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An annealing study of defects induced by electron irradiation of Czochralski-grown Si using a positron lifetime technique

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Abstract

Annealing processes of defects induced by 3 MeV electron irradiation in Czochralski-grown Si were studied by means of positron lifetime measurements. Several annealing processes were identified from a comparison with previous EPR results. The activation energies were also determined from an analysis of isothermal annealing. The results are summarized as follows. Divacancies (V_2s) disappear around 250°C to form divacancy + oxygen (V_2O) complexes. The activation energy for the annealing of divacancies is determined to be 1.30 eV. The V_2O complexes disappear at around 400°C to form trivacancy + oxygen (V_3O) and divacancy + dioxygen (V_2O_2) complexes. The activation energy for the annealing of V_2O complexes is determined to be 2.14 eV. The V_3O and V_2O_2 complexes disappear at around 440°C to form trivacancy–dioxygen (V_3O_2) complexes. The activation energy for the annealings of these defects is determined to be 2.23 eV. The V_3O_2 complexes disappear at around 475°C. The activation energy is determined to be 2.56 eV. The annealing processes of divacancies, vacancy + oxygen (VO) and vacancy + dioxygen (VO_2) complexes were also examined from measurement of their infrared absorption. Temperature dependent changes of the absorption coefficient due to divacancies are in good agreement with temperature dependent changes of the positron trapping rate due to divacancies. Positron trapping at VO and VO_2 complexes was not detected, in contrast to the measurement of optical absorption.

1. Introduction

Radiation-induced defects in Czochralski grown Si (Cz-Si) are more complicated than those in floating-zone grown Si (FZ-Si) due to the existence of the oxygen impurity: Various vacancy–oxygen complexes are introduced in addition to the monovacancy (V), divacancy and vacancy–donor (or acceptor) complexes. It is interesting to study the annealing behaviour of vacancy–oxygen complexes in order to clarify the influence of the vacancy on the motion of oxygen atom. EPR [1–4] and IR [5–7] studies reveal the annealing behaviour of various vacancy–oxygen complexes.

Positron lifetime measurement is a powerful tool to detect vacancy-type defects. Several studies on irradiated Cz-Si have been reported [8,9]. It is not yet clear whether there are any correlations between defects detected from positron annihilation and those detected with EPR and IR. We have thus attempted to clarify the annealing behaviour of vacancy–oxygen complexes using a positron lifetime method and have compared our results with the results of previous works.

2. Experimental

Specimens used in this work were n-type Cz-Si doped with $\sim 1 \times 10^{16} \text{ cm}^{-3}$ antimony (Sb). From the

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infrared absorption measurement, the oxygen concentration was determined to be $1 \times 10^{18} \text{ cm}^{-3}$ with the use of a conversion factor of $3.14 \times 10^{17} \text{ cm}^{-2}$. The specimens were irradiated with 3 MeV electrons up to a dose of $1 \times 10^{18} \text{ cm}^{-2}$ at room temperature. To check the Fermi level position, a Hall effect measurement was done prior to all measurements. The specimens remained n-type and the Fermi level position was located 0.22 eV below the conduction band.

Isochronal annealing was done from 100 to 600°C with a temperature step of 25°C and an annealing duration of 20 min. To determine the activation energy of the annealing processes, isothermal annealings were also carried out at various temperatures.

Positron lifetimes at room temperature were measured using a conventional spectrometer. After the subtraction of source and background components, lifetime spectra were decomposed into two lifetime components, $L(t) = (I_1/\tau_1) \exp(-t/\tau_1) + (I_2/\tau_2) \exp(-t/\tau_2)$, using a computer program called ‘‘POSITRON-FIT’’ [10]. Here, I_i is the intensity ($I_1 + I_2 = 1$) and τ_i is the lifetime. The bulk lifetime of the Si crystal, τ_B , was determined to be 222 ps from a measurement of unirradiated high-purity FZ-Si. To determine the annealing behaviour of divacancies, VO and VO₂ complexes, infrared absorption was also measured at 6 and 296 K using a JEOL JIR-100 type FT-IR spectrophotometer.

