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POSITRON ANNIHILATION STUDY OF ELECTRON-IRRADIATED SILICON-GERMANIUM BULK ALLOYS

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Abstract. As-grown and electron-irradiated Si_xGe_{1-x} bulk crystals (x=0-0.82) have been studied using positron annihilation spectroscopy. Bulk positron lifetime and Doppler parameters were found to change from the value for Ge to that for Si with increasing Si fraction x. However, the dependence was non-monotonic at around x=0.20. Theses results seem to be correlated with the abrupt change of the band gap energy of Si_xGe_{1-x}. After 3 MeV electron irradiation, vacancy-type defects giving rise to the lifetime of 280 ps and 330 ps were detected for $0.63 \leq x \leq 0.82$ and $0.20 \leq x \leq 0.40$. However, no vacancy components were observed for $x < 0.20$. The composition-dependent vacancy production was interpreted in terms of the thermal stability of vacancies with the composition. Through the annealing experiment for the $Si_{0.82}Ge_{12}$ specimen after irradiation, it was found that vacancy-clustering upon heating was suppressed and considerably shifted to high temperatures as compared with the case of Si.

Introduction

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]. It is greatly interesting to study defect properties in Si_xGe_{1-x} alloy from a fundamental view point. Positron annihilation technique is a powerful tool not only to study electronic state but also to detect vacancy-type defects in crystalline solids. It is extensively applied to the study of defects in semiconductors [7]. Despite, the properties of vacancy-type defects in Si_xGe_{1-x} alloy have not been adequately studied so far. In this work, we investigated the annihilation characteristics of positrons in Si_xGe_{1-x} bulk state and also the properties of vacancy-type defects induced by electron irradiation.

Experimental

Specimens used in this work were undoped Czochralski-grown p-type Si_xGe_{1-x} crystals (x=0~0.82). The detail of the growth condition of the crystals was reported in Ref. 8. 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℃ using a dynamitron accelerator in the Japan Atomic Energy Research Institute. Isochronal annealing up to 700 ℃ with a temperature step 25 ℃ for 20 min was carried out using an electric furnace in a dry argon ambience.

The positron source (^{22}NaCl ~0.4 MBq) was sandwiched by two specimens and positron lifetime was measured using a conventional spectrometer at room temperature. 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]:

$L(t)=(I_1/\tau_1)\exp(-t/\tau_1)+(I_2/\tau_2)\exp(-t/\tau_2)$, 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 are give by $\tau_1=1/(\tau_B^{-1}+\kappa)$, $\tau_2=\tau_D$, where τ_B is the positron lifetime in the bulk state, τ_D the positron lifetime at vacancy-type defects, and κ the positron trapping rate due to the vacancy-type defects $\kappa=(I_2/I_1)(1/\tau_B-1/\tau_2)$. The trapping rate is proportional to the concentration of defects. The validity of the analysis based on the trapping model can be checked by the difference of the lifetime τ_1 determined by the fitting procedure and that expected from the trapping model. Doppler broadening measurement of the annihilation γ-rays was also performed using conventional two-γ coincidence method with two pure Ge detectors. About 10^5 counts at peak position (511 keV) were accumulated in each spectrum. The typical signal to noise ratio was about 5×10^3. The line shape parameters (S and W) were determined.

Results and Discussion

A. Positron annihilation in the bulk state

Figure 1 shows Doppler broadening spectra obtained for Ge, $Si_{0.63}Ge_{0.37}$ and Si specimens. The energy shift ΔE=1 keV corresponds to the electron momentum p=0.54 a.u. The spectrum for Ge is broader than that for Si in the high momentum region (i.e., ΔE > 3 keV). The spectrum for $Si_{0.63}Ge_{0.37}$ shows an intermediate shape between Ge and Si. The above result suggests that core electrons of Ge have a higher contribution to the annihilation of positrons than that of Si. It is in good agreement with recent theoretical calculations [11,12]. Figure 2(a) shows the dependence of the line shape parameters (S and W) on the Si fraction x. Here, S and W parameters were

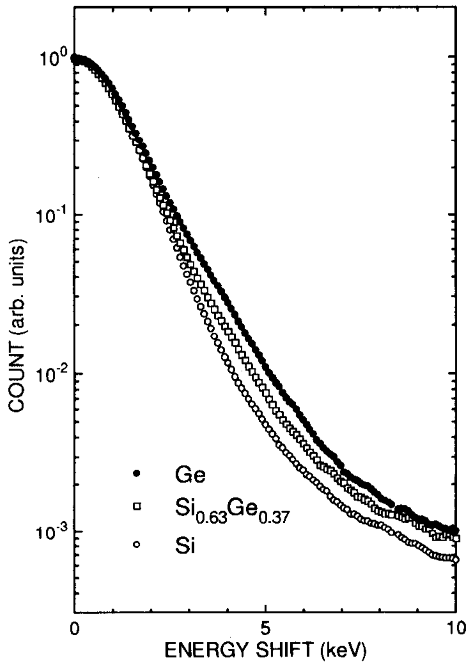

Fig.1 Doppler broadening spectra. Energy shift ΔE=1keV corresponds to electron momentum p=0.54 a.u.

