

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

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## 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  $1.61 \pm 0.07$  eV and a pre-factor of  $\sim 10^{13}$ – $10^{14}$  s<sup>−1</sup>. 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  $4 \times 10^{-17}$  cm<sup>2</sup>. The CCS measured directly by filling pulse variation is found to be  $\sim 6 \times 10^{-18}$  cm<sup>2</sup>. This reveals a relatively high transition entropy for ionization of  $E5^*$ :  $\Delta S/k \approx 2$ , where  $k$  is Boltzmann constant. Such a high  $\Delta S$  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:  $1.05 \pm 0.04$  eV and  $1.10 \pm 0.02$  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 ( $\sim 0.05$  eV) for interaction between  $V_2H$  and  $H_i$  or  $H_2^*$  has been suggested [8].

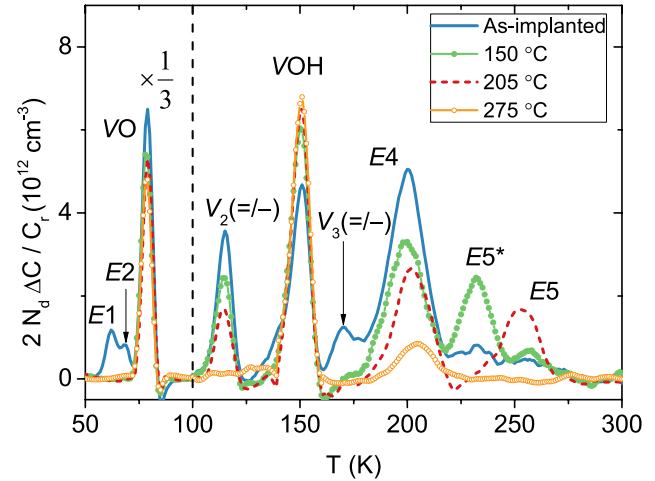
In the present work, we investigate possible identification of  $E5^*$  by studying the annealing kinetics. A series of isochronal and isothermal annealing is performed. We observe that the annealing kinetics of  $E5^*$  is consistent with a dissociation mechanism or structural transformation and deduce 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].



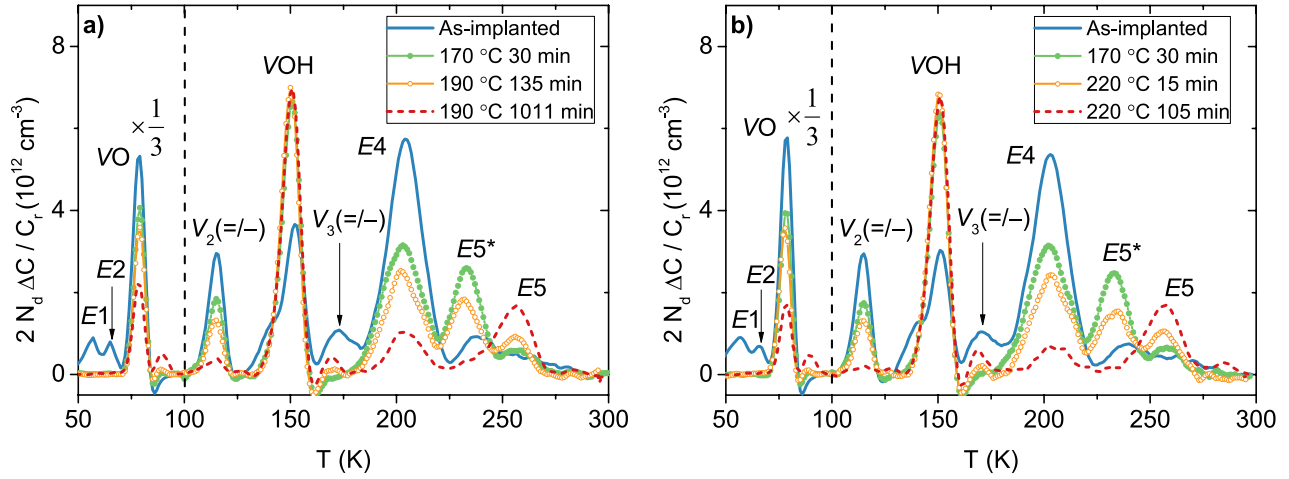
**Figure 1.** DLTS spectra before and after isochronal annealing for 30 min at different temperatures, recorded with a  $(640 \text{ ms})^{-1}$  rate window.

