

Kinetics of the electronically stimulated formation of a boron-oxygen complex in crystalline silicon

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We present experimental data relating to the slow stage of the illumination-induced or electron-injection-induced generation, in crystalline p -type silicon, of the carrier-recombination center believed to be the defect complex $(B_sO_{2i})^+$ formed by diffusion of oxygen interstitial dimers O_{2i}^{++} to substitutional boron atoms B_s^- and, taking account of those data, we consider a detailed theoretical model for the kinetics of the diffusion reaction. The model proposes that the generation rate of the $(B_sO_{2i})^+$ defects is controlled by the capture of a majority-carrier hole by the dimer following the capture of a minority-carrier electron and by the Coulomb attraction of the O_{2i}^{++} to the B_s^- atom, and leads to predictions for the defect generation rate that are in excellent quantitative agreement with experiment.

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I. INTRODUCTION

Investigations of the properties of p - n^+ solar cells fabricated from standard Czochralski-grown single-crystal silicon that contains oxygen and has boron as the p -type dopant have shown¹⁻⁴ that the illumination itself causes a decrease (of about 10% relative) in the energy conversion efficiency of such solar cells. That reduction in the efficiency is detrimental to the economic use of Si(B,O) solar cells, and understanding of the atomic processes occurring during the efficiency loss is required to assist in the development of improved photovoltaic systems. Of importance toward that understanding is that forward-bias-induced electron injection into the p -type region of the cell produces quantitatively the same reduction in conversion efficiency.^{3,4} The efficiency degradation is found²⁻⁴ to occur in two distinct stages, which (for typical conditions) can be described as a fast process of thermal-activation energy 0.23 eV, reaching completion on a time scale of tens of seconds, followed by an independent slow process of thermal-activation energy 0.47 eV, lasting several hours. The degradation is attributed, in each stage, to the formation of a specific defect complex that acts as a recombination center for electrons and holes. The experimental data have indicated also that in each of the two degradation stages, the final concentration of the particular recombination center created is closely proportional to the boron-doping concentration in the silicon and to the square of the oxygen concentration.

Despite those similarities of the fast and slow stages, the experimental data indicate that the fast and slowly formed recombination centers are created independently of each other and that the fast formed center is not a precursor of the slowly formed center. The mechanism for the production of the fast formed center has been proposed³ to be a two-step process in which the illumination- or forward-bias-induced minority-carrier electrons cause the rise of the quasi-Fermi level above the electronic energy level of a preexisting defect and that is followed by a thermally activated process that

leads to the creation of the recombination center that is responsible for the initial, fast degradation of the silicon solar cell. It has been further proposed¹⁻⁶ that the slow stage of the solar-cell degradation is due to the formation of the defect complex $(B_sO_{2i})^+$ by diffusion of oxygen interstitial dimers O_{2i}^{++} to the immobile substitutional dopant boron ions B_s^- , and^{5,6} that that diffusion takes place as a result of a Bourgoin-type migration process involving alternating changes in the structure of the O_{2i}^{++} dimers as they successively capture minority-carrier electrons and majority-carrier holes.

In this paper, we present a detailed theoretical model, for the reaction kinetics of the slow stage of formation of the defect $(B_sO_{2i})^+$, that is based on the previously proposed Bourgoin-type migration process, and show that the predictions given by the model for the defect-formation process are in excellent quantitative agreement with experimental data.

II. EXPERIMENTAL METHODS

The lattice defects that cause reduction in p - n^+ solar-cell efficiency do so by decreasing the lifetime τ of the minority-carrier electrons in the p -silicon active layer of the solar cell, and that change in the magnitude of τ depends on the concentration of the defects. As one method to investigate the kinetics of the formation process of the defects, related to boron and oxygen in silicon, that cause an efficiency loss, we have therefore made direct time-dependent minority-carrier lifetime (τ - t) measurements on appropriate Si(B,O) samples. As a second method to study that defect-formation process, we have measured the time-dependent open-circuit voltage (V_{OC} - t) of p - n^+ solar-cell diodes, the p -silicon in the cells again being boron doped and oxygen containing. As explained below, V_{OC} is a function of the minority-carrier lifetime in the p -type layer of the solar cell, and so is also dependent on the lattice defect concentration in that layer.

