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 (V₂) disappear around 250°C to form divacancy + oxygen (V₂O) complexes. The activation energy for the annealing of divacancies is determined to be 1.30 eV. The V₂O complexes disappear at around 400°C to form trivacency + oxygen (V₃O) and divacancy + dioxygen (V₂O₂) complexes. The activation energy for the annealing of V₂O complexes is determined to be 2.14 eV. The V₂O and V₂O₂ complexes disappear at around 440°C to form trivacency-dioxygen (V₃O₂) complexes. The activation energy for the annealing of these defects is determined to be 2.23 eV. The V₃O₂ 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 (VO₂) 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 VO₂ 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
infrared absorption measurement, the oxygen concentration was determined to be $1 \times 10^{18}$ cm$^{-3}$ with the use of a conversion factor of $3.14 \times 10^{17}$ cm$^{-2}$. The specimens were irradiated with 3 MeV electrons up to a dose of $1 \times 10^{18}$ 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 $\tau_i$ is the lifetime. The bulk lifetime of the Si crystal, $\tau_B$, was determined to be 222 ps from a measurement of unirradiated high-purity FZ-Si. To determine the annealing behaviour of divacancies, VO and VO$_2$ 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 $\tau_2$ 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 V$_2$S. Since the lifetime at a V$_2$ is 320 ps [11], the lifetime 315 ps is probably a weighted average of 320 and 295 ps. The lifetime $\tau_2$ increases to 325 ps at around 400°C. The lifetime $\tau_1$ deviates from that expected from a trapping model. This probably suggests the existence of some defects having lifetimes close to the bulk lifetime. Such defects may be vacancy + antimony (VSB), VO or VO$_2$ 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 $\tau_1$ 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 ($\kappa_1$) and defects which corresponded to the $\tau_2$ component ($\kappa_2$) by the following equations.

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

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

where $\tau_S$ is the lifetime (240 ps) mixed into the bulk lifetime. The trapping rate is proportional to the concentration of the relevant defect.
Fig. 2 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 VSb complexes. The annealing temperature coincides with that of the VSb complexes. The optical absorption coefficient due to VSb complexes is shown in Fig. 3. The increase in the trapping rate for the lifetime 295 ps is explained as due to the formation of V$_2$O complexes due to a reaction of V$_2$ + O $\rightarrow$ V$_2$O. The shortened lifetime suggests a decrease in the open volume due to an additional oxygen atom. The V$_2$O 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$_2$O complexes and the formation of various vacancy–oxygen complexes. A previous EPR study [1] shows that V$_3$O and V$_2$O$_2$ complexes are formed when V$_2$O complexes are annealed. If a V$_3$O captures a vacancy which is released from another V$_2$O, a V$_3$O is formed due to the reaction, V$_3$O + V $\rightarrow$ V$_3$O. If a V$_2$O moves to an oxygen atom, a V$_2$O$_2$ is formed due to the reaction, V$_2$O + O $\rightarrow$ V$_2$O$_2$. Hence it is concluded that the increases in the trapping rates for the lifetimes 325 and 240 ps correspond to the formation of V$_3$O and V$_2$O$_2$ 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.
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 \( V_{2S} \) 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:

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

\[
\frac{d[V_{2O}]}{dt} = K_1[O][V_2], \tag{4}
\]

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

where \( K_i \) is the reaction constant \( = \nu_{eff} \exp(-E_i/KT) \), \( \nu_{eff} \) 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 \( V_{2S} \) 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\(_2\)O), 325 and 240 ps at around 400°C. These show a decrease in V\(_2\)O complexes and formation of other defects. As discussed above, these other defects probably correspond to V\(_3\)O and V\(_2\)O\(_2\) complexes generated due to the reactions:

\[ V_2O \rightarrow 2V + O, \quad V_2O + V \rightarrow V_3O, \quad V_2O + O \rightarrow V_2O_2. \]

Thus, we set up following rate equations:

\[
\text{d}[V_2O]/\text{dt} = -K_1[O][V_2O] - K_2[V_2O] - K_3[V][V_2O], \quad (6)
\]

\[
\text{d}[V]/\text{dt} = 2K_2[V_2O] - K_3[V][V_2O], \quad (7)
\]

\[
\text{d}[V_3O]/\text{dt} = K_3[V][V_2O], \quad (8)
\]

\[
\text{d}[V_2O_2]/\text{dt} = K_1[O][V_2O], \quad (9)
\]

Here, we assume that the concentration of oxygen is constant and \( \text{d}[V]/\text{dt} = 0 \). 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 \([V_2O] = [V_2O]_0\) and \([V_3O] = [V_2O_2] = 0\) at \( t = 0 \), we get \([V_2O] = [V_2O]_0 \exp (-Kt), \quad [V_3O] = (2K_3[V_2O]_0/K) \left[ 1 - \exp(-Kt) \right]\)

and \([V_2O_2] = (K_1[O][V_2O]_0/K) \left[ 1 - \exp(-Kt) \right], \quad \text{where} \quad K = K_1[O] + K_2 + K_3[V]. \]

The solid lines of Fig. 4b are the fitting lines of these equations. The activation energy for the disappearance of V\(_2\)O 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 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:

\[
\text{d}[V_3O]/\text{dt} = -K[V_3O]. \quad (10)
\]

\[
\text{d}[V]/\text{dt} = 3K_1[V_3O] - K_2[V][V_2O_2], \quad (11)
\]

\[
\text{d}[V_2O_2]/\text{dt} = -K_2[V][V_3O], \quad (12)
\]

\[
\text{d}[V_2O_2]/\text{dt} = K_2[V][V_3O]. \quad (13)
\]

Here, we again assume \( \text{d}[V]/\text{dt} = 0 \). Solving Eqs. (10)–(13) with the initial conditions \([V_2O] = [V_3O]_0, [V_2O_2] = [V_2O_2]_0\) at \( t = 0 \), we get \([V_2O] = [V_2O]_0 \exp(-Kt), \quad [V_3O] = [V_3O]_0 \exp(-Kt)\), \([V_2O_2] = [V_2O_2]_0 \left[ 1 - \exp(-Kt) \right], \quad \text{where} \quad K = 3K_1[O]/[V_2O_2]. \]

The dotted and broken lines in Fig. 5a are the fitting lines of the solutions for \([V_2O]\) and \([V_3O]\), respectively. The solid lines in Fig. 5b are the fitting lines of the solution for \([V_2O_2]\). We obtained almost the same activation energy, 2.23 eV, for the annealing of V\(_2\)O and V\(_2\)O\(_2\) complexes. This is consistent with the above discussion. One may, however, expect that the lifetime at a V\(_2\)O is shorter than that at a V\(_3\)O (325 ps) since the open volume of a V\(_3\)O is expected to be smaller than that of V\(_3\)O 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:

\[
\text{d}[V_3O]/\text{dt} = -K[V_3O]. \quad (14)
\]

The solid lines in Fig. 5c show the fitting lines of this solution, \( [V_2O_2] = [V_2O_2]_0 \exp(-Kt) \), where \([V_3O_2]_0\) is the initial concentration of the V\(_3\)O 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\(_2\)O complex captures an oxygen atom to form a V\(_3\)O 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.
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References