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ANNEALING PROCESSES OF VACANCIES IN SILICON INDUCED BY ELECTRON IRRADIATION: ANALYSIS USING POSITRON LIFETIME MEASUREMENT

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ABSTRACT: Annealing processes of vacancies in posphorus doped FZ-Si induced by 15MeV electron irradiation were studied with positron lifetime measurements. It was found that as-irradiated Si contained mainly vacancy-phosphorus pairs (VP) and divacancies (V_2) which gave rise to the positron lifetimes 248ps and 320ps, respectively. Several annealing processes were identified: VP pairs disappeared around 150°C. The mobile vacancies released from VP formed V_3 and V_2 . V_3 decomposed into V and V_2 below 200°C. The mobile V_2 disappeared around 300°C to form V_4 (350ps). V_4 dissociated around 350°C to form V_6 (400ps). V_6 dissociated around 400°C to form larger vacancy clusters (500ps). Thus, it was concluded that vacancy clusters consisting of even number of vacancies were formed after annealing out of V_2. The positron lifetimes 248(VP), 320(V_2), 350(V_4), and 400(V_6) ps identified at present work were in good agreement with the theoretical dependence of lifetimes on the cluster size.

1. INTRODUCTION

The positron annihilation technique has been extensively applied to the studies of defects in semiconductors in last ten years[1,2]. Since the positron lifetime method is a powerful tool to detect vacancy type defects, it is mainly used for the investigations of radiation-induced defects. One intriguiting result is that the positron trapping rate and lifetime strongly depend on the charge state of defect and temperature.

It is known that radiation-induced vacancies form various kinds of vacancy clusters as they are annealed. Despite extensive works, the thermal behaviors of radiation-induced vacancies in Si, such as recovery and clustering, have not yet been clarified in detail by the positron lifetime method. Moreover, theoretical and experimental works show discrepancy with respect to the lifetime at vacancy clusters[3]. Thus, we attempted to identify annealing processes of radiation-induced vacancies and determine positron lifetimes at various kinds of vacancy clusters.

2. EXPERIMENT

A sample ingot for irradiation ($5x8x10mm^3$) was cut from a floating-zone (FZ) grown Si crystal doped with $1.7x10^{16}$ cm^{-3} phosphorus (P). After chemical etching with CP4 solution, it was irradiated with 15MeV electrons to a dose of $3x10^{17}e/cm^2$ at room temperature. Samples for positron lifetime measurements ($5x5x0.8mm^3$) were cut from the irradiated ingot and polished with CP4 solution. To determine annealing temperature, isochronal annealing was done from 100 up to 500°C with a temperature step of 25°C and an annealing duration of 20 min. To determine activation energies of annealing processes, isothermal annealing was done at various temperatures.

^{22}NaCl (~10μCi) was deposited onto a myler thin film with a thickness of 5μm as a positron source. It was sandwiched by two samples. Positron lifetime measurements were done using a conventional spectrometer with a time resolution of 200ps at room temperature. Bulk lifetime (τ_B) of Si (222ps) and the source component (350ps, 10%) were determined from the measurement of unirradiated high-purity FZ-Si. After subtraction of the source and background components, lifetime spectra were decomposed into two or three lifetime components using a computer program "POSITRONFIT"[4]. In the framework of trapping model we assigned the positron lifetimes(τ_1,τ_2,τ_3) obtained from the decomposition to $1/\tau_1=1/\tau_B+\kappa_{D1}+\kappa_{D2}$, $\tau_2=\tau_{D1}$, $\tau_3=\tau_{D2}$, where τ_{D1} and τ_{D2} were the lifetimes at defects 1 and 2, respectively. Positron trapping rates into defects 1 and 2 were estimated from $\kappa_{D1}=(I_2/I_1)[1/\tau_B-(1-I_3)/\tau_2-I_3/\tau_3]$, $\kappa_{D2}=(I_3/I_1)[1/\tau_B-I_2/\tau_2-(1-I_2)/\tau_3]$, respectively, where I_i was the intensity ($I_1+I_2+I_3=100$).

3.RESULTS AND DISCUSSION

Figure 1 shows the results of two-component analysis of isochronal annealing of positron lifetime and intensity. The lifetime τ_2 associated with defects increases from 300 to 320ps around 150°C, from 320 to 350ps around 300°C, from 350 to 400ps around 375°C and from 400 to 500ps around 425°C. (We term these stages I through IV.) It is known that as-irradiated FZ-Si doped with P contains mainly VP and V_2[5]. We confirmed the existence of V_2 from the measurement of infrared absorption. The lifetime at VP is reported to be 248ps[6], and we also verified it in other experiment. Thus, the lifetime 300ps is probably an average for VP (248ps) and V_2 (320ps). We interpret that a stationary lifetime after each annealing stage reflects the dominance of one kind of vacancy clusters. It means that each annealing stage corresponds to the change in the species of dominant vacancy clusters. We therefore carried out three-component analysis with fixed lifetimes, 248 and 320ps, 320 and 350ps, 350 and 400ps, 400 and 500ps in the temperature range 25-225°C, 275-350°C , 350-425°C and 425-500°C, respectively. Figure 2 shows the annealing behavior of trapping rates estimated from three-component analysis. It gives a clear view that larger vacancies are formed from smaller vacancies. Each stage is interpreted as follows:

