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To cite this article: I L Kolevator *et al* 2019 *J. Phys.: Condens. Matter* **31** 235703

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Correlated annealing and formation of vacancy-hydrogen related complexes in silicon

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Received 10 January 2019, revised 23 February 2019

Accepted for publication 1 March 2019

Published 1 April 2019



Abstract

We report on a deep level transient spectroscopy study of annealing kinetics of a deep, vacancy-hydrogen related level, labeled $E5^*$, at 0.42 eV below the conduction band in hydrogen-implanted n-type silicon. The $E5^*$ annealing correlates with the formation of another commonly observed vacancy-hydrogen related level, labeled $E5$, at 0.45 eV below the conduction band. The annealing of $E5^*$ and the formation of $E5$ exhibit first-order kinetics with an activation energy of 1.61 ± 0.07 eV and a pre-factor of $\sim 10^{13}$ – 10^{14} s⁻¹. The pre-factor indicates a dissociation or structural transformation mechanism. The analysis of electron capture cross-sections for $E5^*$ and $E5$ reveals considerable transition entropies for both states and a temperature dependent capture cross-section for $E5^*$. Two possible identifications of $E5^*$ and $E5$ are put forward. Firstly, $E5^*$ can be attributed to $V_2H_2(-/0)$ or $V_2H_3(-/0)$, which dissociate with the emission of VH ($E5$). Secondly, $E5^*$ and $E5$ can be assigned to two different configurations of V_3H .

Keywords: silicon, hydrogen, vacancy-defects, DLTS

(Some figures may appear in colour only in the online journal)

1. Introduction

Hydrogen (H) is probably the most common and, at the same time, controversial impurity in silicon. It can be found in a form of atomic interstitial species (H_i) [1], dimers (H_2^*) [2] and molecules (H_2) [3]. Diffusion of different hydrogen species and their interactions with defects are still not fully understood (see [4] and references therein). Hydrogen is also a crucial impurity in silicon technology due to the ability to passivate dangling bonds. Moreover, recently there have been observed indications that hydrogen may have an effect on the so-called light-induced degradation of solar cells [5–7].

Recently, we have reported on a hydrogen-related level, labeled as $E5^*$ [8]. The level forms during heat treatments in the temperature range 75 °C–95 °C and has a position at $E_c - 0.42$ eV (E_c being the conduction band minimum) and

an apparent capture cross-section (CCS) of 4×10^{-17} cm². The CCS measured directly by filling pulse variation is found to be $\sim 6 \times 10^{-18}$ cm². This reveals a relatively high transition entropy for ionization of $E5^*$: $\Delta S/k \approx 2$, where k is Boltzmann constant. Such a high ΔS can indicate a complex process involving structural changes.

A detailed annealing study of the implantation-induced defects at 75 °C–95 °C observed two processes with different rates [8]. The process with a faster rate is related to the dissociation of phosphorus–hydrogen (P–H) pairs and formation of vacancy–oxygen–hydrogen (VOH) and divacancy–hydrogen (V_2H) complexes by reactions with H_i released from P–H. The second process is slower by a factor of 4, and is associated with formation of $E5^*$. It has been observed that formation of $E5^*$ correlates with annealing of the deep level transient spectroscopy (DLTS) peak, labeled $E4$, that consists of overlapping contributions from single acceptor states of divacancy, $V_2(-/0)$, and divacancy–hydrogen, $V_2H(-/0)$. The

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correlation between $E5^*$ and the double-acceptor state of divacancy, $V_2(=/-)$, has not been observed, and V_2 has been ruled out as a precursor for $E5^*$. Thus, it has been concluded that the precursor for $E5^*$ is likely to be V_2H .

