Higher stability of *p*-type Ga-doped Czochralski silicon for light and elevated-temperature induced degradation: Insights into Ga-related precursors

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ABSTRACT

Light and elevated temperature-induced degradation (LeTID) is still a challenge for crystalline silicon solar cells. In this study, *p*-type Ga-doped Czochralski silicon (Cz-Si) passivated emitter rear contact (PERC) solar cells have been demonstrated to obtain higher stability for LeTID as compared to B-doped counterparts. Meanwhile, the degradation behavior in *p*-type Ga-doped Cz-Si with PERC structure is investigated. It is found that *p*-type Ga-doped Cz-Si behave quite differently than B-doped counterparts: during dark annealing at 170–260 °C, Ga-doped Cz-Si wafers have shown an extremely slower degradation in minority carrier lifetime, i. e., with a temperature-dependent precursor time where the lifetime stays almost stable at the beginning of degradation. In addition, an equivalent activation energy of $E_A = 1.05 \pm 0.05$ eV was obtained from the temperature-dependent precursor time. At last, by density functional theory (DFT) calculations, the molecular structures of the possible LeTID defect precursors, Ga-H and B-H complexes, are optimized, and the formation energies of Ga-H and B-H complexes are derived to be - 1.09 and - 0.96 eV, respectively. Further calculation also confirms a higher equilibrium temperature of reaction of acceptor-hydrogen formation and dissociation for Ga-doped Cz-Si wafers. Therefore, the lower formation energy of Ga-H complex can be one of the root causes for better LeTID stability in Ga-doped Cz-Si, while the participation of dopant in precursor transition of LeTID defect can be confirmed.

1. Introduction

The passivated emitter and rear contact (PERC) solar cells fabricated form *p*-type Czochralski silicon (Cz-Si) wafers have dominated the photovoltaic (PV) industry in recent years and will be still competitive in the future with its relatively low costs and the over 23 % conversion efficiency in mass production [1]. However, the formation of recombination active complex, boron-oxygen (B-O) defects during illumination will cause severe performance loss in *p*-type B-doped Cz-Si wafers, which is called Light-Induced Degradation (LID) [2]. Although the detrimental effect of B-O defects in B-doped Cz-Si wafers has been already solved in

PV industry by post-treatment approaches such as illuminated annealing or current injection annealing [3,4]. Another practical option is to replace the dopant in silicon crystals with gallium (Ga), since the *p*-type Ga-doped Cz-Si wafers will not be affected by B-O defects and hence avoid the additional cost induced by B-O defects elimination post-treatment [5,6]. In addition, Grant et al. have demonstrated that Ga-doped Cz-Si wafers show much smaller degradation in minority carrier lifetime than B-doped Cz-Si wafers, which suggests the great potential of *p*-type Ga-doped Cz-Si as the substrate of PERC solar cells [5]. Thus, *p*-type Ga-doped Cz-Si has become more and more attractive for both PV industry and academia recently.

Although Ga-doped Cz-Si is free from B-O defects, it has been demonstrated that the performance of Ga-doped Cz-Si wafers is also unstable upon illumination at elevated temperature [7,8], which is called Light and elevated Temperature Induced Degradation (LeTID), firstly reported by Ramspeck et al. [9]. Notably, the behavior of LeTID in B-doped crystalline silicon has been studied for years, many experimental results show that hydrogen is required for the activation of LeTID defect [10–13]. However, the root cause of LeTID is still uncertain. Thus, more researches about LeTID in Ga-doped Cz-Si are still needed, since it could provide indications to the underlying mechanism and mitigation strategies of LeTID, which could further enhance the stability of *p*-type Ga-doped Cz-Si PERC solar cells and of is of great significance to global PV industry.

This article presents the advantage of *p*-type Ga-doped Cz-Si PERC solar cells of excellent stability upon light and elevated-temperature. To evaluate the root cause, the degradation behaviors of the effective minority carrier lifetime in *p*-type Ga-doped Cz-Si wafers during dark annealing and illumination are investigated, it is confirmed that the defect activated during dark annealing is identical to the LeTID defect through injection dependent lifetime spectroscopy (IDLS) analysis. By using Density Functional Theory (DFT) calculations, the optimized structures and formation energies of the LeTID defect precursors, B-H and Ga-H complexes are derived. At last, the reaction mechanism of LeTID defect in *p*-type Ga-doped Cz-Si and its correlation with the excellent stability of *p*-type Ga-doped Cz-Si PERC solar cells upon LeTID are discussed.

