Migration energies of point defects during electron irradiation of hydrogenated Si crystals

M. Suezawa,[1] Y. Takada,[2] T. Tamano,[2] R. Taniguchi,[2] F. Hori,[2] and R. Oshima[2]
[1]*I. M. R., Tohoku University, Katahira, Aoba, Sendai 980-8577, Japan*
[2]*R.I.A.S.T., Osaka Prefecture University, Sakai 599-8570, Japan*
(Received 28 January 2002; published 2 October 2002)

To study both generation rates and mobilities of point defects due to electron irradiation, we measured and analyzed optical-absorption spectra of complexes of hydrogen and point defects generated by low-temperature electron irradiation of hydrogenated Si crystals. Specimens were doped with H by heating in H_2 gas at 1300 °C followed by quenching. They were then irradiated with 6-MeV electrons at 270, 200, 130, and 77 K. We measured their optical-absorption spectra at 7 K with an Fourier transform infrared spectrometer. We observed many optical absorption peaks which are due to localized vibrational modes of H bound to various point defects. The irradiation temperature dependence of concentrations of some H-point defect complexes was not monotonic contrary to the prediction of metastable Frenkel pair models. Relative intensities of those peaks depended on the irradiation temperature and were interpreted to be due to the relative mobilities of various point defects. The migration energies of a self-interstitial and a Frenkel pair relative to that of a vacancy were determined.

DOI: 10.1103/PhysRevB.66.155201 PACS number(s): 61.72.Ji, 61.80.Fe, 61.72.Cc

I. INTRODUCTION

One of the most important characteristic quantities of point defects is their migration energy. Migration energies of electron-irradiation-induced vacancies (abbreviated as V hereafter) at various charge states have been determined.[1] Those of Frenkel pairs (FP's) and self-interstitials (I) in electron-irradiated Si, however, have not been clarified since they are very difficult to detect. Instead of direct detection, self-interstitials have been detected in *p*-type Si by the detection of interstitial group-III acceptors which are formed by the change of occupation site from substitutional to interstitial resulting from replacement of these acceptors by I (Watkins' replacement mechanism[2]). Self-interstitials are believed to diffuse in an athermal manner during electron irradiation since acceptors at interstitial sites have been detected after irradiation even at 4.2 K. This athermal motion is explained by the Bourgoin-Corbett mechanism.[3]

As shown in previous papers,[4,5] we succeeded in detecting self-interstitials and Frenkel pairs as well as vacancies, from the measurements of optical absorption of hydrogenated silicon crystals after electron-irradiation at room temperature (RT). Optical-absorption peaks due to localized vibration of H included in complexes of H and point defects enabled their detection. Those complexes were formed due to the diffusion of those point defects to H_2 at RT. Consequently, determination of the relative mobilities of those point defects from the measurement of relative optical-absorption intensities of those complexes is intuitively expected. It is important to know the migration energies of point defects, even their order of magnitude, since they are still controversial.[6] To determine the mobilities of V, I, and FP's, we studied optical-absorption spectra of hydrogenated Si after electron irradiation at low temperatures.

The above explanation of the generation of H-point defect complexes, i.e., that they are determined by the mobilities of those point defects, is an oversimplification. The dependence of the generation rate of point defects, mainly of vacancies, on the irradiation temperature has been studied under another simplified assumption: The concentrations of complexes which include point defects, for example vacancy-oxygen (VO) pairs, depended only on the generation rate of point defects and not on the mobilities of point defects, since the optical-absorption intensity of VO pairs did not change due to annealing at temperatures higher than irradiation temperatures.[7] To explain those dependences, two models,[8,9] termed metastable V-I pair (we term them Frenkel pairs) models have been proposed. Both models assume the existence of metastable V-I pairs: The generation rates of point defects depend on the rates of recombination and dissociation of V-I pairs. The difference of the models depends on whether the charge states influence[9] the recombination or not.[8] Experimentally, the resultant defect concentration was first studied based on the measurement of electrical resistivity,[8] and then by optical-absorption measurement.[7] In the former measurement, defect species, i.e., V, I, and FP's, were not discriminated. In the latter, only a vacancy-oxygen (VO) pair and some other unknown complexes were detected. Within the limits of experimental techniques, these measurements clearly clarified the defect generation process. Subsequently, researchers have studied properties of the irradiation-induced defects themselves, such as vacancies and complexes of vacancies and impurities.

