Influence of high-energy electron irradiation on the formation and annihilation of the photoluminescence *W* center and the center's origin in a proton-implanted silicon crystal

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The population change of the photoluminescence (PL) *W* center (or I_I center) with 2-MeV electron irradiation in proton-implanted silicon crystal was observed to investigate the origin of the center. While a straightforward annihilation of the *W* centers formed by proton implantation with an increase of the electron fluence was observed in the low fluence region, the number of centers increased in the high fluence region ($>2\times10^{18}$ electron/cm^2) due to the predominance of formation over annihilation. The annihilation and formation of the *W* centers were analyzed as first and second order with respect to the numbers of vacancies and self-interstitials, respectively. The efficiency of the *W*-center formation from element pairs produced by electron irradiation was much smaller than that for ion implantation. Considering the findings obtained in the present study and those given by other studies, the $\langle 111\rangle$ split monointerstitial and the $\langle 111\rangle$ ST di-interstitial (ST: split triple) were chosen as the probable candidates for the *W* center.

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I. INTRODUCTION

Nowadays, ion implantation is indispensable for manufacturing silicon electronic devices. Self-interstitials (Si_I's) and vacancies (V's) are intrinsic element pairs plentifully formed in the implanted crystal, which aggregate to form pointlike defects at low temperatures and extended defects at elevated temperatures, bond to impurities to form various complexes, and stimulate complex formation between impurities.[1–3] The structures and behaviors of vacancy-related pointlike defects or small clusters such as V_2 and V_mO_n (m and n are integers) are relatively well characterized by optical, electric, and magnetic resonance measurements.[2,4,5] For interstitial-related clusters, while the structural properties of extended defects such as the {311} defects are well analyzed,[6] even the existence of small clusters is inferred from indirect evidence such as transient enhanced diffusion (TED) of dopants,[7] although a number of theoretical models have been proposed.[8–11] A defect called the *W* or I_I center,[1,12] whose no-phonon photoluminescence (PL) peak is located at 1.018 eV, is commonly observed from Si crystals implanted with various ions[1,12,13] and it has been believed to be a self-interstitial small cluster due to its lack of impurities and its less compressive nature.[10,12] The possibility of assigning the *W* center as a vacancy-related defect such as V_2 has been ruled out from the thermal behaviors of the center[14] and the lack of oxygen participation in the formation of the center[15] except for carbon implantation.[16] Determination of the structure of the *W* center, accordingly, provides a key guide for the theoretical investigation of stable configurations of the self-interstitial small clusters existing at relatively low temperatures ($<500\,°C$). From the uniaxial stress measurement, the symmetry of the *W* center was determined to be $\langle 111\rangle$ trigonal.[12,17,18] Possible self-interstitial models of the center satisfying the $\langle 111\rangle$ trigonal symmetry are a $\langle 111\rangle$-split monointerstitial,[1,12,17] a $\langle 111\rangle$-split di-interstitial,[8] and tri-interstitial clusters.[10,11,14] However, since there are few probes to analyze the *W* center due to the inactivity of the center in electric and magnetic measurements, a determination of the makeup of the center has been quite difficult. In a previous study, the dependence of the formation of the *W* center on the implantation fluence of protons was observed, and the second-order relationship between the *W*-center intensity for the advanced annealing stage and the implantation fluence was analyzed by employing the law of mass action,[15] i.e., the *W*-center formation was second order with respect to the number of the element pairs produced by the implantation. From this observation and the symmetry of the *W* center, the $\langle 111\rangle$ monointerstitial model was chosen to be the most probable. While the observation offers considerable support to construct the *W*-center model, more experiments are needed to promote a sound model of the *W* center. On the other hand, the element pairs produced by an appropriate method are thought to be useful probes to characterize the center, i.e., the observation of population change of the pre-existing centers, occurring through possible interactions between the centers and element pairs, would provide useful information about the formation and annihilation kinetics of the center.

It is well known that the irradiation of high-energy electrons (>400 keV) for Si crystal produces uniform element pairs which lead to various complexes such as *G* (C_S-Si_I-C_S, S stands for substitutional and $_I$ for interstitial) and C (C_I-O_I) centers.[1] Since the production efficiencies of the element pairs by electrons are very small (about 2/cm for a 2-MeV electron),[19] it is preferable to employ electron irradiation to observe the detailed interaction between the *W* centers and element pairs. For the formation of the *W* centers by electron irradiation, however, there are only a few, mostly contradictory reports. While some researchers observed *W* centers on annealing the Si crystal at 200 °C after irradiation of the sample with $1\times10^{17}/cm^2$ electrons having an energy of 2.5 MeV,[20] others found that irradiation with electrons having a lower energy than 10 MeV did not produce the centers.[21] It would also be interesting to know whether the *W* centers are formed by electron irradiation with a lower energy than 10 MeV.

