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 $E_5^*$, at 0.42 eV below the conduction band in hydrogen-implanted n-type silicon. The $E_5^*$ annealing correlates with the formation of another commonly observed vacancy-hydrogen related level, labeled $E_5$, at 0.45 eV below the conduction band. The annealing of $E_5^*$ and the formation of $E_5$ 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$^{-1}$. The pre-factor indicates a dissociation or structural transformation mechanism. The analysis of electron capture cross-sections for $E_5^*$ and $E_5$ reveals considerable transition entropies for both states and a temperature dependent capture cross-section for $E_5^*$. Two possible identifications of $E_5^*$ and $E_5$ are put forward. Firstly, $E_5^*$ can be attributed to $V_2H_3(-/0)$ or $V_2H_4(-/0)$, which dissociate with the emission of VH ($E_5$). Secondly, $E_5^*$ and $E_5$ can be assigned to two different configurations of $V_2H$.

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 $E_5^*$ [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$^2$. The CCS measured directly by filling pulse variation is found to be $\sim 6 \times 10^{-18}$ cm$^2$. This reveals a relatively high transition entropy for ionization of $E_5^*: \Delta S/k \approx 2$, 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$_2$ released from P–H. The second process is slower by a factor of 4, and is associated with formation of $E_5^*$. It has been observed that formation of $E_5^*$ correlates with annealing of the deep level transient spectroscopy (DLTS) peak, labeled $E_4$, that consists of overlapping contributions from single acceptor states of divacancy, $V_2(-/0)$, and divacancy-hydrogen, $V_2H(-/0)$.

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correlation between $E5^*$ and the double-acceptor state of divacancy, $V_{5}(=/-)$, has not been observed, and $V_5$ 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 $(2 \div 25) \times 10^{11}$ s$^{-1}$ and for the slow one in the confidence interval $(3 \div 14) \times 10^{11}$ 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 $H_i^*$ 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 $1.2 \times 10^{15}$ cm$^{-3}$. The oxygen and carbon concentrations were found by Fourier transform infrared spectroscopy to be $7 \times 10^{17}$ cm$^{-3}$ and below $5 \times 10^{15}$ 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 2h 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 300–600keV and a total dose of $4 \times 10^{10}$ cm$^{-2}$ to obtain uniform ‘box-like’ distributions of defects and H. One of the samples underwent 30min isochronal annealings in the range of 75 °C–275 °C. Other samples underwent isothermal annealings at 75 °C–86 °C during 496–860min, 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 ms)$^{-1}$ rate window.](image)

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: $E1$, $E2$, $VO$, $V_3(=/-)$, double acceptor state of trivacancy ($V_5(=/-)$) [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 $V_3(=/-)$ and, presumably, $V_2H(=/-)$ [8, 14, 15]. In addition, $E4$ may have a contribution from the single acceptor state of trivacancy, $V_3(=/-)$ [11].

Before annealing the dominant part of H in the studied samples is stored in P–H [8]. P–H dissociates at $\approx 75$ °C with a release of H, that interacts with the defects. This is manifested in figure 1 in the growth of VOH and $E5^*$, and decrease of VO, $V_3(=/-)$ 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 $V_3(=/-)$ 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 $V_3(=/-)$ peak has disappeared, indicating that $V_2$ is annealed out. This suggest that the remaining amplitude of $E4$ is mainly due to $V_2H(=/-)$. $E5$ 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 annealed 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 ms)^−1 rate window.

Figure 3. Amplitudes of $E_5^*$ and $E_5$ 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 $E_5$ and the loss of $E_5^*$ for all isothermally annealed samples (a), and Arrhenius plot for annealing rate of $E_5^*$ and formation rate of $E_5$ (b).
factor for $E^*$ annealing ($\sim10^{13}$–$10^{14}$ s$^{-1}$) found in the present study indicates a dissociation mechanism. The rates for the $E^*$ 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 $V_d(−/0)$ 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 mono-vacancies and H atoms to form. One could expect that dissociation of hydrogen-vacancy complexes $V_3H_2$ or $V_3H_3(E5^*)$ 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 $V_3H_2(E5^*)$ 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 $\sim10^{13}$–$10^{14}$ s$^{-1}$ [19].

It is tempting to suggest that, similarly to $V_3$, trivacancy-hydrogen complex $(V_3H)$ can also exist in PHR $(V_3^{PHR})$ and FFC $(V_3^{FFC})$ configurations. $V_3^{PHR}$ should exhibit a structure similar to $V_3^{PHR}$, with a H atom passing 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 $V_3^{FFC}$ 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

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![Figure 5. Temperature dependences of CCS for $E5^*$ and $E5$.](image-url)
from a Si dangling bond, while having different structure. Taking this into account one can suggest that the annealing of $E^*$ is not a dissociation, but a structural transformation from $E^*$ to $E$, i.e. from one configuration of $V_3H$ to another. One can notice the similar pre-factors for the $E^*$ → $E$ and $V_3^*(PHR) → V_3^*(FFC)$ kinetics: $\sim 10^{13} – 10^{14}$ s$^{-1}$.

We observe, however, that the amplitude of $E^*$ is almost double of that of $V_3^*(\pm)$ in as-implanted sample (figure 1), and the correlation of $E^*$ versus $E$ is 2-to-1 (figure 4(a)). One could speculate that, for instance, $V_3^*(PHR)$ might be a negative-U defect with an acceptor and a donor levels [21], which emits two electrons upon the ($\pm$) charge transition, resulting in a doubled amplitude in the DLTS spectrum. Both $V_3^*(PHR)$ and $V_3^*(FFC)$ 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 $E^*$ (figure 5) is consistent with the possible negative-U nature. Thus, an identification of $E^*$ as $V_3^*(FFC)$ and $E$ as $V_3^*(PHR)$ can be tentatively put forward. This identification does not contradict our previous observation on the correlation of $E^*$ 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 $E^*$ and $E$, and a reverse identification of $E^*$ as $V_3^*(PHR)$ and $E$ as $V_3^*(FFC)$ 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 $E^*$ and $E$ has been studied by DLTS. $E^*$ anneals out at around 200 °C with a correlated formation of $E$. The kinetics exhibit a first-order behavior 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 for the $E^*$ annealing and the $E$ formation. The analysis of the electron capture cross-sections for $E^*$ and $E$ reveals considerable entropy factors for both states and a temperature dependent capture cross-section for $E^*$. Two possible identifications of $E^*$ and $E$ are put forward. Firstly, $E^*$ can be attributed to $V_3H_3(\pm)$ or $V_2H_3(\pm)$, which dissociate with the emission of VH ($E$). Secondly, $E^*$ and $E$ can be assigned to two different configurations of $V_3H$.

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