

# Boron–Oxygen Complex Responsible for Light-Induced Degradation in Silicon Photovoltaic Cells: A New Insight into the Problem

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Results available in the literature on minority carrier trapping and light-induced degradation (LID) effects in silicon materials containing boron and oxygen atoms are briefly reviewed. Special attention is paid to the phenomena associated with “deep” electron traps (J. A. Hornbeck and J. R. Haynes, *Phys. Rev.* 1955, 97, 311) and the recently reported results that have linked LID with the transformation of a defect consisting of a substitutional boron atom and an oxygen dimer ( $B_5O_2$ ) from a configuration with a deep donor state into a recombination active configuration associated with a shallow acceptor state (M. Vaqueiro-Contreras et al., *J. Appl. Phys.* 2019, 125, 185704). It is shown that the  $B_5O_2$  complex is a defect with negative- $U$  properties, and it is responsible for minority carrier trapping and persistent photoconductivity in nondegraded Si:B+O samples and solar cells. It is argued that the “deep” electron traps observed by Hornbeck and Haynes are the precursors of the “slow” forming shallow acceptor defects, which are responsible for the dominant LID in boron-doped Czochralski silicon (Cz-Si) crystals. Both the deep and shallow defects are  $B_5O_2$  complexes, transformations between charge states and atomic configurations of which account for the observed electron trapping and LID phenomena.

by Hornbeck and Haynes in 1955,<sup>[1]</sup> and 2) defects responsible for light-induced degradation (LID) of solar cells fabricated from silicon materials containing boron and oxygen atoms.<sup>[2–6]</sup>


The information on electron traps observed by Hornbeck and Haynes is very limited.<sup>[1,7–9]</sup> The authors reported long (minutes) two-stage decays of conductivity at room temperature in boron-doped Si crystals after the application of short light pulses. Such phenomena are sometimes referred to as persistent photoconductivity. The authors interpreted the observed effects as being related to temporary trapping and emission of injected electrons by two different (“shallow” and “deep”) traps in the volume of p-type silicon.<sup>[1]</sup> From an analysis of the conductivity decays, the energy level of the “shallow” trap was determined as being at  $E_c - 0.57$  eV, whereas the energy level of the “deep” trap was placed at  $E_c - 0.79$  eV. The concentration of the “deep” trap was

found to increase linearly with the increase in equilibrium conductivity (in the Hornbeck and Haynes case, this is interpreted as being due to the changes in boron concentration) of the samples studied. In the samples with the highest conductivity, the concentration of the “deep” trap was found to be higher than  $1 \times 10^{14} \text{ cm}^{-3}$ . It should be noted that carrier traps with such

## 1. Introduction

In boron-doped silicon crystals grown by the Czochralski technique (Cz-Si), there are two families of defects, which have been known for many years but still lack proper understanding and identification. These are 1) electron traps which were reported

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concentration can be easily detected by deep-level transient spectroscopy (DLTS)<sup>[10,11]</sup> or minority carrier transient spectroscopy (MCTS).<sup>[11,12]</sup> However, only in one article, a carrier trap with an energy level at about  $E_v + 0.48$  eV ( $\approx E_c - 0.64$  eV) and concentration of about  $2 \times 10^{13} \text{ cm}^{-3}$  was detected by means of DLTS in  $n^+/p/p^+$  solar cells made from Cz-grown boron-doped Si wafers.<sup>[7]</sup> The authors suggested that the trap could be related to manganese impurity atoms.<sup>[7]</sup> Schmidt et al.<sup>[8]</sup> detected minority carrier traps in boron- and gallium-doped Cz-Si crystals by means of the quasi-steady-state photo-conductance (QSS-PC) technique. A clear correlation of the trap density with the interstitial oxygen concentration as well as with the boron and gallium concentration was reported.<sup>[8]</sup> The trap energy level was estimated as being at  $0.53 \pm 0.03$  eV below the conduction band edge. Recently, the existence of trap levels for electrons in p-type Cz-grown silicon crystals has been confirmed in experiments on monitoring the transient dynamics of the free electron density in the conduction band by means of a time-correlated single photon counting of photoluminescence (PL).<sup>[9]</sup> As it is mentioned earlier, a correlation between the concentration of deep electron traps and concentrations of acceptor doping atoms and oxygen impurity atoms has been observed.<sup>[1,8]</sup> However, there is no information in the literature about the formation and elimination mechanisms of the electron trapping centers, and there are no suggestions about their atomic structure.

A substantial number of published literature exists on boron-oxygen-related LID (BO-LID) of Si solar cells (>250 papers reporting research and >1000 referring to the effect) with the diagnostic tool being mainly minority carrier lifetime measurements subsequently related to cell performance. The available results and understanding of the problem have been reviewed recently by Niewelt et al.,<sup>[2]</sup> and the readers are directed to this review for details of this phenomenon. It should be emphasized that the BO-LID effect is actually caused not by the light itself but by the excess charge carriers created by the above band-gap illumination. An identical form of degradation occurs in B-doped Si solar cells upon the injection of minority charge carriers by the application of forward bias to the cells.<sup>[2,13]</sup> So, the term “carrier induced degradation” is more appropriate to describe the degradation process; however, the “LID” term is still used by the silicon solar PV community. We use the term BO-LID in this article to distinguish the process from other LID mechanisms.

We would like to highlight that BO-LID progresses via two stages, these are a fast stage with a characteristic time of a few seconds and little temperature dependence, followed by a slower process, typically asymptotic occurring over a period of tens of hours. This latter process is temperature dependent which has been characterized in terms of the formation of a recombination active defect with an activation energy of 0.48 eV.<sup>[2,4]</sup> There is some debate as regards to the relationship between the fast and slow process, with arguments for the two processes being independent or originating from a common defect.<sup>[2–6]</sup> However, the slow degradation is by far the most significant and is predominantly responsible for the loss of efficiency. This article focuses on the slow process.

We have recently obtained some new experimental results on LID in p-type Cz-Si crystals and with supporting ab initio modeling results proposed an alternative explanation of the “slow”



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**Michelle Vaqueiro-Contreras** graduated from Instituto Tecnológico de Celaya, Mexico in 2012 with a B.Sc. in electronic engineering. She received the CONACyT scholarship to study at the University of Manchester, UK, where she was awarded the degrees of M.Phil. and Ph.D. Her Ph.D. work included studies of graphene oxide as a silicon surface passivator and research on degradation mechanisms in solar silicon. Currently, she works at the University of New South Wales in Sydney, on hydrogenation processes and light- and elevated temperature-induced degradation (LeTID) in silicon solar cells.



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BO-LID-related effects.<sup>[14]</sup> In all  $n^+-p$  and Schottky barrier diodes made from boron-doped Cz-Si materials, we have observed a DLTS peak due to a deep trapping center with an activation energy for hole emission of 0.97 eV present in the undegraded samples. This center is a deep donor but has an unusually small majority carrier capture cross section and this, together with the higher than usual DLTS peak temperature, is probably the main reason why it has evaded detection by DLTS previously. This trap is found to be responsible for long (tens of minutes) decays of nonequilibrium hole concentration measured with the use of junction capacitance techniques after application of relatively short (in the range of milliseconds) minority carrier injection (MCI) pulses. After an extended period of carrier injection, which

results in BO-degradation, the concentration of the trapping center decreases. This decrease in concentration correlates strongly with a decrease in minority carrier lifetime suggesting it is the precursor for the BO-LID recombination center.

