

MECHANISMS OF LIGHT-INDUCED DEGRADATION IN MONO- AND MULTICRYSTALLINE SILICON SOLAR CELLS

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ABSTRACT: Light-induced degradation of crystalline silicon solar cells is a frequently observed phenomenon. Two main causes of such degradation effects have been identified in the past, both of them being electronically driven and both related to the most common acceptor element, boron, in silicon: (i) the dissociation of iron-boron pairs and (ii) the formation of recombination-active boron-oxygen complexes. While the first mechanism is particularly relevant in metal-contaminated solar-grade multicrystalline silicon materials, the latter process is important in monocrystalline Czochralski-grown silicon, rich in oxygen. This paper starts with a short review of the characteristic features of the two processes. We then briefly address the effect of iron-boron dissociation on solar cell parameters. Regarding the boron-oxygen-related degradation, the current status of the physical understanding of the defect formation process and the defect structure are presented. Finally, we discuss different strategies for effectively avoiding the degradation.

Keywords: Silicon, Light-Soaking, Defects

1 INTRODUCTION

Two main causes have been identified for the illumination-induced degradation of solar cells fabricated on boron-doped mono- and multicrystalline silicon. Both of them are electronically driven defect reactions involving substitutional boron (B_s), leading to a pronounced decrease in the carrier recombination lifetime under solar cell operating conditions. In multicrystalline silicon (mc-Si), dissociation of interstitial iron-substitutional boron (Fe_iB_s) pairs into isolated Fe_i and B_s has been identified as the most relevant process [1]. This well-known defect reaction is linked to the degree of iron contamination in the material. It can also be observed in single-crystalline iron-contaminated B-doped float-zone (FZ) and Czochralski (Cz) silicon and is not restricted to mc-Si. Another carrier lifetime degradation effect has been observed in metal-impurity-free B-doped Cz-Si [2]. This effect has only recently been attributed to the simultaneous presence of B_s and interstitial oxygen (O_i) [3,4]. Interestingly, as for the Fe_iB_s dissociation, this degradation effect occurs also in the dark when minority-carriers are injected (e.g., by a forward-biased pn junction), leading to the conclusion that the degradation is caused by the presence of minority-carriers and photons are not directly involved [5]. Recently, much research has been devoted to the light-induced B_sO_i -related degradation problem, which is presently the main obstacle for making B-doped Cz-Si an ideal cost-saving material for high-efficiency solar cells. This paper reviews the present physical understanding of the degradation effects and discusses different approaches for reducing or even completely avoiding them.

2 IRON-BORON-RELATED DEGRADATION

In boron-doped p -type silicon, Fe_i is well known to form pairs with B_s [6]. These Fe_iB_s pairs dissociate into Fe_i and B_s under illumination due to a recombination-enhanced dissociation process [7]. If the silicon sample is kept in the dark at room temperature, the Fe_iB_s pairs reform within a couple of hours for typical resistivities of

around $1 \Omega\text{cm}$. Due to this characteristic behavior, the carrier lifetime in iron-contaminated boron-doped silicon is determined by Fe_iB_s pairs, isolated Fe_i or a combination of both species, depending on the history of the sample. The injection level dependence of the carrier lifetimes is much more pronounced for isolated Fe_i than for Fe_iB_s pairs and the corresponding injection-dependent lifetime curves show a characteristic crossover point at an approximately fixed excess carrier concentration for sufficiently low doping concentrations ($N_{\text{dop}} \ll 1.5 \times 10^{17} \text{ cm}^{-3}$) [1]. Using literature data of the energy levels and capture cross sections for Fe_iB_s and Fe_i [1,6,8], the crossover point can be calculated to be at $\Delta n_{\text{cr}} = 1.4 \times 10^{14} \text{ cm}^{-3}$ [1]. Figure 1 shows injection-dependent lifetime curves of an iron-implanted silicon sample before and after optical dissociation of Fe_iB_s pairs, measured using the quasi-steady-state photoconductance technique (QSSPC). In order to distribute the implanted Fe_i homogeneously throughout the wafer, the sample has been annealed at 900°C for 1 h. From the measurements shown in Fig. 1, we are able to determine the crossover point to be at Δn_{cr}

