



Accelerated formation of the boron–oxygen complex in p-type Czochralski silicon

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This Letter reports on the acceleration of the rate of formation of the boron–oxygen defect in p-type Czochralski silicon with illumination intensities in excess of 2.1×10^{17} photons/cm²/s. It is observed that increased light intensities greatly enhance the rate of defect formation, without increasing the saturation concentration of the defect. These results suggest a depend-

ence of the defect formation rate upon the total majority carrier concentration. Finally, a method using temperatures up to 475 K and an illumination intensity of 1.68×10^{19} photons/cm²/s is shown to result in near-complete defect formation within seconds.

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1 Introduction The boron–oxygen (B–O) defect is of significant interest to the photovoltaic community. It can reduce the efficiency of p-type Czochralski (Cz) silicon solar cells by up to 2% absolute when compared to the efficiency measured at the end of fabrication [1]. A number of methods have been discovered for dissolving or passivating this defect once it has been formed [2, 3]. Defect formation has traditionally been performed using a slow light soaking process, which can take many hours or even days to stabilise. The lengthy time taken to form the defect slows research cycles and makes passivating the defect in a commercial setting less practical. It is therefore desirable to develop a rapid process for defect formation.

Two recombination centres, denoted as the fast-forming and slow-forming centres, have been associated with this defect. While the fast-forming defect may reach saturation in a matter of seconds at elevated temperatures, the slow-forming defect typically takes 24–48 hours under 1-sun illumination at room temperature. Ultimately it is this slow-forming defect which is responsible for determining the bulk minority carrier lifetime and hence the performance of the photovoltaic device [4].

Despite considerable research effort, the exact mechanisms responsible for the defect formation (including saturation concentration and formation rate) remain unclear. In

uncompensated boron-doped p-type silicon the formation rate was initially reported to depend upon bulk doping and temperature [5]. Specifically, it was shown that there was a quadratic increase with bulk doping concentration (N_A) and an exponential increase with temperature. In the same study the saturated concentration of the defect showed a quadratic dependence on the interstitial oxygen concentration [4, 6] as well as a linear dependence on N_A . However, recent observations on compensated p-type material doped with boron and phosphorus have demonstrated that the rate of formation and the saturated defect concentration depend upon the equilibrium hole concentration (p_0), rather than the boron concentration, with the rate being proportional to p_0^2 [7–9]. This relationship was shown experimentally by varying the bulk doping in both standard Cz silicon as well as in compensated silicon. This also agrees with results on silicon doped with both B and Ga in which the formation rate was found to depend upon p_0^2 , while the saturated defect density was found to depend upon the boron concentration [10].

All of these works have studied the impact of holes on the defect formation through changing p_0 via various doping strategies. In this Letter, p-type silicon doped exclusively with boron is used to keep p_0 fixed and the silicon is then driven into high injection with laser illumination.

A range of strategies have previously been employed in attempts to accelerate the rate of defect formation. Intensities up to a threshold of 0.1 suns were reported to increase the rate of defect formation in p-type silicon by increasing the concentration of minority carriers [5, 11]. Above this threshold no influence of increasing illumination intensity upon the rate of defect formation was observed. Another study used pulsed laser illumination from a microwave photoconductance tool [12] and noted that the high intensity pulsed illumination significantly enhanced the rate of defect formation in compensated n-type Cz silicon. However the total process time was in excess of 14 hours. A process for accelerated light induced degradation with elevated temperature was also put forward by Wilson et al. [13], using 1-sun illumination which required more than five minutes to achieve full defect formation [14]. Applied electric fields have also been used to accelerate defect formation with the enhancement again saturating at higher excess carrier densities [4]. These techniques have all demonstrated an increase in the defect formation rate, however, in no cases was the formation rate fast enough to allow complete formation in a commercially viable timeframe.

This Letter investigates the use of high intensity laser illumination, combined with elevated substrate temperatures, to accelerate the formation of the boron–oxygen defect in p-type silicon. An examination of the effect of illumination intensity upon formation rate is presented, followed by demonstration of the use of high illumination intensity to achieve defect formation within seconds.

