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Evidence of a second acceptor state of the *E* center in $Si_{1-x}Ge_x$

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We have found evidence of a second acceptor state of the *E* center in $Si_{1-x}Ge_x$ by using positron annihilation spectroscopy. To achieve this, we studied proton irradiated *n*-type $Si_{1-x}Ge_x$ with a Ge content of 10%–30% and a P dopant concentration of 10^{18} cm^{-3}, in which the number of Ge atoms around irradiation induced *E* centers was increased by annealing. When measuring the Doppler broadening of the annihilation line, the shape parameter *S* starts to decreases at 150 K with decreasing measurement temperature. This indicates that a charge transition in the upper half of the $Si_{1-x}Ge_x$ band gap, above the well known $(0/-)$ level, takes place. Hence, we suggest that the increased concentration of germanium around the *E* center pulls down the localized second acceptor state into the $Si_{1-x}Ge_x$ band gap, making the Ge decorated *E* center a more effective trap for conduction electrons.

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Silicon germanium ($Si_{1-x}Ge_x$) has recently received a lot of attention thanks to its promising properties in semiconductor technology. In high performance transistors, strained silicon germanium layers are used to increase electron and hole mobilities.[1–3] In addition, the complete solubility of silicon and germanium offers possibilities for band gap engineering between the values of pure Si and pure Ge. A further advantage is that $Si_{1-x}Ge_x$ is relatively easy to incorporate into existing Si manufacture processes, thanks to the similar structural and chemical properties of Si and Ge.[3]

The electrical properties of semiconductor materials are greatly influenced by the existence of point defects. These defects can form during growth and processing of the material, but they can also be introduced in a controlled way by irradiation. The removal of point defects can be done by annealing the material at high temperatures, where the defects are mobile. Vacancies and vacancy defect complexes are common point defects in semiconductors. They introduce new energy levels into the forbidden band gap, which can trap charge carriers and, thus, act as compensating centers in semiconductor materials.

The *E* center is probably the most studied point defect in semiconductors. It consists of a vacancy and a group V donor impurity (e.g., the *V*-P defect in P-doped Si). In Si, the *E* center is known to affect not only the electrical properties of the material, but also the migration of impurities and dopants.[4] It is a well known fact that the *E* center in Si has an acceptor level at approximately $E_C-0.45$ eV,[5–7] and recently, also a donor level has been found.[8] In Ge, two acceptor levels have been reported.[9]

Due to the increased interest in using $Si_{1-x}Ge_x$ in semiconductor technology, the *E* center has also become the focus of numerous studies in $Si_{1-x}Ge_x$.[10–12,16,17] However, the properties and formation mechanisms of this electrically active defect complex are still not fully understood. Monakhov *et al.* have performed deep level transient spectroscopy studies in *n*-type strained proton irradiated $Si_{1-x}Ge_x$ and report on defect characteristic electronic levels.[10,11] These studies identify the dominating defect in irradiated $Si_{1-x}Ge_x$ as the vacancy phosphorus complex (*V*-P). Kringhøj *et al.* have shown that the distance of the *E* center acceptor level to the conduction band edge is independent of the Ge content in relaxed $Si_{1-x}Ge_x$.[12]

In our earlier studies, positron annihilation spectroscopy has been used to verify that the dominating defect also in relaxed proton irradiated P-doped $Si_{1-x}Ge_x$ layers is the *V*-P pair. It was also shown that the formation of the irradiation induced *E* center does not have any preference for Si or Ge atoms, i.e., the number of Ge atoms around the defect is the same as in the host lattice.[16] Annealing strained $Si_{1-x}Ge_x$ layers results in an increased number of Ge atoms around the *V*-P pair and that the subsequently formed *V*-P-Ge defect complex is by 0.1–0.2 eV more stable than the simple *V*-P pair.[17] Positron annihilation spectroscopy has also previously been used to study charge transitions of vacancy defects in semiconductors, e.g., Refs. 13–15. With this technique, the charge transition is observed as a lattice relaxation induced by the charge transition.

