












# Acceptor-oxygen defects in silicon: The electronic properties of centers formed by boron, gallium, indium, and aluminum interactions with the oxygen dimer

Cite as: J. Appl. Phys. **130**, 245703 (2021); doi: [10.1063/5.0076980](https://doi.org/10.1063/5.0076980)

Submitted: 29 October 2021 · Accepted: 6 December 2021 ·

Published Online: 28 December 2021



Joyce Ann T. de Guzman,<sup>1</sup>  Vladimir P. Markevich,<sup>1,a)</sup>  Ian D. Hawkins,<sup>1</sup>  José Coutinho,<sup>2</sup>   
Hussein M. Ayedh,<sup>3</sup>  Jeff Binns,<sup>4</sup>  Nikolay V. Abrosimov,<sup>5</sup>  Stanislau B. Lastovskii,<sup>6</sup>  Iain F. Crowe,<sup>1</sup>   
Matthew P. Halsall,<sup>1</sup>  and Anthony R. Peaker<sup>1</sup> 

## AFFILIATIONS

<sup>1</sup>Photon Science Institute and Department of EEE, The University of Manchester, Manchester M13 9PL, United Kingdom

<sup>2</sup>Department of Physics and I3N, University of Aveiro, Campus Santiago, 3810-193 Aveiro, Portugal

<sup>3</sup>Department of Electronics and Nanoengineering, Aalto University, Tietotie 3, FI-02150 Espoo, Finland

<sup>4</sup>Nexcel Electronic Technology, Gresham, 97030 Oregon, USA

<sup>5</sup>Leibniz-Institut für Kristallzüchtung (IKZ), Max-Born-Strasse 2, 12489 Berlin, Germany

<sup>6</sup>Scientific-Practical Materials Research Center of National Academy of Sciences of Belarus, Minsk 220072, Belarus

**Note:** This paper is part of the Special Topic on Defects in Semiconductors.

**a)** Author to whom correspondence should be addressed: [V.Markevich@manchester.ac.uk](mailto:V.Markevich@manchester.ac.uk)

## ABSTRACT

It is well established that boron reacts with two oxygen atoms in Czochralski-grown silicon (Cz-Si) to form a defect, which is responsible for the dominant light-induced degradation (LID) in solar cells made from Cz-Si:B material. The detrimental effect of LID has stimulated a move by solar cell manufacturers to the use of silicon with other group-III dopants, particularly with gallium. Cz-Si:Ga is immune to the BO-type LID. The information available in the literature on the interactions of oxygen with either Al, Ga, or In impurities in Si is limited. We use *ab initio* modeling and junction spectroscopy techniques to study a family of defects with unusual electronic properties, which have been detected in Cz-Si samples doped with different shallow acceptor species. We have carried out detailed measurements of the temperature dependencies of hole emission rate, equilibrium occupancy, and hole capture kinetics for the traps observed in differently doped p-type Cz-Si samples. It is found from the analysis of the changes in magnitude of the deep-level-transient signals with temperature that the equilibrium occupancy function of the traps is characteristic for a defect with negative- $U$  properties in all the samples. The positions of the  $E(-/+)$  occupancy level of the defects are very close in differently doped samples,  $E(-/+) = E_v + (0.31 \pm 0.01)$  eV. It is argued that the oxygen dimer interacts with group-III atoms in silicon and these interactions result in the formation of  $A_sO_2$  complexes ( $A$  is either B, Al, Ga, or In atom) with very similar electronic properties.

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## I. INTRODUCTION

A defect with negative electron correlation energy,  $U$ , in a semiconductor is a center, which can emit or capture at least two charge carriers (either electrons or holes), and for which the

ionization energy of the first charge carrier ( $I_1$ ) exceeds the ionization energy of the second carrier ( $I_2$ ):  $U = I_2 - I_1 < 0$ .<sup>1–3</sup> In other words, a negative- $U$  defect has an inverted order of energy levels in the gap. The characteristic features of the defects with negative- $U$

properties and techniques for their analysis have been recently reviewed by Coutinho *et al.*<sup>3</sup> Solid evidence of the negative- $U$  nature of a defect can be obtained from an analysis of its equilibrium occupancy with charge carriers upon changes in the Fermi level position, which can be induced by changes either in temperature or in the concentration of free charge carriers. The occupancy function for a negative- $U$  defect,  $f_{U<0}$ , differs from the Fermi function that describes the charge occupancy of defects with  $U>0$ .<sup>3</sup>

It has been shown recently that a complex consisting of a substitutional boron atom and two oxygen atoms ( $B_sO_2$ ) is a center with negative- $U$  properties, and it is responsible for minority carrier trapping effects, persistent photoconductivity, and light-induced degradation (LID) of minority carrier lifetime in Czochralski-grown silicon (Cz-Si) crystals doped with boron.<sup>4–6</sup> Depending on the position of the Fermi level, the  $B_sO_2$  defect exists either in an atomic configuration with deep donor properties or in several different configurations with a shallow acceptor level. It has been found that the atomic structure of the defect changes from a “square” geometry of the oxygen dimer to a staggered dimer configuration as the defect transforms from the deep donor to a shallow acceptor state.<sup>4</sup> The  $E(-/+)$  occupancy level of the defect has been found to be at  $E_v + (0.30 \pm 0.02)$  eV. Transitions between the different configurations associated with hole/electron emission or capture by the defect can be monitored with the use of junction capacitance techniques.<sup>4–6</sup> From an analysis of temperature dependencies of rates of carrier emission and capture by the  $B_sO_2$  defect in Cz-Si:B samples with different hole concentrations, electronic characteristics of the defect have been determined and its configuration coordinate diagram constructed.<sup>4,5</sup>

Further, a defect with very similar electronic properties to those for the  $B_sO_2$  defect has been detected in Czochralski-grown silicon crystals doped with indium.<sup>7</sup> It has been argued that the defect in In-doped Cz-Si is a complex consisting of a substitutional indium ( $In_s$ ) atom and the oxygen dimer, and its negative- $U$  electronic properties are related to the “square”-staggered configuration transformations of  $O_2$  in the vicinity of an  $In_s$  atom.<sup>7</sup> First-principles modeling results suggest that at equilibrium conditions in p-type Si (in the absence of minority carriers), the ground state of  $InO_2$  is positively charged, comprising close In- and  $O_2$ -square units with the formation of In–O bonds.<sup>7</sup> On the other hand, the location of the occupancy ( $-/+$ ) level was better described by the model assuming that the dimer breaks away from the acceptor and adopts a staggered  $O_2$  configuration in the neutral charge state.

Considering the above, we are immediately confronted with several questions regarding other acceptors: (i) Are all acceptors capable of forming stable  $AO_2$  complexes? (ii) What is the electronic activity of the resulting  $AO_2$  centers? (iii) Are they all powerful recombination centers and do they all lead to a LID effect? This latter point is of considerable importance to the solar industry, which is considering a general shift away from boron doping to gallium doping with the aspiration of improved stability and the possible elimination of LID of the type caused by  $B_sO_2$  defects.

