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Stabilization of Ge-rich defect complexes originating from $E$ centers in $\text{Si}_{1-x}\text{Ge}_x: \text{P}$

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Thermal evolution of vacancy complexes was studied in P-doped ($[\text{P}]=10^{18}$ cm$^{-3}$) proton irradiated $\text{Si}_{1-x}\text{Ge}_x$ with Ge contents of 10%, 20%, and 30% in the range of 250–350 °C using positron annihilation spectroscopy. The radiation damage recovers in the course of anneals but the final state differs from that in as-grown samples indicating the presence of small Ge clusters in the samples, contrary to the initially random Ge distribution. The activation energy for the annealing process was estimated to be $1.4\pm0.3$ eV and attributed to the dissociation energy of the vacancy-impurity-germanium (V-P-Ge) complex.

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Silicon germanium ($\text{Si}_{1-x}\text{Ge}_x$) research has attracted significant attention in the past few years primarily thanks to the wide use of the unique properties of the material in electronics. For example, using $\text{Si}_{1-x}\text{Ge}_x$ was found to be essential in the realization of the 32 nm transistor scaling node¹ utilizing strain and heterojunction engineering provided by $\text{Si}_{1-x}\text{Ge}_x$.² Understanding formation mechanisms and properties of point defects in novel semiconductor materials in general and in $\text{Si}_{1-x}\text{Ge}_x$, in particular, is interesting from a fundamental point of view and crucial for device performance optimization. It is well known that point defects in semiconductors can be generated during device synthesis-processing steps including ion implantation. Interestingly, ion implantation and/or irradiation may also be used as a tool to form specific point defects in specific amounts in order to discriminate the properties. In part as the result of such irradiation-induced defect studies it is now known that vacancy complexes as well as vacancy-impurity complexes (in the case of high enough impurity content in the material) are fundamental point defects in Si-based materials and a long-going effort has been devoted to studying dominant configurations and corresponding electronic signatures.

Out of many different point defect types in semiconductors, the $E$ center in Si is among the most studied. It consists of a vacancy and a group V donor impurity (As, P, or Sb). It has been shown that the $E$ center affects not only the electrical properties but also the migration of impurities (dopants) in Si.³ In pure Si, the $E$ center has two energy levels, an acceptor level at $E_A=0.45$ eV (Ref. 4) and a donor level at $E_D=0.27$ eV, where $E_C$ and $E_V$ are the conduction and valence bands of the material, respectively.³ In the case of pure Ge, two acceptorlike energy levels have been associated with $E$ centers.⁴ The recent interest in $\text{Si}_{1-x}\text{Ge}_x$ has led to a number of studies on the $E$ center also in this material.⁷–¹² While these studies have largely contributed to the understanding of $E$ centers in $\text{Si}_{1-x}\text{Ge}_x$ much is still unknown. For instance, annealing energetics and diffusion of the $E$ center are under debate.¹³–²¹ In particular, experimental documentation is insufficient and largely based on high-temperature dopant redistribution measurements, taking inevitable risks of modifying the delicate $\text{Si}_{1-x}\text{Ge}_x$ matrix itself. Moreover, providing a reliable experimental estimate for $E$ center stability in $\text{Si}_{1-x}\text{Ge}_x$ would make it possible to compare with recently published theoretical data, allowing for the calibration of the models.

The essence of our present work comes from measuring $E$ center annealing in relaxed P-doped and proton irradiated $\text{Si}_{1-x}\text{Ge}_x$ using positron annihilation spectroscopy. A consistent model describing experimental data in terms of different order V-P-Ge$_n$ complexes, where $n=1−3$, is suggested. The annealing behavior of the defects is analyzed by using Arrhenius relations to extract and interpret the corresponding activation energies.

As core electrons predominantly have a wider momentum distribution than valence electrons, the $W$ parameter is sensitive to the identity of the atoms surrounding the vacancy. In order to study the electron-momentum distribution more accurately, we also performed coincidence Doppler broadening measurements using two Ge detectors. With this technique, the peak-to-background ratio can be improved to roughly 10⁶.

