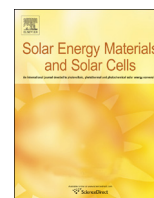




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## Impact of compensation on the boron and oxygen-related degradation of upgraded metallurgical-grade silicon solar cells

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## ABSTRACT

This paper deals with the impact of dopant compensation on the degradation of carrier lifetime and solar cells performance due to the boron–oxygen defect. The boron–oxygen defect density evaluated by lifetime measurements before and after degradation is systematically found proportional to the total boron concentration, showing that compensation cannot reduce light-induced degradation. This result is confirmed by a comparison of upgraded–metallurgical grade silicon solar cells having identical boron, oxygen and carbon but different compensation levels and in which the degradation is found more severe when the compensation is stronger.

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## 1. Introduction

Simultaneous presence of boron (B) and oxygen (O) in crystalline silicon (Si) is known to result in the existence of a strong recombination center – the boron–oxygen (BO) defect – which forms or is activated under excess carrier injection. In its active state, the BO defect dominates bulk recombination in B-doped cast or Czochralski (Cz)-grown Si, on which most of the photovoltaic industry is based. As a consequence, this defect currently represents one of the major wafer-related limitations of the performance of state-of-the-art industrial *p*-type Si solar cells [1].

One would naturally expect that solar cells made with upgraded metallurgical-grade (UMG)-Si are more affected by the BO defect, due to larger B concentration in this material than in Siemens-purified Si. Recent studies, however, found that the BO defect density was proportional in *p*-type Si to the net doping, rather than to the total B concentration, meaning that it could thus be reduced by compensation [2–5]. This finding was more recently contradicted by a study of the BO-related light-induced degradation of compensated Si solar cells, of which the severity was found to depend on the total B concentration [6]. With Ga co-doping offering an efficient tool for compensation engineering [7–9], it becomes important to clarify whether compensation can effectively be employed to mitigate the impact of the BO defect and thus improve the final performance of UMG-Si solar cells.

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Another lately debated issue is the composition of the BO defect complex. Guided by observations that the BO defect density depends on the net doping – or majority carrier density – Voronkov and Falster [10] proposed a model in which the defect complex is made with *interstitial* boron ( $B_i$ ). The dependence of the BO defect density was thereby explained by the proportionality of the solubility of positively charged  $B_i$  to the hole concentration, during the last phase of crystal cooling.

Measurements in *n*-type compensated Si [11–13] and in Si co-doped with B and Ga [14] were nonetheless found inconsistent with the involvement of  $B_i$  but rather suggested the participation of *substitutional* B ( $B_s$ ). Two BO-related recombination centers are observed in *p*-type Si: a fast-forming center (referred to as FRC) and a slow-forming center (SRC). Since the carrier lifetime in *p*-type Si is largely dominated after complete degradation by SRC, previous studies usually focus on this recombination center, as we do in this work. Voronkov et al. argued that the complex responsible for the degradation observed in *n*-type Si corresponds to FRC in *p*-type Si and can thus be made of  $B_s$  without being in contradiction with the  $B_iO_{2i}$  complex they propose for SRC in *p*-type Si. This however infers that despite the fact that the fast and the slow degradations observed in *p*-type Si show numerous similarities, they result from completely unrelated complexes with different precursors.

In addition, the BO-related lifetime degradation was found invariant with respect to the presence of *interstitial* silicon atoms [15,16]—which are themselves likely to influence the concentration of *interstitial* boron. Recent calculations also found that the

concentration of  $B_i$  was too low to explain the observed lifetime degradation and that the calculated characteristics of the  $B_iO_{2i}$  complex were inconsistent with those measured by lifetime spectroscopy for the BO defect [17]. On the other hand, participation of  $B_s$  in the BO defect complex remains very difficult to reconcile with the linearity of the defect density to the net doping [18].

In the present work, we aim at verifying the effect of compensation on the BO recombination center and clarifying the composition of the defect complex. In a first experiment, we study the BO-related lifetime degradation in Si samples with a wide range of dopant concentrations and compensation levels. We evaluate the oxygen-normalized effective BO defect density and find that it depends on the total boron concentration, demonstrating the involvement of *substitutional* boron in the defect complex. In a second experiment, we crystallize two different Cz ingots having identical B, O and C profiles but different compensation levels. Then, we fabricate solar cells with wafers from both ingots and measure their behavior under illumination. We find that the activation of the BO defect leads to stronger performance degradation in solar cells made with heavily compensated Si than with lightly compensated Si. This experiment unambiguously shows that compensation does not mitigate the impact of the BO defect on solar cells but on the contrary worsens it.