The activation energies for the fast and slow rates have been found to be similar: 1.05 ± 0.04 eV and 1.10 ± 0.02 eV, respectively; with the pre-exponential factor for the fast rate in the confidence interval $(2 \div 25) \times 10^{11} \text{ s}^{-1}$ and for the slow one in the confidence interval $(3 \div 14) \times 10^{11} \text{ s}^{-1}$. The difference in the deduced values lies close to the experimental uncertainty, and one can not conclusively claim the nature of the difference between the two rates. However, a small barrier (~ 0.05 eV) for interaction between V_2H and H_i or H_2^+ has been suggested [8].

In the present work, we investigate possible identification of $E5^*$ by studying the annealing kinetics. A series of isochronal and isothermal annealing is performed. We observe that the annealing kinetics of $E5^*$ is consistent with a dissociation mechanism or structural transformation and deduce the activation energy. We also find an anti-correlation between $E5^*$ and a commonly observed hydrogen-related state, labeled $E5$. The origins of both $E5^*$ and $E5$ are discussed.

2. Experimental details

The samples in present work were phosphorus (P) doped n-type Czochralski-grown silicon described in our previous investigation [8]. The P concentration was derived from capacitance-voltage profiles to be $1.2 \times 10^{14} \text{ cm}^{-3}$. The oxygen and carbon concentrations were found by Fourier transform infrared spectroscopy to be $7 \times 10^{17} \text{ cm}^{-3}$ and below $5 \times 10^{15} \text{ cm}^{-3}$, respectively. The wafers were chemically cleaned by standard RCA solutions, and then a dilute hydrofluoric acid was utilized to remove a native oxide layer. Schottky contacts were produced by 150 nm palladium deposition using a circle shadow mask. The samples were annealed at 300 °C during 2 h in nitrogen atmosphere to diffuse-out H that was introduced during chemical treatment. The backside contacts were formed by aluminum film or indium-gallium eutectic.

The H^+ -implantations were performed at room temperature through the Schottky contacts with six different energies in the range 300–600 keV and a total dose of $4 \times 10^{10} \text{ cm}^{-2}$ to obtain uniform ‘box-like’ distributions of defects and H. One of the samples underwent 30 min isochronal annealings in the range of 75 °C–275 °C. Other samples underwent isothermal annealings at 75 °C–86 °C during 496–860 min, which resulted in formation of $E5^*$ (as described in [8]). The samples were then heat treated at 170 °C for 30 min to anneal minor unstable defects prior to isothermal annealings at 190, 200, 210 or 220 °C.

The capacitance-voltage and DLTS measurements were performed using a refined version of the setup described in [9] with Boonton 7200 capacitance meter and a closed cycle helium cryostat. The DLTS signal was deduced by using GS4 weighting function to obtain higher energy resolution in the DLTS spectrum [10].

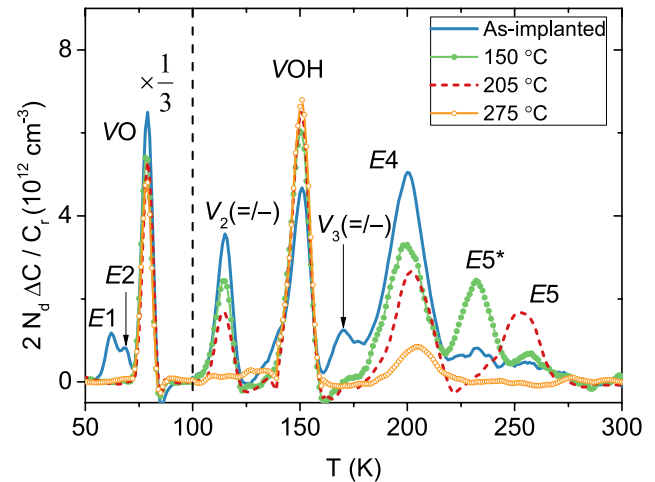


Figure 1. DLTS spectra before and after isochronal annealing for 30 min at different temperatures, recorded with a $(640 \text{ ms})^{-1}$ rate window.