As mentioned, we can detect V, I, and FP's using hydrogen-doped specimens. Contrary to the previous studies and to the intuitive expectation mentioned in the second paragraph of this section, the optical-absorption intensities appear to be determined by both the mobility and generation rate of each point defect. Therefore interpretation of experimental results seems to be difficult. Even so, low-temperature irradiation of H-doped specimens are of value since, as mentioned, generation rates and mobilities of I and FP's have never been studied.

II. EXPERIMENT

Specimens were prepared from floating-zone (FZ) grown Si crystals of *n*-type (phosphorus concentration: 1.0

 ©2002 The American Physical Society

$\times 10^{16}$ cm^{-3}), high-purity (*p*-type: carrier concentration at RT was 4.5×10^{12} cm^{-3}), and *p*-type (boron concentration: 1.5×10^{16} cm^{-3}). After etching to the size of $4\times 6 \times 11$ mm^3, they were doped with hydrogen by being sealed in quartz capsules together with H_2 gas and heated at 1300 °C for 50 min followed by quenching in water. Hydrogen doped with the above method in Si is in a state of H_2 at RT.[10] The H_2 concentration was the same for all specimens since the doping condition of H was the same. The specimens were then irradiated at 270, 200, 130, and 77 K with 6-MeV electrons using a linear accelerator with irradiation doses of 8×10^{15}, 1.5×10^{16}, and 5×10^{16} cm^{-2}. Specimens were placed in a cooled nitrogen-gas flow during irradiation at the three above-mentioned temperatures and in liquid nitrogen during irradiation at 77 K. The specimen temperature was monitored with a thermocouple. We measured optical-absorption spectra of the specimens at about 7 K with an Fourier transform infrared (FTIR) spectrometer equipped with a continuous-flow-type liquid-He cryostat. The resolution was 0.25 cm^{-1}.

Specimens experienced RT for about 3 min while they were being set into the cryostat. Annealing during specimen setting, however, seemed to be absent since the optical-absorption spectrum strongly depended on the irradiation temperature as shown later. Hence the reaction between H_2 and point defects seemed to have finished during irradiation. This is in accordance with Whan and Vook's results[7] that concentrations of VO pairs and of some unidentified complexes did not change due to annealing at temperatures higher than irradiation temperature.

III. RESULTS

A. Defect generation

Prior to presenting the experimental results, we should consider the formation process of various complexes of point defects and H_2, which was briefly described in Sec. I. Due to irradiation of specimens with electrons of moderate energy, probably between 1 and 10 MeV, FP's are first formed. The generation of a FP itself probably does not depend on the irradiation temperature since it occurs due to energy transfer from high-energy electrons to Si atoms; the relevant energy is much higher than the thermal energy. Some FP's disappear due to the recombination of V and I, some diffuse to H_2 and some dissociate into V and I. These processes strongly depend on the irradiation temperature since diffusion and dissociation of FP's are thermally activated processes. The former results in the formation of complexes H_2^* and hence we can determine the concentration of surviving (i.e., neither recombined nor dissociated) FP's from optical absorption due to H_2^*. V and I also diffuse to various sinks and traps during irradiation. Their diffusion processes also depend on the irradiation temperature. There are many kinds of complexes for each point defect. Some form complexes with H_2, such as VH_2, V_2H_2, IH_2, and I_2H_2, where an IH_2, for example, is a complex of one self-interstitial and two H atoms. Some form complexes by themselves, for example, V_2. Hence it is difficult to obtain accurate mobilities of V, I, and FP's from the measurement of the concentrations of relevant complexes. The formation processes of all complexes must be fully analyzed to determine the mobilities of the above point defects. In the following, however, we simply assume that they mainly form complexes of IH_2, VH_2, and H_2^* and neglect the formation of larger complexes. Hence the accuracy of the deduced results may be insufficient. Numerical analyses of the defect formation process and defect migration process should be conducted in the future.

