

Impact of carbon co-doping on the performance of crystalline silicon solar cells

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ABSTRACT

We have investigated the impact of carbon co-doping on the performance of boron-doped Czochralski-grown silicon solar cells. It is found that carbon co-doping will deteriorate the initial performance of Aluminium-back-surface-field solar cells before light-induced degradation (LID), owing to the enhancement effect on the formation of oxygen precipitation. However, carbon co-doping can effectively suppress the formation of boron-oxygen complexes in the solar cells, which becomes more significant with an increase of the carbon concentration. Therefore, the performance of carbon co-doped silicon solar cells is better than that of conventional silicon solar cells after LID. All these results are of great significance for the practical application of carbon co-doped silicon solar cells with low LID effect in photovoltaic industry.

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1. Introduction

Crystalline silicon solar cell is trending towards high efficiency and low cost. However, light-induced degradation (LID) effect deteriorates the efficiency of commercial solar cells based on boron-doped crystalline silicon (c-Si) with loss up to 2–3%, due to the formation of boron and oxygen (B–O) complexes. B–O complexes, acting as effective recombination centers for carriers, form in the presence of excess carriers, particularly under sunlight illumination [1–3]. By annealing at elevated temperatures in dark, B–O complexes can be fully dissociation, but they can generate once again during the subsequent illumination at room temperature [4]. Earlier investigations have shown that the saturated concentration of B–O complexes is primarily proportional to the boron concentration and the square of oxygen concentration [5,6]. Therefore, Schmidt and Palmer et al. proposed that B–O complexes should be formed by the fast-diffusion of oxygen dimer (O_{2i}) towards the immobile substitutional boron (B_s) [7]. Later on, it has been extensively reported that the saturated B–O complex concentration increases linearly with the increase of hole concentration p_0 in compensated (c-Si) [8–10]. Voronkov et al. put forward a B_iO_{2i} model in which the positively charged interstitial boron atoms (B_i) are assumed to be captured by the O_{2i} to form latent centers in as-grown Si, and then the LID occurs via the transformation of latent centers into recombination centers [11]. They further updated this model with a new B_iB_sO model that the B_i atoms are captured by B_sO_i complexes to

be the latent centers but the O_{2i} are totally not involved [11]. Recently, we have presented that B–O complexes could be formed based on a short-distance diffusion of O_{2i} towards B_s in the latent centers [12–14].

Recently, we have reported that carbon (C) co-doping can effectively suppress the formation of B–O complexes in crystalline silicon wafers [7,15]. Furthermore, it is found by both the experiments and first-principle theoretical calculations that this suppression effect is attributed to the tensile stress in silicon lattice induced by carbon with a smaller radius and therefore tending to form more energetically favorable C_sO_{2i} complexes with O_{2i} [15]. Meanwhile, it has also been reported that the C doped in (c-Si) with high concentration will enhance the nucleation of high density oxygen precipitates which might strongly reduce the carrier lifetime in wafers and in turn be detrimental to the performance of solar cells [16–18]. Thus, a systematic study on the impact of C co-doping on the performance of crystalline silicon solar cells, particularly that after LID, is highly needed.

In this paper, we have investigated the performance of C co-doped crystalline silicon solar cells before and after LID, as well as that of conventional crystalline silicon solar cells. It has been demonstrated that C co-doping can effectively improve the performance of solar cells after LID. These results are of significance for the practical application of C co-doped crystalline silicon solar cells with low LID effect in photovoltaic (PV) industry.

2. Experimental procedure

Three 6 in., p -type <100> oriented crystalline silicon crystals were pulled under the same conditions. One is conventional silicon

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crystal for reference, labeled as Ref. The other two are C co-doped silicon crystal with different C doping levels, labeled as C1 and C2, respectively. After slicing the crystals, all the wafers were pre-annealed in Ar ambient for 30 min at 650 °C to eliminate grown-in thermal donors (TDs). Afterwards, the resistivity ρ of these wafers was measured using the four-point-probe (FPP) method. The carbon concentrations and oxygen concentrations were determined by a Fourier transform infrared spectroscopy (FTIR, Bruker IFS 66 V/s) with a calibration factor of $1 \times 10^{17} \text{ cm}^{-2}$ and $3.14 \times 10^{17} \text{ cm}^{-2}$, respectively. The detailed parameters of these wafers are shown in Table 1. It can be seen that the oxygen concentrations of all the samples are similar, but the carbon concentration of C2 sample is almost 3 times higher than that of C1 sample.