We studied relaxed epitaxial $\text{Si}_{1-x}\text{Ge}_x$ layers ($x = 0.1, 0.2, 0.3$) in situ doped with $10^{18}$ P/cm$^3$ and grown by chemical vapor deposition on Czochralski-grown Si(100) substrates as in Ref. 12. The samples were irradiated with 2 MeV protons, creating a homogenous defect distribution within the $\text{Si}_{1-x}\text{Ge}_x$ layer so that the characteristic positron annihilation spectroscopy parameters were constant throughout the layer. The proton flux ($1.6 \times 10^{15}$ cm$^{-2}$) used in the irradiation was high enough to produce saturated positron trapping, i.e., a defect concentration $\approx 10^{18}$ cm$^{-3}$ (Ref. 12) and the defects were identified as V-P pairs ($E$ centers).¹⁰ Further, the samples were isothermally annealed in vacuum at five different temperatures ranging from 250 to 350 °C. The total annealing times were 287 h at 250 °C, 76 h at
Annealed samples, emphasizing the increasing role of excess annealing temperature so that the positron parameters appear to be similar in all samples regardless of the annealing time for samples annealed at 250 and 325 °C. Defect parameter \( W \) decreases to a constant level after an initial decrease. The decrease in the \( W \) parameter region increases considerably already at 150 °C before the irradiation.

Figure 1 shows the measured parameters as a function of annealing time for samples annealed at 250 and 325 °C. Defect annealing trends characterized by the evolution of the positron parameters appear to be similar in all samples regardless of the annealing temperature so that the \( S \) parameter stabilizes to a constant level after an initial decrease. The \( W \) parameter (not shown) behaves otherwise symmetrically but the initial increase in it happens faster than the decrease in \( S \), indicating an increase in the Ge content around the V-P pairs. The decrease in the \( S \) parameter, on the other hand, indicates that the samples are recovering during the annealing and the amount of open volume defects decreases. However, the final values of \( S \) in Fig. 1 (and also those of \( W \), see Fig. 3) reached after long anneals clearly differ from the values in as-grown Si\(_{1-x}\)Ge\(_x\) films, meaning that these anneals do not fully recover the lattice to the state observed before the irradiation (note, in pure Si the \( E \) center anneals already at 150 °C).

The coincidence Doppler broadening results of irradiated samples before and after annealing at 300 °C are shown in Fig. 2. The results are normalized to the values from p-type silicon where no positron trapping into defects occurs. Positron trapping into irradiation-induced vacancy defects is indicated by the increased intensity in the low-momentum region (<0.4 a.u.) compared to the untreated sample. The intensity at high momenta \( W \) parameter region) is also higher than that in the Si reference, indicating the presence of Ge atoms around the annihilation sites. The average number of Ge atoms around the vacancies in the as-irradiated samples depends on the Ge content of the sample and follows the expected statistics. After annealing, the intensity in the high-momentum region increases considerably (see \( W \) parameter region in Fig. 2), showing that the amount of Ge around the annihilation sites is increasing during the annealing series.

Figure 3 summarizes the \( S, W \) parameters in the longest annealed samples, emphasizing the increasing role of excess annealing at 300 °C, 46 h at 300 °C, and 4 h at both 250 and 350 °C. The annealing procedure was identical for all samples regardless of the Ge concentration. \( S \) and \( W \) parameters were measured between annealing in each sample and the obtained values were normalized to the respective values of as-grown Si\(_{1-x}\)Ge\(_x\) samples (e.g., the data from irradiated and annealed Si\(_{0.9}\)Ge\(_{0.1}\) are scaled to untreated Si\(_{0.9}\)Ge\(_{0.1}\) and so on). All measurements were performed at room temperature.

Figure 1 shows the measured parameters as a function of annealing time in samples annealed at 250 °C and 325 °C. The changes in annealing temperature are shown in the symbol size: decreasing symbol size indicates increasing annealing temperature. As seen from Fig. 3, the later stages of annealing have relatively little effect on the obtained line-shape parameter values as long as an equilibrium state is reached (i.e., several subsequent annealing had no significant effect on the parameters—compare with Fig. 1). The values obtained from Si\(_{0.7}\)Ge\(_{0.3}\) and Si\(_{0.8}\)Ge\(_{0.2}\) layers seem to fall on the lines drawn between the as-irradiated and untreated states, with the parameters moving toward the untreated state. Data points from Si\(_{0.8}\)Ge\(_{0.2}\), however, are clearly above the line, suggesting that the Ge decoration of annihilation sites is higher than the “random” Ge content would imply after annealing.

By combining the arguments above with the following two facts evident from the high-momentum region in Fig. 2—(i) the annihilation properties of \( E \) centers in as-irradiated samples follow the average Si/Ge contents of the surrounding matrix so that the \( W \) parameter trend may be explained with only one Ge atom involved and (ii) the enhancement in the \( W \) parameter observed after annealing no longer fol-
ows the average Si/Ge content trends but instead exhibits only minor differences between the samples compared to those seen between as-grown samples in Fig. 7 of Ref. 10—we conclude that regardless of Ge content, high-order V-P-Ge₂ complexes with n ≥ 2 are formed during annealing as long as the Ge content is high enough. The threshold for the formation of these complexes seems to be between 4% and 10% Ge since Sihoto et al. did not observe them in their work but we confirm the appearance of such complexes in our samples. These V-P-Geₙ complexes eventually disappear during the course of the anneals, leaving behind Ge-rich clusters in the samples, thus explaining the differences between the final annihilation states seen in Figs. 1 and 3. Further support for this interpretation comes from the fact that temperature-dependent measurements performed on the same annealed samples in midst of the annealing treatment revealed a charge transition of the defect from a singly to a doubly negative state at around 150 K, an effect not observed for E centers decorated with only a single Ge atom whereas the annealing times and temperatures are too high for these types of defects to survive until the end of the treatment.