In this Brief Report, the effect of the increase in the number of Ge atoms around the *E* center in relaxed P-doped and proton irradiated $Si_{1-x}Ge_x$ is studied. Using the positron Doppler broadening technique, a charge transition of the *E* center is observed in the upper half of the band gap, above the well known $(0/-)$ acceptor level. We suggest that this transition corresponds to a second acceptor state $(-/--)$ of the *E* center and that the increase in the number of Ge atoms around the *E* center pulls down this localized second acceptor state from the conduction band into the $Si_{1-x}Ge_x$ band gap.

We carried out the positron annihilation measurements using a variable energy (0.5–38 keV) slow positron beam with two Ge detectors, with a single detector resolution of 1.3 keV at 511 keV.[18] The sample temperature during the measurement was controlled by a closed cycle He cryostat and with resistive heating. In the single detector measurements, conventional *S* and *W* parameters were used to describe the shape of the Doppler-broadened annihilation line.[18] The low momentum parameter *S* is the fraction of counts in the central part of the line and, thus, it describes mainly annihilation with low momentum valence electrons. Correspondingly, *W* is the high momentum parameter obtained as the fraction of counts in the wing region of the

TABLE I. S and W parameter values at room temperature in the $Si_{1-x}Ge_x$ samples. The x in S_x and W_x refers to the Ge content of the sample.

Parameter	Reference	Annealed at 250 °C	Annealed at 300 °C
S_{10}	0.5264	0.5399	0.5420
S_{20}	0.5242	0.5363	0.5338
S_{30}	0.5257	0.5367	0.5342
W_{10}	0.00793	0.00827	0.00807
W_{20}	0.00920	0.00840	0.00887
W_{30}	0.00957	0.00883	0.00892

annihilation line and it thus describes annihilation mainly with core electrons. The intensity of the background can be reduced by using a coincidence setup, where both annihilation photons are detected. This improves the peak to background ratio up to $\sim 10^6$ and allows the accurate measurement of the momentum distribution of annihilating electrons at high momentum values.[19]

We measured relaxed $Si_{1-x}Ge_x$ samples grown on Czochralski Si (100) substrates as in Ref. 16. A buffer layer with an increasing Ge content was grown on top of the substrate to allow relaxation of the epitaxial layer. The Ge content in the epitaxial layer varied between 10% and 30%, and the thickness of the relaxed layer was $\gtrsim 2\ \mu m$. The samples were of n type with a P concentration of $10^{18}\ cm^{-3}$. A homogeneous defect distribution was generated by irradiating the samples with 2 MeV protons with a fluence of $1.6 \times 10^{15}\ cm^{-2}$ chosen to produce saturated positron trapping, i.e., a defect concentration $\gtrsim 10^{18}\ cm^{-3}$. Also, the range of the protons was high enough to ensure that end-of-range defects remain beyond the the maximum positron implantation depth of $\lesssim 3\ \mu m$ in this experiment. The effect of the irradiation has been shown in Ref. 16.

The samples were annealed isothermally at 250 and 300 °C for 114 and 7 h, respectively. The Doppler parameters S and W were measured between annealings in all samples. The behavior of the Doppler parameters was similar in all the measured samples and at both annealing temperatures. The S parameter decreases as a function of annealing time, whereas the W parameter remains approximately constant after an initial increase. This indicates that the number of annihilations with high momentum electrons increases in the annealings. This behavior is consistent with the previous results from strained $Si_{1-x}Ge_x$,[17] and reveals that the number of Ge atoms around the vacancies increases during the annealing. The continuing decrease in the S parameter suggests that some defect recovery takes place during the annealing.

The Doppler parameter values in the unirradiated reference samples and after the annealings are shown in Table I. The parameter values are not directly comparable to the parameter values in Ref. 16 due to the different measurement apparatus with slightly different resolution and energy windows used to determine the S and W parameters.

Positron trapping into charged vacancy-type defects depends on temperature if the concentration of defects is below the saturation trapping level. Therefore, the Doppler parameters S and W were measured as a function of temperature to check whether the concentration of defects has decreased below the saturation level as a result of annealings at 250 and 300 °C. Figure 1 shows the S parameter as a function of measurement temperature. The parameters are shown without scaling to bulk values, as there is no clear reference to compare the samples with different Ge content and because only the changes in the S parameter are of interest.