2 Experimental details Test structures were prepared using commercial grade 156 mm × 156 mm boron-doped Cz wafers ($1.6 \Omega \text{ cm}$, $N_A = 9.1 \times 10^{15} \text{ cm}^{-3}$). Wafers were subjected to alkaline texturing followed by acidic neutralisation, with a resultant total wafer thickness of approximately 180 μm . This was followed by an RCA clean and HF dip, then a light diffusion ($\sim 250 \Omega/\square$) in a POCl_3 tube furnace (15 min deposition at 795 °C followed by 15 min at 800 °C drive-in) to reduce recombination at the wafer surfaces. Subsequently, hydrogenated silicon nitride ($\text{SiN}_x\text{:H}$) with a refractive index of 2.08 was deposited onto both surfaces of the wafers using a Roth & Rau MAiA plasma-enhanced chemical vapour deposition system. To eliminate the potential passivation of B–O defects by hydrogen during the illuminated annealing process for degradation, the samples were not fired, and hence hydrogen was not introduced into the bulk of the silicon.

The accelerated degradation process was performed on a hotplate under laser illumination. A 938 nm laser was used operating in quasi-continuous wave mode with a pulse length of 0.5 ms and repetition frequency of 2 kHz. A beam shaper was used to illuminate the entire sample, with intensities ranging from $2.1 \times 10^{17} \text{ photons/cm}^2/\text{s}$ to $1.68 \times 10^{19} \text{ photons/cm}^2/\text{s}$, achieved by varying the laser power and/or expansion of the beam.

During laser processing the hotplate set point was adjusted to achieve a similar average wafer temperature at each intensity. A Datapaq Q18 data profiler was used to monitor the temperature of wafers on the hotplate in the dark and under laser illumination. This was used to establish the temperature offsets required to compensate for heating of the wafers under the laser. An offset of 80 K was required for the highest illumination intensity, with decreasing offsets for lower intensities. The temperature of the samples was measured to be 413 K. After processing the illumination was switched off and the wafers were removed from the hotplate to cool in air.

Effective minority carrier lifetimes (τ_{eff}) as a function of minority carrier density (Δn) were measured using a WCT-120 (Sinton Instruments) quasi-steady-state photoconductance lifetime tester [15]. The measured data was analysed using the generalised technique [16]. Where relevant, the lifetimes were extracted at a single excess carrier concentration (Δn) of $9.12 \times 10^{14} \text{ cm}^{-3}$, equivalent to $0.1 \times N_A$, then presented as a ratio of the original starting lifetime. This τ_{eff} value was modified to remove the component due to Auger recombination according to the Richter model [17] as is the standard procedure when analysing such data.

The stabilised degraded lifetimes for the samples were also measured using illumination conditions reported in previous studies [18]. This conventional degradation process was performed under a halogen lamp with a light intensity of $78 \pm 1 \text{ mW/cm}^2/\text{s}$ with wafers maintained at a temperature of $313 \pm 3 \text{ K}$ for a total of 48 hours.

Dark annealing of selected samples was performed on a hot plate with a wafer temperature of approximately 503 K for 10 min.

3 Results and discussion The impact of illumination intensity on the effective lifetime for a one-minute process, shown in Fig. 1a, clearly demonstrated a trend of **reduced lifetime with illumination intensity**. Further processing of the samples with the same laser intensity resulted in the final lifetimes for all samples saturating to the level marked as the stabilized lifetime. The difference in the percentage of total degradation after the first minute of processing indicated that the defect formation rate was accelerated with increasing illumination intensity.

The inverse lifetime as a function of minority carrier density for the sample illuminated with an intensity of $1.68 \times 10^{19} \text{ photons/cm}^2/\text{s}$, shown in Fig. 1b, verified the state of the defect after each process step. The lifetime curves after traditional light soaking and laser processing both matched, indicating that the lifetime of the sample was completely degraded inside 1 min and that the saturated defect concentration for the accelerated process was equivalent to that of the conventional 48 hour process. The recovery in lifetime after dark annealing at 503 K confirmed that the changes in lifetime observed were caused by the boron–oxygen defect, which is widely reported to be deactivated by such anneals.

