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Anisotropic Debye–Waller factor of iodine impurities in p-type silicon

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Abstract. Mössbauer spectroscopy on radioactive ^{125}I impurities implanted in Si was performed using the 35.5 keV transition in $^{125\text{m}}\text{Te}$. Implantation was done at room temperature in Si $\langle 100 \rangle$ crystals that were made p⁺-type by co-implantation of B. After annealing at 875 °C, the I atoms are somewhat displaced from substitutional sites into the $\langle 111 \rangle$ direction, as was shown by previous channelling experiments. Mössbauer experiments were performed as a function of source temperature, with the γ -ray detector along a $\langle 100 \rangle$, $\langle 110 \rangle$ or $\langle 111 \rangle$ direction of the crystal respectively. The spectra were fitted with a quadrupole doublet, the asymmetry of which varied with detector orientation. The areas of all spectra could be fitted consistently assuming different Debye temperatures for vibrations parallel and perpendicular to the nearest-neighbour directions. From the sign of the observed electric field gradient we conclude that the effect is due to the presence of a nearest-neighbour vacancy, in agreement with the interpretation of the channelling experiments.

1. Introduction

The lattice location and the electronic structure of halogen atoms implanted in silicon are only poorly understood at present. For the case of iodine, interesting information was obtained via Mössbauer emission spectroscopy on implanted radioactive $^{129\text{m}}\text{Te}$ parent atoms that were introduced at substitutional sites via ion implantation and subsequent laser annealing [1–3]. It turned out that the daughter I atoms created in the radioactive decay could exist in (at least) three charge states, implying that at least two deep levels are present in the band gap for substitutional I in Si.

In order to study these electronic states with other techniques, stable I was implanted into Si. However, subsequent channelling experiments [4, 5] showed that neither pulsed laser annealing nor conventional oven annealing produced a substitutional solution of I in Si. Laser annealing leads to segregation of the implanted species at the surface. In contrast, oven annealing at 875 °C leads to a nearly substitutional location of the I atoms. In p-type, B-doped crystals a clear shift of the I atoms along $\langle 111 \rangle$ axes in the direction of a nearest neighbour was detected. This was interpreted as association of a nearest-neighbour vacancy with the I impurity.

In order to study this phenomenon in more detail, we performed Mössbauer emission experiments with the parent nucleus ^{125}I (60 d), which decays to the 35.46 keV state in ^{125}Te . Although this level has a lifetime of only 1.48 ns, leading to a large natural width of the Mössbauer transition, it is nevertheless possible to extract meaningful results from

the spectra. In particular, a clear anisotropy in the Debye–Waller factor (DWF) was observed, with a larger vibration amplitude in a nearest-neighbour direction than perpendicular to it. We will argue that this phenomenon, which is observed here for the first time, is indeed caused by the presence of a vacancy at a nearest-neighbour position of the iodine probe atom.

2. Experiment

Floating-zone-refined (100)-oriented Si single crystals with a resistivity of 10–20 Ω cm were implanted at room temperature with I and B ions. For I the implantation energy was 116 keV, while the energy of the B ions was 15 keV, leading to nearly overlapping depth profiles, with a projected range $R_p = 50$ nm and a straggling $\Delta R_p = 15$ nm. Sample 1 had a dose of 4×10^{13} I/cm² and 6×10^{13} B/cm², whereas in sample 2 the doses were 2×10^{14} I/cm² and 5×10^{14} B/cm², respectively. The typical strength of the ¹²⁵I sources obtained was 4 MBq, implying that most of the I implanted was stable ¹²⁷I.

The samples were subsequently annealed at 875 °C for 30 min in vacuum. After this treatment the Si lattice is completely recrystallized, while the depth profile of the implanted I is only slightly broadened and the I atoms occupy near-substitutional lattice sites [4, 5]. Most measurements were performed on the second crystal; in all cases the spectra of both samples were identical when measured under the same circumstances.

