Annealing kinetics of vacancy-related defects in low-dose MeV self-ion-implanted $n$-type silicon

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(Received 26 March 2001; published 30 October 2001)

Silicon samples of $n$-type have been implanted at room temperature with 5.6-MeV $^{28}$Si ions to a dose of $2 \times 10^9 \text{ cm}^{-2}$ and then annealed at temperatures from 100 to 380 °C. Both isothermal and isochronal treatments were performed and the annealing kinetics of the prominent divacancy ($V_2$) and vacancy-oxygen (VO) centers were studied in detail using deep-level transient spectroscopy. The decrease of $V_2$ centers exhibits first-order kinetics in both Czochralski-grown (CZ) and float-zone (FZ) samples, and the data provide strong evidence for a process involving migration of $V_2$ and subsequent annihilation at trapping centers. The migration energy extracted for $V_2$ is $\sim 1.3$ eV and from the shape of the concentration versus depth profiles, an effective diffusion length $\approx 0.1 \text{ µm}$ is obtained. The VO center displays a more complex annealing behavior where interaction with mobile hydrogen (H) plays a key role through the formation of VOH and VOH$_2$ centers. Another contribution is migration of VO and trapping by interstitial oxygen atoms in the silicon lattice, giving rise to vacancy-dioxygen pairs. An activation energy of $\sim 1.8$ eV is deduced for the migration of VO, in close resemblance with results from previous studies using electron-irradiated samples. A model for the annealing of VO, involving only three reactions, is put forward and shown to yield a close quantitative agreement with the experimental data for both CZ and FZ samples over the whole temperature range studied.

DOI: 10.1103/PhysRevB.64.195211 PACS number(s): 61.80.Jh, 71.55.--i, 85.40.Hp

I. INTRODUCTION

It is well established by several fundamental studies that MeV electron irradiation and ion implantation of silicon give rise to similar kinds of point defects, although the relative importance of the different defects hinges on the projectile mass; for a recent review see Ref. 1. This similarity holds if the ion dose is kept below a critical value, which is closely associated with the ion mass and energy. In this “low-dose” regime single collision cascades prevail and the overlap between different ion tracks is small. Hence, agglomeration phenomena, which can lead to the formation of extended clusters and eventually to complete amorphization, are to a large extent suppressed. The main difference between the damage introduced by energetic electrons and ions is, however, to be found in the spatial distribution of the defects. In contrast to MeV electron irradiation, ion implantation gives rise to a localized damage distribution, with a peak region close to the projected ion range and a tail towards the surface. Because of a high concentration of defects, the strain field at the end of the ion range can suppress the capture of free charge carriers by electrically active defects, as well as affect the atomic- and electronic-defect configurations. Furthermore, the flux of the diffusing defects is expected to be influenced by the concentration gradient in the peak region.

For MeV electron irradiation the kinetics of point-defect generation has been studied by different groups,3–8 and today, there is a reasonable understanding of the defect reactions taking place in an irradiated layer. In this respect, it has been crucial to reveal the presence of different impurity atoms in the starting material, e.g., oxygen, carbon, hydrogen, and dopant atoms (phosphorus, in our case). Their role is to act as traps for the mobile vacancies and interstitials, competing strongly in the promotion or suppression of stable complexes.

However, for ion implantation only a few quantitative studies of the point-defect generation exist, 9–13 and the defects primarily investigated are the divacancy ($V_2$) and vacancy-oxygen (VO) centers. $V_2$ and VO are the most prominent vacancy-related defects in silicon after low-dose ion bombardment at room temperature (RT) and their formation has been studied as a function of ion mass, dose, dose rate, sample depth, and implantation temperature. At dose rates below $\sim 10^8 \text{ cm}^{-2} \text{s}^{-1}$, the generation of $V_2$ centers per ion-induced vacancy in the damage peak region is identical, within $\pm 10\%$, for different kinds of ions ranging from $^{11}$B to $^{120}$Sn (this may hold for an even wider range of ions but to the best of our knowledge no such data exist in the literature). In contrast, the VO center shows a decrease in the generation rate per ion-induced vacancy with increasing ion mass, consistent with the picture from molecular-dynamics simulations suggesting that light ions are more effective than heavy ions in generating point defects.14 The concentration of both $V_2$ and VO increases linearly with the ion dose in the regime where single-collision cascades prevail ($\lesssim 10^{10} \text{ cm}^{-2}$), but the generation efficiency per ion de-
creases at high enough dose rates ($\geq 10^8 \text{ cm}^{-2} \text{s}^{-1}$). The dose rate at which the decrease occurs shifts to lower values with increasing ion mass, which is associated with the larger size of the collision cascades for heavy ions. This interpretation is qualitatively supported by computer simulations of the defect reaction kinetics assuming a model where the interaction between single-collision cascades, in the dilute limit, is primarily due to fast-diffusing silicon self-interstitials ($I_s$).