In parallel with the decrease in concentration of the deep donor, an increase in the hole concentration is observed which is greater than that expected from the annihilation of the donor implying the formation of a shallow acceptor. The generation of an acceptor during the degradation process has been confirmed by admittance spectroscopy (AS) and low-temperature PL measurements of the degraded samples. In the PL spectra recorded after degradation, an emission line not present in undegraded material, appears close to the boron-bound exciton line. An analysis of the degradation-associated line indicates that the generated acceptor has a hole binding energy  $\approx 37$  meV from the valence band edge which is consistent with the AS measurements. The new acceptor is annihilated upon dark annealing at temperatures exceeding 150 °C, i.e., under the same conditions which restore the minority carrier lifetime in the BO-LID literature. Its disappearance is accompanied by the recovery of the deep donor signal in the DLTS spectra.

A configuration-coordinate diagram (CCD) has been constructed using the experimentally derived parameters of the deep donor–shallow acceptor transitions and ab initio calculations. It is believed that changes in the charge states result in changes in the atomic configurations of the complex which is identified from experiment and ab initio calculations as a substitutional boron atom and two interstitial oxygen atoms ( $B_sO_2$ ). Depending on the Fermi level ( $E_F$ ), the defect can be either a deep donor (with the atomic configuration referred to as D in the following text) or it can be in one of the two configurations with shallow acceptor levels (referred to as A and A' configurations). The transformation barriers are consistent with the observed degradation/recovery kinetics of the cells. It is postulated that the recombination mechanism associated with the BO-LID is a trap-assisted Auger mechanism. This is supported by the observation of above bandgap luminescence in the degraded samples which is not present in annealed material.

Furthermore, it has been found that the  $B_sO_2$  complex can be formed upon heat-treatments of the Cz-Si:B crystals in the temperature range 350–450 °C where the oxygen dimer is mobile; however, the binding energy of the complex is not very high ( $E_b = 0.48$  eV), so heat-treatments at higher temperatures ( $T \geq 600$  °C) result in its dissociation.<sup>[14]</sup>

In this article, we present additional experimental results and a detailed analysis of data that were presented in the Supporting Information in the study by Vaqueiro-Contreras et al.<sup>[14]</sup> We argue that the  $B_sO_2$  defect in the undegraded Si samples is responsible for electron “deep” traps and persistent photoconductivity effects, which were observed by Hornbeck and Haynes.<sup>[1]</sup> The detailed experimental results on emission and capture of holes by the defect are reported and its electronic properties are explained. We then confirm that the defect has two stable configurations consisting of a substitutional boron atom and staggered oxygen dimer, and transitions between these configurations account for the “degradation” and “annealing” LID-related defect reactions.<sup>[14]</sup> It is further argued that the “deep” level electron trap observed by Hornbeck and Haynes<sup>[1]</sup> can be considered as a precursor of “slow” recombination-active

BO-LID center,<sup>[2–6]</sup> and both centers are related to the same defect,  $B_sO_2$ , in different configurations.

The presence of a deep donor trap with concentrations of the order of  $10^{12}$ – $10^{14}$  cm<sup>−3</sup> (refs. [1] and [14]) in undegraded material and devices, and the resultant persistent photoconductivity has a considerable effect in relation to the measurement of minority carrier lifetime. This can result in significant errors in values of the minority carrier lifetime derived from QSS-PC measurements with the use of a simplified approach which does not take into account the detailed effects of carrier trapping. Several methods have been proposed to reduce errors due to this effect, the most common being the use of a bias light term to subtract out the photoconductance due to the traps. The technique extends, by an order of magnitude, the range of excess carrier of carrier densities over which measurements can be done.<sup>[8,15]</sup> Bardos et al. have compared the QSS-PC measurements with sub-bandgap bias light with PL decay measurements (which are largely immune from trapping artefacts) and shown that in their samples, the overestimate of lifetime measured by QSS-PC can be as much as a factor of five times for excess carrier density below  $5 \times 10^{13}$  cm<sup>−3</sup>.<sup>[16]</sup> Gogolin and Harder<sup>[17]</sup> have undertaken a comprehensive comparison of experiment and modeling to show that specific traps can increase the QSS-PC apparent lifetime while decreasing the actual lifetime derived from the PL measurements. The article provides a consistent description of the observation of both, the increased apparent lifetime from carrier trapping and the decreasing recombination lifetime.<sup>[17]</sup> Unfortunately, a simplified methodology has been used to determine carrier lifetime using QSS-PC in some of the published literature on BO-LID and is one of the factors causing the appearance of some controversial results related to the LID phenomena.

There can be two principal sources of errors in lifetime measurements by means of the QSS-PC technique in the presence of minority carrier traps, which will be briefly considered below. In the QSS-PC technique, a lifetime value is extracted from a photoconductance value measured upon the application of light with a known intensity (or, equally, a known generation rate of excess carriers). The basic equations in the case of absence of minority carrier traps ( $\Delta n = \Delta p$ ) are<sup>[18]</sup>

$$\Delta\sigma = q\Delta n(\mu_n + \mu_p) \quad (1)$$

$$\tau_{\text{eff}} = \Delta n/G \quad (2)$$

where  $\Delta\sigma$  is the photoconductance value,  $q$  is the elementary charge value,  $\Delta n$  is the concentration of generated excess carriers,  $\mu_n$  and  $\mu_p$  are values of mobility of electrons and holes, respectively,  $\tau_{\text{eff}}$  is the effective lifetime of minority carriers, and  $G$  is the generation rate of excess carriers. Considering that the values of  $G$ ,  $\mu_n$ , and  $\mu_p$  are known, with the use of Equation (1) and (2), it is possible to calculate  $\Delta n$  from the measured  $\Delta\sigma$  value and further to derive a  $\tau_{\text{eff}}$  value. In the presence of minority carrier traps,  $\Delta n \neq \Delta p$  and the Equation (1) and (2) are not valid. Let us consider the simplest case when all the generated minority carriers (electrons in p-type Si) are captured by traps. The  $\Delta\sigma$  value in this case will be

$$\Delta\sigma = q\Delta p\mu_p \quad (3)$$

If the Equation (1) is still used for the extraction of  $\Delta n$  value and considering generally cited values of the mobility of electrons and holes in Si ( $\mu_n \approx 1450 \text{ cm}^2 \text{ V}^{-1} \text{ s}$  and  $\mu_p \approx 470 \text{ cm}^2 \text{ V}^{-1} \text{ s}$ ), it is clear that a possible error in determined values of  $\Delta n$  and  $\tau_{\text{eff}}$  can be equal to the  $(\mu_n + \mu_p)$  to  $\mu_p$  ratio, which is about 4 for p-type Si.