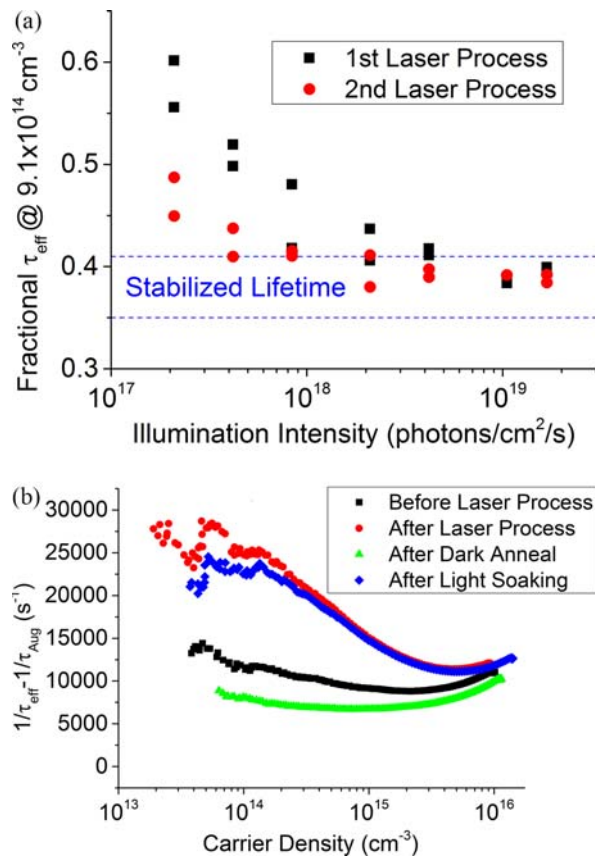


Figure 1 (a) Effective lifetime at a minority carrier density of $9.12 \times 10^{14} \text{ cm}^{-3}$ as a fraction of dark annealed lifetime, after a one-minute laser process (black squares) and after an additional one-minute laser process (red circles) at 413 K, plotted against illumination intensity. The stabilized lifetime of these wafers after 48 hours light soaking lies between the blue dashed lines. (b) Auger corrected inverse effective lifetime plotted against excess minority carrier concentration for a sample before processing (black squares), after laser degradation with an illumination intensity of $1.68 \times 10^{19} \text{ photons/cm}^2/\text{s}$ (red circles), after subsequent dark anneal (green triangles) and after 48 hour light soaking (blue diamonds).

These results are in apparent contradiction with previous studies which have reported that the dependence of defect formation rate on excess carrier density saturates at values greater than ~ 0.1 Suns [5, 11]. A possible explanation is that in this work the illumination intensities used here are high enough to result in a significant increase in the majority carrier concentration which would not have occurred in the previous work. The saturated defect concentration appeared to be independent of the hole concentration during the process, supporting the conclusions of several in the literature [7, 8, 19] that this parameter depends upon p_0 . In contrast, the accelerated defect formation rate with increasing illumination intensity may imply a strong dependence upon the total hole concentration during the annealing process, which in these experiments is estimated to vary between $1.0 \times 10^{16} \text{ cm}^{-3}$ for an illumination

intensity of $2.1 \times 10^{17} \text{ photons/cm}^2/\text{s}$ to $5.2 \times 10^{16} \text{ cm}^{-3}$ for an illumination intensity of $1.68 \times 10^{19} \text{ photons/cm}^2/\text{s}$. This would agree with the previous results presented in which holes are required for the degradation reaction [7], as well as with the observation of Rougieux et al. [20] of an excess carrier dependent defect formation rate in compensated n-type silicon. It would also agree with speculation by Macdonald et al. [8] that the rate of defect formation may possess a dependence on excess hole density.

