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Bulk-doping-controlled implantation site of boron in silicon

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Silicon samples containing various *p*- and *n*-type dopants have been implanted with spin-polarized ^{12}B between 300 and 950 K. Using β-radiation-detected nuclear magnetic resonance, the fraction of ^{12}B in normal substitutional sites has been determined. This fraction increases from about 20% at 300 K to $\simeq$100% at temperatures that systematically depend on the bulk doping. We argue that the diffusive motion of interstitial boron leads to boron in substitutional sites.

The site of implanted dopants in crystalline silicon is of technological and fundamental interest. Usually only substitutional dopants reveal the electrical behavior desired for devices, whereas common dopants on interstitial sites may exhibit rather uncommon properties such as the negative-U behavior of interstitial boron.[1] Channeling studies showed that in contrast to group-V dopants quite large nonsubstitutional fractions of group-III implants are obtained.[2,3] In typical room-temperature implantations of boron, the substitutional fractions varied between 30% and 60% and decreased upon annealing. Only for annealing temperatures above 800 °C were substitutional fractions of $\simeq$90% obtained.[2] The mixed hot implantation of heavy group-III and V elements leads to a considerably increased substitutional fraction compared to group-III implantation alone.[3] It was stated that the suppression of the interstitial fraction of implanted acceptors in the presence of donor species might be due to charge-state effects.[3]

Clearly, only experimental methods that do neither depend on nor introduce high doping levels can be expected to elucidate the influence of the Fermi level and specific mechanisms that determine the implantation site. Moreover, during high-dose implantations as were used in the channeling measurements cited above, problems may arise concerning damage cascade overlap, amorphization during implantation, and solubility limits. Using refined channeling techniques these problems can be avoided to a certain extent so that statements on the as-implanted state of *heavy* acceptors such as In become possible.[4,5] However, implant concentrations of at least $\simeq 10^{17}/\text{cm}^3$ were needed and systematic investigations of the as-implanted site of isolated acceptors do not exist.

We demonstrate that β-radiation-detected nuclear magnetic resonance (β-NMR) using implanted ^{12}B probes allows the determination of the normal substitutional ^{12}B fraction as a function of implantation temperature *and* bulk-doping level without any compensation effects. In two earlier β-NMR studies of ^{12}B in Si only room-temperature implantations were investigated[6] or only one unspecified sample was used.[7] The unique possibilities of β NMR are based on its *extreme* sensitivity and its ability to detect internal fields produced by intrinsic defects and impurities. Furthermore, it is possible to discriminate between cubic and noncubic probe sites.[8] The reactions of boron with interstitials[9,10] and vacancies[11,12] have been thoroughly investigated which allows us to study the relevance of such reactions to the implantation process.

The experiments were performed at the EN Tandem accelerator of the Max-Planck-Institut für Kernphysik in Heidelberg. A detailed description of the β-NMR method can be found in Ref. 8, so we give only a brief outline of the experiment here. A natural boron target is bombarded with a 1.5-MeV deuteron beam. A typical beam current was 2 μA. The reaction $^{11}\text{B}(d,p)$ produces radioactive ^{12}B (nuclear spin $I=1$, lifetime $\tau_\beta = 29$ ms) which leave the target with broadly distributed recoil energies between 0 and 450 keV. Thus a rather homogeneous implantation of the silicon sample (area 14×14 mm^2, thickness $\simeq 500$ μm) up to 1-μm sample depth is achieved. The fixed recoil angle of (45° ± 6°) leads to a nuclear-spin polarization for the ^{12}B probes stopped in the silicon sample. This polarization is parallel to a magnetic field B_0 and can be observed via the asymmetric electron emission in the β decay of ^{12}B by means of two detectors which are mounted on the magnet pole faces on either side of the sample. The measured quantity is the β-decay asymmetry a_β, which is given by $a_\beta = (N-S)/(N+S)$, where N and S denote the counting rates in the electron detectors at the north and the south pole of the magnet, respectively. The quantity a_β is a direct measure of the nuclear-spin polarization. Under the conditions used in this work, the momentary ^{12}B concentration within the implanted volumes never exceeded $10^7/\text{cm}^3$. The probes decayed to ^{12}C which is isoelectronic to Si. The maximum accumulated carbon concentration was $10^{13}/\text{cm}^3$. The Fermi level of the samples is therefore exclusively determined by the initial doping level and by the temperature even for high-resistivity material. The sample characteristics are listed in Table I. All samples were cut from commercially available wafers (Wacker Chemitronic) and used as delivered. The doping levels were chosen in order to obtain an approximately equally spaced spectrum of Fermi levels at 300 K.

The normal substitutional ^{12}B fraction is determined by NMR. A rf field (frequency ν_r) of sufficient power completely destroys the nuclear polarization for those probes

TABLE I. Sample characteristics.

