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The Impact of Thermal Treatment on Light-Induced Degradation of Multicrystalline Silicon PERC Solar Cell

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Received: 31 December 2018; Accepted: 24 January 2019; Published: 29 January 2019

Abstract: Multicrystalline silicon (mc-Si) PERC (passivated emitter and rear cell) solar cells suffer from severe light-induced degradation (LID), which mainly consists of two mechanisms, namely, BO-LID (boron–oxygen complex-related LID) and LeTID (light and elevated temperature induced degradation). The impact of thermal treatment on the LID of a mc-Si PERC solar cell is investigated in this work. The LID of mc-Si PERC solar cells could be alleviated by lowering the peak temperature of thermal treatment (namely sintering), perhaps because fewer impurities present in mc-Si tended to dissolve into interstitial atoms, which have the tendency to form LeTID-related recombination active complexes. The LID could also be effectively restrained by partially replacing the boron dopant with gallium, which is ascribed to the decreased amount of boron–oxygen (B–O) complexes. This work provides a facile way to solve the severe LID problem in mc-Si PERC solar cells in mass production.

Keywords: multicrystalline silicon PERC solar cell; light-induced degradation; thermal treatment; dopant

1. Introduction

The light-induced degradation (LID) phenomenon in crystalline silicon solar cell was first observed by Fischer and Pschunder in 1973 [1]. However, at that time this phenomenon was not taken seriously because improving the photoelectric conversion efficiency was the main concern. When crystalline silicon solar cells began to be practically applied in photovoltaic power plants, the LID gradually attracted more attention in consideration of the long-term output power stability and the cost per kilowatt-hour. At present, it is generally known that the LID in monocrystalline silicon PERC (passivated emitter and rear cell) solar cells is linked to boron–oxygen complexes, and is referred to as BO-LID [2]. However, in addition to BO-LID, there is another LID mechanism affecting the multicrystalline silicon (mc-Si) PERC solar cell, which is called light and elevated temperature induced degradation (LeTID) [3]. Owing to this, mc-Si PERC solar cells suffer severe performance degradation after prolonged exposure to light. Although several defect models have been proposed [4–6], the

LeTID mechanism is not yet fully understood. The greater amount of impurities present in mc-Si is generally considered to be responsible for the LeTID [7].

Several methods have been proposed to restrain the LID in mc-Si PERC solar cells, which are as follows: (1) lowering the sintering peak temperature [8–10]; (2) adopting gallium-doped silicon; (3) the regeneration of light-induced defects [11–13]; (4) adopting N-type silicon. In this work, the first two methods were investigated with the aim of solving the severe LID problem in mc-Si PERC solar cells.

2. Materials and Methods

Boron-doped mc-Si sister wafers (GCL S3L) with length of 156.75 mm, thickness of 180 μm, and resistivity of about 2 Ω·cm were adopted. By using sister wafers, comparable material quality as well as very similar grain and defect structure can be achieved [14]. The manufacturing process flows of an mc-Si PERC solar cell and a corresponding lifetime sample are shown in Figure 1.

