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I. L. Kolevatov, B. G. Svensson, and E. V. Monakhov

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Interaction between the divacancy and hydrogen in silicon: Observation of fast and slow kinetics

I. L. Kolevatov, B. G. Svensson, and E. V. Monakhov

University of Oslo, Department of Physics, Center for Materials Science and Nanotechnology, P.O. Box 1048, Blindern, Oslo, Norway

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The divacancy ($V_2$) is one of the fundamental defects in silicon. However, the interaction of $V_2$ with hydrogen is still not fully understood. In the present work, deep level transient spectroscopy (DLTS) results on hydrogen-assisted annealing of $V_2$ are presented. $H^+$ ions were implanted with multiple energies into n-type Czochralski-grown samples, yielding uniform (box-like) concentration-versus-depth profiles of $V_2$ and hydrogen in the region probed by the DLTS measurements. The evolution kinetics of $V_2$ reveals two distinct processes: (i) a fast one attributed to dissociation of phosphorus-hydrogen pairs and reaction with highly mobile atomic H$_2$ and (ii) a slow one whose origin is not identified yet. During the slow process, we observe the formation of a hydrogen-related electronic state, labeled $E5^*$ and positioned $\sim0.42$ eV below the conduction band edge. The growth of $E5^*$ displays a close one-to-one proportionality with the loss of a $V_2$-related DLTS peak, presumably due to $V_2$H, overlapping with that of the single negatively charged $V_2$. Published by AIP Publishing. https://doi.org/10.1063/1.5037310

I. INTRODUCTION

The divacancy ($V_2$) is perhaps the most fundamental intrinsic defect in silicon stable at room temperature. It has four charge states: positive (+), neutral (0), singly negative (−), and doubly negative (=). Despite a large amount of studies, there is still some controversy regarding its annealing mechanisms in different types of silicon materials. The $V_2$ dissociation prevails in oxygen-lean float zone silicon (Fz-Si), while the diffusion mechanism dominates in oxygen-rich Czochralski-grown silicon (Cz-Si) where $V_2$ can be trapped by interstitial oxygen atoms (O$_i$), forming divacancy-oxygen complexes ($V_2$O$_i$).

However, these two mechanisms become less important in hydrogen-rich silicon materials. The presence of hydrogen significantly reduces the annealing temperature of $V_2$. The interaction of $V_2$ with hydrogen is more complex and considerably less studied than that with O$_i$. EPR and Fourier transform infrared spectroscopy (FTIR) signals of $V_2$H have been identified in hydrogen-implanted samples. However, the identification of electronic levels related to $V_2$H$_n$ with $n = 1$, 3, or 5 is still controversial. On the basis of their atomic structure (Ref. 4), these complexes are anticipated to have three charge states: (+), (0), and (−), and theory predicts that the donor (0+/−) and acceptor (−/0) levels are located close to those of $V_2$(0+/−) and $V_2$(−/0), respectively. Experimentally, this prediction is still not conclusively confirmed. For example, in Deep Level Transient Spectroscopy (DLTS) studies of $H^+$-implanted n-type samples, the amplitude of the DLTS peak assigned to $V_2$(−/0) exceeds that of the double-acceptor state $V_2$(−/−), by almost a factor of two in some cases. $V_2$(−/−) may differ in amplitude in the case of heavy ion implantation. However, for $H^+$ ions, this effect is weak and amounts only to around 10%. It has been suggested, hence, that the enhancement of the $V_2$(−/0) DLTS peak is due to a contribution from $V_2$H−/−, overlapping with $V_2$(−/0), but studies of the annealing kinetics did not result in a fully conclusive identification of $V_2$H.

The general picture of the hydrogen interaction with $V_2$ becomes even more complex when hydrogen is introduced by other techniques than implantation, such as hydrogenation from hydrogen-plasma (Ref. 2) or chemical solution (Ref. 8). In these studies, $V_2$ was generated by MeV electron irradiation, and the $V_2$(−/−) and $V_2$(−/0) DLTS peaks exhibited almost identical amplitudes not only after the irradiation but also during the subsequent hydrogen-assisted annealing. This rules out the formation of an overlapping $V_2$H level in these samples. It has been realized then that diatomic hydrogen (H$_2$), or hydrogen dimers, can play an important role in the $V_2$ annealing. Thus, the absence of a $V_2$H level in these studies has been explained by the interaction $V_2$H$_2$, however, has not been identified via the emergence of an electronic level.

