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Formation of defect complexes by electron-irradiation of hydrogenated crystalline silicon

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We studied properties of complexes responsible for the optical-absorption peaks at about 1870 and 2072 cm^{-1} which were formed by room-temperature electron-irradiation of hydrogenated Si. Specimens were *n*-type, *p*-type, and high-purity Si crystals. They were doped with hydrogen (H) and/or deuterium (D) by annealing at 1300 °C in H_2 and/or D_2 gas followed by quenching. They were then irradiated with 3-MV electrons at room temperature. We measured their optical-absorption spectra by a Fourier transform IR spectrometer at about 7 K. The 1870-cm^{-1} peak was weak in B-doped specimens and strong in high-purity and P-doped specimens. On the other hand, the 2072-cm^{-1} peak was weak in P-doped specimens and strong in high-purity and B-doped specimens. These results support the hypothesis that the 1870- and 2072-cm^{-1} peaks are due to complexes which include I (self-interstitial) and H and V (vacancy) and H, respectively. The intensities of both the 1870- and 2072-cm^{-1} peaks were proportional to the square of electron dose at low doses, which indicates that they are due to I_2H_2 and V_2H_2, respectively. In an isochronal annealing experiment, the 1870- and 2072-cm^{-1} peaks disappeared after annealing below 200 °C and 300 °C, respectively.

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I. INTRODUCTION

One of the issues concerning point defects generated by electron-irradiation of Si crystals is the detection of self-interstitials. Since the commencement of the study of electron-irradiation damages in Si, vacancies (V) and vacancy-related complexes have been detected by electron-spin resonance measurement.[1] Self-interstitials (I), however, have not been detected. This is interpreted to be due to the very fast athermal diffusion rate of I, the so-called Bourgoin-Corbett mechanism.[2] Hence, self-interstitials are interpreted to easily form complexes by themselves during irradiation, even at around 4 K.

We previously proposed a method to study point defects generated by electron-irradiation of Si via complexes of H and point defects using measurements of optical-absorption spectra due to H included in complexes.[3] From the results of experiments[4] conducted according to the above proposal, we experimentally identified complexes that are responsible for optical-absorption peaks, namely, IH_2 and VH_2 complexes for the 1987- and 1990-cm^{-1} peaks and the 2122-cm^{-1} peak[5] (the wave numbers are rounded off at the first decimal point), respectively. In these experiments, we used the effects of impurities on the concentration of intrisic point defects, I and V, in electron-irradiated Si. Namely, the I concentration is known to be low in B-doped Si, and the concentration of isolated V is low in P-doped Si.

In our previous studies,[4,5] we neglected the 1870-and 2072-cm^{-1} peaks. These peaks were not reported in a proton-implanted specimen. Recently, we noticed that the intensity of the 1870-cm^{-1} peak is fairly strong in high-purity and *n*-type specimens and weak in *p*-type specimens and, on the other hand, that the intensity of the 2072-cm^{-1} peak is fairly strong in high-purity and *p*-type specimens and weak in *n*-type specimens. These results strongly suggest that the 1870- and 2072-cm^{-1} peaks are related to complexes which include I and V, respectively. With the use of some additional specimens to those used in Ref. 4, we obtained results reported herein. In the following, we show some properties of the 1870- and 2072-cm^{-1} peaks, such as their spectra, their intensities in various specimens, and their isochronal annealing behaviors.

II. EXPERIMENTAL

Details of the experimental methods employed have been previously reported.[4] Hence, we only briefly describe them for the readers' convenience. Specimens were high-purity (*n* type; P concentration of about $4\times10^{12}\,\mathrm{cm}^{-3}$), *n* type ($1.5\times10^{16}$ P and $2.4\times10^{15}\,\mathrm{P\,cm}^{-3}$, abbreviated hereafter as PH and PL, respectively) and *p*-type (1.5×10^{16} B and $2.6\times10^{15}\,\mathrm{B\,cm}^{-3}$, abbreviated as BH and BL, respectively) floating-zone grown Si crystals. Specimens were prepared from the above crystals by mechanical and chemical treatments. To dope the specimens with H and/or D, they were sealed in quartz capsules together with H_2 and/or D_2 gas. They were heated at 1300 °C for 1 h followed by quenching in water. Most hydrogen atoms are in a state of H_2, HD, or D_2 (Ref. 6) in quenched specimens since hydrogen atoms form pairs during quenching to reduce the solubility which depends on the specimen temperature. Specimens were irradiated with 3-MV electrons at room temperature (RT). To determine the thermal stability of the H point-defect complexes, we conducted an isochronal annealing experiment at intervals of 25 °C with an annealing duration of 30 min. The optical-absorption spectra of those specimens were measured with an a Fourier transform (FT) IR spectrometer and a continuous-flow-type liquid-helium cryostat. The resolution was 0.25 cm^{-1}.

