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Review

Research progress of light and elevated temperature-induced degradation in silicon solar cells: A review

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ABSTRACT

At present, passivated emitter and rear cell (PERC) solar cells dominate the photovoltaic industry. However, light and elevated temperature-induced degradation (LeTID) is an important issue responsible for the reduction of PERC efficiency, which may lead to up to 16% relative performance losses in multicrystalline silicon solar cells, and this degradation occurs in almost all types of silicon wafers. Even in next-generation silicon solar cells like Tunnelling oxide passivated contact (TOPCon) and Heterojunction with Intrinsic Thin-layer (HJT) solar cells, LeTID can still cause an efficiency loss up to 1% relative. LeTID is a long process in terms of time during the whole cycle of degradation and regeneration, which will seriously affect the conversion efficiency and stability of solar modules, and hence increase the cost of electricity generated by solar cells. Furthermore, after years of research on LeTID, researchers are yet to determine the specific cause of LeTID. In this paper, we refer to specific literature, briefly describe the development history of LeTID, introduce the phenomena of LeTID in crystalline silicon solar cells, and describe its characteristics. In addition, we also analyzed the fundamental causes of LeTID, and found that the cause may be related to metal impurities or hydrogen contained in solar cells. At present, in view of the participation of hydrogen in LeTID and other existing related theories, this paper introduces several methods to inhibit LeTID in crystalline silicon. Finally, the content of this paper is summarized, and the development of solar cells in the future is prospected.

Contents

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1. Introduction

Light-induced degradation (LID) is a common phenomenon that leads to the efficiency degradation of crystalline silicon solar cells. The degradation rate of LID is relatively fast and can lead to saturation within few days. The research on LID is also relatively early, and the research has been relatively sufficient, and the cause of degradation has also been unambiguously recognized, mainly boron oxygen defects. In recent decade, a new phenomenon leading to the degradation of crystalline silicon solar cells has attracted the attention of the photovoltaic community. It exists in monocrystalline and multicrystalline silicon (mc-Si) PERC solar cells [1]. This phenomenon is called light and elevated temperature-induced degradation (LeTID). For LID, its degradation phenomenon can reach saturation in a short period of time at normal temperature, whereas LeTID is under high temperature conditions for a longer period of time to reach saturation degradation. LeTID will have a significant and lasting impact on silicon photovoltaic modules [2]. At present, PERC solar cells dominate the commerce, and LeTID can cause up to 16% performance loss in PERC solar cells [3], therefore, the research on LeTID is significant.

LeTID was first discovered in mc-Si solar cells [4]. In 2012, Ramspeck et al. [4] first studied mc-Si PERC solar cells under operating conditions [4]. It was found that without any treatment, the average degradation caused by LeTID can reach 10% relative, and its maximum degradation can reach up to 16% [3]. In 2015, Kersten et al. [5] found that LeTID would accelerate its degradation at high temperature [5]. Moreover, they reported that V_{OC} decreased significantly after 150 h of illumination at a high temperature of 50 – 90 °C. They also showed that the degradation rate correlates with the minority carrier injection level [6]. The behavior of LeTID is complex, showing different degradations under different conditions or due to small changes in device fabrication [2].

Unlike BO-LID, LeTID has been detected in many different materials, such as boron or phosphorus-doped Czochralski silicon [7–9], quasimono-crystalline silicon [10], mc-Si [11], and float-zone (FZ) silicon [12]. Due to the formation of boron–oxygen (BO) defects, the traditional boron doped Czochralski silicon solar cells will suffer serious light-induced degradation (LID) [13], and gallium doping is an effective method to reduce BO defects [14]. Compared with boron doped mc-Si, gallium-doped mc-Si has lower degradation rate [15]. Under the same illumination level, the carrier lifetime of gallium-doped wafers degrades more slowly, but the degree of degradation depends on the carrier injection level. And under typical LeTID conditions (75 °C, illumination of 1 sun equivalent), the degradation degree of gallium-doped silicon is lower than boron-doped silicon in some cases [15,16]. The research on dopants shows that the dopants in silicon wafers may directly participate in the formation of LeTID defects. However, research on LeTID in gallium-doped silicon is quite limited and more research is needed on its degradation characteristics [8].

Currently, PERC solar cells dominate the business [17]. This is due to its relatively low cost and high efficiency. The efficiency of commercial PERC solar cells approach 24%, which indicates that the efficiency of PERC cells approach its upper limit [18]. Tunnelling oxide passivated contact (TOPCon) solar cells and Heterojunction with Intrinsic Thin-layer (HJT) solar cells are potential technologies to replace PERC solar cells [19]. Different from the p-type silicon wafers commonly used in PERC cells, both technologies use phosphorus-doped n-type silicon wafers. Although n-type silicon solar cells will not be affected by BO-LID, it is known from the research report that LeTID will also exist in n-type wafers [7,20,21]. Compared with p-type silicon wafers, the LeTID degradation rate of n-type silicon wafers is much slower. Both TOPCon cells and HJT solar cells can use hydrogen passivation technology to improve the efficiency of solar cells, but hydrogen is likely to cause LeTID. Therefore, the LeTID will also occur in these two solar cells, but their degradation degree will be lower than that of p-type solar cells. Ran Chen et al. [19] studied the effect of the post-hydrogenation steps on the performance and stability of n-type TOPCon solar cells and found that their hydrogenated n-type TOPCon solar cells have lower LeTID [19].

The mechanism of LeTID in crystalline silicon has also been intensively studied. Current research shows that the cause of LeTID may be related to hydrogen or other impurities, such as metals contained in crystalline silicon solar cells, but the specific cause of LeTID has not been determined. Hydrogen plays a very important role in crystalline silicon solar cells. During the heat treatment, hydrogen trapped in the dielectric layer is released, which can passivate most of the defects and improve the efficiency of the solar cells [19]. However, recent studies have shown that hydrogen plays an important role in the degradation of LeTID [22]. Hydrogen-related association and dissociation processes may affect LeTID [22]. Chan et al. found that LeTID could only be observed when samples containing hydrogen dielectric layers (such as SiN_x:H and AlO_x:H films) were fired [23]. By adjusting the AlO_x layer thickness, the degree of LeTID can be reduced [24]. Vargas et al. [25] confirmed that the degradation degree of solar cells was proportional to the amount of hydrogen released from the dielectric film [25]. Utkarshaa Varshney et al. [26] found that the thicker the hydrogen-containing dielectric layer, the greater the degradation of LeTID [26]. Although the understanding of hydrogen has improved significantly, the diffusivity of different H charge states at different temperatures cannot be determined [22].

Other studies have shown that LeTID is caused by dissolved metal-rich precipitates during firing [11]. A study of the recombination activity of LeTID defects at the point of maximum degradation has shown that there are already a range of metal elements that can cause defects, such as titanium, molybdenum and tungsten [27]. Some studies have proposed models to describe LeTID, one of which is that metal precipitates can be dissolved in the process of high-temperature firing [11,28]. With sufficient high peak temperature [29] and rapid cooling rate [28], the metal precipitate

Table 1
Without treatment, the impact of LeTID on the relative power of p-type solar cells and modules [31].
Source: Reproduced from Chen et al. [31], copyright 2021, WILEY Publication.

Source	Year	Type	Deg. (%rel.)	Condition
Petter et al.	2015	Cell	≈ 16(η)	75 °C, CI (1 sun equiv.) 200 h
Chan et al.	2017	Cell	12.7(η)	70 °C, 0.46 kW/m^2, 480 h
Kraus et al.	2016	Cell	11.2(η)	80 °C, 0.8 kW/m^2, 325 h
Luka et al.	2015	Cell	≈ 10(η)	75 °C 1 sun, 48 h
Sen et al.	2020	Cell	10(η)	75 °C 1 sun, 200 h (2015 cell)
			2.5(η)	75 °C 1 sun, 200 h (2019 cell)
			2.7(η)	75 °C 1 sun, 700 h (2019 cell)
Sen et al.	2020	Cell	6(η)	75 °C, 1 kW/m^2, 250 h
Ramspeck et al.	2012	Cell	5–6(η)	75 °C 0.4 kW/m^2, 400 h
Deniz et al.	2018	Cell	4.4(η)	75 °C, CI (J_{SC} equiv.), 45 min
Sio et al.	2018	Cell	4.3(η)	65 °C, 1 sun, 5 h
Padmanabhan et al.	2016	Cell	4.3(η)	90 °C, 1 sun, 21 h
Chunlan et al.	2019	Cell	3.2(η)	70 °C, 0.8 sun, 30 h
Fertig et al.	2015	Module	11(P)	85 °C, CI (1 kW/m^2 equiv.), 425 h
Kersten et al. [32]	2015	Module	11(P)	85 °C, CI MPP, 400 h
Nakayashiki et al.	2015	Module	10(P)	Outdoors-Singapore, ~2 months
Fokuhl et al.	2016	Module	9.2(P)	85 °C, CI (I_{MPP}), 400 min
		Module	7.2(P)	85 °C, CI (I_{SC} – I_{MPP}), 400 min
Kersten et al.	2017	Module	7.5(P)	Outdoors-Germany
		Module	≈ 7(P)	Outdoors-Nicosia, Cyprus, 3 years

can provide interstitial metal atoms to the wafer, and then the metal impurity can participate in LeTID. In addition, Luka et al. [30] reported copper precipitation in the rear contacts of PERC cells after LeTID, which supports this model [30]. Therefore, metal impurities are possible cause of LeTID.

In general, this paper summarizes the important findings in LeTID study and aims to help young researchers to understand this specific research field better.

2. Impact of LeTID

From a number of reports, LeTID has shown significant impact on wafers, solar cells, modules and installed systems.

2.1. Impact on mc-Si solar cells

LeTID was first discovered in mc-Si PERC solar cells. The effect of LeTID on the untreated p-type mc-Si PERC solar cells and the conditions under which LeTID occurs are listed on Table 1. It can be seen from the table that there are different differences in the degradation caused by LeTID measured by different researchers. As early as 2015, Petter et al. [3] found that LeTID can lead to 16% degradation in mc-Si PERC solar cells [3]. For the on-site test of LeTID, Kersten and others have tested the mc-Si PERC module on the outdoor field in Germany and Cyprus [3]. After 3 years, it was found that the solar cell caused a power loss of about 7% in the case of on-site operation. However, the test results show that there is still a big gap compared with the maximum degradation caused by LeTID. This shows that LeTID can last for ten years or more under normal outdoor conditions, until its degradation reaches its maximum. However, under normal circumstances, photovoltaic modules require a warranty of 25–30 years. This causes many problems for consumers and manufacturers. Therefore, researchers attach great importance to this long-term efficiency degradation phenomenon.