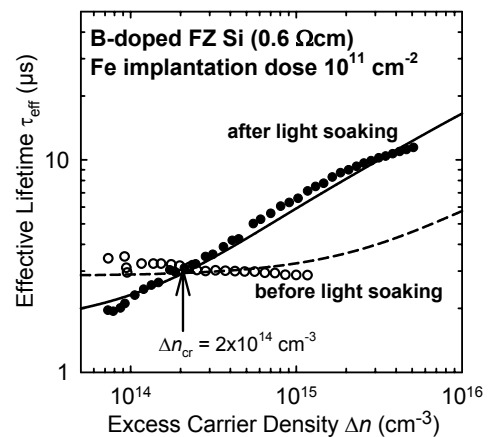


Figure 1: Injection-dependent lifetime curves of an Fe-implanted B-doped silicon wafer before and after optical dissociation of Fe_iB_s pairs, showing the characteristic crossover point Δn_{cr} .

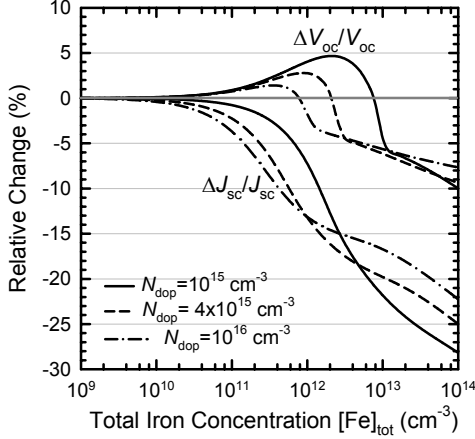


Figure 2: Calculated relative changes in J_{sc} and V_{oc} of a high-efficiency solar cell due to the dissociation of Fe_iB_s pairs [10].

$= 2 \times 10^{14} \text{ cm}^{-3}$ in good agreement with the calculated value. Comparable experimental results have been reported for silicon of various resistivities using different measurement techniques [1].

The effect of the pronounced change in the lifetime caused by the dissociation of Fe_iB_s pairs on the solar cell parameters has been studied by means of PC1D simulations using reported recombination parameters for Fe_i and Fe_iB_s [9,10]. Figure 2 shows the relative changes in the short-circuit current density J_{sc} and the open-circuit voltage V_{oc} of a high-efficiency solar cell for different total iron concentrations. Interestingly, we find that while J_{sc} always decreases as a consequence of the Fe_iB_s dissociation, V_{oc} shows a pronounced increase of up to 5% at relatively high iron concentrations. However, as the degradation in J_{sc} dominates, the cell efficiency always decreases. The very different behavior of V_{oc} and J_{sc} is due to the much larger injection level in the base of the cell under open-circuit than under short-circuit conditions. While under one-sun short-circuit conditions the excess carrier concentration Δn within the base is always below the crossover point Δn_{cr} , the situation is different under open-circuit conditions. In the latter case, whether the injection level is above or below the crossover point depends on the absolute value of the carrier lifetime. Hence, at high iron levels, corresponding to low lifetimes and low injection levels, V_{oc} degrades, whereas at moderate iron contamination levels, corresponding to higher lifetimes and higher injection levels, V_{oc} increases during illumination. The threshold iron contamination level of the V_{oc} -degradation was found to be about one to two orders of magnitude larger than the threshold iron levels of all other cell parameters. Hence, up to relatively high iron concentrations (typically $\sim 10^{12} \text{ cm}^{-3}$ for doping concentrations around 10^{16} cm^{-3}) only a degradation in short-circuit current, fill factor and efficiency may be observed, whereas the open-circuit voltage remains constant or even increases. This effect is characteristic of the Fe_iB_s dissociation and may therefore be used as a simple way of identifying iron contamination problems in silicon solar cells. Note however that Fe concentrations in completed solar cells may be much lower than the Fe concentration in the starting material due to gettering effects of emitter formation.