2. Experiments

2.1. Samples preparation

Hundreds pics of (100) orientation, *p*-type Ga- and B-doped Cz-Si wafers with the resistivity of ~1.0 Ω cm, the thickness of ~170 μm and the size of 166×166 mm^2 were selected to be fabricated into PERC solar cells and PERC structure samples without metal electrodes, respectively, in Chint Co, Ltd. In details, the processing includes chemical cleaning, alkaline texturing, phosphorous diffusion-in (~130 Ω/sq), phosphosilicate glass (PSG) removal, rear surface polishing and deposition of passivation layers (~80 nm hydrogenated silicon nitride (SiN$_x$: H) film on the front surface and ~10 nm AlO$_x$/~75 nm SiN$_x$:H stack films on the rear surface) and then screen printing (noted that the PERC structure samples were fabricated without screen printing process). At last, these wafers were fast fired in a belt furnace for 1 min with a speed of 4.5 °C/min while the measured peak firing temperature is 760 °C. The as-fabricated PERC solar cells were used to evaluate the electrical performance and LeTID stability. The PERC structure samples were laser cleaved into about 41.5×41.5 mm^2 tokens for ease of further treatments and measurements.

2.2. Measurement techniques and evaluation procedures

For *p*-type Ga- and B-doped Cz-Si PERC solar cells, the electrical performance was characterized by an *I-V* tester at the temperature of 25 °C. The long-term stability test was performed on the selected 50 pics of PERC solar cells from each batch, with the set temperature and illumination intensity to be 75 °C and 1 sun for tens of hours. During the above treatment, these PERC solar cells were periodically recorded by an *I-V* tester.

For PERC structure samples, the experiments for LeTID defect activation were carried out under dark annealing and illumination, respectively, at elevated temperature for the test of the evolution of effective minority carrier lifetime. For dark annealing, the samples were placed on a hotplate in the dark (with the illumination intensity lower than 0.1 W m^{-2}) at a temperature of 170–260 °C. In parallel, for illumination, the samples were placed on a hotplate with the temperature of 170 °C and exposed to a halogen lamp simultaneously, the illumination intensity were set to be 0.1 and 0.7 suns, controlled by an illumination intensity meter SM206. Quasi-steady-state photoconductance (QSSPC) measurements were performed periodically during LeTID evolution using Sinton WCT-120 tester at 25 °C with a fixed injection level of $\Delta n = 1.5 \times 10^{15}$ cm^{-3}. The surface saturation current density J_0 was determined at $\Delta n = 3 \times 10^{16}$ cm^{-3}, to monitor the stability of surface passivation quality of the wafers during each treatment [14]. Normalized defect density (*NDD*) was derived from minority carrier lifetime using $NDD(t) = 1/\tau(t) - 1/\tau(0)$, where $\tau(t)$ and $\tau(0)$ denotes the minority carrier lifetime at treating time t and initial state, respectively [15,16].

2.3. DFT calculations

DFT calculations were implemented through the VASP function package. First, a supercell containing 216 silicon atoms was constructed as the basic configuration, denoted as Si$_{216}$. Based on this configuration, a supercell containing one substitutional boron atom (B$_s$), one substitutional gallium atom (Ga$_s$), and one interstitial hydrogen atom (H$_i$) were constructed, respectively. Boron-hydrogen complexes (B-H), and gallium-hydrogen complexes (Ga-H), in which interstitial hydrogen atoms were placed in hexagonal interstitial sites and bridge sites, respectively, to obtain the most stable structure of interstitial hydrogen atoms in silicon. The structures of these supercells were optimized and their energies were calculated, and then the formation energies of B-H and Ga-H complexes were calculated, respectively, through the interaction between these supercells. The entropies for above supercells at different temperatures were calculated by the Phonopy source package. During the DFT calculation, the generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional was used to simulate the interactions between its electrons [17]. In the calculation, a $2 \times 2 \times 2$ k point sampling of the Brillouin zone and a plane wave basis set with a cutoff energy of 450 eV were employed. The structure was optimized until the force on each atom was less than 0.01 eV/Å, and the threshold of calculations for energy comparison was 1.0×10^{-5} eV.

3. Results and discussions

3.1. Advanced electrical performance and long-term stability of Ga-doped Cz-Si PERC solar cells

Recently, *p*-type Ga-doped Cz-Si wafers have been widely applied into PERC solar cells fabrication since they are free from B-O defects. Grant et al. have shown that Ga-doped Cz-Si is superior to B-doped Cz-Si according to the analysis of minority carrier lifetime and PL (photoluminescent) intensity [6]. Herein, we present the certified light *I-V* characteristics of the champion Ga-doped Cz-Si PERC solar cell in Table 1.

As shown in Fig. 1(a), 200 pics of as-fabricated *p*-type Ga- and B-doped Cz-Si PERC solar cells were selected and characterized, where the middle lines are the mean values while the boxes are the interquartile ranges in the figure. Noted that the average conversion efficiencies (η) of the Ga-doped Cz-Si PERC solar cells are slightly higher of 23.40 % while the one of B-doped is 23.26 %. Notably, the relative loss in average η of Ga-doped Cz-Si PERC solar cells during long-term stability test 0.61 %, which is significantly lower than that of B-doped ones of 1.01 %, as given in Fig. 1(b). Since the fabrication processes and the treating

Table 1
Electrical parameters of the certified *p*-type Ga-doped Cz-Si PERC solar cell[a].