Since the discovery of LeTID in 2012, the academic community has paid great attention to the research on the causes of LeTID. LeTID was originally discovered in boron-doped mc-Si PERC devices [4]. First of all, the study on LeTID is analogous to the LID phenomenon that has been discovered, considering whether interstitial oxygen causes of LeTID. As shown in Fig. 1, since the maximum degradation of mc-PERC solar cell is not achieved before several hundreds of hours (see Fig. 2), this ruled out the possibility of boron oxygen

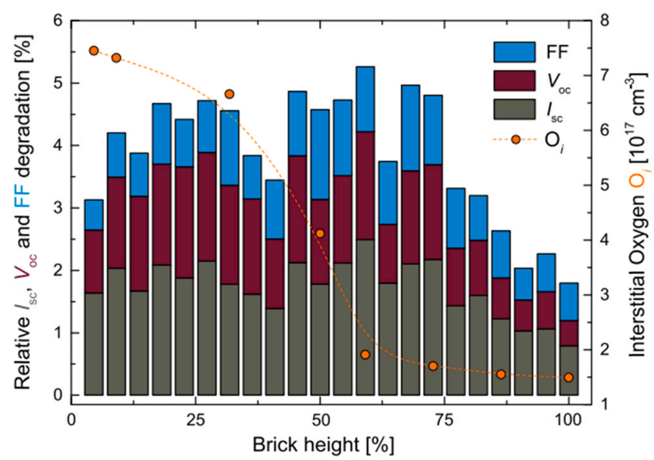

Fig. 1. Under 1,000Wm^{-2} light and 60 °C for 24 h, performance loss and reduction of interstitial oxygen concentration in mc-PERC solar cells [32].
Reproduced from Kersten et al. [32], copyright 2015, IEEE.

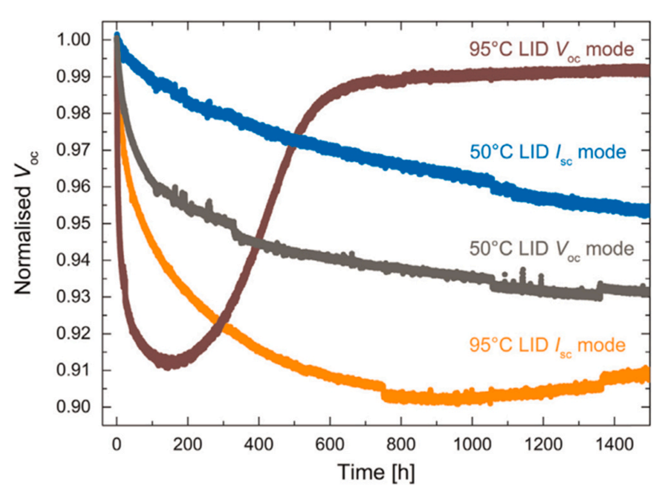

Fig. 2. At two different temperatures and operating modes(50 °C and 95 °C;V_{OC} and I_{SC} mode), light and high temperature cause degradation in p-type mc-perc [32].
Reproduced from Kersten et al. [32], copyright 2015, IEEE.

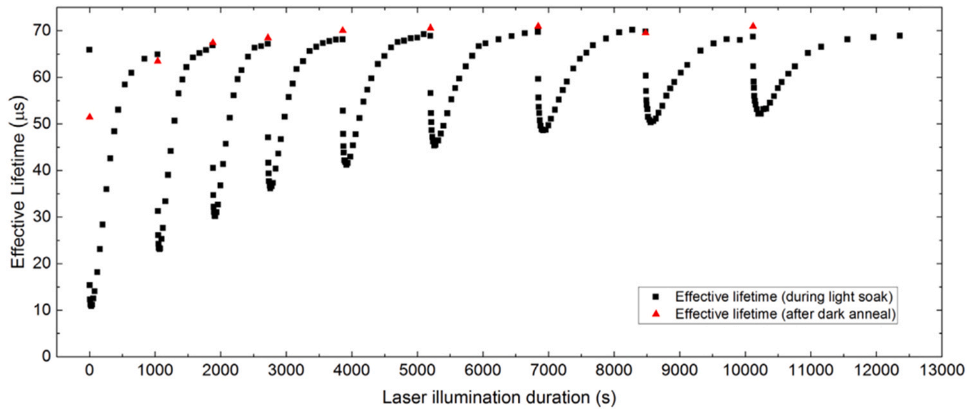

Fig. 3. The effective carrier lifetime is at the injection level of 9.1×10^{14} cm^{-3}, the illumination is 25.7 kW/m^2, and the temperature is 135 ℃. During illuminated processing (black squares), the lifetime is monitored, and measured under dark annealing at 132 °C for 8 min (red triangles) [33].
Reproduced from Fung et al. [33], copyright 2018, Elsevier B.V.

causing the root cause of LeTID, and also ruled out the possibility of iron-boron dissociation [32].

Then, researchers have conducted a lot of research on LeTID to understand the defects that lead to LeTID and the dynamics of its formation [5]. After various studies and investigations, it was found that the degradation rate of LeTID is related to the peak firing temperature and illumination level. As shown in Fig. 2, in the case of higher temperature and stronger carrier injection, the LeTID degradation rate will increase. In addition, Bredemier et al. fired mc silicon wafers at 900 °C and 650 °C respectively, and found that the silicon wafers had severe lifetime degradation at 900 °C [11]. Chan et al. [29] believe that substantial LeTID phenomenon occur only when the firing temperature is greater than 700 °C [29]. Studies by Eberle et al. have shown that wafers with fast firing processes have greater degradation than wafers with the same peak firing temperature but slower heating and cooling speeds. This shows that the cooling rate of the firing process also has an effect on LeTID [28].

There is a lot of confusion about the behavior of LeTID, and the reasons for degradation are currently not clear. Fig. 3 shows the evolution of the effective lifetime in a series of dark annealing and light soaking (DA-LS) cycles. The change in the effective lifetime during accelerated light irradiation shows the formation and subsequent removal of defects in each cycle. After applying the DA process, it will cause the system to become unstable again. After a DA process, the effective lifetime is reduced from 65µs to 51µs, and then LS leads to a minimum of 10µs. As the cycle repeats, it is found that the degree of degradation is gradually decreasing, and finally reaches a minimum in the 9th cycle. The total degradation reduction in each cycle is different from the observation of BO instability. For the samples regenerated after LeTID, the dark annealing process is performed again, which shows that the process cannot be repeated. Regarding this phenomenon, researchers realized that excess interstitial hydrogen might cause its own reorganization. LeTID may be caused by excessive interstitial hydrogen in the silicon, and when the hydrogen moves, it can cause degradation and regeneration of the sample.

2.2. LeTID in p-type and n-type ML-Si and FZ-Si

Although LeTID was first discovered in p-type mc-Si, LeTID will also appear in a variety of silicon materials. ML-Si has a lifetime distribution similar to that of monocrystalline silicon, and contains a similar amount of metal impurities to mc-Si, and has thus become the material for LeTID research. Kang et al. studied LeTID in p-type and n-type ML-Si and FZ-Si [12]. They placed different silicon wafers at 140 °C, under a sun light condition. Using an injection level of 1×10^{15} cm^{-3}QSSPC to measure the lifetime. Fig. 4 shows the effective lifetime and normalised defect density (NDD) of various materials under light at 140 °C. The calculation of NDD is based on the data measured by QSSPC, according to

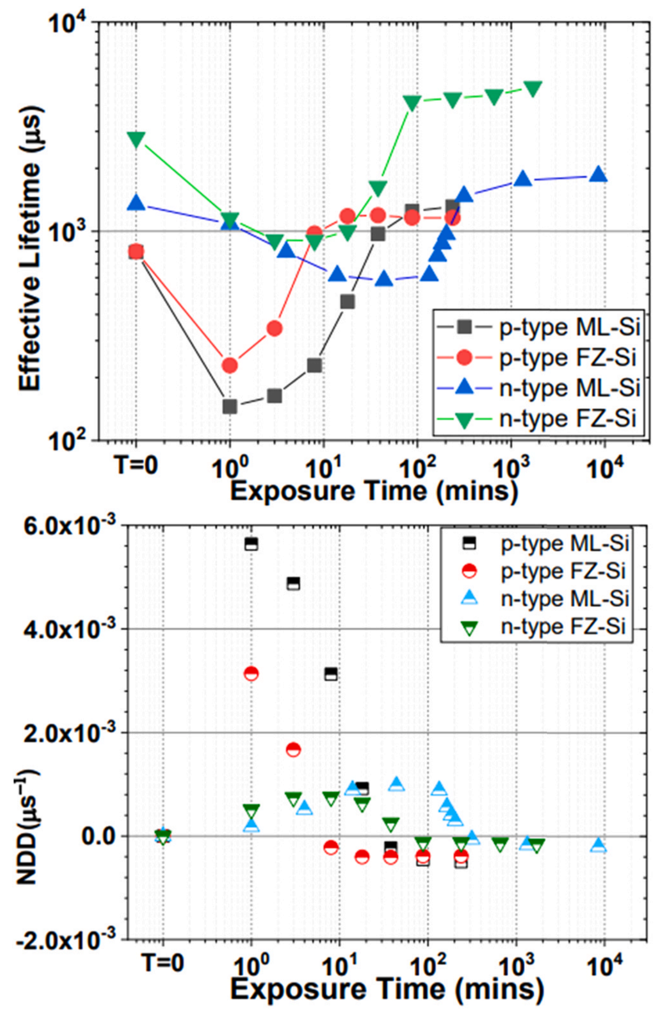

Fig. 4. At injection level of 1×10^{15} cm^{-3}, the effective lifetime and NDD of p-type and n-type ML-Si and FZ-Si silicon wafers measured by QSSPC as a function of time [12]. Reproduced from Kang et al. [12], copyright 2019, EU PVSEC.

$$NDD(t) = \left(\frac{1}{\tau_{eff\,(t)}} - \frac{1}{\tau_{eff\,(t=0)}}\right)$$

$\tau_{eff\,(t)}$和$\tau_{eff\,(t=0)}$ are the effective lifetime under different illumination time. By comparing the LeTID behavior in different materials, it is found that the degradation rate of n-type ML-Si and FZ-Si samples is much slower than that of p-type silicon, and the severity is relatively light. The efficiency degradation of N-type ML-Si and FZ-Si solar cells is not as obvious as that of p-type solar cells. The lifetime degradation of FZ-Si material is lower than that of ML-Si, indicating that defects and impurities in ML Si material may accelerate the degree of LeTID.