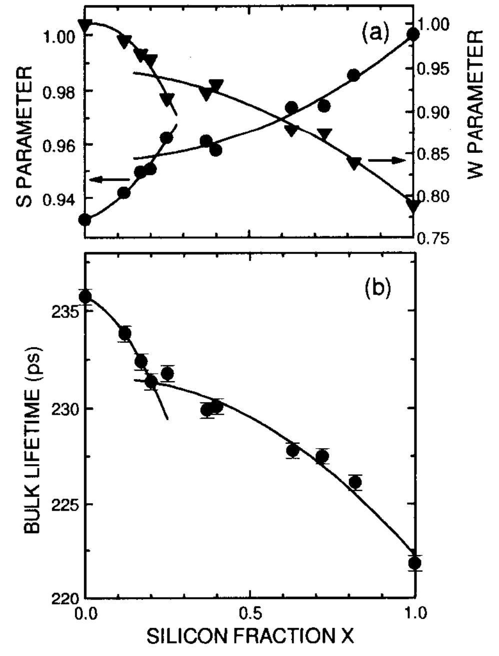

Fig. 2 (a) Doppler parameters (S&W) and
(b) bulk lifetime as a function of x.

normalized by the values of Si and Ge, respectively. These parameters vary between the values for Ge and Si depending on x. The mirror-like behaviors of S and W parameters simply show that the increase (or decrease) in the annihilation rate with core electrons correlates with the decrease (or increase) in the annihilation rate with valence electrons, or vice versa. It should be noted that the variation of the parameters with x is discontinuous at around x=0.20. This is discussed later.

For the as-grown specimens, the two-component analysis of lifetime spectra was not available and hence only one lifetime component was obtained. This shows that positrons annihilate through the delocalized state and not through the trapped state at defects. As shown in Fig. 2(b), although the bulk lifetime changes from 235.6±0.6 ps (bulk lifetime for Ge) to 221.8± 0.6 ps (bulk lifetime for Si) by changing x, the dependence is non-monotonic at around x=0.17-0.20 as well as the cases of S and W parameters.

Now we discussed about the non-monotonic change of the bulk lifetime and Doppler parameters. Since the lattice constant of Si_xGe_{1-x} bulk crystal obeys approximately to Vegard's law [2,3], it is simply expected that the bulk lifetime and Doppler parameters have monotonic dependences on the alloy composition. Therefore, the non-monotonic change of the bulk lifetime and Doppler parameters at around x=0.17~0.20 could not be explained by Vegard's law. It is also hardly expected that the non-monotonic change reflects some ordered structures as observed for Si/Si_xGe_{1-x} strained superlattice, since Si_xGe_{1-x} bulk forms a completly random system [13,14]. Here, it is interesting to note that the above non-monotonic change 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 non-monotonic change is explained as the change in positron annihilation characteristics which is related to the change in the electronic 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 [15], the enhancement factor is a function of dielectric constant. Puska shows that the enhancement factor for semiconductors may be given by $(1-1/\varepsilon)$, where ε is the dielectric constant [16]. This means that electrons respond to positrons through the dielectric polarization. The dielectric constant of semiconductors correlates with the band gap. The dielectric constant for Si_xGe_{1-x} varies depending on the alloy composition [17]. It is therefore expected that the bulk lifetime of Si_xGe_{1-x} alloy is expected to show a non-monotonic change at which the band gap changes discontinuously.

B. Vacancy production by electron irradiation

Figure 3 shows the positron lifetime spectra for the $Si_{0.82}Ge_{0.18}$ specimen before and after 3 MeV electron irradiation. An apparent increase in the lifetime is observed suggesting the introduction of vacancy-type defects due to irradiation. Figure 4 shows the positron lifetimes (τ_1 and τ_2) and the intensity (I_2) after the irradiation as a function of 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 in the bulk and vacancy-type defects, respectively. As seen from Fig. 4, (i) no second lifetime component due to vacancy-type defects is observed for $x \leq 0.17$, (ii) the lifetime τ_2~330 ps related to vacancy-type defects is observed for $0.20 \leq x \leq 0.40$ and the intensity has a plateau up to x=0.40 and (iii) the lifetime τ_2 decreases to 280 ps and the intensity increases for $x \geq 0.63$.

