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Lattice location of ^{12}B in germanium and silicon at 300 K†

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Polarized ^{12}B was produced in the reaction ^{11}B$(d, p)^{12}$B and recoil implanted in single-crystal wafers of Ge and Si. Resonance depolarization spectra taken in the presence of an externally applied field gave linewidths in good agreement with the values expected from second-moment calculations for ^{12}B occupying a substitutional crystallographic site. The measured polarization of ^{12}B was considerably lower than that for several fcc metals. This was attributed to some of the boron occupying a low-symmetry nonsubstitutional site. With this interpretation the substitutional fraction of ^{12}B in Ge = 0.42 ± 0.04 and in Si = 0.67 ± 0.06.

INTRODUCTION

In a previous publication[1] (hereafter referred to as I) we reported a method for determining the lattice location of ^{12}B implanted in fcc metals. This work has now been extended to the semiconductors germanium and silicon. Since a description of the technique has already been given in I, only its salient features are described below.

A beam of ^{12}B ($I = 1$; $t_{1/2} = 20.4$ msec) is produced by the reaction ^{11}B$(d,p)^{12}$B, at a deuteron energy of 1.5 MeV using the Lockheed 3-MeV Van de Graaff, and stopped by the semiconductor host under study. The ^{12}B are polarized in the nuclear reaction. The polarization P is defined in terms of the $I = 1$ nonthermal equilibrium substate populations p_m as

$$P = \sum_m m p_m$$
$$= p_1 - p_{-1} \text{ for } I = 1,$$

where the p_m are normalized by $\sum_m p_m = 1$.

If this polarization is retained during implantation, β particles are emitted anisotropically in the decay process. Thus with the use of two particle detector systems positioned 180° apart on either side of the host, the asymmetry in β-particle emission can be measured.

On combining the polarization production and detection techniques outlined above with conventional NMR procedures, it is possible to determine the crystallographic site of the implanted ^{12}B. Data of major interest are linewidths and the strengths of various quadrupole interactions (QI).

There has been a considerable effort devoted to determining the lattice location of boron implanted in silicon[2] but little if any to that of boron in germanium. Channeling[3,4] experiments have shown that at room temperature boron atoms implanted in silicon are found in comparable numbers on both substitutional and nonsubstitutional crystallographic sites. In addition, these results show that the tetrahedral interstitial site is not occupied by boron.

Frank and Berry[5] analyzed the results of several different experiments on the location of implanted B in Si (in all cases under consideration B was implanted to doses $\gtrsim 1 \times 10^{14}$ atoms cm^{-2}), and concluded that the nonsubstitutional boron component consists of predominantly boron-vacancy complexes and a smaller proportion of boron interstitials. Here the interstitial comprises a boron atom and a silicon atom which together share a substitutional site and form an unsymmetrical dumbbell with its axis along $\langle 100 \rangle$.

The symmetry of Si and Ge is diamond cubic. The substitutional site is coordinated by four nearest neighbors in a tetrahedral configuration. In view of the over-all cubic symmetry of the crystal structure, there is no electric field gradient at the substitutional site. Thus boron atoms implanted in such sites should exhibit a single resonance depolarization line with no quadrupole splitting. In this case, the linewidth Γ for each of the major crystallographic directions can be calculated from the strength of the dipole-dipole interaction using the method of moments[6] (see I). Crystallographic distortions near the boron, engendered for instance by radiation damage, give rise to a nonzero QI which broadens the resonance.

EXPERIMENTAL PROCEDURES AND RESULTS

The Si and Ge samples were single-crystal wafers of thickness 0.40 mm and resistivities of 130 and 1–10 Ω cm, respectively. They were etched in a CP4 solution. The crystals were positioned in the spectrometer and implanted with ^{12}B in the manner described in I. Normally $\approx 10^{10}$ B atoms per cm^{-2} implanted into a 1-μm-thick layer (see I) are sufficient to produce a spectrum. This leads to a total atomic concentration of ^{12}B and its decay product ^{12}C of $\approx 10^{-9}$–10^{-8}. A typical depolarization spectrum is shown in Fig. 1 for a silicon host oriented with $\langle 100 \rangle$ parallel to the holding field H_0. The experimental linewidths (full width at half-maximum) are given in Table I and are to be compared