## 2. Experimental methods

### 2.1. Study of the lifetime degradation in compensated silicon wafers

This study was carried out on *p*-type Cz-Si samples co-doped with Ga and B, B and P or B, P and Ga. These samples originate from a batch of  $<100>$ -oriented Si ingots which were crystallized using the Czochralski pulling technique. They were grown using electronic-grade (EG)-Si to which were added various concentrations of B, P and Ga. In each sample,  $p_0$  was deduced from Hall effect measurement, assuming a Hall factor of  $r_H=0.75$  [19].  $[B]$  was deduced from the sample's position in the ingot, and from the initial concentration of B added into the Si melt, using Scheil's equation [20]. Together with uncompensated B-doped, P-doped and Ga-doped controls, these samples were subsequently acid etched to remove saw damage, RCA cleaned, and underwent a phosphorus diffusion gettering at 820 °C to dissolve oxygen-related thermal donors and eliminate metallic impurities. This ensures that there is no or very little impact of FeB and FeGa pairs during the degradation experiment. Diffused regions were then removed by an additional acid etch and samples were RCA cleaned before being coated on both sides by hydrogenated Si nitride ( $SiN_x:H$ ) at 235 °C, using plasma-enhanced chemical vapor deposition (PECVD).

After deposition, samples were annealed in the dark at 200 °C under air ambient during 30 min, in order to annihilate the boron-oxygen defect. The effective lifetime was then measured using inductively-coupled photo-conductance decay [21], immediately after annealing ( $\tau_0$ ) and after different times  $t$  of illumination under a 10 mW/cm<sup>2</sup> halogen lamp at 25–27 °C.

A fit to Dannhauser and Krause's mobility sum measurements [22–24] is commonly used to convert photo-conductance data into excess carrier density for injection-dependent lifetime measurements [21]. This fit is accurate in uncompensated Si [25] but overestimates the mobility sum in compensated Si [26]. To account for that lower mobility in our samples, we adjust the doping used as input in the fit to Dannhauser and Krause's mobility so that it yields the same low-injection mobility sum as we previously measured in our compensated samples (see [27]).

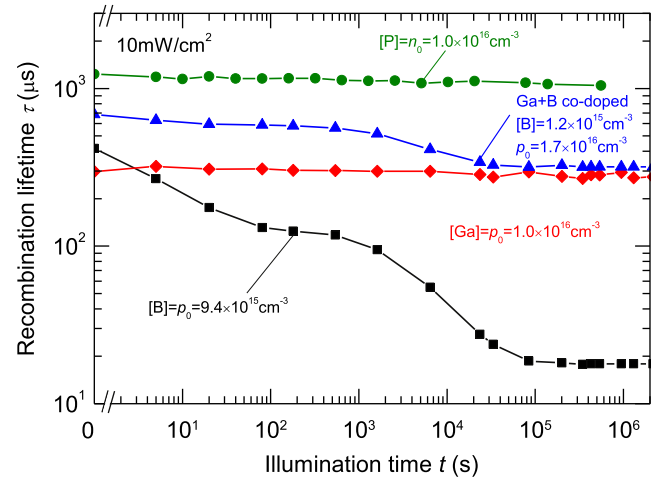


Fig. 1. Measured carrier lifetime, at an injection  $\Delta n=0.1 \times p_0$ , as a function of time under illumination in Si samples with different types of doping.

As illustrated in Fig. 1, the effective lifetime degraded under illumination in all samples except for those which did not contain B, in which it remained stable. This proves that the surface passivation quality of the  $SiN_x:H$  layer did not change throughout the experiment. The observed degradation in samples containing B can thus be attributed to a decrease of the bulk lifetime. After complete degradation, i.e. after saturation of the measured lifetime to its final value  $\tau_{deg}$ , the effective BO defect density is calculated using the following expression:

$$N_t^* = \frac{1}{\tau_{deg}} - \frac{1}{\tau_0} \quad (1)$$

in which  $\tau_{deg}$  and  $\tau_0$  are taken at a fixed injection level of  $\Delta n=0.1 \times p_0$ . It is well known that the effective defect density after complete degradation  $N_{t,sat}^*$  displays a quadratic dependence on  $[O_i]$  [28]. This dependence is thought to be due to the participation of oxygen dimers which are themselves present in a concentration proportional to  $[O_i]$  squared [29]. Since we intend to study the impact of dopants on the BO defect density, a more relevant parameter to focus on is,

$$N_{BC} = \frac{N_{t,sat}^*}{[O_i]^2} \quad (2)$$

This oxygen-normalized parameter reflects the influence of defect components (such as  $[B]$  or  $p_0$ ) not directly related to  $[O_i]$ . To evaluate  $N_{BC}$  in our samples,  $SiN_x:H$  layers were etched off in hydrofluoric acid after the degradation experiment and  $[O_i]$  was measured by Fourier transform infrared spectroscopy (FTIR).

### 2.2. Study of the degradation of compensated Si solar cells

#### 2.2.1. Feedstock preparation

For this study, we used 30 kg of PHOTOSIL UMG-Si [30–32]. The starting metallurgical-grade (MG)-Si was produced by FerroPEM, with careful selection of raw materials, i.e. silica and carbon, enabling to limit the initial impurity concentration. A first segregation treatment was applied during solidification of this MG-Si straight away after carbothermic reduction, decreasing the concentration of phosphorus and metallic impurities. The resulting material was then transferred to the PHOTOSIL facilities where it was purified according to the standard PHOTOSIL process [30–32], involving a plasma treatment to remove B and segregations to remove P and metallic impurities. After purification, the Si feedstock contains 0.25 ppmw of B and 0.60 ppmw of P.

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