

Powerful recombination centers resulting from reactions of hydrogen with carbon–oxygen defects in n-type Czochralski-grown silicon

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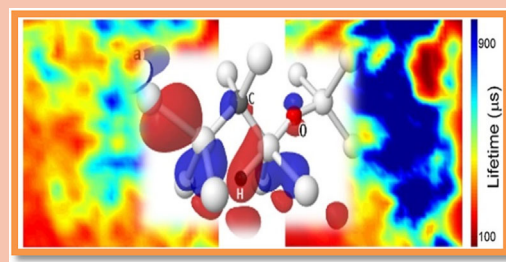
Received 28 April 2017, revised 15 June 2017, accepted 16 June 2017

Published online 27 June 2017

Keywords carbon–oxygen defects, Czochralski silicon, hydrogen, minority carrier transient spectroscopy, recombination centers

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It has been acknowledged for over 50 years that treatments with hydrogen can improve silicon semiconductor devices. In recent years, these have been used to an advantage in silicon solar cells reducing the loss of photo-generated carriers at the silicon surface or at the silicon interface with dielectrics. However, we have found that in some types of silicon the indiffusion of hydrogen can result in the formation of powerful recombination centers composed of carbon, oxygen, and hydrogen which reduce the carrier lifetime and ultimately the efficiency of solar cells made from such material.



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1 Introduction The target for silicon photovoltaics is to approach as closely as possible the Shockley–Queisser limit of efficiency of $\sim 30\%$ at 1 sun [1, 2]. Photovoltaic (PV) cell efficiencies $>25\%$ have been obtained in the lab by using high quality single crystal silicon but this contrasts with commercial devices which typically have module efficiencies $<16\%$. In general these devices use cheaper multi-crystalline silicon. Obtaining materials with long minority carrier lifetime and its maintenance throughout the manufacturing processes is crucial for achieving high efficiencies and this is a major objective for future silicon solar technologies. The carrier lifetime is limited by recombination processes which

depend on the material to be used and the cell processing that it undergoes. The reduction of surface recombination by the passivation of surface and interface states has long been a part of silicon PV manufacture. Among the most widely used materials for surface passivation are hydrogenated silicon nitride (SiN_xH), aluminum oxide [3], and annealed Al/SiO_2 [4]. In these materials, hydrogen content has been found to play an important role for lifetime improvement [5, 6]. Moreover, a recent publication proposed that hydrogen passivation of recombination centers in bulk of Si materials can be enhanced by manipulating the charge states of the hydrogen atoms [7]. Although hydrogen passivation

mechanisms are not fully understood, they are accepted in silicon PV technology as beneficial for Si solar cells.

However, we have found that under some circumstances, contrary to the widely accepted views, hydrogenation can result in degradation of the carrier lifetime in silicon. In our study of n-type Si grown by Czochralski techniques, the appearance of two powerful recombination centers has been observed after the introduction of hydrogen into samples containing relatively high concentrations ($\geq 5 \times 10^{15} \text{ cm}^{-3}$) of carbon impurity atoms. The same centers have been detected irrespective of the hydrogenation method. The most important observations were obtained by the application of the minority carrier transient spectroscopy (MCTS) technique [8], which allows us to measure positions of deep energy levels of the minority carrier traps in the silicon band gap and both the minority and majority carrier capture cross sections. Guided by *ab initio* calculations of possible defect structures and using a combination of MCTS, optical absorption and annealing a range of samples with different oxygen and carbon concentrations, we have obtained data about the composition of the centers and their thermal stability. The work reported here shows conclusively that the centers are related to carbon–oxygen–hydrogen complexes. So, as carbon is present as an impurity in some solar silicon materials including those grown by new methods under development commercially [9], our new findings suggest that this may be an important issue for future silicon PV technologies.

2 Experimental and modeling details In this work, we focus on n-type Czochralski (Cz) Si materials grown by conventional and the newer less expensive continuous Czochralski (C-Cz) techniques [10]. These types of materials are starting to be used in the solar industry for high efficiency products potentially replacing multicrystalline p-type material, at least in part because n-type Cz and C-Cz silicon when compared to p-type silicon has a higher “as grown” lifetime, lesser vulnerability to metallic contamination effects and little light induced degradation [11].