III. RESULTS

A. Spectra

1. The 1870-cm^{-1} peak

The observed absorption peaks were as follows: 2145, 2122, 2072, 2062, 1990, 1987, 1953, 1952, 1870, 1838, 1600, 817 and 719 cm^{-1}. Peak positions of most of these

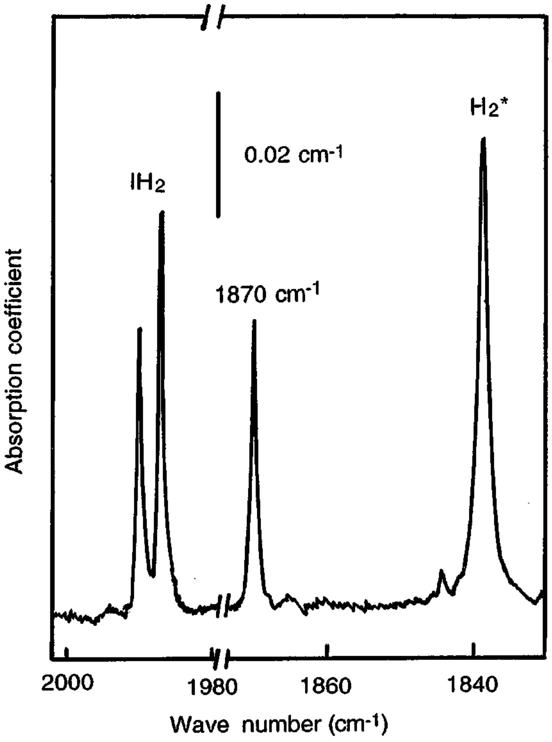

FIG. 1. The optical-absorption spectrum of electron-irradiated high-purity Si doped with H at around 1870 and 1990 cm^{-1}. The irradiation dose was $1.2\times10^{17}\,cm^{-2}$.

absorption peaks agree well with those observed in proton-implanted Si.[7] As mentioned in Sec. I, we herein mainly discuss the 1870- (more accurately, 1870.0) and 2072- (2072.5) cm^{-1} peaks.

Figure 1 shows parts of the optical-absorption spectrum at around 1860 and 1990 cm^{-1} of electron-irradiated Si doped with H_2. As mentioned, the 1870-cm^{-1} peak has not been reported in proton-implanted Si. The linewidth at half maximum [abbreviated as FWHM (full width at half maximum) hereafter] of the 1870-cm^{-1} peak is about 0.9 cm^{-1}. As a measure of defect density responsible for these peaks, we plot the peak intensity rather than the areal intensity in the following since the line shape of each peak does not depend on the irradiation dose and hence peak intensity is sufficient to trace the concentration of the defect with respect to the irradiation dose. Moreover, in the following, we do not discuss relative concentrations of various complexes in a quantitative manner since we do not have any data on oscillator strengths of complexes. The other three peaks are shown for convenience since they are referred to in the following. Defects responsible for the 1838-cm^{-1} peak and the 1987- and 1990-cm^{-1} peaks have been proposed to be H_2^* (Ref. 8) and IH_2 (Ref. 9), respectively. In a D-doped specimen, the 1870-cm^{-1} peak was not observed. Instead, a peak was observed at about 1365 (1364.9) cm^{-1}, as shown in Fig. 2. In a specimen codoped with H and D, those peaks split into two peaks, i.e., 1870- and 1869- (1868.7) cm^{-1} peaks and 1365- and 1364- (1363.8) cm^{-1} peaks, respectively. There is a weak peak at about 1364 cm^{-1} even in a D-doped specimen. This is due to contamination of H which comes from a quartz capsule. Hence, we conclude that the complexes responsible for the 1870-cm^{-1} peak include two H atoms. This conclusion is consistent with the fact that hydrogen atoms doped with the method adopted in this study are not in an isolated atomic state, but rather in a molecular state,[6] and hydrogen molecules are regarded to be immobile during irradiation since the migration energy of H_2 is about 0.78 eV.[10] Small separations of peaks due to codoping suggest that the interaction between two H atoms included in the complex is weak.

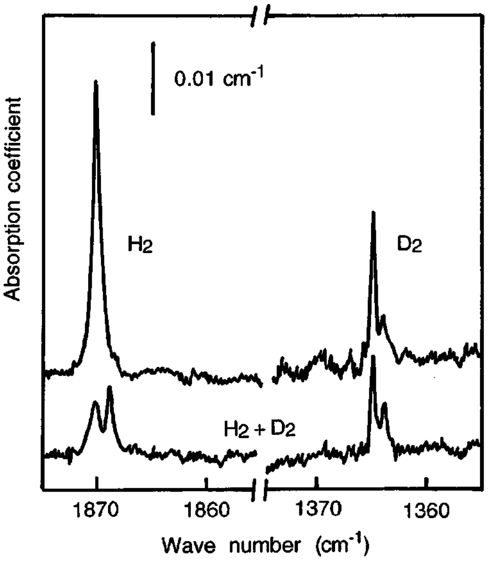

FIG. 2. Spectra around 1870 and 1365 due to doping of H_2 and D_2 and codoping of H_2 and D_2.

