MICROSCOPIC STUDIES OF THE HYDROGEN PASSIVATION IN n-TYPE SILICON: A NEW APPLICATION OF THE $^{73}$As $\gamma$-e$^-$ PAC TECHNIQUE

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The hydrogen passivation of As donors in Si was studied using the g-e$^-$ Perturbed Angular Correlation technique. The samples were doped with $^{73}$As by implanting the parent isotope $^{73}$Se at room temperature and 60 keV energy, to a dose of 2x10$^{13}$ at/cm$^2$. After removing the radiation damage, hydrogen was implanted with low energy (300eV), to a dose of 5x10$^{15}$ at/cm$^2$. Two electric field gradients were observed and assigned to H correlated complexes formed at the As donors. These complexes dissociate at temperatures lower than 1070 K.

1. Introduction

The interest in the hydrogen passivation of shallow impurities in semiconductors has increased in recent years, due to fundamental and technological reasons. While the passivation of shallow acceptors has been extensively studied, less experimental data is available on donor-hydrogen interaction$^1$. Until 1986 it was believed that hydrogen did not affect the electronic properties of n-type silicon. Since then several spectroscopic experiments gave evidence for donor-hydrogen complexes$^2$. The $\gamma$-$\gamma$ perturbed angular correlation ($\gamma$-$\gamma$ PAC) spectroscopy observes the immediate neighbourhood of a specific probe atom on a microscopic scale and is therefore able to investigate the formation and structure of complexes formed with these probes. However, the application of PAC is limited by the small number of suitable probe atoms. As a consequence, PAC experiments up to now have been focused on the passivation of acceptors$^3$. Recently, it was shown that $^{73}$As can be used as a PAC probe, provided the angular correlation between $\gamma$ and e$^-$ emission is measured instead the one between two $\gamma$ quants$^6$. Since the parent isotope $^{71}$As is a donor in Si it is able to trap H. After the radioactive decay ($T_{1/2} = 80$ days) into the excited state ($I = 1/2$) of the isovalent daughter isotope $^{73}$Ge (Fig. 1) hydrogen is...
no more bound to the probe atom by Coulomb interaction. Thus the free H diffusion can be observed as function of temperature within the time window defined by the nuclear half-life ($T_{1/2} = 0.5\text{s}$) of the first excited state of $^{73}\text{Ge}$.

In this work we present first PAC results on the interaction of hydrogen with the probe $^{73}\text{As/Ge}$ in silicon.

2. Experimental Details

The isotope $^{73}\text{Se}$ was implanted into Si $\langle 110\rangle$ single crystals ($10^{15}$ B/cm$^3$) at 300 K and 60 keV energy to a dose of $2 \times 10^{13}$ at/cm$^2$, at the ISOLDE facility at CERN. The Se projected range is 460 Å and the peak concentration is $5 \times 10^{18}$ Se/cm$^3$ (Ref. 8). After the decay of $^{73}\text{Se}$ ($T_{1/2} = 7.1\text{h}$) into $^{73}\text{As}$ ($T_{1/2} = 80\text{d}$) the $\gamma$-e$^-$ PAC spectra were taken at 300 K, in the as-implanted state and after furnace annealing at several temperatures up to 1220(20) K under Ar atmosphere for 10 min. The maximum annealing temperature of 1220 K was chosen to avoid As diffusion. The samples were then implanted with H$^+$ at 400 K to a dose of $5 \times 10^{15}$ at/cm$^2$ and energy of 300 eV.

The $\gamma$-e$^-$ PAC measurements use the 53-13 keV cascade of $^{73}\text{Ge}$, populated by the decay of $^{73}\text{As}$ (Fig. 1). Coincidence spectra are taken between the 53 keV $\gamma$-quants and the L-shell conversion electrons from the 13 keV transition. The intermediate state of the cascade has spin $I = 5/2$ and its quadrupole moment is $Q = 0.70(8)$ b$^6$.

![Figure 1: $^{73}\text{Ge}$ cascade.](image_url)
The experimental setup is described elsewhere. In a PAC experiment, the formation of a complex between the probe atom and a defect or impurity is detected by its characteristic electrical field gradient (EFG) caused by the impurity’s or defect’s charge distribution. The EFG results in a time modulation of the PAC spectrum, $R(t)$, which is described by the quadrupole coupling constant, $v_Q = eQV_{zz}/\hbar$, 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 leads to a distribution of EFGs, which we assume to be of Lorentzian type characterised by an average value $\langle v_Q \rangle$ and a standard deviation $\sigma_Q$. The standard deviation depends on the density and variety of the lattice defects.