3 BORON-OXYGEN-RELATED DEGRADATION

Degradation can also be observed in solar cells made on high-purity monocrystalline Cz-Si without any metal contamination. This effect has been attributed to the formation of a specific boron-oxygen complex [3,4]. Recently, we have shown that the defect concentration of the boron-oxygen complex increases *linearly* with the B_s concentration and *quadratically* with the O_i concentration [11]. Based on these experimental findings, we have proposed a defect model involving an interstitial oxygen dimer (O_{2i}) [11]. In our model, the presence of minority-carriers (i.e., electrons) enhances the diffusivity of the oxygen dimers. The fast-diffusing O_{2i} is then trapped by B_s and forms a B_sO_{2i} complex, acting as a highly effective recombination centre. The oxygen dimers are formed during the cooling of the silicon crystal after its growth or during the subsequent thermal donor annihilation treatment. The oxygen di-interstitial O_{2i} has been detected before in Cz-Si by infrared absorption, and a quadratic dependence of the O_{2i} equilibrium concentration on $[O_i]$ was found [12]. According to our B_sO_{2i} model, this would lead to a quadratic dependence on the O_i content for the concentration of the light-induced recombination centre, in good agreement with the experimental results.

As known from theoretical calculations [13], the stable form of the neutral oxygen dimer has a staggered configuration. Hence, a corresponding staggered configuration had also been proposed for the B_sO_{2i} complex as a possible stable core structure [11]. First results of density-functional theory calculations using the AIMPRO code [14] show that B_sO_{2i} is a bistable defect. The two most stable configurations of B_sO_{2i} are a square form, $B_sO_{2i}^{sq}$ (see Fig. 3 a), and a staggered form, $B_sO_{2i}^{st}$ (see

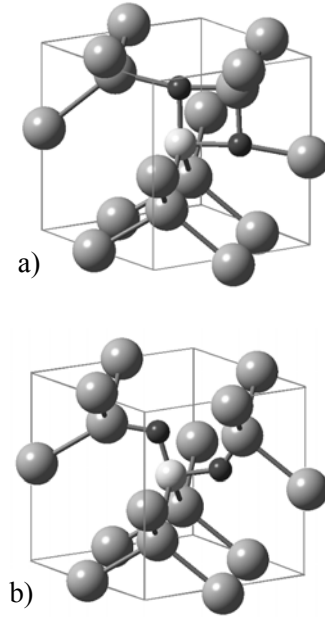


Figure 3: Core structure of the two most stable configurations of B_sO_{2i} according to AIMPRO [14] density-functional calculations. (a) The square form $B_sO_{2i}^{sq}$ is the most stable form in the single positive charge state, while (b) the staggered configuration $B_sO_{2i}^{st}$ is more stable when it's neutral (Si: grey balls, O_i : black balls, B_s : white balls).

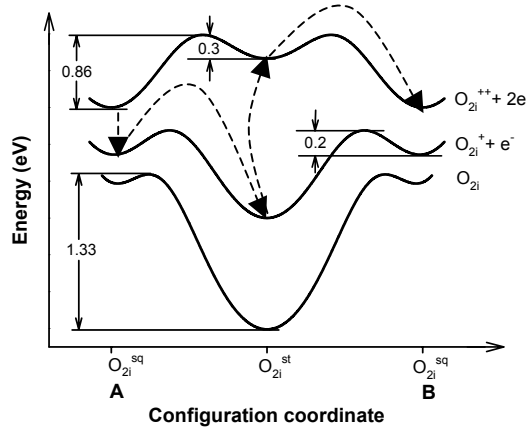


Figure 4: Configuration-coordinate diagram for the oxygen dimer. The arrows indicate the Bourgoin-Corbett diffusion mechanism proposed in Ref. 14.