Sample number	Type of conduction	Dopant	Dopant concentration (cm^{-3})	Production process[a]	Logarithm of preexponent factor[b] $\log_{10}(\mu_0/s^{-1})$	Activation enthalpy[b] E_a (eV)
1	*p*	B	5×10^{18}	CG	$7.3^{+4.2}_{-2.8}$	$0.9^{+0.6}_{-0.4}$
2	*p*	B	2×10^{15}	CG	$5.3^{+2.6}_{-1.7}$	$0.5^{+0.3}_{-0.2}$
3	*p*	B	$\lesssim10^{13}$	FZ	$5.6^{+3.5}_{-2.0}$	$0.5^{+0.4}_{-0.2}$
4	*n*	P	$\lesssim10^{13}$	FZ	$6.5^{+5.5}_{-2.5}$	$0.6^{+0.6}_{-0.3}$
5	*n*	P	9×10^{14}	FZ	$3.3^{+1.5}_{-2.3}$	0.23 ± 0.15
6	*n*	Sb	1.5×10^{18}	CG	4.1 ± 1.8	0.23 ± 0.15

[a] CG = crucible grown, FZ = float zone.

[b] The values for μ_0, and E_a result from the least-squares fit of Eq. (4) to our results shown in Fig. 2. The large errors are due to the fact that not only μ_0 and E_a, but also the top and bottom base lines of the substitutional fraction f_L have been allowed to vary without any restriction. The values of μ_0 and E_a are correlated within their error intervals: if μ_0 takes a value near the upper or lower limit of the given error interval, the same is true for E_a.

showing pure Zeeman splitting, when ν_r equals the Larmor frequency $\nu_L = g_I\mu_N B_0/h$. This leads to a resonance dip in the measurement of a_β as a function of ν_r.[8] Typical resonance curves are shown in Fig. 1.

The depth of the resonance dip can be used to obtain the fraction of the probes f_L that resonate at ν_L. The maximum resonance depths observed in this work were 10%. This value is identified with $f_L = 100\%$.[13] The probes which contribute to f_L must fulfill two conditions. Their local environment must be free of electric field gradients and internal magnetic fields. Both these conditions are satisfied by ^{12}B probes on normal substitutional sites. At the given doping levels and temperatures (>300 K) substitutional boron is an acceptor and hence is in a diamagnetic negative charge state. The cubic symmetry of the charge distribution occurs for this site as long as no intrinsic defects (i.e., vacancies, interstitials) or impurities (other dopants, carbon, oxygen, etc.) cause perturbations in the vicinity of a probe.

^{12}B probes on unperturbed tetrahedral interstitial sites could also contribute to the signal at ν_L. The identification of f_L with the unperturbed *substitutional* fractions alone is justified for the following reasons:

(i) EPR measurements on interstitial boron (B_i) in silicon lead to different possible lattice sites for all three charge states (B_i^-, B_i^0, B_i^+) none of which was the tetrahedral interstitial.[9]

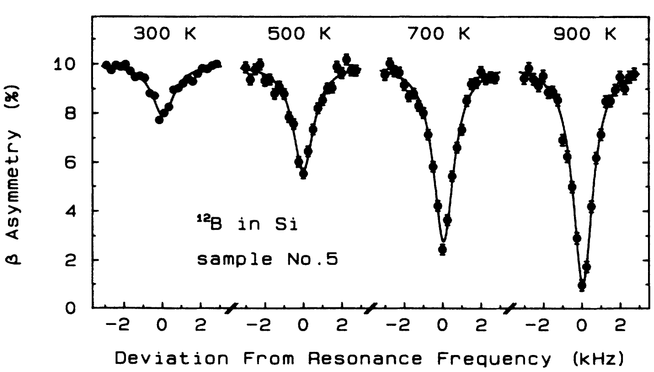

FIG. 1. Typical resonance dips at $\nu_r = \nu_L$ as a function of temperature. The baseline of all dips was shifted to $a_\beta = 10\%$.

(ii) Nuclear reaction channeling studies do not find the tetrahedral interstitial site occupied after boron implantations.[2]

(iii) In earlier β-NMR measurements the resonance linewidth (at ν_L) as a function of crystal direction (at 300 K) has been found to be consistent with the substitutional site only.[6]

In Fig. 2 the normal substitutional ^{12}B fractions f_L are plotted as a function of implantation temperature which is identical to the measuring temperature. For all samples we find $f_L(300\ K) = 20\%-30\%$ which increases continuously up to saturation values of $f_L(950\ K) \simeq 75\%-100\%$.

