Materials Science Forum
ISSN: 1662-9752, Vols. 255-257, pp 548-550
doi:10.4028/www.scientific.net/MSF.255-257.548

Vacancy-Hydrogen Interaction in Proton-Implanted Si Studied by Positron Lifetime and Infrared Absorption Measurements

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Keywords: Vacancy, Hydrogen, Proton Implantation, Positron Lifetime, Infrared Absorption

Abstract Vacancy-hydrogen interaction process in 6 MeV-proton-implanted Si has been studied using conventional positron lifetime and infrared absorption measurements. As a comparison, electron-irradiated and alpha-implanted Si have also been studied The lifetimes of positrons trapped at vacancy-type defects in the electron-irradiated and the alpha-implanted Si were found to increase monotonically with annealing temperatures. This shows the evolution of vacancy-clusters upon heating. On the contrary, the lifetime obtained for the proton-implanted Si was found to repeat decrease and increase several times until the component annealed out. This peculiar annealing behavior is attributed to the interaction between vacancies and hydrogen atoms. In fact, many infrared absorption lines associated with local vibration of hydrogen atoms were observed for the proton-implanted Si. The annealing behavior of some absorption lines could be correlated with that of the positron lifetime and the trapping rates.

Hydrogen in Si has a high reactivity and hence interacts with various impurities and defects to modify their electrical property, e.g., the passivation of electrical active donors and acceptors, the termination of dangling bonds at vacancies, dislocations and surfaces [1]. Hydrogen also activates some electrical "inactive" impurities such as carbon and oxygen due to the formation of complexes. Recently, it has also been shown that hydrogen enhances the thermal donor formation [2]. Defects induced by proton implantation have been studied mainly with infrared (IR) absorption measurement. Many absorption lines related to local vibration of hydrogen atoms trapped at defects are observed after proton implantation. However, infrared absorption method hardly determine if the observed line is vacancy-related or interstitial-related. To elucidate this problem, we performed positron lifetime and infrared absorption measurements with isochronal annealing. We report that some absorption lines are assigned to vacancy-hydrogen complexes.

Specimens used in this work were cut from a floating-zone grown Si single crystal doped with $1\text{x}10^{16}$ cm^{-3} phosphorus. The specimens were implanted with 6 MeV protons up to a dose of $5\text{x}10^{15}$ p/cm^2 at room temperature. As a reference, 3 MeV- electron-irradiated ($1\text{x}10^{18}$ e/cm^2) and 6 MeV-alpha-implanted ($5\text{x}10^{15}$ α/cm^2) specimens were also prepared. Isochronal annealing was carried out from 100 to 700℃ with a temperature step of 25℃ for 20 min in a dry argon atmosphere. Positron lifetime measurement was performed using a conventional spectrometer with a time resolution of 230 ps. Lifetime spectra were decomposed to two exponential terms (bulk and defects): $L(t)=(I_1/\tau_1)\exp(-t/\tau_1)+(I_2/\tau_2)\exp(-t/\tau_2)$. Positron trapping rate (κ) was determined based on the two-state trapping model. The bulk positron lifetime was determined to be 220 ps using unirradiated Si. Infrared absorption measurement was performed at 6 K using a JEOL FT-IR JIR-100 spectrophotometer.

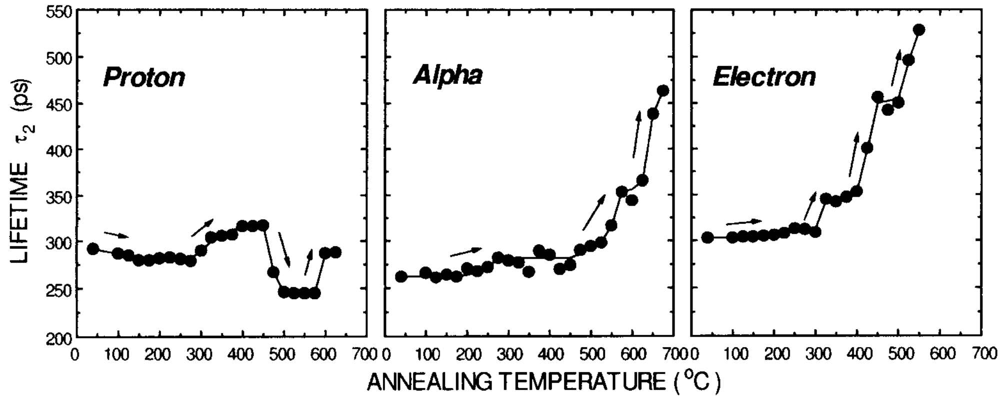

Fig.1 Annealing behavior of lifetime τ_2 for proton and alpha-implanted and electron-irradiated Si.

Figure 1 shows the annealing behavior of the second lifetime (τ_2) related to positron annihilation at vacancy-type defects. In the cases of electron irradiation and alpha implantation, the lifetime τ_2 increases with increasing annealing temperature. This clearly shows the evolution of vacancy-clusters after the annealing of small vacancies. On the contrary, the lifetime τ_2 for the proton-implanted Si first decreases at 100-200℃, increases at 300℃, decreases again at 400℃ and increases again at 600℃. This peculiar annealing behavior is probably caused by the interaction between hydrogen atoms and vacancies. The deviation of the first lifetime (τ_1) from that expected in the two-state trapping model was observed for the proton-implanted Si suggesting the presence of another defect component which gives the lifetime close to the bulk lifetime.

Figure 2 shows the infrared absorption spectra obtained for the proton-implanted Si. In addition to the divacancy-related line (2768 cm^{-1}), many absorption lines are observed from 1900 cm^{-1} to 2250 cm^{-1}. These characteristic lines are originating from local vibration of hydrogen atoms. Thus, the presence of hydrogen-defect complexes is confirmed. It is proposed theoretically that the lines below and above 2000 cm^{-1} are associated with interstitial-hydrogen complexes and vacancy-hydrogen complexes, respectively [1].