The materials that we have studied include a wide range of Cz and C-Cz silicon wafers with interstitial oxygen concentration in the range $12 < [\text{O}_i] < 20 \text{ ppma}$ ($1 \text{ ppma} = 5 \times 10^{16} \text{ cm}^{-3}$) and substitutional carbon concentration of $0.01 < [\text{C}_s] < 9 \text{ ppma}$. A comparison has been made with float zone (FZ) silicon samples with $[\text{O}_i]$ and $[\text{C}_s] < 0.2 \text{ ppma}$. The n-type Si samples that we used were phosphorous doped with resistivities between 1 and $8 \Omega \cdot \text{cm}$. The characterization of the centers was done by means of conventional and high-resolution Laplace deep level transient spectroscopy (L-DLTS) [12], MCTS, and local vibrational mode optical absorption spectroscopy. Samples of each material were cut and RCA cleaned, then the hydrogen was introduced into the silicon by three different techniques: (i) wet etching with either KOH or HF/HNO₃ solutions; (ii) 50 W remote H plasma exposure for 30 min at temperatures between 25 and 250 °C; and

(iii) in-diffusion of hydrogen from H-rich silicon nitride films (SiN_x:H). This latter technique simulates hydrogen introduction in a solar cell fabrication process. After cleaning, the samples were subjected to evaporation of Au through a shadow mask from the front side and Al evaporation without mask on the back side to produce Schottky barrier diodes (SBDs) and an Ohmic contact, respectively. An un-metalized region of the Ohmic contact was left on the back of the MCTS samples to allow optical excitation from a 940 nm light emitting diode (LED). In the case of the samples with SiN_x:H films, the films were etched off in diluted HF prior to metal deposition. Each diode was characterized firstly with current–voltage and capacitance–voltage measurements, and then DLTS, MCTS, and Laplace DLTS/MCTS measurements were carried out for detection and characterization of electrically active defects.

First-principles calculations of CO and COH complexes were carried out within density-functional theory using the projector-augmented wave method to account for the core electrons, and plane-waves limited by a 400 eV kinetic energy cut-off to describe the valence electrons [13, 14]. The generalized gradient approximation was used to describe the exchange and correlation energy, with the application of the Perdew, Burke, and Ernzerhof (PBE) functional [15]. Atomistic models of the CO and COH complexes were introduced in cubic supercells with 216 Si atoms and optimized lattice constant. Atomic coordinates of the resulting defective supercells were relaxed until the maximum force fell below $0.01 \text{ eV } \text{\AA}^{-1}$. The electron density and Kohn–Sham orbitals were calculated self-consistently on a $2 \times 2 \times 2$ Monkhorst–Pack **k**-point grid [16], enforcing a convergence tolerance for the total energy of $1 \mu\text{eV}$. The electrical activity of COH models was investigated using the marker method [17] with the OH defect as a marker [18]. To this end we also used the Heyd–Scuseria–Ernzerhof hybrid functional [19] (HSE06) which mixes a portion of exact exchange with the PBE exchange–correlation potential. The HSE06 functional has the advantage of leading to a theoretical band gap of about 1.2 eV, reducing errors related to the *narrow-gap syndrome* of (semi-) local exchange correlation approximations.

3 Observations and results In Ref. [20], we have shown the MCTS spectra for n-type Cz and C-Cz samples subjected to hydrogenation by the three methods described above. In all the spectra three peaks due to hole emission from defect levels to the valence band have been detected. A detailed analysis of the dominant peak, with its minimum at 180 K for the emission rate window of 50 s^{-1} , with the application of high resolution Laplace MCTS (L-MCTS) [12] has shown that this peak consists of two different emission signals, H₁ and H₂ [20]. Further, it has been shown that the concentration profiles of the H₁ and H₂ traps scale with the hydrogen concentration profiles, so confirming the involvement

of hydrogen atoms into the structure of the corresponding defects.