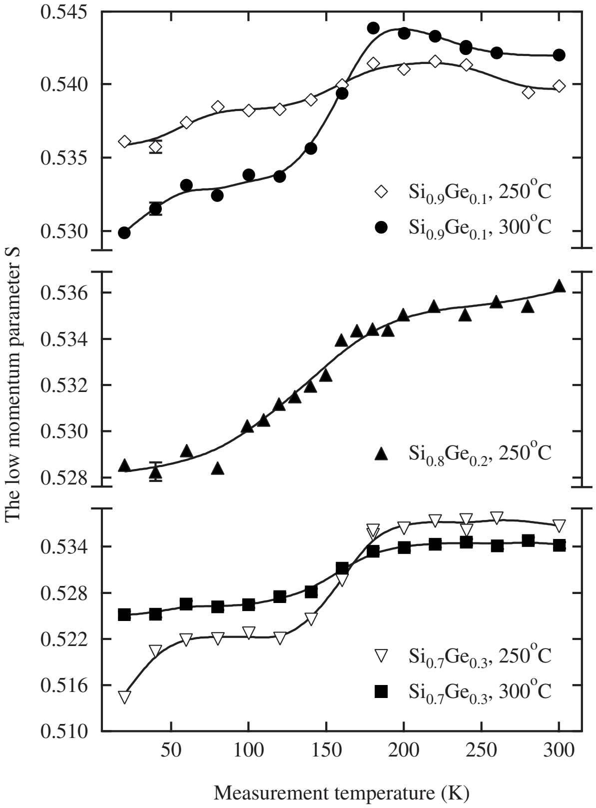

FIG. 1. The low momentum parameter S as a function of measurement temperature. The error bars in the $Si_{0.7}Ge_{0.3}$ samples are of the same size as the markers. The solid curves have been drawn to guide the eye.

The S parameters in the as-grown samples as well as in the samples before the annealings do not show any temperature dependence with decreasing temperature.[16] After the annealings, however, the S parameter increases slightly with decreasing temperature down to 180 K in the $Si_{0.9}Ge_{0.1}$ samples annealed at 250 and 300 °C. This reveals that the positron trapping in these samples is no longer in saturation (i.e., some of the defects have recovered) and that the remaining defects are in a negative charge state. Another notable feature in all the measured samples is that the S parameter decreases approximately at the temperature of 150 K. This suggests that the open volume at the defects decreases. The W parameter, which is sensitive to core electrons, remains constant, indicating that the chemical surroundings of the annihilating positron do not change.

In order to investigate the cause of the observed decrease in the S parameter around 150 K, we performed coincidence Doppler broadening measurements both at room temperature and at 100 K in the irradiated $Si_{0.8}Ge_{0.2}$ sample annealed at 250 °C. The result is shown in Fig. 2, with the data from the

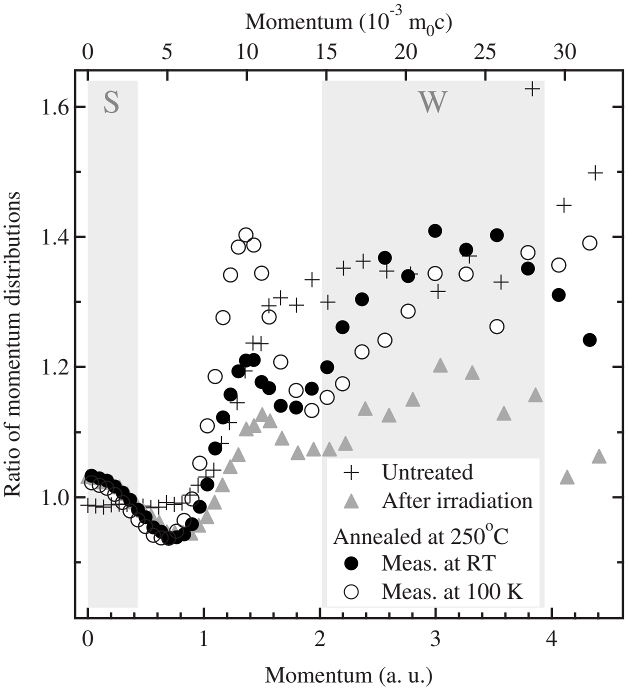

FIG. 2. Coincidence Doppler spectra of the $Si_{0.8}Ge_{0.2}$ layers. The data have been scaled to a Si reference sample, where no positron trapping is observed. The data from both the untreated sample and the sample after irradiation have been measured at room temperature.

untreated and irradiated samples measured at room temperature. The data have been scaled to a *p*-type Si reference, where no positron trapping into defects is observed. The coincidence Doppler spectrum from the as-grown layer is close to the values obtained in Si at low momenta. This is due to the similarity of the valence electrons in Si and Ge. At higher momenta ($p > 1$ a.u.), the 3*d* electrons of Ge increase the intensity above that measured in Si.