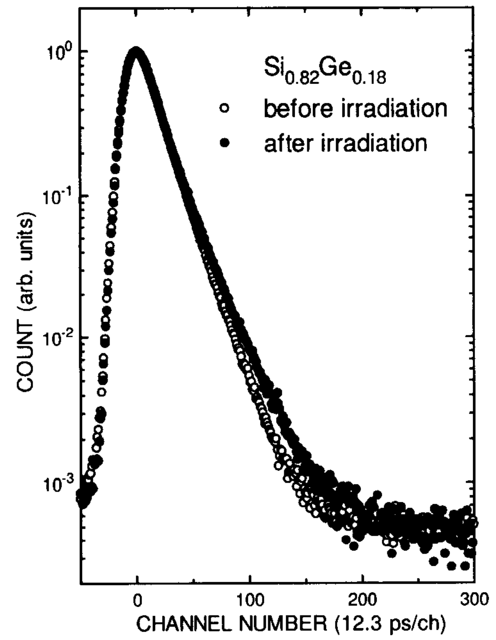

Fig.3 Positron lifetime spectra for the $Si_{0.82}Ge_{0.18}$ specimen before and after 3 MeV electron irradiation with a fluencen of 1×10^{18} e^-/cm^2.

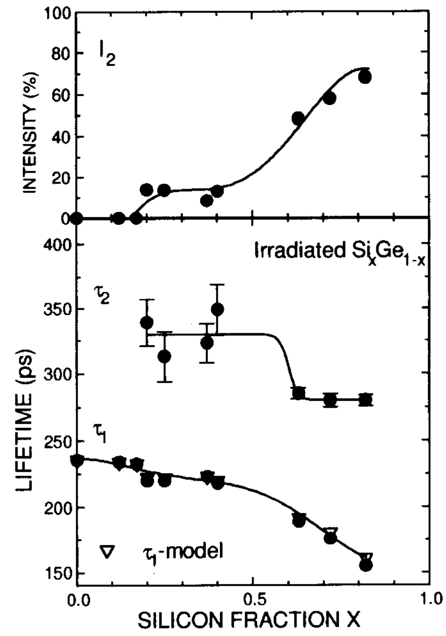

Fig.4 Positron lifetimes τ_1 and τ_2 and intensity I_2 obtained for 3 MeV electron irradiated Si_xGe_{1-x} as a function of Si fraction x.

Monovacancies in Ge are reported to disappear far below room temperature [18]. Divacancies in Ge were proposed to be unstable even at room temperature [19]. Thus, it is probable that both monovacancies and divacancies may disappear in the Ge-rich region ($x \leq 0.17$) since the crystals have a character similar to Ge. The absence of vacancy clusters in the region is explained in terms of the rapid disappearance of divacancies before agglomeration. Monovacancies in Si are also mobile and disappear at sinks or form divacancies or vacancy-impurity complexes below room temperature [20]. Divacancies in Si are stable at room temperature and to form vacancy clusters such as quadrivacancies at 300-350℃ [21, 22]. It is therefore expected that divacancy-like defects and vacancy-impurity complexes are the major defect species in the Si-rich region ($x \geq 0.63$) since the crystals have a character similar to Si. The observed lifetime τ_2~280 ps in the region seems to be an weighted average among these vacancies. The lifetime τ_2~330 ps in the intermediate region ($0.2 \leq x \leq 0.40$) suggests the presence of vacancy clusters larger than divacancies. Probably vacancies have intermediate mobilities between those in Si and Ge. It is therefore expected that divacancies move or dissociate slowly so that vacancy clusters such as trivacancies and quadrivacancies can be formed.

