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DEFECT-ACCEPTOR PAIRS IN GERMANIUM

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The PAC probe ^{111}In was implanted into intrinsic, n- and p-doped germanium. After removing the radiation damage by thermal annealing the samples were irradiated with different ions to study defect-acceptor pairs by means of the PAC technique. In all samples a high electric field gradient could be observed, characterized by a quadrupole interaction frequency of ν_{Q2} = 415 MHz and an axial symmetry (η = 0). Some samples show another frequency of ν_{Q1} = 52.5 MHz and η = 0.The results give evidence for an intrinsic defect trapped at the ^{111}In probe.

1. INTRODUCTION

The time differential perturbed angular correlation technique (PAC) has very successfully proven its applicability to the study of defects in metals /1/. In semiconductors, in spite of intensive investigations with various methods, even today many fundamental questions concerning the properties and behaviour of intrinsic and extrinsic defects remain to be answered. Therefore it seems natural to apply the PAC technique also to these systems.

However, in semiconductors the influence of residual impurities is comparably strong and can interfere with the observation of the defect under study. Therefore for the present work we chose germanium, the semiconductor which can be obtained with the highest purity.

2. EXPERIMENTAL DETAILS

Ge single crystals of ultra high purity (< 10^{10} B/cm^3), polished mechanically to a mirror like surface, were used for the experiments.

The samples were prepared by implanting ^{111}In ions with 160 keV to a dose of 10^{12}-10^{13} ions/cm^2. Subsequently the samples were annealed in vacuum to remove the radiation damage. We used a two-step annealing process, starting with 450°C for 30 min followed by 650°C for 30 min/2/. After the annealing the samples were irradiated with different ions (C, O, P, Ge, As, Se, Sb, Bi) or electrons. The irradiation energy for each ion was chosen appropriately to obtain good overlap with the In profile. The dose was 10^{12}-10^{13} ions/cm^2. The electron irradiation was carried out with 3 MeV e^- and a dose of $2*10^{18}$ e^-/cm^2. The irradiation temperature was 4.2 K. In all other cases the irradiations took place at room temperature.

Some experiments were carried out in samples predoped with Sb (n-Ge) respectively In (p-Ge) to a dose of $5*10^{13}$-$5*10^{14}$ ions/cm^2. Prior to the implantation of radioactive ^{111}In also here the radiation damage was removed using the same annealing process as described above. After the In implantation which was followed again by a two-step annealing the samples were irradiated with O to a dose of $2*10^{12}$ ions/cm^2.

The hyperfine interaction of ^{111}Cd was observed by means of the PAC technique /3/. The excited level of ^{111}Cd, populated by the electron capture decay of the ^{111}In, decays via a γ-γ cascade to the ground level. One observes the angular correlation of the γ rays which is perturbed if an electrical field gradient (EFG) interacts with the quadrupole moment of the intermediate level of the $\gamma-\gamma$ cascade. The EFG arises from a perturbation of the cubic charge symmetry around the In probe. The influence of this perturbation can be described by a perturbation function G(t)

$$G(t) = \sum_n s_{2n}(\eta) * \cos(c_n(\eta)\nu_Q t) * \exp(-c_n(\eta)\tilde{\nu}_Q \delta t)$$

Here ν_Q =eQV$_{zz}$/h is the quadrupole interaction frequency with Q the quadrupole moment of the intermediate level and V_{zz} the maximum component of the EFG tensor. $\eta=(V_{xx}-V_{yy})/V_{zz}$ shows the asymmetry of the EFG. The fourier coefficients s_{2n} and the frequency factors c_n depend on η . The exponential factor describes a possible Lorentzian distribution around a mean value $\tilde{\nu}_Q$.

3. RESULTS

For the samples implanted only with doses of $\sim 10^{12}$ In/cm^2, the annealing process described above led to a complete removal of the radiation damage, i.e. the PAC spectra show that ~100% of the probe atoms occupy sites of perfect cubic charge symmetry. With increasing doses a slight distribution of very weak EFGs at the In site led to a slight decrease of the anisotropy with time. This effect was most pronounced in the samples predoped with $5*10^{14}$ In/cm^2 (p-Ge).

