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The role of hydrogen for crystalline silicon solar cells

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Hydrogen plays a significant role in the hydrogenation and hydrogen-induced degradation (HID) of crystalline silicon solar cells. In solar cells, the main hydrogen source was contributed from hydrogenated silicon nitride (SiN_x: H) to enhance the surface and bulk passivation. This paper depicts a review of the current investigations on mechanisms of hydrogen in the silicon bulk and the defects passivation through manipulating the charge states of hydrogens. Based on the passivation mechanism, we introduced four convertible states of boron-oxygen (BO) related defects in help of understanding the degradation suppression of P-type crystalline silicon. It explains the mechanism of light-induced degradation (LID) because most industrial solar cells are based on boron-doped silicon wafers. Also, we introduced new light sources of laser and light-emitting diodes (LEDs) in the application of hydrogenation. We also explained an efficiency loss that emerged in hydrogenation processes which is considered to be related to the injection of excess hydrogens, similar to the HID of light and elevated temperature induced degradation (LeTID). In the conclusion, optimized methods and conditions of advanced hydrogenation for silicon solar cells are proposed, which can further improve the electrical performance and enhance the stability of silicon solar cells.

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Keywords: Boron-oxygen related defects, Crystalline silicon, Hydrogenation, Hydrogen-induced degradation, Light-induced degradation

1. Introduction

With the continuous optimization of the world's energy structure in recent years, the photovoltaic (PV) industry has received extensive attention and obtained great development under expectations. Among of types of PV productions, crystalline solar cells dominated the fast development, which has championed the market in renewable energy.

In PV field, hydrogenated silicon nitride (SiN_x: H) dielectric film deposited by Plasma Enhanced Chemical Vapor Deposition (PECVD) has attracted much attention due to its excellent anti-reflection properties and surface passivation quality [1-3]. SiN_x: H film was introduced as antireflection coatings, and played the role of surface and bulk passivation, thus improving the Power Conversion Efficiency (PCE) of crystalline silicon solar cells [2-3]. In 2001, J. Schmidt et al. investigated the surface passivation properties of SiNx: H films fabricated by high-frequency direct PECVD on low-resistivity (1 Ω·cm) p-type silicon substrates, and resulted in outstandingly low surface recombination velocities (SRV) below 10 cm/s [4]. Moreover, SiN_x: H film deposited by PECVD is a kind of hydrogen-rich amorphous film, among which contains the smallest atom of hydrogen with a strong permeability [2-3].

In 2009, K. A. Münzer directly proved that hydrogen was required to participate in the recovery of degradation, and published the research results in 24th European Photovoltaic Solar Energy Conference (EU PVSEC) [5], as shown in Fig. 1.

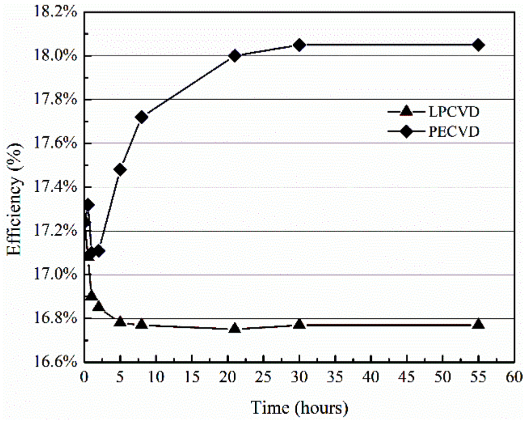


Fig. 1. Comparison of efficiency recovery of silicon solar cells treated with degradation based on PECVD and LPCVD processes [5] (Reproduced with permission. [Ref.5] Copyright of ©2009, 24th European Photovoltaic Solar Energy Conference) (color online)

The results indicated that there would be different performances in the solar cells by respectively using PECVD and Low Pressure Chemical Vapor Deposition

(LPCVD) to deposit SiN_x layer onto the surface of silicon with long time of degradation treatment.

According to the Fig. 1, the conversion efficiency of solar cells with SiN_x: H prepared by LPCVD did not recover after light soaking, and remained in a low attenuation state at last, while the conversion efficiency of the solar cells with SiN_x: H prepared by PECVD began to recover gradually after degradation. The main reason is that the conversion efficiency of solar cells with SiN_x film deposited by LPCVD cannot been restored due to the missing of hydrogen source [5]. As a result, the defects cannot be passivated during long-time degradation. However, the SiN_x: H film deposited by PECVD is abundant hydrogen [2-3], hence the conversion efficiency can be gradually restored during degradation treatment. Therefore, hydrogen played a significant role in the whole recovery of conversion efficiency. Then, the research on hydrogen's participation in suppressing degradation gradually became a hot issue as the rapid expansion of Passivated Emitter and Rear Contact (PERC) solar cells.

With the development of PV technology, PECVD also was applied to deposit hydrogenated aluminum oxide (AlO_x: H) film that also contained abundant hydrogen [6-7]. The AlO_x: H film can provide an outstanding rear surface passivation and back reflection for crystalline silicon solar cells [8-9], which is beneficial to the minority carrier lifetime of PERC solar cells [10]. Therefore, hydrogen also plays a crucial role in passivation of rear surface.

As the rapid industrialization and promotion of PERC solar cells around 2015, the light-induced degradation (LID) on solar cells has been widely discussed again [11]. After years of hard work, the researchers finally found out that the boron-oxygen (BO) related defects was responsible for LID in p-type Czochralski (Cz) silicon solar cells [12-13]. Since the development of high efficiency PERC solar cells, LID became an increasing role in the quality characterization of silicon solar cell. Hence, the suppression of LID gradually become one of the key points for PERCs.

Some researchers began to gradually develop some technologies or measures to suppress LID, such as dark annealing [14] or illumination and heating [15-16], which is called hydrogen passivation. After treatment, the bulk minority carrier lifetime and conversion efficiency of crystalline silicon solar cells can be improved. It is generally acknowledged that the hydrogen from SiNx: H film penetrated into the silicon bulk and passivated the defects or dangling bonds at grain boundaries [17-18]. Under appropriate conditions, hydrogen from SiN_x: H or AlO_x: H films can diffuse into crystalline silicon solar cells and interact with impurities or defects, achieving the conversion efficiency improvement of crystalline silicon solar cells [19-21].

Over the years, researchers have carried out rich research on the effect of hydrogen in LID and hydrogenation, but systematic review on the role of hydrogen was missing. In this review, the charge state of hydrogen and the interaction and transport of hydrogen and impurities from the microscopic level were summarized for the first time, which was crucial to understanding the mechanism of LID and hydrogenation. Based on the role of hydrogen, the mechanisms of LID, hydrogenation and hydrogen-induced degradation (HID) were described, respectively. Then, fast LID treatment was developed to further improve hydrogenation effect.

Additionally, non-equilibrium carriers were noticed to assist the understanding of hydrogen passivation to distinguish the hydrogen passivation process from annealing, which could be called as Advanced Hydrogen Passivation or Hydrogenation. The role of hydrogen in crystalline silicon solar cells discussed in this paper referred to the hydrogen function and dynamic mechanism in hydrogenation, which was reviewed in detail to further clarify the significance of hydrogen in improving conversion efficiency and inhibiting degradation.

2. Advanced hydrogenation for Si solar cells

2.1. The charge states of hydrogen

Note, the major difference between Hydrogenation and conventional hydrogen passivation is the regulation of hydrogen charges by non-equilibrium carriers. The charge state of the diffused hydrogen can be adjusted by tuning the Fermi level in the cell through heating, light irradiation and charge injection [22-24]. Many defects in solar cells are charged defects. For instance, the commonly manufactured p-type crystalline silicon solar cells, minority carrier is electron with negative charge. Therefore, the defect state with the greatest impact on minority carriers is generally positive, such as the boron oxide complex which causes LID. Hence, by adjusting the charge state of hydrogen to form H^-, hydrogenation makes the passivation more efficient and stable compared to conventional hydrogen passivation. Generally, to speed up the process of hydrogenation, thermal treatment and light irradiation, thermal and electric injection are currently applied simultaneously. Therefore, hydrogenation with photon injection is named as HPI and the hydrogenation with electron injection is named as HEI.

The charge states of hydrogen in crystalline silicon could be positive (H^+), negative (H^-) and neutral (H^0) under the irradiation of light at a specific wavelength. [25-26]. These charge states are mainly determined by the effective carrier concentration (hole and electron) in silicon [27-28]. Among these three states, H^0 has a great advantage in transport due to its neutral property, which cannot be affected by the fixed charge defect and external electric field [29-30]. Meanwhile, H^0 has a great advantage in passivation, because it contains one free electron. Hence, H^0 can easily capture an electron to form H^-, or lose an electron to form H^+, so that H^0 can bind impurities with positive or negative charges. The high reactivity of H^0 influenced the concentration of H^0 in silicon.