2.3. The influence of gallium doping on LeTID

According to early studies, solar cells on gallium-doped wafers and boron-doped wafers will experience similar degradation at high temperatures [4]. However, compared with boron-doped mc-Si, the degradation rate of LeTID of gallium-doped mc-Si is lower [14]. And under typical LeTID conditions (75 ℃, illumination of 1 sun equivalent), in some cases, the degradation degree of gallium-doped Cz-Si is lower than that of boron-doped Cz-Si [15]. However, in these studies, the difference in processing conditions and crystal structure will affect LeTID, and the reason for the difference cannot be easily attributed to the dopant.

Fig. 5 shows the normalized lifetime equivalent defect density ΔN_{leq} of gallium-doped and boron-doped samples. It can be seen from Fig. 5 that when the two different dopant types are degraded, the number of activated defects is relatively similar. ΔN_{leq} largely depends on the initial lifetime measurement after the sample is fired. It can be seen from the ΔN_{leq} gradually becoming negative in the boron-doped samples, the LeTID defect has been activated at the beginning. In the Ga-doped samples, the LeTID defects formed at the beginning were not observed, and the samples eventually recovered their original lifetime level.

In the study of boron-doped silicon, it is found that excessive carrier concentration has a strong correlation between the activation and deactivation rate of defects. The higher the carrier injection level, the faster its activation/deactivation rate. This trend can be seen from Table 2. It can be seen from the table that the degradation and regeneration rates of gallium-doped silicon are generally lower than those in boron-doped materials. It can also be seen from the table that the degradation and regeneration rate of the sample with the n + layer is faster than that of the sample with the diffusion region etched. These results show that the effect of carrier injection level on the degradation and regeneration rate of gallium doped silicon is similar to that of boron doped silicon.

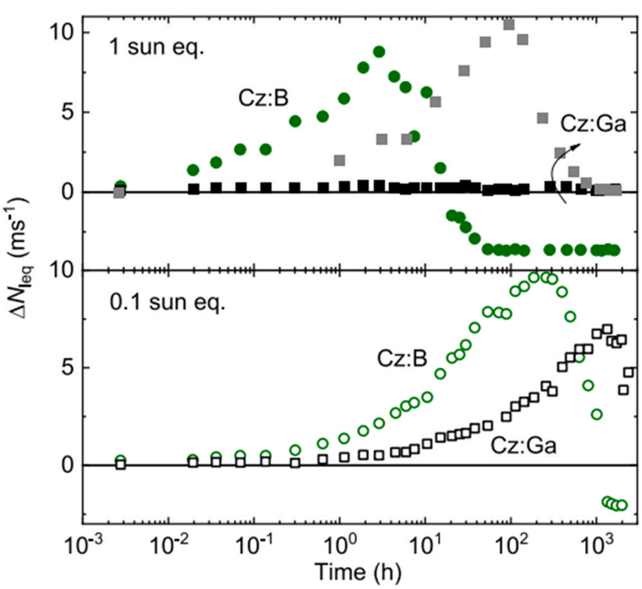

Fig. 5. The equivalent defects of boron-doped silicon and gallium-doped silicon samples under the illumination intensity of 1 sun or 0.1 sun at 75 °C. (rectangles; black: etched-back, gray: diffused) [16].
Reproduced from Kwapil et al. [16], copyright 2021, WILEY Publication.

Table 2
Degradation rate of gallium-doped samples during illuminated Degradation. The residual density of carriers changes with the lifetime of the carriers, and the estimated density range during processing is obtained [16].
Source:Reproduced from Kwapil et al. [16], copyright 2021, WILEY Publication.

Sample	Illumination	Est. excess carrier den. range $[cm]^{-3}$	Degradation rate$[h]^{-1}$
-/Si:Ga/-	1 sun eq.	8×10^{15}	–
-/Si:B/-		$1–5 \times 10^{15}$	-2.0
n^+/Si:Ga/n^+		9×10^{14}-3×10^{15}	-0.06
-/Si:Ga/-	0.1 sun eq.	1×10^{14}-1×10^{15}	-0.004
-/Si:B/-		3×10^{13}-1×10^{14}	-0.07

In general, the existing results show that, compared with boron-doped silicon, gallium-doped silicon has a different dependence on carrier injection and dynamics. But in the case of high-temperature lighting, the same defects are activated in both gallium-doped and boron-doped silicon. The degradation of gallium-doped silicon wafers is generally low. The excessive carrier concentration and degradation degree also indicate that the dopant itself in the silicon wafer may directly participate in the formation of LeTID defects. Therefore, experiments on gallium-doped silicon wafers and boron-doped silicon wafers are expected to provide new insights into LeTID and surface degradation mechanisms. At present, the research on LeTID on gallium-doped silicon wafers has solved a key problem, which can ensure the long-term stability of mass-produced modules [34]. Therefore, considering using gallium doped silicon wafer instead of boron-doped silicon wafers is a possible way to reduce LeTID.

2.4. LeTID's impact on new solar cells and summary

PERC solar cells have lower cost and higher efficiency in commercial manufacturing, and currently dominate the solar market. At present, the efficiency of mass-produced PERC solar cells is close to 24% [18], and it is approaching the limit efficiency of 24.5%. In addition, PERC cells use P-type silicon wafers, which are susceptible to BO defects, and the impact of LID is more serious. Therefore, it is very important to study new solar cell structures that replace PERC cells. TOPCon solar cells and HJT solar cells are currently two mainstream transformation directions.

Both TOPCon solar cells and HJT solar cells can break through the extreme efficiency of PERC solar cells. The ultimate efficiency of TOPCon solar cells can reach 28.7%, and the ultimate efficiency of HJT cells can reach 27.5%. The TOPCon solar cell process can be improved on the basis of PERC and is compatible with the existing PERC production line. It mainly adds steps such as boron diffusion and tunneling oxide layer deposition. The cost is lower than HJT solar cells and has a good cost performance. The HJT solar cell simplifies the process and can form a laminated solar cell with IBC and perovskite, and the ultimate efficiency is expected to exceed 30%. However, HJT solar cells are not compatible with existing equipment, and the cost is relatively high. Both of these new types of solar cells use n-type silicon wafers, which are not susceptible to BO defects. Through research on n-type wafers, it is shown that the degree of LeTID of n-type silicon is lower than that of p-type silicon, but LeTID still exists [12]. Therefore, LeTID still exists in TOPCon solar cells and HJT solar cells. Both of these two types of solar cells use a hydrogenated dielectric layer, a large amount of hydrogen can enter the bulk, and

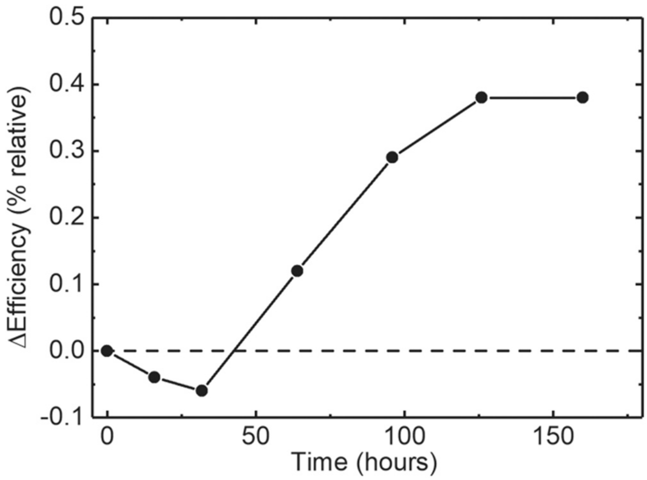

Fig. 6. At 70 ± 5 °C under 1-sun, light- and elevated temperature-induced degradation (LeTID) affects the stability of solar cells [19].
Reproduced from Chen et al. [19], copyright 2021, WILEY Publication.

hydrogen is a possible cause of LeTID, so they will both produce the LeTID phenomenon.

Ran Chen et al. conducted LeTID tests on TOPCon solar cells after hydrogenation treatment [19]. Fig. 6 shows the efficiency stability of TOPCon solar cells after hydrogenation treatment under typical LeTID test conditions (1-sun illumination and 70 ± 5 °C). After 32 h, the maximum degradation of 0.06% was reached, and continuous testing found that the cell efficiency was 0.4% higher than the efficiency at startup. This may be due to hydrogen passivating dangling bonds and defects, releasing excess and problematic hydrogen. Therefore, the efficiency of TOPCon cells can be improved through advanced hydrogenation processes, and there is almost no LeTID. Therefore, n-type TOPCon technology is expected to become the development direction of new solar cells in the future.

In short, the LeTID phenomenon has been basically observed in all silicon materials. Compared with traditional boron-doped silicon, gallium-doped silicon has a lower LeTID. Gallium-doped silicon also reduces BO defects in p-type silicon, so using gallium-doped silicon is a reasonable way to reduce LeTID. Compared with p-type silicon, n-type silicon has a lower degradation rate. Therefore, the transition from p-type solar cells to n-type solar cell technology has also become extremely important. The TOPCon solar cell and HJT solar cell are two types of n-type solar cells currently being transformed, so the research on LeTID in these two new types of solar cells is also very important. In addition, different solar cells have different characteristics under different illumination, temperature, and injection levels. In the following, this article will analyze the factors that affect LeTID and summarize the causes of LeTID.