3. Results and discussion

3.1. Isochronal annealing

Fig. 1 shows the positron lifetime and intensity as a function of annealing temperature. The lifetime τ_2 is associated with vacancy-type defects. It shows a stationary value 315 ps up to 200°C, but decreases to 295 ps around 250°C. This shows a change of the dominant species of defects due to annealing. The appearance of the lifetime 295 ps indicates an increase of the defects associated with this lifetime and the disappearance of V₂s. Since the lifetime at a V₂ is 320 ps [11], the lifetime 315 ps is probably a weighted average of 320 and 295 ps. The lifetime τ_2 increases to 325 ps at around 400°C. The lifetime τ_1 deviates from that expected from a trapping model. This probably suggests the existence of some defects having lifetimes close to the bulk life-

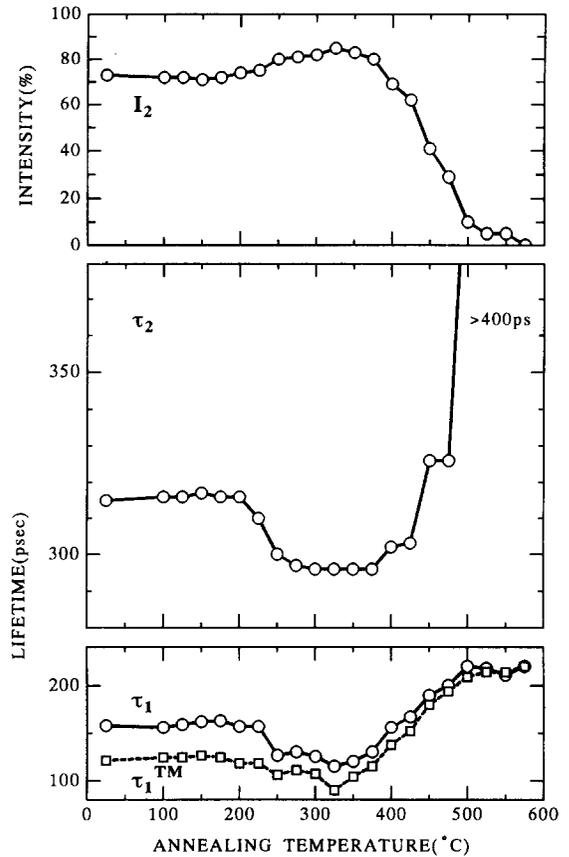


Fig. 1. Positron lifetimes and intensity as a function of annealing temperature. τ_1^{TM} denotes the lifetime τ_1 expected from the trapping model.

time. Such defects may be vacancy + antimony (VSb), VO or VO₂ complexes since the lifetimes at a vacancy–phosphorus (VP) centre and a VO centre are reported to be 248 and 225 ps, respectively [12]. It is, however, very difficult to resolve τ_1 into several components by computer fittings. We therefore assumed the lifetime at those defects to be 240 ps and estimated the trapping rates for such defects (κ_1) and defects which corresponded to the τ_2 component (κ_2) by the following equations.

$$\kappa_1 = \{ \tau_1 [(1/\tau_B) - (I_2/\tau_2)] - I_1 \} / (\tau_S - \tau_1), \quad (1)$$

$$\kappa_2 = I_2 \{ (1/\tau_B) - (1/\tau_2) - [1 - (\tau_1/\tau_2)] I_1 / \tau_S \} / I_1 [1 - (\tau_1/\tau_S)], \quad (2)$$

where τ_S is the lifetime (240 ps) mixed into the bulk lifetime. The trapping rate is proportional to the concentration of the relevant defect.