The second source of errors in determination of  $\tau_{\text{eff}}$  values from the QSS-PC measurements is related to the fact that the measurements of photoconductance as a function of the light intensity are frequently carried out in a mode of decreasing light intensity over a period of a few tens of milliseconds (e.g., light intensity falls from 50 to 0 suns over the period of 12.5 ms for a typical QSS-PC lifetime measurement mode for the widely used Sinton WCT-120 lifetime tester). As characteristic decay times due to the release/capture of carriers by deep traps can exceed 100 s (see e.g., Figure 4 and 7 in the study by Hornbeck and Haynes),<sup>[1]</sup> significant values of persistent photoconductivity can occur at the end of measurements, when  $G$  values are small. The persistent photoconductivity due to minority carrier traps is a reason of frequently observed deviations in  $\tau_{\text{eff}}$  ( $\Delta n$ ) dependencies at small  $\Delta n$  values.<sup>[4,8,19,20]</sup>

## 2. Experimental Section

We have used  $n^+$ -p-p<sup>+</sup> and Schottky barrier diodes on p-type Cz-grown Si materials in this study. The diodes were formed by the implantation and thermal activation of 60 keV phosphorus ions (front side) and 60 keV boron ions (back side) in boron-doped commercial electronic grade Cz-Si wafers with nominal 3 and 10  $\Omega \text{ cm}$  resistivity values reported by wafer suppliers. To activate the doping atoms, the wafers were annealed at 950 °C for 20 min in an  $\text{N}_2$  ambient. The area of the diodes was 4.4 and 6.25 mm<sup>2</sup> for the 3 and 10  $\Omega \text{ cm}$  materials, respectively, and the leakage current was  $<10^{-6} \text{ A}$  at 10 V reverse bias. The concentrations of interstitial oxygen  $[\text{O}_i]$  in the 3 and 10  $\Omega \text{ cm}$  materials were  $(7.5 \pm 1) \times 10^{17}$  and  $(9.5 \pm 1) \times 10^{17} \text{ cm}^{-3}$ , respectively. The  $[\text{O}_i]$  values had been derived from an analysis of the rates of capture of interstitial carbon atoms by the  $\text{O}_i$  atoms measured with the use of DLTS upon annealing of the diodes irradiated with alpha particles at 260 K.<sup>[21,22]</sup> Schottky barrier diodes (1 mm in diameter) were prepared by the thermal evaporation of a titanium/aluminum stack through a shadow mask on samples from p-type Cz-Si crystals with initial resistivity from 1 to 10  $\Omega \text{ cm}$ . The oxygen concentration in the crystals was in the range from  $7 \times 10^{17}$  to  $1 \times 10^{18} \text{ cm}^{-3}$  and the carbon concentration was below  $2 \times 10^{16} \text{ cm}^{-3}$ . The  $[\text{O}_i]$  and  $[\text{C}_s]$  values had been determined from optical absorption measurements at room temperature with the use of  $3.14 \times 10^{17}$  and  $0.94 \times 10^{17} \text{ cm}^{-2}$  calibration coefficients for oxygen and carbon, respectively. Some selected samples have been treated in the temperature range from 350 to 425 °C to generate defects related to boron-oxygen.

Current-voltage and capacitance-voltage ( $C$ - $V$ ) measurements had been used to measure the uncompensated shallow acceptor concentration and width of the probed depletion regions. DLTS and high-resolution Laplace DLTS (L-DLTS)<sup>[23]</sup> had been used for the detection of carrier emission from deep defect states.

For the carrier lifetime measurements, the microwave photoconductance decay technique was used to map the lifetime across

the slices of silicon using a Semilab WT-2000PVN machine, and in the case of the diodes, the reverse recovery method was applied using the analysis methodology described by Kuno.<sup>[24]</sup> In our  $n^+$ -p-p<sup>+</sup> diodes, the technique gives the lifetime of electrons in the p-type region.

## 3. Experimental Results and Discussion

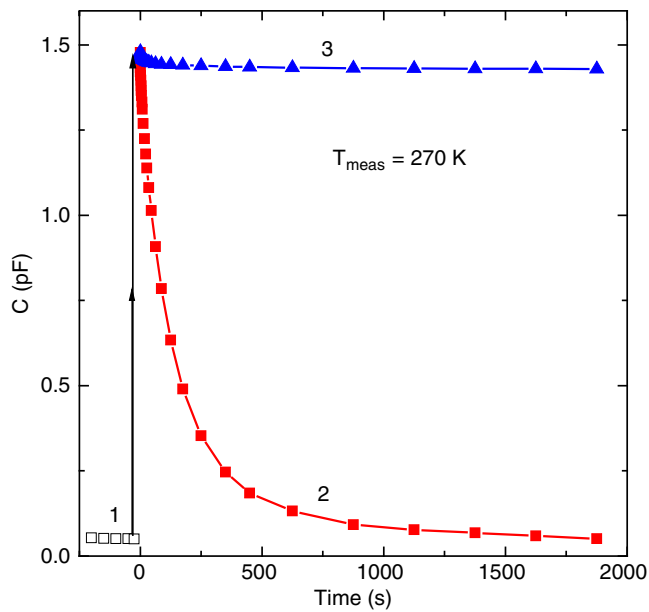
Before proceeding to the description of experimental results, it is necessary to mention that besides the BO-related minority carrier traps and recombination active centers, there are other defects in p-type silicon which can be formed/(de)activated upon the MCI treatments. Among such defects, the most relevant to our study are hydrogen-related complexes (e.g., hydrogen-boron pair) and iron- and copper-related defects.<sup>[25–29]</sup> Special attention has been paid in our study to distinguish the BO-related carrier injection-induced effects from those related to other complexes. Fortunately, there are some clear fingerprints of hydrogen and iron related complexes in the DLTS spectra and capacitance-voltage curves of the diodes on boron-doped Si, which allow us to control the presence of defects other than the BO-related ones. So, we are confident that all the experimental observations reported below are related to the BO complexes.

### 3.1. The $\text{B}_5\text{O}_2$ Defect in Nondegraded Cz-Si Crystals: A Negative- $U$ Center Responsible for the Persistent Photoconductivity

The MCI-induced changes in the conductivity of boron-doped Si samples reported by Hornbeck and Haynes<sup>[1]</sup> are analogous to the changes in capacitance we have observed in nearly all our as-manufactured diodes after the application of short MCI pulses in the temperature range 260–330 K. This applies to both  $n$ -p junctions and Schottky diodes fabricated from the Cz-Si:B material. The MCI pulses were either forward voltage pulses for conventional  $n^+$ -p diodes or light pulses from a 940 nm light emitting diode (LED) for semitransparent Schottky diodes or optically excited  $n^+$ -p diodes with the removed front-side metallization. Figure 1 shows changes in the capacitance of a reverse-biased ( $U_b = -9 \text{ V}$ )  $n^+$ -p diode from 10  $\Omega \text{ cm}$  CZ-Si:B material after application of a 10 ms long forward voltage pulse ( $U_p = +2.5 \text{ V}$ ). The application of the forward voltage pulse results in a strong increase in the diode capacitance, which stays nearly unchanged at the increased value if the diode is kept under reverse bias. However, if the diodes are kept without bias ( $U_b = 0 \text{ V}$ ), a slow decay of the capacitance occurs.