We have determined electronic characteristics of the dominant H_1 and H_2 hole traps from direct measurements of their hole emission rates and capture cross sections of holes and electrons using Laplace MCTS. From Arrhenius plots of T^2 -corrected hole emission rates, the activation energies for hole emission from the defect levels to the valence band and pre-exponential factors have been found to be: 0.38 ± 0.01 eV and $1.8 \times 10^7 \text{ s}^{-1} \text{ K}^{-2}$, and 0.36 ± 0.01 eV and $1.2 \times 10^7 \text{ s}^{-1} \text{ K}^{-2}$ for the H_1 and H_2 traps, respectively. Direct measurements of the capture cross sections of minority carriers (σ_p) by the traps have been carried out by the application of back-side light pulses of different length from an LED. The minority carrier concentration needed for the calculation of σ_p has been determined from the measured value of the diode photo-current at a temperature of trap filling measurements. The values of σ_p for the H_1 and H_2 traps have been determined as 9.8×10^{-16} and $7.9 \times 10^{-16} \text{ cm}^2$, respectively. No significant temperature dependence of the σ_p values has been detected. The values of majority carrier capture cross sections (σ_n) have been determined by the application of the so-called “clearance pulse” pulse of different lengths (“zero” bias voltage in this case) immediately after the application of a long optical filling pulse. The application of the clearance pulse resulted in capture of electrons by the traps filled by holes and corresponding reduction in the magnitude of the hole emission signals. The σ_n values for the H_1 and H_2 traps have been found to be 2.0×10^{-17} and $1.95 \times 10^{-17} \text{ cm}^2$, respectively.

An analysis of the obtained σ_p and σ_n values indicate that both the H_1 and H_2 traps are of acceptor nature, and considering the positions of their levels in the gap it can be suggested that the traps are effective recombination centers for holes in n-type Si. Indeed, using the relationship, that at low injection level, the lifetime depends on the minority carrier capture cross section and trap concentration (N_T) as follows:

$$\tau = (\sigma_p v_{th} N_T)^{-1} \quad (1)$$

where v_{th} is the hole thermal velocity and taking $v_{th} = 1.7 \times 10^7 \text{ cm} \cdot \text{s}^{-1}$ and $N_T = 4 \times 10^{13} \text{ cm}^{-3}$ (an average trap concentration probed by DLTS/MCTS in the sub-surface region of some of our studied samples) we obtain the lifetime value of about 1.5–1.9 μs . For the limit of the high injection level, i.e., when $p \approx n$, the lifetime value is higher, in this case $\sim 40 \mu\text{s}$. These calculations thus confirm the strong limiting impact of the centers on the minority carrier lifetime in the Cz n-type material.

Evidence for the involvement of oxygen impurity atoms in the structure of the H_1/H_2 centers has been presented by us in Ref. [20]. In Ref. [20], we have mentioned a quadratic dependence of concentration of the recombination centers on $[O_i]$ but after measuring many more samples since publishing that paper it appears that the dependence is less

than quadratic. Further, it has been found that the concentration of the H_1/H_2 traps is negligible in some Cz-Si crystals with relatively high oxygen concentrations but with low carbon concentrations. Figure 1 show the MCTS spectra recorded on the hydrogenated n-type Si samples with similar values of the oxygen concentration ($\sim 7.5 \times 10^{17} \text{ cm}^{-3}$) but different concentrations of carbon impurity atoms. An analysis of the data presented in Fig. 1 shows that the concentration of the H_1/H_2 traps is a nearly linear function of the carbon concentration. So, the obtained experimental data clearly indicates that the H_1/H_2 defects consist of centers incorporating oxygen and carbon impurity atoms to which a hydrogen atom is attached.

Substitutional carbon atoms are known to be effective traps for mobile interstitial oxygen atoms. From low-temperature infrared-absorption measurements of carbon and oxygen rich Cz silicon, the local vibrational modes of at least four CO_n complexes with different numbers of oxygen atoms have been identified [21–23]. Concentrations of the complexes can be varied by temperature and duration of heat-treatments in the temperature range 500–1100 °C [22, 23]. To determine which of the CO complexes can be precursors of the H_1/H_2 centers, we have heat-treated a few samples from a Cz-Si crystal with $[O_i] = 7.3 \times 10^{17} \text{ cm}^{-3}$ and $[C_s] = 4.5 \times 10^{17} \text{ cm}^{-3}$ in the temperature range 500–700 °C and carried out infrared absorption (IR) and MCTS measurements on them. Figure 2a shows the IR absorption spectra of the heat-treated samples in the wave-number range 1080–1120 cm^{-1} and Fig. 2b shows the MCTS spectra of the corresponding heat-treated and hydrogenated samples. It appears that there is a good correlation between the intensity of the IR absorption band

