Studies of divacancy in Si using positron lifetime measurement

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The charge state dependence of positron lifetime and trapping at divacancy (V_2) in Si doped with phosphorus or boron has been studied after 15 MeV electron irradiation up to a fluence of 8.0×10^{17} e/cm^2. The positron trapping cross sections for V_2^{2-}, V_2^- and V_2^0 at 300 K were about 6×10^{-14}, 3×10^{-14} and $0.1-3 \times 10^{-14}$ cm^2, respectively. For V_2^+, however, no positron trapping was observed. The marked difference in the cross sections comes from Coulomb interaction between the positron and the charged divacancy. The trapping rates for V_2^0 and V_2^{2-} have been found to increase with decreasing temperature in the temperature range of 10-300 K. These results are well interpreted by a two-stage trapping model having shallow levels with energy of 9 meV (V_2^0) and 21 meV (V_2^{2-}). The appearance of a shallow level for V_2^0 can not be explained by a conventional "Rydberg state" model. The lifetime (290-300 ps) in V_2^0 is nearly constant in the temperature range from 10 to 300 K, while that in V_2^{2-} increases from 260 ps at 10 K to 320 ps at 300 K. The lifetime (260 ps) in V_2^{2-} is shorter than that in V_2^0 at low temperature. which is due to the excess electron density in V_2^{2-}. At high temperature, however, the longer lifetime of V_2^{2-} than that of V_2^0 is attributed to lattice relaxation around V_2^{2-}.

1. Introduction

Defects in semiconductors have the features that they have electronic energy levels in the band gap and hence different charge states, and that atomic structures around defects, such as symmetry and lattice relaxation, change depending on the charge state. For example, the divacancy (V_2) in Si has three energy levels ($E_c - 0.23$, $E_c - 0.41$ and $E_v + 0.27$ eV) and four charge states (2−, −, 0, +), as shown in fig. 1 [1-3], where E_c and E_v are the energies of bottom of the conduction band and top of the valence band. The charge states of defects change with the position of the Fermi level. The trapping and annihilation of positrons at defects are likely to depend upon the charge states because of the positive charge of the positron. Hence, to study defects in semiconductors using positron annihilation, it is necessary to clarify the effects of the charge states on positron trapping into defects and annihilation at defects.

Previous work on V_2 is briefly summarized as follows. (1) The lifetime (300-325 ps) of a positron trapped in V_2 does not depend on the charge state at

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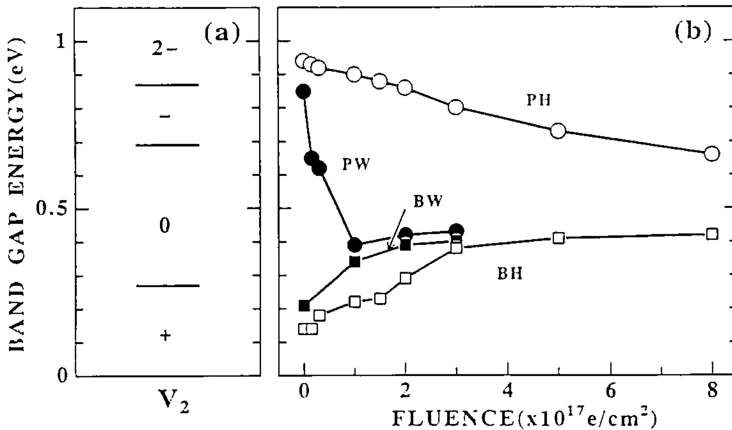

Fig. 1. Ionization energy levels of divacancy (a) and shifts in Fermi level position after irradiation (b).