Mössbauer measurements were performed in transmission geometry, in a liquid He bath cryostat. A single line Sn¹²⁵Te absorber was used with a thickness of 4.9 mg ¹²⁵Te/cm². This absorber was always kept at 4.2 K, leading to an effective reduced thickness $t_A = 3.2$ and a minimum linewidth of 7.4 mm s⁻¹. In most experiments the source was mounted inside a small vacuum chamber that was moved inside the liquid He bath. Different mounts were used to align the $\langle 100 \rangle$, $\langle 110 \rangle$ or $\langle 111 \rangle$ axis of the Si crystal along the vertical direction of observation. For temperature regulation a Si diode temperature sensor and an electrical heater were used in a feedback circuit. In order to separate them efficiently from the intense Te x-rays produced in the decay of ¹²⁵I, the 35.5 keV γ -rays were detected with a 22 mm diameter, 6 mm thick pure planar Ge detector.

3. Results and analysis

Figure 1 shows spectra of the second sample, annealed at 875 °C and measured with source and absorber at 4.2 K. The orientation of the source crystal was varied, so that the observation direction was aligned with the $\langle 100 \rangle$, $\langle 110 \rangle$ and $\langle 111 \rangle$ axis, respectively. The most important feature of these spectra is that they are split by quadrupole interaction, proving that the large majority of the I atoms reside at sites with non-cubic symmetry. The spectra were fitted with a doublet, taking the width of both lines equal. Table 1 lists the position and linewidth parameters obtained from the fits. As can be expected, the parameters are the same for the three spectra within the error limits. The average values are compared with the measurement (taken in the $\langle 100 \rangle$ direction) right after implantation. An increase of the quadrupole interaction of about 20% is observed after annealing, indicating that the local environment of the I atoms did not change very much during recrystallization.

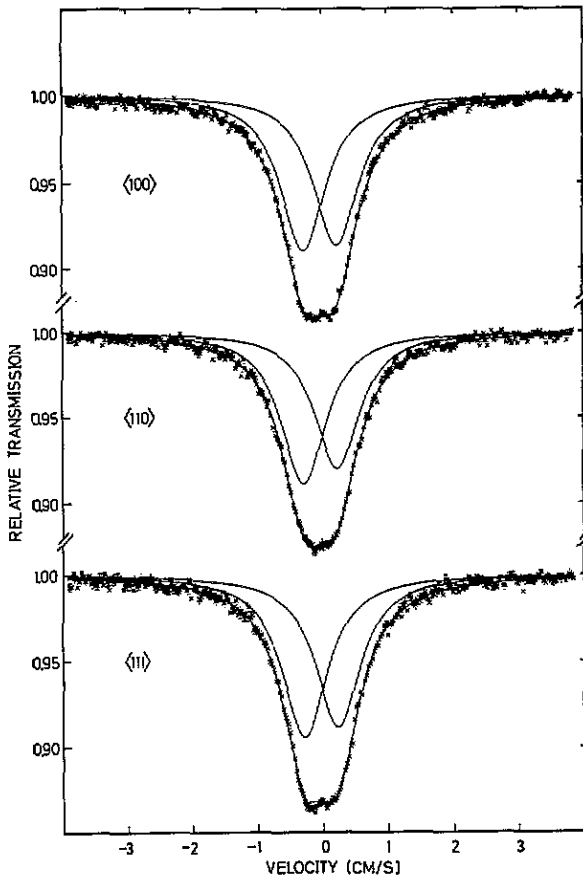


Figure 1. ^{125}I Mössbauer spectra obtained with a source of ^{125}I in B-doped Si and an absorber of Sn^{125}Te , both at 4.2 K. The gamma rays were detected along the $\langle 100 \rangle$, $\langle 110 \rangle$ and $\langle 111 \rangle$ axes of the Si single crystal, respectively.