The materials under investigation in the τ - t measurements were boron-doped Czochralski (Cz) crystalline silicon wafers

with a wide variety of boron and oxygen concentrations from different suppliers and had been heat treated at 650–700 °C to remove thermal donors associated with the presence of oxygen. The boron-doping concentration N_{dop} was evaluated from four-point-probe resistivity measurements. The magnitude of N_{dop} thus found equals the acceptor concentration N_{acc} when no thermal donors are present in the material. Interstitial oxygen concentrations $[O_i]$ were determined from infrared absorption measurements, in accordance with the German Fourier transform infrared standard DIN-50438-1, using a Bruker Equinox 55 spectrometer. Since bulk recombination centers rather than surface effects were to be studied, it was necessary to ensure that the recombination activity at the silicon wafer surfaces was minimal. In order to keep the surface-recombination velocity below 10 cm s⁻¹, both surfaces of the samples were chemically cleaned in accordance with the USA-RCA recommended procedure, and then were passivated using silicon nitride films produced by plasma-enhanced chemical-vapor deposition.⁷ The passivation quality of these films neither degrades during light exposure nor during temperature treatments below 250 °C.

All τ - t data were obtained, on samples held at or above room temperature, by means of a commercial system (Semilab, WT-2000) for measurements by the contactless microwave-photoconductance-decay (MW-PCD) technique.^{4,8} In this technique, the change in the photoconductance of a semiconductor sample is detected using microwaves reflected by the free carriers in the sample. The minority-carrier lifetime τ is then the measured time constant of the decay of the photoconductance following a laser pulse. The Semilab MW-PCD system is equipped with a temperature-controlled sample stage allowing τ - t measurements in the temperature range of 25–250 °C. Prior to each τ - t measurement, the samples were annealed for at least 10 min at 200 °C on an external hot plate; that procedure required initial exposure to room light conditions but that exposure lasted no more than 3–5 s.

The solar cells under investigation in the $V_{\text{OC}}-t$ measurements were 300- μm -thick metal-insulator-semiconductor-contacted p - n^+ structures and also passivated emitter rear locally diffused p - n^+ solar cells.^{9,10} The silicon from which the solar cells were fabricated had been heat treated to remove thermal donors. During each $V_{\text{OC}}-t$ measurement, the solar cell was held at constant temperature and, in order to access the very initial time range instantaneously after annealing, a voltage data-acquisition unit (Agilent 34970A) was used. During the measurements, the solar cell was illuminated with a halogen lamp at an intensity of 10 mW/cm². Before each such measurement, the solar cell was annealed within the cryostat in the dark for 10 min at 200 °C.

From our experimental data obtained by the photoconductance-decay method applied to the p -type silicon samples, we determine an effective minority-carrier lifetime τ_{eff} defined by the expression^{8,11}

$$\frac{1}{\tau_{\text{eff}}} = \frac{1}{\tau_b} + \frac{2S_{\text{eff}}}{d}, \quad (1)$$

where τ_b is the bulk lifetime of the p -type material, S_{eff} is the effective surface-recombination velocity of the sample, and d

is the sample thickness. Thence, we define a time-dependent normalized defect concentration $N_{\tau}^*(t)$ as

$$N_{\tau}^*(t) = \frac{1}{\tau_{\text{eff}}(t)} - \frac{1}{\tau_{\text{eff}}(t=0)}, \quad (2)$$

where the time t is measured from the start of the illumination that causes the reduction in the carrier lifetime. The form of expression (2) ensures that $N_{\tau}^*(t)$ includes only the defects whose production is caused by the illumination.

The open-circuit voltage V_{OC} of the p - n junction solar cell depends¹² on the photocurrent density J_L and the saturation current density J_0 via the following expression:

$$V_{\text{OC}} \cong \frac{nk_B T}{q} \ln\left(\frac{J_L}{J_0}\right), \quad (3)$$

when the ideality factor n of the p - n junction is included if not equal to unity, and where q is the elementary electronic charge. Rearrangement of Eq. (3) gives

$$\exp(qV_{\text{OC}}/nk_B T) \cong J_L/J_0. \quad (4)$$

For the present high efficiency p - n^+ solar cells which have effective rear-surface passivation and in which the p -region minority-carrier diffusion length L_n , equal to $(D_n \tau_n)^{0.5}$, in the p region is large compared to that region's thickness W_p , the saturation current density J_0 in Eq. (4) can be expressed¹³ as