Contrary to the metastable Frenkel pair model where diffusion rates of point defects were neglected, we propose that the observed intensities (OA's) of the above complexes be considered as the multiplication of two factors, i.e., P_1 and P_2, where P_1 and P_2 are the generation rate and the mobility of relevant point defects, respectively. Namely, OA equals $P_1 \cdot P_2$. In the following, we first show the irradiation-temperature dependence of OA and then the results of mobility.

B. Irradiation temperature-dependent intensity

Figures 1(a)–(c) show optical-absorption spectra of Si crystals of high purity, *n* type and *p* type, respectively, irradiated at 270 and 130 K with an irradiation dose of 5×10^{16} cm^{-2}. As can be seen, the absorption due to IH_2 at 1987 and 1990 cm^{-1} in Fig. 1(a) was the strongest of the various peaks after the irradiation at 270 K. On the other hand, after irradiation at 130 K, it was much weaker than that with irradiation at 270 K; those of VH_2 and H_2^* were similar to those with irradiation at 270 K. Figure 1(b) shows spectra of *n*-type specimens. After RT irradiation, the absorption due to IH_2 is the strongest. The intensity due to VH_2 is much weaker than those in Figs. 1(a) and (c). This is due to the preferential formation of V-P pairs as shown in the previous study:[1,5] Vacancies preferentially form pairs with *P* and hence the concentration of VH_2 in *n*-type specimens is smaller than that in high-purity and *p*-type specimens. After irradiation at 130 K, the intensity due to H_2^* is the strongest. Figure 1(c) shows spectra of *p*-type specimens. The intensity due to VH_2 is strong after RT irradiation. The intensity of IH_2 is much weaker than those in Figs. 1(a) and (b), which is due to the action of Watkins' replacement mechanism.[2] Namely, the preferential replacement of occupation sites occurs between an I and a substitutional B:$\mathrm{I}+B(s)\rightarrow B(i)+\mathrm{Si}(s)$, where ($i$) and ($s$) denote the interstitial and substitutional sites, respectively. As shown above, optical-absorption spectra strongly depended on the irradiation temperature. Moreover, the spectra after low-temperature irradiation did not change due to annealing up to 50 °C. Hence, as mentioned, we concluded that the formation of complexes was completed during electron irradiation at low temperatures.

Figures 2(a)–(c) show a summary of the dependence of peak intensities of H_2^* (1838-cm^{-1} peak), IH_2 (1987-cm^{-1} peak), and VH_2 (2122-cm^{-1} peak) on the irradiation temperature in high-purity, *n*-type, and *p*-type specimens, respectively, after an irradiation dose of 5×10^{16} cm^{-2}. Solid, dashed, and chained lines were drawn to guide the eye. In