In the present work, we report results on the observation and characterization of defects with negative- $U$  electronic properties in Czochralski-grown Si crystals doped with either B, Al, Ga, or In impurity atoms during growth. Some preliminary results of this

study have been published earlier in a short conference paper.<sup>8</sup> We have now carried out detailed measurements of temperature dependencies of hole emission rate, equilibrium occupancy, and hole capture kinetics for the detected traps and determined their electronic characteristics in the Cz-Si samples doped with different acceptor impurities. It is argued that the oxygen dimer interacts with all group-III impurity atoms in silicon and these interactions result in the formation of  $A_sO_2$  complexes ( $A$  is either B, Al, Ga, or In atom) with very similar electronic properties. From first-principles calculations, we found that double positive oxygen dimers (forming a squared structure) are strongly stabilized in the vicinity of all acceptors, including the larger ones. The resulting complexes show a calculated hole binding energy of about 1 eV, which depends very little on the location of the acceptor (with respect to  $O_2$ ) and from its chemical identity. The calculations also show that like  $BO_2$ ,  $\{Al, Ga, In\}O_2$  are negative- $U$  complexes and suggest that the complexes that are detected by junction spectroscopy do not involve the formation of direct A–O bonds.

## II. EXPERIMENTAL AND MODELING DETAILS

Mono-crystalline silicon wafers grown by the Czochralski technique and doped with different group-III elements such as boron, aluminum, gallium, or indium during growth have been studied. The acceptor concentrations,  $N_a$ , in the silicon samples range from  $6.5 \times 10^{14}$  to  $9.2 \times 10^{15} \text{ cm}^{-3}$  as determined from the capacitance–voltage ( $C$ – $V$ ) measurements at 300 K. The interstitial oxygen concentration,  $[O_i]$ , in the wafers was in the range from  $5.0 \times 10^{17}$  to  $(9.5 \pm 1) \times 10^{17} \text{ cm}^{-3}$ . The  $[O_i]$  values were determined from infrared absorption measurements at room temperature with the use of  $3.14 \times 10^{17} \text{ cm}^{-2}$  calibration coefficient, which links an absorption coefficient at maximum of the band due to vibrations of  $O_i$  atoms ( $1107 \text{ cm}^{-1}$  band) with  $[O_i]$ . Table I shows some parameters of the wafers studied.

For boron-doped Cz-Si, we have used  $n^+p$ - $p^+$  diodes, which were formed by implantation and subsequent thermal activation of

**TABLE I.** Details of the samples used in the study. The concentration of ionized uncompensated shallow acceptors ( $N_a^-$ ) in as-grown wafers was determined from  $C$ – $V$  measurements on the diodes at 300 K. Oxygen concentration,  $[O_i]$ , in the wafers was determined from infrared absorption measurements at room temperature with the use of  $3.14 \times 10^{17} \text{ cm}^{-2}$  calibration coefficient, which links  $[O_i]$  with an absorption coefficient at maximum of the band due to vibrations of  $O_i$  atoms ( $1107 \text{ cm}^{-1}$  band).

Cz-Si sample	Dopant	Diode structure	$(N_a^-)$ ( $\text{cm}^{-3}$ )	$[O_i]$ ( $\text{cm}^{-3}$ )
B-1	Boron	$n^+p$ - $p^+$ /Schottky	$1.2 \times 10^{15}$	$9.5 \pm 1 \times 10^{17}$
B-2	Boron	$n^+p$ - $p^+$ /Schottky	$4.0 \times 10^{15}$	$7.5 \pm 1 \times 10^{17}$
Al-1	Aluminum	Schottky	$5.2 \times 10^{15}$	$\sim 8 \times 10^{17}$
Ga-1	Gallium	Schottky	$2.0 \times 10^{15}$	$\sim 9 \times 10^{17}$
Ga-2	Gallium	Schottky	$9.2 \times 10^{15}$	$\sim 8 \times 10^{17}$
In-1	Indium	Schottky	$6.5 \times 10^{14}$	$\sim 6 \times 10^{17}$
In-2	Indium	Schottky	$1.7 \times 10^{15}$	$\sim 6 \times 10^{17}$
In-3	Indium	Schottky	$4.0 \times 10^{15}$	$\sim 8 \times 10^{17}$
In-4	Indium	Schottky	$4.5 \times 10^{15}$	$\sim 5 \times 10^{17}$

60 keV phosphorus ions (front side) and 60 keV boron ions (back side). On the other silicon slices doped with either Al, Ga, or In atoms, Schottky barrier diodes have been fabricated by plasma sputtering of titanium/aluminum stack through a shadow mask. Subsequently, gold was deposited at the back of the samples to serve as an Ohmic contact. The diode area for all the samples was  $0.79 \text{ mm}^2$  with a recorded leakage current of about  $1 \mu\text{A}$  at 10 V reverse bias.

We have carried out current–voltage ( $I$ – $V$ ) and capacitance–voltage measurements to assess the quality of the fabricated diodes and to determine the concentration of uncompensated ionized shallow acceptors as well as the width of the depletion regions. Junction spectroscopy techniques such as deep level transient spectroscopy (DLTS) and Laplace-DLTS have been used for the detection and characterization of deep-level defects in the diodes.<sup>9–11</sup> To investigate the possible presence of inadvertent boron atoms in Cz-grown silicon slices doped with either Al, Ga, or In, measurements of bias capacitance as a function of temperature ( $C_b$ – $T$ ) have been carried out.

Modeling of acceptor–oxygen and acceptor–dioxygen complexes was performed within density functional theory using the Vienna *ab-initio* Simulation Package (VASP).<sup>12</sup> The projector augmented-wave (PAW) method was employed to describe core electrons.<sup>13</sup> We used both semi-local (the generalized gradient approximation) and non-local (a mix of exact and semi-local exchange) treatments to the many-body interactions between electrons. The functionals employed were those commonly referred to as Perdew–Burke–Ernzerhof (PBE)<sup>14</sup> and Heyd–Scuseria–Ernzerhof (HSE06),<sup>15</sup> respectively.

A–O<sub>i</sub> and A–O<sub>2</sub> complexes ( $A = \{\text{B}, \text{Al}, \text{Ga}, \text{In}\}$ ) were inserted in 216-, 512- and 1000-Si-atom supercells with cubic shape and calculated lattice constant  $a_0 = 5.4318 \text{ \AA}$ . The Brillouin zone (BZ) of the 216-atom supercell was sampled using a  $2 \times 2 \times 2$  grid of  $\mathbf{k}$ -points, while the  $\Gamma$ -point was used for the BZ sampling of the larger cells. All defect geometries were found within the PBE level. The maximum force acting on every atom was lower than  $0.01 \text{ eV/\AA}$ . From the ground state structure, the total energies were evaluated within the HSE06 level from a single-point energy calculation.