The equilibrium charge state fractions of hydrogen are determined by Fermi level. Herring et al. reported that the donor level of hydrogen is 0.16 eV below the silicon conduction band, and the acceptor level is 0.07 eV below the middle of the band gap [25]. Since the donor energy level is higher than the acceptor, then H^0 would never maintain stable state which is easy to transfer electrons from one to another, as shown in Fig. 2 [24-25]. Because of the existence of energy potential, there are mainly H^- in n-type silicon and H^+ in p-type silicon, while H^0 is always a rarity of rarities among charge states.

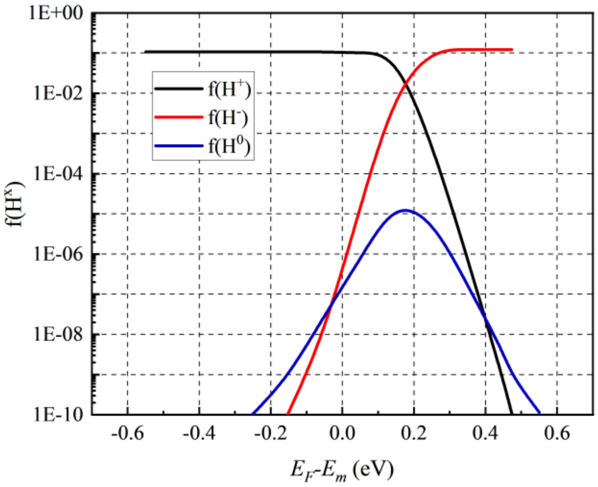
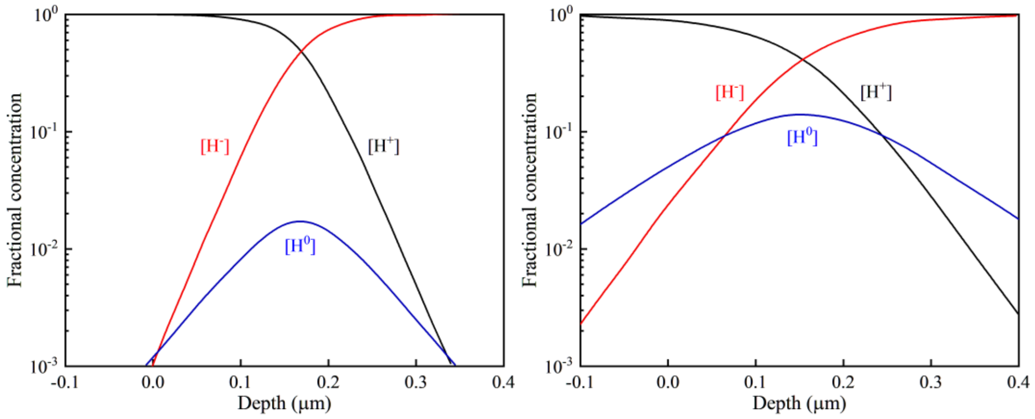


Fig. 2. The fractional hydrogen concentration of each charge states as a function of Fermi level at 423 K [24-25] (Reproduced with permission. [Ref. 24] Copyright of ©2018, Elsevier) (color online)

Recent investigations found that the equilibrium charge state fractions of H are also related to temperature [26,31]. Hamer, P., Sun, C. et al. simulated and calculated the relationship between the fraction of hydrogen in neutral (H^0), negative (H^-) and positive (H^+) charge states and Fermi level (relative to the middle of the bandgap) at 300 °C and 700 °C, respectively, as shown in Fig. 3.



(a) *(b)*

Fig. 3. Fraction of hydrogen in neutral (H^0), negative (H^-) and positive (H^+) charge states as a function of Fermi level (relative to the middle of the bandgap) (a) at 300 °C and (b) at 700 °C [26,31] (Reproduced with permission. [Ref.26] Copyright of ©2018, AIP Publishing) (color online)

As mentioned previously, H^0 is very efficient in passivation of defects. On the other hand, it is hoped that the charge in H^0 can be applied in silicon which the charge is opposite to the polarity of silicon. For instance, the minority carriers in p-type silicon are electrons, and the recombination centers of minority carriers are mainly in positive charge states. To passivate positive recombination centers, H^0 and H^- are then essential sources. It can be seen from Fig. 3 that the Fermi level can be closer to the mid bandgap by thermal treatment. Thus, the concentration of minority charge states of H such as H^0 in silicon substrate can be increased. However, related methods are quite limited as mentioned above for excess carrier injection, such as illumination, electron injection, etc.

P-type crystalline silicon solar cell is the most widely commercialized industrial production. It usually includes an n-type layer, a PN junction and a p-type substrate. For hydrogenation, H^+ and H^0 are needed in n-type layer, while H^- and H^0 are required in p-type substrate. The origin of hydrogen sources has been confirmed, which comes from the dielectric film deposited by PECVD. After the hydrogen permeates into the cell, the charge state is regulated automatically by heating and injecting a large number of non-equilibrium carriers. Taking the p-type crystalline silicon substrate as an example, most of the hydrogen penetrating into the substrate area is H^+. When the Fermi level is changed by heating, meanwhile, a large number of photo-generated carriers are generated in the substrate under the irradiation of high light intensity. The electrons in these photo-carriers are supposed to diffuse to the PN junction, are pushed to n-type region by the built-in electric field of the junction, and wait for outputting. However, the position of Fermi level changes and the built-in electric field of PN junction is weakened under a high temperature and high light intensity condition, so there are more electrons in p-type region. These electrons combine with H^+ to form H^0 or H^-. As a result, the purpose of the state of charge of hydrogen is achieved. P. Hamer et al. studied the manipulation of minority hydrogen charge states by combining temperature conditions and excess carrier density to simulate the concentration of H^0. The simulated H^0 concentration exhibited that a maximum point of H^0 concentration were emerged at specified temperatures for each excess carrier density [32].

2.2. The transport and interaction with impurities of hydrogen

It is reported that the diffusion rate of hydrogen in silicon can vary by several orders of magnitude under different charge states [33-36]. At lower temperatures, it is reported that the diffusivity of hydrogen in silicon varies widely, depending on the silicon doping concentration and temperature [29,37-39]. These differences are mainly due to the interaction of hydrogen with various impurities or defects in crystalline silicon. That is, in many cases, the hydrogen diffusion usually was limited by traps [29,40].

The diffusivity of H^+ is basically consistent with the activation energy between 0.43 and 0.48 eV [38-39]. The diffusion coefficient of H^- is not yet clear, especially at high temperature condition, because it is easily influenced by other elements in silicon, the measurement and calculation of the diffusion coefficient are more challenging. Additionally, the diffusion coefficient of H^0 is hard to be determined as well, because the proportion of H^0 is much lower than that in other charge states. The theoretical calculation of H^0 shows that it should be metastable and migrate rapidly in the entire lattice (activation energy is 0.14 eV) [38].

P. Hamer and B. Hallam et al. [26] from the University of New South Wales recommended to use the low temperature results of Gorelkinskii and Nevinnyi [39] as the diffusion rate of H^+, a conservative diffusivity of H^0 is from the work of Van Wieringen and Warmoltz [40], and the diffusivity of H^- is taken from the work of Johnson and Herring [41]. The diffusivities are as follows,

$$D_{H^+} = 4.24 \times 10^{-4} \exp(\frac{-0.43}{kT}) \tag{1}$$

$$D_{H^0} = 9.67 \times 10^{-3} \exp(\frac{-0.48}{kT}) \tag{2}$$

$$D_{H^-} = 1.3 \times 10^{-2} \exp(\frac{-0.70}{kT}) \tag{3}$$

Due to its high charge-to-mass ratio, the movement of hydrogen in silicon is also strongly impacted by the electric field. The internal electric field was tuned by the doping distribution inside the silicon with a significant impact. So P. Hamer and B. Hallam et al. calculated the mobilities via a Einstein-Smoluchowski relation to the diffusivity [26],

$$\mu_x = \frac{D_x}{kT} \tag{4}$$

Based on these relationships, it is predicted that the diffusion rate of H^- at 400 °C will be 7.30×10^{-6} $cm^2\cdot s^{-1}$, which is about three times higher than that of H^0, while the diffusion rate of H^+ is even lower, only around 2.55×10^{-7} $cm^2\cdot s^{-1}$. These diffusivities are greatly affected by temperature as described in equations.