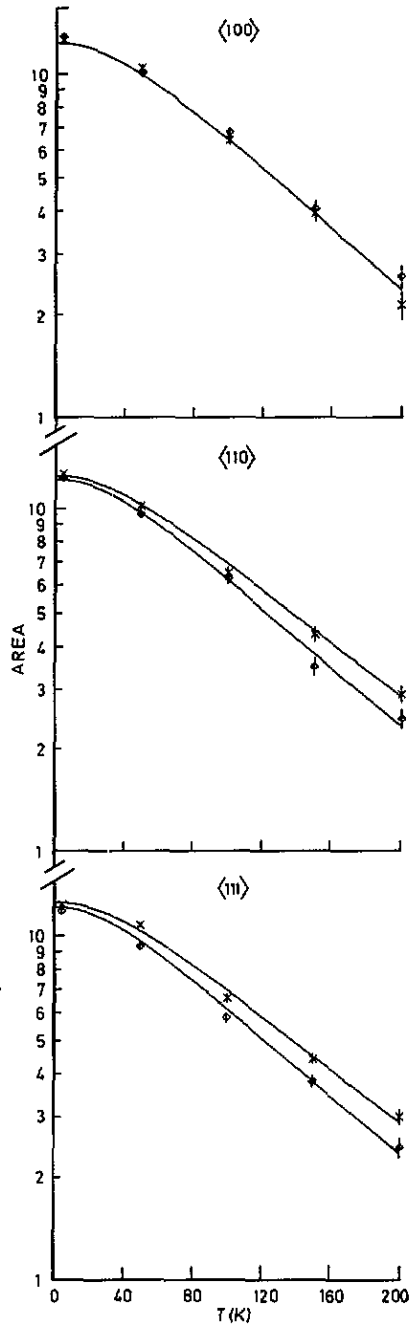


Figure 2. Areas of the two lines of the quadrupole doublet observed in spectra of ^{125}Te in B-doped Si, measured as a function of temperature. The points \times and \diamond denote the lines at negative and positive source velocities, respectively.

Table 1. Parameters of Mössbauer spectra measured with a source of ^{125}I in Si and an absorber of SnTe, both at 4.2 K.

Treatment	Orientation	S (mm s $^{-1}$)	eQV_{zz} (mm s $^{-1}$)	Γ (mm s $^{-1}$)
As implanted	$\langle 100 \rangle$	-0.05(4)	4.47(10)	8.2(2)
Annealed at 875 °C	$\langle 100 \rangle$	+0.19(10)	5.17(20)	8.2(2)
	$\langle 110 \rangle$	-0.11(9)	5.05(17)	8.4(2)
	$\langle 111 \rangle$	-0.03(7)	5.14(14)	8.3(1 3)
	Average	-0.02(6)	5.12(12)	8.3(1)

A slight asymmetry is visible for the $\langle 110 \rangle$ and $\langle 111 \rangle$ orientations. In order to show this more clearly, figure 2 gives the areas of the two lines of the doublet as a function of source temperature for the three different orientations of the Si crystal. A pronounced asymmetry is observed for the $\langle 110 \rangle$ and $\langle 111 \rangle$ orientations, whereas this effect is absent for the $\langle 100 \rangle$ orientation.

Such a behaviour in an otherwise perfect Si crystal must be associated with an anisotropy in the Debye-Waller factor of the I impurity atoms (analogous to the asymmetry in a polycrystalline sample with randomly oriented grains, as was first discussed by Goldanskii and Karyagin [6]. The channelling experiments on a sample prepared in the same way clearly show a shift of the I atoms in the direction of a nearest neighbour, indicating the presence of a near-neighbour point defect. We will therefore analyse the present data starting from the assumption that this anisotropy has axial symmetry along a $\langle 111 \rangle$ direction.

The area of a Mössbauer transition $m_i \rightarrow m_f$ in the source, measured with a single line absorber, is given by

$$I = KF_s(m_i, m_f, \theta) \quad (1)$$

where K is a constant, depending on the absorber thickness and the peak/background ratio in the window set on the Mössbauer γ -ray, while $F_s(m_i, m_f, \theta)$ is the source-dependent factor given by [7]

$$F_s = \begin{pmatrix} \frac{1}{2} & L & \frac{3}{2} \\ m_f & M & -m_i \end{pmatrix}^2 \tau_M^{\frac{1}{2}}(\theta) f_s = S(\theta) f_s. \quad (2)$$

In this expression, the factor within brackets is a $3j$ symbol, $\tau_M^{\frac{1}{2}}(\theta)$ is a factor depending on the angle θ between the quantization axis (the $\langle 111 \rangle$ direction, which is the principal axis of the electric field gradient (EFG)) and the direction of emission of the γ -quanta (the observation direction given by the wavenumber k). In the case of quadrupole interaction, the intensities of the two members of the doublet become

$$\text{I} \quad (m_i = \pm \frac{3}{2}, m_f = \pm \frac{1}{2}) \quad S(\theta) = \frac{1}{2} + \frac{1}{4} P_2(\cos \theta) \quad (3)$$

$$\text{II} \quad (m_i = \pm \frac{1}{2}, m_f = \pm \frac{3}{2}) \quad S(\theta) = \frac{1}{2} - \frac{1}{4} P_2(\cos \theta). \quad (4)$$