Hornbeck and Haynes<sup>[1]</sup> proposed that the decays in conductivity of boron-doped Si samples after the application of MCI pulses are related to the emission of electrons trapped by defects with deep levels in the lower part of the gap. This process is then followed by the recombination of the electrons with available holes through other recombination active centers. We have suggested recently<sup>[14]</sup> and will further argue in this article that the MCI-induced changes in conductivity or capacitance of Cz-Si:B samples are related to transformation from a deep donor to a shallow acceptor state of the  $\text{B}_5\text{O}_2$  center. The center is a defect with negative- $U$  properties, with its CCD and respective atomic configurations presented in Figure 2. In the following, we will





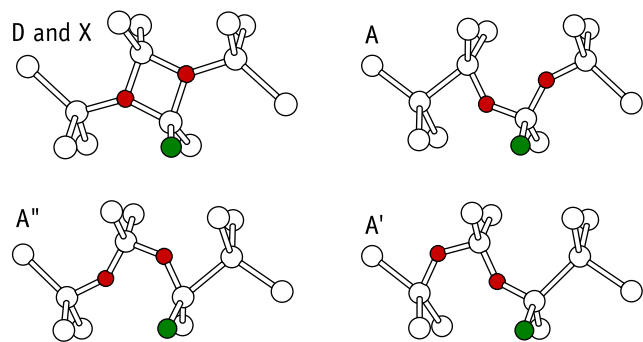
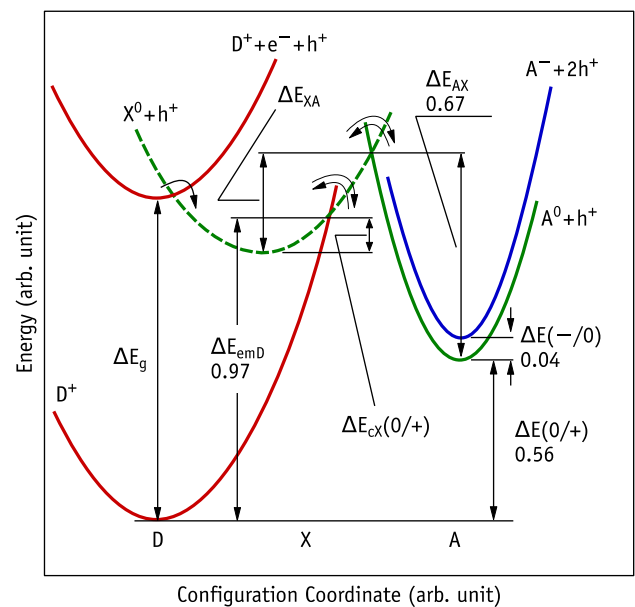
**Figure 1.** Changes in the diode capacitance  $C = C_d - C_b$  at bias voltage  $U_b = -9.0$  V and  $T = 270$  K for an  $n^+ - p - p^+$  diode fabricated from  $10\ \Omega\text{ cm}$  p-type Cz-Si:B material. For the improvement of signal-to-noise ratio in these measurements, we have used a backing-off capacitor of  $C_b = 200$  pF to compensate the capacitance of the diode studied ( $C_d$ ). Diode capacitance, which was measured after relatively long (45 min) storage at  $T = 270$  K with  $U_b = 0$  V, is shown by 1) black open square symbols. A sharp increase in the diode capacitance has been initiated by a short (10 ms) forward bias ( $U_p = +2.5$  V) pulse and recorded after the end of the pulse ( $t = 0$  s) upon keeping the diode either 2) without bias ( $U_b = 0$  V) or 3) under reverse bias  $U_b = -9.0$  V.

present results of a detailed study of hole emission and capture processes by the defect. The results obtained have allowed us to determine the energy differences and barriers for the charge state and structural transitions of the center.

### 3.1.1. Transitions from the Deep Donor State to Shallow Acceptor State (Electron Capture and Hole Emission) of the $B_3O_2$ Center

In the moderately doped p-type Si crystals, the  $B_3O_2$  trap is in the positive charge state (state  $D^+$  in Figure 2) at room temperature. However, the charge state and configuration can be easily changed by short injection pulses of minority carriers (electrons) either by forward biasing of an  $n^+ - p$  diode or by the application of above-band-gap light pulses, which generate carriers. Upon the MCI, the defect captures an electron and transforms to the  $A^-$  state according to the following sequence of transitions:  $D^+ + h^+ + e^- \rightarrow X^0 + h^+ \rightarrow A^0 + h^+ \rightarrow A^- + 2h^+$ .

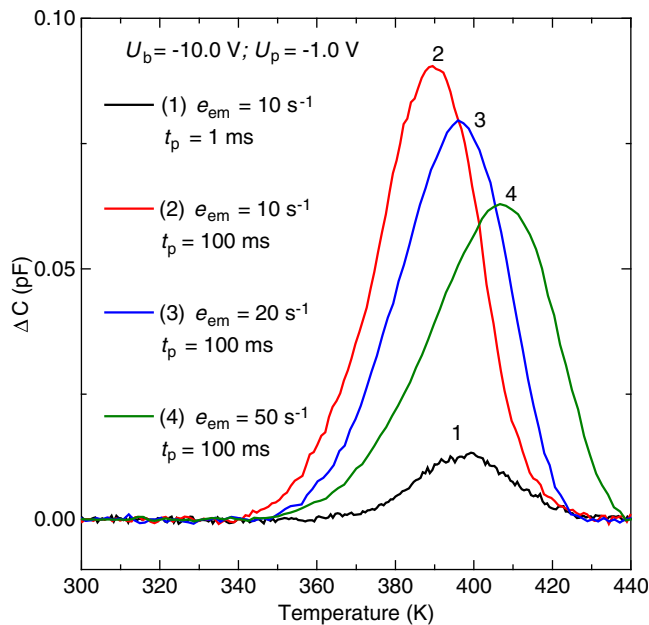
Hole emission from the deep donor state ( $D^+ \rightarrow X^0 + h^+$  transition) of the defect occurs at relatively high temperatures ( $\approx 400$  K) in comparison with those for the majority of defects in silicon because of the large activation energy for the emission process ( $\Delta E_{\text{emD}}$ ). In the conventional DLTS spectra, hole emission from the deep donor state of the defect can be detected as a broad peak with its maximum at about 390 K (for emission rate window,  $e_{\text{em}} = 10\text{ s}^{-1}$  and filling pulse length,  $t_p = 100$  ms)



**Figure 2.** CCD of the  $B_3O_2$  center. The energy differences and barriers parameters for the defect have been derived from the analysis of experimental data on hole emission and capture, which are described below. The lower part of the figure shows atomic configurations of the  $B_3O_2$  complex. Structures D and A are ground states for the singly positive and negative charge states. In p-type Si, D is lowest energy configuration when the Fermi energy is below the  $E(-/+)$  occupancy level of the defect at  $E_v + 0.3$  eV. Structures  $A'$  and  $A''$  are local energy minima 0.23 and 0.38 eV above A, respectively. Adapted under the terms of the Creative Commons CC-BY license.<sup>[14]</sup> Copyright 2019, The Authors, published by AIP Publishing LLC.