3. Experimental results

Figure 1 shows the DLTS spectra for the sample before and after 30 min isochronal annealings at different temperatures. The DLTS spectrum of the as-implanted sample shows signals of several defects: $E1$, $E2$, VO , $V_2(-/0)$, double acceptor state of trivacancy ($V_3(=/-)$) [11], VOH , $E4$, $E5^*$ and $E5$. The $E1$ and $E2$ peaks in figure 1 are observed together only in H-containing samples, and their energy positions are close to those attributed to carbon–oxygen–hydrogen complexes in [12, 13] and labeled there $E1$ and $E2$ as well. The $E4$ peak consists of overlapping contributions from $V_2(-/0)$ and, presumably, $V_2H(-/0)$ [8, 14, 15]. In addition, $E4$ may have a contribution from the single acceptor state of trivacancy, $V_3(-/0)$ [11].

Before annealing the dominant part of H in the studied samples is stored in P–H [8]. P–H dissociates at ≥ 75 °C with a release of H_i that interacts with the defects. This is manifested in figure 1 in the growth of VOH and $E5^*$, and decrease of VO , $V_2(=/-)$ and $E4$ after annealing at 150 °C. After further heat treatment at 205 °C, VO decreases slightly, accompanied by a slight increase in VOH . The $V_2(=/-)$ and $E4$ peaks also decrease. $E5^*$, however, anneals out completely, and growth of $E5$ takes place. After annealing at 275 °C, VO and VOH remain to be the dominant peaks, with a slight decrease in VO and a slight increase in VOH . The $V_2(=/-)$ peak has disappeared, indicating that V_2 is annealed out. This suggests that the remaining amplitude of $E4$ is mainly due to $V_2H(-/0)$. $E5$ is completely annealed out.

Four samples have been annealed isothermally at temperatures of 190, 200, 210 and 220 °C to study the evolution kinetics of $E5^*$ and $E5$. The DLTS spectra before and after different annealing steps at 190 and 220 °C are presented in figure 2. The as-implanted spectra are practically identical to that in figure 1. Prior to the isothermal annealings, the samples were annealed at 75 °C–86 °C to form the $E5^*$ peak (see [8]) and then heat treated at 170 °C for 30 min to anneal out minor peaks. Subsequent isothermal annealings at 190 °C,

