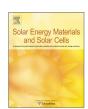
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Study on permanent deactivation of the light-induced degradation in p-type compensated crystalline silicon solar cells



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ABSTRACT

Low-cost upgraded metallurgical grade silicon (UMG-Si) with inherent boron (B) and phosphorus (P) compensation is a novel material for photovoltaic application. In this study, we demonstrate the negative impact of the light-induced degradation (LID) on the efficiency of p-type UMG-Si solar cells. By a following illumination at elevated temperatures, the LID effect in the compensated silicon solar cells can be fully deactivated, and the minority carrier diffusion length is recovered to the original level. The conversion efficiency of the compensated silicon solar cells is increased by a value of more than 3% absolutely compared to the degraded state and is quite stable under the following illumination at room temperature. It is shown that both the boron–oxygen defect density and deactivation energy mainly depend on the total boron concentration rather than the net doping concentration, which strongly suggests that boron is directly involved in the generation and deactivation of boron–oxygen defect at the solar cell level. These results are of significance for understanding the LID effect of the solar cells based on low cost UMG-Si.

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1. Introduction

Terrestrial solar cells are moving toward high efficiency and low cost. However, the currently photovoltaic (PV) industry based on p-type boron-doped Czochralski (CZ) silicon is suffering from a loss in energy conversion efficiency of up to 2-3% absolutely under sunlight illumination, due to a significant degradation of bulk carrier lifetime [1,2]. The reason is ascribed to the formation of boron–oxygen (B–O) defect under the injection of minority carriers induced either by illumination or by forward bias [3-5]. The B-O defect has a strong recombination activity and thus degrades the bulk carrier lifetime [6,7]. It can be dissociated by a 200 °C/10 min anneal in the dark and then the cell efficiency can get recovered [8,9]. However, subsequent illumination will activate the B-O defect again, resulting in renewed efficiency degradation. Recently, it has been recognized that the B-O defect can be permanently deactivated by a strategy of illumination at elevated temperatures [10,11]. The deactivation is a thermal activation process with activation energy of 0.61–0.71 eV [10–12].

Dopant compensation is a universal phenomenon for solar-grade silicon material, especially for low cost upgraded metallurgical grade (UMG) silicon. It is reported that dopant compensation has a strong influence on the properties of the B–O defect in

silicon. The density of the B–O defect mainly depends on the net doping concentration p_0 in p-type compensated silicon, while it mainly depends on the B concentration in the conventional silicon [13]. The deactivation process by illumination at elevated temperatures in p-type compensated silicon is slower than that in the conventional silicon [14]. Recently, Lim et al. have reported that the illumination at elevated temperatures cannot permanently deactivate the B–O defect in n-type compensated silicon [15].

The objective of this study is to directly investigate the deactivation of the LID effect in p-type compensated crystalline silicon solar cells by illumination at elevated temperatures. It is found that after the deactivation pretreatment, the conversion efficiency of the compensated silicon solar cells can be increased by a value of more than 3% absolutely. Afterwards, the conversion efficiency is quite stable under the following illumination at room temperature. The experiments show that both the deactivation rate and the activation energy mainly depend on the total B concentration, which suggests that B is directly involved in the deactivation of LID of solar cells.

2. Experimental procedure

Three 6 in. Czochralski silicon crystals were grown under the same conditions. One is the conventional B-doped silicon crystal for reference. The other two are compensated silicon crystals, labeled as C1 and C2, respectively. After sampling the wafers from

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 Table 1

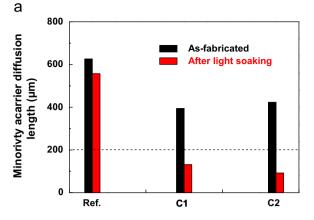
 Detailed parameters of the reference and compensated silicon wafers.