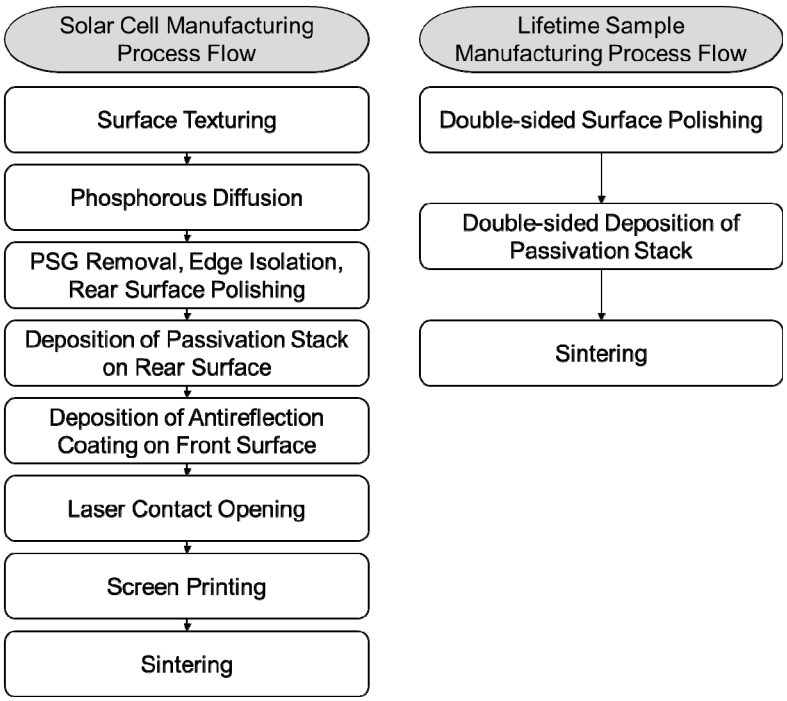

Figure 1. Manufacturing process flows of multicrystalline silicon (mc-Si) passivated emitter and rear cell (PERC) solar cell and corresponding lifetime sample.

As for the solar cell, the as-cut mc-Si wafers were first textured with an acidic etching solution. Then, the samples were transferred into a tubular furnace to complete the phosphorous diffusion and the emitter formation. Subsequently, the phosphosilicate glass (PSG) removal, edge isolation, and rear surface polishing were accomplished with a wet etching technique. After that, a passivation stack (Al_2O_3/SiN_x) and an antireflection coating (SiN_x) were deposited by plasma-enhanced chemical vapor deposition (PECVD) on the rear and front surfaces, respectively. After the Al_2O_3/SiN_x stack was locally opened by laser ablation, the electrode pastes (i.e., rear-side silver, rear-side aluminum, and front-side silver) were screen-printed and dried. Finally, the samples were sintered in a mesh belt furnace to complete the metallization and finish the solar cell manufacturing process. Different peak temperatures were applied in the sintering (thermal treatment) process—which is also called rapid thermal annealing (RTA) [15]—to study the effects on the LID of mc-Si PERC solar cells.

As for lifetime sample, the as-cut mc-Si wafers were first polished on both sides with a concentrated alkaline etching solution. Subsequently, the passivation stack (i.e., Al_2O_3/SiN_x) was deposited by PECVD on both sides. Finally, the samples were also submitted to the sintering process,

which ensured the same thermal history as the solar cell. Likewise, the peak sintering temperature was adjusted to investigate the influence on the LID of the corresponding mc-Si PERC solar cell.

Additionally, gallium-doped mc-Si sister wafers (GCL S4) with the same length, thickness, and resistivity as boron-doped wafers were also adopted to fabricate PERC solar cells. Note that these wafers were co-doped with gallium and boron, but for simplicity, gallium-doped wafer is used to refer to this kind of wafer in this report. The boron concentration in gallium-doped mc-Si was much lower than in the boron-doped mc-Si.

For the lifetime sample, the injection-dependent carrier lifetime was measured by the QSSPC (quasi-steady-state photoconductance decay) method with Sinton WCT-120 [16], and the lifetime at a fixed excess carrier density of 1×10^{15} cm^{-3} was extracted. In order to simplify the analysis of actual defect concentration, the normalized defect concentration concept was introduced here according to the Shockley-Read-Hall theory, as shown below:

$$N_t = \frac{1}{\tau_d} - \frac{1}{\tau_0} \propto N_{defect} \quad (1)$$

The normalized defect concentration (N_t) is proportional to the actual concentration (N_{defect}) [17]. The effective minority carrier lifetime before and after degradation are labeled as τ_0 and τ_d, respectively. The corresponding fitting equation is as below:

$$N_t = N_t^*[1 - \exp(-R_{gen}t)], \quad (2)$$

where N_t* and R_{gen} stand for the saturation defect concentration and defect generation rate, respectively [18].