The subject of this study was to determine the makeup of the *W* center through the observation of the population change of the centers which occurred by electron irradiation. In order to avoid serious lattice damage[15,21] and to minimize formation of by-products such as *G* and *C* centers, protons were employed for the implantation source for the formation of the pre-existing *W* centers. From the observations in the present study, the order of the formation of the *W* center was determined to be second-order with respect to the electron fluence (Sec. III B) and probable structures of the center were proposed (Sec. III D).

II. EXPERIMENT

The samples were 1 mm thick (100) Czochralski (Cz)-grown silicon crystals doped with $(2-7)\times10^{14}/cm^3$ of boron (*p*-type). The oxygen concentration in the crystals was about $9\times10^{17}/cm^3$. The implantation energy for protons was 180 keV with fluences (H_{ip}) between 1×10^{11} and 1×10^{15} ion/cm^2 which produced no amorphous phase.[15] The implantation rates of protons were 4.4×10^9, 4.4×10^{10}, 4.4×10^{11}, and 4.4×10^{12} ion/cm^2 s for fluences of 10^{11}, 10^{12}, 10^{13}, and $10^{14}-10^{15}$ ion/cm^2, respectively. The implantation was done at room temperature using samples mounted with a 7° tilt with respect to the incident beam. In order to understand the depth profiles of the element pairs and implanted ions, Monte Carlo simulation was done using the TRIM (transport of ions in matter) program.[22] The range of the implanted protons simulated from TRIM was about 1.5 μm. After the ion implantation, electron irradiation was performed. The irradiation energy of the electrons (e^-) was 2.0 MeV, with fluences between 1.1×10^{14} and 5.0×10^{18} e^-/cm^2. The rates of the electron irradiation were 3.5×10^{12}, 3.5×10^{13}, and 2.6×10^{14} e^-/cm^2 s for the fluence ranges $1.1\times10^{14}-1.0\times10^{15}$, $1.1\times10^{15}-1.0\times10^{17}$, and $1.1\times10^{17}-5.0\times10^{18}$ e^-/cm^2, respectively. During the electron irradiation, the sample temperature was always kept below 130 °C by mounting the samples on a water-cooled copper plate.

The PL measurements were done in a standard luminescence setup.[23] The samples were kept at constant temperature (4.2 K) in a liquid helium-cooled cryostat. The excitation light was a 488-nm Ar-ion laser line at a laser power of 100 mW in front of the cryostat window. The luminescence was detected by a liquid-nitrogen-cooled Ge photodiode, and a conventional lock-in amplifier processed the signal. The scattering of the intensity of the PL peak of the reference samples was within 10% from run to run.