A subject closely related to the generation of defects is their evolution during post-irradiation annealing. A rather complex scenario then appears, in which the defects can dissociate, migrate to annihilation sinks, interact with each other or with impurities, etc. Given the quite large choice of possible simultaneous reactions, it is important to consider carefully all the factors involved, such as the aforementioned spatial distribution of defects and the impurity content. In some cases, as for the annealing of the vacancy-phosphorus center, a dependence on doping concentration, illumination, and electric field has also to be taken into account.

Quantitative studies of the annealing kinetics for the $V_2$ and VO centers have mainly been performed using infrared spectroscopy (IR) or, to some extent, deep-level transient spectroscopy (DLTS) for the analysis.

Despite their fundamental importance, quantitative annealing data for $V_2$ and VO in ion-implanted samples are scarce. A particular requirement for the latter type of samples is the necessity to determine concentration versus depth profiles because of the non-uniform defect generation. This limits the applicability of IR spectroscopy for implanted samples and favors the use of DLTS. Hence, the defect concentration must be kept low, typically $\lesssim 10^{14} \text{ cm}^{-3}$ for a doping concentration of $\sim 10^{15} \text{ cm}^{-3}$, which is about three to four orders of magnitude below that normally used in IR studies ($\sim 10^{17}$ –$10^{18} \text{ cm}^{-3}$).

In this work the annealing kinetics for the $V_2$ and VO centers are quantitatively determined in MeV self-ion-implanted Czochralski-grown (CZ) and float-zone (FZ) $n$-type silicon samples using DLTS. The annealing of $V_2$ follows first-order kinetics and is attributed to migration of the $V_2$ centers before trapping by immobile defects/impurities. The loss of VO displays a more complex behavior, which can be partly described by passage through reaction with mobile hydrogen atoms originating from a thin surface layer. The passivation is modeled by a two-stage process, where first the VO center appears, being electrically active and possible to monitor by DLTS, before the electrically neutral VOH$_2$ center is formed. A competing reaction, effective at temperatures $\geq 300$ °C, is the migration of VO centers and subsequent formation of vacancy-dioxygen pairs (VO$_2$) via trapping by interstitial oxygen atoms (O$_i$) in the silicon lattice. A close agreement between the experimental data and computer simulations of the annealing kinetics is reached for VO using a model involving only three reactions.

### II. EXPERIMENT

$N$-type [$P_n$] = $9 \times 10^{14}$ cm$^{-3}$, where brackets denote concentration values and subscript $s$ refers to substitutional lattice position) silicon samples were used and cut from CZ and FZ wafers grown in the $\langle 100 \rangle$ direction. According to Fourier-transform infrared (FTIR) absorption measurements the concentrations of interstitial oxygen [O$_i$] and substitutional carbon [C$_s$] were $\sim 5 \times 10^{17}$ and $\sim 1 \times 10^{18}$ cm$^{-3}$, respectively, in the CZ samples while the corresponding concentrations in the FZ samples were both $\leq 5 \times 10^{15}$ cm$^{-3}$.

Shallow $p^+n$ diodes were fabricated using the FZ samples according to the following procedure. The samples were first oxidized in a wet oxygen atmosphere at a temperature of 1000 °C for 120 min, yielding a 5600-Å-thick oxide. Circular diode areas, with a diameter of 2.5 mm, were patterned and etched in a buffered hydrofluoric (HF) solution. A screen oxide, with a thickness of 200 Å, was grown prior to the $p^+$ implantation of 50-keV boron ions with a dose of $5 \times 10^{15}$ cm$^{-2}$. The samples were then implanted on the back-side with $1 \times 10^{15}$ P/cm$^2$ (80 keV), ensuring a good Ohmic contact. Subsequently, annealing was carried out at 1000 °C for 40 min, in order to activate the implanted dopants. Contact holes were defined by means of lift-off lithography, and aluminum was deposited on the front and backside of the samples followed by annealing at 450 °C for 30 min in argon atmosphere. Together with the CZ samples, these $p^+n$ diodes were then implanted at RT with 5.6-MeV Si$^+$ ions using the Uppsala EN tandem accelerator. The implantation energy was chosen to generate a defect distribution suitable for monitoring by DLTS, and the damage peak was located $\sim 3.6 \mu$m below the surface. The ion dose ($2 \times 10^{15}$ cm$^{-2}$) was tuned to avoid doping-compensation effects, and the error in the nominal dose did not exceed 15%.