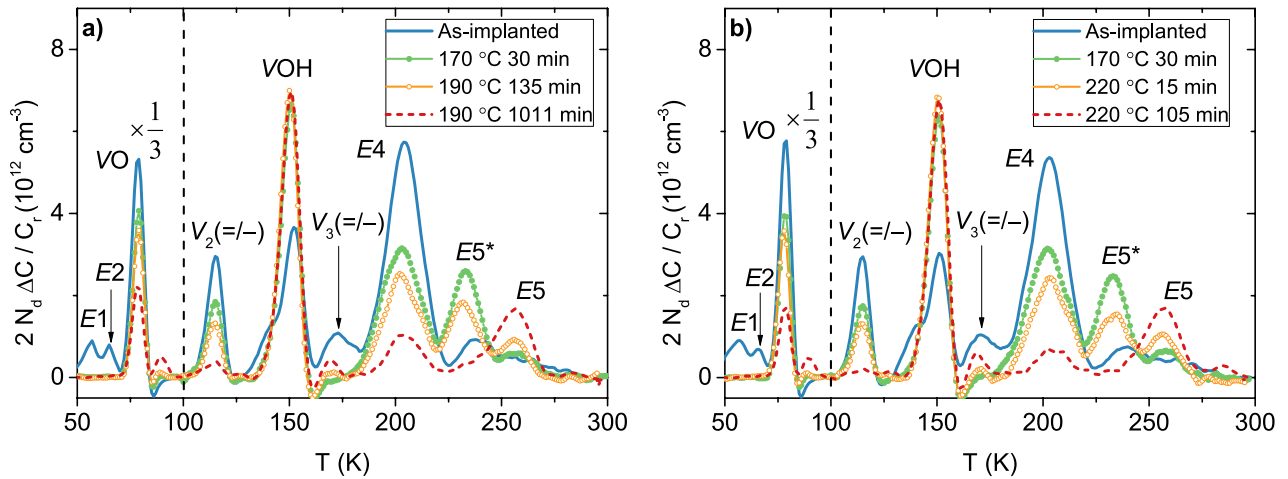


Figure 2. DLTS spectra of the samples annealed isothermally at 190 °C (a) and 220 °C (b) for different durations, recorded with a $(640\text{ms})^{-1}$ rate window.

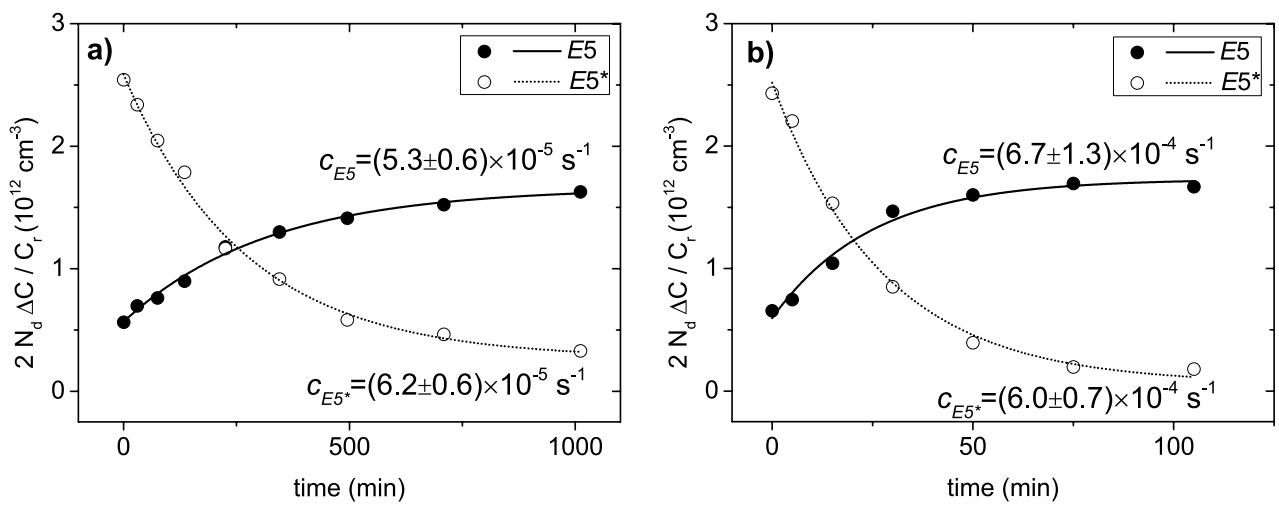


Figure 3. Amplitudes of $E5^*$ and $E5$ as a function of annealing time (symbols) and the corresponding exponential fits (curves) at 190 °C (a) and 220 °C (b).

