Isotopically engineered semiconductors – new media for the investigation of nuclear spin related effects in solids

Kohei M. Itoh[a,]*, Eugene E. Haller[b]

[a] *Department of Applied Physics and Physico-Informatics and PRESTO-JST, Keio University, 3-14-1 Hiyoshi, Yokohama 223-8522, Japan*
[b] *UC Berkeley and Lawrence Berkeley National Laboratory, Berkeley CA 94720, USA*

Abstract

We report on the growth and characterization of isotopically controlled silicon bulk single crystals and germanium superlattice structures in which position and concentration of nuclear spins can be controlled intentionally. The isotopically controlled semiconductor structures enable a wide variety of nuclear-spin related studies involving nuclear-magnetic-resonance and electron-spin-resonance spectroscopy. © 2001 Elsevier Science B.V. All rights reserved.

PACS: 68.55.Bd; 81.10.Fq

Keywords: Nuclear spin; Silicon; Germanium; Superlattice

1. Introduction

Nuclear-spin-related phenomena in semiconductors have attracted considerable attention recently due to the advancement of optically pumped solid-state nuclear magnetic resonance (NMR) techniques [1–3]. The recent development of "All Optical NMR" is especially important since it allows for a convenient and highly sensitive access to nuclear spin states confined in an atomic-scale region. Such NMR techniques are believed to play key roles for the future development of solid-state quantum computers [4]. A wide range of electron-spin-resonance (ESR) investigations of defects in crystalline and amorphous semiconductors also utilizes nuclear spins that are present in the semiconductor matrices.

In contrast to the development of NMR and ESR techniques, manipulations of the nuclear-spin position and concentration within semiconductor structures have received much less attention. All elemental and most compound semiconductors and their alloys contain elements that consist of more than one stable isotope. In order to study nuclear-spin related effects in semiconductors, it is desirable to control the

──────────
* Corresponding author. Tel.: +81-45-566-1594; fax: +81-45-566-1587.
E-mail address: kitoh@appi.keio.ac.jp (K.M. Itoh).

position and concentration of stable isotopes that have nuclear spins. Silicon, for example, is composed of the three isotopes, ^{28}Si, ^{29}Si, and ^{30}Si, with abundances of 92.23%, 4.67%, and 3.10%, respectively. It is therefore of great importance to be able to control the distribution of ^{29}Si for nuclear spin related studies.

In this work, we report on the successful growth of isotopically controlled Si [5] and Ge [6] semiconductor structures in which distribution and concentration of nuclear spins can be controlled intentionally and our Raman results are in good agreement with pioneering studies performed by Cardona and co-workers [7]. We have grown a bulk Si crystal composed of 99.92% ^{28}Si isotopes, i.e., free of ^{29}Si with nuclear spin $I = \frac{1}{2}$. We also have grown ^{70}Ge/^{74}Ge isotope superlattices in which the isotopic composition in the direction of growth has been controlled down to the atomic-level using molecular-beam-epitaxy (MBE). Future MBE growth will involve ^{29}Si and ^{73}Ge isotopes with nuclear spins that will enable us to control the isotopic composition in Si/Ge based superlattices.

2. Growth and characterization of isotopically controlled semiconductors

2.1. Isotopically enriched ^{28}Si bulk single crystal

Growth of isotopically enriched Si requires isotopically separated starting materials in an elemental form in large enough quantity [5]. In the Si separation process, volatile, chemically reactive silicon tetrafluoride (SiF$_4$) was used as a working gas. Highly enriched ^{28}SiF$_4$ was transformed into silicon dioxide ^{28}SiO$_2$, followed by its reduction to the elemental form using high purity aluminum powder: $3\,^{28}$SiO$_2 + 4$Al $\rightarrow$ $3\,^{28}$Si $+ 2$Al$_2$O$_3$. Isotopically enriched elemental ^{28}Si separated from aluminum was in the form of powder with particle diameter 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 $\sim$ 5 mm in diameter and $\sim$ 100 mm in length without reducing the isotopic enrichment of the material, and without introducing any other impurities. Melting of the ^{28}Si powder in quartz crucibles reduces isotopic purity while synthetic crucibles such as PBN and BN are sources of chemical impurities. Therefore, we have employed a crucible-free pre-growth procedure,
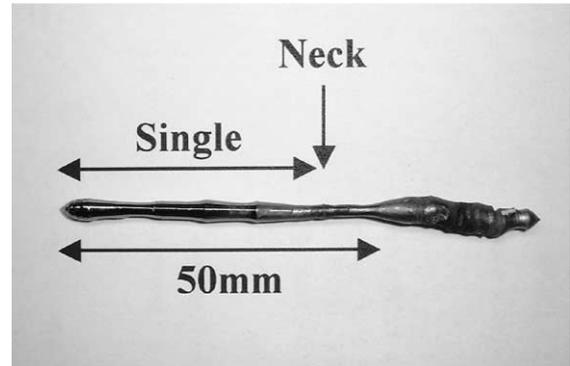