For carrier lifetime measurements, all the wafers were first chemically polished to remove saw damages and then subjected a double-surface passivation with plasma-enhanced chemical vapor deposited silicon nitride ($\text{SiN}_x\text{:H}$) film. The initial minority carrier lifetime (τ) was measured by a quasi-steady-state photoconductance (QSSPC) instrument (Sinton WCT-120). Note that the lifetime values were determined at an injection level of $\Delta n/p_0 = 0.1$ [1,6,7].

Solar cells were fabricated from the 156 mm \times 156 mm conventional and C co-doped crystalline silicon wafers with a thickness of 200 μm on the same production line at the Hareon Solar Company by a standard Al-back-surface-field (Al-BSF) process, including alkaline texture, phosphorus diffusion, Si_3N_4 film deposition, screen-printing and contact firing. For each kind of sample, 10 solar cells are fabricated. Note that the Si_3N_4 film has a refractive index of 2.05, with a thickness of 70 nm, which can act as a good anti-reflection film for the sunlight absorption of solar cell. The illuminated current-voltage characteristics of the solar cells were performed under the standard conditions (one sun, AM 1.5 Global spectrum, 25 ± 1 °C), using a Berger Flasher Pss 10 solar simulator. The illumination intensity was calibrated using a reference cell obtained from Fraunhofer ISE, Germany. After illumination under a halogen lamp with intensity of 100 mW/cm^2 at room temperature for 150 h, the cell efficiencies were investigated again. The internal quantum efficiencies (IQE) of the solar cells were derived from the cell spectral responses and the spectral reflectance. The minority carrier diffusion lengths (L_{diff}) of the solar cells were obtained from the light beam induced current (LBIC) measurement [19].

3. Results and discussion

Fig. 1 shows the initial average minority carrier lifetime of the wafers prior to any light soaking. One can see that with an increase of the C concentrations ([C]s), the initial minority carrier lifetime decreases, which indicates much more recombination centers in the bulk of C co-doped c-Si. As reported in the previous studies [20–22], carbon has an enhancement effect on the formation of oxygen precipitation in c-Si via two mechanisms. On the one hand, carbon bonds with oxygen and then forms $[\text{C}_i\text{-O}]_i\text{C}(3)$ centers at temperatures lower than 800 °C, acting as effective heterogeneous seeding sites for oxygen precipitation. On the other hand, carbon atoms play catalytic roles at temperatures higher than 850 °C.

Table 1
Detailed parameters of the reference and C co-doped silicon wafers.

| Sample | Resistivity ($\Omega \text{ cm}$) | C concentration (cm^{-3}) | O concentration (cm^{-3}) |
|--------|-------------------------------------|--------------------------------------|--------------------------------------|
| Ref. | 1.40 | NA | 1.0×10^{18} |
| C1 | 1.40 | 9.9×10^{16} | 1.0×10^{18} |
| C2 | 1.39 | 3.4×10^{17} | 1.0×10^{18} |

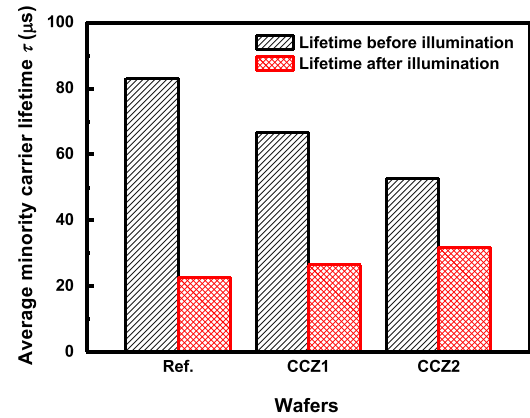


Fig. 1. Average minority carrier lifetime of the reference and C co-doped silicon wafers before and after illumination at room temperature for 150 h.