2. The 2072-cm^{-1} peak

Figure 3 shows a part of the optical-absorption spectrum

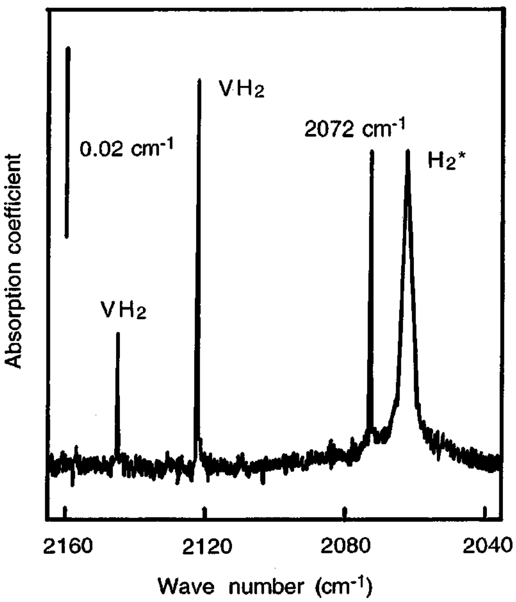

FIG. 3. The optical-absorption spectrum of electron-irradiated high-purity Si doped with H at around 2100 cm^{-1}. The irradiation dose was $1.2\times10^{17}\,cm^{-2}$.

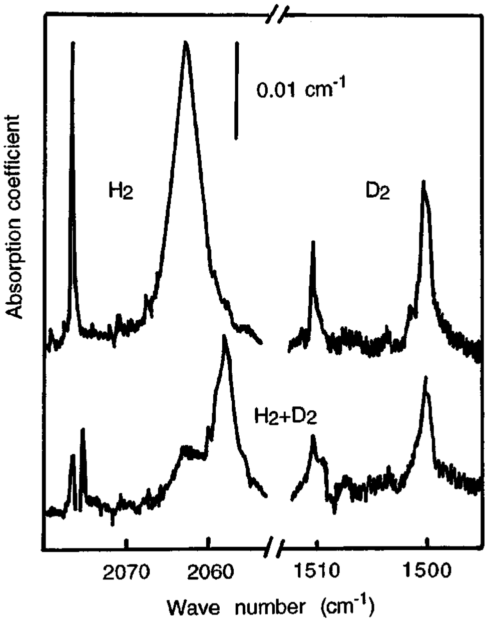

FIG. 4. Spectra around 2070 and 1510 due to doping of H_2 and D_2 and codoping of H_2 and D_2.

at around 2100 cm^{-1} of electron-irradiated Si doped with H_2. As mentioned, the 2072-cm^{-1} peak has not been reported in proton-implanted Si. The FWHM of the 2072-cm^{-1} peak is about 0.3 cm^{-1}. The other three peaks are shown for the sake of convenience since they are referred to in the following. Defects responsible for the 2122- and the 2145-cm^{-1} peaks have been proposed to be VH_2 with different vibrational modes.[7] In a D-doped specimen, the 2072-cm^{-1} peak was not observed. Instead, as shown in Fig. 4, a peak was observed at about 1510 (1510.4) cm^{-1}. In a specimen codoped with H and D, those peaks split into two peaks for each, i.e., 2072- and 2071- (2071.6) and 1510- and 1509-(1509.5) cm^{-1} peaks, respectively. Hence, we conclude that the complex responsible for the 2072-cm^{-1} peak includes two H atoms. Again this conclusion is consistent with the fact that hydrogen atoms doped with the method adopted in this study are not in an isolated atomic state, but rather in a molecular state.[6] Small separations of peaks due to codoping suggest that the interaction between two H atoms included in the complex is weak.

B. Specimen dependencies

1. The 1870-cm^{-1} peak

Figure 5 shows the optical-absorption spectra of a high-purity specimen and a BH specimen after electron-irradiation of 1.2×10^{17} cm^{-2}. The spectra were shifted along the ordinate for the sake of simplicity. The 1870-cm^{-1} peak intensity in the BH specimen was much weaker than that in the high-purity specimen. This result is interpreted to be due to the lower concentration of I in B-doped Si than that in high-purity Si because of the replacement of substitutional B, which becomes interstitial B, by I in the former crystal.[11] Hence, this result clearly shows that this peak is due to a complex of I and H, not V and H. The most remarkable point of this result is that we can detect I-related defects which have not been detected so far by other experimental methods, by its formation of a complex with H_2.