For the solar cell, the photovoltaic performance was measured with a pulsed solar simulator (Halm). The external quantum efficiency was measured with a QEX10 spectral response measurement system (PV Measurements).

During the light-induced degradation process, the lifetime samples and solar cells were illuminated with halogen lamps at the light intensity of 600 W/m^2 and the temperature of 65 °C.

3. Results and Discussion

3.1. Lifetime Sample

Figure 2a shows the effective minority carrier lifetime decay at the injection level of 1×10^{15} cm^{-3} due to illumination for a boron-doped mc-Si lifetime sample with symmetrical passivation structure and sintering peak temperature of 805 °C. The normalized defect concentrations N_t related to illumination time, as shown in Figure 2b, were calculated according to the effective minority carrier lifetime decay. After fitting (the red curve), the values of N_t* and R_{gen} were extracted, which were 0.00464 μs^{-1} and R_{gen} 0.17 min^{-1}, respectively. Because of the limited illumination time (i.e., 30 min), this fitting result is believed to be associated with the BO-LID mechanism only, while the LeTID mechanism takes effect over a much longer period of time.

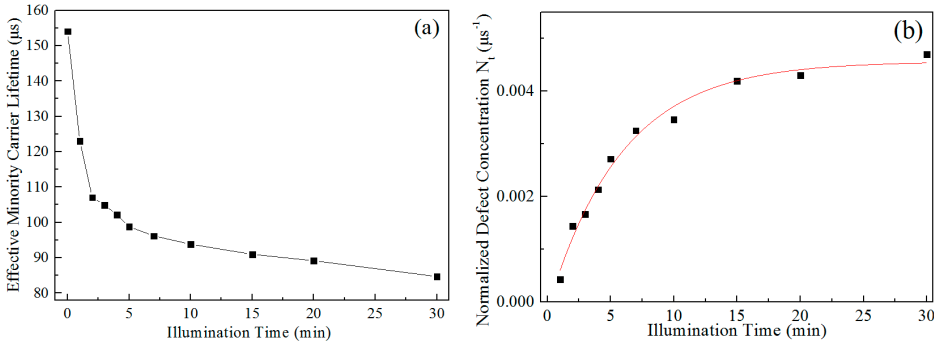

Figure 2. (**a**) Effective minority carrier lifetime decay of a boron-doped mc-Si lifetime sample with symmetrical passivation structure and sintering peak temperature of 805 °C due to illumination at $\Delta n = 1 \times 10^{15}$ cm^{-3}; (**b**) Normalized defect concentrations N_t calculated according to the effective minority carrier lifetime decay. The red curve is the fitting result.

The initial effective minority carrier lifetimes at $\Delta n = 1 \times 10^{15}$ cm^{-3} of boron-doped mc-Si lifetime samples with symmetrical passivation structure were measured after sintering with different peak temperatures, as shown in Figure 3. It was found that along with the decrease of sintering peak temperature from 855 to 685 °C, the initial effective lifetime increased from 66.5 to 134.5 μs. Besides, the degradation ratio after 5 h of illumination also benefited from the lower sintering peak temperature, as shown in Figure 3. However, note that despite the higher initial effective lifetime and lower degradation ratio, the metallization of corresponding solar cell must be taken into account when lowering the sintering peak temperature [19].