Transition levels  $E(q/q+1)$  involving a change in the defect charge state ( $q$ ) via hole emission  $(\text{AO}_2)^{q+1} \rightarrow (\text{AO}_2)^q + h^+$  were evaluated with respect to the valence band top as

$$E(q/q+1) - E_v = E(q) - E(q+1) - \epsilon_v. \quad (1)$$

Here,  $E(q) = \tilde{E}(q) + E_{\text{corr}}(q)$  is a total energy per defect, consisting of the energy per defective periodic cell,  $\tilde{E}(q)$ , subject to a charge correction when  $q \neq 0$ .<sup>16</sup> As a corollary of Eq. (1), the location of a  $E(q-1/q+1)$  negative- $U$  level is obtained as

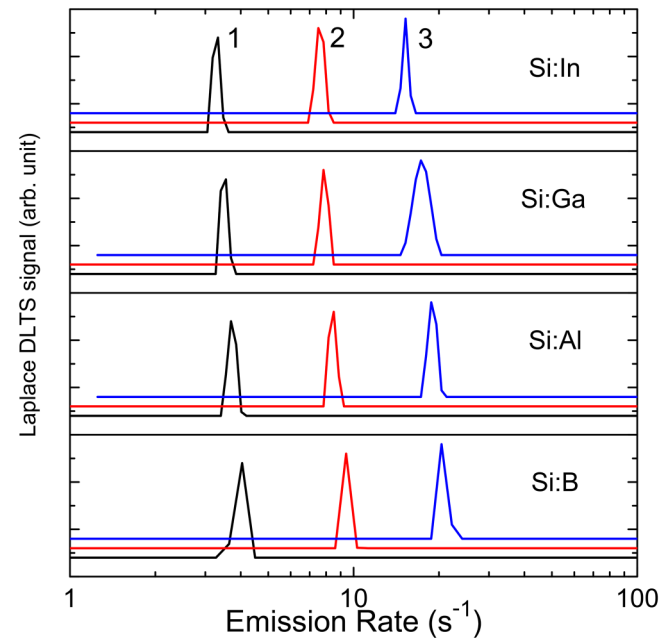
$$E(q-1/q+1) - E_v = \frac{E(q-1) - E(q+1)}{2} - \epsilon_v. \quad (2)$$

Further details of the methodology can be found in Refs. 3, 7, and 17.

### III. EXPERIMENTAL RESULTS AND DISCUSSION

In the conventional DLTS spectra recorded on all diodes (Schottky and  $n^+p$  junctions) from all the  $p$ -type Cz-Si crystals (doped with either B, Al, Ga, or In impurities) studied in this work, a hole-emission-related peak with its maximum at about 390 K for the emission rate window of  $10 \text{ s}^{-1}$  was detected. This peak has been observed earlier in B- and In-doped samples<sup>4–7</sup> and will be referred to as  $H_{390 \text{ K}}$  hole emission signal in the following. The concentrations of the defect(s), which gives rise to the  $H_{390 \text{ K}}$  emission signal, vary from sample to sample and are found to be in the range of a few times of  $10^{13} \text{ cm}^{-3}$  in the majority of as-received samples.

Figure 1 compares the normalized (to the maximum value of the emission signal) Laplace DLTS spectra recorded at 380, 390, and 400 K for the samples doped with either B, Al, Ga, or In impurity atoms. Figure 1 shows that emission rates of holes from the detected trap are very close in differently doped samples. We have carried out measurements of the temperature dependencies of the hole emission rates in the temperature range 335–440 K in differently doped samples with the use of high-resolution Laplace DLTS technique and constructed the Arrhenius plots of  $T^2$ -corrected hole emission rates. Close values of activation energy for hole emission, ( $\Delta E$ ), at approximately  $0.97 \pm 0.02 \text{ eV}$  have been obtained from the Arrhenius plots for the samples with different types and concentrations of dopants. The pre-exponential factors were determined to be in the range of a few times of  $10^8 \text{ s}^{-1} \text{ K}^{-2}$  for all the samples. Table II summarizes the activation energies and pre-exponential factors that have been obtained from the emission rate measurements of different samples.



**FIG. 1.** Normalized (to the maximum value of the emission signal) Laplace DLTS spectra recorded at (1) 380, (2) 390, and (3) 400 K for the Cz-Si samples doped with either B, Al, In, or Ga atoms.

**TABLE II.** Activation energies and pre-exponential factors derived from Arrhenius plots of  $T^2$ -corrected hole emission rates from the  $H_{390\text{ K}}$  trap in different p-type Cz-Si samples.

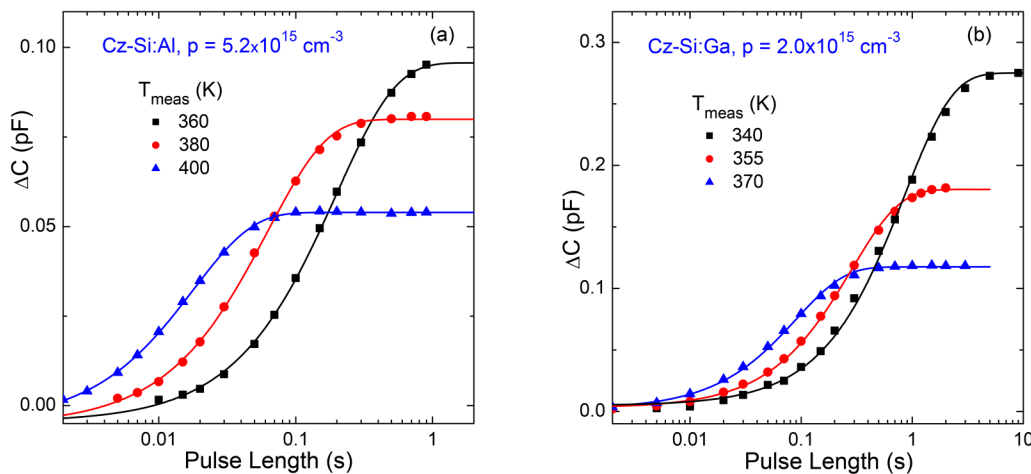
Sample	$N_A$ ( $\text{cm}^{-3}$ )	Activation energy (eV)	Pre-exponential factor ( $\text{s}^{-1}\text{K}^{-2}$ )
B-2	$4.0 \times 10^{15}$	0.97 (0.01)	$2.3 \times 10^8$
Al-1	$5.2 \times 10^{15}$	0.96 (0.01)	$1.4 \times 10^8$
Ga-2	$9.2 \times 10^{15}$	0.99 (0.01)	$3.85 \times 10^8$
In-4	$4.5 \times 10^{15}$	0.97 (0.01)	$2.05 \times 10^8$