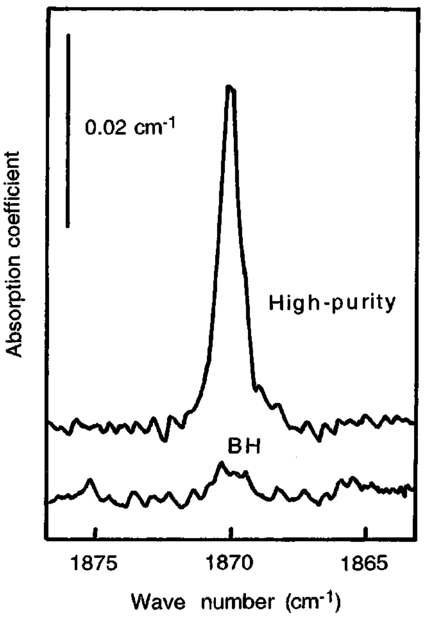

FIG. 5. Optical-absorption spectra of a high-purity specimen and a BH specimen at around 1870 cm^{-1}. The electron dose was $1.2\times10^{17}\,cm^{-2}$.

Figure 6 shows electron dose dependencies of the 1870-cm^{-1} peak intensity in various specimens. The dashed lines without data points are those of the 1987-cm^{-1} peak (IH_2 complex) and are shown for comparison's sake. The

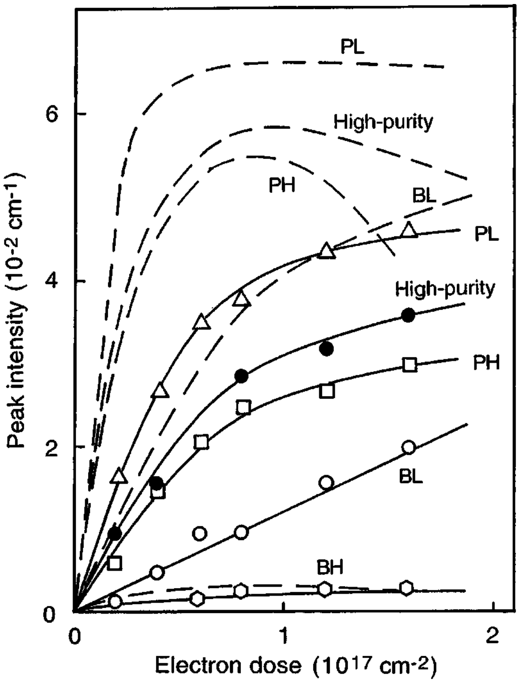

FIG. 6. The dependence of the peak intensity of the 1870-cm^{-1} peak on the electron dose in various specimens. Dashed lines are those of the 1987-cm^{-1} peak (IH_2).

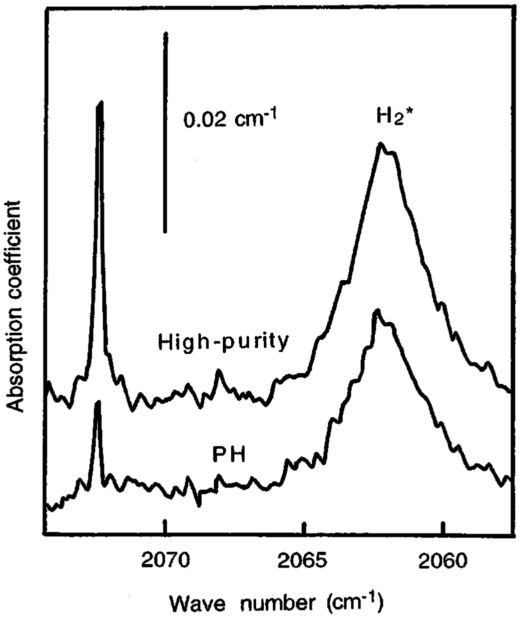

FIG. 7. Optical-absorption spectra of a high-purity specimen and a PH specimen at around 2070 cm^{-1}. The electron dose was $1.2\times10^{17}\,\mathrm{cm}^{-2}$.

most remarkable feature is a much weaker intensity of the peak in BL and BH specimens than those in other specimens. This indicates, again, that the 1870-cm^{-1} defect (termed a wave-number defect since it is responsible for the optical absorption at the wave number) includes self-interstitials. Another feature is that the intensity of the 1987-cm^{-1} peak is stronger than that of the 1870-cm^{-1} peak except in the BH specimen. This suggests that the 1987-cm^{-1} defect is more easily formed than the 1870-cm^{-1} defect under the assumption that oscillator strengths of those peaks are similar. There are differences in the peak intensity in PL, PH, and high-purity specimens. We attempt to explain these based on the interaction between dopants and point defects. In the PL and PH specimens, a V forms a pair with a P atom, resulting in a decrease of isolated V and thereby in a decrease of the mutual annihilation of I and V and finally in an increase in the concentration of I which reacts with H. Such a mechanism, however, cannot explain why the intensity in the PH specimen is lower than that in the PL specimen. We have not yet succeeded in explaining these differences.