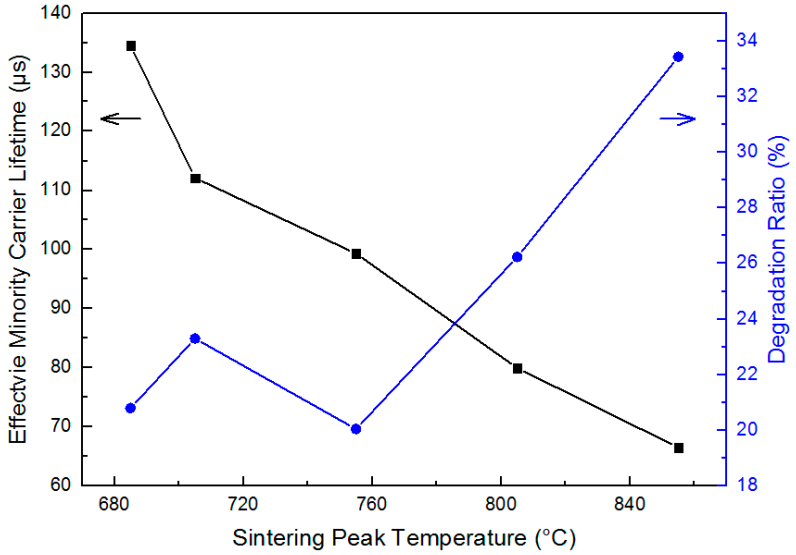

Figure 3. Initial effective minority carrier lifetimes (black squares) at $\Delta n = 1 \times 10^{15}$ cm^{-3} after sintering with different peak temperatures of boron-doped mc-Si lifetime samples with symmetrical passivation structure. The corresponding degradation ratios after 5 h of illumination are shown as blue circles.

3.2. mc-Si PERC Solar Cell

The photovoltaic parameters of mc-Si PERC solar cells with different dopants (i.e., boron or gallium) and sintering peak temperatures degraded under illumination, as shown in Figure 4. In consideration of the metallization, only two peak temperatures were adopted (i.e., 785 and 805 °C). The corresponding degradation ratios after 240 h of illumination are summarized in Table 1. It is obvious that the degradation of the boron-doped mc-Si PERC solar cell was much more serious than the gallium-doped one with the same sintering peak temperature (785 °C), which can be

ascribed to the more severe BO-LID existing in the boron-doped mc-Si with much higher boron concentration. By comparing two gallium-doped samples with different sintering peak temperatures (785 vs. 805 °C), it was found that lowering the temperature moderately was beneficial for the suppression of LID, which was mainly due to the LeTID mechanism here because of the much lower boron concentration. According to the report by Bredemeier et al. [20], when the sintering peak temperature declines, less impurities present in mc-Si can dissolve into interstitial atoms, which form LeTID-related recombination active complexes. From Table 1, the efficiency degradation ratio of the mc-Si PERC solar cell after 240 h of illumination could be improved significantly from 5.18% (boron-doped, 785 °C) to 2.73% (gallium-doped, 785 °C).