3. Factors affecting LeTID

3.1. The influence of substrate thickness on LeTID

The results of Bredemeier et al. [36] show that the degradation degree of LeTID is related to the thickness of the silicon wafer. The silicon substrate with a thickness of less than 120 μm will not be significantly degraded. This result can be explained by two potential theories at present. Because there are metal impurities in mc-Si, according to the activation energy and capture cross-section ratio of titanium, molybdenum, tungsten [37], nickel and cobalt [36], they are considered to be factors that may cause LeTID. Reducing degradation performance through gettering also indicates that metals may participate in LeTID [38]. In addition, people think that hydrogen participates in LeTID, which can explain the existence of

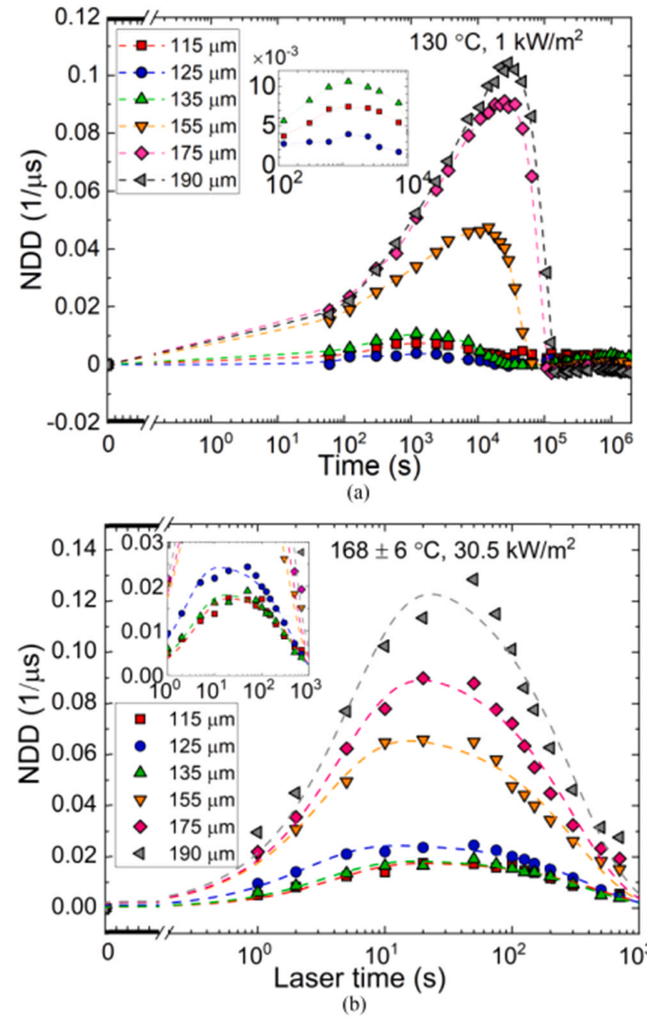

Fig. 7. The mc-Si sample is fired at a temperature of 839 ± 6 °C, (a) using halogen lamp under 1kw/m^2 at 130 °C, (b) under high-intensity laser illumination at 168 ± 6 °C and 30.5 kW/m^2, the NDD changes over time are tested [35].
Reproduced from Varshney et al. [35], copyright 2021,IEEE.

LeTID in all silicon. This is consistent with the reported degradation degree dependent on the properties of hydrogen-rich SiN_x:H films [25,39,40]. When the hydrogen-depleted AlO_x surface passivation layer is used, the degree of degradation is relatively low [23,41].

Utkarshaa Varshney et al. studied the influence of silicon wafer thickness on LeTID [35]. They chose p-type mc-Si wafers (~190 μm and 1.6 Ω·cm) at adjacent wafer positions as the substrate. The n$^+$ layer is chemically removed with nitric acid and hydrofluoric acid (HNO_3/HF) solutions to obtain wafers with a thickness in the range of 115–190 μm. After a series of processes, the required samples are obtained. The change of NDD with time for the samples placed at a temperature of 839 ± 6 °C is shown in Fig. 7.

In two different test cases, NDD will have an initial increase, and the degree of increase is related to the wafer thickness. Except for the 125 μm sample, the increase in defect concentration has a strong positive correlation with the increase in wafer thickness. The reaction kinetics is highly dependent on the injection level. The results show that the degradation range of LeTID will decrease as the thickness of the silicon substrate decreases. Thinner wafers have complete degradation and regeneration at higher firing temperatures. The thinner wafers are also essentially affected by LeTID. In thinner wafers, the decrease of degradation degree may be explained by the possibility of hydrogen exudation during firing. In addition, the optical and physical properties of the wafer have changed during

Table 3
Optical properties of silicon nitride film [26].
Source:Reproduced from Varshney et al. [26], copyright 2018, IEEE.

Sample Name	Thickness (nm)	Optical Constant
SiN_x-1x	49.6	1.02
SiN_x-2x	99.3	1.06
SiN_x-3x	146.7	1.01
SiN_x-4x	201.5	0.97

the thinning process, which may also lead to its lower deterioration. Surface morphology may also have an impact on this.

3.2. Influence of dielectric passivation layer thickness on LeTID

The LeTID in mc-Si is widely considered to originate in the bulk of the silicon substrate, but its surface properties are also very critical. SiN_x:H film is a standard passivation layer on p-type solar cells, with good anti-reflection performance, which is beneficial to passivation of n^+-type crystalline silicon surfaces. After the high-temperature firing process, the SiN_x:H film has the function of hydrogen diffusion in the surface and bulk. The degree of carrier-induced degradation (CID) in mc-Si depends on the deposition characteristics of SiN_x:H and is related to the hydrogen concentration released by the film during the firing process [25]. One way to adjust the atomic hydrogen content in the silicon bulk is to change the thickness of the passivation layer [42]. By adjusting the thickness of SiN_x:H film, the concentration of hydrogen entering mc-Si bulk can be changed, so as to study the effect of the thickness of SiN_x:H film on LeTID. Utkarshaa Varshney et al. used a spectroscopic ellipsometer to measure the thickness of the SiN_x:H film. The thickness of the sample obtained is shown in the Table 3 [26]. The thickness of SiN_x:H will change its optical properties, which will result in a change in the number of photons absorbed by each sample and change the concentration of carriers in the substrate.

Fig. 8 shows the change of NDD with time in the case of dark annealing. NDD increases with the increase of SiN_x:H film thickness. It can be seen from Fig. 8 that the SiN_x:H film has a strong influence on NDD. The degree of degradation increases as the thickness of the silicon nitride film increases, and the thickest SiN_x:H film sample produces the strongest degradation. From this, we can get a hypothesis that a thicker SiN_x:H film can release more hydrogen, so that hydrogen participates in LeTID. It can also be seen from Fig. 9

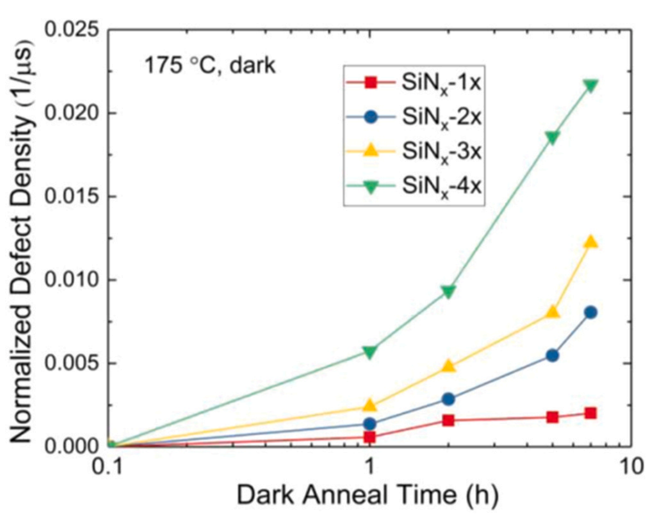

Fig. 8. Logarithmic plot of normalized defect density versus dark annealing time. Degradation condition is 175 ℃ dark annealing [26].
Reproduced from Varshney et al. [26], copyright 2018, IEEE.

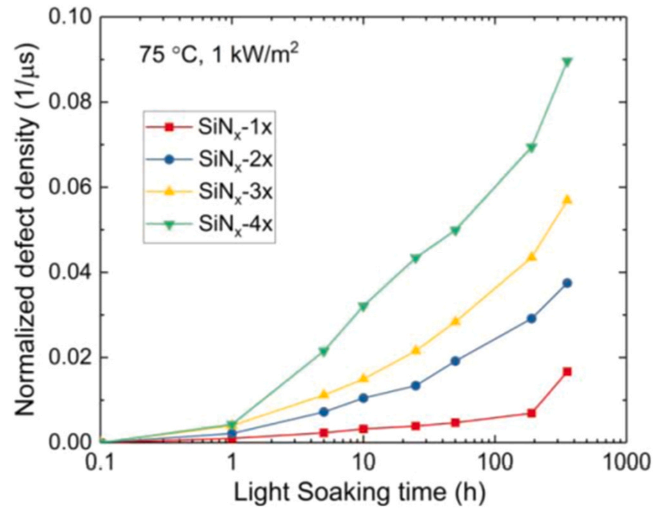

Fig. 9. Logarithmic plot of normalized defect density versus illumination time. The degradation conditions are 75 °C and the lighting intensity is 1 kW/m^2 [26].
Reproduced from Varshney et al. [26], copyright 2018, IEEE.

that the degree of high temperature annealing in the dark is higher than that under light. The degree of degradation depends on the balance between degradation rate and regeneration rate. Both of these rates are affected by temperature and carrier injection. Under illumination, the number of carriers is larger, which accelerates the degradation. In short, the use of a thicker SiN_x:H film results in greater degradation of sample lifetime, and hydrogen may participate in causing LeTID defects.

3.3. The effect of low temperature dark annealing on LeTID

The low-temperature dark annealing process is a typical solar cell processing step. The low temperature dark annealing step is very important for solar cells. It can affect the degradation degree, degradation kinetics and LeTID characteristics of solar cells. Studies have shown that a short dark annealing at a certain temperature will increase the degradation of the solar cell, which will lead to an increase in the degree of LeTID, leading to undesirable results. However, optimized annealing at a specific temperature will improve the performance of solar cells and reduce LeTID. Many researchers have conducted many experiments to explore the effect of low temperature dark annealing on LeTID.

