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Microscopic studies of implanted ^{73}As in diamond

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Abstract

In this work we present results on the lattice location and the microscopic surroundings of As implanted into diamond. A mixture of the isobars ^{73}Se and ^{73}As was implanted to a dose of 1.0×10^{14} at/cm² with 60-keV energy. Complementary γ -e⁻ Perturbed Angular Correlations (PAC), Emission Channeling (EC) and RBS/channeling (RBS/C) measurements were performed for the same sample, after full decay of ^{73}Se to ^{73}As . After annealing at 1400 K the EC and RBS/C spectra show that more than 50% of the As nuclei reside in substitutional positions, although some residual damage is still seen within the implanted range. On the other hand, the PAC data show that significant annealing of the lattice damage occurred only in the vicinity of 30% of the implanted As atoms, and that these have remaining defects in their neighborhood.

1. Introduction

Diamond is an attractive material for applications in high-temperature semiconductor devices. However, the production of reliable p-n junctions is still problematic, due to difficulties in obtaining n-type material [1]. Arsenic is a good candidate to obtain n-type shallow dopant layers in natural diamond, through ion implantation, since large substitutional fractions can be achieved in this way [2,3]. However, in spite of the previous work on the lattice location and on the annealing of the implantation damage, no detailed information is available on the interaction of the remaining defects with the implanted As ions.

In this work the lattice location and microscopic surroundings of implanted As in diamond were studied combining γ -e⁻ Perturbed Angular Correlation (PAC), Emission Channeling (EC) and Rutherford Backscattering/Channeling (RBS/C) measurements for the same sample. These enabled to characterize both the lattice location and the near surrounding of the As dopants.

2. Experimental details

A mixture of the isobars ^{73}Se and ^{73}As isotopes was implanted into a natural IIa diamond (110) single crystal at room temperature (RT) with 60-keV energy to a dose of 1.0×10^{14} at/cm², using the ISOLDE facility at CERN [4]. The Se/As projected range is $R_p = 215$ Å and the peak concentration is $P_C = 6.5 \times 10^{19}$ at/cm³ [5], i.e., about 0.04 at%. The experiments were performed after the full decay of ^{73}Se ($T_{1/2} = 7.1$ h) into ^{73}As ($T_{1/2} = 80.3$ d). First the γ -e⁻ PAC measurements were done at RT, in the as-implanted state and after furnace annealing at several temperatures up to 1400 K in a sealed quartz tube under vacuum (10^{-6} mbar), for 15 min.

Both the γ -e⁻ PAC and the EC measurements took place after the electron capture decay of ^{73}As to the 66.7-keV second excited state of ^{73}Ge (Fig. 1), with a half-life of $T_{1/2} = 0.5$ s. The recoil energy transferred to the ^{73}Ge ion in the decay (0.87 eV) is insufficient to displace it from the lattice position the parent ^{73}As ion occupied.

The γ -e⁻ PAC measurements use the intermediate state of the 53–13-keV cascade (Fig. 1) which has spin $I = 5/2$ and quadrupole moment $Q = 0.70(8)$ b [6]. Conversion electrons from the 13.3-keV transition are detected

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Fig. 1. Simplified level scheme of ^{73}Ge obtained from the ^{73}As and ^{73}Se decays.

due to its high conversion coefficient ($\alpha \approx 1100$). The experimental setup has been described elsewhere [7]. In a PAC experiment [8], the interaction between a radioactive dopant atom and a defect or impurity is detected by its characteristic electric field gradient (EFG), caused by the deviation from cubic symmetry of the charge distribution around the probe atom. This results in a modulation of the PAC spectrum, $R(t)$, which is described by the coupling constant, $\nu_Q = eQV_{zz}/h$, and the asymmetry parameter, $\eta = (V_{xx} - V_{yy})/V_{zz}$, where V_{zz} is the principal component of the EFG. The interaction with randomly distributed defects does not lead to the measurement of a sharp frequency but rather to a distribution of frequencies, which we assume here to be of the Lorentzian type, with an average value $\langle \nu_Q \rangle$ and a standard deviation σ_Q . The standard deviation depends on the density and variety of the lattice defects.