Table 2. Relative intensities of the two components of the quadrupole doublet for different orientations of the observation direction k . It is assumed that the EFG is directed along one of the four equivalent $\langle 111 \rangle$ axes of the silicon crystal; α is the fraction of atoms with an angle θ between the direction of the EFG and k ; $A = -k^2\langle x_{\parallel}^2 \rangle$, $B = -k^2(\langle x_{\parallel}^2 \rangle - \langle x_{\perp}^2 \rangle)$.

Direction	Transition	α	$P_2(\cos \theta)$	$S(\theta)$	$f_s(\theta)$	$\sum_j \alpha_j S(\theta_j) f_s(\theta_j)$
$\langle 100 \rangle$	$\frac{3}{2} \rightarrow \frac{1}{2}$	1	0	$\frac{1}{2}$	$e^A e^{B/3}$	$e^A e^{B/3}/2$
	$\frac{1}{2} \rightarrow \frac{3}{2}$	1	0	$\frac{1}{2}$	$e^A e^{B/3}$	$e^A e^{B/3}/2$
$\langle 110 \rangle$	$\frac{3}{2} \rightarrow \frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{3}{8}$	$e^A e^{2B/3}$	$e^A(3 + 5e^{2B/3})/16$
		$\frac{1}{2}$	$-\frac{1}{2}$	$\frac{3}{8}$	e^A	
	$\frac{1}{2} \rightarrow \frac{3}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{3}{8}$	$e^A e^{2B/3}$	$e^A(5 + 3e^{2B/3})/16$
	$\frac{1}{2}$	$-\frac{1}{2}$	$\frac{3}{8}$	e^A		
$\langle 111 \rangle$	$\frac{3}{2} \rightarrow \frac{1}{2}$	$\frac{1}{3}$	1	$\frac{3}{4}$	$e^A e^B$	$e^A(3e^B + 5e^{B/3})/16$
		$\frac{2}{3}$	$-\frac{1}{3}$	$\frac{5}{12}$	$e^A e^{B/3}$	
	$\frac{1}{2} \rightarrow \frac{3}{2}$	$\frac{1}{3}$	1	$\frac{3}{4}$	$e^A e^B$	$e^A(e^B + 7e^{B/3})/16$
	$\frac{2}{3}$	$-\frac{1}{3}$	$\frac{5}{12}$	$e^A e^{B/3}$		

Furthermore, we assume that the recoilless fraction f_s of the source also depends on this angle θ as

$$f_s = \exp[-k^2(\langle x_{\parallel}^2 \rangle \cos^2 \theta + \langle x_{\perp}^2 \rangle \sin^2 \theta)]. \tag{5}$$

That is,

$$f_s = \exp A \exp(B \cos^2 \theta) \tag{6}$$

with

$$A = -k^2\langle x_{\perp}^2 \rangle \tag{7}$$

$$B = -k^2(\langle x_{\parallel}^2 \rangle - \langle x_{\perp}^2 \rangle). \tag{8}$$

The RMS amplitudes $\langle x_{\parallel}^2 \rangle$ and $\langle x_{\perp}^2 \rangle$ can be calculated as a function of T within the Debye model, with the two Debye temperatures θ_{\parallel} and θ_{\perp} as parameters:

$$\langle x^2 \rangle_T = \frac{3\hbar^2}{mk_B\theta} \left[\frac{1}{4} + \left(\frac{T}{\theta} \right)^2 \int_0^{\theta/T} \frac{x}{e^x - 1} dx \right] \tag{9}$$

where m is the mass of the I atom and k_B is the Boltzmann constant.