$$J_0 \cong \frac{qD_n n_i^2}{L_n N_{\text{acc}}} \tanh(W_p/L_n), \quad (5)$$

where D_n is the minority-carrier diffusivity in the p region, n_i is the temperature-dependent intrinsic carrier concentration of the semiconductor, and N_{acc} is the acceptor doping concentration in the p region. However, $\tanh(W_p/L_n)$ becomes equal to (W_p/L_n) for the condition of large L_n in our solar cells, and therefore J_0 can be written as

$$J_0 \cong C_1/\tau_n, \quad (6)$$

where C_1 , equal to $(qn_i^2 W_p/N_{\text{acc}})$, is a constant. Since, in our experiments, L_n is always much larger than the base thickness of the solar cells W_p , the photocurrent density J_L in Eq. (4) can be considered as constant during our measurement of the light-induced degradation curves.

Therefore, from Eqs. (4) and (6),

$$\frac{1}{\exp(qV_{\text{OC}}/nk_B T)} \cong \frac{C_2}{\tau_n}, \quad (7)$$

where C_2 is a constant equal to C_1/J_L .

However, the right-hand side of Eq. (7) is proportional to the concentration of all lattice defects that reduce the lifetime τ_n by their trapping of minority carriers. Therefore, if we again specify t as the time elapsed since the start of illumination, we can define a normalized concentration $N_{V_{\text{OC}}}^*(t)$ of the illumination-induced defects by the expression

$$N_{V_{OC}}^*(t) = \frac{1}{\exp[qV_{OC}(t)/nk_B T]} - \frac{1}{\exp[qV_{OC}(t=0)/nk_B T]} \quad (8)$$

In using Eq. (8), we need to consider that the ideality factor n of the solar-cell diode may change during the defect-formation process. However, the change of n between the initial and the fully degraded state depends on the base-doping concentration N_{acc} of the solar cell. For solar cells having N_{acc} of the order of 10^{16} cm^{-3} , as investigated in this work, n is very close to unity and has been found¹⁴ not to change significantly during the formation of the boron-oxygen-related recombination centers. Therefore, we have set n as constant equal to unity in our use of expression (8) to determine $N_{V_{OC}}^*(t)$ from our measurements of $V_{OC}(t)$.

In order to investigate the thermal-activation properties and kinetics of the defect-formation process, the τ - t measurements on silicon wafers and the V_{OC} - t measurements on the silicon solar cells were performed at various sample temperatures T .

As in previous works¹⁻⁴ on this topic, we define a generation rate $R_{gen}(T)$ of the boron-oxygen recombination center being investigated as

$$R_{gen}(T) = [dN^*(t)/dt(T, t=0)]/N^*(t \rightarrow \infty), \quad (9)$$

where $N^*(t)$ is equal to $N_{\tau}^*(t)$ of expression (2) for the τ - t measurements and to $N_{V_{OC}}^*(t)$ of expression (8) for the V_{OC} - t measurements. The form of expression (9) for $R_{gen}(T)$ ensures that it is independent of the proportionality constants that relate $N_{\tau}^*(t)$ and $N_{V_{OC}}^*(t)$, respectively, to the absolute concentration of the boron-oxygen lattice defect and, in agreement with that, we have found no difference between $R_{gen}(T)$ values determined from τ - t measurements and V_{OC} - t measurements.

Previous studies¹ of the illumination-induced solar-cell degradation have shown that, in each of the fast and slow stages, $N^*(T, t)$ can be well represented by the expression

$$N^*(T, t) = N^*(t \rightarrow \infty) \{1 - \exp[-R_{gen}(T)t]\}. \quad (10)$$

The present paper includes further experimental data for the slow stage, and we find that they also conform to expression (10).

III. EXPERIMENTAL DATA

Figures 1 and 2 present experimental data that show the respective dependences of the defect generation rate R_{gen} on the boron-doping concentration and on the oxygen concentration. It is seen that R_{gen} is very closely proportional to square of the boron concentration and is independent of the oxygen concentration.