Fig. 3 b), the latter one being equivalent to the structure proposed in Ref. 11. The calculations also show that $B_sO_{2i}^{sq}$ is the more stable configuration in the single positive charge state, while $B_sO_{2i}^{st}$ is the more stable when neutral. The ionization energies of the B_sO_{2i} defect were calculated using the Marker Method [14]. These calculations show that $B_sO_{2i}^{sq}$ has a (0/+) donor level in the upper half of the silicon band gap between $E_C - 0.1$ eV and $E_C - 0.3$ eV, suggesting that $B_sO_{2i}^{sq+}$ is the most likely candidate for the centre responsible for the solar cell degradation.

While there is no disagreement in the literature that neutral O_{2i} has no energy level in the silicon band gap, very different values of the migration energy have been reported. While Ewels [13] calculated a migration energy of ~ 1.3 eV, making the dimer virtually immobile at room temperature, Lee et al. [15] have calculated a much lower migration barrier between 0.3 and 0.9 eV. Adey et al. [14] proposed recently that a positively charged oxygen dimer could be the fast-diffusing species in the defect reaction. In fact, AIMPRO simulations show that the migration of a doubly positively charged oxygen dimer in a square configuration, O_{2i}^{sq++} , would result in a migration barrier of ~ 0.3 eV, in good agreement with the experimental value of 0.37 eV [11] measured for the activation energy of the defect formation. Figure 4 shows how the migration of O_{2i}^{sq++} might proceed via a *Bourgoin-Corbett mechanism*: (i) O_{2i}^{sq++} at position A in the silicon lattice traps an electron and becomes O_{2i}^{sq+} , (ii) O_{2i}^{sq+} transforms into the staggered configuration O_{2i}^{st+} with a barrier of just 0.2 eV, (iii) emission of an electron changes the charge state into O_{2i}^{st++} , (iv) the defect has to overcome a barrier of just 0.3 eV to move to another square configuration at position B. The binding energy E_B of O_{2i}^{++} to B_s^- has been determined by moving O_{2i}^{sq++} away from B_s^- by one and two steps, respectively, along the $\langle 110 \rangle$ direction in a large 144-atom supercell. This increases the total energy by 0.38 eV in both cases, a value which can hence be identified with E_B . Furthermore, the migration energy E_m of O_{2i}^{sq++} has been calculated to be 0.86 eV (see Fig. 4). This results in an activation energy of $E_B + E_m = 1.24$ eV for the dissociation of the boron-oxygen complex, in excellent agreement with the measured value of $E_{ann} = 1.3$ eV [11]. It is interesting

to note that the double charge state of the oxygen dimer may also explain the experimentally observed quadratic increase of the defect generation rate with doping concentration [14].

4 STRATEGIES FOR AVOIDING THE DEGRADATION

4.1 Gallium-doped silicon

In contrast to B-doped Cz-Si, no lifetime degradation is observed in Cz-Si doped with gallium instead of boron [3,11]. Furthermore, very high lifetimes above 1 ms have been measured in Ga-doped Cz-Si materials, despite their large oxygen contents. Using the defect reaction model discussed in the previous Section, we are able to explain the excellent stability of Ga-doped Cz-Si. The key seems to be the tetrahedral radii of the different elements. While the B atom is 25% *smaller* than the Si host atom, the tetrahedral covalent radius of Ga is 7% *greater* compared to that of the Si atom [16]. Hence, there is not enough space available in the vicinity of Ga to accommodate the O_{2i} dimer. AIMPRO calculations show that in fact there seems to be no stable Ga_sO_{2i} complex in silicon. In recent years, several groups have fabricated high-efficiency solar cells on Ga-doped Cz-Si wafers showing stable efficiencies well above 20% [17]. Hence, Ga-doped Cz-Si is a very promising material for the next generation of industrial high-efficiency solar cells.