Stage I: The trapping rate κ_{248} decreases around 150°C. The annealing temperature and activation energy (0.93eV) are consistent with those of VP determined in the past works [7,8]. The trapping rate κ_{320} increases as κ_{248} decreases and shows a peak at 175°C and decreases around 300°C. The increase in κ_{320} is probably due to the formation of V_2 from monovacancies released from VP ($V+V \rightarrow V_2$). Figure 3 shows the annealing behavior of infrared absorption related to V_2. The annealing behaviors in the two measurements are similar to each other. However, the peak at 175°C in κ_{320} is absent in infrared

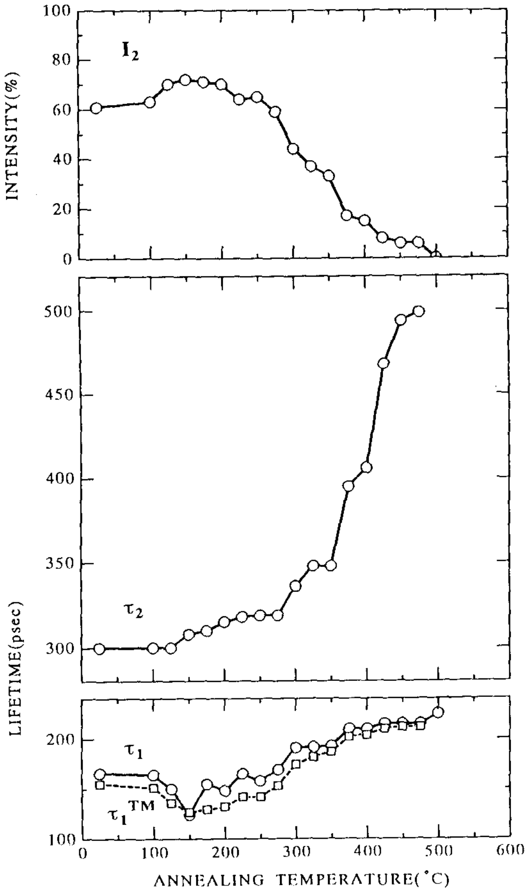

Fig. 1 Variations in positron lifetimes (τ_1, τ_2) and intensity (I_2) from two-component analysis due to isochronal annealing. τ_2 show lifetimes at defects. τ_1^{TM} show the lifetimes of first component expected from trapping model. They are in good agreement with τ_1.

absorption. To explain this peak we assumed the generation of vacancy clusters which have a positron lifetime close to that of V_2 and are less stable than V_2. From the analyses of isothermal annealing, it was found that the reaction $V+V_2 \leftrightarrow V_3$ probably occured. The activation energy of V_3 annealing was determined to be 0.76eV.

Stage II: The trapping rate κ_{320} decreases around 300°C accompanying the appearance of κ_{350}. This is due to the annealing of V_2 and formation of larger clusters. Since the binding energy of V_2 is very high ($\geq$2eV) [9], V_2 diffuses as a whole. Accordingly, the appearance of κ_{350} is probably due to the formation of V_4 ($V_2+V_2 \rightarrow V_4$). This identification is consistent with theoretical study that the lifetime at V_4 is 354ps [3]. From the analyses of isothermal annealing, the activation energy of V_2 annealing was determined to be 1.72eV.

Stage III: The trapping rate κ_{350} decreases around 350°C accompanying the appearance of κ_{400}. This suggests the dissociation of V_4 and formation of larger clusters. If V_4 dissociates into V and V_3, V_5 is formed due to the reaction $V_4+V \rightarrow V_5$. If V_4 dissociates into two V_2's, V_6 is formed due to the reaction $V_4+V_2 \rightarrow V_6$. The formation of V_5 is excluded due to following reasons: (i) The lifetime 400ps is longer than that for V_5, 375ps, predicted from theoretical study [3]. (ii) V_5 is less stable than V_4 and V_6[10]. (iii) The probability of dissociation of V_2 is still low at 350°C. Thus, V_4 dissociates to V_2 and hence V_6 is formed due to the reaction $V_4+V_2 \rightarrow V_6$. From the analyses of isothermal annealing, the activation energy of V_4 dissociation was determined to be 2. 55eV.