It is interesting to note 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. This indicates that the stability of vacancies in Si_xGe_{1-x} alloy is related to the electronic structure of the alloy. It is probably because the electronic structure of crystal correlates with the strength of crystal bonding. For instance, the increase in the band gap energy is closely related to the increase in the strength of crystal bonding in the case of group IV semiconductors. Since the motion of a vacancy requires the

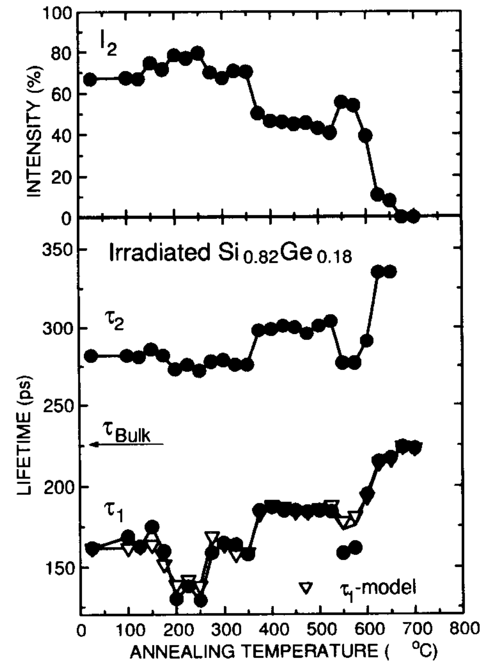

Fig. 5 Positron lifetimes (τ_1 and τ_2) and intensity I_2 for the irradiated $Si_{0.82}Ge_{0.18}$ specimen as a function of annealing temperature.

bond cuttings of the neighboring atoms, the stability of vacancies may depend on the detailed electronic structure of crystal.

C. Annealing of irradiation-induced vacancies

Figure 5 shows annealing behaviors of lifetimes and intensity for the $Si_{0.82}Ge_{0.18}$ specimen irradiated with 3 MeV electrons at a fluence of $1x10^{18}$ e^-/cm^2. The lifetime τ_1 agrees with that expected from the trapping model suggesting the second lifetime component represents vacancy-type defects. The lifetime τ_2 is about 280 ps and changes as 280 ps → 275 ps → 300 ps → 275 ps → 330 ps at 150℃, 350 ℃, 550 ℃ and 600 ℃, respectively. At these annealing temperatures, the intensity I_2 increases and then decreases, increases again and finally diminishes. At 700 ℃, intensity I_2 reaches the detection limit and the lifetime τ_1 fully recovers to the bulk lifetime.

It is known that in the case of lightly doped Si small vacancies generated by electron irradiation develops to large vacancy clusters upon heating and hence the positron lifetime has a tendency to increase at elevated temperatures [22]. Whereas in the heavily doped case vacancy-impurity interaction is a dominant process and hence positron lifetime does not increase drastically and sometimes decreases [23]. The above results seems to be similar to the case of heavily doped Si. Probably, vacancy-impurity interaction is a dominant defect reaction below 600 ℃. If we think that this specimen ($Si_{0.82}Ge_{0.18}$) is a heavily Ge-doped Si, vacancies at Si site easily interact with Ge atoms. Since the atomic radius of a Ge atom (1.23 Å) is slightly larger than that of a Si atom (1.17 Å), the dilatational strain field may be formed around Ge atom site. Thus, vacancies will be bound at Ge atom site. The lifetime of positron trapped at a vacancy-Ge complex may be shorter as compared to as isolated vacancy since the effective open volume of the complex is smaller due to the larger atomic radius of a Ge atom. In addition, excess core electrons of a Ge atom also results the shortening of the positron lifetime. Possibly, the decreases in the lifetime τ_2 at 150 ℃ and 550 ℃ may be caused by the combination of vacancy-type defects with Ge atoms. The increases in the lifetime τ_2 at 350 ℃ and 600 ℃ may be caused by the dissociation of vacancy-Ge complexes and/or vacancy-clustering. The lifetime τ_2 ~330 ps observed after the annealing at 600 ℃ is comparable to the lifetime of a positron trapped at trivacancy or quadrivacancy in Si. For instance, quadrivacancies in Si are formed due to the migration and combination of divacancies at 300~350 ℃. The above clustering temperature 600℃ is somewhat higher as compared to the case of Si. This indicates that the existence Ge atoms retards the growth of vacancy-clusters.

Summary

The results of this work are summarized as follows: The bulk positron lifetime and Doppler parameters of Si_xGe_{1-x} bulk crystal show a non-monotonic change at around x=0.17~0.20. This phenomenon is very similar to the abrupt change of the band gap width of Si_xGe_{1-x} bulk crystal. In irradiated Si_xGe_{1-x} crystals vacancy-type defects are observed for $x \geq 0.20$ but not for $x \leq 0.17$. This implies that the mobility of vacancies depends on the electronic structures of crystal itself. From the annealing behavior of the positron lifetime, it is found that vacancy-clustering is suppressed unlike to the case of lightly-doped Si. This may be due to the strong interaction between vacancies and Ge atoms.

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