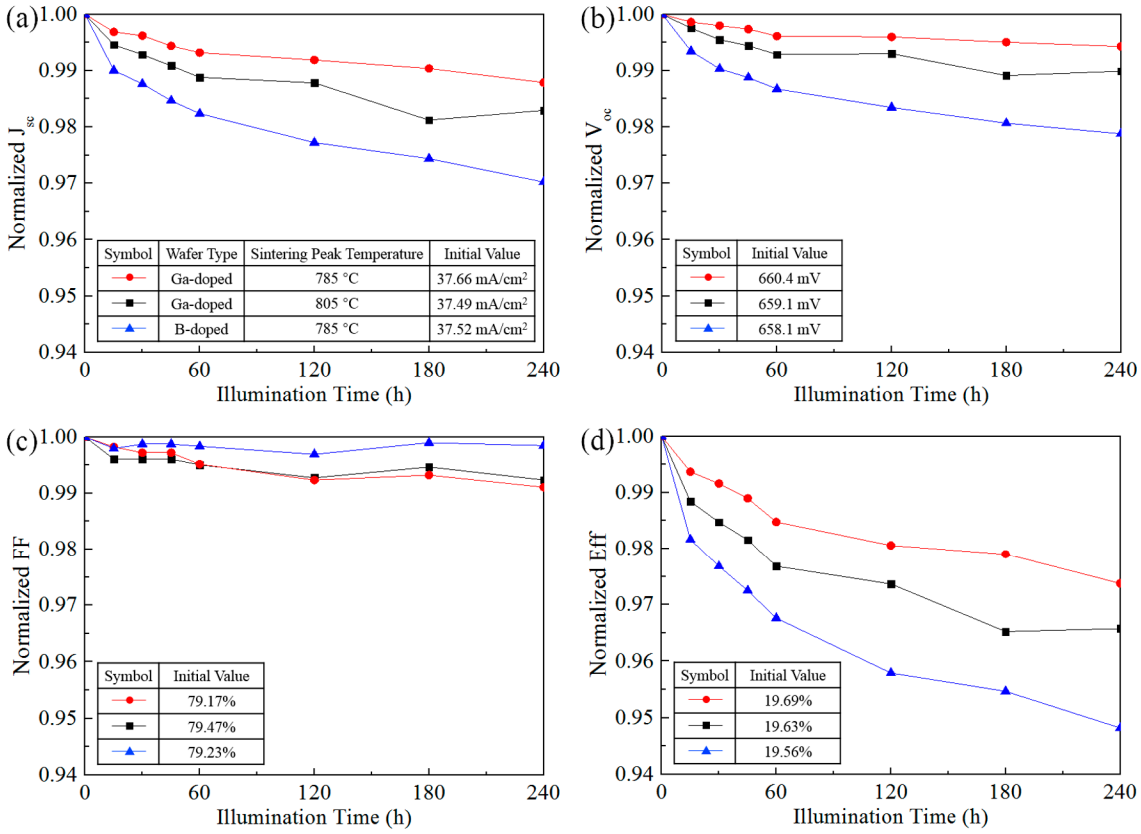

Figure 4. (**a**) Short circuit current density decay, (**b**) open circuit voltage decay, (**c**) fill factor decay, and (**d**) conversion efficiency decay of mc-Si PERC solar cells with different dopants (i.e., boron or gallium) and sintering peak temperatures (785 or 805 °C) due to illumination. These data were normalized, and the corresponding initial values are listed. For each kind of solar cell, 10 samples were chosen at random, and the average values of photovoltaic parameters and degradation ratios were extracted.

Table 1. Change in short circuit current density (J_{sc}), open circuit voltage (V_{oc}), fill factor (FF) and conversion efficiency (Eff) of mc-Si PERC solar cells with different dopants (i.e., boron or gallium) and sintering peak temperatures (785 or 805 °C) after 240 h of illumination.

Wafer Type	Sintering Peak Temperature (°C)	ΔJ_{sc} ($\%_{rel}$)	ΔV_{oc} ($\%_{rel}$)	ΔFF ($\%_{rel}$)	ΔEff ($\%_{rel}$)
Ga-doped	785	−1.23	−0.62	−0.91	−2.73
Ga-doped	805	−1.71	−1.02	−0.77	−3.46
B-doped	785	−2.98	−2.12	−0.16	−5.18

External quantum efficiency curves of mc-Si PERC solar cells with different dopants (i.e., boron or gallium) and sintering peak temperatures (i.e., 785 or 805 °C) were measured before and after 240 h of illumination, as shown in Figure 5a. For the sake of observation, the external quantum efficiency decline was calculated, and is displayed in Figure 5b. It was found that with the same sintering

peak temperature of 785 °C, the spectral response of the boron-doped sample began to degrade at a wavelength of about 650 nm after illumination, while the gallium-doped sample began to degrade at a longer wavelength (about 850 nm). Besides, the boron-doped sample had much more serious degradation than the gallium-doped one at wavelengths above 850 nm. We thus concluded that the much more plentiful boron–oxygen (B–O) complexes present in boron-doped mc-Si seemed to severely influence the base effective diffusion length [21]. By comparing the gallium-doped samples with different sintering peak temperatures, the lower temperature was found to be beneficial for the suppression of quantum efficiency degradation at long wavelengths. According to the report of Luka et al. [22], the dissolved impurities due to sintering may accumulate at the rear surface of mc-Si and form LeTID-related recombination active complexes, which affect the passivation effect of the Al_2O_3/SiN_x stack. This explains why the quantum efficiency degradation worsened only at long wavelengths for gallium-doped samples when increasing the sintering peak temperature.