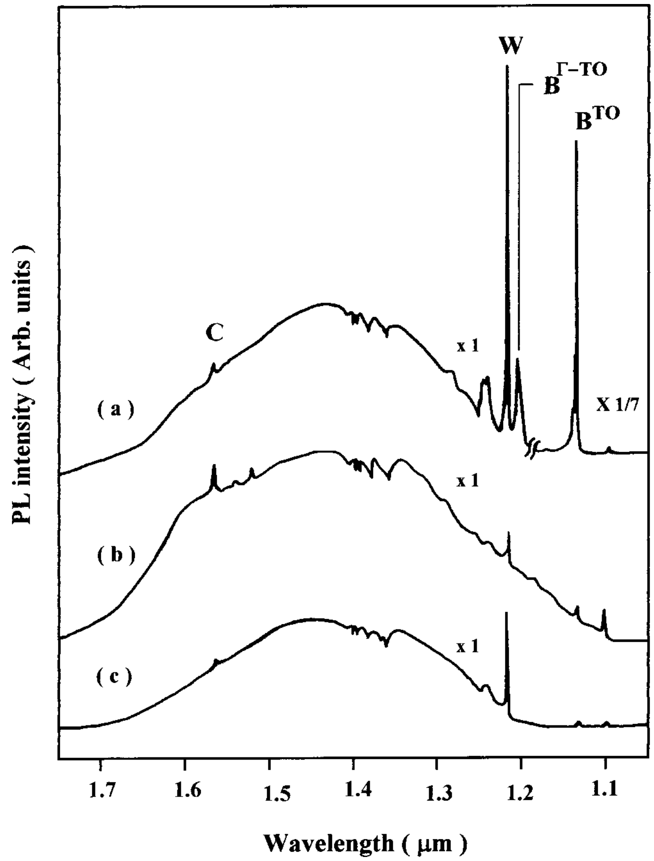

FIG. 1. Changes in the PL spectrum caused by electron irradiation for proton-implanted *p*-type Cz samples. The proton fluence was $1\times10^{13}/cm^2$ at an energy of 180 keV. (a) The PL spectrum for as-proton implanted sample. (b) and (c) The PL spectra for samples electron-irradiated with fluences of 6.3×10^{17} and $5.0\times10^{18}/cm^2$ at an energy of 2.0 MeV, respectively, after proton implantation with the same fluence as for sample (a).

III. RESULTS AND DISCUSSION

A. Change of PL intensity with electron fluence

Changes of the PL spectrum with electron irradiation fluence for the proton-implanted samples were measured. Figure 1(a) shows the PL spectrum for the sample immediately after the proton implantation (as-implanted) with the fluence of 1×10^{13} ion/cm^2. Figures 1(b) and 1(c) show the PL spectra for the samples electron irradiated with fluences 6.3×10^{17} and 5.0×10^{18} e^-/cm^2, respectively, after proton implantation with the same fluence as for sample (a). For the as-implanted sample, the strongest peak at 1.135 μm is due to the transverse optical (TO) phonon replica of boron bound excitons B^{TO}. A significantly large no-phonon peak (1.22 μm: 1.018 eV) for the *W* centers and their phonon replica peaks on the longer wavelength side are seen. A small peak for the C centers at 1.57 μm is also seen in the same spectrum. A broad peak which has been thought to be due to the strained region[24] occurs between 1.2 and 1.6 μm. The fine structure formed on this peak at around 1.3–1.4 μm is due to water vapor absorption. With the increase of the irradiation electron fluence on the implanted sample, a decrease of the PL intensities of the *W* centers and B^{TO}, and an increase of

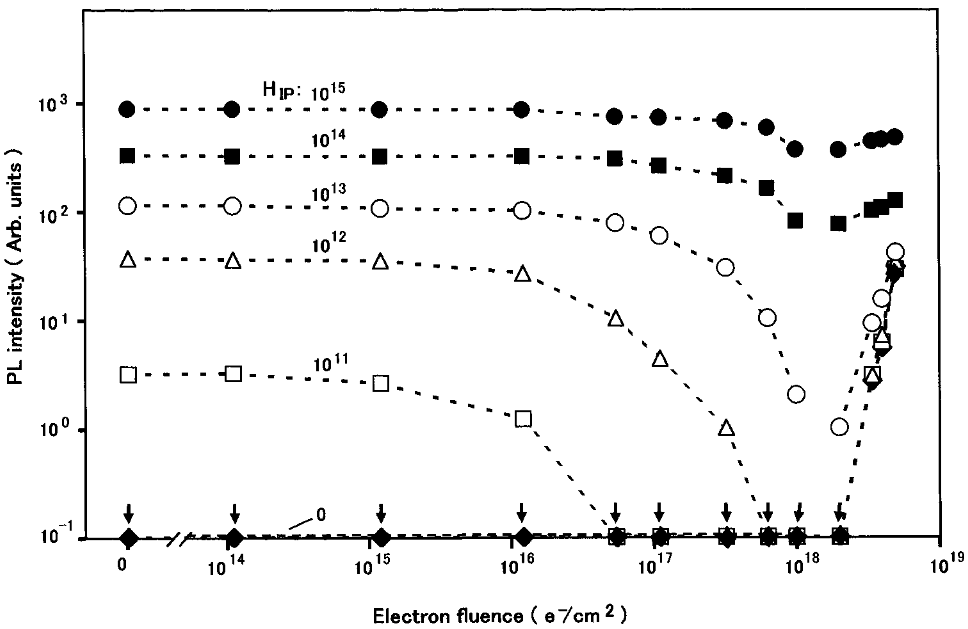

FIG. 2. Changes of the PL intensity of the no-phonon 1.018-eV peak of the *W* center with electron fluence for proton-implanted samples of various fluences. The numbers in the figure are the implantation fluences (H_{IP}) of protons. The arrows indicate that the intensities are below the detection limit of the instrument. The broken lines are only visual guides.

the *C*-center PL intensity are seen [Fig. 1(b)]. It is significant that the PL intensity of the *W* centers again increases with a further increase of the electron fluence [Fig. 1(c)].