If we want to calculate the intensities of the two members of the quadrupole doublet (denoted by I and II respectively) for certain orientations of the EFG with respect to the observation direction k , we have to sum over the different possible orientations θ_j with fractions α_j . Table 2 gives the expressions for the intensities of the two lines, assuming that the EFG is oriented along one of the four equivalent $\langle 111 \rangle$ axes. For $e^B = 0$ (maximum anisotropy) we find that $I(\text{I})/I(\text{II})$ is equal to 1 for k along $\langle 100 \rangle$, equal to 3/5 for k along $\langle 110 \rangle$ and equal to 5/7 for k along $\langle 111 \rangle$. The fact that we indeed do not observe any anisotropy for k along a $\langle 100 \rangle$ axis is important evidence in favour of the proposed model.

The model described above implies that all Mössbauer measurements taken as a function of temperature, with the γ detector in three different directions, can be fitted with only three parameters, the two Debye temperatures θ_{\perp} and θ_{\parallel} and an overall scale

factor K . The curves drawn in figure 2 give the results of such fits. We allowed for a slight variation of K due to different geometries when measuring along the three main axes of the crystal. The resulting values of K differed less than 10%. Finally we find for the effective Debye temperatures: $\theta_{\perp} = 213(4)$ K and $\theta_{\parallel} = 160(5)$ K.

The value for θ_{\perp} can be compared with the value found for substitutional Te in B-doped Si, measured after implanting $^{125\text{m}}\text{Te}$ and performing a pulsed laser anneal [8]: $\theta = 207(3)$ K. The nice agreement is expected in our model, because the vibrations perpendicular to the impurity-defect axis are not supposed to be influenced appreciably by the presence of the point defect.

4. Interpretation

The present Mössbauer results, combined with the previous channelling data, very strongly suggest the presence of a point defect at a nearest-neighbour position of the iodine atoms. There are two possibilities: the defect is a monovacancy or it is a boron atom. The channelling experiments are interpreted adopting the first possibility, but they cannot exclude the second one. Fortunately, the observed asymmetry in the doublet enables us to obtain the sign of the EFG V_{zz} . Transition I, corresponding to $m_i = \pm\frac{3}{2}$ and $m_f = \pm\frac{1}{2}$, has always the smallest intensity and is found at positive velocity (negative isomer shift with respect to SnTe). Using $Q = -0.20$ b [9] we find $V_{zz} = +6.1 \times 10^{22}$ V m⁻². This sign is in disagreement with a result from Langouche *et al* [10], who obtained a negative sign for V_{zz} from an analysis of the ^{125}Te Mössbauer spectrum from a ^{125}ISi source oriented at very low temperatures. In fact, this experiment only shows that the sign of V_{zz} is the same for the 35 keV state in ^{125}Te and for the ground state of ^{125}I . The negative sign is then derived referring to ^{129}I Mössbauer spectroscopy using $^{129\text{m}}\text{Te}$ sources [2]. We note, however, that the sample studied by Langouche *et al* was amorphized during implantation of 10^{15} Te/cm² and was not annealed subsequently. Consequently the environment of the radioactive ^{125}I probe atoms may be quite different in both cases. Even if vacancy trapping is the main origin for the EFG in both cases, the sign is not necessarily the same because the charge on the vacancy depends on the position of the Fermi level [11, 12].

A monovacancy in p⁺-type silicon is positively charged [11, 12]. Located at a nearest-neighbour site, it will lead to a positive V_{zz} at the position of the I nucleus. This is immediately clear in a point-charge picture. A more sophisticated treatment, in which the electronic structure of the Te vacancy cluster plus the surrounding Si atoms is explicitly calculated, is not expected to yield a different result for the sign of V_{zz} . The opposite sign is expected for a negatively charged B atom at a nearest-neighbour site. We conclude that monovacancies, being sufficiently mobile during the annealing treatment at 875 °C, are trapped by the I atoms in the neighbourhood. This gives rise to a slight shift of the iodine atoms from substitutional positions and an anisotropic Debye-Waller factor.

5. Conclusions

Mössbauer experiments on a source of ^{125}I in recrystallized B-doped Si show a quadrupole doublet whose asymmetry depends on the observation direction of the γ -rays. All experimental information, including previous channelling data, can be consistently

interpreted assuming the presence of a nearest-neighbour point defect at the impurity site, leading to an anisotropic Debye–Waller factor for the impurity atom. Such an effect is observed here for the first time. From the sign of the EFG it is concluded that the point defect is a monovacancy.

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