Subsequently, Schottky-barrier junctions were prepared on the CZ samples. Following a standard cleaning process, which includes a final dip in diluted HF solution (10%), thermal evaporation of Au contacts was performed at a pressure of $\sim 1 \times 10^{-6}$ mbar. The temperature of the samples during contact growth did not exceed 50 °C.

Isochronal and isothermal anneals of both types of samples were performed in nitrogen atmosphere at temperatures between 100 and 380 °C. DLTS analysis was then carried out using a refined version of the setup described in Ref. 25. Up to nine different spectra, each of them corresponding to a particular time window, could be recorded simultaneously. In this way, the measurement time was minimized and a high-energy resolution was achieved when characterizing the deep levels observed. A filling pulse of 10 ms duration was applied, ensuring that even traps with small capture cross sections, of the order of $10^{-18}$ –$10^{-19}$ cm$^2$, were fully saturated and contributed to the recorded emission. Furthermore, capture-cross-section measurements were undertaken by variation of the filling pulse width.

Concentration versus depth profiles of the defect levels were obtained by selecting one rate window and holding the temperature constant at the maximum of the DLTS peak of interest. The steady-state reverse-bias voltage was kept constant while gradually increasing the amplitude of the filling pulse. The depth profiles were then extracted from the dependence of the recorded DLTS signal on the pulse amplitude, where the voltages used were converted into...
depth according to the conventional square-root dependence for a Schottky-barrier or $p-n$ junction.

### III. RESULTS

Figure 1 shows DLTS temperature scans after isochronal (30 min) annealing of implanted CZ samples. The characteristic peaks primarily attributed to the VO center at $E_C - 0.17$ eV and to the doubly and singly negative charge states of $V_2$ at $E_C - 0.23$ eV and $E_C - 0.42$ eV, respectively, are identified (see Refs. 2, 5, 20, 26–31) ($E_C$ denotes the conduction-band edge). These two centers dominate the majority carrier spectrum for $n$-type samples and are normally the prime defects after implantation at low doses, together with the interstitial-carbon–interstitial-oxygen complex ($C_iO_i$) having a level at $-0.35$ eV above the valence-band edge (not shown here). The apparent deviation from a 1:1 ratio between the singly negative ($V_2^-$) and doubly negative charge state ($V_2^{2-}$) of $V_2$ is a characteristic feature of ion bombardment, together with a highly nonexponential capture rate of the $E_C - 0.23$ eV level as a function of the filling-pulse duration. Both phenomena are enhanced as the mass of the impinging ions increases and can be regarded as two different aspects of the suppression of $V_2^{2-}$ in the damage peak region, as has been discussed in detail in Refs. 2, 9, and 34.

It is well established that the $E_C - 0.42$ eV peak contains contributions from both the vacancy-phosphorus (VP) center and possibly from the interstitial-carbon–substitutional-phosphorus ($C_iP_s$) complex. Even if it is difficult to directly resolve the contributions of these additional defects by means of conventional DLTS their thermal stability is less than that of $V_2$. Both VP and $C_iP_s$ disappear rapidly at 150 °C and as shown in Fig. 1, the amplitude of the $E_C - 0.42$ eV peak decreases by $\sim 10\%$ after 30 min, consistent with the magnitude expected for these centers in moderately doped ($[P_i] \sim 10^{15}$ cm$^{-3}$) CZ samples. It may be noted that the peak shifts to slightly higher temperatures after annealing, in accordance with a somewhat higher rate of electron emission from VP than $V_2$ at a given temperature. Moreover, at 150 °C a small level at $E_C - 0.36$ eV disappears. This level was also found in the FZ $p+/n$ samples and investigated after reverse-bias cooling or minority-carrier injection. The behavior and thermal stability of the $E_C - 0.36$ eV level resemble closely those of one (metastable) state of the $C_iP_s$ complex, studied in detail for electron-irradiated samples. $[E_C - 0.36$ eV] is quite small ($\sim 10^{13}$ cm$^{-3}$), as expected with $[P_i] \sim 1 \times 10^{15}$ cm$^{-3}$, and does not affect the stability of VO and $V_2$. Further, it was verified that the concentration of the substitutional-carbon–interstitial-carbon pair ($C_iC_i$) is negligible in both sets of samples at any stage of the annealing experiments. The DLTS signal of $C_iC_i$ overlaps strongly with that of VO, but its presence can be readily resolved by variation of the filling-pulse width.