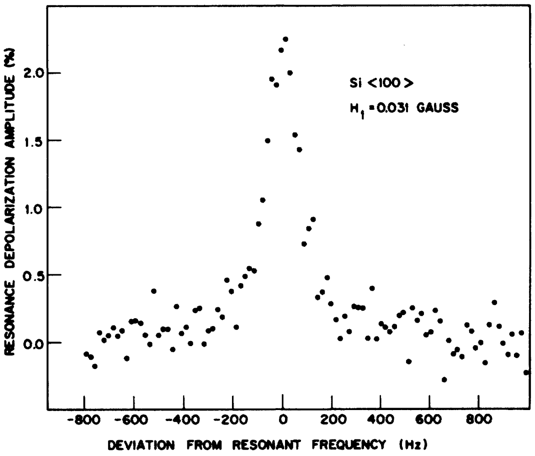

FIG. 1. Depolarization spectrum obtained with a silicon host oriented with ⟨100⟩ parallel to the holding field for a depolarizing field amplitude $H_1 = 0.031$ G (24 Hz). The resonant frequency ≈3.8 MHz.

with the calculated values obtained using the method of moments and assuming a Gaussian for the depolarization line shape. The second-moment calculation was carried out to the fifth-nearest-neighbor shell (a total of 40 atoms). Residual dipole-dipole effects owing to the remainder of the crystal were estimated roughly and found to be negligible. The experimental data values are within ≈30% of the calculated linewidths. This agreement between theory and experiment is gratifying and shows that the ^{12}B nuclei contributing to the resonance are situated in substitutional sites in Si and Ge.

The adiabatic fast passage (AFP) technique (see I) allows the determination of the fraction of implanted ^{12}B that contributes to the resonance. The AFP through the resonance reverses the spins of the ^{12}B and gives rise to an effective doubling of the magnitude of depolarization (detected as a change in anisotropy). Expressed as a function of polarization, the change in anisotropy is

$$A = (1+P)^2/(1-P)^2 .$$

In the metals Al, Ag, Pt, and Pd, the anisotropy change is 1.45 ± 0.03, the maximum value we have observed after investigating a large number of different systems. We use this value to calculate the maximum polarization $P_0 = 0.093 \pm 0.05$ when all ^{12}B nuclei resonate at the same frequency. For Si and Ge after AFP, $A = 1.28 \pm 0.01$ and 1.17 ± 0.01, respectively. We take these values to reflect the loss in polarization of ^{12}B atoms situated on low-symmetry crystallographic sites since spin-lattice relaxation effects with time scales greater than 1 msec were found to be undetectable within experimental error. Thus the boron substitutional fraction is found by taking the ratio of the individual semiconductor polarization to P_0. Thus in Si the fraction is

$$\frac{0.062 \pm 0.02}{0.093 \pm 0.05} = 0.67 \pm 0.06 ,$$

and in Ge it is

$$\frac{0.039 \pm 0.02}{0.093 \pm 0.05} = 0.42 \pm 0.04 .$$

TABLE I. Resonance linewidths for silicon and germanium.

Crystal	Crystal direction	Linewidth (Hz) Experiment	Linewidth (Hz) Theory
Silicon	⟨100⟩	107 ± 19	80
	⟨110⟩	168 ± 19	196
	⟨111⟩	194 ± 19	220
Germanium	⟨100⟩	124 ± 20	90
	⟨110⟩	170 ± 20	222
	⟨111⟩	170 ± 20	248

A search was carried out for other resonances within ±250 kHz of the substitutional site value. None were detected, indicating ≲10% of the ^{12}B atoms (except for those previously observed) resonated in this frequency interval.

DISCUSSION

Channeling measurements[3] show that the fraction of boron implanted substitutionally in silicon is 0.63 for an atomic concentration $\approx 10^{-4}$. In view of the four-to-five orders-of-magnitude difference in boron concentration between this result and our own it is possible that the agreement is fortuitous. It is more likely, however, that at room temperature for boron concentrations $\lesssim 10^{-4}$ the probability of a boron atom becoming substitutional is independent of concentration. This type of behavior is exhibited, for instance, when group V dopants (As, Sb, Bi) are implanted in Si at 40 keV and 350–450° C.[7] A threshold dose (or concentration) is observed below which the substitutional component becomes constant.

The nonsubstitutional boron fraction could either be depolarized and/or resonate at a frequency quite different from the substitutional site value. In the former case this would happen if the ^{12}B is located in a low-symmetry site where a large depolarizing QI exists. Such a situation arises when the boron has a nearest-neighbor point defect, e.g., vacancy, divacancy, self-interstitial (forming the B-Si dumbbell[5]). All such defects are created when the kinetic energy of the implanted ion is dissipated.

A change in resonant frequency could arise also for the case of the boron atom-vacancy complex. Here the B may not be bonded to four nn host atoms, and so one or more unsaturated bonds will give rise to an enhanced contact field that shifts the resonance. It is not yet possible to elucidate which of the above mechanisms is responsible for the loss of polarization in Si and Ge. Experiments performed with host temperatures up to 500 °C and also with prior radiation-damaged samples are now in progress, in order to help clarify the depolarizing mechanisms existing in B implanted Si and Ge.

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