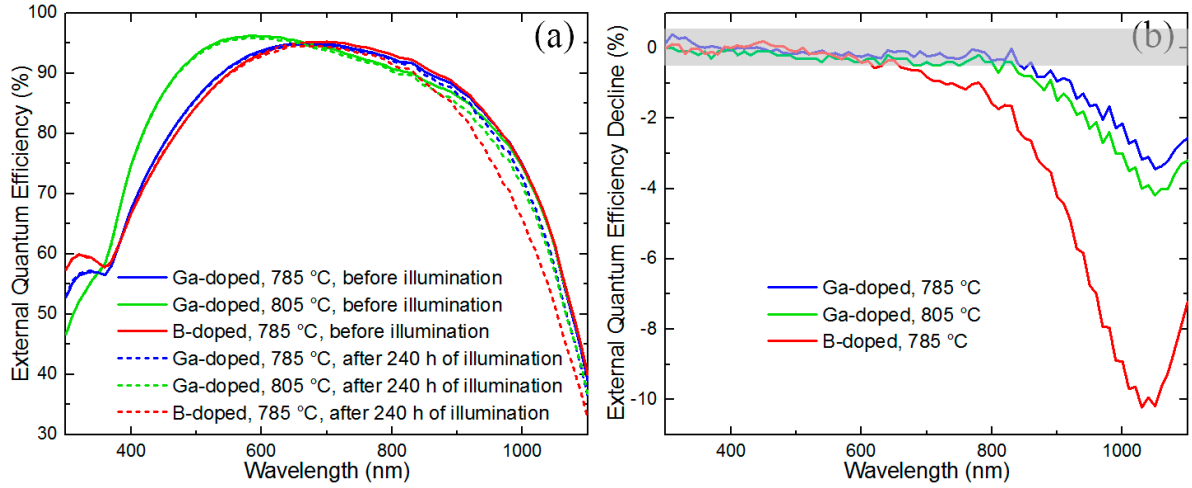

Figure 5. (**a**) External quantum efficiency curves of mc-Si PERC solar cells with different dopants (i.e., boron or gallium) and sintering peak temperatures (i.e., 785 or 805 °C) before and after 240 h of illumination. (**b**) Calculated external quantum efficiency decline curves. The grey area represents the fluctuation range (±0.5%), in which the value change is considered as the measurement tolerance.

Apart from the impurities existing in mc-Si, Fung et al. speculated that the hydrogen coming from the dielectric layers has a major impact on the LeTID [4]. When the sintering peak temperature changes, the amount and bound state of hydrogen varies correspondingly, which influences the LeTID. This interpretation explains why the higher sintering peak temperature led to more severe efficiency degradation after illumination for gallium-doped samples, but cannot explain why the quantum efficiency degradation only worsened at long wavelengths. Therefore, according to the results in this report, the interpretation of Luka et al. [22] seems to be more reasonable.