Although the diffusion rate of hydrogen is relatively low in silicon bulks compared with the defects inside of the solar cell, the hydrogen content in the dielectric layers such as SiN_x: H and AlO_x: H deposited by PECVD is far excessive, and the mobility of hydrogen will increase under heating. Therefore, the probability of hydrogen reacting with defects is considerable. Only a few studies have observed that interstitial hydrogen passivate the doped impurities, bond to both shallow acceptors and donors [28,42-43]. That is, H^- and the positively charged phosphorus dopant P^+ form a [HP] complex, and H^+ and the negatively charged phosphorus dopant B- form a [HB] complex.

Meanwhile, there are publications have proved that hydrogen can passivate metal impurities and crystal defects in silicon [44-45], including dislocations [46-47], vacancies [48]. Additionally, interstitial hydrogen can also interact strongly with itself and form hydrogen dimers [49]. The situation in multi-silicon is more complicated due to the interaction of hydrogen and grain boundaries. It has been proposed that the diffusion of hydrogen at the grain boundary can be enhanced [50]. Moreover, the grain boundaries act as a trap for hydrogen, which increases the probability of hydrogen reaction at the grain boundaries, but reduces the ability of hydrogen to diffuse into silicon bulks [51-53].

In summary, the phenomenon of passivation reaction between hydrogen and various types of defects has been observed in many types [22, 44-46]. It is generally believed that hydrogen with different charge states will passivate defects with the opposite charge states under the action of the electric field caused by the formation of defects.

$$D^+ + H^- \rightarrow [HD] \tag{5}$$

$$D^- + H^+ \rightarrow [HD] \tag{6}$$

Of course, for H^0, it can be combined with different types of defects, which has the universality of passivation. When it encounters defect D^+, it can provide its free electron to saturate it, when it encounters defect D^-, the H^0 can from a covalent bond with defect as well. Since the hydrogen controlled by the state of charge can react with the defects inside the cell in a wide range, hydrogenation is beneficial to the improvement of the performance of crystalline silicon solar cells, mainly in the attenuation recovery and the improvement of conversion efficiency.

2.3. Light-induced degradation and hydrogenation

More than 90% of crystalline silicon apply p-type silicon wafers as substrates [54]. The solar cells made of boron-doped crystalline silicon grown by Cz have strong effect of LID. Reports showed that the LID was serious in Cz p-type solar cells even in room temperature under the natural sunlight condition [55-56]. LID has plagued the PV industry for decades without effective solution. Although it is now clear that this is the attenuation caused by BO related defects, the specific mechanism of this defect is still ambiguous [57-59]. The attenuation of BO-related LID can reach more than 10% under a standard sunlight attenuation characterization [60]. But in fact, it did not show such a bad situation. Usually the LID rate of conventional aluminum back-field solar cells is only about 3% [11]. The LID of PERC can reach up to 5% [61]. And this attenuation can also be expressed as a gradual recovery. Due to different environments in actual application, this recovery time will vary greatly, often ranging from weeks to years [62]. This brings an unwelcomed uncertainty to photovoltaic investment. Although this attenuation brings uncertainty to solar cells, and the LID has not yet been fully determined, for more than ten years, research on overcoming LID has been ongoing, such as reducing oxygen content, changing dopants and avoiding the use of boron. The LID improvement in the cell manufacturing process is the use of hydrogenation which is previously described.

Actually, without replacing the silicon material, two methods can be used to alleviate BO-related LID: (1) Pure thermal treatment heat to the cells at a relatively high temperature, (2) Thermal treatment at a moderately low temperature while irradiating or applying a voltage bias to inject non-equilibrium carriers. However, these two methods have significant differences in mechanism and degree of attenuation inhibition. The BO-related LID is relieved from the cell manufacturing technology, mainly due to the mutual conversion of boron and oxygen in the three states, as shown in Fig. 4.

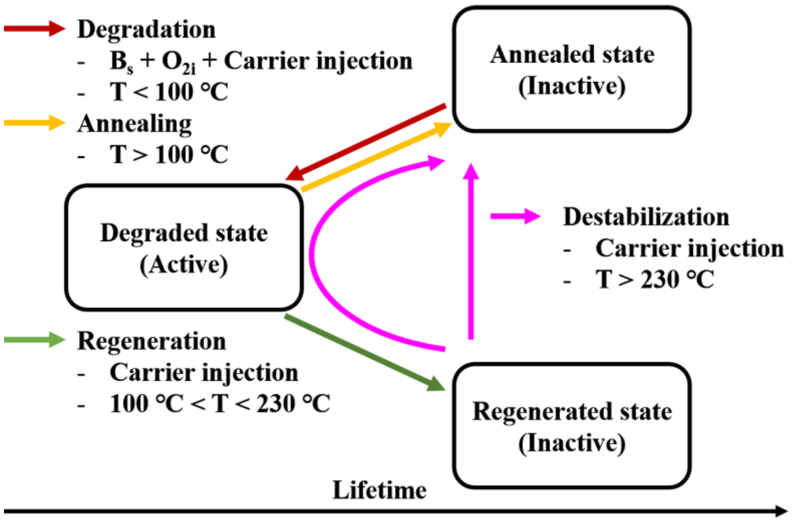


Fig. 4. Transition between three states model of BO defect and required conditions for each transition [24] (Reproduced with permission. [Ref. 24] Copyright of ©2018, Elsevier) (color online)

In terms of technology, the difference between pure thermal treatment and Hydrogenation is that simple thermal treatment excites BO defects return to the original inactive state again, while Hydrogenation is another re-ecology that passivate BO in the cell enter inactive state. And this re-ecology will not decompose until 230 °C. To elucidate these differences, B. Hallam et al. expressed the above triangle relationship as a straight-line parallel relationship [12], as shown in Fig. 5.

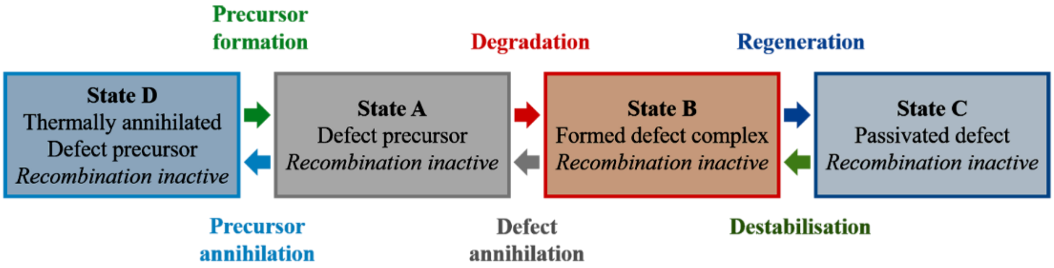


Fig. 5. Simplified diagrammatic representation of the BO defect system [12] (Reproduced with permission. [Ref. 19] Copyright of ©2018, MDPI-Open Access) (color online)

In Fig. 5, state A represents an unstable defect precursor state, that is, an initial state. State B represents the activation state of the BO defect. State C represents the stable regeneration state of BO defect after subsequent hydrogenation. State D represents the thermal decomposition state of the BO defect precursor, which is decomposed into boron and oxygen species. The process from state A to B is attenuation, which means that the minority carrier lifetime is reduced under light exposure. The reaction from state B to state A indicates the recovery of minority carrier lifetime under dark annealing conditions, but this is an unstable recovery. The process from state B to state C is irradiated annealing at an appropriate temperature, so that the life can be restored stably. Therefore, eliminating the need for BO-related LID to form defects and then regenerate. The reverse reaction (destabilization) from state C to B is the passivation failure due to excessively high temperature. There are reports that the reaction is usually a two-step reaction from state C to state B, first from state C to A (that is, the destabilized line in the triangle diagram in Fig. 4), and then transfer from state A to state B [63].