It is interesting to note that theory predicts that $V_2$H$_2$ is electrically active as well. It is expected that the acceptor state $V_2$H$_2$(−/0) occurs at $\sim E_c − 0.32$ eV ($E_c$ being the edge of the conduction band). This predicted level position of $V_2$H$_2$(−/0) coincides with that of VOH(−/0), which is also located at about $E_c − 0.32$ eV (Ref. 8 and references therein), and a strong overlap between $V_2$H$_2$(−/0) and VOH(−/0) in DLTS spectra can be expected. VOH is one of the most dominant complexes in irradiated and hydrogen-enriched silicon, with a concentration significantly exceeding that of $V_2$H$_2$. This makes the detection of $V_2$H$_2$(−/0) challenging. With respect to the donor state $V_2$H$_2$(0+/−), theory does not predict any level in the bandgap.
In the present work, we report on the evolution of \( V_2 \) and associated complexes upon heat treatments of H\(^+\)-implanted samples using high-resolution DLTS analysis. The H\(^+\)-implantation was performed with multiple energies to form a uniform box-like profile of \( V_2 \) and hydrogen, facilitating the data analysis and interpretation. Upon annealing, a new hydrogen-related level, labeled \( E5^* \), is revealed. Its formation kinetics is slower than that of other defect reactions involving H\(_2\), and it anticorrelates in a one-to-one ratio with the state commonly ascribed to \( V_2\text{H}(\text{–}/0) \).\(^{4,6,7}\)

II. EXPERIMENTAL DETAILS

The samples investigated in this study were cut from three different phosphorus (P) doped n-type Cz-Si wafers; their dopant concentrations are presented in Table I. The oxygen and carbon concentrations were about \( 7 \times 10^{17} \text{ cm}^{-3} \) and below \( 5 \times 10^{15} \text{ cm}^{-3} \), respectively, as measured by FTIR spectroscopy. The samples were cleaned in a standard RCA solution, and the native oxide layer was dissolved by a dilute HF dip during 10–20 s. Using a shadow mask, circular palladium contacts with a diameter of 1 and 2 mm and a thickness of 150 nm were then deposited to form Schottky diodes. The samples were annealed at 300\( \degree \text{C} \) during 2 h in nitrogen ambient to diffuse out residual hydrogen that penetrated into the samples during the chemical treatment. Indium-gallium eutectic was used as backside Ohmic contacts. Here, it should be pointed out that the use of palladium Schottky contacts does not appear to influence the defect evolution observed. In a previous study of samples implanted with multiple energy H ions for analysis by DLTS and MCTS, gold Schottky contacts with a protective aluminum layer were used.\(^{9}\) Isochronal annealing of these samples up to 300 \( \degree \text{C} \) revealed identical trends in the defect annealing and formation as those found in the present study.

H\(^+\) ions were implanted into samples A and C0–C4 at room temperature with multiple energies to obtain a box-like profile. The projected ion range was selected to cover the depletion region during the subsequent DLTS measurements. A high energy implantation was performed for the B samples such that the H\(^+\) ions penetrated far beyond the DLTS probing depth, \( \sim 48 \mu \text{m} \) versus 4–6 \( \mu \text{m} \) as estimated by SRIM simulations.\(^{12}\) Thus, in the B samples, only hydrogen-free irradiation-induced defects were monitored, and in accordance with previous results, in the literature,\(^{13}\) their evolution during annealing can be used as a control to unveil the influence of hydrogen in samples A and C. The implantation parameters for all the studied samples are given in Table I. All the samples were exposed to RT for a few hours (maximum 24 h) after the implantation before the first DLTS measurement was undertaken. The samples were then stored in a freezer (-18 \( \degree \text{C} \)) between every stage of annealing and analysis. Isochronal and isothermal annealings were carried out at temperatures of 75–150 \( \degree \text{C} \). DLTS and capacitance-voltage (CV) measurements were performed after each annealing stage using a refined version of the setup described in Ref. 14, having a Boonton 7200 capacitance meter, a closed cycle helium cryostat operating in the temperature range from 30 \( \text{K} \) to 300 \( \text{K} \), and an in-house LabView code for controlling the system. All the DLTS spectra were recorded adopting the GS4 weighting function to obtain high spectral energy resolution.\(^{15}\)