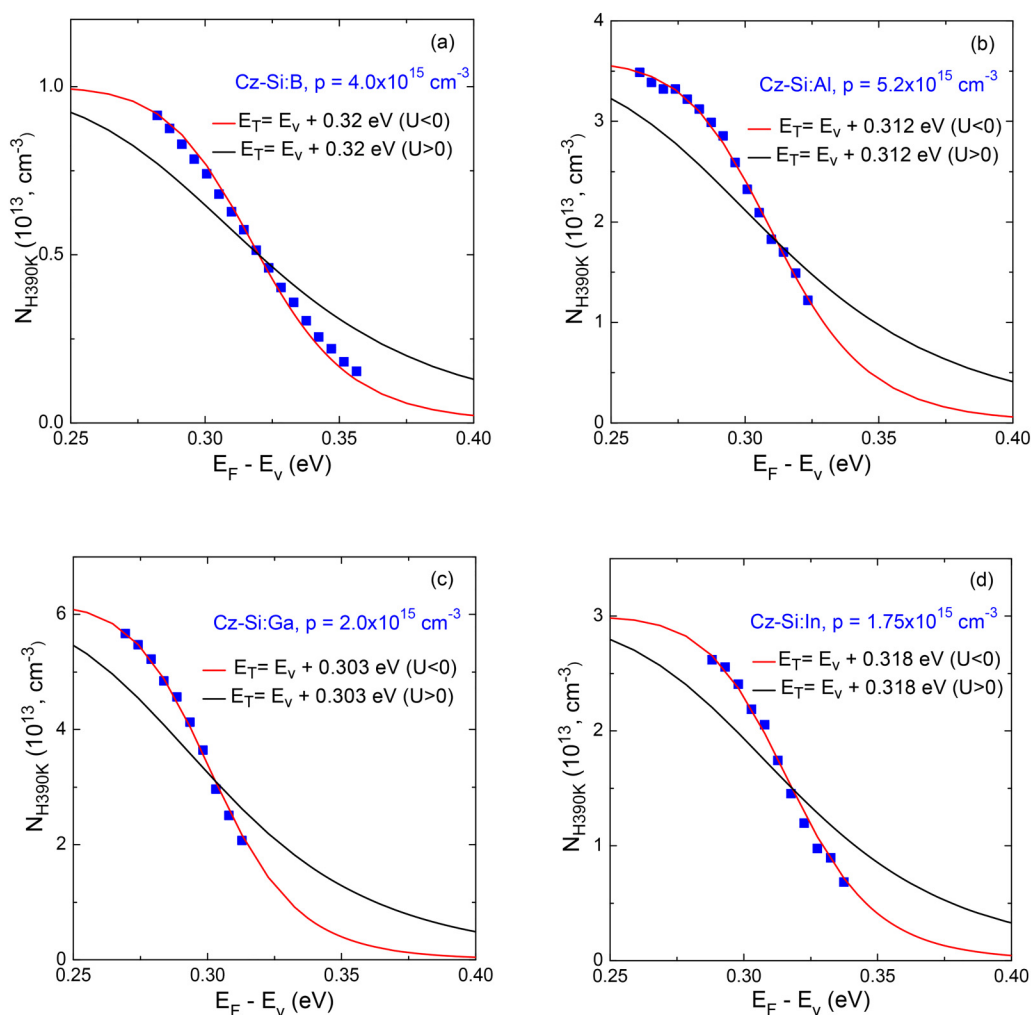
Figure 2 shows the changes in the magnitude of the emission signal due to the  $H_{390\text{ K}}$  trap upon changes in the filling pulse length,  $t_p$ , at different temperatures for the Cz-Si samples doped with either Al or Ga atoms. The obtained  $\Delta C(t_p)$  dependencies are related to the hole capture by the  $H_{390\text{ K}}$  trap. The dependencies presented in Fig. 2 are described well by a mono-exponential-growth equation and resemble those observed earlier for Cz-Si samples doped with either B or In.<sup>4,5,7</sup> The characteristic features of the  $\Delta C(t_p)$  dependencies in all the samples are as follows: (i) the capture rates,  $C_p$ ,<sup>11</sup> are temperature dependent and (ii) the maximum values of the emission signal,  $\Delta C_{\text{max}}$ , reachable at long filling pulses, are temperature dependent. The  $\Delta C_{\text{max}}$  value is a measure of equilibrium occupancy of a defect with charge carriers.<sup>11</sup> The decrease in the  $\Delta C_{\text{max}}$  values with increasing temperature, which is observed for the  $H_{390\text{ K}}$  trap, indicates that there is a competition between the capture and emission of holes by the defect in the temperature range 340–430 K when holes are available in the probed regions during the filling pulse period.

Figure 3 shows dependencies of the concentration of the occupied  $H_{390\text{ K}}$  traps calculated from the measured  $\Delta C_{\text{max}}$  values at different temperatures vs the Fermi level position at the

corresponding temperature in Cz-Si samples doped with different group-III impurities. We have attempted to describe the obtained experimental dependencies with the use of occupancy functions for defects with negative and positive  $U$  values.<sup>3</sup> The solid red lines in Fig. 3 represent the results of the best fitting of the occupancy function for a defect with  $U < 0$  to the experimental results with fitting parameters being the trap occupancy level relative to the valence band top and the trap concentration. The black lines in Fig. 3 show the concentration values vs the Fermi level position calculated with the use of occupancy function for a defect with  $U > 0$  and the fitting parameters are the same as for the solid red lines. It is evident that the experimentally obtained dependencies can be described well with the use of occupancy function for a negative- $U$  defect. Furthermore, the occupancy levels extracted from the fits are very similar for samples with different group-III dopants,  $E(-/+)=E_v+(0.31 \pm 0.01)$  eV. The results presented in Fig. 3 can be considered a solid evidence that the  $H_{390\text{ K}}$  trap is related to a defect with negative- $U$  properties and with very similar occupancy level positions in differently doped p-type Cz-Si samples.

Figure 4 shows the Arrhenius plots of emission and capture rates of holes by the  $H_{390\text{ K}}$  trap for the samples doped with either Al or Ga. These dependencies are similar to those obtained earlier for the B- and In-doped samples.<sup>4–7</sup> All the temperature dependencies of  $C_p$  values given in Fig. 4 consist of two slopes, which show that a dominant mechanism of the hole capture process is changed within the measured temperature range.<sup>3</sup> The Fermi level position at temperatures corresponding to the change in the slopes is found to be at about  $E_v+0.31$  eV that coincides with the position of the  $E(-/+)$  occupancy level of the  $H_{390\text{ K}}$  trap in the Si:Al and Si:Ga samples. An inspection of the  $e_{\text{em}}(1/kT)$  and  $C_p(1/kT)$  dependencies presented in Fig. 4 indicates that there are two other features, which are characteristic of the defects with negative- $U$  properties. First, the emission rate values measured by Laplace-DLTS differ

**FIG. 2.** Capture kinetics of holes by the  $H_{390\text{ K}}$  trap in diodes on (a) Al-doped (Al-1) and (b) Ga-doped (Ga-1) samples. Changes in the magnitude of the capacitance transients,  $\Delta C$ , due to hole emission from the  $H_{390\text{ K}}$  trap upon changes in the filling pulse length are shown. The capacitance transients have been measured and analyzed with the use of the L-DLTS technique. The solid lines are calculated for the mono-exponential growth process with least-square fitting values of  $\Delta C_{\text{max}}$  and characteristic growth rates.



