Positron annihilation in electron-irradiated Si_xGe_{1-x} bulk crystals

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Position lifetime measurement for Si_xGe_{1-x} bulk crystals has been performed. The bulk lifetime of positron in the crystals varied between those for Ge and Si. The dependence of the lifetime on the alloy composition showed an abrupt change at $x=0.17$–0.20 which seems to be correlated with that of the band gap energy. After 3 MeV electron-irradiation, vacancy-type defects giving rise to the lifetimes of ~280 and ~330 ps were detected for $0.63 \leqslant x \leqslant 0.82$ and $0.20 \leqslant x \leqslant 0.40$, respectively, but not for $x \leqslant 0.17$. The composition-dependent vacancy production was interpreted in terms of the thermal stability of vacancies with the composition.
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Silicon-germanium (Si_xGe_{1-x}) alloy forms a complete series of solid solution.[1] By changing the alloy composition, physical parameters such as lattice constant and band gap energy can be controlled at arbitrary values between those of Si and Ge.[2–6] This property is useful for material design and the development of optoelectronic devices based on Si-Si_xGe_{1-x} strained superlattice is recently accelerated. From a fundamental view point, it is intriguing to study the effect of alloying on defect properties in atomic and electronic sense. Positron annihilation technique is a powerful tool to detect vacancy-type defects in crystalline solids. Recently, it is extensively applied to the study of defects in semiconductors.[7] The properties of vacancy-type defects in Si_xGe_{1-x} alloy have not been adequately studied so far. We therefore investigated the properties of vacancy-type defects in Si_xGe_{1-x} bulk crystals induced by electron irradiation using positron lifetime measurement.

Specimens used in this work were undoped Czochralski-grown Si_xGe_{1-x} crystals ($x=0$–0.82). As a reference specimen, commercially supplied floating zone-grown Si crystals were used. The detail of the growth condition of the Si_xGe_{1-x} crystals was reported in Ref. 8. The conduction type of the specimens was p-type and the residual carrier density was of the order of 10^{15} cm^{-3}. The dislocation density was determined to be of the order of 10^4 cm^{-2} by counting the number of etch-pit. The specimens were irradiated with 3 MeV electrons at the fluence of 1×10^{18} e^-/cm^2 at about 70 °C using a dynamitron accelerator at the Japan Atomic Energy Research Institute. The radiation effect on the Si specimen was not studied here since the specimen was not produced in the same growth procedure as the Si_xGe_{1-x} crystals. Positron source was prepared by depositing ^{22}NaCl (~0.4 MBq) onto a titanium thin film with a thickness of 3 μm. The positron source was sandwiched by two specimens and positron lifetime was measured using a conventional spectrometer at room temperature. About 2×10^6 counts were accumulated in each spectrum. The source components (136 ps: 12%, 507 ps: 0.7%) were determined from the measurement of unirradiated Si crystals. After subtracting the source and background components, lifetime spectrum was decomposed into two lifetime components (bulk and defect) using a computer program of PATFIT-88:[9]

$$L(t)=(I_1/\tau_1)\exp(-t/\tau_1)+(I_2/\tau_2)\exp(-t/\tau_2), \qquad (1)$$

where I_i ($i=1,2$) are the intensities ($I_1+I_2=1$) and τ_i are the lifetimes. If the two-state trapping model[10] is a good approximation, the above lifetimes have the following relations

$$\tau_1 = 1/(1/\tau_B+\kappa), \qquad (2)$$

$$\tau_2=\tau_D, \qquad (3)$$

where τ_B is the positron lifetime in a bulk determined from the measurement of unirradiated specimens, τ_D the positron lifetime at vacancy-type defects, and κ the positron trapping rate due to the vacancy-type defects:

$$\kappa=(I_2/I_1)(1/\tau_B-1/\tau_D). \qquad (4)$$

The trapping rate is proportional to the concentration of defects. The validity of the analysis based on the trapping model is checked by Eq. (2) since quantities of left and right hand side are determined independently.

For the unirradiated specimens, the two-component analysis was not available and hence only one lifetime component was obtained. It allows us to conclude that the lifetime is related to the positron annihilation in a bulk. The defect concentration is deduced to be under the detection limit ($<10^{14}$ cm^{-3}). Figure 1 shows the dependence of the lifetime on the Si composition x. The lifetime decreases from 235.6±0.6 ps (bulk lifetime for Ge) to 221.8±0.6 ps (bulk lifetime for Si) with the Si composition x. However, the dependence of the lifetime on the composition is not monotonic at around $x=0.17$–0.20 as shown by the solid guide lines. It is known that bulk lifetime in semiconductors changes linearly with the unit cell volume.[11] On the other hand, the lattice constant of Si_xGe_{1-x} alloy is reported to obey approximately to Vegard's law.[2,3] The broken line in the figure is the bulk lifetime expected from Vegard's law. The line is nearly linear due to the small difference of lattice constants of Si (5.43 Å) and Ge (5.66 Å). The nonmonotonic change of the lifetime at around $x=0.17$–0.20 could not be