Stage IV: The trapping rate κ_{400} decreases around 425°C accompanying the appearance of κ_{500}. This suggests the dissociation of V_6 and formation of larger clusters. From the analyses of isothermal annealing, the activation energy of V_6 annealing was determined to be 3.74eV. If the similar argument as discussed above is applicable, V_8 is

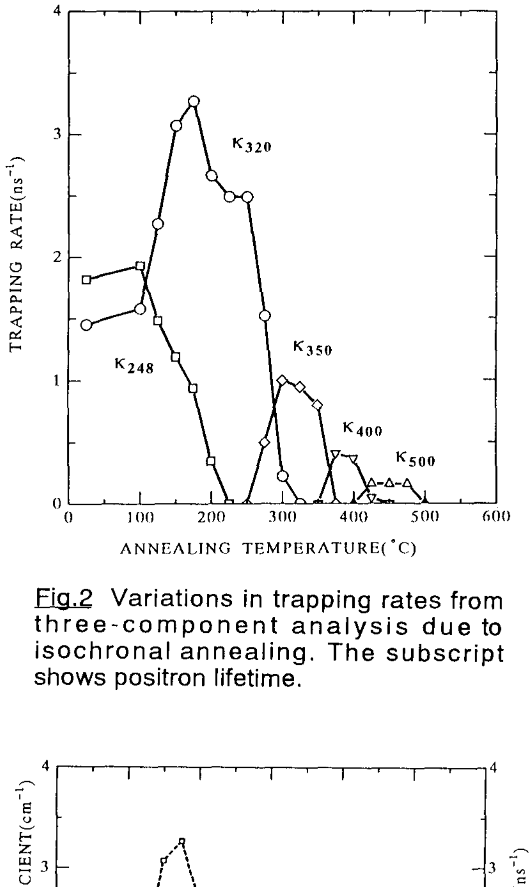

Fig.2 Variations in trapping rates from three-component analysis due to isochronal annealing. The subscript shows positron lifetime.

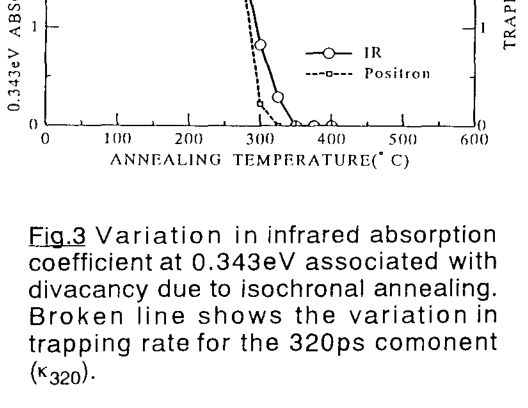

Fig.3 Variation in infrared absorption coefficient at 0.343eV associated with divacancy due to isochronal annealing. Broken line shows the variation in trapping rate for the 320ps comonent (κ_{320}).

formed due to the reaction $V_6+V_2 \rightarrow V_8$. Since there are various ways for the dissociation of V_6, it is not known whether such a reaction is dominant or not. It is shown that the most stable cluster is V_{10} among V_7~V_{12}[10]. However, present theory[3] does not predict the lifetime 500ps for V_{10}. It is thus difficult to identify the clusters giving rise to the lifetime 500ps. The identification is a future problem.

Figure 4 shows the positron lifetimes at various vacancy clusters. The present results are in good agreement with the result of theoretical calculation by Puska et al.[3] up to V_6 unlike to the result of Dannefaer [2]. This discrepancy is probably because Dannefaer used neutron-irradiated Si. It is known that the damage by neutron irradiation is more complicated compared to the case of electron irradiation. For example, his result shows that the lifetime τ_2 increases from 320 to 435ps around 150°C and decreases around 250°C. Present result shows that the lifetime τ_2 increases with annealing temperature monotonously.

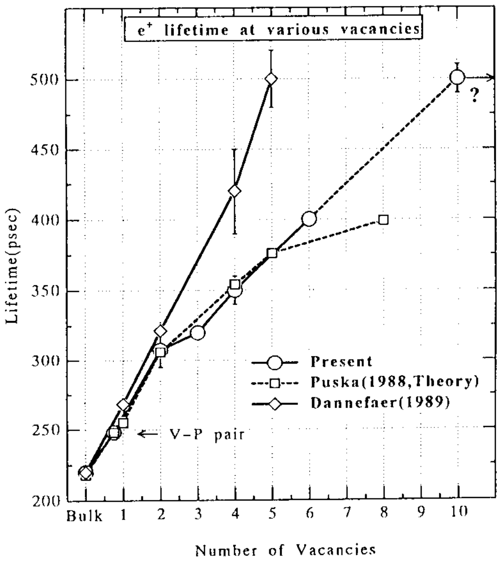

Fig.4 Positron lifetimes at various vacancy clusters. Open circles, squares and diamonds show the results of present work, Puska et al.[3] and Dannefaer [2], respectively.

3.SUMMARY

Thermal behaviors of various types of vacancy clusters in Si are clarified. It is found that the mobile species are V_2 after stage II and hence vacancy clusters of even number of vacancies are formed. This owes to a large binding energy of V_2. Positron lifetimes at various vacancy clusters are also determined. They are consistent with the result of theoretical calculation up to V_6. However, the lifetime 500ps is not predicted by any theory. The further study is necessary to elucidate this point.

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