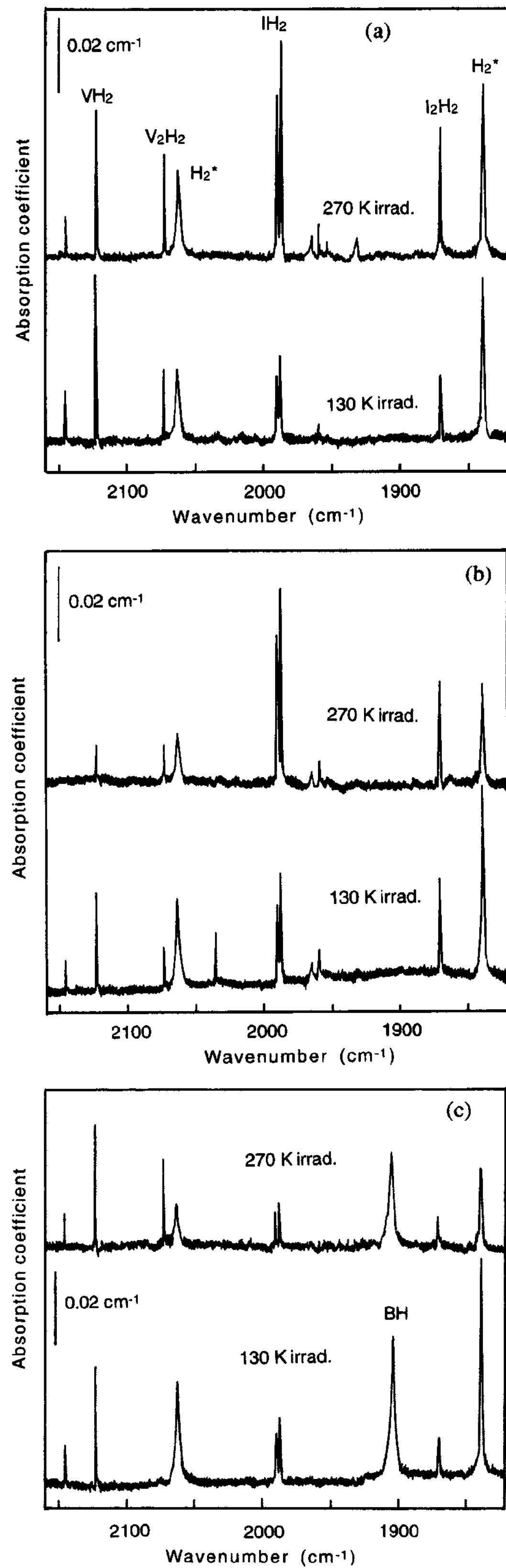

FIG. 1. Optical-absorption spectra of specimens of (a) high purity, (b) *n* type, and (c) *p* type, irradiated at 270 and 130 K. Electron dose was 5×10^{16} cm^{-2}. Complexes responsible for peaks were determined in previous studies.[3,4] BH denotes a boron-hydrogen pair.

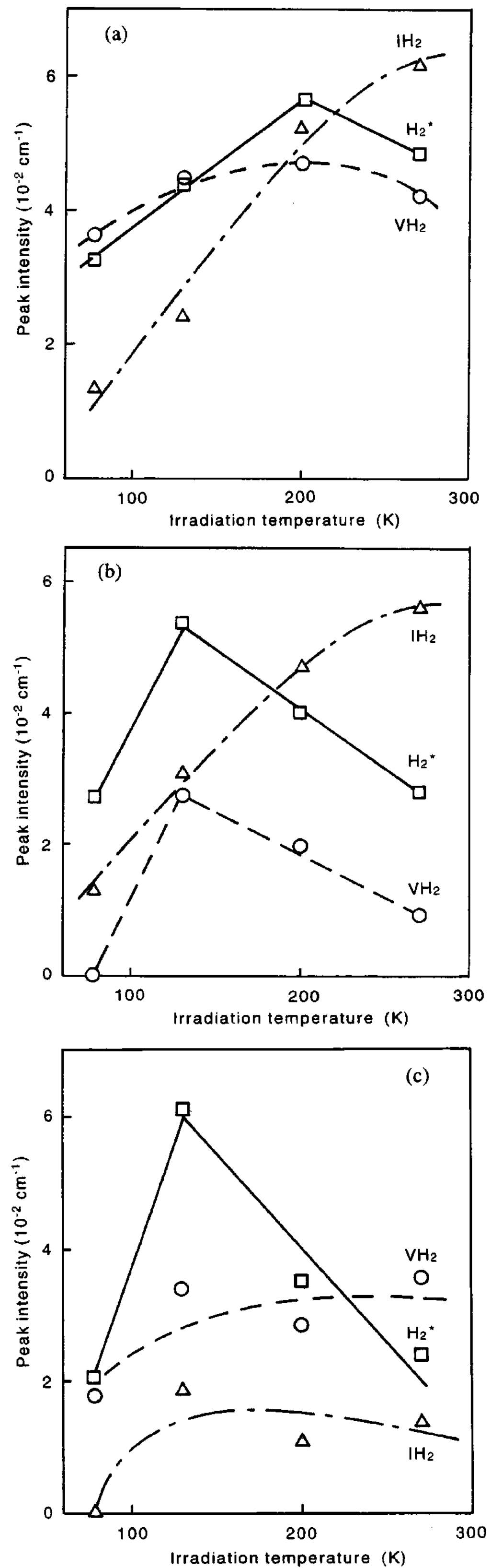

FIG. 2. Irradiation-temperature-dependence of peak intensities of high-purity (a), *n*-type (b), and *p*-type (c) specimens. Electron dose was 5×10^{16} cm^{-2}.

case of *n*-type specimens, the intensity of VH_2 was weak after 270-K irradiation. This is explained above.