In p-type mc-Si, post-fire thermal processing is used to suppress LeTID. Sharma et al. [43] demonstrated that the degree of lifetime degradation was reduced by 20% by firing at 550 ℃ for 20 min [43]. Yli-Koski et al. [44] reported that dark annealing at 300 °C for 40 h can completely inhibit the V_{OC} degradation in PERC [44]. However, the process is too long to be suitable for solar cell production. Marko Yli-Koski et al. [45] used commercial boron-doped high-performance mc-Si wafers with a resistivity of 1.3 Ω/cm and a thickness of 190 µm [45]. At different temperatures and times, the samples were annealed in the dark, while one sample was retained as a reference. The wafer was then placed under 0.6suns and 80 °C, and continuously exposed to degraded conditions for 1000 h. The light source is a LED lamp, the spectrum range is 400–800 nm, and the peak value is 550 nm.

As shown in Fig. 10, it is the normalized defect density (NDD) obtained by dark annealing at different temperatures for 0.5 h and then under long-time illumination. As shown in Fig. 10, it can be seen that the dark annealing temperature has a great influence on LeTID. When the dark annealing temperature is lower than 300 °C, the maximum degradation rate is faster than that of the reference sample. However, after illumination for 15–25 h or 35 h, and then

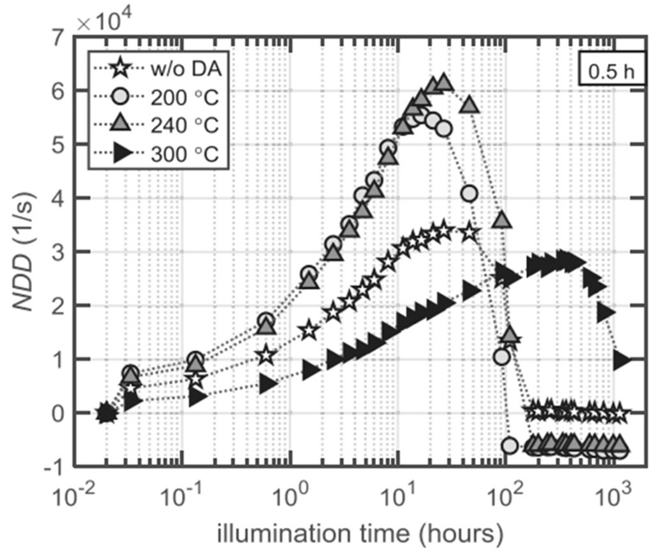

Fig. 10. The normalized defect density of the sample was dark annealed for 0.5 h under the light of 0.6 suns and 75 °C at 200 °C, 240 °C, and 300 °C. The samples without dark annealing are also used as reference [45].
Reproduced from Yli-Koski et al. [45], copyright 2019, Elsevier B.V.

through the dark annealing step, the measured NDD is much higher than that of the reference sample, even up to twice. When the dark annealing temperature reaches 300 °C, the degradation rate of LeTID is significantly slower than that of the reference sample, and reaches the maximum when it reaches 400 h. It can be shown that a temperature of 300 °C or higher may reduce the LeTID of the solar cell. It can also be seen from Fig. 10 that the NDD measured after regeneration and saturation has a negative value compared to the sample without dark annealing. This shows that some defects may be produced during the dark annealing process, and then regenerated in the subsequent lighting. Therefore, the dark annealing treatment slightly increases the initial NDD.

Because the samples obtained by dark annealing at 300 °C have interesting characteristics, Marko Yli-Koski et al. studied the effect of dark annealing time on LeTID. As shown in Fig. 11, it shows the normalized defect density of samples with different dark annealing times at 300 °C as the illumination time increases. It can be seen from Fig. 11 that the degree of LeTID has a great correlation with the

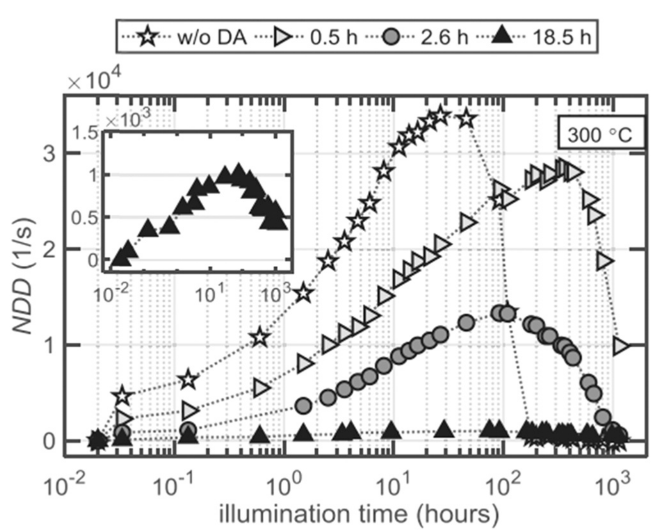

Fig. 11. Normalized defect density of samples after dark annealing at different times at 300 °C under 0.6 suns, 75 °C light [45].
Reproduced from Yli-Koski et al. [45], copyright 2019, Elsevier B.V.

dark annealing time. The shorter the duration of dark annealing, the lower the degree of LeTID. After the dark annealing time reaches 18.5 h, LeTID is almost completely suppressed. Through the analysis of the results, the researchers also carried out a long-term dark annealing by lowering the temperature. The obtained results show that long-term dark annealing at 220 °C and 240 °C also has the same trend. And in the case of lower temperature, the time required to alleviate LeTID is longer, so it is impractical to completely suppress LeTID. According to some studies, low-temperature dark annealing in a short period of time has an effect on the characteristics of LeTID. Within 5 h, it was able to increase LeTID while accelerating degradation [29,46]. So far, through literature references, it is found that the LeTID in the solar cell samples still exists at 700 °C or higher. When the temperature is lower than 675 ℃, low temperature dark annealing can reduce LeTID.

According to the above experimental analysis, it is shown that low-temperature dark annealing will affect LeTID, and the defects produced during dark annealing are the same as those produced during LeTID. This conjecture can be confirmed by injection dependent lifetime spectroscopy (IDLS) analysis [7]. Studies have shown that the longer dark annealing time and higher the temperature, the closer initial conditions are to the optimum. However, there has not yet been a unified speculation about how low-temperature dark annealing affects LeTID. Most theories believe that hydrogen plays a very important role [47], while other studies believe that it is caused by the participation of metals.

In summary, the research shows that the low-temperature dark annealing treatment will have a great impact on LeTID before the solar cell is illuminated by light. The temperature and time of low temperature dark annealing will affect LeTID and its degradation kinetics. Extending the annealing time in the dark for several hours can inhibit LeTID and almost completely remove it at 300 °C. When dark annealing is performed at 300 °C for 0.5 h, it greatly slows down the degradation and regeneration rate of LeTID. In the case of lower temperature, compared with the sample without dark annealing treatment, resulting in stronger LeTID. Therefore, the researchers will further study the effect of dark annealing on the degree of LeTID in different solar cells.

3.4. The impact of carriers on LeTID

In addition to light, defect degradation can also be observed in the case of current injection, which also suggests a carrier-induced degradation (CID) mechanism [5]. In addition to degradation, it was also found that the carrier lifetime of the solar cell would regenerate after a period of observation. Degradation and regeneration depend on injection conditions and temperature [5,48]. Higher injection and temperature conditions will accelerate degradation and regeneration cycles [5,48]. Wolfram Kwapil et al. studied the relationship between the degradation rate of solar cells and the excess carrier density of the p-n junction at a constant temperature [6]. They used 156 mm × 156 mm PERC solar cells made from p-type polysilicon wafers from three different material suppliers. The three different solar cells are called "HPM1" (base resistivity 1.7Ωcm), "HPM2" (2.2Ωcm) and "HPM3" (1.9Ωcm).

In most studies on LeTID, the generation rate of electron and holes in solar cells is constant when constant illumination is used. However, over time, the excess carrier concentration Δn decreases significantly as the carrier lifetime decreases. Under dark conditions, applying a constant voltage across the solar cell keeps the excess carrier density constant. To some extent, the carrier density depends on the carrier lifetime of the bulk. Using this method, the change of carrier density with time is minimal. The saturation current density will change with the change of defect density, and the two are in positive proportion. Fig. 12 shows the relationship between solar cell current and degradation time. The resulting value can be normalized

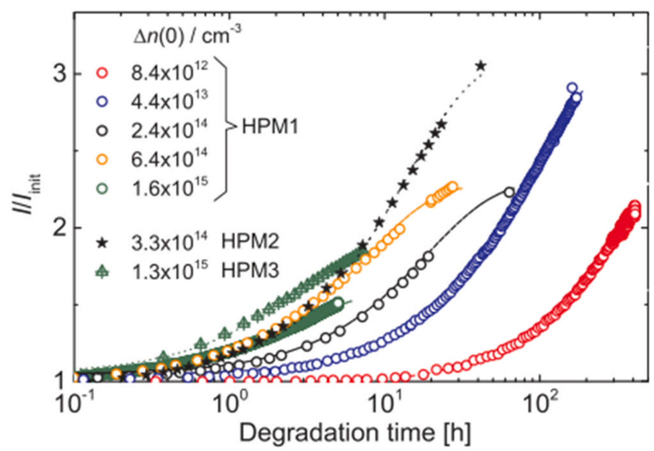

Fig. 12. Semi-logarithmic plot of relative current increase and degradation time [6]. Reproduced from Kwapil et al. [6], copyright 2017, Elsevier B.V.