(Figure 3). The magnitude of the observed peak depends significantly on the  $t_p$  value (Figure 3). Detection of the peak requires long filling pulses  $\approx 100$  ms. These are unusual detection conditions for Si defects in terms of both the high temperature and the long filling pulse required, which are outside the typical experimental conditions used for surveying traps in Si with DLTS. It has been found that the concentration of the defect, which gives rise to the observed DLTS signal, varies in the range  $5 \times 10^{11} - 5 \times 10^{12}\text{ cm}^{-3}$  in the as-manufactured diodes from different Cz-Si:B materials.

Figure 4a shows high-resolution L-DLTS spectra recorded in the temperature range 390–410 K for an  $n^+ - p - p^+$  diode from  $3\ \Omega\text{ cm}$  Cz-Si:B material, which was subjected to a heat-treatment



**Figure 3.** Conventional DLTS spectra recorded in the temperature range 300–440 K on as-manufactured  $n^+ \cdot p \cdot p^+$  diodes from 3  $\Omega$  cm p-type boron-doped Cz-Si material.

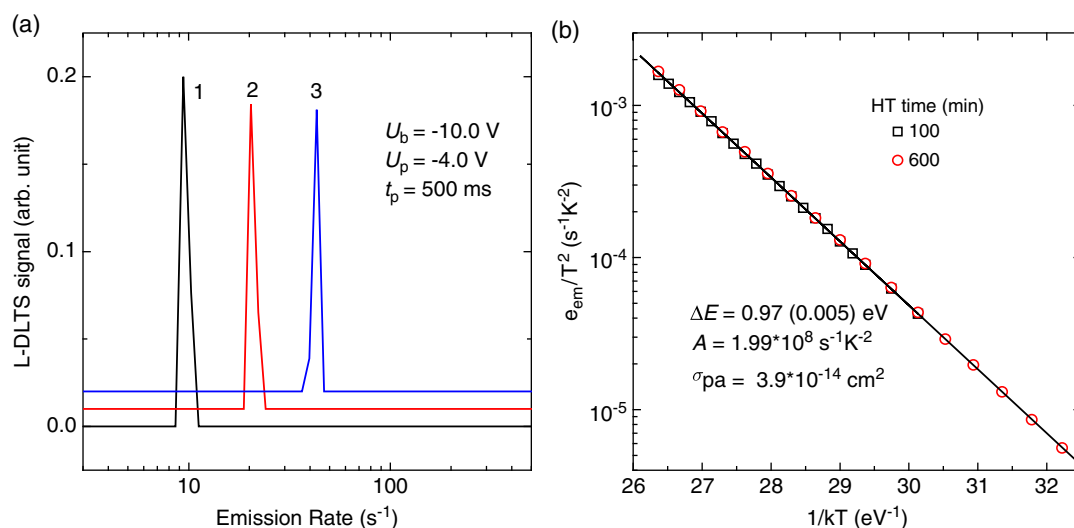
at 350 °C for 10 h. It can be seen that the L-DLTS spectra contain a single sharp emission line indicative of 1) hole emission being from a point-like defect and 2) that the level of strain in the material is low or uniform throughout the material.<sup>[23]</sup> Figure 4b shows an Arrhenius plot of the  $T^2$ -corrected hole emission rate for the  $B_sO_2$  center from which we have determined an activation energy for hole emission ( $\Delta E_{emD}$ ) as  $0.97 \pm 0.005$  eV. Such high  $\Delta E_{em}$  values are very unusual for defects in silicon, although similar values of  $\Delta E_{em}$  have been observed recently

for oxygen-related bistable thermal double donors (BTDDs) in n-type Cz-Si crystals.<sup>[30]</sup> BTDDs are known to be centers with negative- $U$  properties, which have two very different atomic configurations for deep and shallow donor states.<sup>[30–34]</sup> Detailed information about the electronic structure of BTDDs have been obtained from the analysis of temperature dependencies of electron capture rates for these defects in Si crystals with different concentrations of free electrons.<sup>[30,31,34]</sup>

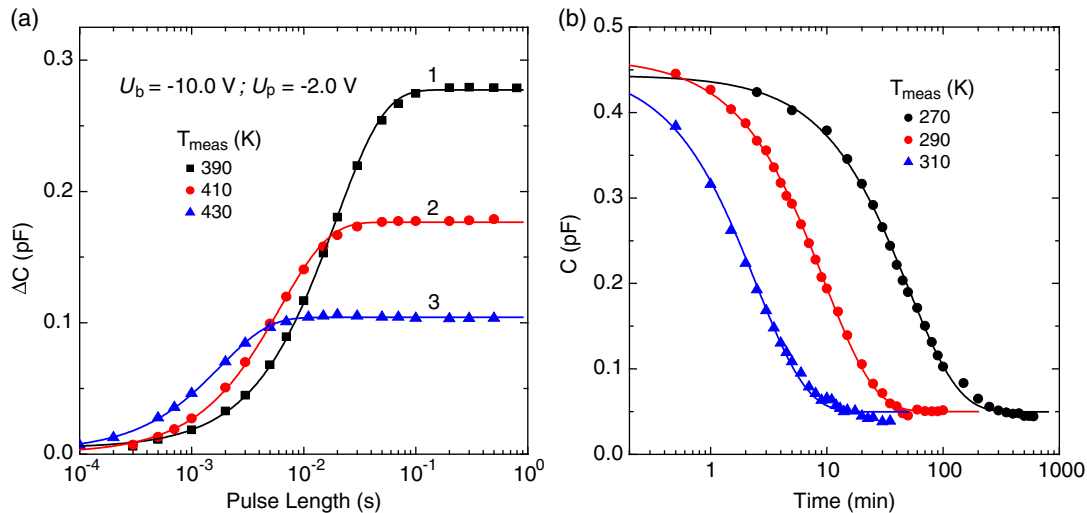
### 3.1.2. Transitions from the Shallow Acceptor to the Deep Donor State of the $B_sO_2$ Center: Long Decays of Conductivity

We have carried out measurements of the temperature dependencies of capture rates of holes by the  $B_sO_2$  defect (a transition from the  $A^-$  shallow acceptor state to the  $D^+$  deep donor state) in the Cz-Si:B samples with different doping levels. **Figure 5a** shows changes in the hole population of the defect upon changes in filling pulse length measured at different temperatures in the range 390–430 K. It can be seen that the capture rate of holes is temperature dependent as is the maximum achievable hole population of the  $B_sO_2$  center, which is the result of competition between capture and emission of holes in this temperature range.