In case of *p*-type Si specimens, the intensity of IH_2 was weak after 270-K irradiation. As explained above, this is due to Watkins' replacement effect. According to Fig. 2(c), the probability of the replacement of occupation sites seems to decrease due to irradiation at 130 K. No 1987- and 1990-cm^{-1} peaks, however, were observed after irradiation at 77 K. This is probably due to the lower concentration of I after irradiation at 77 K, as well as to the fact that Watkins' replacement mechanism works well at 77 K.

Intensities of some complexes in Figs. 2(a)–(c) show non-monotonic dependence on the irradiation temperature. This seems to support the proposal in Sec. III A that processes of more than one kind are involved in the formation of complexes.

As previously mentioned, complexes of H-point defects were formed due to the migration of point defects, i.e., V, I, and FP, to H_2. As shown in Figs. 2(a)–(c), the magnitudes of peak intensities due to IH_2, VH_2, and H_2^* (formed by a reaction between an H_2 and a FP) are different but more or less similar. Hence, qualitatively, these results show that the migration energies of V, I, and FP's are similar during electron irradiation. To our knowledge, no one has shown the diffusion of FP's. The migration of FP's suggests that it has a long lifetime, i.e., the annihilation of some FP's is difficult and there is probably an energy barrier for pair annihilation of V and I. This will be discussed in Sec. IV.

C. Migration energy of point defects

Migration energies of vacancies at various charge states in Si have been determined, i.e., 0.33,[11] 0.45,[12] and 0.18 (Ref. 13) eV for V^{--} (double-negatively charged V), V^0 (neutral V), and V^{++} (double-positively charged V), respectively. There has been no report of electron irradiation enhancement of vacancy diffusion. We adopted the above values as bases. Namely, we determined the migration energies of I and FP's relative to the above values. We estimated the dependences of relative quantities (initial slopes of intensities as explained below) of IH_2 and VH_2, and of H_2^* and VH_2, on temperature to determine the relative migration energies of I and FP's to that of V. Such a procedure is necessary to cancel the possible change of irradiation condition depending on the irradiation temperature and to cancel the irradiation temperature dependence of production of elementary point defects, i.e., V, I, and FP's, which is not fully understood as shown in Sec. III B. We studied the irradiation dose dependence of peak intensity at and above 130-K irradiation in detail. Figure 3 shows the dependence of peak intensities of VH_2 (circles), IH_2 (triangles), and H_2^* (squares) on the irradiation dose in high-purity specimens. With irradiation at 270 K, peak intensities were easily saturated. At 130 K on the other hand, they increased much more slowly with the electron dose than those at 270 K. From Fig. 3, we determined the initial slope of intensity of each complex, which is proportional to the initial formation rate. Figure 4 shows the dependence of the ratio of the initial slope on the irradiation temperature in high-purity specimens. From the dependence, we