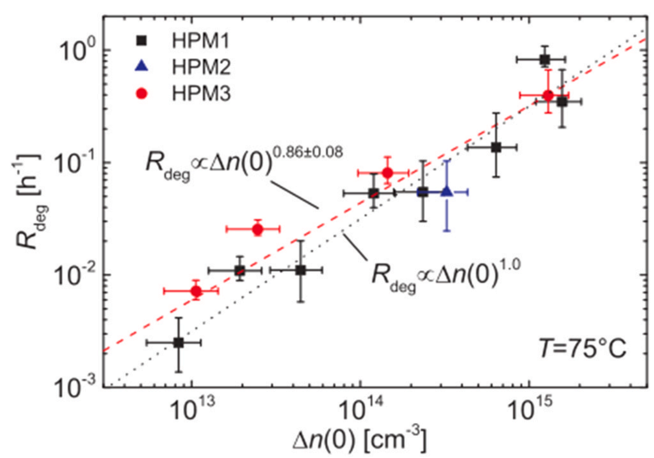

Fig. 13. The relationship between the decay rate constant and the excess carrier density of the P-N junction [6].
Reproduced from Kwapil et al. [6], copyright 2017, Elsevier B.V.

to the corresponding initial current measurement value I_{init}. When the applied voltage increases, the degradation rate will accelerate. Fig. 13 shows the relationship between the degradation rate constant and the excess electron concentration at the p-n junction. Studies have shown that the carrier degradation rate at high temperatures is almost linearly related to the excess carrier density in mc-Si. The explanation is that the LeTID precursor must change its charge state as a prerequisite.

3.5. Influence of initial sample conditions on LeTID

LeTID will produce two degradation phenomena, the first is bulk-related degradation(BRD), and the second is surface-related degradation (SRD). Changing the initial sample state may affect LeTID. The state of the initial sample can be changed by silicon-based materials, SiN_x:H film deposition, firing and annealing, etc. Benjamin Hammann et al. studied the degradation kinetics of LeTID and its surface by changing the initial sample conditions of solar cells [49].

Changing the initial state of the sample can influence the kinetics of BRD and SRD on LeTID. Combining one or two temperature steps on the studied sample can affect the density and conversion rate of composite active defects. The combination of steps at different temperatures will produce different kinetics. Different temperature steps and annealing time will also cause different effects. Almost all samples will be affected by SRD, and the kinetics of BRD is different from that of SRD.

The root cause of BRD and SRD is still uncertain. Existing research suggests that hydrogen may affect BRD [29,47]. These two degradation behaviors may be related to the firing of the high-temperature treatment process steps. Within a certain range, when the temperature rises, the degradation phenomenon becomes stronger.

Through the research of Benjamin Hammann et al., it is found that the LeTID of FZ-Si is affected by many factors. They found that LeTID was found in p-type samples of 2 and 200 Ω·cm. The LeTID phenomenon found in the n-type sample is weaker, and no typical LeTID behavior is found in the 2 Ω·cm sample. Different SiN_x:H deposition tools and subsequent steps at different temperatures will lead to different BRD kinetics. H can diffuse from the SiN_x:H film into the Si bulk, resulting in a greater lifetime-equivalent defect density through the firing step. The firing step may change the defect precursor density and transition rate, so that the lifetime-equivalent defect density increases. The annealing step may reduce the precursor defect density, But its mechanism is not yet clear.

By BRD involving the movement of defects and defect precursors, the influence of SiN_x:H deposition and subsequent temperature on the degradation rate can be described. Different temperature treatment steps can change the distribution of defect precursors and affect their movement, so that degradation occurs faster or slower.

For SRD kinetics, there is a clear difference between the fired sample and the unfired sample. The degradation rate of fired samples is lower than that of unfired samples. The study also found that SRD is not affected by atmospheric humidity, nor does it occur under ultraviolet light. The SRD phenomenon depends on light intensity and temperature, and may be due to degradation induced by one of the carriers.

By changing the state of the initial sample, various parameters can be measured, and then LeTID can be studied. Factors such as silicon-based materials, SiN_x:H deposition, firing and annealing steps will all have a certain impact on LeTID.

4. Causes of LeTID

The root cause of LeTID had intensively been conducted by researchers and some series of hypotheses had also been provided. One of the most common assumptions made before is that metal impurities cause LeTID [37]. And now more and more evidences prove that hydrogen has a great influence in the production of LeTID. The researchers found that the characteristics of silicon hydride nitride (SiN_x:H) affect LeTID, and the film can release hydrogen into the silicon bulk during the firing process [39,40]. Jensen et al. also proved that hydrogen has an effect on LeTID through plasma hydrogenation [50]. This article will then combine the references to analyze the common causes of LeTID.

4.1. Metal impurities as a possible candidate for LeTID

After the discovery of LeTID, metal impurities were one of the first reasons that cause of LeTID. As early as 2016, Bredemier proposed that metal impurities may be the root cause of LeTID. For this reason, Bredemier proposed a defect model [11]. As shown in Fig. 14, it is a simple model suitable for the participation of metal impurities from the theory proposed by Bredemeier et al. [11] It is first assumed that there are precipitates of a particular metal (M_p) in the mc-Si material. From Table 4, it is observed that there are high concentrations of various metals in mc-Si. It can be dissolved under high temperature to form interstitial metal atoms (M_i). This precipitate will not dissolve at a lower temperature of 650 °C. Due to the relatively low density of metal precipitates, their impact on bulk lifetime is also small. When these metal precipitates (M_p) dissolve into interstitial atoms. They are captured by the evenly distributed

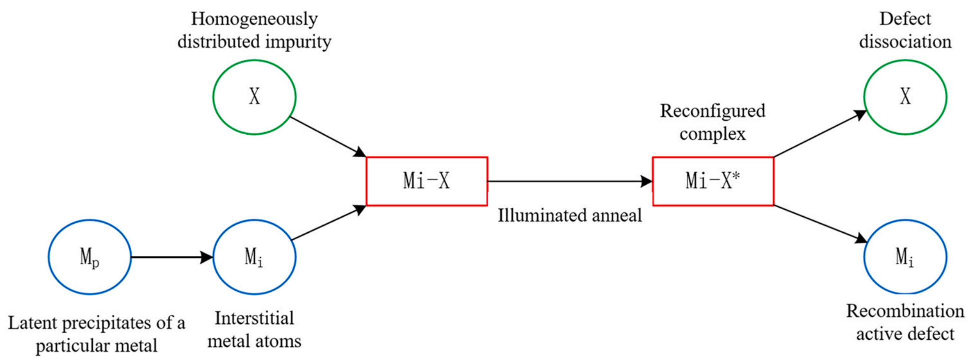

Fig. 14. A simple model suitable for the participation of metal impurities from the theory proposed by Bredemeier et al. [11].

Table 4
List of metal impurities with a total concentration of more than 10^{-12} cm^{-3} detected using mc-Si wafers , detection by inductively-coupled plasma mass spectrometry (ICP-MS) [11].
Source:Reproduced from Bredemeier et al. [11], copyright 2016, AIP.

Metallic impurity	Concentration in cm^{-3}
Aluminum	3.72×10^{15}
Zirconium	8.19×10^{14}
Silver	3.97×10^{14}
Titanium	3.26×10^{14}
Iron	2.02×10^{14}
Tungsten	1.58×10^{14}
Copper	8.30×10^{13}
Yttrium	7.72×10^{13}
Nickel	4.26×10^{13}
Chromium	1.17×10^{13}
Vanadium	7.26×10^{12}
Molybdenum	6.45×10^{12}
Cobalt	5.27×10^{12}
Manganese	3.07×10^{12}

impurities X (such as O_i, C_S, N_2, H) in Si to form a M_i-X complex. M_i-X is a weaker recombination center, in the case of high-temperature illumination, the complex may change its configuration to a more active complex M_i-X*. Through continuous light annealing, the complex M_i-X* will decompose again to form a highly reorganized activity M_i. During long-term illumination at high temperatures, movable M_i atoms diffuse to the surface of the wafer, and M_i is captured by the surface. Due to the unevenness of the wafer thickness and other characteristics, the diffusion of M_i to the surface of the wafer is also uneven, and the lifetime of its regeneration also depends on the location. The surface of the wafer is not the only place to diffuses and receives M_i. Inhomogeneous crystal defects in mc-Si can also adsorb M_i. This proposed model shows that LeTID is related to the thickness of the crystal and also related to the distribution of defects in the crystal. However, hydrogen may also play a role in the formation of defects. After rapid thermal annealing , The hydrogen in the SiN_x:H film deposited on the surface of the wafer enters the bulk of polysilicon.

Afterwards, many researchers studied the influence of metal impurities on LeTID. By using both injection dependent and temperature dependent lifetime spectroscopy, Morishige et al. proposed that LeTID may be related to the presence of tungsten [51]. Later, Niewelt et al. found an ablation zone near the polysilicon grain boundary, the solubility and diffusion coefficient of most metal impurities in the industry are known, and the researchers also proposed that the metal cobalt may be related to LeTID [47]. Wagner et al. correlated the degradation degree of LeTID with various impurities detected, including interstitial oxygen (O_i), substitutional carbon (C_S), iron (Fe), chromium (Cr), Cu, aluminium (Al), Ni and Ti [52].

Researchers investigate the effect of rapidly diffusing metal impurities on LeTID. Using elemental analysis techniques, Luka et al. [27] found copper precipitation in the grain boundaries of LeTID sensitive wafers through elemental microanalysis techniques. Yli-Koski et al. studied the effect of long-term low-temperature dark annealing on LeTID to understand the defects that have not been found so far. Because after the high temperature, some metals still exist in the wafer [53], they investigated whether the degradation and regeneration of low-temperature dark annealing are similar to the kinetics of metal precipitation. And they studied whether dark annealing has an effect on LeTID recombination. For this reason, they used dark annealing at different temperatures (200–300 °C) and time (0.5–44 h) to study LeTID in mc-Si. For this reason, they used a copper precipitation model to explain the results of dark annealing [54]. They found that higher temperature annealing for several hours can always cause LeTID, and lower temperature and shorter time will lead to stronger LeTID. This is consistent with the defect mechanism caused by metal precipitation and dissolution.

Through the study of LeTID defect recombination activity at the maximum degradation point, a series of possible defects including metal titanium, molybdenum and tungsten were found [37], and a deep understanding of the evolution of the defect recombination activity part has been obtained [55]. Research on the distribution of iron precipitation and point defects in the high temperature process has shown that time and temperature can change the distribution of metals to achieve a balance between solubility, diffusibility and segregation effects. Researchers use solubility and diffusivity to find the root cause of LeTID. Jensen MA et al. studied the distribution of metal precipitates in specific grain boundaries based on synchrotron technology and found that copper (Cu) and nickel (Ni) are aligned together during the growth process [27]. Both high temperature and low temperature roasting can reduce the size of these precipitates. They found that there is no direct correlation between precipitation and degradation. However, process simulation can be used to provide a better understanding of the root cause of LeTID. They believe that the precipitation dissolution hypothesis is only applicable to metals with high solubility and rapid diffusion, such as Ni and Cu. And in the firing process, the mechanism of increasing the concentration of point defects is related to the activation of LeTID defects. It may be that the precipitate dissolves or the getter metal segregates back into the bulk.