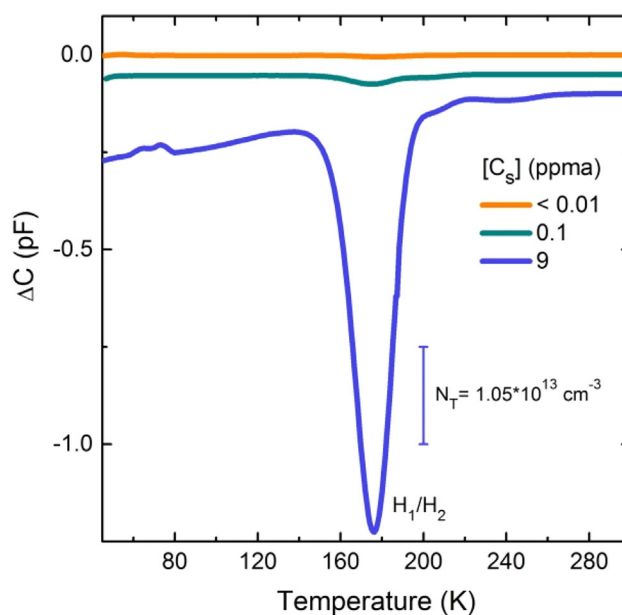


Figure 1 MCTS spectra for n-type Cz-Si samples with $[O_i] = 7.5 \times 10^{17} \text{ cm}^{-3}$ and different $[C_s]$. Hydrogen was introduced by etching in 1HF/7HNO₃ solution for 3 min.

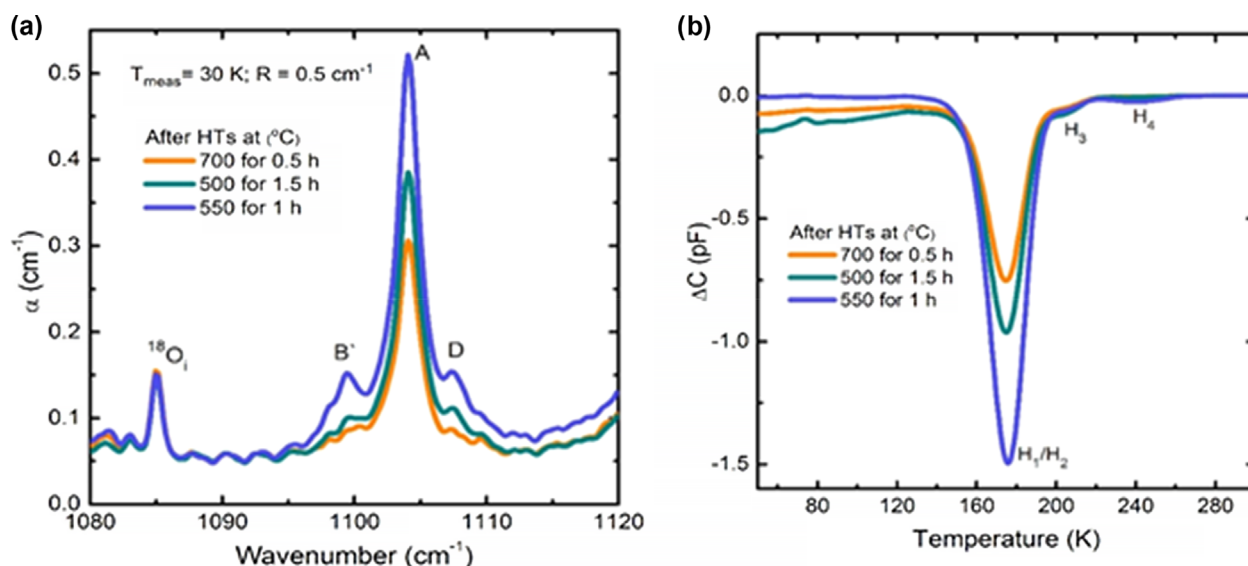


Figure 2 (a) Infrared-absorption spectra of a set of carbon and oxygen rich n-type Cz-Si samples after heat-treatments: at 700 °C for 30 min, at 500 °C for 1.5 h, and at 550 °C for 1 h. The absorption peaks, which are labelled as A, B', and D in the spectra are related to the CO_n complexes [22, 23]. (b) MCTS spectra recorded on neighboring samples to those used in the IR absorption measurements after same heat-treatments. All the samples we subjected to hydrogenation by etching in 1HF/7HNO₃ solution for 3 min prior to the measurements.

at 1104 cm⁻¹ (A band), which has been related to a complex incorporating one oxygen and one carbon atom [21–23], and the magnitudes of the MCTS signal due to the H₁/H₂ traps.