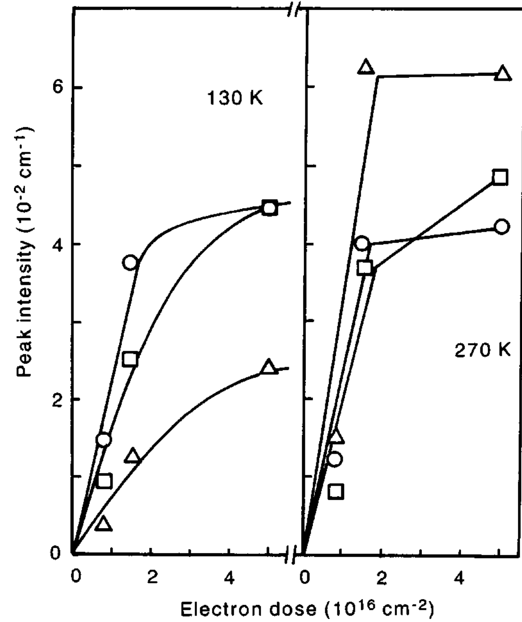

FIG. 3. Dose dependence of peak intensities of high-purity specimens irradiated at 130 and 270 K. Circles, triangles, and rectangles denote the intensities of VH_2, IH_2, and H_2^*, respectively.

obtained energies of 6.5 and 37.4 meV for H_2^*/VH_2 and IH_2/VH_2, respectively. These energies are thought to be the differences of migration energies of FP's and V and of I and V. They are much smaller than the migration energy of V^0 which is about 0.45 eV as shown above. Hence these results show that the migration energies of V, I, and FP's are similar during electron irradiation. This seems to be a rather unexpected result. One supporting evidence for our result is that the activation energies of self-diffusion via vacancy and self-interstitial have been reported to be rather similar.[14,15] Such small difference is expected to occur due to the difference of formation energies of those point defects. Table I shows a summary of the migration-energy difference in various crystals. The magnitude of migration energy of each point defect is the sum of the values in Table I and the migration energy of the vacancy in an appropriate charge state.

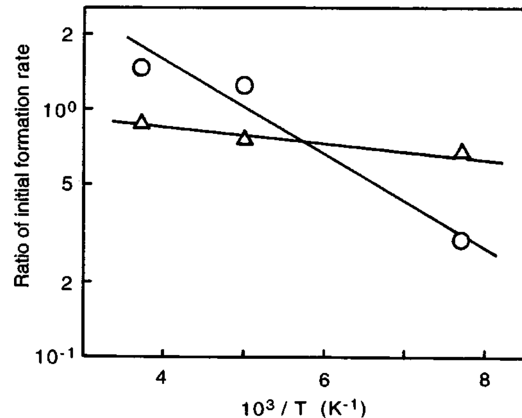

FIG. 4. Dependence of relative intensities on the irradiation temperature. Triangles and circles denote H_2^*/VH_2 and IH_2/VH_2, respectively.

TABLE I. Migration energies of I and FP's relative to that of V during electron irradiation.

	I, meV	FP, meV
High purity	−37	−6
n type	−50	−24
p type	+15	+21

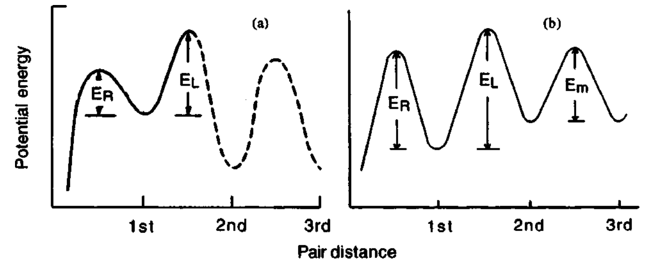

FIG. 5. Schematic of the metastable Frenkel pair model. (a) Slight modification of Fig. 3 of a paper by Vook and Stein and (b) proposed picture. In (b), the migration energy of the relevant point defect is smaller than the energy of recombination and liberation.

IV. DISCUSSION

A. Lifetime of Frenkel pair

As shown in Sec. III, some FP's diffuse to H_2 during electron irradiation and form H_2^*. This means that some FP's exist as pairs of V and I until arriving at H_2 after generation due to electron irradiation. Here, we roughly estimate the lifetime of FP's. The average separation of H_2 is about 46 nm (the H_2 concentration is around $1\times10^{16}\ \mathrm{cm}^{-3}$) and some FP's should survive longer than about 0.19 s as estimated from the diffusion time ($[Dt]^{1/2}=46$ nm, where D and t are the diffusion constant and diffusion time, respectively) of FP's to form H_2^* at RT. Here, the diffusion constant of FP's is assumed to be the same as that of V^0 [about $4\times10^{-3}\exp(-0.45\ \mathrm{eV/kT})$].[12] Recently, Tang *et al.*[16] studied the lifetime of Frenkel pairs by molecular-dynamic calculation. Their results do not agree with our results. According to them, the lifetime of an ordinary Frenkel pair is around 1 ps at RT. This lifetime is negligibly small compared with the above value. They also found a greatly stabilized configuration of a FP. The energy barrier for the recombination of that FP is estimated to be about 1.1 eV, which is too large to explain the above value.