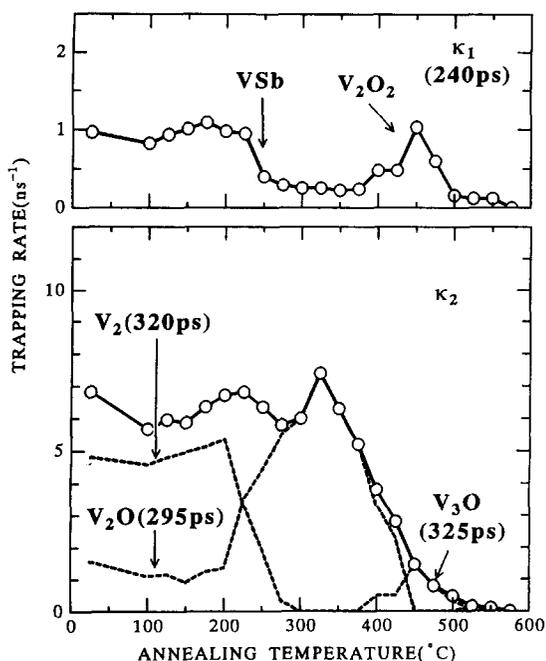


Fig. 2. Positron trapping rates κ_1 for a lifetime of 240 ps (upper figure) and κ_2 (solid lines in the lower figure) with two-component analysis of lifetime spectra as a function of annealing temperature. The broken lines in the lower figure show the trapping rates for the lifetimes 320, 295 and 325 ps, respectively.

Fig. 2 shows the annealing behaviour of the trapping rates. The trapping rate for the lifetime 240 ps decreases at 250°C. This shows the disappearance of VSb complexes since the annealing temperature is in good agreement with that obtained from previous work concerned with Hall effect measurements [13]. The trapping rate for the lifetime 320 ps decreases at around 250°C with an increase in the trapping rate for the lifetime 295 ps. The decrease in the trapping rate for the lifetime 320 ps is explained as due to the disappearance of V_2s since the annealing temperature coincides with that of the optical absorption coefficient due to V_2s as shown in Fig. 3. The increase in the trapping rate for the lifetime 295 ps is explained as due to the formation of V_2O complexes due to a reaction of $V_2 + O \rightarrow V_2O$. The shortened lifetime suggests a decrease in the open volume due to an additional oxygen atom. The V_2O complexes disappear at around 400°C with increases in the trapping rates of lifetimes 325 and 240 ps. These are probably due to the dissociation or migration of V_2O complexes and the formation of various vacancy–oxygen complexes. A previous EPR study [1] shows that V_3O and V_2O_2 complexes are formed when V_2O com-

plexes are annealed. If a V_2O captures a vacancy which is released from another V_2O , a V_3O is formed due to the reaction, $V_2O + V \rightarrow V_3O$. If a V_2O moves to an oxygen atom, a V_2O_2 is formed due to the reaction, $V_2O + O \rightarrow V_2O_2$. Hence it is concluded that the increases in the trapping rates for the lifetimes 325 and 240 ps correspond to the formation of V_3O and V_2O_2 complexes, respectively.

Fig. 3 shows the annealing behaviour of VO and VO_2 complexes [5–7] determined from the measurement of optical absorption. The VO complexes disappear around 350°C with the appearance of VO_2 complexes which disappears around 500°C. As shown in Fig. 2, we could not detect these annealing processes in the case of the positron trapping rate in contrast to previous works [12,14]. We conclude that positron trapping rates at VO and VO_2 complexes at room temperature are too small to be detected.

3.2. Isothermal annealing

In order to determine the activation energies for the annealing processes, we carried out isothermal annealings. As shown in Fig. 2, the annealing process is separated into several temperature ranges.