Figure 3 shows, as an Arrhenius plot, the temperature dependence of the experimental parameter R_{gen} for the slow stage of the solar-cell degradation for two concentrations, 1.25×10^{16} and $3.85 \times 10^{16} \text{ cm}^{-3}$, of the boron-doping concentration $[B_s]$ in Czochralski-grown silicon. The figure indicates that R_{gen} can be represented by the expression

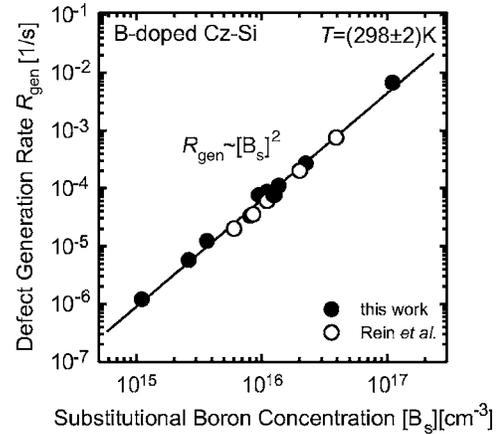


FIG. 1. Measured rate R_{gen} of the slow defect-formation process at 298 K as a function of the boron-doping concentration $[B_s]$. It is seen that the defect-generation rate is proportional to the square of the boron concentration over more than two orders of magnitude of $[B_s]$. The data of Rein *et al.* are from Ref. 15.

$$R_{gen} = \kappa_0 \exp(-E_{gen}/k_B T), \quad (11)$$

where the thermal-activation energy E_{gen} is equal to 0.47 eV, independent of the $[B_s]$ value. Also, as stated in Fig. 3, the analysis of the data indicates values of the preexponential factor κ_0 of 7.8×10^3 and $8.1 \times 10^4 \text{ s}^{-1}$ for the two boron concentrations.

We now present a theoretical model, for the defect-formation rate R_{gen} , whose predictions agree very well with those experimental observations in terms of the dependences of R_{gen} on the boron and oxygen concentrations and also with the values of the preexponential factor κ_0 .

IV. THEORETICAL MODEL

As previously,¹⁻⁶ it is envisaged, on the basis of experimental and theoretical data, that the slowly forming recom-

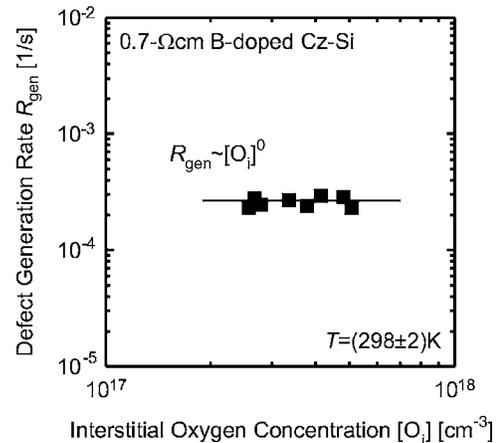


FIG. 2. Measured rate R_{gen} of the slow defect-formation process at 298 K as a function of the interstitial oxygen concentration $[O_i]$ in silicon having a boron-doping concentration of $2.2 \times 10^{16} \text{ cm}^{-3}$. The data show that the defect-generation rate is independent of the oxygen concentration.

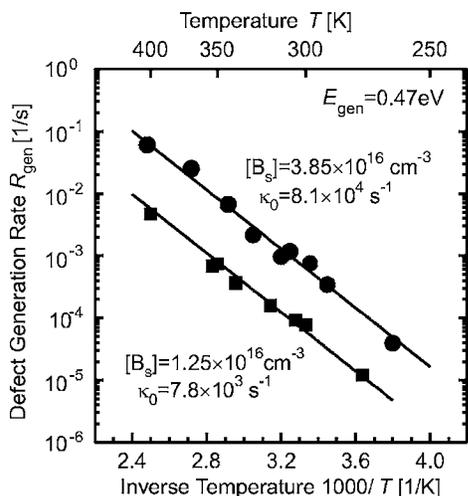


FIG. 3. The measured temperature dependence of the defect generation parameter R_{gen} of the slowly forming degradation defect for two silicon samples having boron-doping concentrations $[B_s]$ of 1.25×10^{16} and $3.85 \times 10^{16} \text{ cm}^{-3}$, respectively. The symbol κ_0 indicates the values of the preexponential factors of the Arrhenius plots as deduced from the experimental data shown.