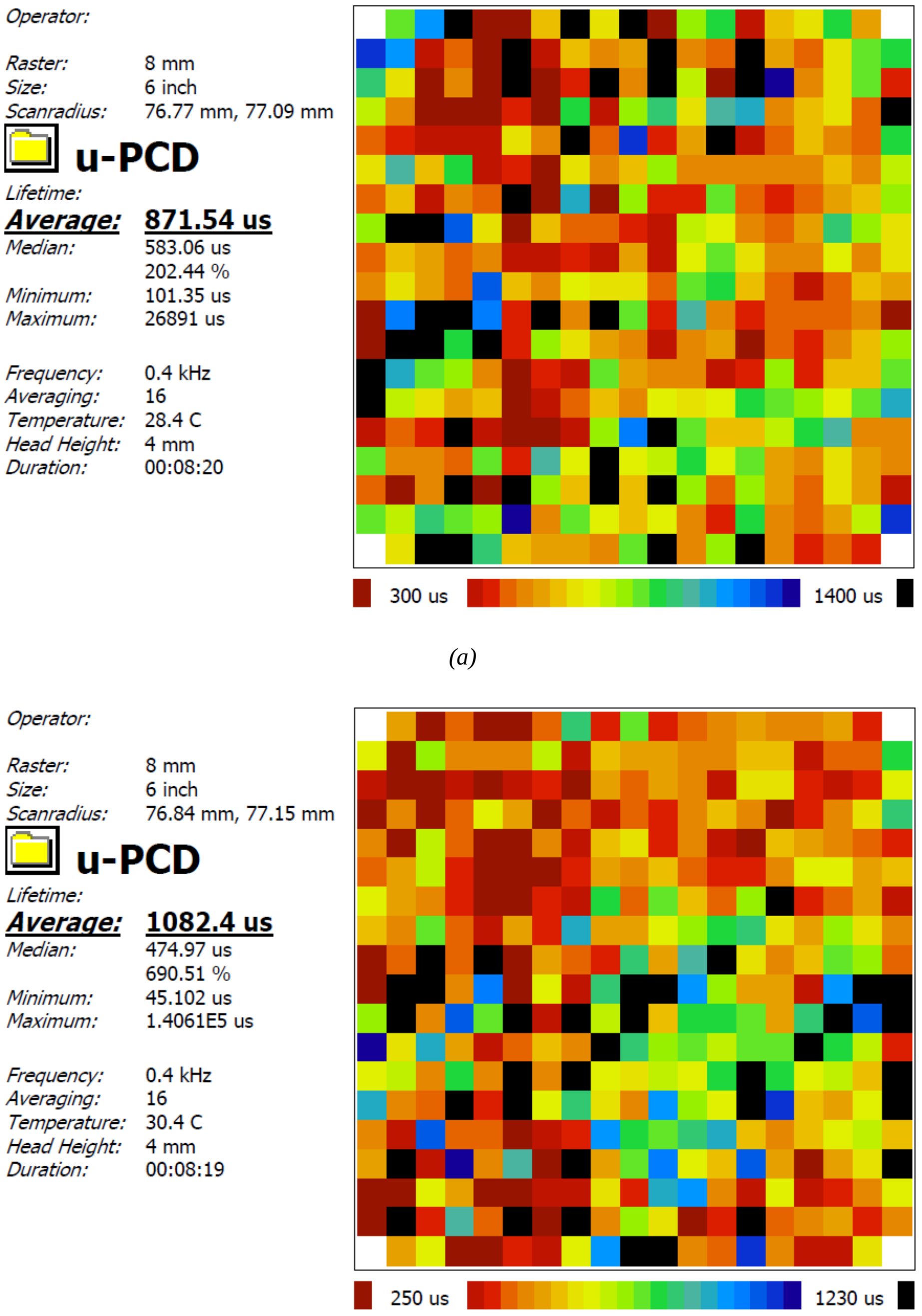
Annealing under non-equilibrium minority carrier injection can lead to the neutralization of the electrical properties of the formed defects and the recovery of carrier lifetime. In 2006, Herguth et al. first discovered the permanent inactivation of BO defects by the light annealing process at high temperature [64-65]. It was worthy mentioned that the lifetime recovery caused by hydrogenation is stable after subsequent exposure to light. Under the temperature conditions below 230 °C, hydrogenation shows the ability to completely overcome BO-related LID [66-68]. This breakthrough provides new hope for industrial p-type solar cells made of boron-doped Cz silicon wafers to overcome the LID for PV industry.

The hydrogenation of BO defects involves defect formation and passivation. Defects must be generated before hydrogen can be passivated. To achieve a fast LID control process, a high-intensity light source is required. On the one hand, the high-intensity light source will accelerate the generation of BO-related defects. Meanwhile, abundant unbalanced carriers will be generated by the high-intensity light source will facilitate the regulation of the three charges of hydrogen. High-intensity lighting accelerates defect formation and hydrogen charge state manipulation requirements tend to setup laser-based hydrogenation processes [69]. Wilking et al. proved that in the hydrogenation process based on local laser, the passivation time is about 0.1 s when the defect conditions have been generated [70]. Subsequent research using full-area laser radiation hydrogenation showed that BO defects can be simultaneously formed and passivated within tens of seconds within a time range suitable for mass production, thereby completely eliminating the BO defects related LID on the aluminum back-field solar cell [22,33]. However, these fast processes are carried out at a temperature of about 300 °C, which is somewhat different from the upper limit of 230 °C in previous theoretical studies. In 2018, J. Shao et al. developed a high-intensity LED-based planar light source for hydrogenation [71]. They performed Hydrogenation on Cz boron-doped PERC solar cells at 240 °C (closer to the theoretical temperature of 230 °C), which greatly improved the LID of the cells.

Currently, irradiance of hydrogenation is in the range of 5 to 20 sunlight (1 sunlight =1000 W/m^2) are acknowledged in most cases [72-74]. Usually each cell requires 25-45 seconds of processing time. An alternative to high-intensity irradiation is to use current injection to improve the anti-degradation ability for solar cells. In this case, the cells are stacked and the current flows through the entire stack [75-76]. However, since the level of injected current cannot reach the effect of high-intensity irradiation to over ten suns, the processing time of this process is very long. Fortunately, the process is carried out in a stacking manner, which can process hundreds of cells at a time, so the production capacity can still match the existing production status. However, this process causes additional stress, and the temperature uniformity within and among the cells is difficult to control, which may reduce the effect of inhibiting LID.

2.4. Refine hydrogenation

The hydrogenation can passivate BO-related defects and inhibit LID. BO defects exist in boron-doped P-type Cz silicon wafers, and their minority carriers are electrons. The generation of BO defects reduces the lifetime. Therefore, BO defects should keep in positive charge state. Similarly, other minority carrier recombination centers should also be positive in p-type silicon. It can be speculated that in the process of hydrogenation inhibiting LID, while excited H^- and H^0 passivate BO defects, H^- or H^0 must also react with other defects, so that the minority carrier lifetime in the cell is improved and the conversion efficiency is increased. In the process of researching the high-intensity LED hydrogenation platform, J. Shao tested the minority lifetime before and after the hydrogenation treatment to infer the effect of the high-intensity LED hydrogenation platform, as shown in Fig. 6 [71]. The minority lifetime test uses the WT-2000 minority carrier lifetime test equipment produced by Semilab of Hungary in Suntech Power Co., Ltd. of China. The measurement range of minority carrier lifetime of WT-2000 tool is 0.1 ms to 30 ms, and the test resolution is not less than 0.1%.



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u-PCD
Lifetime:
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Median: 583.06 us
202.44 %
Minimum: 101.35 us
Maximum: 26891 us

Frequency: 0.4 kHz
Averaging: 16
Temperature: 28.4 C
Head Height: 4 mm
Duration: 00:08:20

(a)

Operator:

Raster: 8 mm
Size: 6 inch
Scanradius: 76.84 mm, 77.15 mm
u-PCD
Lifetime:
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Median: 474.97 us
690.51 %
Minimum: 45.102 us
Maximum: 1.4061E5 us

Frequency: 0.4 kHz
Averaging: 16
Temperature: 30.4 C
Head Height: 4 mm
Duration: 00:08:19

(b)

Fig. 6. The minority carrier lifetime of cells (a) initial and (b) after the infrared LED hydrogen passivation [71] (Reproduced with permission. [Ref. 71] Copyright of ©2018, AIP Publishing) (color online)

In the hydrogenation process, hydrogen passivates BO-related defects. The generation of BO defects reduces the minority carrier lifetime. Hydrogen deactivates most of the BO defects, that is, hydrogen can make these BO defects enter the re-ecology after hydrogenation. The minority carrier lifetime is in accordance with the initial state, as shown in Fig. 4, the re-ecology and the initial state of the minority carrier lifetime are at the same level. Then the increase in the lifetime expectancy of minority carriers in Fig. 6 must come from the suppression of other defects.

