Kuitunen, Katja; Tuomisto, Filip; Slotte, Jonatan; Capan, Ivana

Divacancy clustering in neutron-irradiated and annealed n-type germanium

Published in:
Physical Review B

DOI:
10.1103/PhysRevB.78.033202

Published: 01/07/2008

Please cite the original version:
I. INTRODUCTION

Germanium as an elemental semiconductor has been shadowed by silicon, when it comes to the use of semiconductor materials in integrated circuits and devices. The supreme properties of silicon include a larger band gap, a stable oxide, and an extremely low surface-state density. However, electron and hole mobilities are much higher in germanium than in silicon, which has lead to the use of strained Si$_x$Ge$_{1-x}$ heterostructures to increase mobility in modern transistors. Even higher charge carrier mobilities could be pursued if transistors were built out of germanium, which is something that is attempted by many groups.

Even though the history of germanium as a material for semiconductor devices is over 50 years old, very little is known about its material properties, e.g., very few irradiation-induced defects such as vacancies and vacancy impurity complexes have been identified in germanium. Gaining knowledge on the formation, migration, and annealing properties of vacancy defects in germanium is therefore of utmost importance. The apparent low formation energies of vacancy defects in germanium make them suitable agents for, e.g., self-diffusion and diffusion of impurities. Also knowledge of the annealing behavior of different defects is very much needed.

The investigations of irradiation-induced defects in Ge have been carried out using different techniques, e.g., deep-level transient spectroscopy (DLTS), Hall measurements, and infrared absorption spectroscopy. Fage–Pedersen et al. reported on energy levels of several majority and one minority carrier traps in irradiated Ge. Vanmeerbek et al. have used local vibrational mode spectroscopy to study oxygen-related defects in irradiated and annealed Ge. Computational studies on vacancy defects in germanium have recently been carried out by Coutinho et al., who studied deep carrier traps in a divacancy, and by Janke et al., who made calculations concerning the thermal stability of the divacancy in germanium. The calculations by Janke et al. suggest that most divacancies anneal by migration to trapping centers. Peaker et al. have used multiple experimental techniques to study ion-implanted Ge. They propose that the vacancy and interstitial clustering are important mechanisms in implanted germanium.

Positron annihilation spectroscopy (PAS) has been established as a versatile tool for studying open volume defects in semiconductors. However, as with other techniques, very little work has been published on germanium. Early work from the 1960s on single-crystal Ge include pioneering works by Fabri et al. and Fieschi et al. However, it is difficult to relate to these studies due to the poor time resolution available in the early days of PAS, which makes comparison between lifetime components questionable. Among the first annealing studies on (neutron) irradiated Ge were Yeh et al. and Arifov and Arutyunov. It seems that the as-grown samples used in both studies contain native defects, since the average lifetime calculated from the reported annihilation rates ($\lambda=4.17 \times 10^9$ s$^{-1}$) is around 240 ps, i.e., approximately 15–20 ps above the bulk lifetime in Refs. 14 and 19 and in the present study. Yeh et al. observed that the trapping rate in as-irradiated samples saturate at $3.32 \times 10^9$ s$^{-1}$ after an irradiation fluence of $7 \times 10^{15}$ cm$^{-2}$, corresponding to a lifetime of 301 ps. Similar results were observed by Arifov and Arutyunov after a 2 x 10$^{18}$ cm$^{-2}$ irradiation. Both studies report that the annealing of the irradiation-induced defects is divided into two steps. The first one at around 573 K apparently results in the formation of larger vacancy clusters. Open volume defects of monovacancy size, with positron lifetimes varying from 278–292 ps have been reported by Moser et al., Corbel et al. and Wurschum et al. More recently, Polity et al. have studied the formation and annealing of Frenkel pairs and vacancy-oxygen pairs in electron-irradiated Ge with positrons. Va-
cancy clustering and the annealing of these clusters have been studied by Krause–Rehberg et al. Similar results in self- and Si-implanted Ge have been reported by Peaker et al.\textsuperscript{12} Recrystallization of ion-implanted amorphous Ge have been studied with PAS by Slotte et al.\textsuperscript{13}

In this Brief Report, we have studied neutron-irradiated Ge samples doped with Sb with positron lifetime spectroscopy. We show that irradiation generates vacancy defects that tentatively are identified as divacancies. At the annealing temperature of 473 K, the majority of the vacancy defects turns mobile and form bigger vacancy clusters. However, temperature dependence in the defect lifetime component shows that some defects of divacancy size that are in a negative charge state are stable after annealing at 473 K. Annealing at 673 K removes most of the clusters and also a considerable fraction of negatively charged vacancy defects of divacancy size. An annealing temperature of 773 K is required to remove these defects.