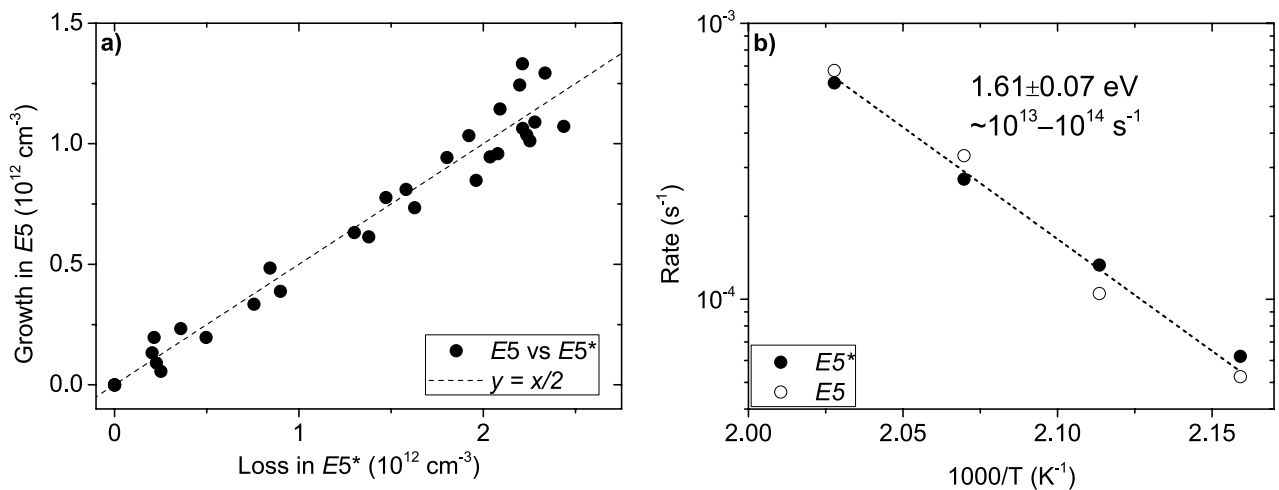


Figure 4. Correlation between the growth of $E5$ and the loss of $E5^*$ for all isothermally annealed samples (a), and Arrhenius plot for annealing rate of $E5^*$ and formation rate of $E5$ (b).

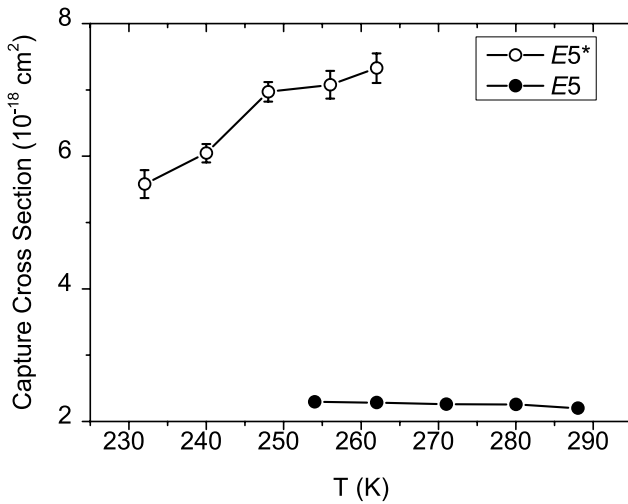


Figure 5. Temperature dependences of CCS for $E5^*$ and $E5$.

200 °C, 210 °C and 220 °C demonstrate a trend similar to the sample annealed isochronally: $E5^*$ decreases gradually with a simultaneous growth of $E5$. The kinetics for both peaks at 190 and 220 °C are shown in figure 3. The $E5^*$ annealing and the $E5$ formation follow the first order kinetics. The rates, c in figure 3, are deduced by exponential fitting, and show similar values for annealing of $E5^*$ and formation of $E5$ for all the annealing temperatures.

Moreover, the amplitudes of $E5^*$ and $E5$ show a strong anti-correlation upon annealing. That is shown in figure 4(a) where the growth of $E5$ is plotted versus the loss of $E5^*$ for all the samples isothermally annealed at 190 °C–220 °C during the investigation. The data points demonstrate a linear correlation and lie close to the line $y = x/2$, i.e. $\Delta E5 = -\Delta E5^*/2$. The Arrhenius plot for the $E5^*$ annealing rate and the $E5$ formation rate is shown in figure 4(b). The rates follow Arrhenius behavior, and the deduced activation energy and the pre-exponential factor are 1.61 ± 0.07 eV and $\sim 10^{13}$ – 10^{14} s⁻¹, respectively.