Gettering procedures can reduce the severity of LeTID, which is a behavior that supports LeTID caused by metal impurities. Zuschlag et al. have observed that the LeTID of the wafer obtained by the subsequent passivation and firing is reduced by using the phosphorous diffusion gettering (PDG) process and the emitter removal method [56], which means that this process removes the related defect components.

However, the claim that metal impurities lead to LeTID in FZ-Si has been questioned. Many people think that some non-metallic impurities may cause LeTID. They believe that inherent defects such as silicon self-interstitial and lattice vacancies lead to LeTID. At present, any relationship between non-metallic impurities and LeTID has not been explored clearly, so no specific conclusions have been obtained. The concept of hydrogen leading to LeTID mentioned below also shows that hydrogen atoms can be paired with almost all impurities, including carbon, oxygen and metal atoms, and these impurities may act as hydrogen receivers, so that the metal will cause LeTID.

4.2. Hydrogen as a possible candidate for LeTID

Through years of research on solar cells, there are now many convincing reasons to prove the role of hydrogen in solar cells [28,37]. Varshney et al. have demonstrated that the degree of LeTID degradation is related to the amount of hydrogen introduced during firing [39]. The lower the hydrogen content, the smaller the degree of LeTID observed. Some of these studies focused on the performance of the passivation dielectric layer, especially the hydrogenated silicon nitride (SiN_x:H) film. The film is rich in hydrogen. When the film is fired, the hydrogen in the film will release the hydrogen into the silicon bulk [39,40]. Jensen et al. linked LeTID with hydrogen itself, and proved the effect of hydrogen on LeTID through plasma hydrogenation. Nakayashiki et al. put forward a theory about hydrogen reduction defect recombination [37]. They believe that under light conditions, the change in the charge state of the hydrogen passivation defect causes the hydrogen to dissociate, and the defect is restored to the original state of composite activity. In the dark, the quasi-Fermi levels return to the valence band, so that the constituent atoms return to their original state of charge, and hydrogen can passivate the defect again. However, under the same circumstances, this theory cannot explain the formation and regeneration of defects in the dark. Most researchers believe that hydrogen is involved in LeTID, especially the Stuart team's research on hydrogen provides good support for hydrogen-induced degradation [21]. Chen et al. conducted a specific study on the effect of firing temperature on degradation [29].

Although researchers have shown that hydrogen may have an effect on the formation of LeTID, it is very difficult to characterize the hydrogen content in silicon. This is limited by characterization tools and the high mobility of hydrogen [57]. There are two main methods for researchers to study the effect of hydrogen on LeTID. Changing the hydrogen content in the passivation dielectric film or performing heat treatment can change the hydrogen diffusion effect. Fig. 15 shows the change of lifetime under different temperatures. If there is

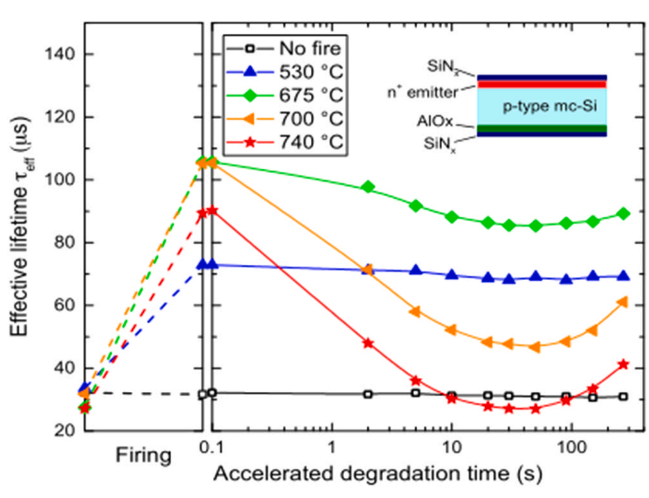

Fig. 15. Lifetime after LeTID testing at different temperatures [29]. Reproduced from Chan et al. [29], copyright 2016, IEEE.

no heating, hydrogen will not enter the silicon bulk to passivate defects. When the temperature rises, the hydrogen in the SiN_x:H film will be released into the silicon bulk to passivate the dielectric and increase the lifetime. But when the temperature rises to a certain value, the effect of improving the lifetime will be reduced, because excessive hydrogen will cause harmful effects. The study also found that the degree of degradation is related to the ratio of hydrogen released by different SiN_x:H films during the firing process [25]. The greater degree of degradation is also related to the thickness of the SiN_x:H film. From cast multi-crystalline silicon [7], cast- mono-like crystalline silicon [3], Czochralski grown silicon [7], and even float-zoned [58] and n-type silicon [20], hydrogen is found to be one of proposed causes for LeTID.

The behavior of hydrogen that causes specific degradation in any form of carrier injection (including in the dark) is called hydrogen-induced degradation (HID). If there is excessive interstitial hydrogen in the solar cell, HID will occur, which will lead to LeTID and reduce the efficiency of the solar cell. HID mainly has the following several methods that can cause the performance of solar cells to decrease.

(1) First of all, hydrogen will lead to the formation of bulk defects. The direct interaction between hydrogen atoms and the crystal lattice can lead to crystal defects. Hydrogen atoms will also interact with silicon atoms or other impurity atoms present in the solar cell to form chemical substances, resulting in complex active defects. Hydrogen can also cause hydrogen-induced recombination, which is caused by interstitial hydrogen atoms as defects.
(2) Hydrogen may increase the contact resistance of solar cells. Due to the increase of hydrogen in the solar cell, the accumulation of hydrogen in the contact area of the solar cell leads to an increase in its contact resistance and an increase in the series resistance of the solar cell, resulting in a decrease in the efficiency of the solar cell.
(3) Hydrogen may lead to increased recombination in the surface region. Deactivation of the dopant or counter-doping effect of hydrogen leads to deterioration of defects. Or the accumulation of a large amount of hydrogen on the surface of the solar cell lead to a large amount of crystal damage in the surface region. And Increased recombination in surface regions of the solar cell leads to a decrease in solar cell efficiency.

In general, among mc-Si, HID is mainly caused by the above-mentioned reasons. Since hydrogen can move and diffuse in the bulk area and surface of the solar cell, HID can cause bulk defects or surface defects, which leads to a decrease in the efficiency of the solar cell.

As many theories about recombination centers, hydrogen has attracted a lot of attention. Wenham et al. put forward a hypothesis on this, based on the high concentration of hydrogen can lead to recombination, thus creating the hydrogen-induced recombination (HIR) theory. The donor energy level H^+ of hydrogen is higher than the acceptor energy level H^-, and there is no stable neutral state H^0. A H^0 atom will convert the H^0 atom into H^- or H^+ according to the position of the Fermi Energy level (E_F) to reduce its energy. Fig. 16 shows the fractional charge state of hydrogen based on the Fermi level.

When H(+/-) is the position of EF, the probability of H^+ and H^- are equal. If E_F is higher than this value, the interstitial atoms almost exist as H^-, and if E_F is lower than this value, the interstitial atoms almost exist as H^+. This property of hydrogen means that if there is a sufficient concentration of hydrogen, E_F can be controlled and maintained at the level of H (+/-), so that the probability of forming H^+ and H^- from additional hydrogen is equal. However, H^0 is unstable, it will accept an electron or give an electron to make it H^- or H^+. In order to maintain the equilibrium fractional concentration of

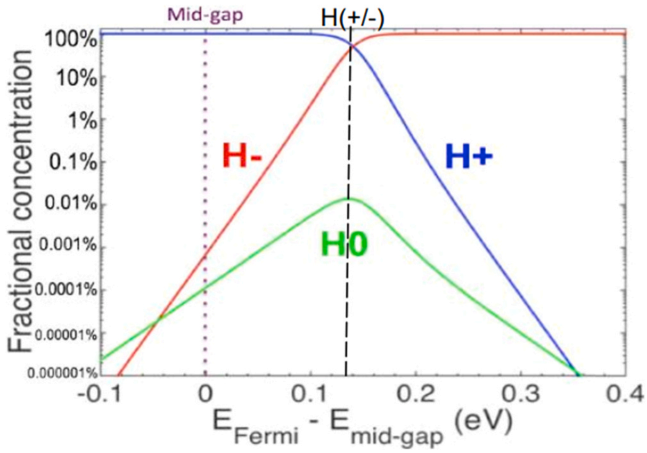

Fig. 16. Fractional charge states of hydrogen in silicon based on Fermi level, reference [59].
Reproduced from Herring et al. [59], copyright 2001, APS.

hydrogen, H^- or H^+ must form another H^0. This dynamic situation leads to hydrogen-induced recombination. Since hydrogen is the smallest atom, it is difficult to measure, whether this special mechanism will cause recombination in LeTID/HID is currently not clear evidence.

4.3. Summary

In the current research on the causes of LeTID, the root cause of LeTID has not been determined. At present, most people believe that metal impurities and hydrogen are the key reasons that affect LeTID. By changing the thickness of the substrate, the thickness of the film, the firing process, etc., the content of hydrogen in the solar cell can be altered to change the degradation degree of LeTID. The metal is a ubiquitous impurity in silicon, and it can also change the degree of LeTID degradation by changing methods such as phosphorus gettering. However, it has not been determined what role metal impurities and hydrogen play in causing LeTID, and the study of LeTID by other non-metals has not been ruled out. Therefore, the mechanism of crystalline silicon solar cell LeTID still needs to be studied in depth.

5. Methods to mitigate LeTID

5.1. Introduction to LeTID mitigation

At present, PERC solar cells still account for a large proportion in the photovoltaic industry, and LeTID has a huge impact on the efficiency of solar cells. Therefore, it is very important to find a commercial solution that can suppress LeTID defects. The various mitigation strategies proposed in the literature are summarized in the Table 5.