We have also carried out measurements of the transformation rate from the  $A^-$  shallow acceptor state to the  $D^+$  deep donor state of the  $B_sO_2$  defect by monitoring changes in bias capacitance,  $C$ , of the diodes upon keeping them without bias ( $U_b = 0$  V) in the temperature range 260–320 K after application of 10 ms long MCI pulses or after cooling the diodes down under applied reverse bias from a temperature above 400 K (all the defects are in the  $A^-$  state at these conditions) to a measurement temperature ( $T_m$ ). **Figure 5b** shows changes in compensated diode capacitance  $C$  at different temperatures in the range 270–310 K for a diode from 3  $\Omega$  cm Cz-Si:B material.



**Figure 4.** Hole emission from the deep donor state of the  $B_sO_2$  complex. a) L-DLTS spectra recorded at 1) 390 K, 2) 400 K, and 3) 410 K on an  $n^+ \cdot p \cdot p^+$  diode from 3  $\Omega$  cm p-type boron-doped Cz-Si material that was subjected to a heat-treatment at 350 °C for 10 h. b) Arrhenius of  $T^2$ -corrected hole emission rates from the deep donor trap in  $n^+ \cdot p \cdot p^+$  diodes from 3  $\Omega$  cm p-type boron-doped Cz-Si material, which were subjected to heat-treatments at 350 °C for 100 and 600 min. Reproduced under the terms of the Creative Commons CC-BY license.<sup>[14]</sup> Copyright 2019, The Authors, published by AIP Publishing LLC.



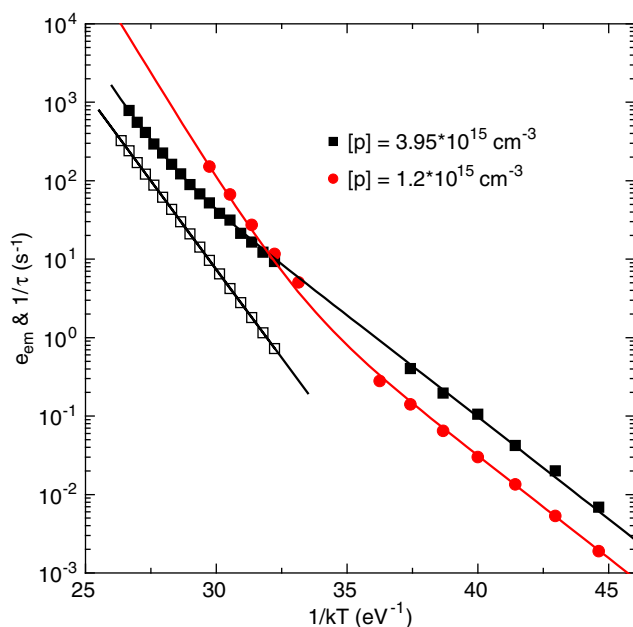
**Figure 5.** Capture kinetics of holes by the  $B_sO_2$  center. a) Changes in magnitude of the L-DLTS signal due to the deep donor trap upon changes in the filling pulse length. The solid lines are calculated for monoexponential growth process with least-square fitting values of  $\Delta C_{max}$  and characteristic growth rates. b) Changes in the diode capacitance  $C = C_d - C_b$  at bias voltage  $U_b = -10.0$  V and different temperatures in the range 270–310 K. For the improvement of signal-to-noise ratio in these measurements, we have used a backing-off capacitor of  $C_b = 200$  pF to compensate the capacitance of the diode studied ( $C_d$ ). The changes were induced by the application of multiple filling pulses with  $U_p = -2.0$  V. Further details of the measurements are described in the text. The solid lines are calculated for a monoexponential decay process with least-square fitting values of  $\Delta C_{max}$  and characteristic decay rate. All the measurements were carried out on an  $n^+-p-p^+$  diode from 3  $\Omega$  cm p-type boron-doped Cz-Si material which was subjected to a heat-treatment at 375 °C for 10 h. Reproduced under the terms of the Creative Commons CC-BY license.<sup>[14]</sup> Copyright 2019, The Authors, published by AIP Publishing LLC.

In **Figure 6**, the temperature dependencies of hole capture rates for the  $B_sO_2$  defect are plotted together with hole emission rates for the samples from 3 and 10  $\Omega$  cm Cz-Si:B materials. There are some similarities in temperature dependencies of carrier emission and capture for the  $B_sO_2$  center and oxygen-related BTDDs,<sup>[30,34]</sup> which indicate that the  $B_sO_2$  defect is related to a defect with negative- $U$  properties, similar to those for BTDDs. Occupancy kinetics for defects with  $U < 0$  and different structures have been considered in detail in previous studies.<sup>[34,35]</sup> There are some characteristic features in temperature dependencies of occupancy and emission rates for defects with  $U < 0$ , which provide details of their electronic structure. From a quick analysis of such characteristic features in the temperature dependencies of emission and occupancy rates presented in Figure 6 and taking into account positions of the Fermi level at the measurement temperatures, some preliminary information about the electronic and structural properties of  $B_sO_2$  defect has been obtained. First, a remarkable feature is that in the high-temperature region, the capture rate of holes is faster in the material with lower hole concentration. Such a feature is very unusual and, according to our knowledge, has never been observed for defects in semiconductors. Furthermore, the occupancy rates exceed the emission rates, which are identical in the materials studied, in the high-temperature region. These observations indicate that there is an intermediate state (state  $X^0$  in Figure 2) between the stable deep and shallow defect configurations.<sup>[35]</sup>

The temperature dependencies of the emission and capture rates for the  $B_sO_2$  defect in all the materials studied have been described using occupancy statistics developed in the study by Markevich et al.<sup>[35]</sup> for a defect with negative- $U$  and an

intermediate metastable state between the stable configurations. The values of energy barriers, which are derived by fitting the calculated and experimental curves in Figure 6, are given in the CCD diagram in Figure 2. It should be noted that a unique set of derived defect parameters has been obtained which describes experimental results for all the samples studied. From the junction capacitance measurements, we could not determine precisely the activation energy for hole emission in the shallow acceptor state  $\{\Delta E(-/0)\}$  as the corresponding hole emission rate was faster than we have been able to observe experimentally. However, from the experimental data presented in Figure 6, we have determined the value of  $\Delta E(0/+)$  as  $0.56 \pm 0.02$  eV, and from the analysis of temperature dependencies of occupancy of the  $B_sO_2$  defect with holes, we have estimated its occupancy level  $E(-/+)=0.5[\Delta E(0/+) + \Delta E(-/0)]$  to be at  $E_v + 0.30 (\pm 0.02)$  eV. So, a combination of the obtained  $\Delta E(0/+)$  and  $E(-/+)$  values gives  $\Delta E(-/0) \approx 0.04$  eV.