For boron-doped Cz PERC, due to the high quality of silicon wafers, this repair rate is very fast, often within 1 minute. It can be seen from Fig. 7 that when the same batch of PERC cells are subjected to hydrogenation treatment at different times, although there is a slight difference in conversion efficiency between the cells, after 1 minute, the gain of conversion efficiency is basically constant with the continued hydrogenation treatment [77].

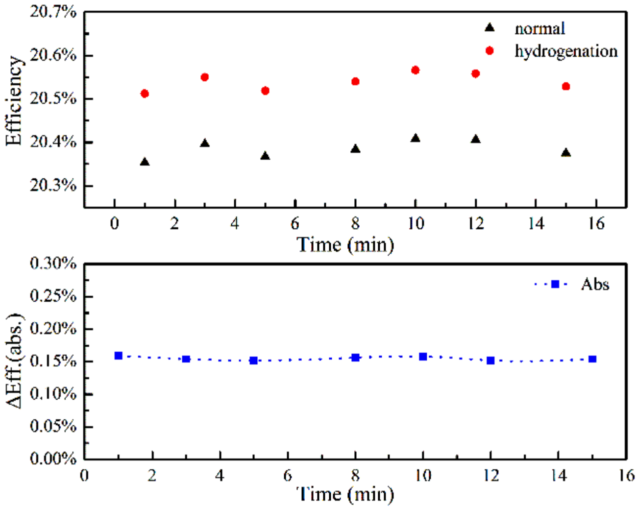


Fig. 7. The electrical performance of mono-Si PERC cells at different hydrogenation duration [77] (Reproduced with permission. [Ref. 77] Copyright of ©2019, Elsevier) (color online)

Superior performance of hydrogenation in monocrystalline silicon cells is naturally reminiscent of using it in multi-crystalline or lower quality silicon wafers to greatly reduce the cost of solar cells. L. Song et al. used a laser to hydrogenate the cast monocrystalline silicon solar cell [69]. After the laser hydrogenation treatment, the open circuit voltage and short circuit current density of the cast monocrystalline silicon solar cell were both increase, thereby increasing the absolute efficiency by 0.6%. Detailed studies have shown that the improvement in electrical performance is mainly due to the excellent passivation of dislocation clusters in the cells. The increased H^- or H^0 under laser irradiation by L. Song et al. causes the positively charged dangling bonds in the dislocation cluster to be further passivated. We conducted Fourier transform infrared spectroscopy tests before and after the hydrogenation of the multi-crystalline silicon PERC cells, and the increase in Si-H bonds can also be seen in Fig. 8. The FTIR test uses the Fourier infrared spectrometer produced by Thermo Company of the United States in State Key Laboratory of Food Science and Technology of Jiangnan University. The model is Nexus, the wavenumber range is 378 cm^{-1}-4000 cm^{-1}, the resolution is less than or equal to 0.5 cm^{-1}, and the wavenumber accuracy is 0.01 cm^{-1}.

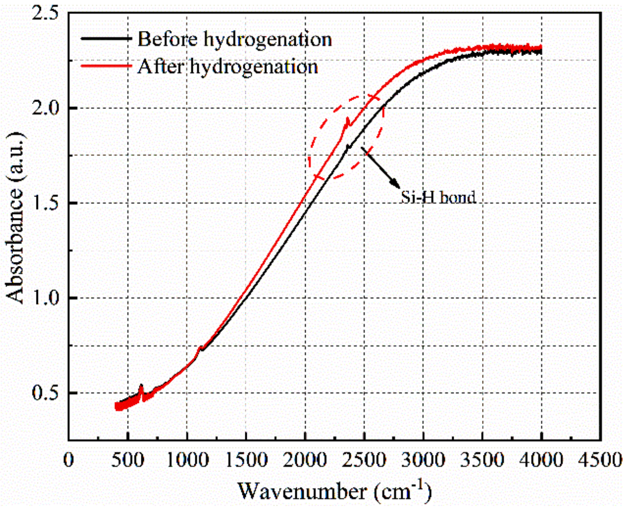


Fig. 8. Measurement of Si-H bond using FTIR

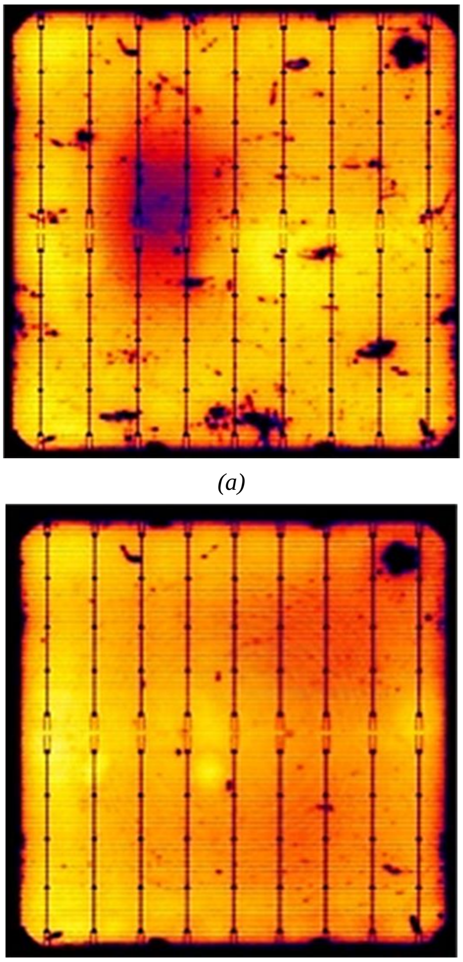
L. Song et al. found that a laser annealing process with a laser power density higher than 4.08×10^3 W/cm^2 is likely to cause laser damage. Meanwhile, hydrogenation only occurs when the laser power density is higher than a threshold power density (in this case, 32.6 W/cm^2) [69]. Irradiation is very important to improve the effectiveness of hydrogenation, because it can increase the concentration of the required minority charge states of hydrogen and bond with certain defects. The rapid cooling rate helps maintain the effect of advanced hydrogen passivation because it can reactivate the defects by reducing the time. And thereby preventing the dissociation of the hydrogen defect complex under a high temperature.

Hydrogenation technology has strong versatility [78]. It has a good effect on improving efficiency of conventional structure aluminum back-field silicon solar cells, PERC solar cells, N-type bifacial cells, heterojunction with Intrinsic Thin-layer (HIT) cells, etc. For HIT cells that use n-type silicon wafers, which have a high minority carrier lifetime and have excellent surface passivation, hydrogenation may be of bit use in terms of this substrate and structure. However, we have found in our experiments that the conversion efficiency improvement of HIT cells after hydrogenation treatment is as high as $0.4\%_{abs.}$, which is higher than the general increase of $0.2\%_{abs.}$ for Cz PERC cells, as shown in Table 1.

Table 1. Electrical performance of HIT cell before and after hydrogenation

	Area (cm^2)	**I_{sc} (A)**	**V_{oc} (V)**	**FF (%)**	**Eff. (%)**
Before Hydrogenation	244.32	8.9919	0.7343	80.121	21.652
After Hydrogenation	244.32	9.0873	0.7393	80.208	22.055

The photoluminescence (PL) image was used to study the passivation of defects in HIT cells. After hydrogenation, the change in PL images of HIT cells was shown in Fig. 9. Since the particularity of HIT cells, the hydrogenation temperature was lower than conventional crystalline silicon solar cells. The results indicated that the defect area of treated HIT cell decreased significantly after hydrogenation. Thus, compared with the HIT cell without hydrogenation treatment, the defects of the treated HIT cell have been greatly improved.


(a)

(b)

Fig. 9. PL images of HIT cells, (a) before hydrogenation (b) after hydrogenation (color online)

2.5. Hydrogen induced degradation

As mentioned earlier, hydrogenation has the function of suppressing LID and improving conversion efficiency. When J. Shao studied the hydrogenation of multi-crystalline silicon PERC cells, he found that the processing time of multi-crystalline PERC is much longer than that of Cz single crystal hydrogenation within 1 min [77]. The main reason is that the grain boundary acts as a trap for hydrogen, which increases the probability of hydrogen reaction at the grain boundary, but reduces the ability of hydrogen to diffuse into silicon [51-53]. More importantly, when the hydrogenation processing time of multi-silicon PERC is extended for a longer time, the magnitude of improvement in conversion efficiency will gradually decrease, as shown in Fig. 10 [77]. This situation seems to be due to excessive hydrogenation leading to a new unknown attenuation.