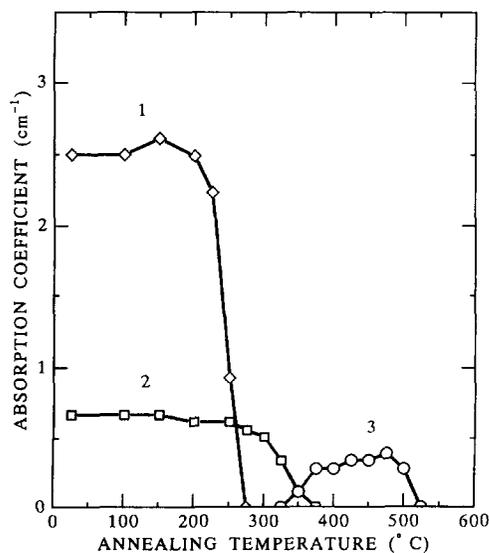


Fig. 3. Infrared absorption coefficients associated with VO, VO_2 complexes and divacancies as a function of annealing temperature. Curves 1–3 show the behaviour of divacancy, VO and VO_2 complexes, respectively. The peak positions of divacancy, VO and VO_2 complexes are 2768, 830 and 889 cm^{-1} , respectively.

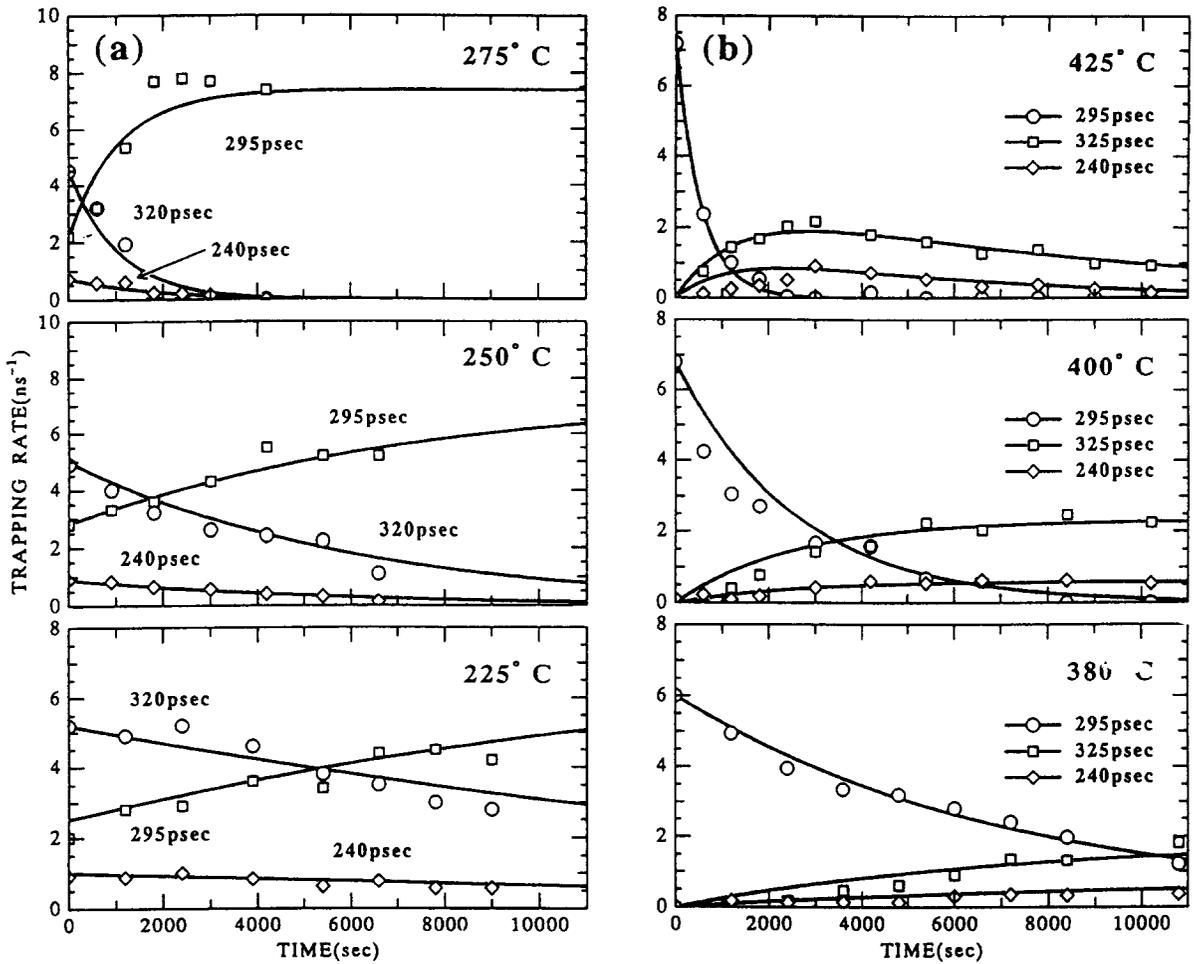


Fig. 4. (a) Positron trapping rates responsible for the lifetimes 320, 295 and 240 ps, respectively, as a function of annealing time. (b) Same as (a) for the lifetimes 325, 295 and 240 ps.

3.2.1. ~250°C

Fig. 4a shows the results of isothermal annealings of trapping rates for the lifetimes 320, 295 and 240 ps. As discussed above, the decrease and increase in the trapping rates for the lifetime 320 and 295 ps, respectively, are described by the migration of V_2 s to oxygen atoms and the formation of V_2O complexes, $V_2 + O \rightarrow V_2O$. The decrease in the trapping rate for the lifetime 240 ps is probably described by the migration of VSb complexes to oxygen atoms. Thus, we set up the following rate equations:

$$d[V_2]/dt = -K_1[O][V_2], \tag{3}$$

$$d[V_2O]/dt = K_1[O][V_2], \tag{4}$$

$$d[VSb]/dt = -K_2[O][VSb], \tag{5}$$