Detailed changes of the PL intensity of the no-phonon *W*-center peak with the electron fluence for the samples with various implantation fluences are shown in Fig. 2. The result for the sample without proton implantation ($H_{IP}=0$ ion/cm^2) is also shown. The PL intensities of the *W* centers for all the implanted samples decrease in a straightforward manner with the increase of the electron fluence until around 1×10^{18} e^-/cm^2. The PL intensities for the samples with the proton fluence smaller than 1×10^{12} ion/cm^2 drop to the detection limit of the instrument before reaching an electron fluence of 1×10^{18} e^-/cm^2. However, when the electron fluence is increased above 2×10^{18} e^-/cm^2, the PL intensities for the implanted samples increase again. The important items seen are the emergence of the *W* centers for the unimplanted sample ($H_{ip}=0$ ion/cm^2) at the electron fluence of 3.4×10^{18} e^-/cm^2 and the further increase of the intensity of the centers with an increase of the electron fluence, indicating that increases of the PL intensity above the fluence of 2×10^{18} e^-/cm^2 for the implanted samples are also due to the centers newly formed by the electron irradiation. The trends of Fig. 2 are thought to result from a competition between the annihilation and formation of the *W* centers. It is reasonable to assume that the annihilation of the *W* centers occurs by a reaction of the center with different kind of elements from that of the center. When the annihilation is assumed to occur by the attack of the same kind of elements as the *W* center or by a direct hit of an incident electron, the increase (and the new formation) of the centers in the higher-fluence region cannot be explained. Since Si_I is assumed to be the element of the *W* center, an annihilation of the centers occurs by the attack of *V* and the formation occurs by aggregation of Si_I. Results of this study emphasize that the *W* centers are formed by the irradiation of 2-MeV electrons with considerable fluences ($>2\times10^{18}$ e^-/cm^2). The reason why the *W* centers were not observed by electron irradiation at a lower energy than 10 MeV, as reported by others,[21] is thought to be due to the lack of sufficient electron fluence. The observation of the *W* centers for the sample irradiated with low fluence of 1×10^{17} e^-/cm^2 at 2.5 MeV and a subsequent annealing at 200 °C (Ref. 20) is thought to be due to more than one order enhancement of the PL intensity by the annealing (see Ref. 15).

For comparison, changes of the PL intensities for B^{TO} and the *C* center with the electron fluence are shown in Fig. 3, where only the data for two end samples (H_{IP}:0 and 1×10^{15} ion/cm^2) are shown. For the intermediately implanted samples (H_{ip}:1×10^{11}–1×10^{14} ion/cm^2), the data points are located between the data for the two end samples. The PL intensities of B^{TO} for both samples decrease to the detection limit of the instrument at the electron fluence of 1×10^{17} e^-/cm^2, slightly recover by a further increase of the fluence, and peak at around 1×10^{18} e^-/cm^2. There is no difference in the decrease trend of the PL intensity of B^{TO} between the implanted and unimplanted samples. The PL intensities of the *C* center increase with the increase of the electron fluence, form a hill at around 1×10^{17} e^-/cm^2, and decrease gradually with the further increase of the fluence. There is also no essential difference in the intensity curves of the *C*-center peak between the implanted and unimplanted samples, except that the intensity of the former was slightly larger than that of the latter in the low electron fluence region due to the preexisting center formed by the implantation before the electron irradiation.

The changes of the PL intensities of B^{TO} and the *C* center with the electron irradiation are explained by the known reactions of the elements. The straightforward decrease of the PL intensity of B^{TO} in the region of lower electron fluence than 1×10^{17} e^-/cm^2 is explained by the formation of a complex *B*-Si_I due to the reaction of neutral *B* with free Si_I produced by the electron irradiation.[25,26] The reincrease of the B^{TO} intensity in the region of high fluence around 1×10^{18} e^-/cm^2 is explained by the recovery of neutral *B* due