## 3. Experimental results

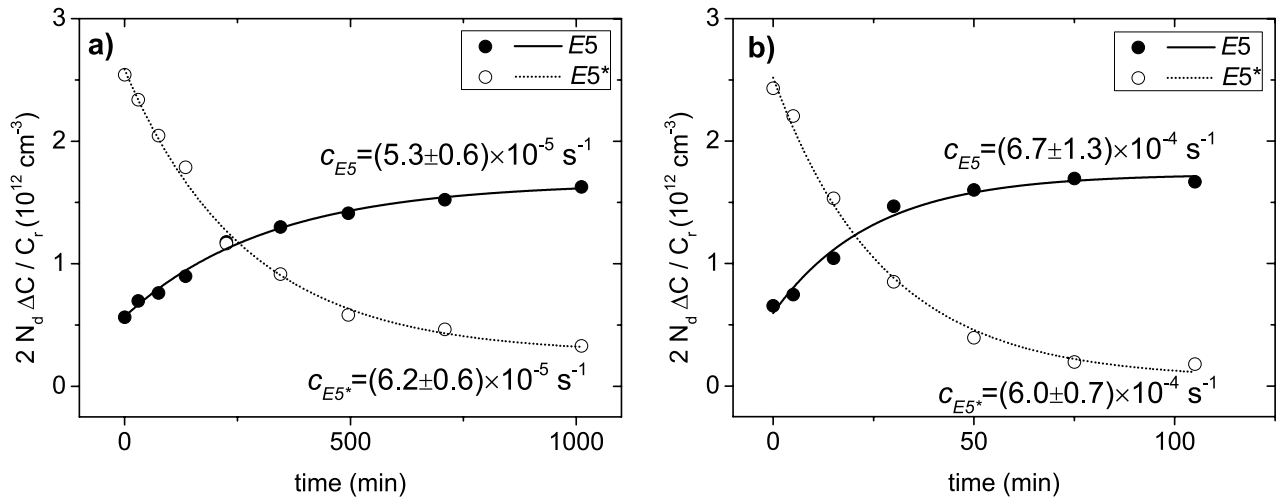
Figure 1 shows the DLTS spectra for the sample before and after 30 min isochronal annealings at different temperatures. The DLTS spectrum of the as-implanted sample shows signals of several defects:  $E1$ ,  $E2$ ,  $VO$ ,  $V_2(-/0)$ , double acceptor state of trivacancy ( $V_3(=/-)$ ) [11],  $VOH$ ,  $E4$ ,  $E5^*$  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  $\geq 75$  °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.

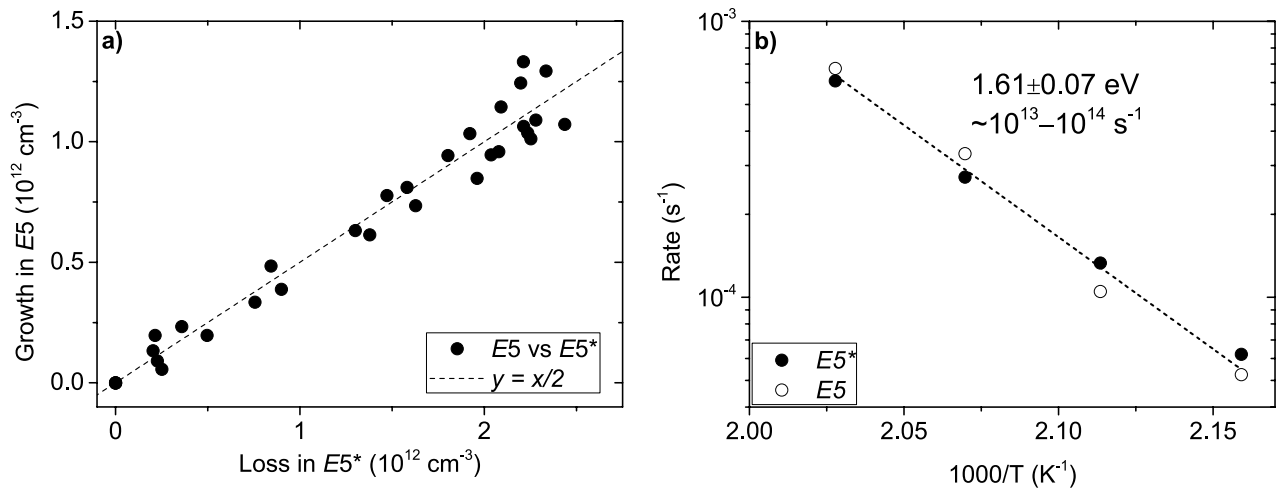
Four samples have been annealed isothermally at temperatures of 190, 200, 210 and 220 °C to study the evolution kinetics of  $E5^*$  and  $E5$ . The DLTS spectra before and after different annealing steps at 190 and 220 °C are presented in figure 2. The as-implanted spectra are practically identical 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,



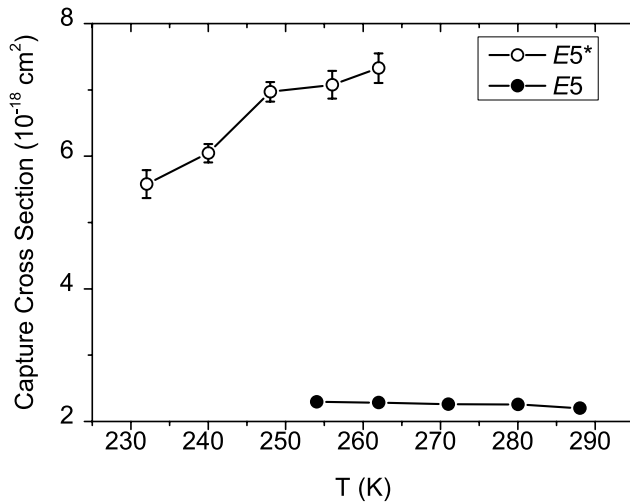
**Figure 2.** DLTS spectra of the samples annealed isothermally at 190 °C (a) and 220 °C (b) for different durations, recorded with a  $(640 \text{ ms})^{-1}$  rate window.



**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  $1.61 \pm 0.07$  eV and  $\sim 10^{13}$ – $10^{14}$  s<sup>-1</sup>, 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  $50 \pm 10$  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<sup>-1</sup>) 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<sup>-1</sup> [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  $V_3H$ .

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