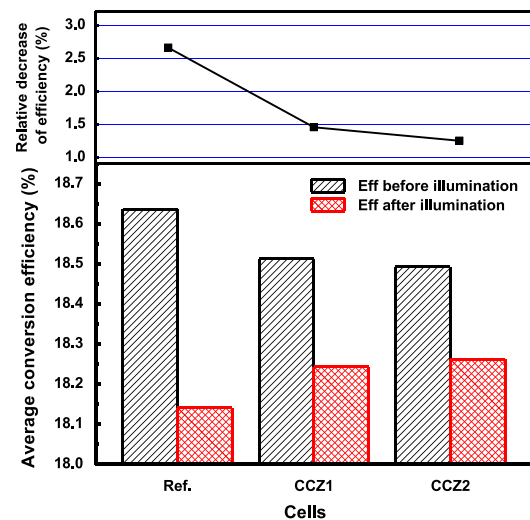


Fig. 2. Average conversion efficiency of the reference and C co-doped silicon solar cells before and after illumination at room temperature for 150 h, as well as its relative decrease.

Meanwhile, oxygen precipitates can cause deep energy levels in band gap of silicon, which have strong electrical recombination activity for carriers [17,23–25]. Therefore, the reduction of initial τ in C co-doped silicon wafers should be attributed to the generation of high density oxygen precipitates. This implies that carbon co-doping may deteriorate the performance of solar cells before LID.

Fig. 2 shows the average conversion efficiency of the corresponding solar cells before and after illumination at room temperature for 150 h. It should be mentioned here that the conversion efficiencies don't change any more with additional light soaking. Thus, the 150 h illumination at room temperature has proved to be long enough to saturate solar cells degradation completely. As we predicted above, the conversion efficiency of the solar cells before LID decreases with the increase of [C]s, due to more oxygen precipitates recombination centers. However, after light soaking, the conversion efficiency of the C co-doped silicon solar cells decreases less significantly than that of the reference cell. The relative decrease in these solar cells is also shown in Fig. 2 (top). Our previous work has demonstrated that C co-doping in (c-Si) can effectively suppress the formation of B-O complexes, owing to the formation of more energetically favorable CO_{2i} complexes [15]. As a consequence, the conversion efficiency of these solar cells after LID increases with the increase of [C]s is shown for the first time. These results suggest that carbon co-doping is beneficial

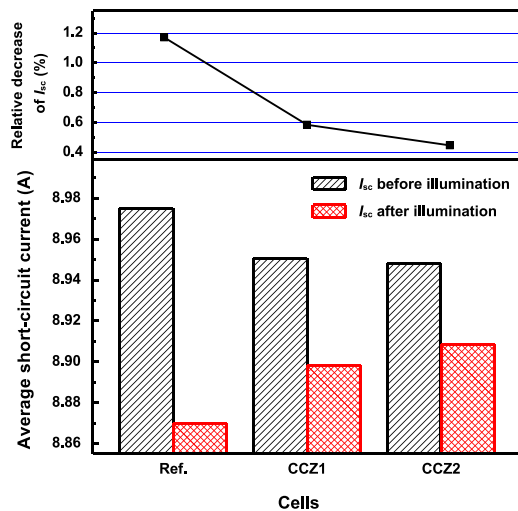


Fig. 3. Average short-circuit current of the reference and C co-doped silicon solar cells before and after illumination at room temperature for 150 h, as well as its relative decrease.

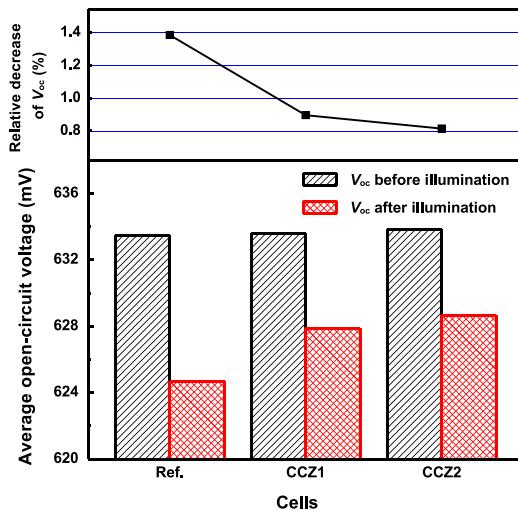


Fig. 4. Average open-circuit voltage of the reference and C co-doped silicon solar cells before and after illumination at room temperature for 150 h, as well as its relative decrease.

to improve the performance of solar cells after LID, which is of significance in PV application.