As shown in Fig. 1, annealing of the CZ samples at and above 200 °C results in a progressive reduction in the concentration of both $V_2$ and VO. The concentration of $V_2$ is below the detection limit at 300 °C, while VO still persists at temperatures well above 300 °C. At this stage small signals originating from levels at about $E_C - 0.20$ eV and $E_C - 0.59$ eV are detected. There is scarce information in the literature regarding these two levels, and their small intensities preclude any accurate characterization. We could not establish any correlation between their presence and the annealing of $V_2$ and VO, but it is worth mentioning that they appear simultaneously with the growth of a level at $E_C - 0.32$ eV. This latter level originates from a defect already present in small concentration directly after implantation in the CZ samples and which then gradually increases with annealing up to 300 °C. In accordance with previous notations, we label this level as $E_3$.

A similar isochronal annealing study for the FZ samples yields different results compared to those in Fig. 1. As illustrated in Fig. 2, an overall higher thermal stability of the defects is observed, especially for the VO center. The annealing of $V_2$ and VO take place in two distinctly different temperature regimes, and moreover, $E_3$ is not detected until temperatures where VO starts to disappear. It may also be noted that even at the lowest temperature (150 °C) in Fig. 2 [VO] is larger in the FZ samples, despite two orders of mag-
implies that an oxygen concentration in the low 10–15 cm³ tends to be lower than that in the CZ samples. However, the sum [VO] and [E3] is identical in the two materials at 150 °C, providing further indication that the loss of VO is correlated with the growth of E3, as will be discussed in detail in Sec. IV B. Moreover, the identical sum of [VO] and [E3] in the two materials implies that an oxygen concentration in the low 10¹⁵ cm⁻³ range is sufficient to efficiently trap migrating monovacancies that have escaped recombination or higher-order defect formation in the collision cascades. For the ion dose used in this work (2 × 10⁸ Si ions/cm²) the peak concentration of monovacancies surviving annihilation is estimated to be in the low 10¹³ cm⁻³ range.¹¹

By performing isothermal treatments of the CZ and FZ samples in the 190–260 °C temperature range, the annealing kinetics of V₂ has been explored. In the whole interval an exponential decrease as a function of annealing time holds with a high accuracy, Fig. 3. The integrated intensity of [V₂(x,t)] after each annealing step can be expressed by

\[ \int [V_2(x,t)]dx = \int [V_2(x,t=0)]dx \exp[-c(T)t], \]

where x is the sample depth and t is the annealing time, i.e., the process follows first-order kinetics with a temperature-dependent rate constant c(T). As shown in Fig. 4, c(T) exhibits an Arrhenius dependence,

\[ c(T) = c_0 \exp(-E_a/kT), \]

where c₀ and E_a are the frequency factor and the activation energy, respectively, k is Boltzmann’s constant and T is the absolute temperature. The values of c(T) obtained for the CZ samples are about a factor of 2 higher than those for the FZ samples, and the extracted values for c₀ and E_a are ~1 × 10⁸ (~5 × 10⁸) s⁻¹ and 1.27 ± 0.04 (1.25 ± 0.05) eV in the CZ (FZ) samples, respectively. No electrically active defects have been detected with a growth correlated to the loss of V₂. This is true even for shallow energy levels extending the temperature range of the DLTS measurements to below 30 K where the phosphorus donor starts to freeze out.

In Figs. 2–4, the V₂ center is represented by the E_C − 0.23 eV level (V₂⁺) but well within the experimental accuracy of the data; the E_C − 0.42 eV level (V₂⁻) displays the same annealing rate. In this context it should be emphasized that no broadening of the concentration versus depth profiles of V₂ is revealed during the annealing. The profile shape remains the same except for an initial narrowing around the peak region after the first annealing step at each temperature. A similar behavior is also observed for the VO center and the narrowing is due to a decrease of the tail towards the surface. This has been discussed in detail previously²² and the narrowing exhibits a transient behavior with no temperature dependence in the studied range (100–380 °C). Consequently, for the annealing kinetics the depth distributions of V₂ and VO can be considered as invariant. In the following, [V₂(t)] and [VO(t)] will denote \(\int [V_2(x,t)]dx\) and \(\int [V_0(x,t)]dx\), respectively.