**FIG. 3.** Equilibrium occupancy with holes of the H<sub>390K</sub> trap as a function of Fermi level position in the gap for Cz-Si samples doped with either (a) B, (b) Al, (c) Ga, or (d) In impurities. The equilibrium concentrations of defects occupied with holes have been calculated from the  $\Delta C_{\text{max}}$  values at a certain temperature determined from hole capture kinetics measurements such as those shown in Fig. 2. The solid red lines represent the results of the best fitting of the occupancy function for a defect with  $U < 0$  to the experimental values with fitting parameters being the trap occupancy level relative to the valence band top and the trap concentration. The black lines are the values of concentration of traps occupied with holes vs the Fermi level position, which have been calculated with the use of occupancy function for a defect with  $U > 0$  and the fitting parameters being the same as for the solid red lines.

from the capture rate values in the range of temperatures where  $E_F > E_v + 0.31 \text{ eV}$  in the samples, that is an indication of bistability of the defect in the charge state, which occurs after emission of the first hole.<sup>3,4</sup> Second, it appears that the capture rate values are inversely proportional to the hole concentrations in the samples ( $C_p \sim p^{-1}$ ) when  $E_F > E_v + 0.31 \text{ eV}$ . That cannot occur for defects with positive  $U$  values.<sup>3</sup> Further, all the experimental  $C_p(1/kT)$  dependencies have been described well using equations for non-equilibrium occupancy statistics for defects with negative- $U$  properties.<sup>3,18</sup> The solid lines for the  $C_p(1/kT)$  dependencies in Fig. 4 have been calculated according to equations from that statistics with the energy barriers between the D, X, and A configurations shown in

configuration-coordinate diagram (CCD) in Fig. 5 as fitting parameters for matching the experimental dependencies. The detailed analysis of the experimental temperature dependencies of hole capture rates in the differently doped p-type-Cz samples is beyond the scope of the present work and will be reported in a separate paper.

The experimental results and analysis presented above show that in Czochralski-grown Si crystals doped with different group-III impurities there are defects with very similar electronic properties. All the defects have negative electron correlation energy and close positions of the  $E(-/+)$  occupancy level at about  $E_v + 0.31 \text{ eV}$ . In Refs. 4–6, the results of experimental studies of electronic



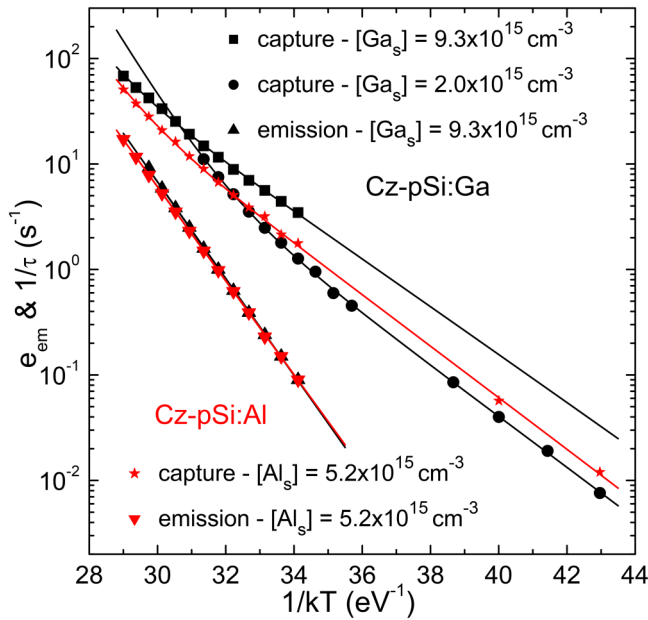


FIG. 4. Temperature dependencies of hole emission and capture rates for the  $H_{390\text{ K}}$  trap in Cz-Si samples doped with either Al or Ga impurity atoms.

properties of this defect and its formation and annihilation conditions in B-doped Cz-Si crystals were reported. A comparison of the obtained results with the results available in literature allowed the authors of Ref. 4 to suggest that the defect consists of a substitutional acceptor atom and the oxygen dimer. With the use of *ab initio* modeling calculations, the changes in atomic configurations of the  $B_sO_2$  defect, which could explain all the observed experimental data, were elucidated. Figure 5 reproduces the configuration-coordinate diagram and atomic configurations of the  $B_sO_2$  defect in different charge states as proposed in Ref. 4.

The first question to be answered to arrive at an explanation of the results of the present study is whether the  $H_{390\text{ K}}$  trap in either Al-, Ga-, or In-doped Cz-Si samples is due to contamination with boron and hence is related to the  $B_sO_2$  defect. It is known that in conventional Cz growth (as distinct to continuous growth Czochralski technique variants) some manufacturers combine boron and other group-III impurity doping to reduce the variation in hole concentration along the ingot. That is because of the more favorable segregation coefficient of boron in silicon in comparison with those for other shallow acceptor impurities. It should be noted that according to the information from growers of the wafers used in the present study, no boron was intentionally added to the melt during growth of the Al-, Ga-, and In-doped ingots.

To verify the absence of boron in the samples doped with either Al, Ga, or In, we have obtained information about the ensemble of shallow dopant impurities in the studied p-type-Si crystals by means of electrical measurements. Measurements of temperature dependencies of bias capacitance,  $C_b$ , of the diodes on the differently doped samples were carried out. Figure 6 compares