bination center is a defect complex $(B_s O_{2i})^+$ of a substitutional boron atom B_s and a dimer O_{2i} consisting of two oxygen atoms in interstitial sites, in which the boron is either bound directly to the two oxygen atoms^{5,6} or is bound to a silicon atom itself bound to the oxygen atoms.^{16,17} The formation of the defect complex is considered¹⁻⁶ to occur by the capture of a mobile dimer O_{2i}^{++} by an immobile B_s^- , in which the thermally activated diffusion of the dimer through the p -type silicon lattice is enhanced by recombination of minority-carrier electrons with majority-carrier holes. The model proposed by Adey *et al.*^{5,6} for that recombination-enhanced diffusion is based on calculations using the local electron-density functional theory computer program AIM-PRO. It assumes, in accordance with other work,¹⁸ that some of the oxygen in the Cz-Si is in the form of doubly positive oxygen dimers O_{2i}^{++} , and that those oxygen dimers can undergo thermally activated diffusion by a process in which they move from their stable site in the silicon lattice to an adjacent equivalent lattice site by successive atomic rearrangements and charge-state changes that include thermal energy activation, capture of a minority-carrier electron by O_{2i}^{++sq} that has a structure described as “square,” and the subsequent capture of a majority-carrier hole by O_{2i}^{+st} having a “staggered” structure. The overall process allows the oxygen dimer O_{2i}^{++} to diffuse randomly through the silicon lattice until captured by a substitutional boron atom B_s^- , so forming the $(B_s O_{2i})^+$ defect complex that is the proposed electron-hole recombination center responsible for the observed efficiency degradation of the solar cell.

We proceed by considering a general atomic reaction of the form $A+B \rightarrow C$ in a crystalline solid, in which a defect A , here representing the oxygen dimer O_{2i}^{++sq} , diffuses randomly until it is trapped by an immobile atom B , representing the substitutional boron atom B_s^- , and so forms the complex C that represents the $(B_s O_{2i})^+$ defect.

The experimental data indicate that the efficiency of the Cz-Si (B) solar cell is only partially reduced by the illumi-

nation and that the active part of the cell remains p type. Since the $(0/+)$ level of the $(B_s O_{2i})$ complex has been measured¹⁹ to be at $(E_C - 0.41 \text{ eV})$, i.e., in the upper half of the silicon band gap, it cannot be that the $(B_s O_{2i})$ is an active acceptor, and so we deduce that it is because of electrically active boron atoms that the silicon remains p type and therefore that most of the boron dopant atoms do not capture oxygen dimers. In accordance with that, we assume that the concentration N_A (per unit volume) of oxygen dimers is small compared to that of the boron atoms, i.e., that $N_A \ll N_B$ in our notation. We assume, furthermore, that the concentration N_A of the oxygen dimers and the concentration N_B of the isolated boron atoms B decrease only because of the reaction $A+B \rightarrow C$, that therefore N_B can be considered as essentially constant during the degradation process, and that the efficiency degradation ceases when all the oxygen dimers A in the p -type silicon have been captured by the boron atoms B .

The rate of change of the concentration of the oxygen dimers A can then be written as

$$dN_A/dt = -N_A \nu_A \exp(-E_{mA}/k_B T) n_j, \quad (12)$$

where ν_A is the jump-attempt frequency of the defect A (i.e., the oxygen dimer), E_{mA} is the thermal activation energy for the migration (lattice jumping) of A , k_B is Boltzmann’s constant, and n_j is the mean number of random jumps that A needs to make to cause formation of the complex C .

We now define γ as the number of sites around a boron atom B that, when reached by A , constitute automatic formation of the complex C . Then, n_j is given by

$$n_j = N_{Si}/(\gamma N_B), \quad (13)$$

where N_{Si} is the silicon atomic density. Because of the assumption of the constancy of N_B , n_j stays constant during the degradation process.

Therefore, from Eq. (12),

$$dN_A/dt = -\nu_A (\gamma N_B / N_{Si}) \exp(-E_{mA}/k_B T) N_A. \quad (14)$$

Integration of that expression from $[t=0, N_A(t=0)]$ to $[t, N_A]$ gives

$$N_A(t) = N_A(t=0) \exp[-\nu_A (\gamma N_B / N_{Si}) \exp(-E_{mA}/k_B T) t]. \quad (15)$$

However, because $N_C(t)$ is equal to $[N_A(t=0) - N_A(t)]$ and $N_A(t=0)$ equals $N_C(t \rightarrow \infty)$, the result is, from Eq. (15), that $N_C(t)$ is given by the expression

$$N_C(t) = N_C(t \rightarrow \infty) \{1 - \exp[-\nu_A (\gamma N_B / N_{Si}) \exp(-E_{mA}/k_B T) t]\}. \quad (16)$$

We note that expression (16) for $N_C(t)$ has the same form as Eq. (10), above, shown by the experimental solar-cell data. Since the value of $N_C(t \rightarrow \infty)$ equal to $N_A(t=0)$, is the initial concentration of oxygen dimers in the silicon, and since it is known¹⁸ that that is proportional to the square of the total oxygen concentration in device-quality silicon, theoretical expression (16) is in agreement with the oxygen concentra-

tion dependence of $N_C(t)$ demonstrated by the experimental data for the solar-cell degradation.