Figs. 3 and 4 show the average short-circuit current (I_{sc}) and open-circuit voltage (V_{oc}) of the solar cells before and after illumination at room temperature for 150 h, as well as its relative decrease, respectively. It can be seen that the value of I_{sc} and V_{oc} in the solar cells before LID decreases with the increase of [C] and reverses after LID, which is the same trend as the conversion efficiency of the solar cells. Considering that the B-O complexes can directly affect the I_{sc} due to the effective recombination of carriers generated in the solar cells under illumination, and the V_{oc} is affected by changes in I_{sc} in this case, the variation in the conversion efficiency should mainly originate from the variation of the I_{sc} .

Fig. 5(a) and (b) show the measured IQE data as a function of wavelength for the solar cells before and after illumination at room temperature for 150 h, respectively. For a better impression of the difference among these curves, the same data is plotted as an inset. It can be seen that the IQE of the C co-doped silicon solar cells is slightly worse than that of the reference solar cell before LID, which should account for the generation of higher density

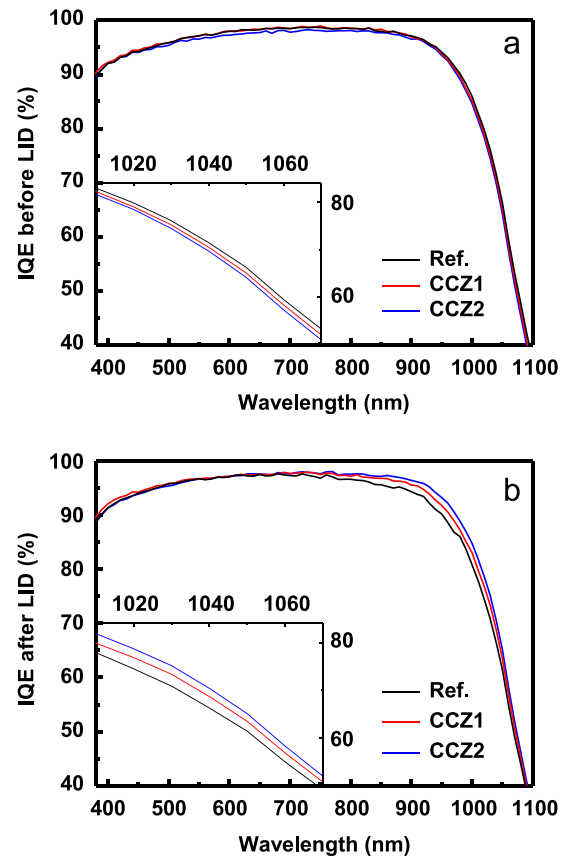


Fig. 5. IQE spectra of the reference and C co-doped silicon solar cells (a) before and (b) after illumination at room temperature for 150 h.

oxygen precipitates as discussed above. Meanwhile, the IQE of the C co-doped silicon solar cells is much better than that of the reference solar cell after LID, especially in the region from 800 to 1070 nm. It is known that IQE in the short wavelength range denotes information about the recombination in the emitter junction as well as the front surface [26], while the long wavelength region reveals messages about the quality of bulk materials and recombination at the rear side of solar cells [27]. This leads us to believe that the better response at long wavelength is ascribed to the suppression of B-O complexes in the bulk by carbon co-doping. Obviously, this effect becomes much more remarkable with the increase of co-doped [C]s, as can be seen from Fig. 5(b). This result strongly suggests that carbon co-doping has a positive influence on the performance of solar cells after LID.