II. EXPERIMENTAL DETAILS

The measured samples were $n$-type Ge (110) bulk crystals, in which the dopant Sb concentration was $1.5 \times 10^{15}$ cm$^{-2}$. The samples were irradiated with fast neutrons up to a fluence of approximately $10^{16}$ cm$^{-2}$ and annealed in 473, 673, and 773 K.

We used a conventional fast-fast coincidence system with a resolution of 260 ps and a 20 $\mu$Ci $^{22}$NaCl source to measure positron lifetime spectra. The reference (bulk) lifetime in the measurements was $\tau_B = 224$ ps. Prior to the analysis, the positron annihilations in the source material and in the Al foil covering the source, as well as positronium annihilations as positronium and in the reference sample, were subtracted from the lifetime spectra. The sample temperature during the measurements was controlled by a closed-cycle He cryostat with resistive heating.

The lifetime spectra $n(t) = \sum I_i \exp(-t/\tau_i)$ were analyzed in terms of exponential decay components convoluted with the Gaussian resolution function of the spectrometer. The indexes $i$ correspond to the different lifetime components in the spectra with individual lifetimes $\tau_i$ and intensities $I_i$. The increase of the average positron lifetime $\tau_{\text{ave}} = \sum I_i/\tau_i$ above the bulk lifetime is a signal of vacancy defects being present in the material. This parameter also corresponds to the center of mass of the lifetime spectrum and is insensitive to the decomposition process.

In the case of one type of the vacancy defect with a specific lifetime of $\tau_d$, the decomposition of the lifetime components is straightforward to interpret. In this simple case, the higher lifetime component $\tau_2 = \tau_d$ and the lower lifetime component $\tau_1 = (\tau_d^2 + \kappa)^{-1} \tau_d$. The separation of two lifetime components is typically possible, only if the ratio of the annihilation rates is $\lambda_1/\lambda_2 > 1.5$, where the annihilation rate $\lambda_i$ is defined as $\lambda_i = 1/\tau_i$ (Ref. 14).

III. RESULTS

We have carried out positron lifetime experiments as a function of temperature and the results for the as-irradiated and annealed samples are shown in Fig. 1.

The average positron lifetime in the samples is shown in Fig. 1(e). In the as-irradiated sample, $\tau_{\text{ave}} = 293$ ps is clearly above the bulk lifetime, proving that vacancy defects are present in the samples after the neutron irradiation. It can be noted that this is approximately 10 ps less than in the studies by Arifov and Arutyunov,\textsuperscript{18} who used a 100 times larger neutron fluence. In the annealing at 473 K, the average positron lifetime increases to 345 ps. In the sample annealed at 473 K, the average positron lifetime decreases with decreasing temperature, unlike in the unannealed sample. After annealing at 673 K, $\tau_{\text{ave}}$ has decreased to 238 ps at room temperature (RT) indicating that the defects have started to

FIG. 1. (a) The intensity of the higher lifetime component $I_2$, (b) the higher lifetime component $\tau_2$, (c) the average positron lifetime $\tau_{\text{ave}}$, and (d) the lower lifetime component $\tau_1$.
annihilate. The annealing at 773 K removes all the remaining vacancy defects from the samples.