Further, from Eqs. (10) and (16), the value of R_{gen} is given by

$$R_{\text{gen}}(T) = \nu_A(\gamma N_B/N_{\text{Si}})\exp(-E_{mA}/k_B T), \quad (17)$$

which, also in agreement with the experimental data, is independent of the oxygen concentration.

We now consider the lattice-jump-attempt frequency ν_A of the oxygen dimers A . In a usual situation, the jump rate of a defect A can be expressed as $\nu_0 \exp(-E_{mA}/k_B T)$, where ν_0 represents an effective atomic vibration frequency of the order of 10^{12} s^{-1} associated with the defect, and E_{mA} is the lattice-jump enthalpy. However, in the present case we are considering^{5,6} that the long-range diffusional motion of the oxygen dimer cannot occur unless the oxygen dimer in the form O_{2i}^{+st} changes to O_{2i}^{++st} by capture of a positive hole. Because ν_0 is much larger than the hole-capture rate, the situation is that, as soon as an O_{2i}^{+st} dimer captures a hole, the resultant O_{2i}^{++st} immediately changes its structure to O_{2i}^{++sq} , and so it is the rate of hole capture by O_{2i}^{+st} , instead of ν_0 , that is the preexponential frequency in the diffusion of the oxygen dimer. Therefore, ν_A in Eq. (17) is set equal to the rate of hole capture by O_{2i}^{+st} , and that capture rate is $v_h \sigma_h p$, where v_h is the mean thermal velocity of the holes, σ_h is the hole-capture cross section of the O_{2i}^{+st} , and p is the hole concentration. In consequence, expression (17) becomes

$$R_{\text{gen}}(T) = v_h \sigma_h p [\gamma N_B/N_{\text{Si}}] \exp(-E_{mA}/k_B T). \quad (18)$$

However, the hole concentration p is essentially equal to the boron concentration N_B , and therefore

$$R_{\text{gen}}(T) = [v_h \sigma_h (\gamma N_B^2/N_{\text{Si}})] \exp(-E_{mA}/k_B T). \quad (19)$$

Thus, in agreement with the experimental data, R_{gen} is proportional to the square of the boron concentration and independent of the oxygen concentration.

We note that E_{gen} in expression (11) corresponds to E_{mA} in Eq. (18) and that, similarly,

$$\kappa_0 = [v_h \sigma_h (\gamma N_B^2/N_{\text{Si}})], \quad (20)$$

which we need to evaluate for comparison with the experimental data.

We now therefore consider the value of γ , which, here, is the number of sites around a substitutional boron atom B_s^- , which, when reached by an oxygen dimer O_{2i}^{++} , causes the automatic formation of the $(\text{B}_s \text{O}_{2i})^+$ complex. It is clear that the rate of formation of the $(\text{B}_s \text{O}_{2i})^+$ is enhanced by the Coulomb attraction between the mobile positively charged dimer O_{2i}^{++} and the negatively charged boron atom B_s^- . We consider that enhancement, in the standard way, in terms of a capture radius r_c , such that there is automatic formation of the $(\text{B}_s \text{O}_{2i})^+$ complex (by inevitable correlated jumping of the O_{2i}^{++} towards the B_s^-) when the randomly jumping oxygen dimer reaches any point that is a radial distance r_c from the boron atom. It is usual²⁰ to estimate r_c by setting the Coulomb attraction energy between the two species at that radial distance (taking account of the dielectric constant of the semiconductor) to be equal to the Boltzmann thermal

energy $k_B T$. Use of that procedure in the present case for T equal to 298 K (the dielectric constant of silicon being 11.9) produces a value of r_c of 9.424 nm.

The number of lattice sites per B_s atom for which the $(\text{B}_s \text{O}_{2i})^+$ is inevitably formed, which is the value of γ in expression (19) above for R_{gen} , is then $4\pi r_c^2 [N_{\text{O}_{2i}}]^{2/3}$, where $N_{\text{O}_{2i}}$ is the volume concentration of oxygen dimer sites in the silicon. In order to calculate an approximate value for γ , we assume that the concentration of possible sites for the oxygen dimers is about the same as the concentration of silicon substitutional sites. Then, setting r_c as 9.424 nm gives a value of γ of approximately 1.5×10^4 .