room temperature [4–10]. This seems to be strange at first sight, because the lifetime is a function of the electron density at the positron. (2) Positron trapping strongly depends on the charge state of V_2 [10]. (3) The trapping cross section for negatively charged V_2 increases with decreasing temperature [4,5,9,10], while that for V_2^0 does not depend on temperature [10]. The negative temperature dependence is explained in terms of a phonon cascade model [11]: positrons are attracted to negatively charged V_2 and lose their energy by emission of multi-phonons. In this context, similar temperature dependence has been observed for a negatively charged vacancy–phosphorus (V–P) pair and a single vacancy, and explained in terms of a two-stage trapping model with a shallow level originating from a Rydberg state [15]. Thus, it is interesting to see whether this model is applicable to negatively charged V_2 or not. (4) The positron lifetime in V_2^{2-} decreases with temperature (<300 K) [4]. This has been attributed to the splitting of the divacancy [4].

Since the Fermi level is known to change by irradiation, a precise determination of Fermi levels is necessary for the study of a charged divacancy. However, previous work has shown no experimental information about them. Thus, to clarify the interactions between the positron and V_2, we studied the dependences of lifetime and cross section at V_2 on charge states and temperature with the use of sample for which Hall effect measurements were made after irradiation.

2. Experimental

The crystals used in this study were grown by the floating zone method. Defects were introduced by 15 MeV electron irradiation at room temperature. In order to obtain different charge states for V_2, n- and p-type crystals with various doping levels were irradiated up to 8.0×10^{17} e/cm^2. Sample characteristics are shown in table 1.

Table 1

Characteristics of specimens.

Sample	Dopant	Dopant concen. (cm^{-3})
PH	P	1.7×10^{16}
PW	P	7.0×10^{14}
BH	B	1.1×10^{16}
BW	B	4.0×10^{14}

A positron source ^{22}Na of 10 μCi was deposited onto mylar and aluminum thin films for measurements at room temperature and low temperature, respectively. These were then sandwiched with two samples. Positron lifetime measurement was carried out using two conventional spectrometers with time resolutions (FWHM) of 200 and 250 ps, respectively. The source components of the mylar and aluminum films were about 350 and 280 ps, with intensities of about 10 and 5%, respectively. After source and background subtraction, the spectra were decomposed into two lifetime components using the fitting program of POSITRONFIT [12].

After irradiation, the Fermi level positions were evaluated from Hall effect measurements by the van der Pauw method. Fermi level positions are shown in fig. 1, together with energy levels of V_2.

The characteristics of the samples are summarized in table 1. After electron irradiation at room temperature, most of the irradiation-induced vacancies in FZ-Si (PW, BH, BW) annihilate by mutual recombination with the interstitial atoms, and only a few exist as V_2. However, in the highly phosphorus-doped sample (PH), some vacancies can be trapped by phosphorus atoms and survive as a V–P pair. Since in the present study our concern is V_2, the V–P pair was eliminated by annealing at 170 °C so as to limit possible trapping to V_2.

3. Results and discussion

3.1. METHOD OF ANALYSIS

The lifetime spectra were well decomposed into two lifetime components (bulk and V_2). In a two-state trapping model, decomposed annihilation rates λ_i and intensities I_i are written as