The annealing kinetics of the defects were determined using a first-order diffusion model. The vacancy concentration in the lattice can be estimated from the annihilation parameters if the defect type in which the annihilations occur is known. The positron trapping rate into a defect is given by κ_D = κ₀ exp(−λr)b(S−S₀)/(S₀−S), where λ⁻¹ = τ_b is the positron lifetime in the defect-free lattice—and τ_b = 220 ps was adapted in the calculations—and S is the measured parameter while S₀ and Sₐ correspond to annihilations in the bulk and the defect, respectively. The defect concentration is related to the annihilation rate via c_D = κ_D µ_D, where µ_D is the trapping coefficient of the defect with a typical value of around 10₁⁵ s⁻¹ (10¹³ s⁻¹ adapted for calculations) for negatively charged vacancies in Si.

By combining the expressions for κ_D and c_D with the Arrhenius-type behavior of the defect concentration, c₀ exp(−EA/kbT) + K, where λ = λ₀ exp(−E_a/k_bT) and K is a factor taking into account the irreversible changes in the lattice compared to the initial state, the activation energies of the process can be obtained. The factor describing the irreversible changes to the lattice, K, was fitted to the data along with λ and the initial concentration of the annealing defects c₀. These fits are shown in Fig. 1 for samples annealed in 250 and 325 °C. The activation energies were obtained by making Arrhenius plots of λ versus annealing temperature. These plots are found in Fig. 4, resulting in activation energies E_a of 1.5(2) eV for Si₀.₉Ge₀.₁, 1.3(2) eV for Si₀.₃₇Ge₀.₆₃, and 1.3(2) eV for Si₀.₇Ge₀.₃. These activation energies are attributed to the dissociation of the vacancy-impurity complexes.

The difference in dissociation energies between samples with different Ge contents is reflected in the behavior seen in the (S, W) plot of Fig. 3. The V-P-Geₙ complexes have a larger dissociation energy in Si₀.₉Ge₀.₁ because the surrounding lattice differs more from the immediate vicinity of the defect than in Si₀.₃₇Ge₀.₆₃ and Si₀.₇Ge₀.₃ which have more Ge in the host lattice. Chronoes et al. calculated the binding energy of the V-P pair in Si₀.₇₅Ge₀.₂₅ to be 1.0(2) eV. This value is in agreement with our results since the calculated binding energy is the difference between the vacancy and the impurity states in the energy scale and does not take into account the potential barrier which is included in the measured dissociation energy, as shown in the inset of Fig. 4. An interesting remark regarding the stability of the V-P-Geₙ complexes in the samples studied in this work compared to the defects observed in strained samples with 4–7% Ge studied in Ref. is that the annealing temperatures needed to cause changes after irradiation were considerably higher. In the strained samples with low Ge content, a few hours of annealing at 150 °C was enough for changes to occur whereas a similar treatment at 250 °C was needed for the relaxed samples measured in this work.

In summary, we have studied the evolution of E centers during isothermal annealing in relaxed Si₁₋ₓGeₓ layers (x=0.1,0.2,0.3) in situ doped with 10¹⁸ P/cm². The annealing was performed at five temperatures ranging from 250 to 350 °C. The experimental data are described in terms of different order V-P-Geₙ complexes, where n=1–3. In each case, the sample recovered during the anneal but the end state after a lengthy annealing period clearly differed from the state measured from samples before irradiation. This behavior is attributed to the initially random Ge distribution turning into one containing small Ge clusters which can be seen with positrons during the course of the anneal. We fitted a first-order reaction model to the data and obtained an activation energy of 1.4 ± 0.3 eV for the process. This activation energy is attributed to the dissociation energy of the V-P-Geₙ complexes and is in agreement with theoretical predictions. Judging from the higher annealing temperature required for changes to occur after irradiation (250 vs 150 °C), the defect complexes observed in the relaxed samples with 10–30% Ge are considerably more stable than those observed in strained samples with 4–7% Ge.

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24. The 3d electrons of Ge enhance the annihilation signal in the W parameter range compared to the 2p electrons of Si.