In the present model for the slow stage of the solar-cell degradation, the preexponential factor κ_0 given by expression (20) above includes the hole thermal velocity v_h and the hole-capture cross section σ_h of the staggered form O_{2i}^{+st} of the oxygen dimer. Using the thermal velocity effective mass m_h^* of holes in silicon at 298 K as $0.41 m_0$,²¹ then v_h , equal to $(8k_B T / \pi m_h^*)^{0.5}$, is $1.675 \times 10^7 \text{ cm s}^{-1}$. No experimental value is available for the value of the cross section σ_h , but the cross section of a positive defect species, in this case O_{2i}^{+st} , for the capture of a positive hole is likely to be significantly smaller than the corresponding value of the order of 10^{-16} cm^2 for a neutral defect. In order to proceed, we assume a range of values for σ_h , in particular, of 5.0×10^{-18} , 1.0×10^{-17} , and $5.0 \times 10^{-17} \text{ cm}^2$ and calculate theoretical values of κ_0 for those cross-section values.

Then, the values of the preexponential factor κ_0 equal to $[v_h \sigma_h \gamma (N_B)^2 / N_{\text{Si}}]$ in this model for the boron concentrations N_B of 1.25×10^{16} and $3.85 \times 10^{16} \text{ cm}^{-3}$, are as shown in Table I, in comparison with the corresponding experimental values stated in Fig. 3. It is seen that, for the assumed range of values of σ_h , the theoretical value of the preexponential factor κ_0 is of the same order of magnitude as the respective experimental value for each of the two boron-doping concentrations. Furthermore, very good agreement between the theoretical and experimental data is obtained if σ_h is assumed to be $1.0 \times 10^{-17} \text{ cm}^2$.

We need, however, to consider also the rate at which an oxygen dimer O_{2i}^{++sq} captures a minority-carrier electron created by the illumination or forward biasing of the solar cell. Because that is a capture of a negative electron by a doubly positive defect, the cross section σ_e for that capture is likely to be large, and we assume a value of $1 \times 10^{-14} \text{ cm}^2$ for it. Noting that the induced concentration n of minority-carrier electrons is typically about $0.1 N_B$ in the experiments and that the mean thermal velocity of electrons is $1.3 \times 10^7 \text{ cm s}^{-1}$ [the thermal velocity effective mass of electrons in silicon at 298 K being $0.28 m_0$ (Ref. 21)], we estimate the capture rate $v_e \sigma_e n$ of the electrons by O_{2i}^{++sq} dimers as about $3 \times 10^8 \text{ s}^{-1}$ when N_B is $1.25 \times 10^{16} \text{ cm}^{-3}$. Since that rate of electron capture by the O_{2i}^{++sq} dimers is much larger than the hole-capture rate $v_h \sigma_h p$ of the order of $2 \times 10^6 \text{ s}^{-1}$, by the O_{2i}^{+st} dimers, it is clear, as was assumed above in the derivation of expression (19) for R_{gen} , that hole capture by the oxygen dimers controls the lattice-jump rate of the dimers.

The theoretical model presented above that leads to the calculated prefactor κ_0 values shown in Table I is therefore

TABLE I. The values of the preexponential factor κ_0 calculated from expression (20) for assumed hole-capture cross sections of 5.0×10^{-18} , 1.0×10^{-17} , and 5.0×10^{-17} cm², in comparison with the experimental values.

N_B (cm ⁻³)	κ_0 (s ⁻¹) Experimental value from Fig. 3	κ_0 (s ⁻¹) Theoretical value from expression (20)		
		σ_h (5.0×10^{-18} cm ²)	σ_h (1.0×10^{-17} cm ²)	σ_h (5.0×10^{-17} cm ²)
1.25×10^{16}	7.8×10^3	4.1×10^3	8.2×10^3	4.1×10^4
3.85×10^{16}	8.1×10^4	3.9×10^4	7.8×10^4	3.9×10^5

seen to provide a valid description of the solar-cell slow degradation process as the trapping of diffusing oxygen dimers by immobile substitutional boron-doping atoms, in which the overall rate of that process in terms of the defect generation rate R_{gen} is, in agreement with the experimental data, proportional to the square of the boron-doping concentration and independent of the oxygen concentration. In this model, that dependence of the rate upon the square of the boron concentration arises because that rate is proportional to the product of two terms, (a) the lattice-jump rate of the dimers controlled by hole capture and (b) the probability per second that a diffusing dimer becomes trapped by a boron atom, in which each of those terms is proportional to the boron concentration. Furthermore, the assumption that the hole-capture cross section of O_{2i}^+ has the very plausible value of 1.0×10^{-17} cm² and the inclusion of the Coulomb attraction between the O_{2i}^{++} dimers and the B_s^- leads to theoretical values of the preexponential factor in R_{gen} that agree very well with the measured data.