III. RESULTS AND DISCUSSION

The charge carrier profiles of the as-implanted A samples, deduced from the CV measurements, reveal a decrease in the effective doping concentration from \( 7.5 \times 10^{14} \text{ cm}^{-3} \) to \( 5.0 \times 10^{14} \text{ cm}^{-3} \) in the H\(^+\)-implanted region. This is primarily attributed to passivation of the phosphorus donors by hydrogen with formation of electrically inactive phosphorus-hydrogen (PH) pairs.\(^{16}\) CV-profiles of the B sample do not show a significant decrease in the charge carrier concentration after the high-energy implantation. This indicates that the implantation-induced defects alone do not considerably affect the carrier concentration, and the dominant mechanism is the passivation of phosphorus by hydrogen. Based on this observation, we estimate the concentration of PH pairs in the implanted region of the A samples as \( 2.5 \times 10^{14} \text{ cm}^{-3} \), while the average hydrogen concentration, estimated from the total implantation dose and the width of the box-like implantation profile, is \( 3 \times 10^{14} \text{ cm}^{-3} \).

Figure 1 shows DLTS spectra for the samples A and B after implantation and after annealing at 150 \( \degree \text{C} \). The DLTS signal is represented as \( 2N_d \Delta C/C_r \), where \( N_d \) is the effective doping concentration, \( \Delta C \) is the amplitude of the capacitance transient, and \( C_r \) is the steady-state capacitance at the reverse

![FIG. 1. DLTS spectra for samples A and B before and after annealing at 150 \( \degree \text{C} \) during 30 min. The spectra were acquired with a (640 ms)\(^{–1}\) rate window.](image-url)
bias used. In the case of uniform distributions, the concentration of carrier traps, \( N_j \), equals \( 2N_i \Delta C/C_i \) at the maximum of the corresponding DLTS peak. Before annealing, the DLTS spectrum of sample B contains peaks attributed to vacancy-oxygen pairs (VO)\(^1\), \( V_2(=/-) \), planar-coordinated trivacancies \( V_3(=/-) \)\(^1\), and a peak labeled E4 which is an overlap of \( V_2(=/-) \) and \( V_3(=/-) \)\(^1\). In addition to these peaks, the corresponding DLTS spectrum for sample A demonstrates several hydrogen-related states. The peak E1 is tentatively attributed to a donor state of complexes involving substitutional carbon, oxygen, and hydrogen\(^1\). The spectrum includes also the prominent VOH peak \( \Delta E \approx 4 \leq 10 \text{ eV} \), \( \Delta E \approx 0.45 \text{ eV} \), respectively, with apparent electron capture cross-section (CCS) values of \( 4 \times 10^{-17} \) and \( 2 \times 10^{-17} \text{ cm}^2 \), respectively. The CCS values deduced from direct CCS measurements by the variation of filling pulse duration are equal to \( 6.0 \times 10^{-18} \text{ cm}^2 \) and \( 2.5 \times 10^{-18} \text{ cm}^2 \) for \( E_4 \) and \( E_5 \), respectively. Thus, the transition entropies \( \Delta S/k \) are similar and equal to \( \sim 2 \) for both \( E_4 \) and \( E_5 \). Furthermore, the electron emission rates of both states do not exhibit any dependence on the electric field. That is, together with their small CCS, these results strongly favor an assignment of \( E_4 \) and \( E_5 \) to acceptor-like transitions.

Upon annealing at 150°C for 30 min, the charge carrier profile of sample A recovers, indicating the dissociation of the PH pairs\(^1\), while the carrier profile of sample B remains unchanged. \( V_4 \) modifies its configuration from the planar-coordinated to the more stable fourfold one\(^1\), and the \( V_2(=/-) \) and \( V_3(=/-) \) signals disappear in both samples. The amplitudes of \( V_2(=/-) \) and \( V_3(=/-) \) peaks become practically equal, as expected for unperturbed/isolated \( V_2 \) centers. In contrast, the spectrum of sample A evolves substantially, indicating the defect interaction with “free” hydrogen, presumably originating from the dissociating PH pairs\(^1\). In particular, the presence of hydrogen is manifested by the growth of VOH and the decrease in VO, \( V_2(=/-) \), and E4. \( E_5 \) does not change significantly, while \( E_5^* \) grows noticeably and is concluded to be a hydrogen-related state. In fact, the amplitude of \( E_5^* \) exceeds now that of \( V_2(=/-) \) and \( E_5 \). It should also be pointed out that simulation of DLTS spectra for the \( E_5^* \) peak shows an excellent fit, assuming one contributing level only, and no evidence for an overlapping level is found.