If a dependence of the defect formation upon the hole concentration is accepted it would be expected to be either linear or quadratic based upon results in the Refs. [5, 7, 8]. In which case it may therefore be supposed that instead of the reported quadratic dependence of degradation rate upon p_0 the actual dependence should be replaced with either pp_0 or p^2 to reflect the enhancement of the defect formation rate under medium to high injection levels. From these initial results it is not possible to conclusively determine which applies in this case.

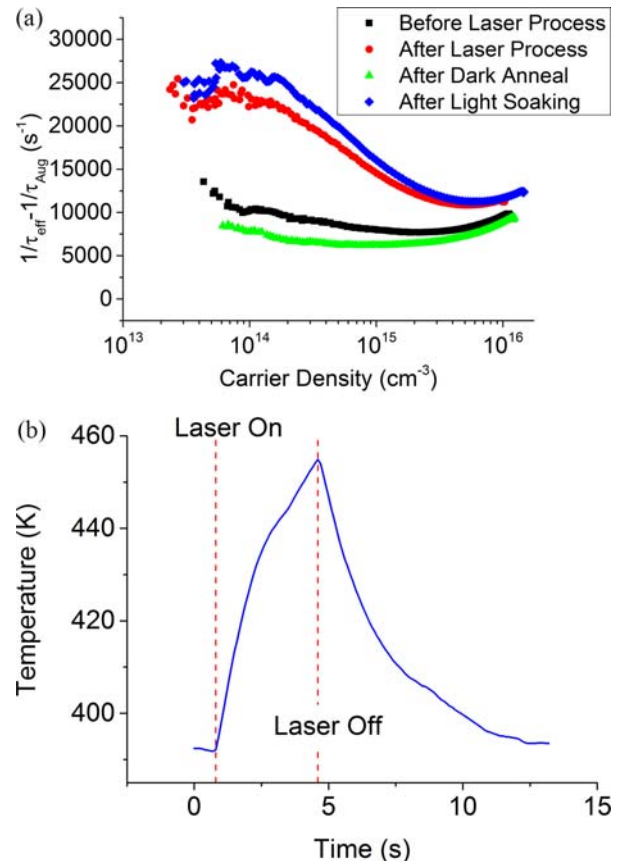


Figure 2 (a) Auger corrected inverse effective lifetime as a function of minority carrier density. The inverse lifetimes are given before laser degradation (black squares), after laser degradation with an illumination intensity of $1.68 \times 10^{19} \text{ photons/cm}^2/\text{s}$ and a temperature profile as shown in (b) (red circles), after dark annealing (green triangles), and finally after 48 h light soaking (blue diamonds). (b) The temperature profile for the sample in 2(a) as measured using the Datapaq Q18 profiler. The laser is turned on at 0.8 s and turned off at 4.6 s.

For a commercially viable process it is desirable that complete degradation be achieved as rapidly as possible. In order to investigate how quickly complete formation of the boron–oxygen defect might be achieved, the wafers were illuminated at 1.68×10^{19} photons/cm²/s with an initial hot-plate temperature of 413 K. The temperature profile for this process is shown in Fig. 2b, with a peak temperature of 475 K reached after 3.8 s. Figure 2a presents the inverse lifetime as a function of minority carrier density for these wafers. As may be seen through comparison with the lifetimes after conventional light soak, these samples exhibited almost complete degradation after the rapid degradation process.

It may be expected that there is still significant room for further acceleration of this process with optimised temperature and/or illumination throughout the process. It is a matter for further investigation whether degradation accelerated with high intensity illumination will dominate over annealing at temperatures above those previously reported.

4 Conclusion This work has demonstrated that the rate of formation of the boron–oxygen defect in crystalline silicon can be significantly accelerated under high-intensity illumination. It was also shown that this process increases the rate of formation of the defects without increasing the saturated concentration. By using light intensities of 1.68×10^{19} photons/cm²/s and temperatures of 475 K it was shown that near-complete formation of such defects may be achieved within four seconds, with the potential for even more rapid degradation using increased intensities and/or temperatures.

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