The EC experiments were performed using the Konstan three-axis goniometer, after the annealing at 1400 K. Conversion electrons from the 53.4-keV transition in ^{73}Ge were detected using a silicon surface barrier detector with an angular resolution of $\sigma = 0.25^\circ$. For the quantitative determination of lattice site fractions, calculated emission distributions using the many beam formalism of the dynamical theory of electron diffraction were fitted to the experimental spectra [9,10]. Thermal vibrations of the lattice and impurity atoms were taken into account in the calculation.

The RBS/C experiments were performed at the 3.1-MeV Van de Graaff accelerator at Sacavém, using a 1.6-MeV He^+ beam. The backscattered particles were detected at 140° and 180° using silicon surface barrier detectors located in the same horizontal plane (IBM standard geometry), with energy resolutions of 13 and 18 keV, respectively. The channeling data were simulated using a modified version of the FLUX code [11]. The thermal vibrations of the lattice and impurity atoms were included

in the simulations. These experiments were done after the annealing at 1400 K when more than 80% of the ^{73}As had already decayed to ^{73}Ge . The $^{73}\text{As}/^{73}\text{Ge}$ projected range and peak concentration were then measured to be $R_p = 330(50) \text{ \AA}$ and $P_c = 1.8(8) \times 10^{19} \text{ at/cm}^3$, respectively. R_p and P_c are respectively higher and lower than the as-implanted values estimated with TRIM [5]. This can be due either to As/Ge inward diffusion or to the fact that the implantation was performed along the $\langle 110 \rangle$ channeling direction.

3. Results and discussion

Fig. 2 shows the $R(t)$ functions measured in the as-implanted state and after annealing at 1400 K. After implantation most of the As nuclei, $f_D = 83(5)\%$, are located in highly damaged lattice sites, leading to a strong attenuation of the $R(t)$ function in the first channels. The remaining fraction, $f_U = 17(5)\%$, accounts for the As nuclei which are already in regular positions, either substitutional or interstitial with tetrahedral symmetry, but that are still interacting with randomly distributed defects, characterized by a distribution of frequencies with $\langle \nu_{QU} \rangle = 0 \text{ MHz}$ and $\sigma_{QU} = 1.5(1) \text{ MHz}$. After annealing at 1400 K there is an increase to $f_U = 29(8)\%$ of the regular fraction and an increase of the σ_{QU} to 3.9(7) MHz. This shows that the recovery is incomplete at the atomic scale. In case of complete recovery f_U would increase up to 100% and σ_{QU} would decrease to zero. The fact that σ_{QU} increased reveals that the set of nuclei now contributing to f_U are interacting with a spectrum of EFG that is larger than in the as-implanted state. This can be interpreted as due to a

Fig. 2. PAC spectra taken after the full decay of ^{73}Se in the as-implanted state (top) and after annealing at 1400 K (bottom). The dotted line in the bottom figure represents the expected $R(t)$ spectrum, for 100% unperturbed As nuclei.

Fig. 3. Evolution with the annealing temperature of the fraction f_U and of the standard deviation σ_{QU} that characterizes the As nuclei which are in regular positions but are still interacting with randomly distributed defects.

variety of remaining defects which are randomly located around those nuclei that only could achieve regular positions after annealing. The evolution with the annealing temperature of the fraction f_U and of the distribution of EFG's, σ_{QU} are shown in Fig. 3.

Fig. 4 shows the normalized electron emission yields measured along the $\langle 110 \rangle$, $\langle 100 \rangle$, and $\langle 111 \rangle$ axial directions after the annealing at 1400 K. The channeling peaks observed for all three axes are evidence for a significant fraction of As atoms on substitutional (S) sites. Arsenic atoms on tetrahedral interstitial (T) sites contribute to the channeling peaks in $\langle 111 \rangle$ and $\langle 100 \rangle$ but produce an almost isotropic emission distribution in the $\langle 110 \rangle$ direction [10]. It is therefore possible to determine the T fraction. The best fit to the data is obtained considering a fraction of 65(5)% of ^{73}As on S sites and no significant fraction on T sites. The remaining fraction of 35(%) is attributed to sites giving an isotropic electron emission distribution. Such sites could be other interstitial sites, like antibonding or hexagonal sites, or randomly distributed As atoms trapped in defect complexes. Since electron emission channeling is extremely sensitive to small displacements of emitters from an atomic row position, static or dynamic displacements from the substitutional sites exceeding about 0.1–0.2 Å can be excluded.