V. CONCLUSIONS

We have presented a theoretical model for the slow stage of the illumination-induced or electron-injection-induced for-

mation, in boron-doped p -type crystalline silicon, of a boron-oxygen complex defect $(\text{B}_s\text{O}_{2i})^+$ that acts as an efficient electron-hole recombination center. The model envisages that the defect is formed by diffusion of interstitial oxygen dimers O_{2i}^{++} to immobile substitutional boron atoms B_s^- , that that diffusion is enhanced by the dimer's successive capturing of minority-carrier electrons and majority-carrier holes, and that the formation of the complex is strongly assisted by the Coulomb attraction between the O_{2i}^{++} and the B_s^- . It is shown that the model provides a complete quantitative understanding of the experimental data on the oxygen-concentration dependence, the boron-concentration dependence and the reaction kinetics in the formation of the $(\text{B}_s\text{O}_{2i})^+$ defect, and of the illumination-induced reduction in the photovoltaic efficiencies of p - n^+ solar cells fabricated from oxygen-containing crystalline silicon in which the p -type dopant is boron.

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¹J. Schmidt and K. Bothe, Phys. Rev. B **69**, 024107 (2004).

²K. Bothe and J. Schmidt, Appl. Phys. Lett. **87**, 262108 (2005).

³K. Bothe and J. Schmidt, J. Appl. Phys. **99**, 013701 (2006).

⁴K. Bothe, Dipl. Phys. thesis, University of Hanover, 2006.

⁵J. Adey, R. Jones, D. W. Palmer, P. R. Briddon, and S. Öberg, Phys. Rev. Lett. **93**, 055504 (2004); **93**, 169904(E) (2004).

⁶J. Adey, Ph.D. thesis, University of Exeter, 2005.

⁷T. Lauinger, J. Schmidt, A. G. Aberle, and R. Hezel, Appl. Phys. Lett. **68**, 1232 (1996).

⁸J. Schmidt and A. G. Aberle, J. Appl. Phys. **81**, 6186 (1997).

⁹J. Knobloch, A. Noel, E. Schäffer, U. Schubert, F. J. Kamerewerd, S. Klüßmann, and W. Wettling, Proceedings of the 23rd IEEE Photovoltaic Specialists Conference (IEEE, New York, 1993), pp. 271–276.

¹⁰A. Metz and R. Hezel, Proceedings of the 26th IEEE Photovoltaic Specialists Conference, Anaheim, CA (IEEE, New York, 1997), pp. 283–286.

¹¹A. Cuevas and D. Macdonald, Sol. Energy **76**, 255 (2004).

¹²S. M. Sze, *Semiconductor Devices: Physics and Technology* (Wiley, New York, 1985).

¹³M. A. Green, *Solar Cells* (University of New South Wales, Sydney, 1992).

¹⁴J. Schmidt, A. Cuevas, S. Rein, and S. W. Glunz, Prog. Photovoltaics **9**, 249 (2001).

¹⁵S. Rein, T. Rehri, W. Warta, S. W. Glunz, and G. Willeke, Proceedings of the 17th European Photovoltaic Solar-Energy Conference, Munich, Germany (WIP, Munich, 2001), p. 1555.

¹⁶M. Sanati and S. K. Estreicher, Phys. Rev. B **72**, 165206 (2005).

¹⁷M. Sanati and S. K. Estreicher, Physica B **376-377**, 133 (2006).

¹⁸L. I. Murin, T. Hallberg, V. P. Markevich, and J. L. Lindström, Phys. Rev. Lett. **80**, 93 (1998).

¹⁹S. Rein and S. W. Glunz, Appl. Phys. Lett. **82**, 1054 (2003).

²⁰M. Lannoo and J. Bourgoin, *Point Defects in Semiconductors I* (Springer-Verlag, Berlin, 1981), pp. 203–204.

²¹M. A. Green, J. Appl. Phys. **67**, 2944 (1990).