$$\lambda_1 = \lambda_B + \kappa, \tag{1}$$

$$\lambda_2 = \lambda_D, \tag{2}$$

$$\kappa = (I_2/I_1)(\lambda_B - \lambda_2), \tag{3}$$

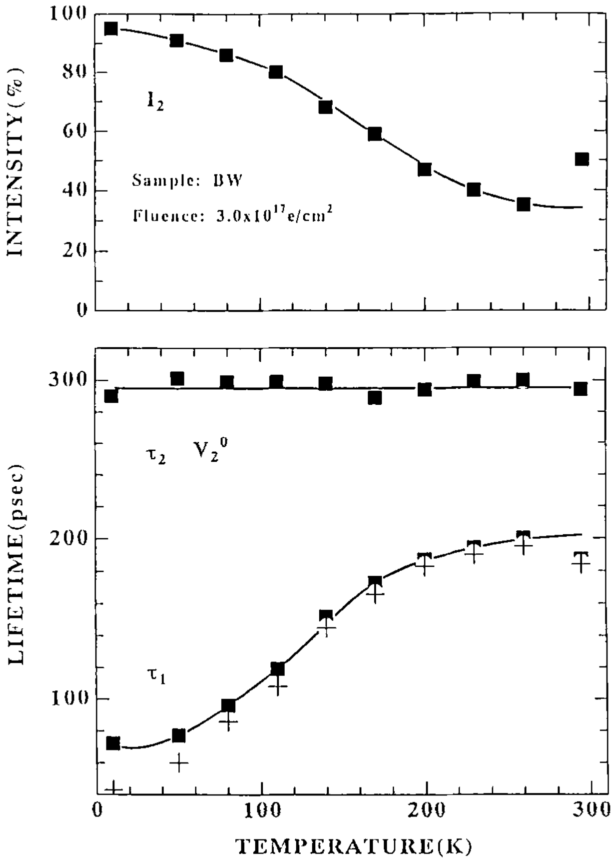

Fig. 2. Positron lifetimes τ_1 and τ_2 and intensity I_2 as functions of temperature for sample BW irradiated with 3.0×10^{17} e/cm^2. The symbol (+) denotes τ_1 calculated from eqs. (1) and (3).

where $\lambda_{1,2}$ and $I_{1,2}$ are the annihilation rates and their intensities, respectively, and λ_B and λ_D are the annihilation rates at bulk and defect state, respectively. The κ is the positron trapping rate to the defect. The inverse of λ_i is equal to the lifetime (τ_i). The bulk lifetime (221 ps) was determined for high-purity floating zone Si. To check our simplified assumption that the long lifetime component is due to positron annihilation from only one type of trap (V_2), we calculate τ_1 by eq. (1) from experimental values of λ_B and κ. The calculated τ_1 shown in figs. 2 and 3 is in good agreement with the observed one, which gives strong support to the above assumption.

The trapping rate is given by

$$\kappa = \mu C = \sigma v C, \tag{4}$$

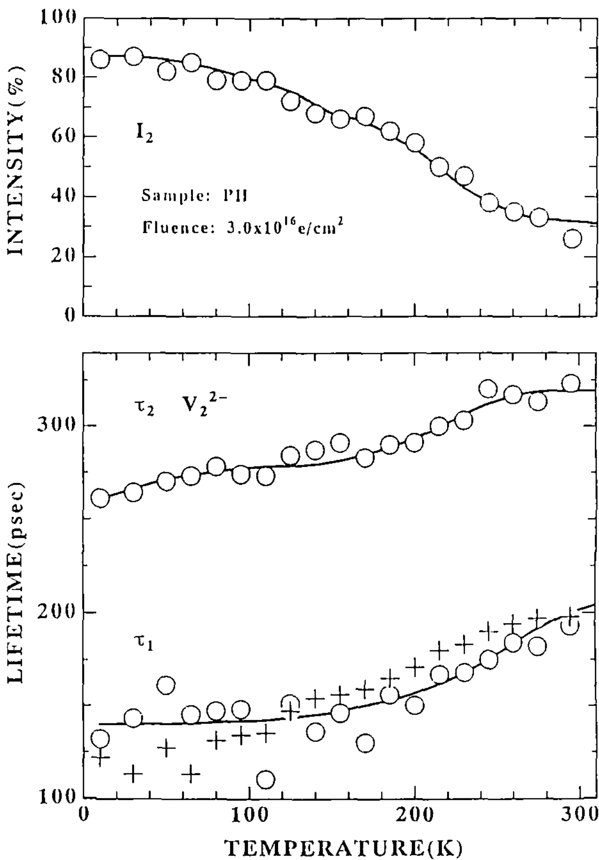

Fig. 3. Positron lifetimes τ_1 and τ_2 and intensity I_2 as functions of temperature for sample PH annealed at 170 °C for 30 min after irradiation with 3.0×10^{16} e/cm^2. The symbol (+) refers to the same as in fig. 2.

where μ is the specific trapping rate, C the concentration of defect, σ the cross section for positron trapping, and υ the thermal velocity of positrons. The value of σ was obtained from this equation.