From density functional calculations, the minimum energy configuration of the CO center consists of a substitutional carbon atom with an interstitial bond-centered oxygen atom separated from C_s by a silicon atom. The binding energy of the pair is 0.51 eV. This agrees with the results of previous calculations [24]. The calculated asymmetric stretching-mode frequency of the Si–O–Si unit in CO is 1074 cm⁻¹, which is about 20 cm⁻¹ below the analogous mode frequency calculated for isolated O_i, and in good agreement with the infrared absorption data reported above. The CO pair is found to be an effective trap for hydrogen impurity atoms and the minimum energy configuration of the COH complex in the negative charge state (stable in n-type material) is shown in Fig. 3a. The binding energy of the H⁻ anion to the CO defect is found to be 0.74 eV, in line with the thermal stability of the H₁/H₂ traps. We predict that the COH complex shown in Fig. 3a introduces an acceptor level at about $E_v + 0.39$ eV into the band gap, which is very close to the experimentally determined values for the acceptor levels of the H₁/H₂ traps. Figure 3a also shows that the acceptor level of COH corresponds to a bonding state mostly localized on the Si–H bond and particularly on Si–Si bonds, therefore having a similar character to the topmost valence band states of Si. Combining this property with the fact that a negatively charged COH defect will attract holes, we may conclude that this complex has the right ingredients to be a rather effective minority carrier recombination center in n-type Si. As represented in Fig. 3b the mechanism involves capture of

photo-generated holes, followed by capture of a majority carrier to recover equilibrium.

It has been found that like many other H-related defects in silicon the H₁/H₂ recombination centers anneal out at quite low temperatures, they have been shown to be eliminated after a 30-min anneal at 175 °C [20]. We have used this fact for studying an effect of the H₁/H₂ centers on minority carrier lifetime in silicon. Measurements of effective minority carrier lifetime in silicon wafers were carried out with the use of a Semilab WT-2000 PVN μ-PCD machine with the excitation of non-equilibrium carriers by pulses from a 904 nm semiconductor laser and microwave

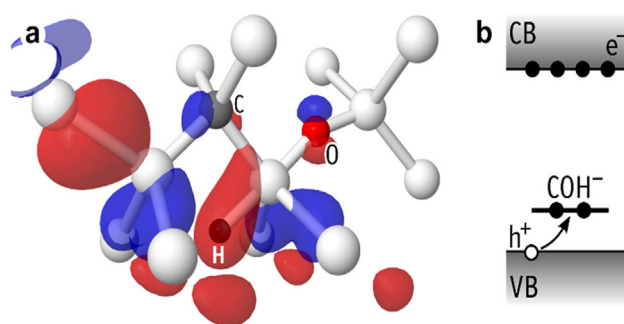


Figure 3 Structure of the COH complex. (a) Minimum energy configuration of the COH complex in the negative charged state. The isosurface depicts the highest occupied state for $\psi(\mathbf{k} = \Gamma, \mathbf{r}) = \pm 0.02$, with positive and negative phases shown in blue and red, respectively. (b) Band gap diagram showing the fully occupied acceptor state of COH depicted in (a), and how it interacts with minority carriers (h⁺) in n-type material.

