}Si isotope was transformed into silicon oxide SiO_2 followed by its reduction to the elemental form using high purity aluminum powder: $3SiO_2 + 4Al \rightarrow 3Si + 2Al_2O_3$. Isotopically enriched elemental ^{28}Si separated from aluminum was in the form of powder with the particle diameters 10–50 μm. In order to melt the material using our vertical floating-zone (Fz) system, it was necessary to form the powder into a bar of ~5 mm in diameter and ~100 mm in length *without reducing the isotopic enrichment of the material, and without introducing any other impurities into the material.* Melting of the ^{28}Si powder in quartz crucibles reduces isotopic purity as was demonstrated severely in ref. 13. Crucibles made of synthetic materials such as PBN, BN, etc., introduce impurities into the material. Therefore, we have employed a cruicible-free pre-growth procedure which is commonly used for the growth of high T_c oxide superconductors. The ^{28}Si powder was packed into a rubber tube of an appropriate size and it was hydorostatically pressured up to $3000\,\mathrm{kgf/m^2G}$ at room temperature to form a bar of loosely bound ^{28}Si particles. The particles were then sintered at 1200°C for 90 minutes in the pure Ar gas atmosphere to form a bar which has a enough mechanical strength for the floating-zone process. A molten-zone of approximately 10 mm was produced in the pure Ar gas atmosphere by optical heating in our floating-zone system. After several zone-refining passes, the width of molten-zone was reduced to form a neck for single crystal growth. No seed crystal was used in order to preserve the isotopic purity of the starting charge. Once a single crystal grain was formed in the necking region, the bar was pulled upward with the speed of 50 mm/s. As a result of careful control of the heating power and the growth speed, a single crystal shown in Fig. 1 has been produced successfully. The growth direction turned out to be parallel to ⟨310⟩.

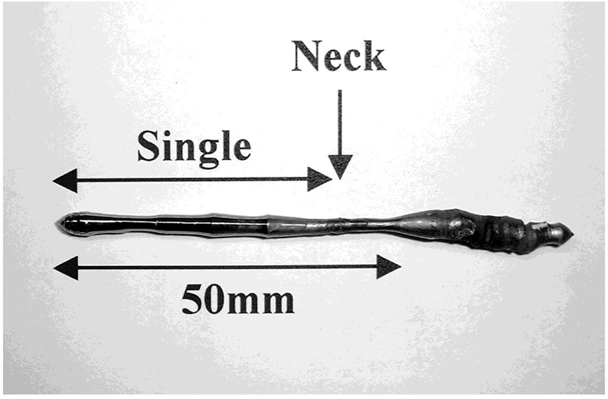

Fig. 1. Isotopically enriched ^{28}Si single crystal.

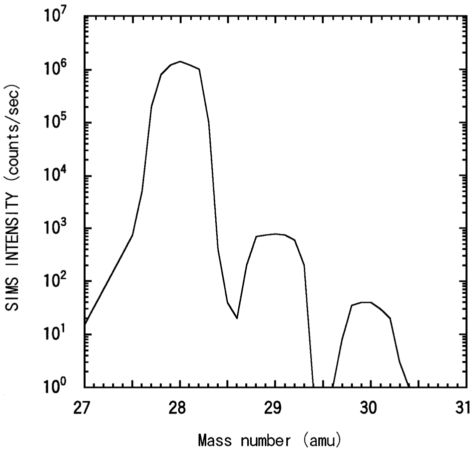

Fig. 2. Typical SIMS results showing the intensity vs mass number for the isotopically enriched ^{28}Si bulk single crystal.

Figure 2 shows the mass spectrum (intensity vs. mass number) of the crystal revealed by secondary-ion-mass spectroscopy (SIMS). The isotopic composition (ratio of ^{28}Si, ^{29}Si, and ^{30}Si) was found by integration of the counts of each peak within the area of full width at half maximum (FWHM). The resulting ratio was ^{28}Si (99.924 at%), ^{29}Si (0.073 at%), and ^{30}Si (0.003 at%). The same SIMS results were obtained for several different positions along the growth direction of the crystal. Moreover, this isotopic composition was exactly the same as that of starting charge, i.e., our purification and growth procedure did not reduce the isotopic purity at all.

Figure 3 shows the free-hole concentration $p(T)$ as a function of inverse temperature determined by Hall effect for a 1 mm thick wafer cut near the tail-end of the crystal. The crystal was entirely p-type. The data shown in Fig. 3 has been fitted by the following standard carrier statistics equation in order to determine the ionization energy of the acceptor E_A and the concentrations of acceptors N_A and compensating donors N_D:

$$\frac{p\,(p+N_D)}{N_A - N_D - p} = \frac{1}{\beta} N_g \exp\left(-\frac{E_A}{2k_{BT}}\right), \tag{1}$$

where β is the degeneracy factor 4 for acceptors and $N_g = 2 \times 10^{15} T^{3/2}\,\mathrm{cm}^{-3}$ is the effective density of the states in the valence band. The best fit (solid curve) shown in Fig. 3 has been obtained with $N_A = 1 \times 10^{18}\,\mathrm{cm}^{-3}$, $N_D = 4 \times 10^{17}\,\mathrm{cm}^{-3}$, and $E_A = 67\,\mathrm{meV}$. The ionization energy 67 meV corresponds to aluminum in Si. Aluminum was detected also in our SIMS measurement while no other acceptors including boron was detected in the same measurement. Aluminum was introduced most likely during the reduction process of $^{28}SiO_2$

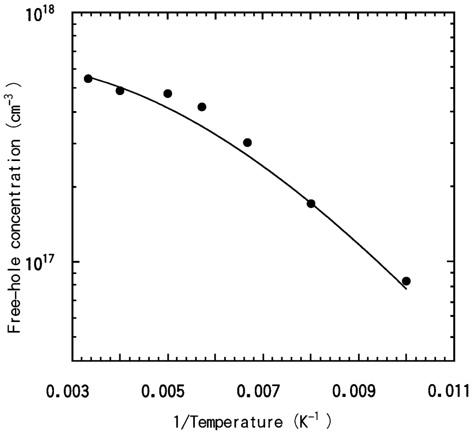

Fig. 3. The free hole concentration vs inverse temperature determined by the Hall effect measurement (filled circles). The solid curve represents the best fit using eq. (1).

involving the high purity aluminum powder. Aluminum is a favorable specie to have as a residual impurity since its small distribution coefficient $k = 2 \times 10^{-3}$ in Si allows for the efficient zone-purification process. On the other hand, boron with $k = 0.8$ is extremely difficult to remove by zone-refining. The zone-purification process to reduce the aluminum concentration in the crystal is currently on the way.

In summary, we have grown successfully a semiconductor-grade, isotopically enriched ^{28}Si bulk single crystal. A special attention has been paid to maintain the isotopic purity of the material throughout our purification and growth process. The isotopic enrichment of 99.924 at% is remarkably high that we expect to observe large isotope effects on various properties including the one on thermal conductivity.

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