CCS for both $E5^*$ and $E5$ have been directly measured by varying the DLTS filling pulse duration at different measurement temperatures, and the experimental results are shown in figure 5. Similarly to $E5^*$, the transition entropy $\Delta S/k$ for $E5$ is close to 2. However, we observe a temperature dependence of CCS for $E5^*$, while CCS for $E5$ remains constant in the range 254–288 K. Assuming an activation mechanism for CCS, we deduce the energy barrier for electron capture to be 50 ± 10 meV. The relatively high entropies together with the temperature dependence of CCS for $E5^*$ may indicate structural changes between occupied and empty levels, and could be attributed to a complex structure for both $E5^*$ and $E5$.

4. Discussion

4.1. $E5^*$ as a divacancy-hydrogen complex

In the previous study [8], we have tentatively attributed $E5^*$ to an acceptor state of a defect formed by reaction of V_2H with H_i or H_2 , i.e. $V_2H_2(-/0)$ or $V_2H_3(-/0)$. The pre-exponential

factor for $E5^*$ annealing ($\sim 10^{13}$ – 10^{14} s⁻¹) found in the present study indicates a dissociation mechanism. The rates for the $E5^*$ and $E5$ evolutions are similar at each studied temperature and follow Arrhenius behavior. The correlation between $E5^*$ and $E5$ is valid for all the samples. All these facts lead to an assumption that $E5$ can be a product of the $E5^*$ dissociation. Previously, $E5$ has been tentatively attributed to the acceptor state of VH [15]. Indeed, the electrical activity of VH also originates from the dangling bonds, and its electrical level $VH(-/0)$ is predicted to have an energy position close to those of $V_2(-/0)$ and the vacancy-phosphorus (VP) state at $\sim E_c - 0.42$ eV [16]. $E5$ is known to form in H⁺-implanted samples [8, 15], but not in irradiated material with subsequent hydrogenation [17, 18]. This supports the identification of $E5$ as VH that requires simultaneous presence of both monovacancies and H atoms to form. One could expect that dissociation of hydrogen-vacancy complexes V_2H_2 or V_2H_3 ($E5^*$) leads to emission of VH ($E5$).

This mechanism, however, has difficulties in explaining the quantitative correlation between $E5^*$ and $E5$, where $\Delta E5 = -\Delta E5^*/2$. Indeed, annealing of, for instance, one V_2H_2 ($E5^*$) would result in formation of two VH ($E5$), while we observe the opposite: annealing of two $E5^*$ centers is required to form one $E5$ center. Thus, one has to assume a more complex dissociation mechanism, where several reaction channels are possible, and the probability of VH formation is 50%.

4.2. $E5^*$ as a trivacancy-hydrogen complex

On the other hand, the significant transition entropy $\Delta S/k \approx 2$, together with temperature dependent CCS for $E5^*$, can indicate another, more complex structure of $E5^*$. It is known that V_3 has a considerable concentration in irradiated and ion implanted silicon ([11] and figure 1). V_3 can be presented in two configurations in silicon lattice: (i) so-called ‘part of a hexagonal ring’ ($V_3^{(PHR)}$) with two deep acceptor levels at $E_c - 0.36$ eV and $E_c - 0.46$ eV originated from two Si dangling bonds, and (ii) so-called four-fold coordinated ($V_3^{(FFC)}$) with one acceptor level at $E_c - 0.075$ eV [11]. In the as-implanted samples $V_3^{(PHR)}$ is the dominant configuration. As the temperature increases to 50 °C–70 °C, $V_3^{(PHR)}$ starts to transform to $V_3^{(FFC)}$. The transformation follows an activation mechanism with an activation energy of around 1.2 eV and a pre-factor of $\sim 10^{13}$ – 10^{14} s⁻¹ [19].