Analogous isothermal annealing as for V₂ was performed for the VO center. As already demonstrated, substantially higher temperatures are required in order to affect the stability of VO in the FZ samples than in the CZ samples. Apart from this important difference, the annealing of VO displays similar features in the two materials. As illustrated in Fig. 5 for the CZ samples, at each annealing temperature two different stages can be identified, a fast initial process followed by a considerably slower one. An analytical expression to fully describe the annealing of VO in the whole temperature range studied has not been found. It is apparent from Fig. 5 that a composition of two first-order processes, which would result in two linear regions, is not adequate for all the temperatures. Furthermore, the rate of the initial drop increases with [VO(t=0)], as revealed by the inset in Fig. 5, comparing results of samples implanted with 1 × 10⁸ and 2 × 10⁸ ions/cm².

If a second-order process is put forward, then [VO(t)] should evolve according to

\[ d[VO(t)]/dt = -K(T)[VO(t)]^2, \]

where K(T) is a second-order rate constant. In this case the annealing rate depends on [VO(t=0)], as one finds by integrating Eq. (3),
portionality holds between the increase of annealing rate of VO after the initial stage is always accompanied by an onset of saturation in the growth of \( E_3(t) \) saturates while simultaneously the decrease of \( [\text{VO}(t)] \) slows down. The second regime is even more clearly observed, after the initial short stage, at the intermediate temperature (220 °C), Fig. 7(b). Finally, \( E_3 \) starts to anneal out with about the same rate as VO. This third stage is readily observed at 250 °C, Fig. 7(c).

In the FZ samples the annealing kinetics for VO shows the same trend as in the CZ samples but at substantially higher temperatures. As mentioned previously, in the FZ samples \( E_3 \) is not detected until temperatures \( \geq 300 \) °C. All the three annealing stages can be found in Fig. 8 showing results after isothermal treatment at 330 °C. The first stage occurs for \( t \leq 150 \) min followed by a saturation in the growth of \( [E_3(t)] \) and a decrease in the loss of \( [\text{VO}(t)] \) (second stage) before both centers decrease simultaneously for \( t \geq 400 \) min (third stage). Analogous results are obtained at all the temperatures explored for isothermal annealing of VO in the FZ samples (300–380 °C).

**IV. DISCUSSION**

**A. \( V_2 \) center**

The annealing of \( V_2 \) is established to follow first-order reaction kinetics, irrespective of FZ or CZ samples. Further,
in the FZ samples the loss of $V_2$ and VO take place in two well-separated temperature regimes, and as shown in Ref. 42, the progressive decrease of $[V_2(x,t)]$ in the 200–250 °C interval occurs without any noticeable change in the concentration of VO centers. This implies that the annealing of $V_2$ cannot be ascribed to a flux of silicon self-interstitials annihilating vacancy-type centers since it would simultaneously affect $[\text{VO}(x,t)]$, which is of the same magnitude as $[V_2(x,t)]$. Moreover, dissociation of $V_2$ can be ruled out as a dominant process since it would increase $[\text{VO}(x,t)]$, as observed in the case of dissociation of $\text{V}_\text{B}$.

In addition, the frequency factors obtained are in the $10^8$–$10^9$ s$^{-1}$ range (Fig. 4), which is a factor of $10^4$–$10^5$ lower than expected if dissociation prevails ($10^{12}$–$10^{13}$ s$^{-1}$).

This suggests strongly that the annealing is predominantly controlled by migration of $V_2$ and subsequent annihilation at trapping centers. In order to fulfill the first-order kinetics, the concentration of traps must be at least one order of magnitude higher than that of $V_2$, i.e., $\geq 10^{15}$ cm$^{-3}$.

However, no broadening of the original $V_2$ depth profile, which would be a direct evidence for migration, was detected at any stage of the study. This holds even for the FZ samples, having a low concentration of impurities/traps, and in order to make a proper interpretation, quantitative estimates based on the observed annealing kinetics are required. The activation energy $E_a$ is regarded as the migration energy of $V_2$ (involving partial dissociation), while the frequency factor $c_0$ is related to the number of jumps before $V_2$ is captured. The values extracted from the experiments are in accordance with the proposed model. $E_a$ being independent on the material quality while $c_0$ is smaller in the FZ samples, as expected for a material with a low concentration of traps. If the total concentration of traps for $V_2$ is denoted by $[Z]$, the following relation can be derived by applying the theory for diffusion-limited reactions:

$$\frac{\partial [V_2(x,t)]}{\partial t} = -4 \pi RD_{V_2}[V_2(x,t)][Z] + D_{V_2} \frac{\partial^2 [V_2(x,t)]}{\partial x^2},$$