2. The 2072-cm^{-1} peak

Figure 7 shows the optical-absorption spectra of a high-purity specimen and a PH specimen after electron-irradiation of $1.2\times10^{17}\,\mathrm{cm}^{-2}$. The spectra were shifted along the ordinate for the sake of simplicity. The 2072-cm^{-1} peak intensity in the PH specimen was much weaker than that in the high-purity specimen. This result is interpreted to be due to the lower concentration of V in P-doped Si than that in high-purity Si because of the formation of a VP pair in the former specimen. Hence, this result clearly shows that this peak is due to a complex of V and H, not I and H. The most remarkable point of this result is that we can detect V-related defects by its formation of a complex with H_2.

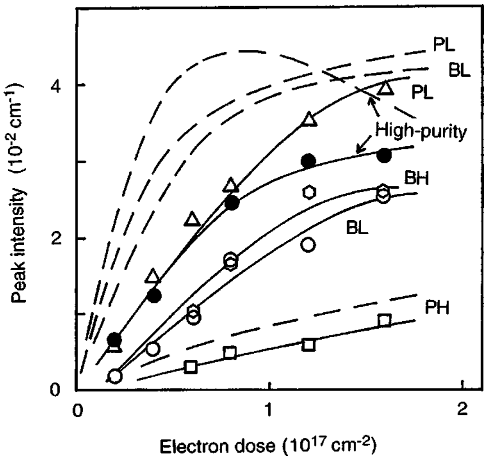

FIG. 8. The dependence of the peak intensity of the 2072-cm^{-1} peak on the electron dose in various specimens. Dashed lines are those of the 2122-cm^{-1} peak (VH_2).

Figure 8 shows electron dose dependencies of the 2072-cm^{-1} peak intensity in various specimens. The dashed lines without data points are those of the 2122-cm^{-1} peak (VH_2 complex) and are shown for comparison's sake. The most remarkable feature is the much weaker intensity of the peak in PH specimens than those in other specimens. This indicates that the 2072-cm^{-1} defect includes vacancies. Another feature is that the intensity of the 2122-cm^{-1} peak is stronger than that of the 2072-cm^{-1} peak. This suggests that the 2122-cm^{-1} defect is more easily formed than the 2072-cm^{-1} defect, assuming similar oscillator strengths of those peaks. Again, we have not yet succeeded in explaining the difference of the intensities in high-purity, BL, BH, and PL specimens.

C. Dose dependencies at low doses

To determine the number of I and V included in the 1870- and 2072-cm^{-1} defects, respectively, we studied dose dependencies of the intensities of 1870- and 2072-cm^{-1} peaks in high-purity specimens. If the number of I or V included in the complexes is n, the optical-absorption intensity should have nth power dependence on the electron dose at small doses since the concentrations of I and V are expected to be proportional to the electron dose at low doses. Figure 9 shows the dependencies of the intensities of the 1870- and 2072-cm^{-1} peaks on the electron dose. The intensities seem to be proportional to the square of the dose at low doses and then show weaker dependencies at higher doses, probably a tendency to become saturated. To ascertain these dependencies at small doses, we plot those intensities as functions of the square of the electron dose since a logarithmic plot sometimes does not give the correct dependence at small quantities. As shown in Fig. 10, the intensities are proportional to the square of the electron dose since the lines pass through the origin. Hence, we conclude that the number of I and V included in the 1870- and 2072-cm^{-1} defects, respectively, are two. Accordingly, combining these results with those of Sec. III B, we conclude that an I_2H_2 and a V_2H_2 are responsible for the 1870- and 2072-cm^{-1} peaks, respectively.

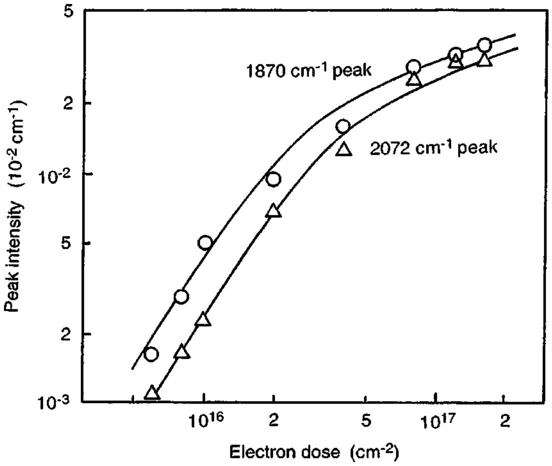

FIG. 9. The dependences of the 1870- and 2072-cm^{-1} peak intensities on the electron dose in high-purity specimens.