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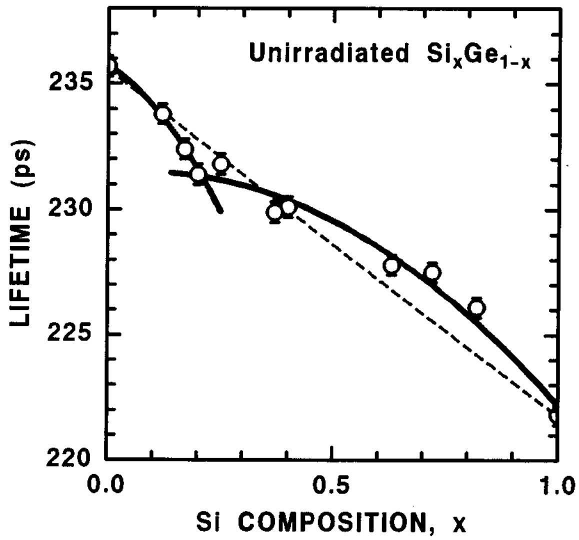

FIG. 1. Positron lifetime observed for unirradiated Si_xGe_{1-x} crystals as a function of the Si composition x. The broken line shows the bulk lifetime expected from Vegard's law. The solid lines are the guides for eye.

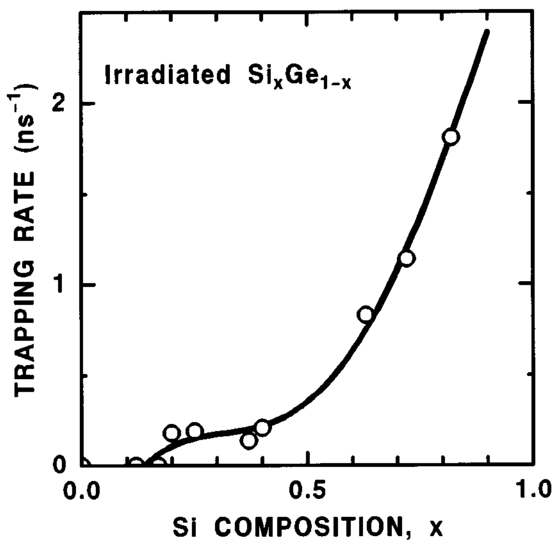

FIG. 3. Positron trapping rate due to the vacancy-type defects represented by the lifetime τ_2 in Fig. 2 as a function of the Si composition x.

explained by Vegard's law. One may think that the nonmonotonic change reflects some ordered structures of Si_xGe_{1-x} alloy. However, the atomic configuration of Si_xGe_{1-x} bulk alloy is reported to be completely random and to have no ordered structures unlike to the case of

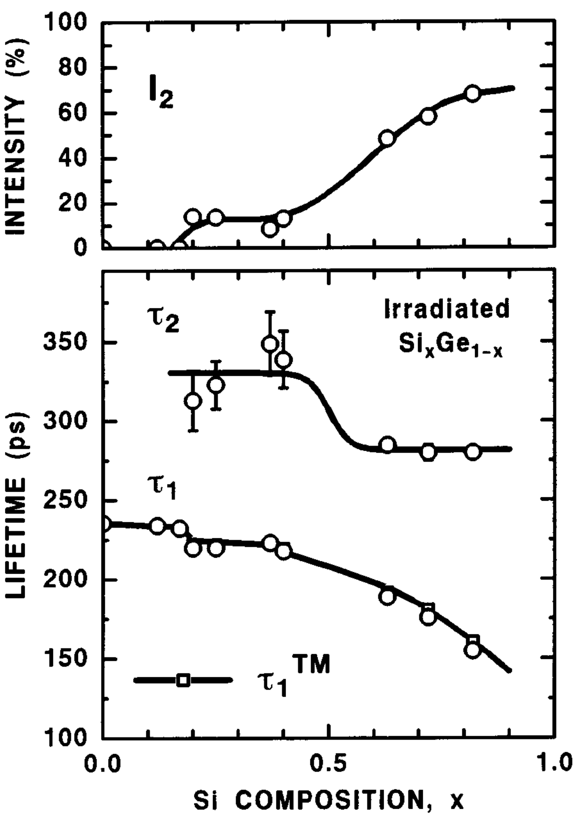

FIG. 2. Positron lifetimes (τ_1 and τ_2) and intensity (I_2) observed for electron-irradiated Si_xGe_{1-x} crystals as a function of the Si composition x. The lifetime τ_1™ denotes the τ_1 value expected from the trapping model.