FP's cannot diffuse if it keeps the same neighbor pair, for example, the first neighbor pair. It should change the kind of neighbor, for example, the first neighbor to the second neighbor and vice versa during diffusion. We have no idea, however, about the detailed diffusion mechanism of FP's.

B. Irradiation temperature dependence of optical-absorption intensities

As shown in Figs. 2(a)–(c), the intensities of optical absorptions due to complexes show different dependences on the irradiation temperature. As already mentioned, two models have been proposed,[8,9] both of which assume a metastable configuration of FP's. The issue of those models is whether the charge state of FP's affects the annihilation rate (a charge-state-limited model)[9] or not (a barrier-limited model).[8] In any case, the defect production rate depends on the irradiation temperature as $\{1+g\exp(E/kT)\}^{-1}$, where g, E, T, and k are a geometrical factor, an energy, the irradiation temperature and Boltzmann's constant. Energy E varies with the models. In case of the charge-state-limited model, it is the difference between the Fermi level and the energy level of the metastable pair. In the case of the barrier-limited model, it is the difference between the liberation barrier (E_L) and the recombination barrier (E_R) of the metastable pair.

When applying the above models to the experimental results, there has been no discussion on the mobility of point defects. As previously mentioned, this is because the optical-absorption spectrum did not depend on the annealing at temperatures higher than the irradiation temperature. For example, Whan and Vook[7] studied the formation of VO pairs in electron-irradiated Czochralski-grown Si crystals from the measurement of optical absorption due to VO pairs. They found "the formation energy" of VO pairs to be about 50 meV, assuming the barrier-limited model. This energy is an apparent one, namely, the difference between E_L and E_R in Fig. 5(a),[7] as interpreted by Vook and Stein.[17] To form a V-O pair, a V should diffuse to an O atom. The above value, however, is much smaller than the vacancy migration energy. This means that both E_L and E_R should be much larger than the migration energy of a point defect, V or I, because one successful jump is sufficient to liberate or recombine the Frenkel pair but long-distance migration is necessary for formation of a VO pair. Therefore, if the difference between E_L and the migration energy of V or I is small, the activation energy obtained should have been the same as the migration energy of V or I. Hence we propose an energy diagram as schematically shown in Fig. 5(b). In this model, E_L and E_R are larger than the migration energy of the relevant point defects. We could not determine the magnitudes of E_L and E_R.

According to Figs. 5(a) and (b), we can explain the result of Ehrhart and Zillingen.[15] From the measurement of the x-ray diffraction of Si crystals electron irradiated at 4.2 K, they observed that a high concentration of defects can be frozen in at 4 K and that a large fraction of defects is stabilized in the form of close FP's. This result clearly shows that a FP is stable at 4.2 K, suggesting the existence of the recombination barrier E_R. The models in Fig. 5, however, cannot be said to be superior based on experiments performed at such a low temperature.

C. Mobility of self-interstitials

It is well known that an I in *p*-type Si crystals diffuses in an athermal manner even at 4.2 K.[1] This athermal motion is explained as being due to the Bourgoin-Corbett mechanism.[3] According to this, the position where an I in one charge state is at a potential minimum which corresponds to a potential maximum for an I in another charge state. Thus an I will move toward its new minimum-potential position each time its charge state changes. How is this I generated? According

to Fig. 5(b), there is a barrier against liberation of FP's. Hence this liberation barrier itself should be almost 0 in *p*-type Si during electron irradiation. This means that there is excitation-induced liberation of FP's in a *p*-type Si crystal at 4.2 K.