D. Isochronal annealing

Figure 11(a) shows the isochronal annealing behaviors of the 1870- 1987-, and 1838-cm^{-1} peaks, the latter two of which are due to IH_2 (Ref. 9) and H_2* (Ref. 8), H_2* being a metastable state of H_2.[12–14] The 1870- and 1838-cm^{-1} peaks have similar thermal stability. It is interesting that the thermal stability of the 1870-cm^{-1} peak is much lower than that of another I-related complex, IH_2.

Figure 11(b) shows the isochronal annealing behaviors of the 2072-, 2122-, 2166-, and 2223-cm^{-1} peaks. As shown in a separate paper,[5] the 2223-cm^{-1} defect (VH_4) is formed by the reaction between the 2122-cm^{-1} defect (VH_2) and H_2. The 2072-cm^{-1} defect is thermally more stable than the 2122-cm^{-1} defect. What is interesting is that the 2166-cm^{-1} peak seems to increase in parallel with the decrease of the 2072-cm^{-1} peak.

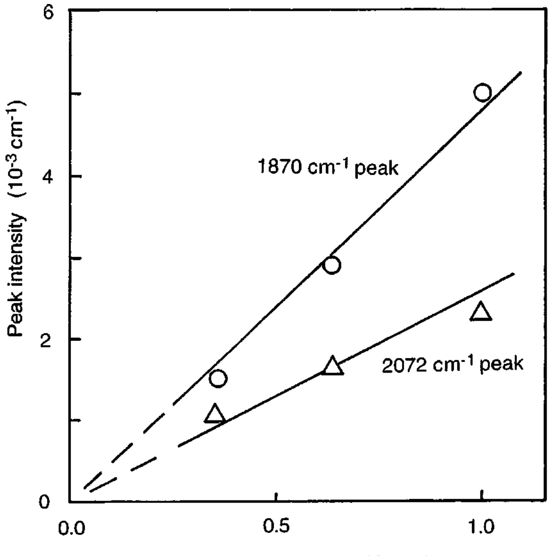

FIG. 10. The dependences of the 1870- and 2072-cm^{-1} peak intensities on the electron dose at low doses in high-purity specimens.

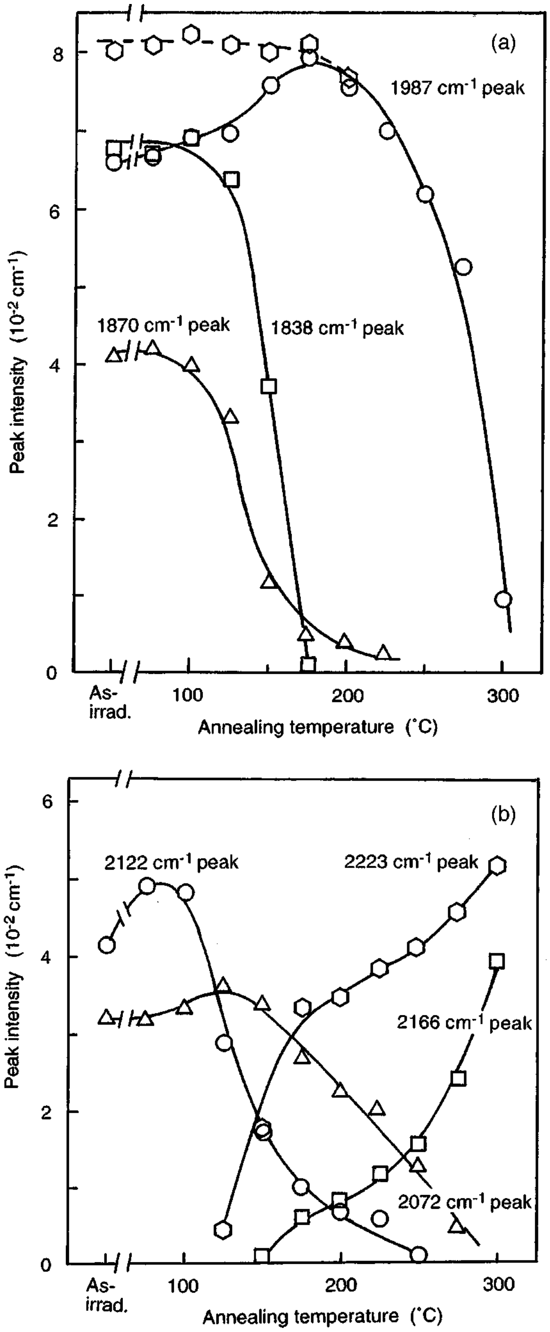

FIG. 11. Isochronal annealing curves of (a) the 1870-, 1838-, and 1987-cm^{-1} peaks and of (b) the 2072-, 2122-, 2223-, and 2166-cm^{-1} peaks in an electron-irradiated high-purity specimen. Annealing duration was 30 min at each temperature.