4.2 Magnetic-field-assisted growth of Cz-Si

The oxygen content of Cz-Si can be strongly reduced by damping the melt flows with strong magnetic fields. This so-called magnetic-field assisted Cz (MCz) silicon has O_i concentrations which are up to one order of magnitude below that of conventional Cz-Si. B-doped MCz-Si shows an almost vanishing light degradation and has bulk lifetimes comparable to that of Ga-doped Cz-Si. Different high-efficiency solar cell concepts have been successfully applied to B-doped MCz-Si and efficiencies $>20\%$ have been achieved after extensive light-soaking [17].

4.3 N-type silicon

The third alternative silicon material showing very high carrier lifetimes in the ms range and virtually no light degradation despite the presence of oxygen is phosphorus or arsenic-doped *n*-type Cz-Si [3]. The main problem of this class of materials is that most cell structures used in the past have been designed for *p*-type silicon. However, since a couple of years new cell structures are being developed in several groups aiming at exploiting the high potential of *n*-type silicon materials. One very successful example is the HIT (Heterojunction with Intrinsic Thin Layer) cell giving efficiencies up to 21.3 % on *n*-type Cz-Si [18]. In our lab, we are currently developing a low-cost cell process for *n*-type silicon based on screen-printed $Al-p^+$ rear emitters. Up to now we have achieved independently confirmed efficiencies up to 18.3% on 2 Ω cm P-doped *n*-type Cz-Si using this simple screen printing process [19].

5 CONCLUSIONS

In this paper, we have discussed two different boron-related, electronically driven defect reactions, which are of particular importance for solar cells as they cause a severe degradation in the energy conversion efficiency under illumination. If the silicon wafer is contaminated with iron, as is frequently the case for solar-grade multicrystalline silicon, iron-boron pairs form in equilibrium. Under illumination with white light, these pairs split up due to a recombination-enhanced dissociation reaction. As the recombination properties of iron-boron pairs and isolated iron are very different, the injection-dependent lifetime curves change considerably during light-soaking and a characteristic crossover point exists. For injection levels below this characteristic crossover point the lifetime decreases during the dissociation of iron-boron pairs, while for injection levels above the crossover point it increases. On the basis of numerical device simulations, we have shown that the dissociation of iron-boron pairs always results in a degradation of the solar cell efficiency. However, the existence of the crossover point leads to a completely different behavior for the short-circuit current and the open-circuit voltage, as the two cell parameters are measured at very different excess carrier concentrations. While the short-circuit current, measured at injection levels below the crossover point, always degrades during iron-boron dissociation, the open-circuit voltage may decrease, be constant or even increase, depending on the excess carrier concentration under open-circuit conditions relative to the position of the crossover point.

A pronounced degradation in solar cell efficiency under illumination can also be observed if high-purity monocrystalline Czochralski-grown boron-doped silicon is used as the base material. This effect is attributed to the formation of a recombination-active boron-oxygen complex. The defect concentration depends linearly on the boron concentration and quadratically on the interstitial oxygen concentration, suggesting a defect complex made up of one substitutional boron and two interstitial oxygen atoms. *Ab-initio* calculations using density-functional theory show that such a defect exists in different stable configurations in crystalline silicon. In our defect formation model, a fast-diffusing oxygen dimer is captured by a substitutional boron atom. The diffusivity of the oxygen dimer is electronically enhanced via a recombination-enhanced or a Bourgoin-Corbett mechanism.

Various approaches to avoid the boron-oxygen-related degradation exist. Alternative dopants, such as gallium or phosphorus, have been demonstrated to completely avoid the degradation. Reducing the oxygen content by applying a strong magnetic field during crystal growth is another way of improving the stable cell efficiency. In B-doped Cz-Si, high-temperature treatment can significantly reduce the magnitude of degradation [17]. In combination with adapted cell structures, currently being developed in several labs, strongly improved stable efficiencies may also be expected in the near future on conventional B-doped Cz-Si.

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