	Sample	Resistivity (Ω cm)	B concentration (cm ⁻³)	P concentration (cm ⁻³)	O concentration (cm ⁻³)
_	Reference C1 C2	2.20 0.64 2.84	$6.3 \times 10^{15} \\ 4.1 \times 10^{16} \\ 1.1 \times 10^{17}$	$\begin{array}{c} \text{NA} \\ 1.2 \times 10^{16} \\ 9.1 \times 10^{16} \end{array}$	$\begin{array}{c} 1.0\times10^{18}\\ 1.0\times10^{18}\\ 1.0\times10^{18} \end{array}$

these three crystals, the resistivity ρ of wafers was measured using the four-point-probe technique after 650 °C/30 min annealing in Ar ambient to eliminate the grown-in thermal donors (TDs). The concentrations of B and P in the compensated wafers were determined by a secondary ion mass spectrometer (SIMS), while the B concentration in the reference wafers was directly derived from the measured resistivity. The interstitial oxygen concentrations in these wafers were determined by a Fourier transform infrared spectroscope (FTIR, Bruker, IFS 66V/S) with a calibration coefficient of 3.14×10^{17} cm⁻². The detailed parameters of these wafers are shown in Table 1. All the samples were then fabricated into solar cells on the same production line at the Trina Solar Company by a standard process, including acid etching, P diffusion, anti-reflection coating deposition, screen-printing and contact firing. The solar cells were first illuminated for 12 h by a halogen lamp with a light intensity of 100 mW/cm² at room temperature. Then, the solar cells were continually illuminated at elevated temperatures for different times. Afterwards, the solar cells were again illuminated at room temperature for the investigation of the deactivation stability. The illuminated current-voltage (I-V) characteristics of the solar cells were performed under AM 1.5G (100 mW/cm², and 25 °C). The minority carrier diffusion lengths (L_{diff}) of the solar cells were derived from the light-beam-induced current (LBIC) measurement [16].

3. Results and discussion

Fig. 1 shows the minority carrier diffusion length and conversion efficiency of the solar cells before and after illumination for 12 h at room temperature. We have checked that there are no more changes in the L_{diff} and conversion efficiency with additional light soaking. Therefore, the solar cells suffer from a complete degradation. The value of L_{diff} in the compensated silicon solar cells decreases more significantly than that in the reference cells, as shown in Fig. 1(a). For instance, the $L_{\rm diff}$ in the C2 solar cells decreases by 78%, while the L_{diff} in the reference cells decreases only by 11%. It should be mentioned that after light soaking, the L_{diff} in the compensated silicon solar cells is less than the solar cell thickness, while the L_{diff} in the reference cells is still much higher than the solar cell thickness. Our previous work has reported that the value of the short-circuit current J_{sc} is very sensitive to the L_{diff} for the solar cells with the L_{diff} shorter than the solar cell thickness [17]. Therefore, it is the reason that the $J_{\rm sc}$ in the C2 solar cells decreases by 16.2%, from 35.57 mA/cm² to 29.81 mA/cm², while the J_{sc} in the reference cells decreases only by 0.7%, from 36.12 mA/ cm² to 35.85 mA/cm². As a result, the efficiencies of the C1 and C2 solar cells are decreased by a value of 2.4% and 3.9% absolutely, respectively, while that of the reference cells by a value of 0.5% absolutely, as shown in Fig. 1(b). The larger degradation in the L_{diff} and conversion efficiency of the compensated silicon solar cells should be attributed to the generation of higher density B-O defect. The B-O defect density in all these solar cells scales with the B concentration rather than the net doping concentration, which is contrary to recent lifetime results by Lim et al. [13]. After passivating the surfaces of wafers by a plasma-enhanced chemical



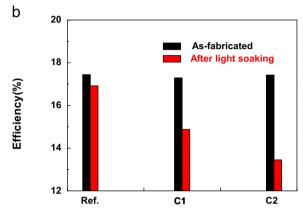


Fig. 1. (a) Minority carrier diffusion length and (b) conversion efficiency of the reference and compensated silicon solar cells before and after illumination for 12 h at room temperature. The dashed line in the Fig. 1(a) represents the value of the solar cell thickness.

vapor deposited silicon nitride (SiN:H) film, the carrier lifetimes of the degraded C1 and C2 wafers measured by a microwave–photoconductance decay system (MW–PCD) are about 7.2 μ s and 6.5 μ s, respectively. Therefore, the difference of the $L_{\rm diff}$ in the C1 and C2 solar cells should be solely due to the minority carrier mobility [18].

Fig. 2 shows the evolution of the open-circuit voltage $V_{\rm oc}$ and conversion efficiency of the solar cells by illumination at 200 °C. Note that both $V_{\rm oc}$ and conversion efficiency of these solar cells can get fully recovered after some time. It can be seen that the recovering time constant for the reference cells is about 10 min, while it is about 60 and 100 min for the C1 and C2 solar cells, respectively. This indicates that the recovering process of the compensated silicon solar cells needs more time than that of the reference cells.