Fig. 5 shows random and $\langle 111 \rangle$ -aligned RBS spectra obtained after the annealing at 1400 K. Several impurities

Fig. 4. Normalized conversion electron intensities measured along the $\langle 110 \rangle$, $\langle 100 \rangle$, and $\langle 111 \rangle$ directions after the annealing at 1400 K. The solid lines represent fits to the data of calculated yields based on the dynamical theory of electron diffraction.

are clearly visible, mainly O ($2(1) \times 10^{15}$ at/cm²) and Si ($2(1) \times 10^{14}$ at/cm²) lying at the surface of the sample, possibly originating from the quartz tube. The spectrum taken along the $\langle 111 \rangle$ axis shows that even after annealing at 1400 K there is some residual damage, which becomes evident on comparing the spectrum with the one taken along the same direction in a non-implanted region. The remaining damage is centered at a depth of 280(50) Å and corresponds to a defect density of $5(2) \times 10^{20}$ at/cm³. The present set of data cannot distinguish if these are mainly point defects or small agglomerates of C randomly distributed. Table 1 shows the theoretical and the measured minimum yield ($\chi_{\min}$) values obtained for the main axis of the C lattice and for the corresponding As/Ge scans. For comparison the $\chi_{\min}$ of the $\langle 111 \rangle$ and $\langle 110 \rangle$ axes in an annealed but not implanted region are included.

Fig. 6 shows the RBS angular scans of the normalized yields for C and $^{73}\text{As}/^{73}\text{Ge}$ measured along the $\langle 100 \rangle$, $\langle 110 \rangle$, and $\langle 111 \rangle$ directions after the annealing at 1400 K. The narrowing mainly seen in the $\langle 100 \rangle$ axis suggests that the impurities are slightly displaced from the ideal position. The continuous lines are Monte Carlo simulations, considering an S fraction of 48(5)% and a random fraction of 52(5)%. The best fits were obtained considering a static displacement of about 0.15(5) Å of the As/Ge atoms from the ideal position towards the center of the $\langle 100 \rangle$ channel.

Table 1

Theoretical and measured RBS/C minimum yield ($\chi_{\min}$) values obtained for the main axis of the diamond lattice and for the corresponding As/Ge scans

Axis	$\chi_{\min}$ (%) of the C lattice			$\chi_{\min}$ (%) $^{73}\text{As}/^{73}\text{Ge}$
	theory	not-implanted	implanted	implanted
$\langle 100 \rangle$	2	–	12.6	56
$\langle 110 \rangle$	1.4	3	4.6	59
$\langle 111 \rangle$	1.7	4	6.1	50

For comparison the $\chi_{\min}$ of the $\langle 111 \rangle$ and $\langle 110 \rangle$ axes in an annealed but not implanted region are included.

Fig. 5. Random and $\langle 111 \rangle$ -aligned RBS spectra obtained after the annealing at 1400 K. A spectrum taken along the $\langle 111 \rangle$ direction in a non-implanted region is also shown for comparison.

The dotted lines represent the corresponding fits when no displacement is considered. Within the accuracy of the present measurements done with RBS and EC, it is possible that small displacements from the perfect substitutional site in the order of the vibrational amplitude of the impurities (~ 0.07 Å) are present. From the RBS data the T fraction is less than 5%, which is in agreement with the EC results.

Fig. 6. RBS angular scans measured along the $\langle 100 \rangle$, $\langle 110 \rangle$, and $\langle 111 \rangle$ directions after the annealing at 1400 K and respective Monte Carlo fits, detailed in the text. The dotted lines are fits of the As/Ge scans when no displacement from the substitutional sites is considered.

4. Conclusions

^{73}Se was implanted in diamond at a dose of 1×10^{14} at/cm² and 60-keV energy. Combined PAC, EC and RBS/C measurements were performed in the same sample, after the complete decay of ^{73}Se to ^{73}As . After annealing at 1400 K the PAC data show that only about 30% of the As atoms significantly recovered in the diamond lattice, but have still randomly distributed defects in their neighborhood. Both the EC and RBS/C data show that more than 50% of the As nuclei reside in substitutional positions. Therefore, we can conclude that even the As atoms achieving substitutional positions have unrecovered point defects nearby. Although some residual damage is still seen within the implanted range the RBS/channeling results show that there was a significant recovery of the diamond lattice, in spite of the relatively high implanted dose of 1.0×10^{14} at/cm².

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