IV. DISCUSSION

As stated above, we propose that the 1870- and 2072-cm^{-1} peaks are due to the vibration of the H atom included in the I_2H_2 and V_2H_2 complexes, respectively. The I_2H_2 and I_2D_2 complexes have optical-absorption peaks at 1870 and 1365 cm^{-1}, respectively. On the other hand, the optical-absorption peaks of V_2H_2 and V_2D_2 are at 2072 and 1510 cm^{-1}, respectively. The frequency ratios of the former and the latter are about 1.370 and 1.372, respectively. These values are smaller than that (1.41) expected from the mass ratio of D and H. The latter value is deduced under the assumption that only an H atom vibrates.[15] This discrepancy is explained by introducing the reduced mass for a H vibrational mode, i.e., both H and Si atoms vibrate.[15] The above values are slightly smaller than that (1.39) deduced from such assumption, but such a discrepancy is often observed in the case of H included in complexes with point defects such as V and I.[7]

We suppose that both V and I bind with one H atom, namely, for example, a V_2H_2 is not $V \cdot VH_2$ but $HV \cdot VH$, where ''·'' means a binding of units of the left-hand side and the right-hand side and is herein used only when we need to emphasize the bonding state. This means that the properties of V_2H_2 and I_2H_2 complexes are expected to be rather similar to those of VH and IH pairs, respectively. Two supporting evidences for the above proposal are as follows. First, if a V_2H_2 is $V \cdot VH_2$ one would expect a spectrum similar to that of VH_2, i.e., two stretch modes separated by about 20 cm^{-1},[7] which is not consistent with the present results. Second, if it has the $HV \cdot VH$ structure proposed above, the frequency of H vibration is expected to be similar to that (2068 cm^{-1}) of V_2H,[16] which is consistent with our results. Based on the above models, a study of detailed vibrational modes of V_2H_2 and I_2H_2 appears to be necessary to fully understand the effect of codoping of H and D on the splittings of those peaks.

As already mentioned, the interaction between two H atoms seems to be small since the separations due to codoping are small. Theoretical studies of the IH pair have been conducted.[9,17] Van de Walle and Neugebauer[17] studied such properties as vibrational frequency and binding energy of the IH pair and the IH_2 complex based on the density-functional theory. According to them, the vibrational frequency of the IH pair is 1870 cm^{-1}. This agrees remarkably well with our experimental result. Of course, this agreement should not be over emphasized because their estimated frequency of IH_2 was 1915 cm^{-1}, while experimentally the frequencies are 1987 and 1990 cm^{-1}.[9]

As stated above, we propose that the 1870- and 2072-cm^{-1} peaks are due to an I_2H_2 complex and a V_2H_2 complex, respectively. What are the formation mechanisms of these complexes? Prior to discussion of this question, we should remember that most hydrogen atoms doped with our procedure are in the state of H_2.[6] Two mechanisms are possible for the formation of these complexes under this condition. One is the initial formation of VH_2 (IH_2) followed by the capture of another diffusing V (I) by VH_2 (IH_2). The other is the initial formation of V_2 (I_2) followed by the diffusion of V_2 (I_2) to an H_2. The former seems to be the case since the diffusion rate of V (I) is sufficiently fast to realize such formation and those of V_2 (I_2) and H_2 are too small to realize the latter case at around room temperature.[10] In reality, V_2 is known to be stable below about 250 °C,[18] which means that there is no diffusion motion of V_2 below this temperature. After the formation of $V \cdot VH_2$ ($I \cdot IH_2$), one H atom probably changes sites and forms an $HV \cdot VH$ ($HI \cdot IH$) since the latter seems to be in a lower-energy state because of the interaction between two H atoms. Figures 6 and 8 semiquantitatively support these formation mechanisms: The formation rates of I_2H_2 and V_2H_2 are smaller than those of IH_2 and VH_2 and the saturations of I_2H_2 and V_2H_2 seem to appear at higher doses than those of IH_2 and VH_2.