where K_i is the reaction constant ($= \nu_{\text{eff}} \exp(-E_i/KT)$), ν_{eff} : effective jump frequency, E_i : activation energy). Solving these rate equations with the initial conditions of $[V_2] = [V_2]_0$, $[V_2O] = [V_2O]_0$ and $[VSb] = [VSb]_0$ at $t=0$, we get $[V_2] = [V_2]_0 \exp(-Kt)$, $[V_2O] = [V_2O]_0 + [V_2]_0 [1 - \exp(-Kt)]$ and $[VSb] = [VSb]_0 \exp(-K't)$, where $K = K_1[O]$ and $K' = K_2[O]$. The solid lines in Fig. 4a are the fitting lines of these equations. The results are well-reproduced. From the Arrhenius plots of reaction constants shown in Fig. 6, the activation energies for the disappearances of V_2 s and VSb complexes were determined to be 1.30 and 1.27 eV, respectively. These are in good agreement with those obtained in past works [13,15,16].

3.2.2. $\sim 400^\circ\text{C}$

Fig. 4b shows the results of isothermal annealings of trapping rates for the lifetimes 295 (V_2O), 325 and 240 ps at around 400°C . These show a decrease in V_2O complexes and formation of other defects. As discussed above, these other defects probably correspond to V_3O and V_2O_2 complexes generated due to the reactions: $\text{V}_2\text{O} \rightarrow 2\text{V} + \text{O}$, $\text{V}_2\text{O} + \text{V} \rightarrow \text{V}_3\text{O}$, $\text{V}_2\text{O} + \text{O} \rightarrow \text{V}_2\text{O}_2$. Thus, we set up following rate equations:

$$d[\text{V}_2\text{O}]/dt = -K_1[\text{O}][\text{V}_2\text{O}] - K_2[\text{V}_2\text{O}] - K_3[\text{V}][\text{V}_2\text{O}], \quad (6)$$

$$d[\text{V}]/dt = 2K_2[\text{V}_2\text{O}] - K_3[\text{V}][\text{V}_2\text{O}], \quad (7)$$