where $R$ is a capture radius for the trapping reaction and $D_{V_2}$ is the diffusion constant of $V_2$. $Z$ is considered to be immobile and to have a uniform depth distribution. The first term on the right-hand side of Eq. (5a) accounts for the loss of $[V_2]$ and we can write

$$\frac{\partial [V_2(x,t)]}{\partial t} = -c(T)[V_2(x,t)] + D_{V_2} \frac{\partial^2 [V_2(x,t)]}{\partial x^2}$$

with $c(T)$ given by Eq. (2) and putting $c_0 = 4 \pi RD_{V_2}[Z]$ and $D_{V_2} = D_{V_2}^0 \exp(-E_a/kT)$. $R$ is put equal to 5 Å and Eq. (5b) is solved numerically with $[V_2(x,t=0)]$ and $c(T)$ taken from the experimental data. The evolution of $[V_2(x,t)]$ is then compared with the measured profiles as a function of annealing time and temperature, and Fig. 9 shows the results (both with and without trapping) for FZ samples after 450 min at 220 °C. In order to reproduce the lack of broadening of the $V_2$ profile, $D_{V_2}$ has to be low. In fact, the effective diffusion length must be smaller than the accessible depth resolution ($\sim 0.1 \mu m$), and the comparison between experimental and simulated data gives a maximum value of $\sim 10^{-3} \text{cm}^2/\text{s}$ for $D_{V_2}^0$. This value is in the anticipated range and differs less than a factor of $\sim 30$ compared to the preexponential factor estimated for migration of the monovacancy assuming a small migration entropy ($\sim 0 \text{ k}$), as expected in the studied temperature range.

Hence, $D_{V_2}^0 \leq 10^{-1} \text{ cm}^2/\text{s}$ implies $[Z] \geq 10^{15}$ cm$^{-3}$ in the FZ samples and $[Z] \geq 8 \times 10^{15}$ cm$^{-3}$ in the CZ samples, which may be regarded as reasonable lower limits. In addition, these values are fully consistent with the trap concentrations required for the first-order kinetics to apply. The identity of $Z$ is not known but it should be emphasized that $O_i$ can be ruled out as a main candidate; the $c_0$ values for the FZ and CZ samples differ only by a factor of 2 while $[O_i]$ differs by at least two orders of magnitude ($\approx 5 \times 10^{15}$ versus $\approx 5 \times 10^{17}$ cm$^{-3}$). A more likely candidate is a carbon-related trap since carbon can be present with comparable concentrations in FZ and CZ samples. However, no correlation was found between the loss of $V_2$ and the growth of any electrically active center. In fact, this provides additional support
for the conclusion that $O_i$ can be excluded as a prime trap since $V_2O$ ($V_2 + O_i → V_2O$) is expected to be electrically active.\(^{30,47,48}\)

The values deduced for $c(T)$ are in close agreement with those obtained from previous studies on electron-irradiated samples, and the same holds for the proposed annealing mechanism. Indeed, a migration energy in the range of 1.25–1.30 eV has been found by studying reorientation of $V_2$ under uniaxial stress using electron paramagnetic resonance\(^*\) or photoconductivity.\(^{49}\) Slightly higher values for $E_m$ and $c_0$ than those obtained in the present work were extracted from samples irradiated with MeV electrons to high doses ($10^{18}$ cm\(^{-2}\)) and analyzed by FTIR.\(^{22}\) In Ref. 22, $[V_2(x,t) = 0]$ is in the range of $10^{16}$ cm\(^{-3}\) and approaches the concentration of traps. As a result, at long enough annealing times the dissociation rate of $V_2$ becomes comparable with the loss through migration and subsequent trapping. Since both processes can be approximated by first-order kinetics, Eq. (1) is still applicable and the extracted values represent a mixed annealing regime. In fact, two individual contributions were deduced yielding an activation energy of \(\sim 1.28\) eV for migration and \(\sim 1.7\) eV for dissociation.\(^{22}\)

### B. VO center

The annealing kinetics of VO shows clearly that it cannot be described by a single dissociation or migration/trapping mechanism. In both sets of samples the concentration versus depth profiles of VO exhibit no broadening after thermal treatment.\(^{45}\) Another key result is that the decrease in $[VO(x,t)]$ is followed by an evolution of the $E_3$ defect ($E_c = 0.32$ eV level). Furthermore, VO displays an increased stability in the FZ samples relative to that in the CZ samples, with a corresponding inhibition of the appearance of $E_3$.