There are some remarkable similarities between the diode capacitance changes related to recharging of the  $B_sO_2$  defect induced by the application of MCI pulses at temperatures close to  $T = 300$  K, and conductance changes due to “deep traps” for electrons in bulk boron-doped Si crystals induced by the application of light pulse which were observed by Hornbeck and Haynes.<sup>[1]</sup> It is highly likely that the trap observed in our work and the “deep traps” observed in the work of Hornbeck and Haynes are related to the same defect. It is worth noting that while these “deep traps” were considered by Hornbeck and Haynes to be trapping centers for minority carriers (electrons), they did not consider them to be effective recombination centers. With the knowledge of the electronic structure of  $B_sO_2$  (Figure 2), it is possible to discuss its effect on minority carrier



**Figure 6.** Temperature dependencies of hole emission (empty symbols) and capture (filled symbols) rates for the  $B_sO_2$  defect. The values have been derived from an analysis of capacitance measurements described above on  $n^+-p^+$  diodes from 3 and 10  $\Omega$  cm Cz-Si:B materials, which were subjected to heat-treatments at 375 °C for 10 h. Solid lines were calculated with the use of Equation (8) and (9) from ref. [22] and values of energy barriers as fitting parameters. Concentrations of uncompensated shallow acceptors determined from capacitance determined from capacitance–voltage measurements were  $(3.95 \pm 0.1) \times 10^{15}$  and  $(1.2 \pm 0.1) \times 10^{15} \text{ cm}^{-3}$  in diodes from 3 and 10  $\Omega$  cm materials, respectively. Reproduced under the terms of the Creative Commons CC-BY license.<sup>[14]</sup> Copyright 2019, The Authors, published by AIP Publishing LLC.

lifetime in boron-doped silicon crystals, which have not been subjected to the extended LID. The recombination of light- or forward-bias-injection-induced electrons with holes through the  $B_sO_2$  defect with its initial state being  $D^+$  can occur via two different paths. The first step in both processes consists of the capture of an electron by the  $B_sO_2$  trap in the deep donor configuration and its transition to the metastable  $X^0$  state ( $D^+ + h^+ + e^- \rightarrow X^0 + h^+$ ). The rate of this process is likely to be fast; in other words, the capture cross section of electrons by the  $D^+$  state is large due to coulombic attraction. In the  $X^0$  state, the  $B_sO_2$  defect can either a) capture a hole and return to the  $D^+$  state ( $X^0 + h^+ \rightarrow D^+$ ) or b) transform to the more stable neutral  $A^0$  state and then emit a weekly bound hole and go to the  $A^-$  state ( $X^0 + h^+ \rightarrow A^0 + h^+ \rightarrow A^- + 2h^+$ ). The  $D^+ + h^+ + e^- \rightarrow X^0 + h^+ \rightarrow D^+$  transitions result in the recombination of injected electrons with available holes. However, the results presented by Hornbeck and Haynes<sup>[1]</sup> and our analysis indicate that the rate of process b) is higher than that of process a) at room temperatures in Si crystals with hole concentration lower than  $10^{17} \text{ cm}^{-3}$ . So, it appears that electron–hole recombination via the  $B_sO_2$  defect in nondegraded Cz-Si:B samples proceeds mainly through the  $A$  state of the center with the further sequence of transitions: b-ii) capture of a hole by the defect in  $A^-$  with the following reconfiguration from the  $A^0$  state to the

$X^0$  state; and b-iii) capture of a hole by the defect in  $X^0$  state and its transformation back to the initial deep donor  $D^+$  configuration ( $X^0 + h^+ \rightarrow D^+$ ). Results shown in Figure 5 and 6 indicate that the rate of process b-ii) is not high in the temperature range of operation of solar cells around 300 K ( $1/kT \approx 38.7 \text{ eV}^{-1}$ ),  $\approx 10^{-1} \text{ s}^{-1}$ . The  $A^0 \rightarrow X^0$  process is slow because of the existence of a relatively large energy barrier,  $\Delta E_{AX} = 0.67 \text{ eV}$  (Figure 2). So, the whole cycle of the  $D^+ \rightarrow A^- \rightarrow D^+$  transformations of the  $B_sO_2$  defect, which can be considered as a recombination event, is relatively long, in the range of tens of seconds. This is consistent with the predictions of Hornbeck and Haynes,<sup>[1]</sup> so the  $B_sO_2$  defect in the deep donor state can be considered as minority carrier trapping center in p-type Cz-Si crystals but not as an effective recombination center. It has been mentioned in the Section 1 that the presence of such trapping centers in relatively high concentrations can result in significant errors in the values of minority carrier lifetime measured by the QSS-PC technique.<sup>[8,15–17]</sup>

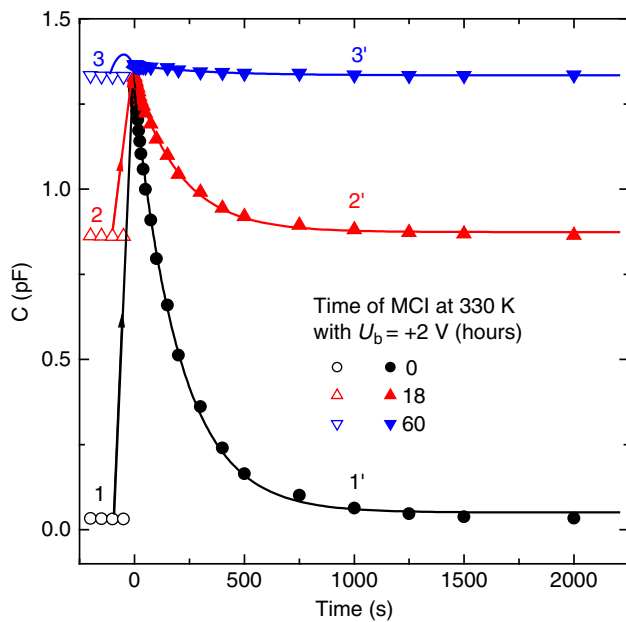
### 3.2. Light-Induced Degradation: Changes in Configurations of the $B_sO_2$ Defect upon Extended MCI and Dark Annealing

In agreement with the literature results on the LID in boron-doped Cz-Si crystals, we have observed a decrease in minority carrier lifetime in either bulk samples or the diodes studied upon extended light soaking or forward bias-induced MCI. It has been found in our previous work<sup>[14]</sup> that the reductions in lifetime occur simultaneously with the decrease in the concentration of the deep donor state of the  $B_sO_2$  defect and is accompanied by the appearance of a shallow acceptor state, which is different from the  $A^0(A^-)$  state shown in Figure 2.

Figure 7 shows that the magnitude of the capacitance transient, which is induced by short MCI pulses and are associated with the  $D^+ \rightarrow A^- \rightarrow D^+$  transformations (Figure 2), decreases in an  $n^+-p$  diode after its treatment with forward bias ( $U_b = +2.0 \text{ V}$ ,  $I_b \approx 1 \text{ A cm}^{-2}$ ) induced injection of minority carriers at 330 K for 18 h and becomes negligible after the treatment for 60 accumulated hours. The capacitance of the diode after the MCI treatment for 60 h is close to the value corresponding to that with the  $B_sO_2$  defect in the  $A^-$  shallow acceptor state (Figure 2) so indicating a transformation of the defect to another configuration ( $A'$ ) with a shallow acceptor level. The transitions from the  $A'$  state back to the  $A$  and  $D$  state are suppressed at room temperature under any bias conditions. It has been observed that the back  $A' \rightarrow A \rightarrow D^+$  transitions can be initiated by annealing of the degraded samples at temperatures higher than 150 °C.