It is tempting to suggest that, similarly to V_3 , trivacancy-hydrogen complex (V_3H) can also exist in PHR ($V_3H^{(PHR)}$) and FFC ($V_3H^{(FFC)}$) configurations. $V_3H^{(PHR)}$ should exhibit a structure similar to $V_3^{(PHR)}$, with a H atom passivating one of the two dangling bonds [20]. The remaining dangling bond should give rise to one deep acceptor state, $V_3H^{(PHR)}(-/0)$, close to that of $V_3^{(PHR)}(-/0)$ at around $E_c - 0.46$ eV. It is interesting to note that $V_3H^{(FFC)}$ should also have a deep acceptor level since the H atom will break one of the reconstructed bonds, resulting in one dangling bond. Thus, both $V_3H^{(PHR)}$ and $V_3H^{(FFC)}$ should have a deep acceptor level originating

from a Si dangling bond, while having different structure. Taking this into account one can suggest that the annealing of $E5^*$ is not a dissociation, but a structural transformation from $E5^*$ to $E5$, i.e. from one configuration of V_3H to another. One can notice the similar pre-factors for the $E5^* \rightarrow E5$ and $V_3^{(PHR)} \rightarrow V_3^{(FFC)}$ kinetics: $\sim 10^{13} - 10^{14} \text{ s}^{-1}$.

We observe, however, that the amplitude of $E5^*$ is almost double of that of $V_3(=/-)$ in as-implanted sample (figure 1), and the correlation of $E5^*$ versus $E5$ is 2-to-1 (figure 4(a)). One could speculate that, for instance, $V_3H^{(FFC)}$ might be a negative- U defect with an acceptor and a donor levels [21], which emits two electrons upon the $(-/+)$ charge transition, resulting in a doubled amplitude in the DLTS spectrum. Both $V_3H^{(PHR)}$ and $V_3H^{(FFC)}$ can have a $(0/+)$ donor and a $(0/-)$ acceptor transition similarly to V_2 , V_2H and V_3 .

The negative- U behavior implies a considerable structural change of the center upon electron capture and emission. It is interesting to note that the temperature dependence of CCS for $E5^*$ (figure 5) is consistent with the possible negative- U nature. Thus, an identification of $E5^*$ as $V_3H^{(FFC)}$ and $E5$ as $V_3H^{(PHR)}$ can be tentatively put forward. This identification does not contradict our previous observation on the correlation of $E5^*$ formation with the annealing of $E4$ [8], since $E4$ has a contribution from V_3 as well.

We can not conclude at the moment on the exact configurations for $E5^*$ and $E5$, and a reverse identification of $E5^*$ as $V_3H^{(PHR)}$ and $E5$ as $V_3H^{(FFC)}$ can not be ruled out. Theoretical studies on the atomic configurations and electronic properties of V_3H are, thus, necessary to substantiate or rule out these assignments.

5. Conclusion

The annealing kinetics of the hydrogen-related states $E5^*$ and $E5$ has been studied by DLTS. $E5^*$ anneals out at around 200 °C with a correlated formation of $E5$. The kinetics exhibit a first-order behavior with an activation energy of $1.61 \pm 0.07 \text{ eV}$ and a pre-factor of $\sim 10^{13} - 10^{14} \text{ s}^{-1}$. The pre-factor indicates a dissociation or structural transformation mechanism for the $E5^*$ annealing and the $E5$ formation. The analysis of the electron capture cross-sections for $E5^*$ and $E5$ reveals considerable entropy factors for both states and a temperature dependent capture cross-section for $E5^*$. Two possible identifications of $E5^*$ and $E5$ are put forward. Firstly, $E5^*$ can be attributed to $V_2H_2(-/0)$ or $V_2H_3(-/0)$, which dissociate with the emission of VH ($E5$). Secondly, $E5^*$ and $E5$ can be assigned to two different configurations of V_3H .

Acknowledgments

This work was performed within ‘The Norwegian Research Centre for Solar Cell Technology’ (project number 460976)

co-sponsored by the Norwegian Research Council and research and industry partners in Norway. The Research Council of Norway is acknowledged for the support to ‘The Norwegian Micro- and Nano-Fabrication Facility, NorFab’ (project number 245963).

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