frequency of about 10 GHz. The wafers have been subjected to either wet chemical or H plasma treatments and their lifetime was then measured with iodine/ethanol surface passivation. The slices studied had a thickness of about 180 μm and resistivity 5 $\Omega\cdot\text{cm}$. The combination of microwave skin depth and LASER extinction depth results in the measured conductivity decay indicating a lifetime which is weighted to the region between the surface and a depth of $\sim 50\ \mu\text{m}$. This is much wider than the region in which we generate the H_1/H_2 recombination centers in our etching experiment ($\sim 3\ \mu\text{m}$) [20] so this has to be considered when analyzing the effect of the recombination centers on the measured lifetime. The slices were then annealed at 200 $^\circ\text{C}$ for 10–20 min on a hot plate exposed to air so as to eliminate the COH defects and the lifetime measurements repeated. Figure 4 shows the comparison of two lifetime maps after KOH hydrogenation before (Fig. 4a) and after (Fig. 4b) a 200 $^\circ\text{C}$ anneal, the results show an increase of $\sim 45\%$ in average lifetime. Overall the 200 $^\circ\text{C}$ anneal of the hydrogenated n-type Si:O + C samples resulted in an increase of the effective lifetime of 40–100% [20], so confirming the strong effect of the H_1/H_2 traps on the minority carrier lifetime despite the recombination due to H_1/H_2 being concentrated in a narrow surface region.

It should be mentioned, however, that the sample in which the annealing behavior of the H_1/H_2 traps was studied had hydrogen only present in a narrow sub-surface layer; during heat-treatments the hydrogen diffuses away to the surface and into the bulk. If hydrogen is retained in the slice (e.g., in samples with a $\text{SiN}_x\text{:H}$ coating) then on cooling down after heat-treatments the recombination centers will reform and the minority carrier lifetime will remain degraded after thermal cycles. So, it is likely that the H_1/H_2 traps can survive after normal cell fabrication

processes and hence reduce the efficiency of solar cells using n-type Si containing oxygen and carbon impurity atoms.

4 Conclusions It is shown in our work that very powerful recombination centers can be formed in n-type silicon by the interaction of hydrogen and carbon–oxygen defects. Our measurements indicate that under common manufacturing conditions the concentration of these recombination centers is sufficiently high to have an important effect on the minority carrier lifetime and, in consequence, on the efficiency of solar cells. The probability of this happening is large as carbon and oxygen are the main light element impurities in recent commercial Cz and C-Cz solar silicon [9], and hydrogen is readily introduced during solar cell processing. The properties of the defects are identical whether the hydrogen is introduced from wet etching, hydrogenated silicon nitride, or from remote hydrogen plasma. Hydrogen is thought to be a beneficial impurity in Si solar cells technology, however, as the solar industry moves to cheaper material manufacturing processes with higher carbon concentrations, care should be taken in order to prevent hydrogen interactions with carbon–oxygen defects and the formation of the detrimental COH complexes.

Acknowledgements The work was funded in the UK by EPSRC contract EP/M024911/1, and in Norway by the Research Centre for Solar Cell Technology (FME – Solar United). In Portugal, the work was funded by the FCT under projects PTDC/CTM-ENE/1973/2012 and UID/CTM/50025/2013, and funded by FEDER funds through the COMPETE 2020 Program. Computer resources were partially provided by the Swedish National Infrastructure for Computing (SNIC) at PDC. We would like to thank Alexander Hupfer at the University of Oslo for his assistance in the optical absorption measurements. Financial support was also given by CONACyT-Mexico.

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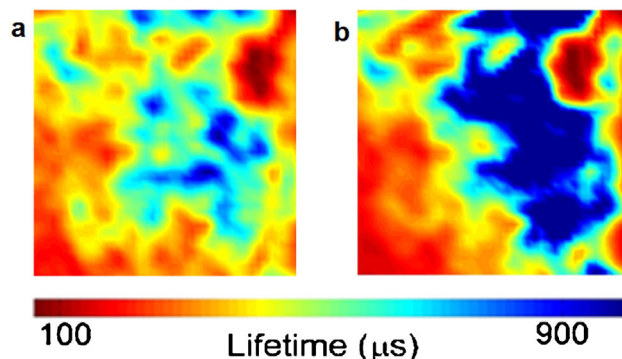


Figure 4 Maps of effective lifetime for an n-type C-Cz sample (4 cm \times 4 cm) with iodine/ethanol surface passivation. (a) KOH etched sample to inject hydrogen into the sub-surface region. (b) Same sample after annealing at 200 $^\circ\text{C}$ to dissociate the hydrogen–oxygen recombination center. The averaged lifetime shows an increase from 381 to 549 μs after the annealing.

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