$$d[\text{V}_3\text{O}]/dt = K_3[\text{V}][\text{V}_2\text{O}], \quad (8)$$

$$d[\text{V}_2\text{O}_2]/dt = K_1[\text{O}][\text{V}_2\text{O}]. \quad (9)$$

Here, we assume that the concentration of oxygen is constant and $d[\text{V}]/dt = 0$. These assumptions are valid since (i) the concentration of oxygen is much higher than those of the defects and (ii) the monovacancy is highly mobile and hence the concentration will rapidly reach an equilibrium value. Solving Eqs. (6)–(9) with the initial conditions $[\text{V}_2\text{O}] = [\text{V}_2\text{O}]_0$ and $[\text{V}_3\text{O}] = [\text{V}_2\text{O}_2] = 0$ at $t=0$, we get $[\text{V}_2\text{O}] = [\text{V}_2\text{O}]_0 \exp(-Kt)$, $[\text{V}_3\text{O}] = (2K_3[\text{V}_2\text{O}]_0/K)[1 - \exp(-Kt)]$ and $[\text{V}_2\text{O}_2] = (K_1[\text{O}][\text{V}_2\text{O}]_0/K)[1 - \exp(-Kt)]$, where $K = K_1[\text{O}] + K_2 + K_3[\text{V}]$. The solid lines of Fig. 4b are the fitting lines of these equations. The activation energy for the disappearance of V_2O complexes was determined to be 2.14 eV from Fig. 6.

3.2.3. $\sim 450^\circ\text{C}$

Figs. 5a and 5b show the results of isothermal annealings of trapping rates for the lifetimes 325 and 240 ps at around 450°C . It shows that the trapping rates for the lifetime 240 ps decrease and that the trapping rates for the lifetime 325 ps approach a constant. The former process corresponds to the disappearance of V_2O_2 complexes. The latter suggests the disappearance of V_3O complexes and the formation of another defect having a similar lifetime to the V_3O complexes. Previous EPR work shows that V_3O_2 complexes are formed when V_2O_2 complexes disappear. This suggests that a V_2O_2 captures a vacancy which is released from a V_3O complex and hence a V_3O_2 is formed ($\text{V}_2\text{O}_2 + \text{V} \rightarrow \text{V}_3\text{O}_2$). Thus, we set up the following rate equations:

$$d[\text{V}_3\text{O}]/dt = -K_1[\text{V}_3\text{O}], \quad (10)$$

$$d[\text{V}]/dt = 3K_1[\text{V}_3\text{O}] - K_2[\text{V}][\text{V}_2\text{O}_2], \quad (11)$$

$$d[\text{V}_2\text{O}_2]/dt = -K_2[\text{V}][\text{V}_2\text{O}_2], \quad (12)$$

$$d[\text{V}_3\text{O}_2]/dt = K_2[\text{V}][\text{V}_2\text{O}_2]. \quad (13)$$

Here, we again assume $d[\text{V}]/dt \approx 0$. Solving Eqs. (10)–(13) with the initial conditions $[\text{V}_3\text{O}] = [\text{V}_3\text{O}]_0$, $[\text{V}_2\text{O}_2] = [\text{V}_2\text{O}_2]_0$ at $t=0$, we get $[\text{V}_3\text{O}] = [\text{V}_3\text{O}]_0 \exp(-K_1t)$, $[\text{V}_2\text{O}_2] = [\text{V}_2\text{O}_2]_0 \exp(-Kt)$ and $[\text{V}_3\text{O}_2] = [\text{V}_2\text{O}_2]_0[1 - \exp(-Kt)]$, where $K = 3K_1[\text{V}_3\text{O}]/[\text{V}_2\text{O}_2]$. The dotted and broken lines in Fig. 5a are the fitting lines of the solutions for $[\text{V}_3\text{O}]$ and $[\text{V}_3\text{O}_2]$, respectively. The solid lines in Fig. 5b are the fitting lines of the solution for $[\text{V}_2\text{O}_2]$. We obtained almost the same activation energy, 2.23 eV, for the annealing of V_3O and V_2O_2 complexes. This is consistent with the above discussion. One may, however, expect that the lifetime at a V_3O_2 is shorter than that at a V_3O (325 ps) since the open volume of a V_3O_2 is expected to be smaller than that of V_3O due to the additional oxygen atom. To clarify this point, the theoretical lifetime must be calculated.