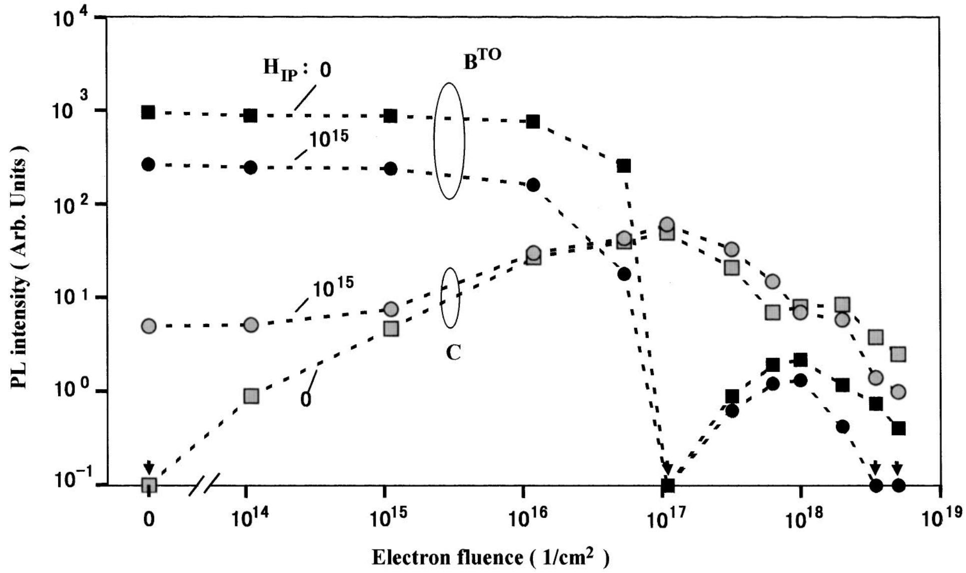

FIG. 3. Changes of the PL intensity of B^{TO} (full marks) and the C-center peak (hatched marks) with electron fluence for the sample proton implanted with $1\times10^{15}/\mathrm{cm}^2$ and the sample without proton implantation. The numbers in the figure are the implantation fluences (H_{IP}) of protons. The arrows indicate that the intensities are below the detection limit of the instrument. The broken lines are only visual guides.

to the reaction of B-Si_I with V, although the reason why it occurs in this region is not clear. For the C-center peak, the increase in intensity in the low fluence region is explained by the formation of a complex C_I-O_I due to the successive reactions: $Si_I+C_S\rightarrow Si+C_I$ and the $C_I+O_I\rightarrow C_I$-O_I.[19,25] The decrease of the intensity in the high fluence region is explained by the predominant formation of a complex $(C_I$-$O_I)Si_I$.[19,25] The gentle change of the intensity is due to the competing reactions of formation and annihilation of the C center. Assuming the law of mass action, these reactions of the complex formation are explained as first-order with respect to the number of Si_I (or electron fluence). The observation that changes of the PL intensities of B^{TO} and the C center with electron fluence are not influenced by the number of W centers (i.e., ion implantation fluence) does not contradict the assumptions that the W centers are composed of Si_I's, and are annihilated by V's.

B. Analysis of the population change of the *W* centers

In order to investigate the annihilation kinetics of the W centers, decreases of the PL intensity of the center from the as-implanted values, obtained from Fig. 2, are shown in Fig. 4 for electron fluences between 10^{16} and 10^{18} e^-/cm^2, where the change of the PL intensities is remarkable for all the implanted samples. A linear relationship between decrease of the PL intensity and the electron fluence is seen in the region of the remarkable change of the intensity for each implantation fluence except for the sample with the implantation fluence 1×10^{11} ion/cm^2 (an accurate slope is not obtained for this sample due to the lack of data points). There is a tendency, however, that the decrease of the PL intensity for the larger implantation fluences is slightly larger than that for smaller implantation fluences for the same electron fluence, indicating that the annihilation of the centers is influenced by vacancy-capturing impurities such as oxygen, and is not