From the results of the isochronal annealing experiment shown in Fig. 11(a), we know that the thermal stability of I_2H_2 is similar to that of H_2^*. Hence, the activation energy necessary for the decrease of I_2H_2 may be similar to that [about 1.5 eV (Ref. 5)] of H_2^*, which well agrees with that (1.34 eV) estimated by Van de Walle and Neugebauer.[17] We should, however, be careful since we previously found that much different activation energies were obtained for two kinds of defects which showed similar isochronal annealing behaviors.[5] Generally, two annealing processes are possible. The first is the dissociation of complexes and the second is the growth of complexes by capture of other defects. Applied to this case, the former corresponds to a dissociation reaction of, for example, $I_2H_2 \rightarrow I_2H + H$, and the latter corresponds to a growth reaction of $I_2H_2 + H_2 \rightarrow I_2H_4$. If these processes occur in similar temperature ranges, we can discriminate them by their activation energies and the frequency factors which dominate the time constants of the annealing processes.[5] In the former case, both the activation energy and the frequency factor, the so-called attempt frequency, are large since only one successful jump of a constituent defect, for example H, of the complex is sufficient to dissociate a complex. On the other hand, they are small in the latter case since diffusion of the other defect, for example H_2, is involved in the annealing process (i.e., growth process). In this case, the observed frequency factor is the concentration of the complex (I_2H_2) multiplied by the attempt frequency of the other defect (H_2). According to Fig. 11(a), the annealing temperature range of the 1838-cm^{-1} peak is much smaller than that of the 1870-cm^{-1} peak. As shown in a separate paper, the annealing of the 1838 cm^{-1} peak is due to the dissociation of H_2^*.[5] This strongly suggests that the annealing process of the 1870-cm^{-1} peak is not dissociation but rather growth due to a reaction with a diffusing H_2 molecule. In the latter case, there is a tendency for the annealing temperature range to widen since there is a distribution of the complex (I_2H_2 in this case), and hence distribution of the time constant of the annealing. Another possible support for the growth process comes from the behaviors of the hexagons in Fig. 11(a), which are the sum of the 1987-cm^{-1} peak intensity and 1/3 of the 1870-cm^{-1} peak intensity. They are almost constant at temperatures below the annealing temperature of the 1987-cm^{-1} peak. One interpretation of this is as follows. As already shown in a separate paper,[10] H_2 molecules in Si diffuse over a long distance at around 100 °C with an activation energy of about 0.78 eV. A H_2 molecule is captured by an I_2H_2, resulting in the formation of an I_2H_4 which is thought to result from the bonding of $H_2I \cdot IH_2$. The frequency of H in the I_2H_4 may be the same as that of IH_2 since the separation between H atoms in the complexes of I and H is expected to be large because of a split configuration of I as schematically shown by Van de Walle and Neugebauer.[17] If this interpretation is correct, the oscillator strength of I_2H_2 is 1.5 times greater than that of IH_2 because the contribution of one I_2H_4 to the optical absorption is effectively that of two I_2H_2.

In Fig. 11(b), the intensities of the 2122- and 2072-cm^{-1} peaks increase slightly at low temperatures. We cannot offer any explanation of this phenomenon. As shown in a separate paper,[5] the 2223-cm^{-1} defect is generated by a reaction between a 2122-cm^{-1} defect and H_2. The 2166-cm^{-1} peak intensity seems to increase in parallel with the decrease of the 2072-cm^{-1} peak intensity. We have already determined the activation energy [1.2 eV (Ref. 5)] and frequency factor (4.4×10^9 s^{-1}) for the generation of this defect. This energy is larger than that of H_2 diffusion. Hence, this annealing process does not seem to correspond to the reaction of $V_2H_2+H_2\rightarrow V_2H_4$. However, there is a possibility that the activation energy (1.2 eV) corresponds to that of the dissociation of the H_2 supplier. The number of H atoms included in the 2166-cm^{-1} defect should be determined by an experiment of codoping of H and D and the activation energy of the decrease of the 2072-cm^{-1} defect. Recently, Budde *et al.*[19] proposed that the 2166-cm^{-1} defect observed in proton-implanted Si is due to V_2H_6. They observed another peak at 2191 cm^{-1}, which is interpreted to be due to another vibrational mode of the 2166-cm^{-1} defect. Our 2166-cm^{-1} defect seems to be different from V_2H_6 because of the following two reasons. First, we did not observe a 2191-cm^{-1} peak associated with the increase of the 2166-cm^{-1} peak. Second, the probability of the formation of V_2H_6 seems to be small since two H_2 should come to a V_2H_2.

Finally, we should refer to the 2073.2-cm^{-1} peak observed in proton-implanted Si (Ref. 16) since this peak position is very near our 2072-cm^{-1} peak. The complexes responsible for these two peaks, however, seem to be much different. According to Stallinga *et al.*,[16] the 2073.2-cm^{-1} peak is due to a V_nH^0, $n=3$ and 4. In our specimen, the probability of the formation of such a large cluster of V seems to be low since the electron dose is not high. Moreover, complexes in our specimen include two hydrogen atoms. Hence, we again conclude that the above two peaks are due to different complexes.

V. CONCLUSION

From the dependence of the intensity of the 1870- and 2072-cm^{-1} peaks on dopants and from the peak positions and peak splitting due to codoping of H and D, we conclude that the 1870- and 2072-cm^{-1} peaks are due to an I_2H_2 complex and a V_2H_2 complex, respectively. The determination of the activation energies necessary for the decrease of these complexes by isothermal annealing experiments is of interest.

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