### 3. Results and Discussion

Fig. 2 (left) shows two $R(t)$ spectra of a Si sample after implantation and subsequent annealing at 570(5) K and at 1220 K. After annealing at 570 K a fraction $f_S = 62(8)\%$ of the $^{73}$Ge probe atoms are located on lattice sites within a slightly perturbed environment, characterised by an EFG distribution centered at $\langle v_{QS} \rangle = 0$ MHz with a standard deviation $\sigma_{QS} = 3.4(3)$ MHz. The rest of the probe atoms $f_D = 38(8)\%$ are located in a heavily perturbed environment. With increasing annealing temperature the fraction $f_D$ decreases while the fraction $f_S$ increases and the standard deviation $\sigma_{QS}$ of the corresponding EFG distribution decreases. To illustrate this annealing behaviour $f_S$ and $\sigma_{QS}$ are plotted in Fig. 2 (right) as function of annealing temperature. After annealing at 1220 K a fraction to a weak EFG distribution characterised by $\langle v_{QS} \rangle = 0$ MHz and $\sigma_{QS} = 0.16(2)$ MHz. This indicates the removal of the implantation damage for the majority of the probe nuclei which we assume to be located on substitutional lattice sites in agreement with recent Emission Channeling measurements. The temperature of 1220 K is typical for annealing radiation damage after implantation of heavy ions in Si.

![Figure 2](image-url)
After annealing, the samples have been implanted with low energy H\(^+\). Fig. 3 (top) shows the PAC spectra taken at 300 K after H\(^+\) loading and after annealing at 1070(5) K. Immediately after H\(^+\) loading a modulation of the R(t) spectrum appears which was fitted considering two EFG distributions characterised by their average values \(\langle \nu_{Q1} \rangle = 65(2) \text{ MHz} \) and \(\langle \nu_{Q2} \rangle = 204(10) \text{ MHz} \) and the corresponding standard deviations \(\sigma_{Q1} = 4.6(6) \text{ MHz} \) and \(\sigma_{Q2} = 14.2(2) \text{ MHz} \), respectively. More than 50 \% of all probe atoms interact with these EFGs \(f_1 = 17(4)\%\), \(f_2 = 36(4)\%\).

After annealing at 1070 K both the fractions \(f_1\) and \(f_2\) vanish but without recovering the previous situation before hydrogen was loaded. In fact the fraction of the probe atoms which are located on almost unperturbed lattice sites, \(f_S = 72(5)\%\) is smaller and the standard deviation \(\sigma_{QS} = 0.28(1) \text{ MHz} \) is greater than the corresponding values measured before hydrogenation.

The observed EFGs which give origin to the non-vanishing \(\langle \nu_{Q1} \rangle\) and \(\langle \nu_{Q2} \rangle\) frequency average values must be due to \(^{73}\text{As}/\text{Ge}\) trapped hydrogen atoms or hydrogen correlated defects which are not yet mobile at 300 K. At 300 K the diffusion of a single H atom should be fast enough to leave the next nearest neighbourhood of the probe atom already within the first 0.5 s after the decay of \(^{73}\text{As}\) into \(^{73}\text{Ge}\) which is isovalent to Si.

Therefore we propose that the observed complexes are hydrogen related, either consisting of several H atoms or H-defect clusters, which are immobile at 300 K. Since the implanted H dose of \(5 \times 10^{15} \text{ at/cm}^2\) was rather high it might well be that complexes consisting of more than one H atom or of H and additional other defects are formed. The high hydrogen dose could also be the reason for the failure in recovering the original conditions after annealing at 1070 K since it is well known that hydrogen introduced into Si to high concentrations produces many defects such as stable agglomerates\(^\text{13}\).

![PAC spectra](image)

Fig. 3 PAC spectra taken after hydrogen loading (top) and after annealing at 1070(5) K (bottom). The dashed line in the top figure represents the \(T_A = 1220\) K annealed spectrum, before the hydrogen loading.
4. Conclusions

First results were reported on PAC experiments in Si using $^{73}\text{As}^{73}\text{Ge}$ as $\gamma$-e$^-$ PAC probe. It was aimed to study the annealing of the radiation damage after heavy ion implantation and the interaction of hydrogen with As.

It was shown that after implantation and annealing at 1220 K about 90% of all As nuclei are located on almost unperturbed substitutional lattice sites. After low energy H$^+$ implantation, 50% of the $^{73}\text{Ge}$ atoms obtained from the radioactive decay of $^{73}\text{As}$ interact with hydrogen related defects at 300 K. Two different complexes can be distinguished, but for a further characterisation measurements at lower temperatures are necessary.

The probe atom As is a n-type dopant in Si and Ge, enabling the trapping of H. PAC measurements at temperatures below the onset of the hydrogen diffusion should allow the observation of the single, unbound hydrogen at the probe atom $^{73}\text{Ge}$ after the decay of $^{73}\text{As}$ into the isovalent impurity $^{73}\text{Ge}$. Thus it would be possible to observe directly the diffusion of the isolated hydrogen in Si and Ge.

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