First of all, it is necessary to select suitable starting materials for the inhibition of LeTID. The thickness of the wafer can affect the degree of LeTID, and the degree of LeTID will decrease as the thickness of the wafer decreases. However, reducing the thickness of the wafer will have an impact on the number of solar cells produced and subsequent processing, especially for screen-printed solar cells [60]. Therefore, it is necessary to reasonably control the thickness of the wafer. Research has also shown that wafers with different ingots, or even wafers with the same ingot, can lead to different LeTID characteristics. Currently there is no silicon wafer without LeTID on the market, so choosing silicon wafers with lower LeTID is a way to reduce LeTID.

According to the research of phosphorus gettering process, it is found that it can reduce LeTID [56]. Therefore, LeTID can be suppressed by improving the process of solar cell diffusion in the emitter. The composition and thickness of the dielectric layer also have a significant effect on LeTID, which may be due to hydrogen diffusion in the film. The refractive index of SiN_x:H film will also have an impact. The researchers found that when the refractive index of SiN_x:H film is greater than 3 or lower than 1.9, it will cause a decrease in LeTID. Therefore, adjusting the various parameters of the film may have an impact on the optical and electrical properties of the solar cell. By post-processing methods, LeTID can also be suppressed. The method used is mainly to anneal the finished solar cell through light and current injection or in the dark. Forward current injection and annealing as a pretreatment can mitigate p-type Cast-Mono silicon and multicrystalline silicon PERC solar cells.[61,62].

5.2. Control hydrogen to reduce LeTID

Since hydrogen has a high possibility of causing LeTID, removing hydrogen may have a significant effect on reducing LeTID. However, the presence of hydrogen in solar cells plays an important role. The hydrogenation step is widely used in the commercial production of solar cells. Hydrogen can passivate defects in solar cells, thereby improving the voltage and efficiency of solar cells, and hydrogen has a more significant improvement on low-quality silicon substrates. PERC solar cells use p-type silicon wafers, which are susceptible to LID caused by boron-oxygen defects. Using hydrogen can passivate BO defects and alleviate degradation. Therefore, in order to suppress LeTID, it is necessary to make solar cells rationally and maximally utilize hydrogen, and then remove the excess and harmful hydrogen.

How to control the hydrogen in the solar cell is the key to stabilizing the cell. An excellent solution needs to remove excess hydrogen from the solar cell. Stable samples can be obtained through proper temperature, time, cooling and injection levels, and then heat treatment. However, there may be problems in the optimization of solar cells. Hydrogen can move in the solar cell, and hydrogen can move to the contacts, causing contact resistance problems [66]. Hydrogen can also move from the bulk to the surface in the dark at around 400 °C [67]. Therefore, researchers have paid attention to the technology that can remove hydrogen without affecting solar cell stability and without increasing contact resistance. However, at present, because hydrogen has different effects on solar cells of different wafers and different structural types, different optimizations are required, and general commercial solutions are still under development.

Table 5
Summary of Methods to mitigate LeTID.

Source	Treatment
Bredemeier et al.[36]	Reduce the thickness of the silicon wafer
Zuschlag et al.[56]	Inhibition of leTID by phosphorus diffusion gettering (PDG)
Varshney et al.[39]	Reduce the thickness of SiN_x film
Bredemeier et al.[40]	Tune the SiN_x film to high (close to 3) or low (close to 1.9) refractive index
Sen et al.[63]	Low temperature annealing (~650 °C) should be performed before metallization firing
Sharma et al.[64]	The firing conditions were optimized and dark annealing was carried out after metallization at medium temperature (300–550 °C)
Wang et al.[65]	Using single or double current injection annealing (CIA) (260 °C, 14.5 A) on finished solar cells

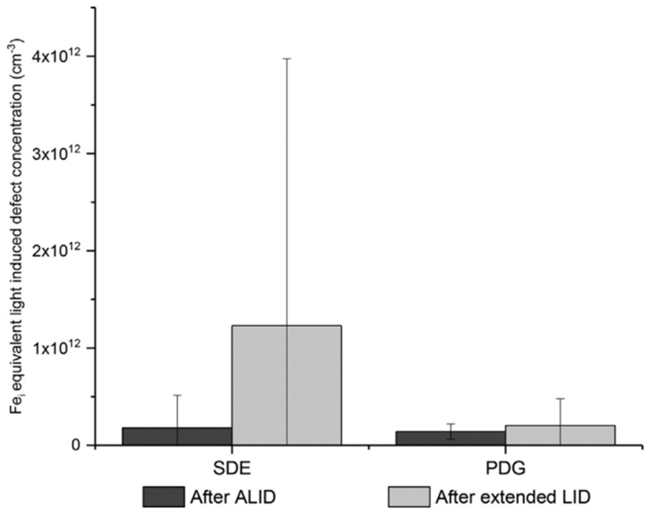

Fig. 17. The equivalent defect concentration of light induced defect before and after phosphorus gettering. The detection limit of Fe_i is 10^8 cm^{-3} [68].
Reproduced from Chakraborty et al. [68], copyright 2018, WILEY Publication.

5.3. Phosphorus diffusion gettering reduces LeTID

Researchers conducted trace element analysis by inductively coupled plasma mass spectrometry and showed that the polycrystalline silicon wafer grains at the edge of the ingot contained high concentrations of impurities, such as copper, nickel, and titanium, compared to adjacent grains. Therefore, researchers have proposed a method to reduce LeTID in mc-Si PERC solar cells using PDG.

The photovoltaic industry has successfully reduced the degradation of polysilicon by optimizing the screen-printed metal process. The researchers also studied the effect of phosphorus diffusion getters on PERC cells made of industrially produced high-performance polysilicon wafers, hoping to improve their performance. Therefore, researchers studied the impurity distribution in polycrystalline silicon wafers, hoping to find the influence of different impurity concentrations on the degradation of solar cells.

Fig. 17 shows that after accelerated light induced degradation (ALID), the difference in light induced defect concentration between the control sample and the gettering sample is more obvious, and the measured value differs by 21%. Extending LeTID at high temperature (75 °C, 1 Sun, 24 h), this difference becomes more obvious, and the difference increases to 83%. Therefore, it shows that the method of absorbing impurities can significantly change the performance of solar cells.

At present, researchers need to understand and solve LeTID in polycrystalline silicon wafers in order to reduce the cost of polycrystalline PERC cells. The dynamics of Fe_i-B or B-O defects cannot explain this phenomenon. According to recent studies, it is found that transition metal defect complexes involve this process through experiments of lifetime spectroscopy [37] and deliberate contamination of metal impurities. During the spatial analysis of defect dynamics in samples fired at different temperatures, the observation of the ablation zone also indicated that metal precipitates were found in LeTID. After PDG, the researchers measured the significantly reduced concentration of light-induced defects. Under high temperature conditions, the defects that cause LeTID may be effectively absorbed. However, it cannot be determined that the gettering process reduces LeTID, but it may be that the heat treatment step reduces LeTID defects better. Therefore, absorbing transition metal impurities can possibly be solved which indicates that the impurity concentration has a correlation with the degradation performance of solar cells. By determining the difference in the performance and concentration of impurities in different parts of the edge wafer, it shows that the regions with higher metal impurity concentrations are more concentrated. Sagnik Chakraborty and others introduced a method to inhibit LeTID [68]. Through the use of an etch-back step to analyze the sample in the emitter manufacturing process, this hypothesis is proved.

In crystalline silicon solar cells, transition metal impurities will affect the carrier lifetime and can aggravate the degree of LeTID. The more severe the LeTID, the higher the concentration of metal impurities, such as Cu, Ni, and Ti. In order to prove that phosphorus diffusion gettering (PDG) can reduce LeTID, the researchers measured the concentration of light-induced defects before and after degradation. The study found that compared with a specific sample, the light-induced defect concentration of the PDG-treated wafer was 83% lower than that of the untreated sample. Because there are many impurities in solar cells that may cause LeTID, phosphorus gettering has become a method to reduce LeTID.

6. Conclusion

LeTID is ubiquitous in various solar cells. In the case of long-term high temperature and sunlight, the efficiency of solar cells can be reduced, and the cost of solar modules can be increased. Although LeTID has been studied for nearly ten years since it was discovered, the specific cause of LeTID has not yet been determined. But the hypothesis that causes LeTID in solar cells is mainly due to the metallic impurities or hydrogen in the solar cell. A large number of experiments have proved that hydrogen plays a very important role in solar cells. Hydrogen can passivate a variety of defects in solar cells, but excessive hydrogen may also cause hydrogen-induced defects and cause LeTID. PERC solar cells are easily affected by LeTID in industrial production. First of all, choosing suitable starting materials and choosing suitable doping materials in the manufacture of solar cells have an important influence on LeTID. Using gallium-doped silicon can reduce BO defects and is a way to improve LeTID. Secondly, it is also very important to control the hydrogen contained in the solar cell and remove excess impurities. Phosphorus gettering can reduce impurities in solar cells and reduce LeTID. Using proper post-processing methods can reduce LeTID. Light, current injection or annealing in the dark can effectively reduce LeTID.

At present, the efficiency of PERC solar cells is close to the limit, and the degradation of n-type solar cells LeTID is relatively low, so n-type solar cells will become the mainstream direction of future development. TOPCon solar cells and HJT solar cells are two transformational technological directions. TOPCon solar cell is compatible with the PERC solar cell production line and is very cost-effective. The HJT solar cell has the advantages of simplified process flow, high conversion efficiency, both front and back light can generate electricity, high open circuit voltage, good temperature characteristics, etc., but its cost is relatively high. But in n-type solar cells, LeTID can still cause up to 1% efficiency loss. In the past 10 years, a lot of work has led to the development of the hydrogenation process in p-type technology, but there is less research on hydrogenation process in high-efficiency n-type solar cells. Hydrogen is one of the possible causes of LeTID, and it is also extremely important to study the role of hydrogen in n-type high-efficiency solar cells. Therefore, in the follow-up research, researchers need to continue to study the characteristics of LeTID in the new type of solar cell, and explore the most fundamental reason for LeTID, and develop a more efficient solar cell.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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