Our results confirm the trend already observed by Minamisono *et al.*[7] However, a substitutional ^{12}B fraction as high as 67(6)% at 300 K which was deduced by McDonald and McNab[6] appears to be inconsistent with our data. Since these authors did not measure the maximum polarization for ^{12}B in silicon they had to use a normalization in order to infer a substitutional fraction from a single measured polarization value. In this they erroneously assumed that the maximum polarization observed in certain metallic systems could be used to normalize their silicon data point.[6] A reanalysis including the maximum polarization observed in the present work shows that in Ref. 6 the substitutional fraction was overestimated by a factor of $\simeq 2$. The corrected value falls into the range of our data.

The most remarkable feature of our data is the dramatic temperature shift of the $f_L(T)$ curves as a function of bulk-doping level. This shows that both temperature *and* bulk-doping control the lattice site of isolated boron atoms after implantation.

The typical *S* shape of the $f_L(T)$ curves which is common to all samples suggests that thermally activated processes are important for the probe's site. In a simple model we consider a two-state system of resonant (substitutional) and nonresonant (nonsubstitutional) probes in which nonresonant probes may become resonant at a tem-

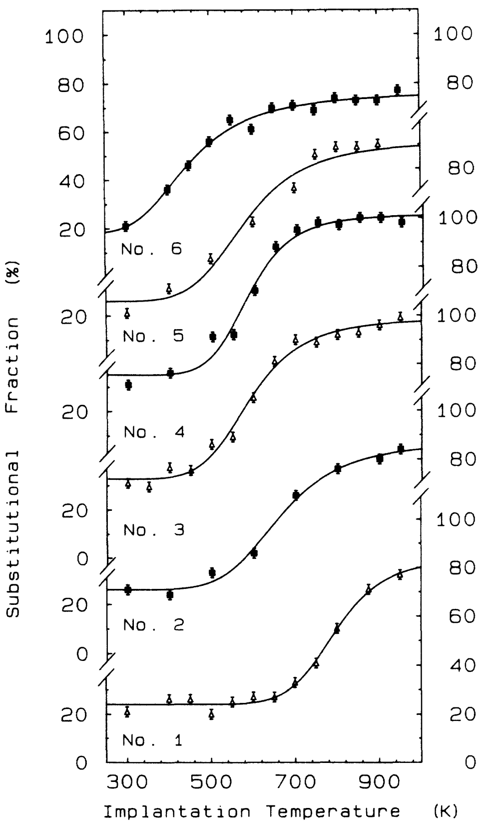

FIG. 2. The fractions f_L of unperturbed substitutional ^{12}B probes as a function of implantation temperature for samples of different doping levels (compare Table I). The temperatures of high substitutional fractions vary with doping level. The solid lines correspond to least-squares fits according to Eq. (4).

perature dependent rate $\mu(T)$. Hence, the absolute numbers of resonant and nonresonant polarized probes, r and n, respectively, are described by the following rate equations:

$$dr/dt = -\lambda r - T_{1,r}^{-1} r + \mu(T) n + \rho , \qquad (1)$$

$$dn/dt = -\lambda n - T_{1,n}^{-1} n - \mu(T) n + \nu . \qquad (2)$$

The decay rate λ is given by $1/\tau_\beta$, while ρ and ν describe the production rates of resonant and nonresonant probes by the implantation process. $T_{1,r}$ and $T_{1,n}$ are the spin-lattice relaxation times for resonant and nonresonant probes, respectively. We have measured $T_{1,r}$ at different temperatures and always found $T_{1,r} \gg \tau_\beta$. We could not measure $T_{1,n}$, but it is probable that it is of the same order of magnitude as $T_{1,r}$ for the following reasons: (i) boron is diamagnetic also on nonsubstitutional sites[1] and paramagnetic relaxation does not take place, (ii) possible quadrupole contributions to relaxation should be small because of the small quadrupole interaction of ^{12}B.[14] Therefore we neglect the relaxation terms in Eqs. (1) and (2).

For the stationary case we obtain the following solution of the equation system [(1) and (2)]

$$f_{\mathrm{res}}(T) = [f_0 + \mu(T)/\lambda]/[1 + \mu(T)/\lambda] , \qquad (3)$$

where $f_0 = \rho/(\nu+\rho)$ and $f_{\mathrm{res}} = r/(n+r)$. The experimentally observed high-temperature values for $f_L(T)$ are below 100% for several samples. This can be caused by two effects. First, a minor fraction of ^{12}B nuclei is not found on substitutional sites even at the highest temperatures accessible to us because they are either located in stable traps or were depolarized before reaching the substitutional sites. Second, the initial probe polarization varied somewhat between different runs due to instrumental instabilities. We account for these effects by introducing a scaling factor F which varies between 0.75 and 1. Further, we assume a single thermally activated process of the form $\mu(T) = \mu_0 \exp(-E_a/kT)$, where μ_0 is the transition rate for $T = \infty$ and E_a is an activation enthalpy. When these assumptions are combined with Eq. (3) we obtain

$$f_L(T) = F[f_0 + \tau_\beta \mu_0 \exp(-E_a/kT)] \times [1 + \tau_\beta \mu_0 \exp(-E_a/kT)]^{-1} . \qquad (4)$$