3.2. CHARGE STATE DEPENDENCE OF POSITRON LIFETIME AND TRAPPING

Fig. 1b shows the Fermi level position (E_F) at room temperature obtained from Hall effect measurements after electron irradiation. The Fermi level position varies with the fluence, which results from the remaining irradiation-induced defects of an amphoteric nature. Details will be reported elsewhere [13]. From the obtained E_F, most of V_2 are charged as V_2^{2-} in sample PH at a low fluence range ($< 1.0 \times 10^{17}$ e/cm^2), while as V_2^- with further increasing fluence. Since this sample

contains phosphorus of density 1.7×10^{16} cm^{-3}, the V–P pair can also be formed. We observed a lifetime of 310–320 ps after annealing at 170 °C, at which temperature the V–P pair annihilated [13]. This indicates that the lifetime at negatively charged V_2 is 310–320 ps at room temperature. We decomposed the spectrum into three lifetime components (bulk, V–P pair, V_2). In this case, the analysis was made in accordance with a three-state trapping model instead of the two-state one described above. Details will be reported elsewhere [13]. We only mention that these two analyses are essentially the same.

With the use of concentrations of V_2 determined from the carrier reduction given by the Hall effect measurement, the capture cross sections for V_2^{2-} and V_2^- were obtained as being about 7×10^{-14} and 3×10^{-14} cm^2, respectively, at room temperature.

From E_F shown in fig. 1, most of V_2 are neutral in samples PW, BW and BH ($>2.0 \times 10^{17}$ e/cm^2). The decomposed lifetime (τ_2) at the defect was 290–300 ps. No other longer defect component (τ_3) was observed after annealing at 170 °C, unlike sample PH. Hence, this lifetime component comes from V_2^0. This result was also confirmed from the comparison with the infrared absorption peak associated with V_2 [13]. The trapping cross section for V_2^0 at room temperature was estimated to be about $1.0–3.0 \times 10^{-15}$ cm^2 in the same way as above.

Since the Fermi level position of sample BH is located below the level of V_2^0 ($E_v + 0.27$ eV) in the fluence range up to 1.0×10^{17} e/cm^2, as shown in fig. 1, the charge state of most of V_2 is single-positive. Contrary to the cases of V_2^{2-}, V_2^- and V_2^0, no positron trapping was observed for V_2^+: its cross section is less than 10^{-17} cm^2.

The values of the cross sections for each charge state of V_2 are listed in table 2, together with those by Mascher et al. [10]. We note that the cross sections for negatively charged V_2 are one order of magnitude larger than that for V_2^0, and

Table 2

The positron trapping cross sections for divacancy.

Charge state	Cross section[a] at RT (cm^2)	Cross section[b] at RT (cm^2)	Cross section[c] at 10 K (cm^2)
V_2^{2-}	6.9×10^{-14}	$0.7 \sim 1.4 \times 10^{-14}$	2.8×10^{-12}
V_2^-	2.7×10^{-14}	$3.5 \sim 7.0 \times 10^{-15}$	–
V_2^0	$1 \sim 3 \times 10^{-15}$	1.0×10^{-15}	$0.9 \sim 2.6 \times 10^{-13}$
V_2^+	$< 10^{-17}$	–	–

[a,c] Present work. [b] Mascher et al. [10].

that for V_2^+ is effectively zero. This result suggests that a long-range Coulomb interaction exists between the positron and the charged V_2. This plays an important role for positron trapping: Coulomb attraction works between positron and negatively

charged V_2, whereas Coulomb repulsion works for positively charged V_2. We note that the positron can be trapped even at V_2^0, which has no long-range Coulomb attraction.