Fig. 1. Isotopically enriched ^{28}Si single crystal.

which is commonly used for the growth of high T_C oxide superconductors. The ^{28}Si powder was packed into a rubber tube of appropriate size and it was hydrostatically pressured up to 3000 kgf/m^{2}G at room temperature to form a bar of loosely bound ^{28}Si particles. The particles were then sintered at 1200°C for 90 min in a pure Ar gas atmosphere to form a bar that has enough mechanical strength to be Fz processed. A molten-zone of approximately 10 mm was produced in the pure Ar gas atmosphere by optical heating in our Fz system. After several zone-refining passes, the width of the 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 $\langle 3\,1\,0 \rangle$.

The isotopic composition of the crystal as determined by secondary-ion-mass spectroscopy (SIMS) is as follows: ^{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. The crystal is entirely p-type with the room temperature free-hole concentration 5×10^{17} cm^{-3}. The majority impurity is found to be aluminum. The aluminum was introduced most likely during the reduction process of ^{28}SiO$_2$ involving the high purity aluminum powder. Aluminum is an acceptable residual impurity species since its small distribution coefficient $k = 2 \times 10^{-3}$ in Si allows for

efficient zone-purification processing, i.e., it can be removed quickly.

The isotopically enriched ^{28}Si single crystal depleted of nuclear spins (^{29}Si isotopes) is expected to be useful for a wide variety of nuclear-spin related investigations. For example, a new quantum computer construction scheme proposed by Kane [4] makes use of interactions between nuclear spins and electron spins of phosphorus donors in Si. In this scheme, the relaxation of the phosphorus nuclear spins via interaction with ^{29}Si nuclear spins needs to be suppressed. 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 $\frac{1}{2}$, is important. Besides Si, we have grown successfully isotopically enriched ^{70}Ge, ^{73}Ge, ^{74}Ge, and ^{76}Ge single crystals sometime ago [8]. Among the five stable isotopes of Ge (^{70}Ge, ^{72}Ge, ^{73}Ge, ^{74}Ge, and ^{76}Ge), only ^{73}Ge has a nuclear spin $\frac{9}{2}$. Isotopically controlled Ge enriched in or depleted of ^{73}Ge is also useful for a variety of nuclear-spin related studies.

2.2. ^{70}Ge$_n$ ^{74}Ge$_n$ isotope superlattices

In order to control at the atomic level the position and concentration of stable isotopes having nuclear-spins in semiconductors, it is necessary to employ a layer-by-layer growth technique such as molecular beam epitaxy (MBE). The development of MBE has lead to the successful fabrication of semiconductor superlattices that are composed of alternating thin layers of different chemical constituents, e.g. GaAs/GaAlAs, GaN/GaAlN, etc. In these conventional structures, the periodicity in the alternating layers in the growth direction leads to zone-folding of both the electronic band structures and the phonon dispersion curves [7]. In this work we have grown ^{70}Ge$_n$/^{74}Ge$_n$ isotope superlattices [6] composed of alternating layers of the stable isotopes ^{70}Ge and ^{74}Ge. n denotes the thickness of the each isotope layer in units of atomic monolayers. These superlattices are unique in the sense that the alternating layers are composed of the same chemical elements but with different atomic masses, i.e. while the electronic band structure is practically the same as that of bulk Ge, the phonon dispersion curve is zone-folded due to the mass periodicity in the direction of the growth. Therefore, the quality of isotope superlattices
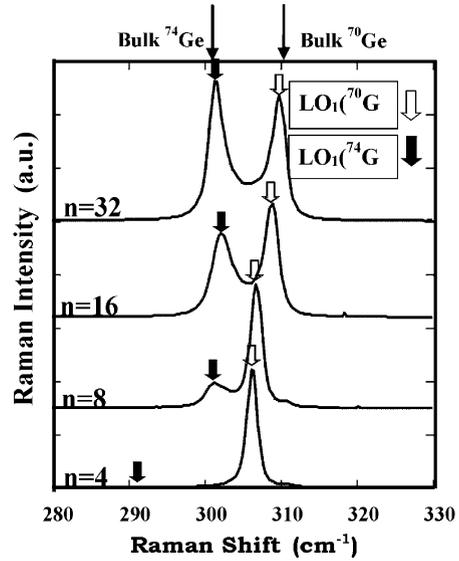

Fig. 2. Raman Spectra of ^{70}Ge$_n$ ^{74}Ge$_n$ isotope superlattices.

can be evaluated by probing the phonon properties. Raman scattering is a convenient method to characterize the short period isotope superlattices, since for example X-ray diffraction analysis can be used only for superlattices composed of different chemical constituents. The depth resolution of the SIMS is not sufficient to permit characterization of isotope superlattices of a hundred angstroms or less thick.