The exact identification of the $E_3$ center has been a subject of speculation for some time. In one of the first reports,\(^{25}\) it was assigned to a migrating impurity from the surface, coupling with a primary defect introduced by electron irradiation. Moreover, the hypothesis that VO was the affected defect was put forward, since the production rate of $E_3$ was comparable with that of VO. DLTS experiments after proton implantation\(^{41,50}\) or hydrogenation\(^{51}\) revealed a defect level with the same emission rate as the $E_c = 0.32$ eV level, leading to the firm conclusion that hydrogen is one of the constituents of $E_3$. More recent studies have finally agreed on the assignment of $E_3$ as a VOH complex.\(^{23,32-34}\) In this study we provide additional evidence for this identification, based on the annealing kinetics for VO and $E_3$.

In fact, hydrogen diffusion from the surface is anticipated to take place in the investigated samples. Initially, a significant amount of hydrogen is confined to the surface region, resulting from the cleaning steps in the diode manufacturing. Because of the high mobility and reactivity of hydrogen, a progressive aggregation with irradiation-induced defects occurs even at RT.\(^{55}\) Hydrogen is known to modify the electrical properties of point defects and ultimately, full passivation may occur. By means of DLTS, it is possible to follow the evolution of these phenomena, e.g., the transformation of VO to VOH. In the case of electron irradiation, the in-diffusing hydrogen faces a uniform defect distribution\(^{51,53}\) and initially, the depth profile of the VOH centers formed shows a diffusion-like shape from the surface. At later annealing stages, while the hydrogen front advances into the bulk, passivation of the VOH centers occurs in the near-surface region and neutral VOH\(_2\) centers form. These reactions can be observed until the electrically active defects in the explored region are fully saturated, or the supply of free hydrogen is exhausted.

In ion-implanted samples the defects are mostly confined to the peak region, and a somewhat more complex scenario appears than in electron-irradiated samples since the diffusing hydrogen reacts with a nonuniform distribution of defects. It may be noted that even without intentionally introducing hydrogen, its initial surface concentration is large enough to affect the defect production/annealing in the low-dose regime studied. In order to quantitatively validate this interpretation of our DLTS data, a comparison is made with computer simulations of the annealing kinetics assuming the following reactions:

\[
\begin{align*}
\text{VO} + \text{H} & \rightarrow \text{VOH} \\
\text{VO} + \text{O}_i & \rightarrow \text{VO}_2 \\
\text{VOH} + \text{H} & \rightarrow \text{VOH}_2
\end{align*}
\]

(6)

where the first reaction represents the formation and dissociation of VOH, the second one formation of VO\(_2\) pairs, and the third one formation of VOH\(_2\) centers. Both VO\(_2\) and VOH\(_2\) are electrically inactive. The capture radius $R$ is put equal to 5 Å, and only hydrogen and VO are considered to be mobile. The set of differential rate equations corresponding to Eq. (6), derived from the theory for diffusion-limited reactions,\(^{45}\) is listed in Table I.

The numerical values used for the hydrogen diffusion coefficient are given by $D_H = 5 \times 10^{-3} \exp [-0.8 \text{ (eV)/}kT]$. 

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**Table I.** Set of simultaneous differential rate equations derived from the reactions in Eq. (6). See text for explanation of the symbols used. $K_1 = 4 \pi R(D_H + D_{VO})$, $K_2 = 4 \pi R D_{VO}$, $K_3 = 4 \pi R D_H$. In the CZ samples, $\Theta_{BH} = 0$.
cm$^2$/s and are almost identical with those proposed by Rizk et al. for diffusion of negatively charged hydrogen (H$^-$) in n-type silicon. Here, it should be pointed out that a quite large interval exists in the literature regarding the activation-energy values for hydrogen diffusion, ranging from 0.48 eV at high temperatures to 1.2 eV at 225–350 °C, presumably reflecting a strong dependence of the mobility on the hydrogen charge state. It may also be mentioned that an activation energy of ~0.8 eV has been deduced for the diffusion of H$_2$ complexes but the pre-exponential factor is only of the order of a few times 10$^{-4}$ cm$^2$/s. For the diffusion constant of VO, a value of $D_{VO}=6 \times 10^{12}$ cm$^2$/s is employed, which agrees closely with previous values extracted from FTIR studies of electron-irradiated samples. The dissociation rate for VOH is set to $\Theta_{VOH}=5 \times 10^{12}$ exp$[-1.3 \text{ (eV)/} kT]$ s$^{-1}$. A frequency factor of this order is typical for a pure dissociation process, and the activation energy of 1.3 eV is consistent with the thermal stability of the E3 center.