Fig. 6 shows the LBIC measurements for solar cells under the same limits from 600 to 950 nm. Note that the LBIC measurement is performed on the whole solar cell and the LBIC image of every kind of solar cells in Fig. 6 are integrated by two half parts corresponding to the data before (left side) and after (right side) illumination at room temperature for 150 h, respectively. The blue regions in Fig. 6 correspond to low carrier recombination zones where the minority carrier diffusion length (L_{diff}) is large, while the red regions are related to high carrier recombination regions. Therefore, it can be seen clearly that the value of L_{diff} in the reference solar cell is slightly larger than that in the C co-doped silicon solar cells, which is caused by a smaller oxygen precipitation density. However, a significant degradation of L_{diff} in all kinds of the solar cells after LID was also observed. Moreover, the L_{diff} degradation in the reference solar cell is the most serious, and the LID effect alleviates with an increase of co-doped [C]s. This further suggests that the C co-doping is conducive to the improvement of the L_{diff} in solar cells after LID.

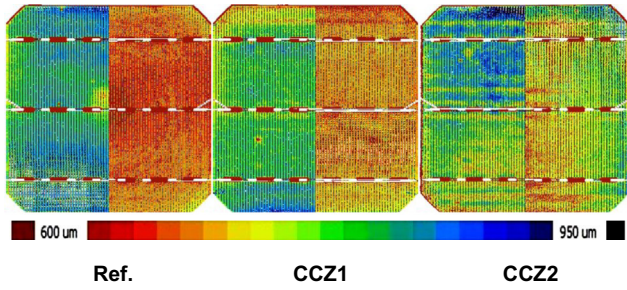


Fig. 6. Mappings of LBIC measurement for the reference and C co-doped silicon solar cells before and after illumination at room temperature for 150 h.

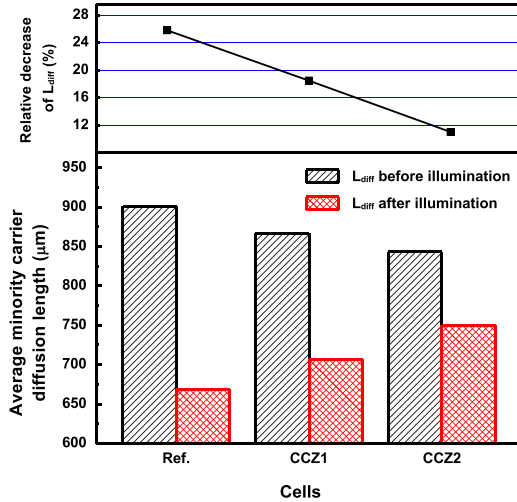


Fig. 7. Average minority carrier diffusion length of the reference and C co-doped silicon solar cells before and after illumination at room temperature for 150 h, as well as its relative decrease.

Fig. 7 shows the concrete average value of L_{diff} in these solar cells mentioned in Fig. 6, as well as its relative decrease. As we discussed above, the average value of L_{diff} in the reference cell decreases more severely than that in the C co-doped silicon solar cells. For instance, the decrease of the L_{diff} in the reference cell is more than twice as large as that in the C2 solar cells, which should be attributed to the suppression of B-O complexes by C co-doping and in turn the reduction of the bulk recombination in C co-doped silicon solar cells.

For *p*-type standard cells, L_{diff} can be expressed as follows,

$$L_{diff} = \sqrt{D_e \tau_{eff}} \quad (1)$$

where D_e is the electron diffusion coefficient and τ_{eff} is the effective minority carrier lifetime. According to Klaassen's model, the D_e is mainly influenced by ionized acceptor and donor impurities scattering, electron-hole scattering and lattice scattering [28,29]. In fact, carbon, as an isovalent impurity in silicon, is electrically inactive. Meanwhile, the concentration of C co-doped in our solar cells does not exceed $3.4 \times 10^{17} \text{ cm}^{-3}$, which could be negligible compared with the atomic density of silicon itself. Therefore, the D_e in reference and C co-doped silicon solar cells should be the same.