The higher lifetime component \( \tau_2 \) is shown in Fig. 1(b) and its intensity in Fig. 1(a). Prior to the annealings, \( \tau_2 \) is \(~330\) ps with an intensity of \( \sim 68\% \). This lifetime value is similar to the calculated value for a divacancy (\( V_2 \)) of \( 316\) ps in Ge (Ref. 25) and clearly above the calculated value of \( 265 \) ps for a monovacancy,25 and the experimental values of \( 290, 292, \) and \( 278 \) ps.19–21

Annealing at \( 473 \) K increases \( \tau_2 \) to a value of \(~410\) ps at RT, while the intensity remains the same. A positron lifetime of \(~400\) ps in a semiconductor indicates a vacancy cluster of \(~10\) missing atoms in size.26–28 This indicates that the smaller irradiation-induced defects form bigger clusters during the annealing. The intensity of the higher lifetime component drops during the annealing at \( 673 \) K, suggesting that most of the cluster defects start to anneal. The temperature dependences of \( \tau_2 \) after the annealings at \( 473 \) and \( 673 \) K are similar. In both cases, the higher lifetime decreases with decreasing temperature.

The lower lifetime component \( \tau_1 \) is shown in Fig. 1(d). In the unannealed sample and the sample after \( 473 \) K, \( \tau_1 \) is larger than the bulk lifetime of \( 224 \) ps, which indicates that the two trap model used to fit to the lifetime data does not describe the data accurately enough. An explanation could be that there also exists a lifetime component, with a value in between the divacancy lifetime of \( \sim 330 \) ps and the bulk lifetime. This defect of monovacancy size would give a lifetime that in these two fits (\( 473 \) K and \( 673 \) K annealings) becomes mixed with the lifetime \( \tau_1 \). It is however, very difficult to separate this smaller lifetime component from the lifetime spectrum, since the concentration of the defects having this positron lifetime component is small compared to the concentrations of the observed clusters or the divacancies.

IV. DISCUSSION

As mentioned, the samples are of \( n \)-type with an Sb concentration of \( 1.5 \times 10^{15} \) cm\(^{-3} \), prior to irradiation and annealing. The dominant vacancy defect after irradiation is expected to be the divacancy,29 which is also supported by the \( \tau_2 \) value of \( 330 \) ps found in the as-irradiated sample. Taking into account the approximately \( 100 \) ps wider resolution of Yeh et al. compared to this study, it can also be speculated that the saturated trapping rate of \( 3.32 \times 10^9 \) s\(^{-1} \) observed in this old neutron fluence-dependence study is due to a divacancy. Neither \( \tau_{\text{ave}} \) nor the defect component \( \tau_2 \) shows any temperature dependence. This is a clear indication that the dominant positron trap after irradiation is in a neutral charge state. It has previously been established that the divacancy has an acceptor level of \( 0.29 \) eV below the conduction band.3 recent calculations have also indicated the presence of a donor state close to the valence band.11 In order for the divacancy to be neutral after irradiation, the samples thus have to be \( p \)-type or the Fermi level has to be very close to midgap.

After annealing at \( 473 \) K both \( \tau_{\text{ave}} \) and \( \tau_2 \) at RT have increased, indicating the formation of larger vacancy clusters. In order for this agglomeration of divacancies to be possible, the agglomerating divacancies have to be neutrally charged at the annealing temperature. However, as the measurement temperature decreases, both parameters \( \tau_{\text{ave}} \) and \( \tau_2 \) also decrease, indicating that two competing positron traps are present in the samples and that the smaller one is negatively charged. It can be estimated that the lifetime component of the defect with a smaller open volume is \( 280–320 \) ps, i.e., most likely a negatively charged divacancy. Hence, we conclude that as the crystal recovers from the irradiation and neutral divacancies agglomerate into larger clusters, the samples gradually become more \( n \)-type and at least part of the divacancies change charge state into a more negative one. At the annealing temperature of \( 473 \) K, the thermal movement of the Fermi level towards midgap works against the movement upwards, due to the recovery of the crystal. Calculations by Janke et al.12 indicate that the negatively charged divacancy is more stable than the neutral one, i.e., a possible explanation for the presence of the negative divacancies after the \( 473 \) anneal is that, as the divacancies change charge state into a more negative one, they also become immobile and no longer contribute to the vacancy cluster formation.