It was not possible to determine the activation energy for hole emission from the LID-induced shallow acceptor state by the capacitance transient measurements as the corresponding hole emission was faster than we have been able to observe experimentally. Further results on electronic properties of the defect appearing upon the LID process have been obtained from low-temperature PL and AS measurements on the samples subjected to the LID and dark annealing at about 200 °C.<sup>[14]</sup> In both the low-temperature PL and AS spectra of the degraded samples, signals due to a defect with an energy level slightly shallower ( $E_b = 40 \pm 3 \text{ meV}$ ) than that of the single substitutional boron atoms have been detected.





**Figure 7.** Changes in the diode capacitance  $C = C_d - C_b$  at bias voltage  $U_b = -10.0$  V and  $T = 270$  K for an  $n^+-p-p^+$  diode from  $10\ \Omega\text{ cm}$  p-type Cz-Si:B material after treatments with forward bias ( $U_b = +2.0$  V;  $I_b \approx 1\text{ A cm}^{-2}$ ) induced MCI at 330 K. For the improvement of signal-to-noise ratio in these measurements, we have used a backing-off capacitor of  $C_b = 200$  pF to compensate the capacitance of the diode studied ( $C_d$ ). Values of diode capacitance, which were measured after relatively long (45 min) storage at  $T = 270$  K with  $U_b = 0$  V, are shown by open symbols (1, 2, and 3). Sharp increases in the diode capacitance before the MCI treatments and after the treatments for 18 h were initiated by a short (10 ms) forward bias ( $U_b = +2.5$  V) pulse, and capacitance transients were recorded after the end of the pulse ( $t = 0$  s) upon keeping the diode without bias ( $U_b = 0$  V). The solid lines (1', 2', and 3') are calculated dependencies for a monoexponential decay process with least-square fitting values of  $\Delta C_m$  and characteristic decay rate.

It has been widely proposed that the light-soaking-induced minority carrier lifetime degradation is associated with the appearance of Shockley–Read–Hall (SRH) recombination center with deep levels in the band gap.<sup>[2–6,36,37]</sup> According to the recent literature results obtained from the analysis of injection-level dependencies of minority carrier lifetime in the degraded boron-doped Si crystals, the degradation-induced recombination center is a defect with negative- $U$  properties having a donor level at about  $E_C - 0.41$  eV and an acceptor level at about  $E_V + 0.26$  eV.<sup>[2,6,37]</sup> The ratio of electron to hole capture cross sections for the donor level has been found to be in the range between 10 and 20.<sup>[6,37]</sup> Assuming physically feasible maximum values for  $\sigma_n$  and the observed lifetime changes, observation of the responsible SRH center using standard techniques, such as DLTS and MCTS,<sup>[10–12]</sup> should present no difficulty. We have carefully examined the DLTS and MCTS spectra of the Cz-Si:B samples subjected to the LID treatments, and in consistency with the previously published results, Markevich et al.<sup>[38]</sup> have not observed emission signals from deep-level defects, which have been argued to be responsible for the LID. An important distinction must be made here between recombination behavior which

can be modeled or fitted to SRH kinetics and SRH recombination which takes place with the necessary involvement of a deep state.

From the analysis of all the data obtained and previous searches for a correlation between the defects responsible for LID and deep-level states observed in DLTS and MCTS by us and others,<sup>[2,38]</sup> we come to the conclusion that SRH recombination through a defect with deep levels is not the dominant recombination mechanism in Cz-Si:B samples subjected to the LID treatments. Our hypothesis is therefore that the shallow acceptor, the presence of which we have observed by low-temperature PL and electrical measurements in the samples after the LID treatments, is directly or indirectly responsible for the additional recombination produced by the BO degradation. It is likely that the enhanced recombination is associated with trap-assisted Auger recombination<sup>[39–41]</sup> of charge carriers through the  $B_sO_2$  complex, which, in its recombination active state, is a shallow acceptor. This assignment is supported by the observation of above band-gap luminescence due to hot carriers resulting from the Auger process.<sup>[14]</sup> However, further experimental work is necessary for clear understanding of details of the Auger process.

Ab initio calculations have shown that there are a few (at least three) stable configurations of the  $B_sO_2$  defect consisting of a substitutional boron atom and staggered oxygen dimer.<sup>[14]</sup> These configurations are shown in the lower part of Figure 2. In all of these configurations (labeled as A, A', and A''), the defect has a shallow acceptor level close to that of the single substitutional boron atom. We have argued that the LID process is associated with an exciton recombination enhanced transition from the A state to the A' state, and the recombination activity in the long-term degraded samples is associated with trap-assisted Auger recombination involving the A' state. For some reasons, which are not fully understood at the moment, the recombination activity of the  $B_sO_2$  defect in the A' state is significantly stronger than that due to the single substitutional boron atom.

## 4. Conclusion

It is shown in our work that persistent photoconductivity and “deep” electron traps observed many years ago by Hornbeck and Haynes<sup>[1]</sup> in boron-doped Cz-grown Si crystals are associated with transitions between the deep donor and shallow acceptor states of the  $B_sO_{2i}$  complex. We have investigated processes associated with electron and hole emission and captured the defect and constructed its CCD. It is argued that the  $B_sO_{2i}$  complex is a defect with negative- $U$  properties with its  $E(-/+)$  occupancy level at  $E_V + 0.3$  eV and it is responsible for MCI-induced conductivity and capacitance transients in nondegraded Si:B+O samples and solar cells. From ab initio modeling, atomic configurations of the defects have been found,<sup>[14]</sup> with calculated energy differences and barriers close to those derived from experiments.

Extended (hours) treatments of the samples having the negative- $U$   $B_sO_2$  defect-related features (high-temperature DLTS signal, persistent photoconductivity, capacitance transients) under MCI conditions (LID) result in the disappearance of these features and degradation of minority carrier lifetime. A combination of our experimental results gives an evidence that the LID

treatments are associated with the transformation of the  $B_sO_2$  defect into a metastable shallow acceptor configuration (the A' configuration in Figure 3) with an associated enhanced recombination activity. The deep donor state concentration decreases as the minority carrier lifetime decreases, and its measured parameters show it to be a trap with insignificant recombination activity. We have presented in a previous study<sup>[14]</sup> evidence supporting the hypothesis that the recombination mechanism in BO-LID is a trap-assisted Auger process involving the shallow acceptor state of the  $B_sO_2$  complex. An experimental complication of some of the previous work on BO-LID, which remains to be investigated in detail in relation to the concentrations and properties of the deep donor, is that this state acting as a trap, in certain circumstances, influences the measurement of minority carrier lifetime and so increasing the apparent lifetime.

In summary, we argue that the “deep” electron traps observed by Hornbeck and Haynes can be considered as precursors of the “slow” defects responsible for the LID in boron-doped Cz-Si crystals. Both the defects are  $B_sO_2$  complexes, transformations between charge states and atomic configurations of which account for the observed electron trapping and LID phenomena.

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## Conflict of Interest

The authors declare no conflict of interest.

## Keywords

boron–oxygen defects, light-induced degradation, persistent photoconductivity, recombination enhanced reactions, silicon

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