The [VO(x,t=0)] profile and a uniform interstitial oxygen concentration of $[O_i]=5 \times 10^{17}$ cm$^{-3}$, as determined by FTIR for the CZ samples, were used as input for the simulations. The initial hydrogen concentration was put to 4.5 \times 10^{14} \text{cm}^{-3} and confined to a 0.2-$\mu$m-thick surface layer, i.e., $[H(x \leq 0.2 \mu m, t=0)]=4.5 \times 10^{14} \text{cm}^{-3}$ and $[H(x > 0.2 \mu m, t=0)]=0$. This value is in accordance with the surface concentration of hydrogen on HF cleaned p-type Si wafers, as observed by deactivation of boron acceptors using surface-charge profiling. Further, it is considerably smaller than that found after intentional hydrogenation processing, which lead to a hydrogen incorporation of the order of 10$^{16}$ cm$^{-3}$ in the bulk or 10$^{18}$ cm$^{-3}$ at the surface.

Results for two CZ samples annealed at 220 and 250 °C are shown in Fig. 10, and close quantitative agreement with the experimental data is obtained. Moreover, the assumption of an initial surface concentration of hydrogen is strongly supported by the evolution of the [VO(x,t)] and [VOH(x,t)] profiles during annealing. The transient reduction of the original [VO(x,t)] profile towards the surface is associated with a concurrent drastic change in the shape of the [VOH(x,t)] profile, starting from a broad distribution and ending with a peaked profile resembling that of VO in as-implanted samples. These important features are reproduced by the proposed model, as illustrated for VOH in Fig. 11.

In the $p^+/n$ FZ samples, the incorporation of hydrogen from the surface is retarded by trapping at the boron acceptors in the $p^+$ layer. For instance, atomic hydrogen and the boron acceptor form readily a complex with an estimated dissociation energy in excess of 1.3 eV. Thus, the $p^+$ layer acts as an efficient diffusion barrier for hydrogen, explaining the high temperatures needed to observe the interaction between H and VO in the $p^+/n$ FZ samples. In the simulations, this is taken into account by introducing a thermally activated injection rate of hydrogen from the $p^+$ layer into the n region, $\Theta_{BH}=5 \times 10^{12}$ exp$[-2 \text{ (eV)/} kT]$ s$^{-1}$. Otherwise, the parameter values used are the same as for the CZ samples, except for a lower oxygen concentration, $[O_i]=2 \times 10^{15}$ cm$^{-3}$.

In Fig. 12, the simulated and measured values of [VOH(x,t)] in the $p^+/n$ FZ samples are compared for annealing at 300, 320, 350, and 370 °C. Indeed, a close agreement is reached, especially considering the limited number of reactions included in Eq. (6) and the lack of reliable data for hydrogen diffusion/incorporation in highly doped surface layers. Hence, we do not claim that the proposed model is complete but it provides a satisfactory and quantitative picture of the main mechanisms responsible for the annealing of VO in low-dose implanted CZ and FZ samples.

**V. CONCLUSIONS**

Annihilation with mobile interstitial-type defects plays a minor role for the annealing of $V_2$ and VO centers in the studied concentration regime ($10^{12} - 10^{14}$ cm$^{-3}$). Instead, both centers transform into more complex defects with higher thermal stability. The annealing of $V_2$ centers occurs via migration of $V_2$ and subsequent annihilation with traps.
centers, and (ii) migration of VO and reaction with O$_2$ to form VO$_2$ pairs. The latter process becomes important above $\sim$300 °C, and computer simulations of the annealing kinetics, based on the processes (i) and (ii), yield a close quantitative agreement with the experimental data for both CZ and FZ samples. VOH is electrically active with a distinct DLTS peak while VOH$_2$ and VO$_2$ are electrically inactive. Hence, a substantial amount of the implantation-induced vacancies survive at high temperatures as constituents of neutral complexes. For instance, after 1000 min at 370 °C, about 65% of the initial VO centers in the FZ samples have been transformed into VOH$_2$ and the remaining fraction occurs as VO$_2$ pairs. Thus, the persistence of these vacancies cannot be neglected at temperatures above 400 °C when such phenomena as thermal donor formation and generation of extended implantation-induced defects with DLTS signatures$^{66–68}$ start to appear.

**ACKNOWLEDGMENTS**

Enlightening discussions with Professor J. L. Lindström are gratefully acknowledged. Financial support was kindly provided by the Swedish Research Council for Engineering Sciences (TFR), the Swedish Foundation for International Cooperation in Research and Higher Education (STINT) and the EU Commission, Contract No. ERBFMRXCT980208 (ENDEASD–TMR network).

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