Fig. 3 shows the dependence of the $V_{\rm oc}$ and conversion efficiency of the solar cells on the illumination time at room temperature after processing the deactivation pretreatment by illumination at 200 °C/3 h. It can be seen that no efficiency degradation is discernible after illumination for 12 h at room temperature. Noticeably, the stable conversion efficiency of the C2 solar cells is 17.3%. To our best knowledge, this is the highest stabilized efficiency reported for the solar cells based on such highly-doped and compensated material.

Fig. 4 shows the $L_{\rm diff}$ of the solar cells before and after illumination for 12 h at room temperature as well as firstly processing the deactivation pretreatment by illumination at 200 °C/3 h and then illumination for 12 h at room temperature. It can be seen that after processing the deactivation pretreatment, the $L_{\rm diff}$ of the solar cells could get fully recovered and decay no

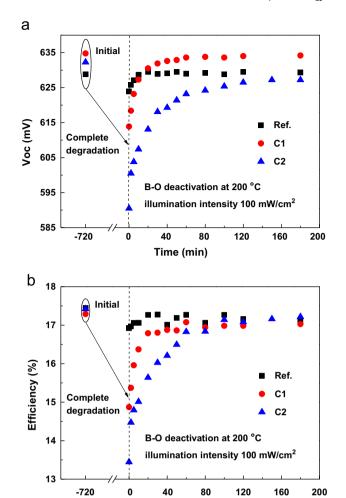


Fig. 2. Evolution of (a) the open-circuit voltage and (b) conversion efficiency of the reference and compensated silicon solar cells which are illuminated at 200 °C. Prior to the deactivation procedure, all the solar cells have performed the complete degradation by illumination for 12 h at room temperature.

Time (min)

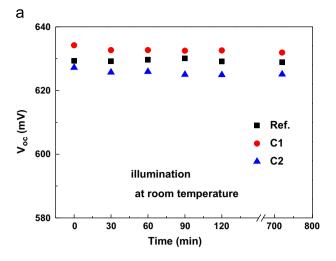
longer under the continual illumination at room temperature. Therefore, the B–O defect responsible for the LID in the compensated silicon solar cells could be permanently deactivated by illumination at elevated temperatures. It suggests that the deactivation strategy could supply an effective way to the improvement of the stable $L_{\rm diff}$ in the UMG-Si solar cells.

Fig. 5 shows the evolution of the $V_{\rm oc}$ in the C2 solar cells which are illuminated at elevated temperatures. It can be seen that with the temperature increasing, the deactivation process in the C2 solar cells proceeds faster in the temperature range from 160 to 200 °C. The normalized concentration (N^*) of the light-induced B–O defect can be described by the $V_{\rm oc}$ under illumination as follows [19]:

$$N^* = \frac{1}{\exp[mqV_{oc}(t)/k_BT]} - \frac{1}{\exp[mqV_{oc}(t=0)/k_BT]}$$
 (1)

$$N^*(t,T) = N^*(t \to \infty)[1 - \exp(-R_{de}t)]$$
 (2)

where $k_{\rm B}$ is the Boltzman constant, T is the absolute temperature and m is the ideality factor. Dubois et al. have reported that m is equal to 1 for the solar cells with the $L_{\rm diff}$ longer than the solar cell thickness, while it is equal to 2 for the solar cells with the $L_{\rm diff}$ smaller than the cell thickness [20]. During the deactivation process, the $L_{\rm diff}$ in the compensated silicon solar cells shows a very large variation, which results in the value of m changing from



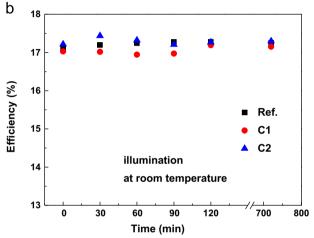


Fig. 3. Time dependence of (a) the open-circuit voltage and (b) conversion efficiency of the reference and compensated silicon solar cells during illumination at room temperature. No efficiency degradation is discernible after illumination for 12 h at room temperature.

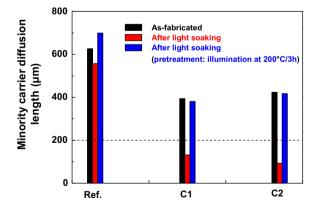


Fig. 4. Minority carrier diffusion length in the reference and compensated silicon solar cells before and after illumination for 12 h at room temperature as well as firstly processing the deactivation pretreatment by illumination at 200 $^{\circ}$ C/3 h and then illumination for 12 h at room temperature.