The nature of \( E_5 \) is still not conclusively identified. However, its position in the bandgap is in the same range as the theoretically predicted acceptor level of VH\(^2\), and it is reported to anneal out simultaneously with the EPR signal of VH\(^5\). Furthermore, \( E_5 \) is only observed in H-implanted samples and not in irradiated ones subjected to subsequent hydrogenation. Hence, the simultaneous presence of hydrogen and mobile primary intrinsic defects, such as \( V \), appears to be a necessary condition for \( E_5 \) formation, corroborating an assignment to VH. The \( E_5^* \) state has recently been reported in Ref. 9, and it grows after annealing at 75–100°C before disappearing at temperatures above 225°C. A DLTS peak with a similar signature as \( E_5^* \), labeled E10, was briefly mentioned in Ref. 20 but without any detailed investigation.

In order to gain further understanding of the formation of \( E_5^* \), the low doped samples C0–C4 (Table I) have been implanted with \( \text{H}^+ \) ions. Similar to sample A, the charge carrier profiles of the samples C0–C4 exhibit a decrease after implantation, attributed to the formation of PH pairs with a concentration of \( 2 \times 10^{13} \text{ cm}^{-3} \), while the average (uniform) concentration of implanted hydrogen is \( 5 \times 10^{13} \text{ cm}^{-3} \) in the probed volume.

DLTS spectra of the C0 sample after different stages of 30 min isochronal annealing are shown in Fig. 2. In comparison to sample A, the \( E_1 \) amplitude is higher, relative to the other peaks, presumably indicating that residual carbon is more prominent in this material as a trap for hydrogen and implantation-induced defects. The net carrier concentration recovers with annealing, attributed to the dissociation of the PH pairs, and despite the low doping concentration, the evolution of the DLTS spectra is similar to that in sample A. \( E_5^* \) grows gradually, and VO and \( V_2 \) react with “free” hydrogen. There is also a noticeable anticorrelation between the amplitudes of \( E_4 \) and \( E_5^* \) upon the annealing.

To analyze the evolution kinetics of \( E_5^* \) in detail, we have conducted isothermal annealing of the samples C1–C4 in the temperature range of 75–95°C. The development of the peak amplitudes is presented in Fig. 3. VO and \( V_2 \) react with \( \text{H}_2 \), as inferred from a rapid decrease in VO (data not shown) and \( V_2(=/-) \) and an increase in VOH during the initial stages of annealing. The growth of \( E_5^* \) is substantially slower, which indicates a different migrating species, for instance \( \text{H}_2 \), or a reaction mechanism involving a barrier.

![FIG. 2. DLTS spectra of sample C0 after different stages of isochronal annealing, recorded with a (640 ms)\(^{-1} \) rate window.](image-url)
The formation of H₂ in silicon is a somewhat controversial issue, and it is well established that H₂ does indeed form, but the exact mechanism is still under debate (see, for instance, Refs. 23 and 24). It is generally accepted that Hᵢ in silicon is an amphoteric, negative-U defect, and the dominant fractions are either negatively or positively charged depending on the Fermi level position.²⁵ Thus, formation of H₂ by the direct interaction of two identically charged Hᵢs (Hᵢ⁺ + Hᵢ⁻ → H₂) has a low probability due to the Coulomb repulsion. It has been suggested, however, that dopants (donors and acceptors) can in fact mediate the formation of H₂.²⁶–²⁸ In addition, hydrogen is also known to form weakly bound complexes with substitutional carbon (Cₛ)²⁹ and interstitial oxygen (Oᵢ).³⁰ This opens another possible mechanism, where Cₛ and Oᵢ mediate H₂ formation. Besides, the interaction of hydrogen with monovacancies and self-interstitials, present during the implantation, should not be excluded as a path to form H₂.²⁸