This formula was used for a least-squares fit of the data. The fit parameters for μ_0 and E_a which correspond to the solid lines in Fig. 2 are included in Table I. The data are remarkably well described by our model. Hence it appears reasonable to consider possible simple mechanisms which, after implantation, convert nonsubstitutional to substitutional boron via thermal activation. These may include reactions with vacancies and silicon self-interstitials which were produced during implantation. We note that each implanted ^{12}B probe, due to the extremely low probe concentration, can only undergo reactions with those defects that were produced in its own spatially correlated damage cascade. We can exclude interfering effects of either damage or carbon accumulation or implantation of inactive boron since the $f_L(T)$ values were independent of the total measuring time.

The low preexponential factors of 10^4–10^7 s^{-1} (compare Table I) suggest neither the simple dissociation of a ^{12}B-defect pair, nor the annealing of a ^{12}B-defect pair or a ^{12}B interstitial by the respective spatially correlated antidefect. Attempt frequencies of the order of 10^{10}–10^{13} s^{-1}, i.e., a characteristic vibrational frequency for the boron atom ($\sim 10^{13}$ s^{-1}) divided by a low number of jumps, would be expected for these processes. Rather, a thermally activated long-range migration with $\sim 10^6$ jumps is compatible with our analysis. The most likely candidate for such a process is interstitial boron. The annealing rate for interstitial boron in moderately boron doped electron-irradiated p-type silicon was determined by Watkins to be $5.3 \times 10^6 \exp(0.60 eV/kT)$ s^{-1} (Ref. 9). This rate is well reproduced by the parameters we found for the samples 2, 3, and 4. These samples, concerning the position of the Fermi level, are comparable to those used by Watkins since electron irradiation tends to shift the Fermi level towards midgap.[9] Therefore, the identical positive charge state of interstitial boron is expected for these cases. It is assumed by Watkins that the given rate describes the *disappearance* of interstitial boron via the migration to unidentified traps. We assign a comparable rate to the *appearance* of ^{12}B in normal substitutional sites. Hence we propose the following description of the implantation process of single boron atoms. About 75%–80% of the implanted ^{12}B probes are initially present as ^{12}B interstitials which were produced either directly in the implantation process or via Watkins' replacement mechanism. Thermal activation of the ^{12}B interstitials leads to long-range migration during which the probes may become substitutional via a hitherto unknown mechanism. As a result all or nearly all ^{12}B probes occupy normal substitutional sites at sufficiently high temperatures *and* contribute to the Larmor resonance.

The remaining samples yield either higher (sample 1) or lower (samples 5 and 6) activation enthalpies in the transition rate μ compared to the cases discussed above. It is tempting to assume that in the highly boron doped sample 1 interstitial ^{12}B is trapped by substitutional boron and is thus hindered from becoming substitutional at temperatures as low as in the close-to-intrinsic samples. However, our data for this sample are not compatible with the reported high temperature stability of such boron-boron pairs.[10] The low activation enthalpies of interstitial boron in the n-type samples 5 and 6 may reflect the now dominating negative equilibrium charge state of interstitial boron. It has been demonstrated experimentally[15] and theoretically[16] for the case of aluminum in silicon that the addition of electrons to a common acceptor atom on an interstitial site can cause a barrier lowering for migration. However, barrier lowering was hitherto not observed for the case of interstitial boron in silicon.[1]

A comparison of our data to the channeling studies[2] reveals two major differences. First, the typical decrease of the substitutional boron fraction upon annealing in those experiments finds no counterpart in our data. Second, in the channeling experiments despite the *longer* time scale (30 min compared to 29 ms) comparable saturation values of $\simeq 90\%$ for the substitutional fraction are obtained only at *higher* temperatures (between 1100 and 1300 K in contrast to values between 650 and 950 K in our experiment). These differences are probably due to the complex phenomena that occur in high dose implantations.[17]

In conclusion, we have demonstrated that β NMR with ^{12}B is presently the only method which allows the investigation of the behavior of isolated boron atoms when implanted into silicon samples with varying doping levels and implantation temperatures. A pronounced dependence of the substitutional ^{12}B fraction on bulk doping and temperature was observed. The unexpectedly simple temperature dependence is compatible with the assumption of a thermally activated process for each sample. A comparison to existing data[1,9] leads us to suggest that the underlying mechanism which produces boron in normal substitutional sites after implantation includes the long-range migration of interstitial boron.

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