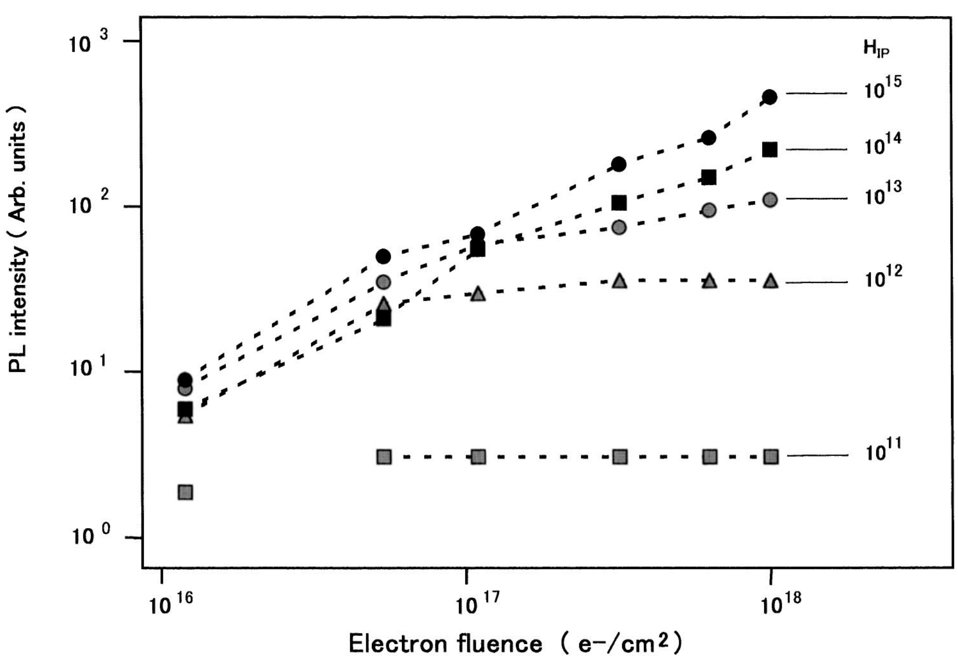

FIG. 4. Decrease of the PL intensity of the no-phonon 1.018-eV peak of the W center from the as-implanted value with electron fluence. The numbers in the figure are the implantation fluences (H_{IP}) of protons. The broken lines are only visual guides.

completely independent of the concentration of the centers. The considerably large discrepancy of the values for the implantation fluence of 10^{11}-ion/cm^2 from those for other fluences is explained by the relatively large capture ratio of vacancies by oxygen ($V+O \rightarrow VO$).[4,5] In spite of these discrepancies, it is evident that the annihilation of the *W* centers by electron irradiation is explained as first order with respect to the electron fluence. In order to explain the features throughout the fluence region of Fig. 2, however, formation of the *W* centers should occur by a higher order reaction with respect to the electron fluence. For proton implantation, the *W*-center formation reaction was analyzed as second order with respect to the implantation fluence.[15] For electron irradiation, as well, it seems reasonable to assume second-order *W*-center formation with respect to electron fluence. The number of the *W* centers n_W is formally described by the electron fluence n_e as

$$n_W = C - K_A n_e + K_F n_e^2, \quad (1)$$

where C is the number of the pre-existing *W* centers formed by proton implantation, and K_A and K_F are the constants for annihilation and formation of the center, respectively. In Eq. (1), the condition that n_W is positive or zero should always be satisfied. When appropriate values of the constants in Eq. (1) are chosen, the change of the PL intensity with the fluence for each implantation curve (Fig. 2) is well fitted up to the fluence of 5×10^{18} e^-/cm^2. The best-fit values of K_A are slightly different for various implantation fluences, as expected from Fig. 4. On the other hand, K_F is independent of the number of the pre-existing *W* centers. When the cubic dependence on the electron fluence is assumed in place of the square dependence for the *W*-center formation term in Eq. (1), the agreement between the experiment and calculation becomes significantly worse. Accordingly, it is concluded that the annihilation and formation of the *W* centers are of first and second order with respect to the electron fluence (or element pairs), respectively, in which formation order agrees with that obtained from proton implantation.[15]