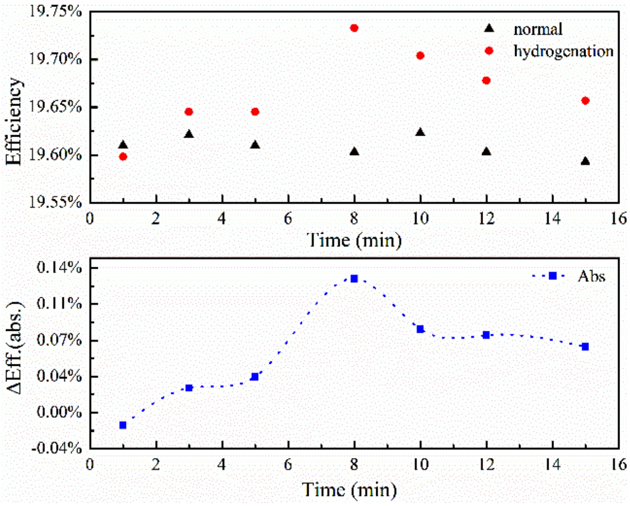


Fig. 10. Changes in conversion efficiency of mc-Si PERC cells at different hydrogenation duration [77] (Reproduced with permission. [Ref. 77] Copyright of ©2019, Elsevier) (color online)

The unknown decrease we mentioned above in efficiency improvement may be related to hydrogen injection, which is a HID. At present, LID can be efficiently suppressed, but the new attenuation under heating and light (carrier injection) conditions---Light and elevated temperature induced degradation (LeTID) has rapidly attracted wide attention. LeTID requires heating and light to exist simultaneously. The HID just drops in this condition. Therefore, it can be assumed that HID is related to LeTID.

LeTID refers to the cell efficiency degradation phenomenon of crystalline silicon solar cells under certain temperature and light (or carrier injection) conditions [80-81]. A series new emerged studies have shown that LeTID exists in a variety of crystalline silicon materials, including monocrystalline silicon, multi-crystalline silicon and cast mono silicon. LeTID can cause up to 16% efficiency degradation (relative value) of crystalline silicon solar cells, and the duration can be up to over 10 years [82]. It should be noted that LeTID is not only produced under light irradiation, but can also be produced by applying a forward voltage bias to the crystalline silicon solar cell with injected current. It means that LeTID is not merely related with photons, but directly related to the non-equilibrium carriers. Regarding the formation mechanism of LeTID, there are currently two hypotheses, that is, (1) hydrogen causes LeTID or (2) metal impurities cause LeTID. Wenham et al [83]. and Vargas et al. [84] found that LeTID only occurs when hydrogen exists in silicon, and the degree of LeTID is positively correlated with the content of hydrogen in silicon. Therefore, we speculate that hydrogen causes LeTID. Although the exact form of the LeTID defect is still a topic of debate, more evidences show that the degree of attenuation is proportional to the amount of hydrogen released from the dielectric layer into the body during the firing process [84].

2.6. Applications of advanced hydrogenation

As previously mentioned, the application of hydrogenation is to suppress the LID in solar cells. The conventional method was excited the LID defects first, and then passivate them by applying hydrogen sources. As a result, the detection of defects is important for the whole process. However, the detection of LID usually spends over hours or even days under an exposure of a standard sunlight (AM 1.5G). Several hours of LID irradiation treatment even can significantly destroy the real-time performance of solar cells which blocks the further manufacture of solar modules. On the other hand, once the devices failed to pass the LID test, the quality of the products produced online will all share the same risk of LID. As described above, there are time overlaps between hydrogenation and LID. To clear distinguish the hydrogen and LID, as a result, fast LID is essential for PV industry which can achieve online characterization for solar cells. This aspect is mainly relied in the control of light intensity and temperature to achieve sufficient LID. Meanwhile, the rapid LID can also sufficient block cells entering the hydrogenation process. Related research has been carried out [85], as shown in Fig. 11.

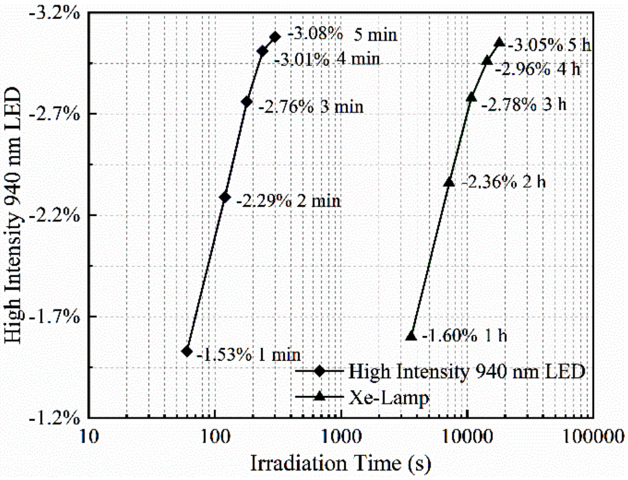


Fig. 11. The average efficiency LID ratio contrast between high intensity LED source and Xe-lamp [85] (Reproduced with permission. [Ref. 85 Copyright of ©2017, AIP Publishing) (color online)

Based on investigation of fast LID, the fast LeTID can also be achieved if the temperature can be precisely manipulated. In current methods, the processing time of LeTID is longer than that of LID, which extends to hundreds of hours [69]. The long-time of LeTID test is also a great challenge to quality control of photovoltaics. To solve this problem, major photovoltaic companies have devoted tremendous effort. In June 2020, LONGi Solar Technology Co, Ltd, with the assistance of UMS Information Technology Co., Ltd., transformed UMS's fast LID equipment, and conducted research on the fast attenuation treatment of Ga-doped PERC solar cells, and the results published on the official WeChat social platform of LONGi Solar, as shown in Fig. 12.

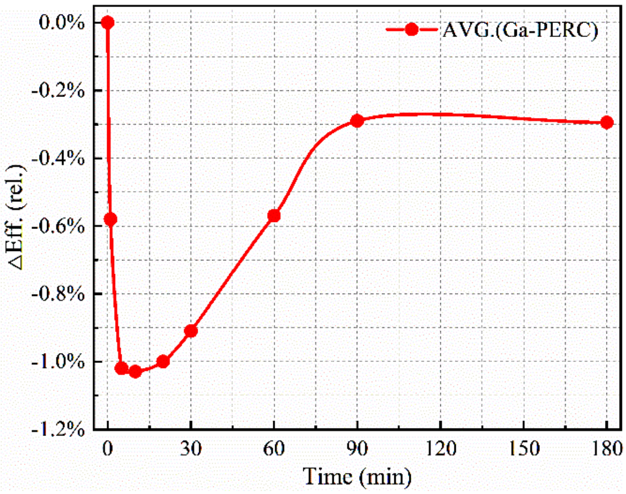


Fig. 12. Change in conversion efficiency of Ga-doped PERC solar cells treated by fast attenuation treatment (color online)

Note, BO defects are invisible in Ga-doped silicon solar cells, which means the LID is missing in Ga-doped solar cells. As a result, the attenuation should refer to LeTID. Then, under appropriate temperature conditions, a method similar to hydrogenation can be used to rapidly express LeTID, and the time can be dramatically accelerated from hours to minutes, which greatly improves the timeliness of the feedback of production sampling results.

3. Conclusion

This article reviews the significant roles of hydrogen in crystalline silicon solar cells and discusses the functional evolution of hydrogen with different charge states during the processes of hydrogenation and HID. Many researchers have proved that the manipulated hydrogen ions with appropriate charge states can efficiently decrease the surface recombination and achieve bulk passivation. However, the injection of excess hydrogen introduces a decrease in efficiency improvement. Hence, the optimized hydrogenation process is required to be stable for the subsequent module fabrication with light welding. For these reasons, the key points for effective hydrogenation are summarized as follows. First, the excess carrier injection should be accompanied with appropriate temperature conditions, such as illumination or electron injection, is required to manipulate for increasing the concentration of minority charge states of hydrogen, such as H^0 in the silicon substrate. Secondly, for ensuring the diffusion rate of hydrogen to migrate a large amount of hydrogen into the silicon bulk, the control process of temperature and doping concentration is worthy optimized based on the build-in electric field of solar cells. Thirdly, we summarized two methods to alleviate BO-related LID: 1) pure thermal treatment with a relatively high temperature, 2) thermal treatment at a moderately low temperature while irradiating or applying a voltage bias to inject non-equilibrium carriers. Then, hydrogenation, such as LED hydrogenation and laser hydrogenation, can accelerate the hydrogen regeneration process by regulating illumination intensity with precisely time and temperature control. Moreover, both hydrogenation and LeTID are required to prevent HID from excessive hydrogen ions by blocking the amount of hydrogen that migrates into the silicon bulk. In the future, through manipulating the appropriate charge states for crystalline silicon solar cells, efficiency and reliability of the various types of silicon solar cells can be significantly improved. In particular, the hydrogenation on BO-related defects, which introduce LID, has a substantial improvement since the substrates of most industrial solar cells are made of the boron-doped p-type silicon wafer. Also, some significant performance improvements emerge in conventional cell structures due to the influence of hydrogenation, such as aluminum back-field silicon solar cells, PERC solar cells, N-type bifacial cells, HIT cells, etc. However, the application of hydrogenation to perovskite solar cells needs further research. Therefore, advanced platforms combined with proper methods and conditions of advanced hydrogen passivation for silicon solar cells will be successfully developed and will spread out quickly to the PV industries in the future.