2 to 1. Therefore, the Eqs. (1) and (2) will be invalid for directly describing the deactivation kinetics in the compensated silicon solar cells. As can be seen from Figs. 2 and 5, the values of the $V_{\rm oc}$ show a logarithmic scale with time. We use the logarithmic fitting

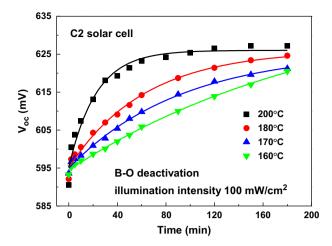


Fig. 5. Evolution of the open-circuit voltage of the C2 solar cells which are illuminated at elevated temperatures between 160 and 200 $^{\circ}$ C.

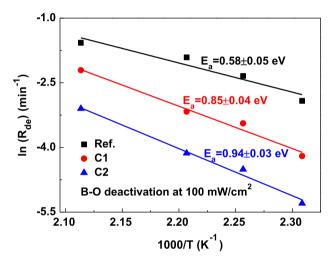


Fig. 6. Arrhenius plot of the deactivation rate $R_{\rm de}$ for the reference and compensated silicon solar cells. The $R_{\rm de}$ for the compensated cells is lower than that for the reference cells, and the activation energy $E_{\rm a}$ for the compensated silicon solar cells is higher than that for the reference cells.

of the $V_{\rm oc}$ to describe the deactivation kinetics as follows:

$$V_{oc}(t,T) = V_{oc}(t \to \infty)[1 - \exp(-R_{de}t)]$$
(3)

Note that even though the B–O defect is fully activated, the $L_{\rm diff}$ in the reference cells is still much higher than the solar cell thickness. So, the Eqs. (1) and (2) will be still available for describing the deactivation kinetics in the reference cells. Therefore, it is possible to compare the difference of two methods by analyzing the results from the reference cells. The time constant of the deactivation rate $R_{\rm de}$ by illumination at 200 °C for the reference cells based on the Eq. (3) is 4.81 min, which is basically in agreement with the value of 4.55 min based on the Eqs. (1) and (2). This suggests that the logarithmic fitting of the $V_{\rm oc}$ is suitable to describe the deactivation kinetics.

Fig. 6 shows the temperature dependence of the $R_{\rm de}$ for the compensated and reference silicon solar cells. It can be seen that the value of $R_{\rm de}$ for the compensated silicon solar cells is lower than that for the reference cells at all temperatures. Noticeably, the $R_{\rm de}$ for the C2 solar cells is the lowest. Note that the $R_{\rm de}$ for these solar cells is an exponential function of temperature, which can be

presented as

$$R_{de}(T) = k_o \exp\left(-\frac{E_a}{k_B T}\right) \tag{4}$$

where $k_{\rm o}$ is the pre-exponential factor and $E_{\rm a}$ the activation energy. By fitting the experimental data, the value of $E_{\rm a}$ can be derived, as shown in Fig. 6. It can be seen that the value of the $E_{\rm a}$ for the reference cells is 0.58 eV, which agrees well with the values reported in the conventional silicon wafers [10,11]. However, the values of the $E_{\rm a}$ for the C1 and C2 solar cells are 0.85 eV and 0.94 eV, respectively, which are much higher than that for the reference cells. Since the C1 sample has the highest $p_{\rm 0}$ and the C2 sample has the highest B concentration, the experiments evidence that both the $R_{\rm de}$ and $E_{\rm a}$ mainly depend on the total B concentration rather than on the $p_{\rm 0}$. The results strongly suggest that B is directly involved in the deactivation of LID of solar cells.

4. Conclusions

In summary, we have demonstrated the effectiveness of the B–O defect permanent deactivation in p-type UMG silicon at the cell level. After processing a deactivation pretreatment, the conversion efficiency of the compensated silicon solar cells is increased by a value of more than 3% absolutely, compared to the degraded state. In agreement with other lifetime studies, the deactivated state is shown to be stable upon subsequent illumination at room temperature. The boron–oxygen defect density and deactivation energy mainly depend on the total boron concentration rather than the net doping concentration, which strongly suggests that boron is directly involved in the generation and deactivation of B–O defect at the solar cell level. These results are of significance for understanding the LID effect of solar cells based on low cost UMG silicon.

Acknowledgments

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