C. Efficiencies for the formation of the *W* centers

While the *W* centers are easily observed in the implanted samples, it seems, in general, very difficult to observe them in the electron-irradiated samples. In order to investigate the formation kinetics of the *W* centers, the efficiencies for the formation of the centers between the element pairs produced by the ion implantation and electron irradiation are compared. Since the lowest fluence case of the proton implantation is the most ideal due to the low lattice damage,[15] the level of the PL intensity of the *W* centers for an as-implanted sample with the fluence of 1×10^{11} ion/cm^2 in Fig. 2 is referred to for comparison. Since one proton with an energy of 180 keV produces about 11 element pairs, as calculated from TRIM,[22] in total $1.1\times10^{12}/\mathrm{cm}^2$ element pairs are produced within the depth of 2.0 μm from the surface by the reference proton fluence (1×10^{11} ion/cm^2). Since the *W* centers are formed inside the collision cascade volume and/or not so far from it, it can be assumed that they are distributed within 3.0 μm from the surface at the deepest. Since the concentrations of all the *W* centers and impurities are sufficiently small (Fig. 1) and the lattice damage is very slight[15] for the reference sample, the penetration depth of the excitons produced by the excitation light near the surface ($\sim$1 μm) is deeper than 50 μm estimated from the exciton capture cross section of the impurities.[27] All the signals of the *W* centers formed by the proton implantation in the reference sample are, accordingly, observed by PL. As seen from Fig. 2, the electron fluence corresponding to the same level of the PL intensity as that for the reference sample is about 3×10^{18} e^-/cm^2. Accordingly, $1.8\times10^{15}/\mathrm{cm}^2$ element pairs are produced by this fluence within 3 μm from the surface employing the production efficiency 2/cm for one electron;[19] this number is three orders larger than the number of element pairs produced by ion implantation in the reference sample, indicating that the number of *W* centers is not simply determined by only the number of the element pairs produced by incident particles. Considering the large penetration depth of the excitons (>50 μm) for the electron-irradiated samples as well as for the proton-implanted samples, the efficiency of the element pairs produced by proton implantation for the *W*-center formation is more than four orders larger than that produced by electron irradiation. This large difference in the efficiency is not explained by the difference in the production rates of the element pairs for both methods employed in this study because the production rate of the element pairs for the proton implantation with the present condition (4.4×10^9 ion/cm^2 s) is $1.2\times10^{15}/\mathrm{cm}^3$ s at the maximum density of element pairs 2.8×10^5/cm per ion calculated by TRIM and is 5.2 $\times10^{14}/\mathrm{cm}^3$ s for the electron irradiation calculated with the present irradiation condition (2.6×10^{14} e^-/cm^2 s), i.e., the former is only about two times larger than the latter. In spite of the large difference in the formation efficiency of the *W* center between ion implantation and electron irradiation, it is evident that the *W*-center formation is expressed as second-order with respect to the fluences of both species.

D. *W*-center model

In modeling the *W* center, requirements of the ⟨111⟩ trigonal symmetry[12] and the second-order formation of the center with respect to the fluences of both incident ions and electrons are essential. In addition to these requirements, the higher efficiency of the *W*-center formation by ion implantation than electron irradiation is a strong point for the model. In the previous study,[15] the ⟨111⟩-split monointerstitial model was proposed for the *W* center by simply satisfying the requirements of the symmetry and formation order with respect to implantation fluence. The procedure of the center formation was that (1) many element pairs produced by ion implantation formed V-Si_I close pairs around the range of protons; (2) then the center was directly formed by the attack of a free Si_I onto the V-Si_I close pair through the mediation of V to satisfy the ⟨111⟩ symmetry of the center, which is second order with respect to the fluence of ions. Although this explanation has a basic importance considering that the intermediate V-Si_I complex at the recombination of Si_I with V, proposed by Tang, *et al.*,[28] has considerable stability (the recombination barrier is ~1.1 eV), a more advanced explanation based on the findings obtained in the present study and those given by other studies is needed. The high efficiency of the *W*-center formation by ion implantation is thought to originate from a special configuration of the element pairs produced by this method. While the same numbers of Si_I's and *V*'s are uniformly distributed everywhere in the crystal for electron irradiation, for proton implantation, not only the distribution of each element has a sharp peak at around the range of protons, but there are an excessive number of Si_I's deposited at a deeper position than that of the maximum distribution of *V* also, which is theoretically expected by TRIM and is experimentally observed by deep level transient spectroscopy for boron implantation.[29] The high efficiency of the *W*-center formation is assumed to be due to these split distributions of both elements around the range of protons. The excessive number of Si_I's at the end of the range of protons are assumed to reside as isolated interstitials and have a probability to directly bond to another Si_I immediately after implantation. Most of the other Si_I's tend to combine with *V* to form the V-Si_I close pair or to recombine when there is no impurity. On the other hand, homogeneous formation of the V-Si_I close pairs or a recombination of the pairs occurs everywhere in electron-irradiated sample.