Author contributions

X. Xi and J.B. Shao contributed equally to this work. Writing-original draft preparation, X. Xi and J.B. Shao; writing-review and editing, J.B. Shao; visualization and supervision, X. Xi, G.L. Liu and F. Luo; All authors have read and agreed to the published version of the manuscript.

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Conflicts of interest

The authors declare no conflict of interest.

References

[1] Y. Lee, D. Gong, N. Balaji, Y. J. Lee, J. Yi, Nanoscale Res. Lett. **7**, 50 (2012).
[2] A. G. Aberle, Sol. Energy Mater. Sol. Cells **65**, 239 (2001).
[3] B. Hallam, B. Tjahjono, S. Wenham, Sol. Energy Mater. Sol. Cells **96**, 173 (2012).
[4] J. Schmidt, M. Kerr, Sol. Energy Mater. Sol. Cells **65**, 585 (2001).
[5] K. A. Münzer, K Proc. 24th European Photovolt. Sol. Energy Conf., 1558 (2009).
[6] B. Vermang, H. Goverde, L. Tous, A. Lorenz, P. Choulat, J. Horzel, J. John, J. Poortmans, R. Mertens, Prog. Photovolt. Res. Appl. **20**, 269 (2012).
[7] D. Kania, P. Saint-Cast, D. Wagenmann, M. Hofmann, J. Rentsch, R. Preu, Proc. 24th European Photovolt. Sol. Energy Conf., Hamburg, Germany, 2275 (2009).
[8] A. G. Aberle, Prog. Photovolt. Res. Appl. **8**, 473 (2000).
[9] H.-P. Sperlich, D. Decker, P. Saint-Cast, E. Erben, L. Peters, Proc. 25th European Photovolt. Sol. Energy Conf., Valencia, Spain, 1352 (2010).
[10] Q. Qiao, H. Lu, J. Ge, X. Xi, R. Chen, J. Yang, J. Zhu, Z. Shi, J. Chu, Appl. Surf. Sci. **305**, 439 (2014).
[11] E. Cho, J.-H. Lai, Y. Ok, A. D. Upadhyaya, A. Rohatgi, M. J. Binns, J. Appel, J. Guo, H. Fang, E. A. Good, Proc. IEEE 42nd Photovolt. Specialists Conf. (PVSC), 2015.
[12] B. Hallam, A. Herguth, P. Hamer, N. Nampalli, S. Wilking, M. Abbott, S. Wenham, G. Hahn, Appl.

Sci. **8**, 10 (2018).

[13] B. Hallam, C. Chan, D. N. R. Payne, D. Lausch, M. Gläser, M. Abbott, S. Wenham, Photovolt. Int. **33**, 37 (2016).

[14] C. Chan, T. H. Fung, M. Abbott, D. Payne, A. Wenham, B. Hallam, R. Chen, S. Wenham, Solar RRL **1**, 1600028 (2017).

[15] J. B. Shao, X. Xi, G. L. Liu, S. M. Li, R. Y. Peng, G. Q. Chen, Y. F. Jiang, J. G. Sun, Superlattices and Microstructures **151**, 106839 (2021).

[16] M. Kim, P. Hamer, H. Z. Li, D. Payne, S. Wenham, M. Abbott, B. Hallam, Frontiers in Energy **11**, 32 (2017).

[17] B. J. Hallam, P. G. Hamer, S. R. Wenham, M. D. Abbott, A. Sugianto, A. M. Wenham, C. E. Chan, G. Q. Xu, J. Kraiem, J. Degoulange, R. Einhaus, IEEE J. Photovolt. **4**, 88 (2013).

[18] J. B. Shao, X. Xi, G. L. Liu, S. M. Li, R. Y. Peng, G. Q. Chen, T. Zhu, Bull. Mater. Sci. **44**, 48 (2021).

[19] M. A. Jensen, A. E. Morishige, J. Hofstetter, D. B. Needleman, T. Buonassisi, IEEE J. Photovolt. **7**, 980 (2017).

[20] S. Wilking, S. Ebert, A. Herguth, G. Hahn, J. Appl. Phys. **114**, 194512 (2013).

[21] D. Bredemeier, D. C. Walter, J. Schmidt, Solar RRL **2**, 1700159 (2018).

[22] B. Hallam, P. Hamer, S. Wang, L. Song, N. Nampalli, M. Abbott, C. Chan, P. Lu, A. Ciesla, L. Mai, N. Borojevic, A. Li, D. Chen, M. Kim, A. Azmi, S. Wenham, Energy Proc. **77**, 799 (2015).

[23] B. Parida, G. Lim, J. Choi, S. Palei, K. Kim, Solar Energy **122**, 486 (2015).

[24] S. H. Lee, M. F. Bhopal, D. W. Lee, S. H. Lee, Mater. Sci. Semicon. Proc. **79**, 66 (2018).

[25] C. Herring, N. Johnson, C. G. Van de Walle, Phys. Rev. B **64**, 125209 (2001).

[26] P. Hamer, B. Hallam, R. S. Bonilla, P. P. Altermatt, P. Wilshaw, S. Wenham, J. Appl. Phys. **123**, 043108 (2018).

[27] E. C. Chan, D. M. Abbott, J. B. Hallam, N. R. D. Payne, B. Hoex, Phys. Status Solidi Rapid Res. Lett. **10**, 237 (2016).

[28] D. N. R. Payne, C. E. Chan, B. J. Hallam, B. Hoex, M. D. Abbott, S. R. Wenham, D. M. Bagnall, Sol. Energy Mater. Sol. Cells **158**, 102 (2016).

[29] P. Hamer, S. S. Wang, B. Hallam, S. Wenham, C. M. Chong, A. Wenham, Phys. Status Solidi Rapid Res. Lett. **9**, 111 (2015).

[30] L. H. Song, J. J. Lou, J. Y. Fu, Electronic Materials Lett. **14**, 574 (2018).

[31] C. Sun, F. E. Rougieux, D. Macdonald, J. Appl. Phys. **117**, 045702 (2015).

[32] P. Hamer, B. Hallam, S. Wenham, M. Abbott, IEEE J. Photovolt. **4**, 1252 (2014).

[33] P. Hamer, B. Hallam, M. Abbott, C. Chan, N. Nampalli, S. Wenham, Sol. Energy Mater. Sol. Cells **145**, 440 (2016).

[34] D. Bredemeier, D. Walter, S. Herlufsen, J. Schmidt, AIP Adv. **6**, 035119 (2016).

[35] M. V. Contreras, V. P. Markevich, M. Halsall, A. Peaker, P. Santos, J. Coutinho, S. Oberg, L. Murin, R. Falster, J. Binns, E. V. Monakhov, B. G. Svensson, Phys. Status Solidi RRL **11**, 1700133 (2017).

[36] V. Markevich, M. V. Contreras, J. Mullins, M. Halsall, B. Hamilton, L. Murin, R. Falster, J. Binns, E. Good, J. Coutinho, Proceeding of the 2016 IEEE 43rd Photovoltaic Specialists Conference (PVSC), 2016.

[37] L. H. Song, A. Wenham, S. Wenham, Sol. Energy Mater. Sol. Cells **149**, 221 (2016).

[38] S. Estreicher, A. Docaj, M. Bebek, D. Backlund, M. Stavola, Phys. Status Solidi A **209**, 1872 (2012).

[39] Y. V. Gorelkinskii, N. N. Nevinnyi, C, H, N and O in Si and Characterization and Simulation of Materials and Processes. Elsevier, 133 (1996).

[40] T. Zundel, J. Weber, Physical Review B **46**, 2071 (1992).