The lifetime at negatively charged V_2 is longer than that at V_2^0 at room tempeature. Here, a natural question would be why are the positron lifetimes (320 ps) in V_2^{2-} and V_2^- longer than that of V_2^0 (290–300 ps) at room temperature, if we consider a larger electron number at a negatively charged V_2 than that at V_2^0? This may be due to a lattice relaxation around V_2 and will also be discussed later.

3.3. TEMPERATURE DEPENDENCE OF POSITRON LIFETIME AND TRAPPING

Figs. 2 and 3 show the temperature dependence of lifetimes (τ_1, τ_2) and intensity (I_2) for samples BW (3.0×10^{17} e/cm^2, V_2^0) and PH (3.0×10^{16} e/cm^2, V_2^{2-}), respectively.

The lifetime (τ_2) at V_2^0 is nearly independent of temperature, while that at V_2^{2-} varies from 260 ps at 10 K to 320 ps at 300 K. These different behaviors can be interpreted as follows. The increase in lifetime at V_2^{2-} from 10 K to 300 K suggests a decrease in the electron density, possibly due to outward lattice relaxation. However, V_2^0 is lacking in bound electrons so that this relaxation effect is supposed to be negligible, and hence the lifetime at V_2^0 is nearly independent of temperature.

The lifetime at V_2^{2-} is shorter than that for V_2^0 at low temperature, but it becomes longer than that for V_2^0 at room temperature. This result reflects the fact that the electron density in V_2^{2-} is higher than that in V_2^0 at low temperature and it becomes lower due to outward lattice relaxation at high temperature. Thus, the question of why the lifetime at V_2^{2-} is longer than that for V_2^0 at room temperature, in spite of the excess electrons, is solved by taking into account the temperature dependence of the electron density.

The above discussion is consistent with a prediction of the LCAO model for V_2 [1]. According to the model, the electrons of V_2^0 occupy bonding orbitals, while the excess electrons of V_2^{2-} occupy anti-bonding orbitals. Namely, the bonding between atoms through V_2^{2-} is more unstable as compared with V_2^0. In addition, the Coulomb repulsion between two electrons of V_2^{2-} which occupy anti-bonding orbitals also results in an outward lattice relxation.

Fig. 4 shows the temperature dependence of the trapping rate for V_2^0 and V_2^{2-}, calculated from eq. (4). In both charge states, the trapping rate increases with decreasing temperature. Dannefaer et al. [4,5] have claimed that such a negative temperature dependence appears only for negatively charged V_2 but not for V_2^0 [10], and described it in terms of a phonon cascade mechanism [11]. Similar conclusions are also reported by other authors [8,9]. However, in most cases, they supposed that the charge state of V_2 is negative without an experimental determination of the Fermi level position which shifts after irradiation, as mentioned above. We found that even V_2^0 shows such a negative temperature dependence. Thus, we should note the importance of precise monitoring of the Fermi level position.