It is well-established that the saturated B-O complex concentration N_{∞}^* can be determined by

$$N_{\infty}^* = \frac{1}{\tau_{\infty}} - \frac{1}{\tau_0} \quad (2)$$

where τ_0 is the initial lifetime and τ_{∞} is the lifetime after illumination at room temperature for 150 h, i.e. suffered from a complete degradation [7]. Based on the discussion about D_e above and

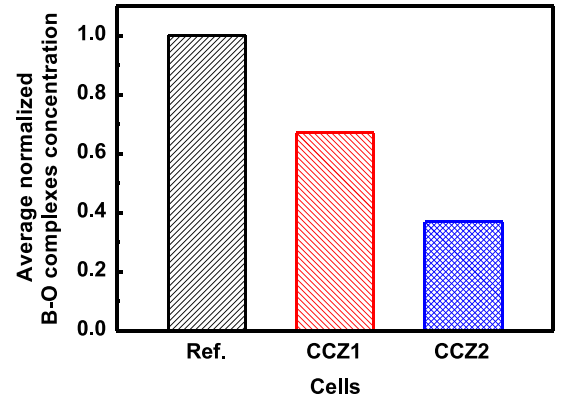


Fig. 8. Average normalized concentration of B-O complexes generated in the reference and C co-doped silicon solar cells after illumination at room temperature for 150 h.

Eq. (1), the N_{∞}^* can be further described in terms of the L_{diff} as

$$N_{\infty}^* = D_e \left(\frac{1}{L_{diff, \infty}^2} - \frac{1}{L_{diff, 0}^2} \right) \quad (3)$$

where $L_{diff, 0}$ and $L_{diff, \infty}$ are the initial and saturated minority carrier diffusion lengths, respectively. Thus the normalized concentration of B-O complexes in these solar cells is shown in Fig. 8. It should be noted that we have normalized the saturated B-O complex concentrations in the reference solar cell to 1 for better comparison. One can see that the normalized N_{∞}^* decreases with an increase of [C], which exactly coincides with those results of cell performance above. This indicates that the C co-doping can efficiently suppress the formation of B-O complexes in (c-Si), and in turn improve the performance of solar cells after LID. Even though the microstructure of B-O defect is still controversial, various models have been put forward. The classical model is that the formation of B-O defect is a process of oxygen dimer moving toward substitutional boron atom. However, Voronkov et al. have questioned the participation of oxygen dimers in the formation of B-O defects [30]. Taking into consideration the fact that the B-O complex is composed of a substitutional boron and an oxygen dimer, and the boron concentrations derived from the corresponding resistivity with ASTM F723 are almost the same in our solar cells, it naturally leads us to believe that the suppression of B-O complexes by C co-doping is associated with the reduction of O_{2i} . This conclusion is in good agreement with our previous studies [15].

So far, our results seem to indicate that even though C co-doping will detrimentally influence the initial performance of solar cells by enhancing as-grown oxygen precipitates, it is still beneficial to the performance of solar cells after LID via suppressing the formation of B-O complexes, and a higher concentration of C can cause a more significant suppression effect. However, a point that should be stressed is that an extremely high concentration of carbon co-doped in (c-Si) will trend to form silicon carbide inclusions, which might increase the cutting breakage rate of wafers and the leakage current of solar cells and therefore may be not practical for the fabrication of high efficiency solar cells [31,32].

It should be mentioned here that the efforts have been made to overcome B-O complexes related LID limitations [33], and much higher carrier lifetime can be obtained from the treatment of permanent deactivation of the B-O complexes [34]. While, it should be noted that the permanent deactivation of the B-O complexes should be done by an additional light irradiation combined with heat treatment, which cannot be accomplished on a common Al-BSF celling line. In contrast, carbon co-doping will be done during the silicon crystals growth, which has no incompatible problem with the

common ceiling line. Meanwhile, carbon co-doping is quite cheap and its positive and stabilized effect can be seen above obviously. These results make us believe that carbon co-doping is more hopefully for overcoming the lifetime limitations of the LID practically.

4. Conclusions

In summary, we have investigated the impact of C co-doping on the performance of crystalline silicon solar cells. It is found that C co-doping will deteriorate the initial performance of solar cells before LID, relying on the enhancement effect on oxygen precipitation. This is a non-negligible issue which might be overcome via thermal process elimination or passivation in the future. On the other hand, C co-doping can effectively suppress the formation of B–O complexes, and the saturated B–O complexes concentration decreases with the increase of [C]. Therefore, the performance of C co-doped silicon solar cells is better than that of conventional silicon solar cells after LID. It is believed that C co-doping in (c-Si) with an appropriate concentration could be a promising strategy of fabricating silicon solar cells with low LID in practical PV industry due to its conveniences and economy.

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