Figures 3 and 4 show the annealing behaviors of the positron lifetime (τ_2), the trapping rates (κ_1, κ_2) and the IR absorbance (>2000cm^{-1}). At 100-200℃, the 2768 cm^{-1} absorbance decreases. Since divacancies in Si start to migrate above 250℃ [3], the decreases in the 2768 cm^{-1} absorbance is attributed to the capture of hydrogen atoms by divacancies. The trapping rate κ_2 decreases and the lifetime τ_2 shortens in the same temperature range. The shortening of the lifetime τ_2 is explained as the

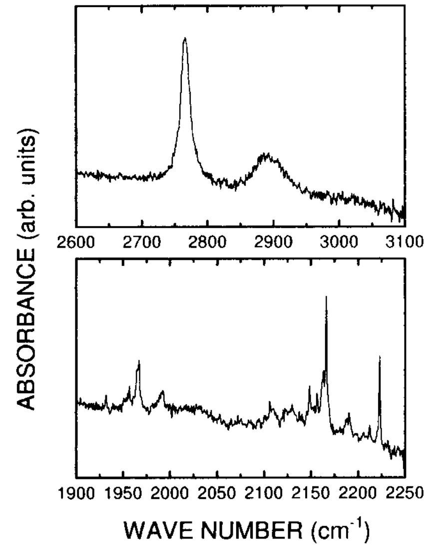

Fig. 2 IR spectra for proton-implanted Si.

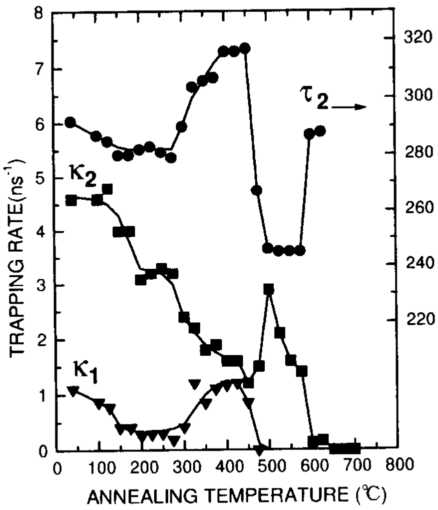

Fig. 3 Annealing behavior of positron lifetime and trapping rates for proton-implanted Si

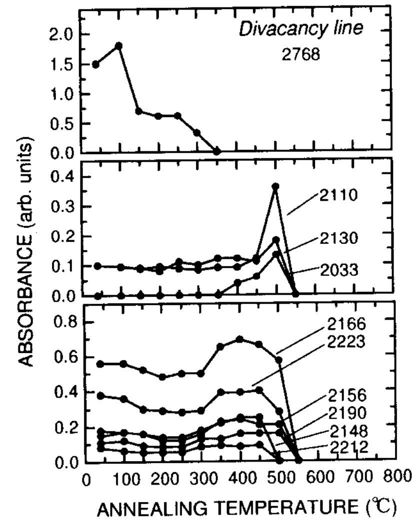

Fig. 3 Annealing behavior of absorbances (>2000 cm^{-1}) for proton-implanted Si

reduction of divacancy open volume due to the attachment of hydrogen atoms. At 300-350℃, the 2768 cm^{-1} absorbance and the trapping rate κ_2 decrease and the lifetime τ_2 prolongs towards 318 ps. These results suggest the formation of vacancy-clusters due to the migration of divacancies. At 450-500℃, the lifetime τ_2 suddenly decreases to 245 ps. It is worth to note that no vacancy-cluster formation proceed. This result suggests the break-up of vacancy-clusters and the formation of higher-order vacancy-hydrogen complexes, such as divacancy and multi-hydrogen complexes. The trapping rate κ_2 shows a peaked behavior at 500℃. The 2033, 2110 and 2130 cm^{-1} absorbances also show similar features. Accordingly, these lines can be correlated with the positron annihilation centers giving rise to the lifetime 245 ps. The trapping rate κ_1 in Fig.3 is arising from another vacancy component which contributes to the first lifetime (τ_1) as mentioned above. The positron lifetime responsible for the defects is expected to be close to the bulk lifetime. (Here, it is assumed to be 230 ps.) Probably, such defects are related to single-vacancy and mult-hydrogen complexes. The trapping rate κ_1 first decreases at 150℃, increases at 300-350℃ and finally diminishes at 500℃. The 2148-2223 cm^{-1} absorbances show the similar annealing behavior. Thus, these absorption lines can be correlated with the above positron annihilation centers. All the absorption lines diminish above 550 ℃. The trapping rates κ_1 and κ_2 also reach the detection limit up to 600℃. These results show that all hydrogen-vacancy complexes anneal out up to 600℃.

In this research, it is clearly shown that the annealing behavior of positron lifetime for the proton-irradiated Si is quite different from that for alpha or electron-irradiated Si. From the combination with IR measurement, it is clarified that the peculiar annealing behavior of the lifetime is caused by the vacancy-hydrogen interaction. The annealing behavior of the IR lines above 2000-2250 cm^{-1} is well correlated with that for positron lifetime and trapping rates.

[1]Hydrogen in Semiconductors, eds. J.I.Pankove and N.M.Johnson, Academic Press, 1991.
[2]H.J. Stein and S.K.Hahn, J. Appl. **75** (1994) 3477.
[3]G.D.Watkins and J.W.Corbett, Phys. Rev. **138** (1965) 543.

Positron Annihilation - ICPA-11

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