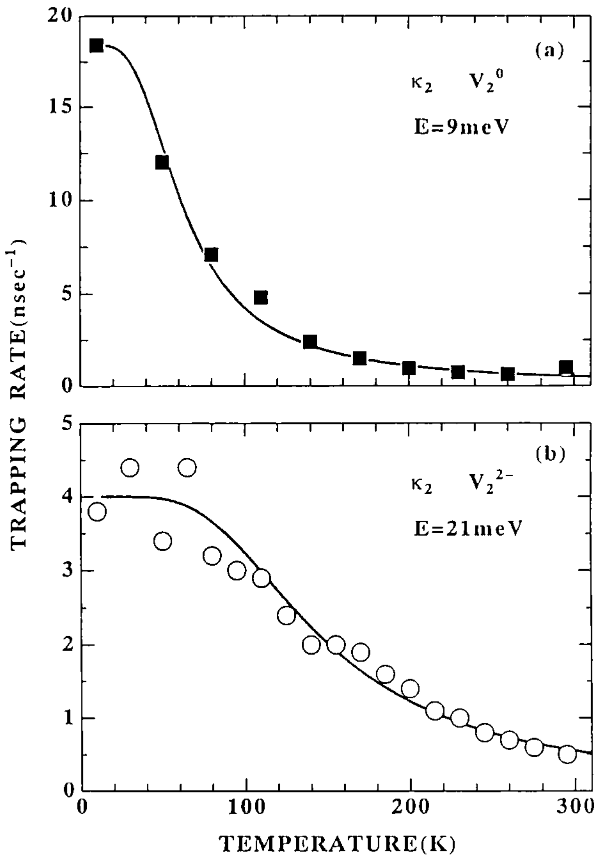

Fig. 4. Positron trapping rates as a function of temperature for samples BW irradiated with 3.0×10^{17} e/cm^2 and PH annealed at 170 °C for 30 min. Solid lines are the best fit of eqs. (5) and (6) to the experimental data.

It has been assumed by several authors [14,15] that the negative temperature dependence of the trapping rate can be described in terms of a two-stage trapping model with an additional shallow level. According to Puska et al. [14], the trapping rate is written as follows:

$$\kappa = \kappa_0/[1 + CT^{1.5}\exp(-E/kT)], \qquad (5)$$

$$C = (2\pi mk/h^2)^{1.5}\kappa_0/\eta C_v), \qquad (6)$$

where κ_0 is the trapping rate from the bulk state to the shallow state, E the shallow level energy, η the trapping rate from the shallow state to the ground state, and C_v the defect concentration. The solid lines in fig. 4 are the bet fit of eqs. (5) and (6) to experimental data. The values of the shallow level E for V_2^0 and V_2^{2-} were thus

obtained as 9 and 21 meV, respectively. The shallow level is attributed to a Rydberg state between positron and negatively charged defects [14, 15]. A theoretical study [14] has reported an energy of 25 meV for a single-negatively charged single vacancy in Si. The present results yield nearly the same order of magnitude for this energy. These results suggest that the shallow level of V_2^{2-} is also originated by a Rydberg state. The cross sections for V_2^{2-} and V_2^0 at 10 K are evaluated as being about 3×10^{-12} and 1.8×10^{-13} cm^2, respectively. The large trapping cross section at low temperature suggests that it is based on a long-range Coulomb interaction. It should be noted that the shallow level is suggested even for V_2^0 having no Coulomb interaction. In this case, the interaction is the relatively short-range type, such as a deformation or polarization potential. Further study is now in progress to elucidate this point.

4. Conclusion

In this study, we investigated the dependence of positron lifetime and trapping for V_2 in Si on its charged state and temperature by the use of sample irradiated by 15 MeV electrons. A summary of results is as follows:

(i) The cross sections for V_2^{2-}, V_2^-, V_2^0 and V_2^+ are about 7×10^{-14}, 3×10^{-14}, $1-3 \times 10^{-15}$ cm^2 and effective zero at room temperature, respectively. This charge state dependence of cross sections is due to the Coulomb interaction between the positron and the charged V_2.

(ii) The cross sections for both V_2^0 and V_2^{2-} increase with decreasing temperature. This is explained in terms of a two-stage trapping model with shallow levels of 9 and 21 meV, respectively. The latter can be due to a Coulomb potential, but the former needs another interaction to give a shallow level.

(iii) The lifetime of a positron trapped in V_2^{2-} is 260 ps at 10 K, that is, shorter than when trapped in V_2^0 (295 ps). This is due to the excess electrons in V_2^{2-}. The lifetime at V_2^{2-} increases with temperature and becomes longer than that of V_2^0. This is attributed to the lattice relaxation around V_2^{2-}, which depends upon temperature.

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