After the irradiation with electrons and various ions two well defined interaction frequencies were observed, characterized by the hyperfine parameters ν_{Q1} = 52.5 (10) MHz, η = 0 and ν_{Q2} = 415 (1) MHz, η = 0. Figure 1 shows a typical spectrum obtained after irradiation with O. The fractions f_i of probe atoms decorated with the corresponding defects vary for different irradiations. f_2 (ν_{Q2}) has values in the range between 30% and 7.5% whereas f_1 (ν_{Q1}) reaches a maximum of 10% and even vanishes in some cases.

Orientation measurements yielded a ⟨111⟩ orientation of the main EFG component produced by both defects.

The temperature dependence of the EFGs has been investigated in the O irradiated sample. The result is shown in figure 2. In both cases only a slight decrease of the interaction frequencies between 13 K and 293 K is observed.

The behaviour of the fraction f_2 was studied in the electron irradiated sample in an isochronal

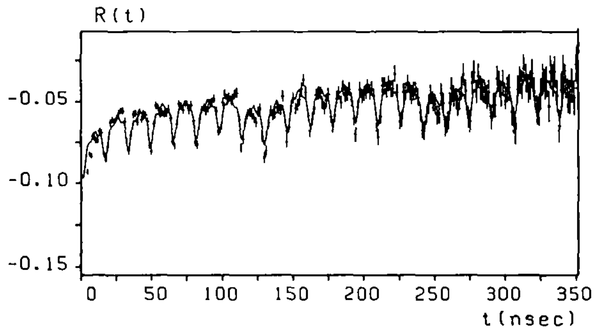

Figure 1. PAC spectrum measured after O irradiation for ^{111}In in Ge at room temperature.

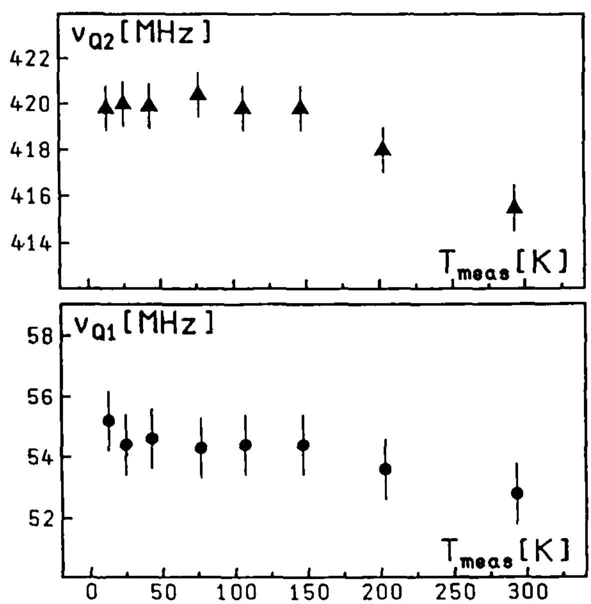

Figure 2. Temperature dependence of ν_{Q1} and ν_{Q2}.

annealing program (annealing the samples for 10 min at different temperatures). It was found that f_2 has its maximum value immediately after the irradiation. Annealing up to 350 K showed only a slight decrease of f_2.
Annealing at temperatures above 350 K caused a quick decrease of f_2 which resulted in the disappearance of ν_{Q2} at about 430 K. The fraction f_1 equally vanished at this temperature.

Another sample, irradiated with 3 MeV electrons, was transferred cold (T= 4.2 K) into the measuring apparatus and measured at 4.2 K. The obtained PAC spectrum corresponds to a wide distribution of quadrupole frequencies arising from radiation damage. An isochronal annealing program (measuring temperature T = 4.2 K) carried out for this sample below room temperature showed that ν_{Q2} is not observed up to 200 K and appears only after warming up the sample to room temperature.

After O irradiation of the predoped samples the quadrupole interaction frequency ν_{Q1} appeared as well as ν_{Q2}. The isochronal annealing programs showed no significant differences to the results in the intrinsic samples.