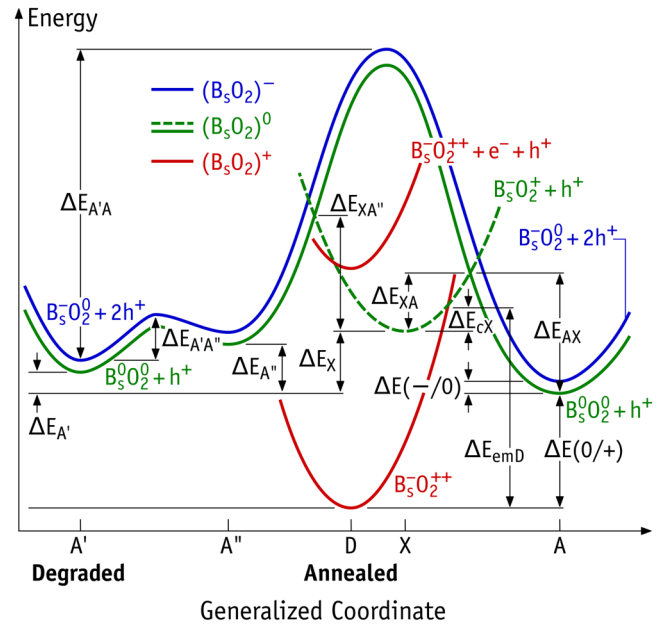
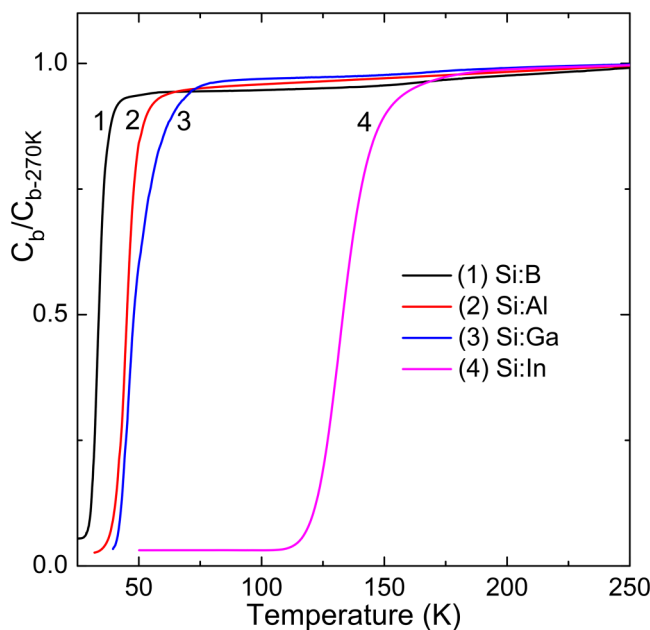


FIG. 5. Configuration coordinate diagram and atomic configurations of the  $B_sO_2$  defect in different charge states. Reproduced with permission from Vaqueiro-Contreras *et al.*, J. Appl. Phys. **125**, 185704 (2019). Copyright 2019 AIP Publishing LLC.

$C_b/C_{b-270\text{ K}}(T)$  dependencies for the samples intentionally doped with either B, Al, Ga, or In impurities ( $C_{b-270\text{ K}}$  is the bias capacitance of the diodes at 270 K). The sharp drops in the  $C_b/C_{b-270\text{ K}}$  values with decreasing temperature are related to the so-called “carrier freezing” effect, which depends on the activation energy of carrier emission from a shallow trap. The temperature ranges of “carrier freezing” differ in differently doped samples. It appears that there is no “carrier freezing” induced step in the  $C_b/C_{b-270\text{ K}}(T)$  dependencies in the temperature range below 40 K for the Al-, Ga-, and In-doped samples but the changes in the  $C_b/C_{b-270\text{ K}}$  values for the B-doped sample occur in this temperature range. The results presented in Fig. 6 indicate that there is no significant concentration of boron  $\{[B_s] \leq 0.02 N_d\}$  in the wafers doped with either Al, Ga, or In atoms, which have been studied.

*Ab initio* calculations reported in Ref. 7 showed that in In-doped Cz-Si samples the  $H_{390\text{ K}}$  trap is related to the  $In_sO_2$



**FIG. 6.** Capacitance of Schottky diodes at a bias voltage ( $U_b$ ) normalized to bias capacitance at 270 K as a function of temperature for the Cz-Si samples doped with different group-III impurities. The presented dependencies have been measured with the temperature rise rate ( $R_T$ ) of 3 K/min.

defect with slightly different configurations of the  $\text{In}_s$  and oxygen atoms in different charge states compared to those for the  $\text{B}_s\text{O}_2$  defect, the CCD and atomic configurations of which are shown in Fig. 5. The common feature of the  $\text{B}_s\text{O}_2$  and  $\text{In}_s\text{O}_2$  defects is that their electronic properties are associated mainly with the transformation of the oxygen dimer between the “square” and the staggered configurations upon capture or emission of electrons/holes.<sup>4,7</sup> It has been further concluded that the best description of the measured hole emission energy and  $(-/+)$  occupancy level is obtained for the  $\text{B}_s\text{O}_2$  and  $\text{In}_s\text{O}_2$  complexes without direct A–O bonds.<sup>4,7</sup> On the basis of the results obtained in the present study, it is reasonable to suggest that the  $\text{H}_{390\text{ K}}$  traps in the Al- and Ga-doped Cz-Si crystals are related to complexes of the oxygen dimer with Al and Ga substitutional atoms and the deep-donor–shallow-acceptor transformations of the  $\text{Al}_s\text{O}_2$  and  $\text{Ga}_s\text{O}_2$  complexes are related to the “square”–staggered transformations of  $\text{O}_2$  in the vicinity of  $\text{Al}_s$  and  $\text{Ga}_s$  atoms.

The formation mechanisms of the  $\text{B}_s\text{O}_2$  defect in Si crystals have been discussed by Voronkov and Falster.<sup>19</sup> It has been argued that the complex is formed by the interaction of mobile oxygen dimers with substitutional boron atoms in the temperature range from 550 to 450 °C upon cooling down the growing ingots or heat-treated wafers. The concentration of the  $\text{B}_s\text{O}_2$  complexes created depends on several parameters such as concentrations of the boron and oxygen atoms, binding energy of the complex, and cooling rate.<sup>19</sup> The binding energy of the  $\text{B}_s\text{O}_2$  defect in the negatively charged state relative to the separated  $\text{B}_s^-$  and  $\text{O}_2$  species has been

found to be 0.48 eV.<sup>4</sup> It appears, from the results reported here, that all the group-III substitutional atoms in silicon are traps for the mobile oxygen dimers and all the  $\text{A}_s\text{O}_2$  complexes (A is either B, Al, Ga, or In atom) are stable at temperatures below 500 °C. Furthermore, close concentrations of the  $\text{H}_{390\text{ K}}$  traps in the studied crystals with close values of  $[\text{O}_i]$  and concentrations of shallow acceptors of different types indicate that the binding energies of  $\text{O}_2$  and different group-III acceptors do not differ significantly.