4. Prospect

It can be concluded from the above that lowering the sintering peak temperature and adopting gallium-doped silicon are effective methods to restrain the light-induced degradation of mc-Si PERC solar cells. However, in consideration of the metallization of solar cells, the adjustment range of sintering peak temperature is limited. Therefore, constrained by the present technical level of metallization paste, it is difficult to further suppress the LID of mc-Si PERC solar cells with screen-printing technology. The high-temperature sintering can be avoided by adopting another industrial metallization method such as plating. Accordingly, the LeTID-related recombination active complexes accumulated at the rear surface of mc-Si due to sintering [22] are expected to be eliminated, which ensures the passivation effect of the Al_2O_3/SiN_x stack and significantly inhibits the LeTID. On the other hand, it is known that most of the gallium-doped mc-Si wafers on the market—such as GCL

G4 used in this report—are co-doped with boron, which is largely owing to the small segregation coefficient of gallium in silicon. It is believed that along with the development of casting technology, gallium single-doped mc-Si wafers will overcome the problem of broad resistivity distribution. By then, by replacing the co-doped mc-Si wafers with single-doped ones, the BO-LID will be further inhibited. Ultimately, combining these two improved methods will lead to a full suppression of the LID of mc-Si PERC solar cells, which consists of LeTID and BO-LID.

However, we are presently looking for an easily and rapidly realized method in our production line to further suppress the LID of mc-Si PERC solar cells. Regeneration has been demonstrated to passivate the light-induced defects effectively, which include both LeTID-related and BO-LID-related defects [11–13]. Besides, only a simple carrier injection device needs to be added to complete the regeneration process. Consequently, regeneration of the light-induced defects in mc-Si PERC solar cells is the next research direction.

In terms of cost, the price of one co-doped mc-Si wafer was about 0.2 RMB higher than that of a boron-doped wafer a year ago. At present, the price gap has been reduced to about 0.02 RMB. However, the unit price of gallium single-doped mc-Si wafer is not available right now, because we have not found a company supplying the commercial version of this kind of wafer. The regeneration device costs only about 0.5 million RMB, which is quite cheap compared with the other equipment in solar cell production lines. As for the plating device, the investment cost is relatively high. Nevertheless, in spite of the high price of more than 10 million RMB per device, the total cost of ownership is only about 0.1 RMB/Wp due to the much lower cost of consumables. On the other hand, on account of the expensive silver pastes, the total cost of ownership is about 0.3 RMB/Wp for screen-printing technology.

5. Conclusions

Multicrystalline silicon PERC solar cells suffer from severe LID, which mainly consists of two mechanisms—namely, BO-LID and LeTID. By lowering the peak temperature of thermal treatment (i.e., sintering), higher initial effective minority carrier lifetime and lower degradation ratio due to illumination can be achieved for boron-doped mc-Si samples with symmetrical passivation structure. However, for mc-Si PERC solar cells, the decline of sintering peak temperature should be restricted with the quality of metallization. By combining the moderate decline of sintering peak temperature and the partial alternation of dopants from boron to gallium, the photovoltaic parameter degradation ratios of mc-Si PERC solar cells after illumination can be improved significantly. It was found that the impurities existing in mc-Si may dissolve into interstitial atoms, which accumulate at the rear surface of mc-Si and form LeTID-related recombination active complexes, affecting the passivation effect of the Al_2O_3/SiN_x stack. Therefore, the quantum efficiency degradation under illumination worsened when increasing the sintering peak temperature only at long wavelengths for gallium-doped samples. With regard to the boron-doped case, the spectral response began to degrade at a much shorter wavelength under illumination, which means that the much greater quantity of boron–oxygen (B–O) complexes in boron-doped mc-Si seem to severely influence the base effective diffusion length. Finally, a conversion efficiency degradation ratio as low as 2.73% after 240 h of illumination at the light intensity of 600 W/m^2 and the temperature of 65 °C was achieved for an mc-Si PERC solar cell. This work provides a facile way to solve the severe LID problem of mc-Si PERC solar cells in mass production.

Author Contributions: Investigation and writing—original draft preparation, S.Z. and J.P.; Conceptualization and methodology, H.Q. and W.L.; Supervision, H.S.; Project administration, Q.W.; Resources, Z.N.; Writing—review and editing, J.J., X.Z., and L.X.

Funding: This research received no external funding.

Conflicts of Interest: The authors declare no conflict of interest.

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