4. DISCUSSION

The completely undisturbed spectra and the full anisotropy observed after annealing of the samples with In concentrations below 10^{18} In/cm^3 (implantation dose ~ 10^{12} at/cm^2) show that 100% of the implanted probe atoms occupy sites of perfect cubic charge symmetry. Although in the Ge lattice the substitutional and the tetrahedral interstitial site show this cubic symmetry a comparison with Rutherford backscattering / channeling experiments /4/ allow to conclude that all In probes occupy the substitutional site.

The damping observed in the samples with higher dopant concentrations (~ 10^{21} at/cm^3) can be attributed to the influence of other impurity atoms on the EFG at the substitutional site.

As far as the nature of the two defects trapped at the In probes is concerned we can draw the following conclusions:
- The corresponding quadrupole interaction (QI) frequencies ν_{Q1} and ν_{Q2} appear after room temperature irradiations with electrons, Ge and various other impurities (C, O, P, As, Se, Sb, Bi). Hence it follows that the defects are either intrinsic (selfinterstitials, vacancies) or previously present in the sample. Due to the high purity of the material only hydrogen incorporated during the production process or from the atmosphere is a possible candidate for an extrinsic defect.
- After the electron irradiation at 4.2 K a strong damping of the anisotropy is observed which is due to the uncorrelated damage produced in the vicinity of the In probes. In an isochronous annealing program no unique frequency appears up to 200 K. ν_{Q2} appears only after the sample is warmed up to 293 K. Thus the corresponding defect becomes mobile between 200 K and 293 K, a temperature region where vacancy migration is expected /5/. Selfinterstitials are mobile at much lower temperatures and can be ruled out by this observation.
- In the case of ν_{Q1} additional evidence for the intrinsic nature of the defect comes from neutrino recoil experiments /6/. The neutrino recoil transfered to the Cd nucleus after the electron capture decay of ^{111}In creates very localized damage around the probe atoms. The fact that ν_{Q1} is observed in samples kept at 77 K can only be explained by assuming the creation of an intrinsic defect in the vicinity of the probe and not the trapping of a migrating impurity like H.

In view of these facts we suggest that the QI frequencies observed in the present experiments are most probably due to In - vacancy complexes. In the case of ν_{Q2} = 415 MHz a vacancy is trapped in the nearest neighbour position (V - S complex in figure 3). This configuration explains the symmetry of the

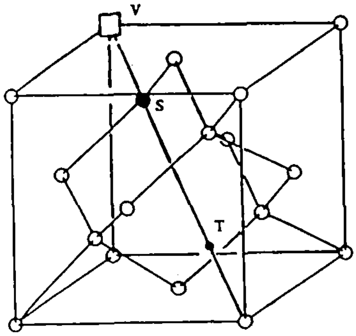

Figure 3. Structure of the Ge lattice V-vacancy, S-substitutional site, T-tetrahedral interstitial site

EFG, the $\langle 111 \rangle$ orientation of its main component and the high value of V_{ZZ}. In this context it is interesting to note that in Si a QI frequency of comparable magnitude has been found, which also is attributed to a trapped monovacancy /7/.

Regarding the second QI frequency ν_{Q1} = 52.5 MHz it is striking that its value is quite precisely 1/8 of ν_{Q2}. Due to the $1/r^3$ dependence of the EFG one would expect such a reduction of the QI frequency if the distance between the In probe and the disturbing charge is increased by a factor of two. However, no regular lattice site, where a vacancy could be trapped, exists in the Ge lattice at the double nearest neighbour distance.

A possible configuration explaining the hyperfine parameters of this complex would be an In probe on the tetrahedral interstitial site (T in figure 3) with a vacancy trapped on the substitutional position along the $\langle 111 \rangle$ direction at the double nearest neighbour distance (S - site in figure 3). The fact that ν_{Q1} is also observed in the neutrino recoil experiment /6/ can be explained by assuming that the neutrino emitting In probe is displaced from its substitutional site to the T site leaving a vacancy at its previous site. In the present experiments the displacement could occur during the postirradiation with heavy ions.

However, in many systems a decoration (passivation) of acceptors in semiconductors by hydrogen has been reported /8/. Therefore further experiments seem to be necessary to finally exclude hydrogen as a possible partner in the observed In - defect complexes.

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