Si/Si_xGe_{1-x} strained superlattice.[12,13] Here, it is interesting to note that the nonmonotonic change of the lifetime is similar to that of the band gap of Si_xGe_{1-x} alloy at $x=0.15–0.25$ due to the switch of conduction band minima from the Ge-like L points to the Si-like X points.[2,4–6] Possibly, the nonmonotonic change is explained as the change in positron annihilation characteristics caused by the change in the band structure of Si_xGe_{1-x} alloy: The positron annihilation rate with valence electrons is basically determined by the valence electron density felt by positrons. The annihilation rate is enhanced by the correlation effect that positrons tend to gather electrons around themselves. According to Bandt and Reinheimer,[14] the enhancement factor in semiconductors is a function of dielectric constant. This means that electrons respond to positrons through the dielectric polarization. On the other hand, the dielectric constant of semiconductors correlates with the band gap. Accordingly, the bulk lifetime of Si_xGe_{1-x} alloy is expected to show a nonmonotonic change at which the band gap of the alloy change discontinuously.

Figure 2 shows the positron lifetimes (τ_1 and τ_2) and the intensity (I_2) obtained for the irradiated specimens as a function of the Si composition x. It is found that the lifetime τ_1 agrees well with that expected from the two-state trapping model. This assures that the first and second components are related to the positron annihilations at bulk and vacancy-type defects, respectively. Figure 3 shows the positron trapping rate due to the vacancy-type defects calculated from Eq. (4) with the lifetime and intensity shown in Fig. 2. As seen from Figs. 2 and 3:

(i) no second lifetime component due to vacancy-type defects is observed for $x \leqslant 0.17$,
(ii) the lifetime $\tau_2 \sim 330$ ps related to vacancy-type defects is observed for $0.20 \leqslant x \leqslant 0.40$ and the trapping rate has a plateau up to $x=0.40$, and
(iii) the lifetime τ_2 decreases to 280 ps and the trapping rate increases for $x \geqslant 0.63$.

Monovacancies in Ge are reported to annihilate far below room temperature.[15] From the analysis of the Hall effect measurements, Hirata proposed that divacancies in Ge were unstable even at room temperature.[16] Thus, it is probable that both monovacancies and divacancies disappear in the Ge-rich region ($x \leqslant 0.17$) since the crystals have a character similar to Ge. The absence of vacancy clusters in the region is explained in terms of the disappearance of divacancies too quickly to agglomerate. Monovacancies in Si are also mobile and annihilate at sinks or form divacancies below room temperature.[17] Divacancies in Si are stable at room temperature and to form vacancy clusters such as quadrivacancies at 300–350 °C.[18,19] It is therefore expected that divacancy-like defect is a major defect species in the Si-rich region ($x \geqslant 0.63$) since the crystals have a character similar to Si. However, the observed lifetime $\tau_2 \sim 280$ ps in the region seems to be a little bit shorter than the lifetime at a divacancy in Si (290–295 ps).[20] It indicates the presence of monovacancy-like defects in addition to the divacancy-like defects. It is probable that monovacancies are trapped by residual impurities and/or by some irregular parts in the crystals to survive as positron trapping centers. The observed lifetime $\tau_2 \sim 330$ ps in the intermediate region ($0.2 \leqslant x \leqslant 0.40$) suggests the presence of vacancy clusters larger than divacancies. Probably divacancies have intermediate properties between those in Si and Ge. It is therefore expected that divacancies move or dissociate slowly to form vacancy clusters such as trivacancies and quadrivacancies.

One of the intriguing points of the above results is that vacancies start to survive at $x = 0.17–0.20$ where the conduction band minima switch from the Ge-like X points to the Si-like L points. The electronic structure of crystal correlates with the strength of crystal bonding. For instance, the band gap energy of group IV semiconductors has a tendency to increase with the strength of crystal bonding. It is therefore expected that the stability of vacancies depends on the electronic structure of crystal since the motion of a vacancy requires the bond cuttings of the neighboring atoms. It is easily known from the general trend that the stability of vacancies is higher in wide band gap semiconductors such as silicon carbide than in Si and Ge.[21] The above result just shows that the stability of vacancies in Si_xGe_{1-x} alloy depends on the electronic structure of the alloy.

In summary, we emphasize two important results of this work: One is that in unirradiated Si_xGe_{1-x} crystals the bulk lifetime of positron shows an abrupt change at around $x = 0.17–0.20$. The other is that in irradiated Si_xGe_{1-x} crystals vacancy-type defects are observed for $x \geqslant 0.20$ but not for $x \leqslant 0.17$. The former result reflects the change of positron annihilation characteristics with the composition. The latter result may be because the behavior of vacancies depends on the electronic structures of crystal itself.

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