3.2.4. $\sim 475^\circ\text{C}$

Fig. 5c shows the results of isothermal annealings of the trapping rates for the lifetime 325 ps. The trapping rates decrease and approach to zero. Although the process for the disappearance of the defects is not clear, we assume a first-order process and set up following rate equation:

$$d[\text{V}_3\text{O}_2]/dt = -K[\text{V}_3\text{O}_2]. \quad (14)$$

The solid lines in Fig. 5c show the fitting lines of this solution, $[\text{V}_3\text{O}_2] = [\text{V}_3\text{O}_2]_0 \exp(-Kt)$, where $[\text{V}_3\text{O}_2]_0$ is the initial concentration of the V_3O_2 complex. The activation energy was determined to be 2.56 eV from Fig. 6. This is comparable to the migration energy of an oxygen atom [17]. This suggests that a V_3O_2 complex captures an oxygen atom to form a V_3O_3 complex.

4. Summary

Annealing processes of radiation-induced defects in Cz-Si have been identified, and activation energies for

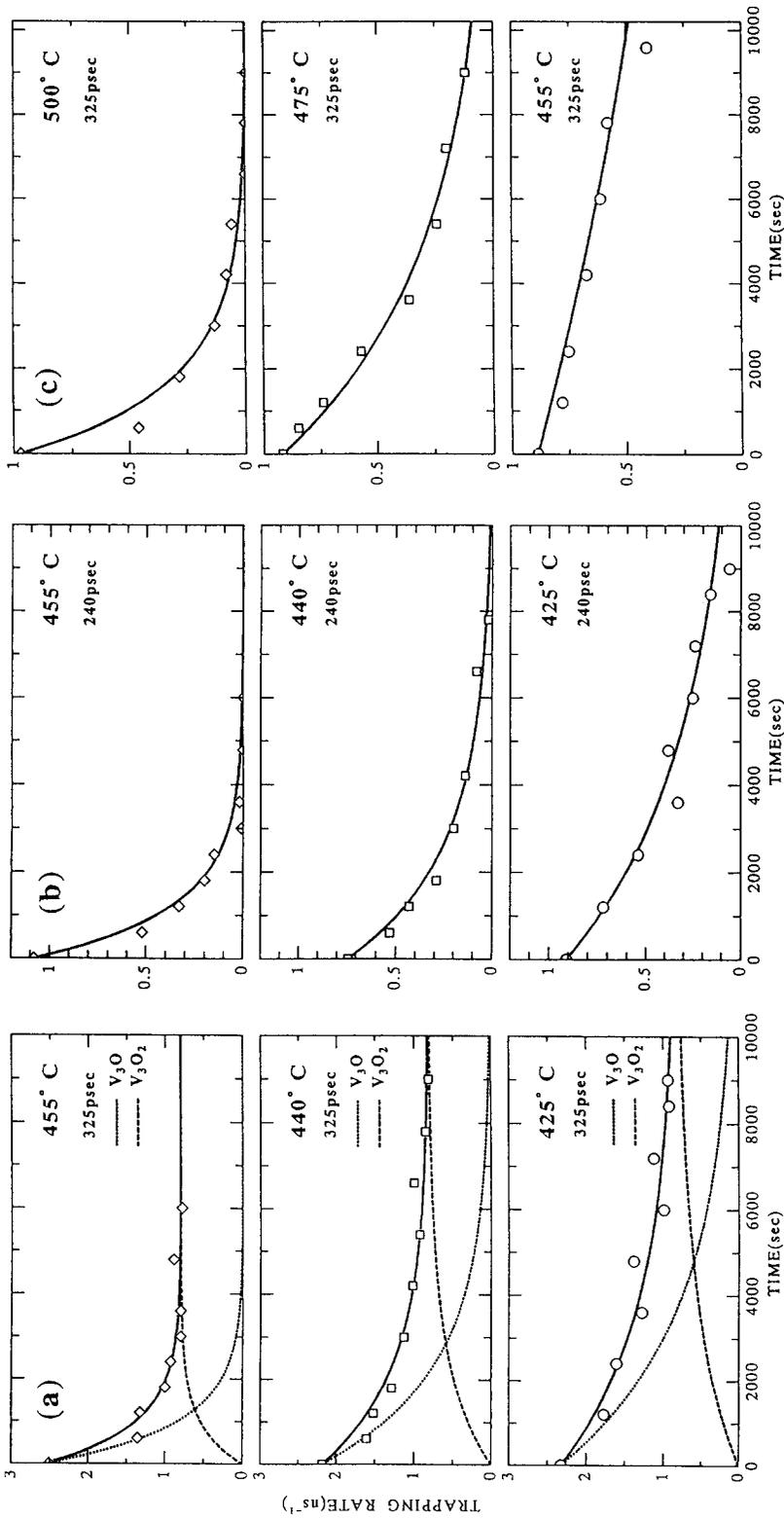


Fig. 5. (a)–(c) Same as Fig. 4 (a) for 325, 240 and 325 ps, respectively.

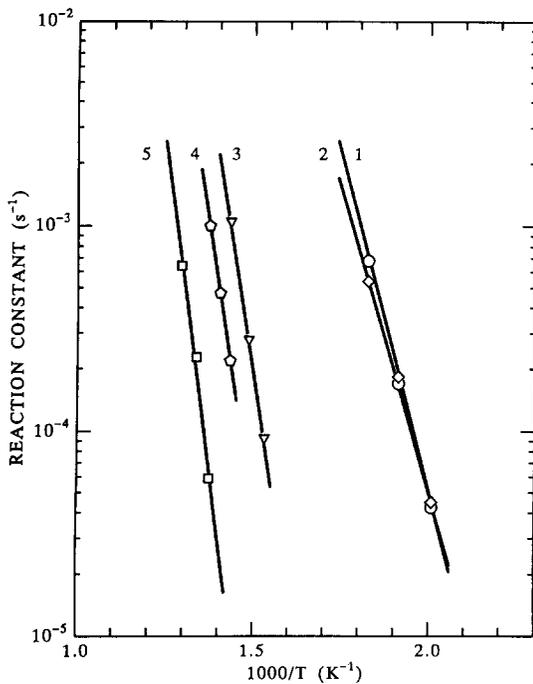


Fig. 6. Arrhenius plots of reaction constants. Lines 1–5 show the fitting lines, $6.4 \times 10^8 \exp(-1.30 \text{ eV}/kT)$ for V_2 , $3.1 \times 10^7 \exp(-1.27 \text{ eV}/kT)$ for VSb, $2.7 \times 10^{12} \exp(-2.14 \text{ eV}/kT)$ for V_2O , $2.6 \times 10^{12} \exp(-2.23 \text{ eV}/kT)$ for V_3O and V_2O_2 , $3.4 \times 10^{13} \exp(-2.56 \text{ eV}/kT)$ for V_3O_2 , respectively.

the annealing processes were determined by means of positron lifetime measurements. It was found that various vacancy–oxygen complexes were formed due to the annealing. The annealing processes identified in this work are consistent with the results of EPR works. Theoretical calculations of positron lifetimes at vacancy–oxygen complexes are necessary for further study.

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