The aforementioned anti-correlation between E₅* and E₄ becomes even more apparent upon the isothermal annealing (Fig. 3), and the increase in the E₅* concentration versus the loss of E₄ for the isothermally annealed samples C₁–C₄ is depicted in Fig. 4. The data points are close to the line y = x, evidencing a nearly one-to-one proportionality between the E₅* growth and the E₄ loss. As discussed above, E₄ contains contributions from at least two levels: V₂(−/0) and an unknown one, presumably V₂H(−/0).⁶⁷ The contribution from V₂(−/0) can be estimated from the amplitude of the V₂(−/) peak arising from the same defect center and with no overlapping levels. It should be emphasized that the interaction V₂ + Hᵢ → V₂H does not decrease the E₄ peak since E₄ is a sum of V₂(−/0) and V₂H(−/0). Thus, the annealing of E₄ can be either (i) due to an interaction of V₂ with another hydrogen species instead Hᵢ or (ii) due to an interaction of V₂H with Hᵢ or other hydrogen species. No correlation is found between the growth of E₅* and the loss of V₂(−/0), i.e., V₂ appears not to be a direct precursor of E₅*. Hence, V₂H(−/0) seems to be directly associated with the formation of E₅*.

The defect evolution upon the isothermal annealing has been fitted by exponential decay to deduce reaction rates (curves in Fig. 3). Figure 5 shows the temperature dependencies of the formation rates for VOH and E₅*. The rates exhibit an Arrhenius behavior, yielding activation energies of EᵥOH = 1.05 eV and Eₑ₅* = 1.10 eV and pre-exponential factors rᵥOH and rₑ₅* of around ~10¹¹–10¹² s⁻¹. The “slow” rate is about a factor of 4 slower within the investigated temperature interval, and the similar activation energies indicate strongly that the diffusing species are the same or very similar in the two cases.

As mentioned above, the origin of the fast kinetics, which governs the annealing of VO and V₂(−/) and the formation of VOH, is attributed to the PH dissociation and subsequent diffusion of atomic Hᵢ. Hence, based on the correlation plot in Fig. 4 and the Arrhenius analysis of the experimental rates in Fig. 5, it is tempting to ascribe the E₅* formation to the interaction V₂H + Hᵢ → V₂H₂, where the acceptor transition V₂H₂(−/0) can be associated with E₅*. However, one should emphasize that the amplitudes of VOH and V₂(−/) saturate faster during the isothermal anneals in
hydrogen-related complex, presumably of H₂E₂E₂ nature. The hydrogen-enriched material, evidencing its hydrogen-related nature, has been observed. The presence of a small barrier (∼0.05 eV) for the transition to V₂H₂.

Based on the kinetics rates, one can rule out the involvement of hydrogen molecules in the E₅* formation since the estimated diffusivity of the hydrogen species involved is several orders higher compared to that obtained by Markевич and Suezawa for the molecules.30 Another potential candidate for the slow E₄ and E₅* kinetics could be the so-called H₂E₂E₂ dimer,31 which can result in the interaction V₂H + H₂ → V₂H₂. The diffusivity of H₂E₂E₂ is poorly investigated but can be anticipated to be slower than that of H₂, although it may not seem probable that the difference is only a factor of 4.

IV. CONCLUSIONS

The V₂ evolution in hydrogen-implanted Czochralski-grown silicon samples upon isochronal and isothermal annealing has been studied by DLTS. An acceptor-like electronic state, labeled E₅*, with the energy position Eᵣ ≈ 0.42 eV has been observed. The E₅* center is present only in the hydrogen-enriched material, evidencing its hydrogen-related nature. E₅* anticorrelates, in a close one-to-one ratio, with a hydrogen-related complex, presumably V₂H, which contributes to the V₂-containing E₄ peak. Isothermal heat treatment reveals slower formation kinetics for E₅*, by a factor of 4, compared to the interactions of VO and V₂ with H₂. It implies the presence of a small barrier (∼0.05 eV) for the interaction of H₂ with V₂H or another slower diffusing hydrogen species being involved in the formation of E₅*.

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FIG. 5. Arrhenius plot of formation rates for VOH and E₅* deduced from the isothermal annealing at 75 °C, 86 °C, 90 °C, and 95 °C.