According to our experiment, however, an I has migration energy even in *p*-type Si crystals at above 77 K. There are two possible reasons. The first is that the lifetime of the charge state at the maximum potential of I is shorter than the time for one atomic "movement" (not "jump" according to the Bourgoin-Corbett mechamism) for diffusion motion because of the thermal escape of the trapped charge at high temperatures. The other reason is that nonradiative recombination becomes dominant at high temperatures, making it difficult for the charge state of I to change. We have no idea now to determine which is the case.

V. CONCLUSION

We studied the effect of irradiation temperature on the formation of complexes of point defects and H_2 in hydrogenated Si crystals. Concentrations of complexes were found to depend on the irradiation temperature in a nonmonotonic manner. This was interpreted to be due to the fact that two kinds of processes, namely, the generation of point defects and the diffusion of point defects to H_2, were involved in the formation of complexes. We proposed a modified metastable Frenkel pair model in which the migration energy of the relevant point defect is smaller than the energies of recombination and liberation of the Frenkel pair. Relative initial slopes of intensities of optical-absorption peaks due to complexes of point defects and H_2 were found to strongly depend on the irradiation temperature. We interpreted those results under a simplified assumption that the relative initial slopes of intensities correspond to the relative mobilities of relevant point defects and determined the migration energies of self-interstitials and Frenkel pairs relative to that of vacancies.

ACKNOWLEDGMENTS

The authors thank the Laboratory for Advanced Materials for allowing us to use their FTIR spectrometer. This work was partly supported by the JSPS Research for the Future Program under the project "Ultimate Characterization Technique of SOI Wafers for Nano-scale LSI Devices" and a Grant-in-Aid for Scientific Research on Priority Area (B) "Manipulation of Atoms and Molecules by Electron excitation" from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

[1] As a review, see G. D. Watkins, *Materials Science and Technology*, edited by R. W. Cahn, P. Haasen, and E. J. Kramer (VCH, Weinheim, 1991), Vol. 4, Chap. 3, p. 105.
[2] G. D. Watkins, *Radiation Damage in Semiconductors*, edited by M. Hullin (Dunod, Paris, 1965), p. 97.
[3] J. Bourgoin and J. W. Corbett, Phys. Lett. **38A**, 135 (1972).
[4] M. Suezawa, Phys. Rev. B **63**, 035201 (2001).
[5] M. Suezawa, Phys. Rev. B **63**, 035203 (2001).
[6] As a review, see K. Wada, *Properties of Crystalline Silicon*, edited by R. Hull (INSPEC, London, 1999), p. 33.
[7] R. E. Whang and F. L. Vook, Phys. Rev. **153**, 814 (1967).
[8] G. K. Wertheim, Phys. Rev. **115**, 568 (1959).
[9] J. W. MacKay and E. E. Klontz, J. Appl. Phys. **30**, 1269 (1959).
[10] R. E. Pritchard, M. J. Ashwin, J. H. Tucker, R. C. Newman, E. C. Lightowlers, M. J. Binns, S. A. McQuaid, and R. Falster, Phys. Rev. B **56**, 13 118 (1997).
[11] G. D. Watkins, J. Phys. Soc. Jpn. Suppl. II **18**, 22 (1963).
[12] J. R. Troxell and A. P. Chatterjee, Inst. Phys. Conf. Ser. **46**, 16 (1979).
[13] J. R. Troxell and G. D. Watkins, Phys. Rev. B **22**, 921 (1980).
[14] H. Bracht, E. E. Haller, and R. Clark-Phelps, Phys. Rev. Lett. **81**, 393 (1998).
[15] A. Ural, P. B. Griffin, and J. D. Plummer, Phys. Rev. Lett. **83**, 3454 (1999).
[16] M. Tang, L. Colombo, J. Zhu, and T. Daiz de la Rubia, Phys. Rev. B **55**, 14 279 (1997).
[17] F. L. Vook and H. J. Stein, *Radiation Effects in Semiconductors*, edited by F. L. Vook (Plenum Press, New York, 1968), p. 99.