It has been shown in Ref. 4 that upon prolonged injection of minority carriers (electrons) the  $\text{B}_s\text{O}_2$  defect transforms from the A configuration that is the most energetically favorable configuration for the Fermi level positions above  $E_v + 0.31$  eV to the metastable A' configuration (Fig. 5), which has enhanced recombination activity, and the  $\text{D} \Leftrightarrow \text{A} \Rightarrow \text{A}'$  transformations cause the degradation of minority carrier lifetime (BO-LID). The back  $\text{A}' \Rightarrow \text{A} \Rightarrow \text{D}$  transformations can be induced by heat treatment of the degraded samples in the dark at temperatures above 150 °C.<sup>4,6</sup> The detrimental effect of the BO-LID on the conversion efficiency of solar cells based on B-doped Cz-Si has resulted in the recent movement of Cz-Si-based photovoltaic industry to the replacement of Cz-Si:B wafers with Cz-Si:Ga ones.<sup>20,21</sup> It is known from the literature that LID does not occur in Ga-doped Cz-Si samples.<sup>20–23</sup> We have tried to understand what happens with the  $\text{H}_{390\text{ K}}$  trap in Ga-doped Cz-Si samples upon prolonged minority carrier injection. A Ga-doped Cz-Si sample from Ga-1 wafer has been subjected to light soaking for 60 h at 320 K with about 0.5 sun illumination intensity. The DLTS measurements on this sample after the light soaking have shown an insignificant change in the magnitude of the  $\text{H}_{390\text{ K}}$  trap compared to that for the untreated sample. Hence, the prolonged minority carrier injection treatments do not result in the transformation of the  $\text{Ga}_s\text{O}_2$  defect into a metastable configuration with the enhanced recombination activity as it happens for the  $\text{B}_s\text{O}_2$  defect.

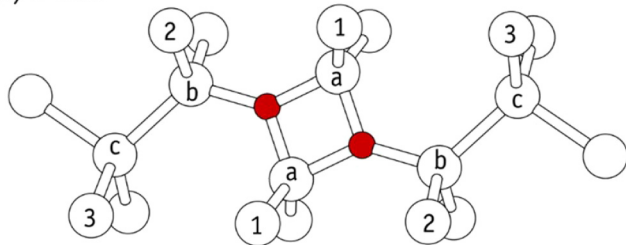
## IV. MODELING RESULTS

### A. A–O complexes

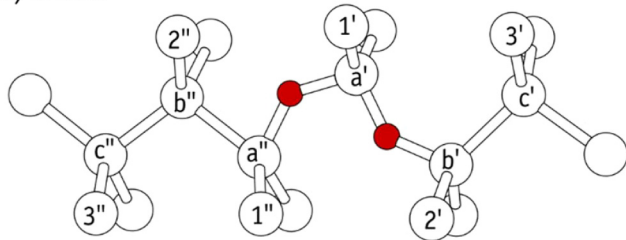
We start by analyzing the interaction between a single interstitial oxygen and the acceptors. Pairs of  $\text{O}_i$  and  $\text{A}_s^-$  ionized dopants were placed in 1000-Si atom supercells separated by several distances and the binding energy evaluated. Overall, the binding energies are very small, they are dominated by a minimization of strain fields around the impurities, and they can be attractive or repulsive depending on their relative alignment within the crystal. Among all, only  $\text{Al}_s\text{O}_i$  shows a positive (stabilizing) binding energy ( $E_b = 22$  meV) when a direct bond is formed between oxygen and the acceptor. This result contrasts with  $E_b = -70$  meV,  $-0.83$  eV, and  $-7.25$  eV, for analogous structures involving B, Ga, and In. Binding energies of  $\text{B}_s-\text{O}_i$ ,  $\text{Al}_s-\text{O}_i$ ,  $\text{Ga}_s-\text{O}_i$ , and  $\text{In}_s-\text{O}_i$  pairs separated by at least one Si–Si bond were in the range  $[+0.15; +0.27]$ ,  $[-0.02; +0.02]$ ,  $[+0.02; +0.07]$ , and  $[+0.07; +0.15]$  eV, respectively.

The smallest and largest acceptors, namely, B and In, produce the largest tensile and compressive strain fields, respectively. This explains how their interaction with  $\text{O}_i$  leads to the largest binding energies. Notably,  $\text{O}_i$  is compressive along the Si– $\text{O}_i$ –Si unit and tends to sit on Si–Si bonds aligned toward the tensile boron atom. Conversely, the Si– $\text{O}_i$ –Si unit is tensile along the directions

(a) D-form



(b) A-form



**FIG. 7.** Atomistic structures of  $A_5O_2$  complexes in silicon. Oxygen and silicon atoms are shown in red and white, respectively. Donor (D) and acceptor (A) forms are depicted in (a) and (b), respectively. Defect states are referred to as  $A_5O_2(X^q)$  or simply  $X^q$ , standing for the case where the p-type dopant replaces the Si atom with label  $X$  and the net charge of the defect is  $q$ .

perpendicular to its axis, and that elastic field can be compensated by a compressive In atom. Aluminum, and to some extent gallium, show a smaller size mismatch when replacing Si atoms, hence the weaker binding energies for complexes involving these species.

### B. A- $O_2$ complexes

As previously found for  $BO_2$  and  $InO_2$ , the energy balance regarding the formation of positively charged  $AlO_2$  and  $GaO_2$  complexes in p-type Si is particularly favorable. This is owed to both the formation of strong acceptor-oxygen bonds and to the Coulomb attraction between doubly positive  $O_2$  (squared form) and the ionized acceptor. Following Ref. 7, we use the notation of Fig. 7 to refer to a particular atomistic structure. The most stable  $(AO_2)^+$  defects are  $1^+$  for  $BO_2$  and  $a^+$  for  $\{Al, Ga, In\}O_2$ . Binding energies for reaction  $A_s^+ + O_2 + 2h^+ \rightarrow (AO_2)^+$  are 2.2, 1.4, and 1.5 eV for  $A = Al, Ga,$  and  $In$ , respectively, and the positive figures indicate that the processes are all exothermic. The  $a^+$  structures differ markedly from  $1^+$  of  $BO_2$ , where the O atoms do not connect directly to the acceptor, and the binding energy is 1.0 eV.

Another difference between  $BO_2$  and other  $AO_2$  complexes is found in the ground state structure of the neutral states. While  $(BO_2)^0$  adopts the  $1'^0$  state [A-form cf. Fig. 7(b)], other  $(AO_2)^0$  are most stable in the  $a^0$  state [D-form cf. Fig. 7(a)]. Hence, besides involving the formation of direct A-O bonds, neutral  $\{Al, Ga, In\}O_2$  complexes adopt a squared  $O_2$  structure. From the calculated ionization energies of 512-atom cells with defects, we found  $(0/+)$  transitions (with respect to the valence band top)

rather insensitive to the acceptor species involved in the complex. According to Eq. (1), we found  $E(0/+) - E_v$  in the range 1.04–1.09 eV for all four  $AO_2$  complexes with an acceptor atom in position  $a$ . Interestingly, this result was also found for  $(0/+)$  transitions for the configurations with more remote  $A_s$  and  $O_2$  units like those with the A atom in positions 2, 3, or  $c$  [see Fig. 7(a)]. For such structures,  $E(0/+) - E_v$  were found to be in the range 0.95–0.99 eV.