In the irradiated samples, the positrons annihilate trapped into irradiation induced vacancies, which increases the intensity of the momentum distribution at low momentum values ($p < 0.4$ a.u.). The reduced intensity at high momenta is due to the reduced overlap of the positron wave function with core electrons. The peak at approximately 1.4 a.u. is caused by the fact that in a vacancy, the overlap of the positron wave function with the anisotropic electron momentum distribution in the diamond structure is reduced.[18,20]

The result after the annealing at 250 °C shows that the annealing increases the intensity of the momentum distribution at high momentum values. This is due to the increased number of Ge atoms around the *V*-P pair. The slight shifts in the position of the minimum at ∼0.85 a.u. and the peak at ∼1.4 a.u. between the untreated and irradiated sample and the annealed samples are due to the different resolutions of the measurement systems used in the present and previous studies.[16] Interestingly, the intensity of the peak observed at ∼1.4 a.u. increases considerably in the coincidence Doppler spectra measured at 100 K. This indicates that the overlap of the positron wave function with the anisotropic bulk distribution is further reduced. Thus, the positron state is narrower and the positron is more localized in the vacancy.

As the *S* parameter represents the open volume of the defect, we interpret the decrease in the *S* parameter with decreasing temperature at the temperature of 150 K as the inward relaxation of the *E* center. This is supported by the fact that the *W* parameter does not show any change in the chemical surroundings of the positron annihilation site. Hence, we infer that this relaxation and the stronger localization of the positron at low temperatures are due to the transition of the *E* center to a more negative charge state.

The charge transition (0/−) of the *E* center has been observed in deep-level transient spectroscopy studies in $Si_{1-x}Ge_x$.[10,12] However, the energy level of this transition lies close to or below the midgap at high Ge contents like the ones in this study.[21] Therefore, this transition cannot be the one we observe here, since the vacancies in the annealed samples with 10% of Ge and a P concentration of 10^{18} cm^{-3} clearly are in a negative charge state in the temperature interval of 200–300 K.

In the case of pure Si, it has been shown that the neutral *E* center relaxes inward when it captures an electron.[13] However, energy levels above the already mentioned (0/−) have not been observed in Si. Introducing Ge atoms at high concentrations can change the situation, since the energy level (−/− −) of the *E* center in Ge has been observed.[22] Thus, we conclude that the charge transition we observe corresponds to the energy level (−/− −) of the *E* center. This transition was not detected in Ref. 17, where the *V*-P defects were decorated by one Ge atom only. This indicates that the *V*-P defect needs to be decorated by several Ge atoms for the (−/− −) level to be pulled down into the $Si_{1-x}Ge_x$ band gap. This conclusion is also supported by the higher annealing temperature compared to Ref. 17, where it was shown that one neighboring Ge atom stabilizes the *E* center by 0.1–0.2 eV. The appearance of the (−/− −) level, thus, makes the *E* center decorated with several Ge atoms a more effective trap for the conduction electrons than the simple *E* center.

In summary, we used positron annihilation spectroscopy to study the effect of the increased number of Ge atoms around the *E* center in relaxed P-doped $Si_{1-x}Ge_x$, with Ge content of 10%–30%. An inward relaxation of the *E* center is observed at the temperature of 150 K when measuring Doppler broadening parameters as a function of temperature. The coincidence Doppler measurements further reveal that the positron localization into the *V*−P defect is enhanced at these temperatures. We interpret this as the charge transition (−/− −) of the *E* center enabled by the increased number of neighboring Ge atoms. The comparison to the previous results from strained $Si_{1-x}Ge_x$ layers also shows that the *E* center must be decorated by several Ge atoms for this level to be pulled down into the band gap.

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