To understand the atomistic model of the *W* center, probable configurations of isolated Si_I are considered. The stable configurations of several charge states of Si_I have been calculated by a number of authors at various levels of theory.[8,11,28] While the *T* interstitial (situated at the *T* site) is the most stable according to an empirical tight-binding calculation,[8] the ⟨110⟩-split and *H* (situated at hexagonal site) configurations are more stable than *T* by the first-principles local-density approximation,[11,28,30] i.e., the stability of isolated Si_I has a considerable variation with different theoretical bases. However, since the isolated Si_I has not yet been observed, there is no experimental information to which theory can be compared. Since the ⟨110⟩-split interstitial is the basic building unit for the {311} defects[6] which occur by annealing the sample above 650 °C and it is thought to play a central role in TED of dopants,[7,31] there is an opinion that it should also be the building unit for small clusters. However, since at least five PL peaks due to thermally more stable clusters than the *W* center are observed (not shown here) before occurring the {311} defects, which are also seen from the data given by other authors,[24,32] and structural transformations are reported to occur in the evolution from these clusters to the {311} defects,[24,33,34] it is unnecessary to assume that the small clusters including the *W* center have the same building unit as that of the {311} defects. This idea is also supported by a recent calculation[35] that showed that compact-type clusters composed of 2–4 self-interstitials form a more stable group than ⟨110⟩ elongated-type clusters which are the building blocks of the {311} defects and have a discontinuity in the formation energy with the latter group. Accordingly, it is reasonable to assume that several stable structures of Si_I such as *T* and ⟨110⟩-split interstitials all have a possibility to be the building unit(s) for the formation of the *W* center.

According to calculations, it is general thought that stability of interstitial clusters increases by successive combination with interstitials,[8,35,36] although there is one experimental analysis in which clusters containing four and eight interstitials are only stable until forming larger clusters containing more than 15 interstitials.[37] Within the second-order formation of the *W* center with respect to the number of the element pairs, there are two ways to form the interstitial products at the end of the range; one is the formation of a new interstitial through the combination of the metastable V-Si_I close pair with an isolated Si_I, and the other is the formation of a di-interstitial through the direct combination of two isolated Si_I's. In the former case, when either or both Si_I's are *T* interstitials, a ⟨111⟩-split monointerstitial is easily formed, as stated earlier.[15] Several types of di-interstitials was predicted by a number of authors,[8,10,11,28,35,36] however, among them, the model proposed in Ref. 8 is the only one which satisfies the ⟨111⟩ symmetry. This model, synthesized from a ⟨110⟩-split interstitial and a *T* interstitial and designated as the ⟨111⟩ ST di-interstitial (ST: split triple), consists of three Si atoms sharing one lattice site and forming an equilateral triangle in a ⟨111⟩ plane. The +2 charge state of the ⟨111⟩ ST di-interstitial is the most stable (the formation enthalpy is 3.0 eV) among several charge states of three di-interstitials calculated in Ref. 8. Accordingly, the ⟨111⟩ ST di-interstitial is also assumed as the candidate for the *W* center. Considering, from molecular-dynamic simulations,[38] that there is a strong attractive interaction between two Si_I's to form a di-interstitial when they approach very close to one another, the formation of this species seems as easy as the ⟨111⟩-split monointerstitial in implanted samples. It is worth noting that excessive interstitials at the end of the range play a central role for the formation of both models of the *W* center. Since the distribution of the element pairs is homogeneous everywhere in an electron-irradiated sample, the increase of the number of the *W* centers seen above the fluence of 1×10^{18} e^-/cm^2 (Fig. 2) is simply explained by the increase of the probability to approach two Si_I's (or a V-Si_I pair and Si_I) to bring about an attractive interaction between them when the number of the element pairs increases.

The tri-interstitial (I_3^b in these reports) model involving three Si_I's at three adjacent puckered *BC* sites on one ⟨111⟩ plane was proposed for the *W* center by several authors.[10,11,14] However, this cluster does not seem to be a candidate for the *W* center due to the following reasons. First, it is difficult to suppose the formation of a tri-interstitial by the second-order reaction with respect to the number of Si_I's. Second, according to molecular-dynamics simulations given by other authors, the cluster is highly stable and does not diffuse for a long time even at 1000 K,[11] and at the melting point,[38] which differs from the observations that the *W* centers are not so stable and are completely extinguished below 500 °C.[15,21] It seems reasonable to assign the highly stable simulated clusters such as I_3^b and Si_{14} (Ref. 9) to the above-mentioned high temperature clusters which are present at higher temperatures than 550 °C. Accordingly, only the ⟨111⟩-split monointerstitial and the ⟨111⟩ ST di-interstitial remain as candidates for the *W* center model.

E. Summary

The annihilation and formation of the *W* centers by electron irradiation in the sample containing the pre-existing centers were explained by first- and second-order reactions with respect to the number of element pairs, respectively. The efficiency of the *W*-center formation from element pairs produced by electron irradiation is much smaller than that for ion implantation. Considering the symmetry and formation order of the *W* centers and the configurations of element pairs produced by incident particles, the ⟨111⟩-split monointerstitial and the ⟨111⟩ ST di-interstitial were chosen as the probable candidates for the center.

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