From the above, we are tempted to assign the conspicuous  $H_{390\text{ K}}$  hole traps observed by DLTS and reported in Table II to a hole emission process  $1^+ \rightarrow 1^0 + h^+$  involving  $BO_2$ , and  $a^+ \rightarrow a^0 + h^+$  involving  $\{Al, Ga, In\}O_2$  complexes. However, except for  $BO_2$ , that cannot be correct. For the case of  $BO_2$ , hole emission from  $1^+$  is followed by a transformation  $1^0 \rightarrow 1'^0$  (the neutral A-form is more stable than the D-form) and by a second hole emission  $1'^0 \rightarrow 1'^- + h^+$  (the  $1'$  state is a shallow acceptor). Our results indicate that the  $1'^- + 2h^+$  state is 0.48 eV above  $1^+$ , which according to Eq. (2) translates into a  $BO_2(-/+)$  level at  $E_v + 0.24$  eV. Hence, the  $1^+ \leftrightarrow 1'^- + 2h^+$  transition can be observed in a p-type diode because the  $(-/+)$  level is below midgap.

For  $AO_2$  complexes involving Al, Ga, and In, the negatively charged structures that can be readily converted from state  $a^+$ , namely,  $a'^-, a''-,$  and  $b'^-$  are relatively unstable. For instance, the energy of  $a'^- + 2h^+$  with respect to  $a^+$  is calculated as high as 2.1, 2.9, and 2.2 eV, respectively. Even considering the most stable negatively charged states, namely,  $\{a''-, 3'^-, 2''-\} + 2h^+$  for  $\{Al, Ga, In\}O_2$  complexes, respectively, they still are 2.0, 1.4, and 1.4 eV above their respective  $a^+$  ground state. These figures imply that the  $(-/+)$  level is well above the middle of the gap and that hole emission from  $a^+$  cannot be observed in a reverse biased p-type diode.

We have recently suggested that although the most stable  $InO_2$  complexes ( $a^+$  and  $2''-$ ) could not be held accountable for the junction capacitance observations in In-doped samples, a population of close In- $O_2$  pairs could explain the measured hole emission and the negative-U properties.<sup>7</sup> Formation of such pairs could take place during the cool down of the material (under intrinsic condition) or during thermal treatments, where the Fermi level is close to midgap and entropy could play an important role. Due to their structures and shallow levels, remote A- $O_2$  pairs could be stabilized by high configurational and electronic entropy. Another explanation for our observations would be the existence of a barrier for the formation of positively charged  $\{Al, Ga, In\}O_2$  complexes in the D-form. Such a barrier was indeed suggested to hinder the reaction of  $Ga_s^-$  and  $O_2$  defects in close proximity.<sup>24</sup> Our results extend this idea to the case of Al- and In-doped Si, and we also add that the final reaction step, which involves a jump of the staggered dimer for the formation of the ground state structure,  $O_2-Ga_s^- + 2h^+ \rightarrow (GaO_2)^+$ , is further obstructed due to the slow capture of two holes.

Analogously to the donor level, we found that separated  $\{Al, Ga, In\}-O_2$  pairs have  $E(-/+)$  levels that are quite insensitive to the chemical identity of the acceptor. For instance, transitions of all three complexes involving  $c^+ \leftrightarrow c'^- + 2h^+$  have  $E(-/+)$  transitions within  $E_v + 0.34 \pm 0.04$  eV. These are very close to the levels obtained from the capacitance measurements and reported above. The calculations are also not far from  $E(-/+)$  =  $E_v + 0.24$  eV obtained for  $BO_2$ . The difference between  $E(-/+)$  levels of  $\{Al, Ga, In\}-O_2$  and  $BO_2$  may reside on the rather peculiar  $1^+ \leftrightarrow 1'^- + 2h^+$  configurations of the boron related complex.



## V. CONCLUSIONS

By means of junction capacitance techniques, we have observed a family of defects with negative- $U$  properties in Czochralski-grown silicon wafers doped with different group-III elements. It is suggested that the defects are formed by the interaction of mobile oxygen dimers with substitutional shallow acceptor atoms, either B, Al, Ga, or In, upon cooling down the growing ingots. We argue that the common feature of all the  $A_sO_2$  defects is the reversible transformations of the oxygen dimer from its “square” configuration to the staggered configuration upon capture or emission of charge carriers, and these transformations are origin of the negative- $U$  properties. Concentration of the  $A_sO_2$  defects is found to be a few times of  $10^{13} \text{ cm}^{-3}$  in the as-grown Cz-Si crystals doped with different group-III elements. Further studies are necessary for elucidating the behavior of the  $Al_sO_2$ ,  $Ga_sO_2$ , and  $In_sO_2$  defects upon prolonged treatments with minority carrier injection, which are known to result in the transformation of the  $B_sO_2$  defect into a recombination active configuration that is responsible for the degradation of minority carrier lifetime and conversion efficiency of solar cells on Si:B + O materials.

From first-principles modeling of  $AO_i$  and  $AO_2$  complexes in Si (with  $A = \{B, Al, Ga, In\}$ ), we found that the interaction of dopants with neutral  $O_i$  and staggered- $O_2$  defects is dominated by strain cancellation. The binding energies are low ( $< 0.3 \text{ eV}$ ) and direct A– $O_i$  bonds are only expected for the case of  $A = Al$ .

Double positively charged squared  $O_2$  defects are markedly stabilized in the vicinity of ionized acceptors. The resulting  $(AO_2)^+$  complexes show calculated hole binding energies of about 1 eV, which depend very little on the chemical identity of A and its placement with respect to  $O_2$ . These results agree well with the experimental observations.

Important differences were found when comparing  $BO_2$  with the most stable  $\{Al, Ga, In\}$ - $O_2$  structures. While  $(BO_2)^+$  has a binding energy of about 1 eV (with respect to staggered- $O_2$ ,  $B^-$  and two free holes) and there is no direct connection between B and  $O_2$  units, other  $(AO_2)^+$  show binding energies as large as 1.4–2.2 eV with the acceptor making two bonds with oxygen. This feature leads to a  $(-/+)$  transition level in the upper half of the gap for  $\{Al, Ga, In\}$ - $O_2$  complexes [in opposition to  $BO_2$ , which has a  $(-/+)$  transition calculated at  $E_v + 0.24 \text{ eV}$ ]. On the other hand,  $AO_2$  structures that avoid the formation direct A–O bonds show  $E(-/+)$  levels close to the experimentally determined negative- $U$  level at about  $E_v + 0.3 \text{ eV}$ , suggesting that the complexes detected by junction spectroscopy measurements are related to the A– $O_2$  pairs with remote  $A_s$  and  $O_2$  units.

## ACKNOWLEDGMENTS

We would like to thank EPSRC (UK) for funding this work via Grant No. EP/TO25131/1. J.A.T. de Guzman would like to thank the Government of the Philippines through the Department of Science and Technology (DOST) for her PhD funding. J.C. acknowledges the support of the i3N projects, Ref. Nos. UIDB/50025/2020 and UIDP/50025/2020, financed by the Fundação para a Ciência e a Tecnologia in Portugal.

## AUTHOR DECLARATIONS

### Conflict of Interest

The authors do not have any potential conflict of interest to disclose.

### DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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