[41] N. M. Johnson, C. Herring, Phys. Rev. B **46**, 15554 (1992).

[42] S. Q. Ding, C. Yang, C. Qin, B. Ai, X. P. Sun, J. H. Yang, Q. Liu, X. Q. Liang, Energies **15**, 7764 (2022).

[43] M. G. Seok, Y. Kim, S. M. Kim, Energies **15**, 3563 (2022).

[44] A. A. Istratov, T. Buonassisi, R. J. McDonald, A. R. Smith, R. Schindler, J. Rand, J.P. Kalejs, E. R. Weber, J. Appl. Phys. **94**, 6552 (2003).

[45] B. Hallam, C. Chan, M. Abbott, S. Wenham, Sol. Energy Mater. Sol. Cells **141**, 125 (2015).

[46] N. Chen, S. Y. Qiu, G. H. Liu, Crystals **6**, 130 (2016).

[47] M. I. Bertoni, S. Hudelson, B. K. Newman, D. P. Fenning, H. F. W. Dekkers, E. Cornagliotti, A. Zuschlag, G. Micard, G. Hahn, G. Coletti, B. Lai, T. Buonassisi, Progress in Photovoltaics **19**, 187 (2011).

[48] M. A. Roberson, S. K. Estreicher, Phys. Rev. B **49**, 17040 (1994).

[49] M. Matsubara, J. Godet, L. Pizzagalli, Phys. Rev. B **82**, 024107 (2010).

[50] N. M. Johnson, D. K. Biegelsen, M. D. Moyer, Appl. Phys. Lett. **40**, 882 (1982).

[51] B. Hammann, L. Rachdi, W. Kwapil, F. Schindler, M. C. Schubert, Phys. Status Solidi RRL **15**, 2000584 (2021).

[52] Y. Park, J. Lu, G. Rozgonyi, Electronic Mater. Lett. **6**, 1 (2010).

[53] B. J. Hallam, A. M. Ciesla, C. C. Chae, A. Soeriyadi, S. Y. Liu, A. M. Soufiani, M. Wright, S. Wenham, Australian Journal of Chemistry **71**, 743 (2018).

[54] International Technology Roadmap for Photovoltaic: 2016 Results, 8th ed.; VDMA: Berlin, Germany, 2017.

[55] J. Lindroos, H. Savin, Sol. Energy Mater. Sol. Cells **147**, 115 (2016).

[56] K. Ramspeck, S. Zimmermann, H. Nagel, A. Metz, Y. Gassenbauer, B. Birkmann, A. Seidl, Proceedings of the 27th European Photovoltaic Solar Energy Conference, Frankfurt, Germany, 24-28 September, 861 (2012).

[57] B. Hallam, M. Abbott, T. Nærland, S. Wenham, Phys. Status Solidi RRL **10**, 520 (2016).

[58] B. Hallam, M. Kim, M. Abbott, N. Nampalli,

T. Nærland, B. Stefani, S. Wenham, Sol. Energy Mater. Sol. Cells **173**, 25 (2017).

[59] V. Voronkov, R. Falster, Phys. Status Solidi B **13**, 712 (2016).

[60] H. Ichikawa, I. Takahashi, N. Usami, K. Shirasawa, H. Takato, Energy Procedia **92**, 801 (2016).

[61] K. Lee, M.-S. Kim, J.-K. Lim, J.-H. Ahn, M.-I. Hwang, E.-C. Cho, E.-C. Proceedings of the 31st European Photovoltaic Solar Energy Conference and Exhibition- EU PVSEC, Hamburg, Germany, 14-18 September, 1837 (2015).

[62] B. Hallam, J. Bilbao, D. Payne, C. Chan, M. Kim, D. Chen, N. Gorman, M. Abbott, S. Wenham, Proceedings of the 32nd European Photovoltaic Solar Energy Conference and Exhibition, München, Germany, 21-24 June, 555 (2016).

[63] B. Hallam, P. Hamer, M. Kim, N. Nampalli, N. Gorman, D. Chen, D. Chan, M. Abbott, S. Wenham, Proceedings of the 43rd IEEE Photovoltaic Specialists Conference, 5-10 June, 2430 (2016).

[64] A. Herguth, G. Schubert, M. Käs, G. Hahn, Proceedings of the 4th IEEE World Conference on Photovoltaic Energy Conversion, Waikoloa, HI, USA, 7-12 May, 940 (2006).

[65] A. Herguth, G. Schubert, M. Kaes, G. Hahn, Proceedings of the 21st European Photovoltaic Solar Energy Conference, Dresden, Germany, 4-8 September, 530 (2006).

[66] A. Herguth, G. Hahn, J. Appl. Phys. **108**, 114509 (2010).

[67] B. Lim, S. Hermann, K. Bothe, J. Schmidt, R. Brendel, Proceedings of the 23rd European Photovoltaic Solar Energy Conference, Valencia, Spain, 1-5 September, 1018 (2008).

[68] B. Lim, K. Bothe, J. Schmidt, Phys. Status Solidi Rapid Res. Lett. **2**, 93 (2008).

[69] L. Song, A. Wenham, S. Wang, P. Hamer, A. Shakil, B. Hallam, L. Mai, M. Abbott, E. Hawkes, C. Chong, Int. J. Photoenergy **501**, 193892 (2015).

[70] S. Wilking, J. Engelhardt, S. Ebert, C. Beckh, A. Herguth, G. Hahn, Proceedings of the 29th European Photovoltaic Solar Energy Conference and Exhibition, Hamburg, Germany, 4-18 September, 366 (2014).

[71] J. Shao, X. Xi, C. Li, G. Liu, G. Li, Y. Zhu, X. Wang, W. Qian, G. Chen, R. Chen, T. Zhu, J. Renew. Sustain. Ener. **10**, 013507 (2018).

[72] G. Fischbeck, PV-Magazine, 44 (2015).

[73] T. Pernau, O. Romer, W. Scheiffele, A. Reichart, W. Jooß, Proceedings of the 31st European Photovoltaic Solar Energy Conference, Hamburg, Germany, 14-18 September, 918 (2015).

[74] B. J. Hallam, C. E. Chan, R. Chen, S. Wang, J. Ji, L. Mai, M. D. Abbott, D. N. R. Payne, M. Kim, D. Chen, Jpn. J. Appl. Phys. **56**, 08MB13 (2017).

[75] A. Herguth, G. Hahn, Proceeding of the 28th European Photovoltaic Solar Energy Conference, Paris, France, 1507 (2013).

[76] S. M. Li, J. Shao, X. Xi, G. Liu, R. Peng, R. Chen, L. Chen, Y. Jiang, X. Gu, Bull. Mater. Sci. **43**, 104 (2020).

[77] J. B. Shao, X. Xi, S. M. Li, G. L. Liu, R. Y. Peng, C. Li, G. Q. Chen, R. L. Chen, Opt. Commun. **450**, 252 (2019).

[78] B. Hallam, D. Chen, M. Kim, B. Stefani, B. Hoex, M. Abbott, S. Wenham, Phys. Status Solidi A **214**, 1700305 (2017).

[79] C. Y. Wei, C. H. Lin, H. T. Hsiao, P. C. Yang, C. M. Wang, Y. C. Pan, Materials **6**, 5440 (2014).

[80] B. Grübel, G. C. Theil, S. Roder, T. Niewelt, S. Kluska, IEEE J. Photovolt. **10**, 444 (2020).

[81] D. Chen, P. Hamer, M. Kim, C. Chan, A. C. Wenham, F. Rougieux, B. Hallam, Sol. Energy Mater. Sol. Cells **207**, 110353 (2020).

[82] C. Sen, C. Chan, D. Chen, M. Wright, U. Varshney, M. Kim, M. Abbott, Asia-Pacific Solar Research Conference. **2**, 3 (2020).

[83] A. C. Wenham, S. Wenham, R. Chen, C. Chan, D. Chen, B. Hallam, M. Abbott, 2018 IEEE 7th world conference on photovoltaic energy conversion (WCPEC) (A joint conference of 45th IEEE PVSC, 28th PVSEC & 34th EU PVSEC), 1 (2018).

[84] C. Vargas, K. Kim, G. Coletti, D. Payne, C. Chan, S. Wenham, Z. Hameiri, IEEE J. Photovolt. **8**, 1 (2018).

[85] X. Xi, J. B. Shao, C. Li, G. L. Liu, G. H. Li, Y. Q. Zhu, X. Wang, W. Y. Qian, R. L. Chen, J. Renew. Sustain. Ener. **9**, 053502 (2017).

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