W have grown four ^{70}Ge$_n$/^{74}Ge$_n$ isotope superlattices with $n = 4, 8, 16$, and 32 using solid-source MBE. The sources of ^{70}Ge and ^{74}Ge we used were isotopically enriched to 96.3 and 96.8 at.%, respectively. The superlattices were grown on the top of a 20 nm thick ^{70}Ge buffer layer along the (1 0 0) direction. The temperature of the substrate during the growth was kept at 350°C. All superlattices are p-type having a net-impurity concentration of $\approx 10^{16}$ cm^{-3}. High resolution (0.3 cm^{-1}) Raman spectra of the four SLs were recorded in back scattering geometry at $T = 10$ K using the Ar$^+$ 514 nm-line.

The measured Raman spectra of the $n = 4, 8, 16$ and 32 ^{70}Ge$_n$/^{74}Ge$_n$ isotope superlattices are shown in Fig. 2. At the top of this figure, the positions of bulk ^{70}Ge and bulk ^{74}Ge LO phonon peaks are indicated by arrows. Two major phonon peaks due to LO$_1$(^{70}Ge) and LO$_1$(^{74}Ge) phonons are observed clearly in the $n = 8, 16$, and 32 samples. We also can find a weak
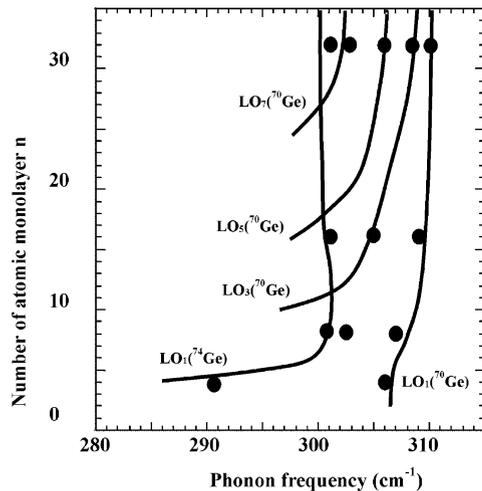
Fig. 3. Direct comparison of the LO phonon frequencies determined by Raman experiments (filled circles) and calculations (solid curves). The calculated results have been adopted from Ref. [7].

$LO_1(^{74}Ge)$ phonon peak near 290 cm^{-1} in the $n = 4$ sample when magnified. The $LO_1(^{70}Ge)$ phonon peak position shifts to higher frequency and approaches the frequency of the bulk ^{70}Ge LO-phonon as n is increased. On the other hand the $LO_1(^{74}Ge)$ phonon peak position stays at the same frequency, but grows in intensity when n is increased. Further analysis has shown that it is necessary to combine more than two Lorentzian peaks in order to reproduce our Raman spectra [6]. Fig. 3 shows the direct comparison of the phonon peak positions found from the experiment (filled circles) and from calculations using the planer bond-charge model (solid curve) [9]. The over all agreement between experiment and calculation is excellent for phonon frequencies. Detailed analysis of the Raman spectra lets us conclude that the degree of interface mixing between the ^{70}Ge and ^{74}Ge layers for our typical growth condition is less than two monolayers [6]. This level of ability to control of the distribution of stable isotopes will allow us to grow isotope superlattices with well controlled distributions of nuclear-spins.

3. Summary

We have grown successfully isotopically controlled silicon bulk single crystals and germanium isotope superlattices. Our ability to control the position of stable isotopes will allow manipulation of the nuclear-spin distribution in semiconductors down to atomic levels.

Acknowledgements

References

[1] R. Tycko, J.A. Reimer, J. Phys. Chem. 100 (1996) 13240.
[2] P. Khandelwal et al., Phys. Rev. Lett. 81 (1998) 673.
[3] J.M. Kikkawa, D.D. Awschalom, Science 287 (2000) 473.
[4] B.E. Kane, Nature 393 (1998) 133.
[5] K. Takyu, K.M. Itoh, K. Oka, N. Saito, V.I. Ozhogin, Jpn. J. Appl. Phys. 38 (1999) L1493.
[6] K. Morita, K.M. Itoh, J. Muto, K. Mizoguchi, N. Usami, Y. Shiraki, E.E. Haller, Thin Solid Films 369 (2000) 405.
[7] J. Spitzer et al., Phys. Rev. Lett. 72 (1994) 1565.
[8] K. Itoh, W.L. Hansen, E.E. Haller, J.W. Farmer, V.I. Ozhogin, A. Rudnev, A. Tikhomirov, J. Mater. Res. 8 (1993) 1341.
[9] P. Molinas-Mata, M. Cardona, Phys. Rev. B. 43 (1991) 9799.