As the samples are annealed at \( 673 \) K, the decrease in the average lifetime at RT shows that the vacancy clusters have started to anneal. The thermal budget has, however, not been enough to dissociate all clusters, indicated by high value of \( \tau_2 \) at RT. Interestingly there is still negatively charged smaller vacancy defects of divacancy size left in these samples, even though the annealing temperature is higher than the reported annealing temperature for divacancies.30 Even though these defects seem more stable than divacancies, they are still most likely divacancies formed during the cooling of the crystal from dissociated vacancy clusters. These divacancies are negatively charged, indicated by the increase in \( \tau_{\text{ave}} \) with decreasing temperature. The increase in \( \tau_{\text{ave}} \) is due to the fact that the smaller negative positron traps of divacancy size trap positrons better at low temperatures compared to neutral vacancy clusters. This effect can also be seen in the intensity \( I_2 \) after the annealing at \( 673 \) K, where the intensity increases from \(~10\% \) at RT to approximately \( 45\% \) at \( 40 \) K. Similar behavior in the defect component intensity [(Fig. 1(a))] is not seen in the sample annealed at \( 473 \) K, since the intensity from the vacancy clusters is too high to make the weaker divacancy signal observable in the intensity. However, as mentioned above the influence of the divacancies is observed in the defect component \( \tau_2 \) and in the average positron lifetime \( \tau_{\text{ave}} \).

It should be noted that a small fraction of the signal from the negatively charged defects of divacancy size in the annealed samples could be coming from \( V_2 \)-Sb complexes. The concentration of these complexes cannot be higher than the Sb concentration of \( 1.5 \times 10^{15} \) cm\(^{-3} \), which is very close to the detection limit of PAS for point defects in semiconductors.31 Thus, the \( V_2 \)-Sb complexes can only explain a small fraction of the \( 60 \) ps increase in \( \tau_{\text{ave}} \) with decreasing measurement temperature in the sample annealed at \( 673 \) K. From the results for the as-irradiated sample, where the defect concentration is of the order of \( 1 \times 10^{17} \) cm\(^{-3} \), it is however clear that the neutral divacancy is not mobile at RT.
V. CONCLUSIONS

To conclude, we have used positron annihilation spectroscopy to study the neutron-irradiation-induced vacancy defects in Ge. The irradiation was found to produce vacancy defects with a neutral charge state and a characteristic lifetime of 330 ps, which is identified as the positron lifetime of defects with a neutral charge state and a characteristic lifetime of defects in Ge. The irradiation was found to produce vacancy copy to study the neutron-irradiation-induced vacancy defect. The concentration of time of 330 ps, which is identified as the positron lifetime of defects with a neutral charge state and a characteristic lifetime of defects in Ge. The irradiation was found to produce vacancy copy to study the neutron-irradiation-induced vacancy defects.

To conclude, we have used positron annihilation spectroscopy to study the neutron-irradiation-induced vacancy defects in Ge. The irradiation was found to produce vacancy defects with a neutral charge state and a characteristic lifetime of 330 ps, which is identified as the positron lifetime of defects with a neutral charge state and a characteristic lifetime of defects in Ge. The irradiation was found to produce vacancy copy to study the neutron-irradiation-induced vacancy defects.

V. CONCLUSIONS

To conclude, we have used positron annihilation spectroscopy to study the neutron-irradiation-induced vacancy defects in Ge. The irradiation was found to produce vacancy defects with a neutral charge state and a characteristic lifetime of 330 ps, which is identified as the positron lifetime of defects with a neutral charge state and a characteristic lifetime of defects in Ge. The irradiation was found to produce vacancy copy to study the neutron-irradiation-induced vacancy defects.

To conclude, we have used positron annihilation spectroscopy to study the neutron-irradiation-induced vacancy defects in Ge. The irradiation was found to produce vacancy defects with a neutral charge state and a characteristic lifetime of 330 ps, which is identified as the positron lifetime of defects with a neutral charge state and a characteristic lifetime of defects in Ge. The irradiation was found to produce vacancy copy to study the neutron-irradiation-induced vacancy defects.

V. CONCLUSIONS

To conclude, we have used positron annihilation spectroscopy to study the neutron-irradiation-induced vacancy defects in Ge. The irradiation was found to produce vacancy defects with a neutral charge state and a characteristic lifetime of 330 ps, which is identified as the positron lifetime of defects with a neutral charge state and a characteristic lifetime of defects in Ge. The irradiation was found to produce vacancy copy to study the neutron-irradiation-induced vacancy defects.