	I_{sc} (A)	V_{oc} (mV)	I_{max} (A)	V_{max} (mV)	P_{max} (W)	*FF* (%)	η (%)
Ga-PERC	11.22	696.6	10.68	605.7	6.47	82.8	23.6

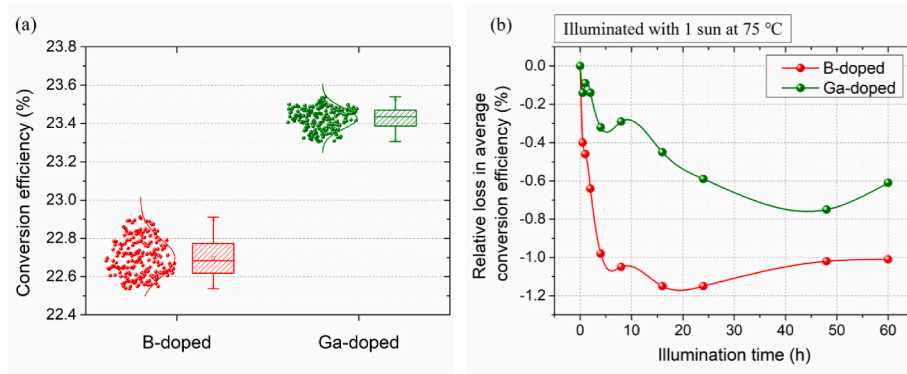[a] Certified by National Institute of Metrology, China.

Fig. 1. (a) The conversion efficiency of a batch of as-fabricated p-type Ga- and B-doped Cz-Si PERC solar cells and (b) evolutions of relative loss in conversion efficiency during stability test with 1 sun illumination at 75 °C.

conditions were identical for Ga- and B-doped Cz-Si PERC solar cells, the variations in relative loss of η should be attributed to the different response of LeTID defect in Ga- and B-doped Cz-Si upon light and elevated-temperature. Noted that although the B-O defects in B-doped Cz-Si will induce some interference when comparing the η loss, its effects are negligible under prolonged stability test of light and elevated-temperature due to the rapid degradation and regeneration rates under such a treating condition. This observation indicates that the composition of LeTID defect or related defect precursor in crystalline silicon PERC solar cell is associated to dopant in it, which has been proposed before [7,15,18,19], moreover, the deactivation and reactivation of LeTID defect may also be closely related to dopant.

3.2. Characteristics of the defect generated in Ga-doped Cz-Si during dark annealing

In order to explore the underlying mechanism for the different degradation response of the industrial p-type Ga- and B-doped Cz-Si PERC solar cells upon light and elevated-temperature, further experiments were conducted on p-type Ga- and B-doped Cz-Si PERC structure samples which are available for the assessing of surface passivation quality and defect properties. Firstly, it is of significance to figure out the differences between the behavior of LeTID defect in Ga- and B-doped Cz-Si. Fig. 2(a) depicts the evolution of effective carrier lifetimes of the Ga- and B-doped Cz-Si PERC structure samples during 170 °C dark annealing. Notably, the initial carrier lifetimes of Ga- and B-doped Cz-Si samples prepared by the same processes are comparable, however, the degradation of lifetime occurs much earlier in B-doped Cz-Si wafers than in Ga-doped Cz-Si wafers. For detailed, obvious degradation of lifetime in B-doped wafers can be observed after dark annealing for only several minutes, which is similar to the previous studies on LeTID defect [20], while the lifetime of Ga-doped Cz-Si wafers will not become unstable

until being dark annealed for over 1000 min. Although the degradation rates vary much for Ga- and B-doped Cz-Si wafers, similar amounts of degradation in lifetime can be observed. The slow degradation behavior of Ga-doped Cz-Si wafers during dark annealing is a quite confusing phenomenon, which makes some studies have reported that the Ga-doped Cz-Si wafers are much more stable than B-doped wafers without further demonstration [6], however, the root cause should be detailed discussed.

The extracted J_0 during the dark annealing process is shown in Fig. 2 (b), indicating no notable changes in the surface passivation quality during dark annealing, which further supports the hypothesis that the different degradation behaviors of lifetime in Ga- and B-doped Cz-Si wafers are caused by a bulk effect, i. e., reactions of bulk-related defect during dark annealing. Noted that only the degradation processes of lifetime in Ga- and B- doped Cz-Si wafers during dark annealing are compared, because the reaction of B-O complex would induce uncertainty in the extraction of carrier lifetime degradation when treated during illumination.

The observation of such a slow degradation behavior in p-type Ga-doped Cz-Si wafers during 170 °C dark annealing is quite interesting. For comparison, illumination with 0.1 and 0.7 suns at the temperature of 170 °C is performed, with the changes in the effective carrier lifetime and extracted J_0 during each treating condition depicted in Fig. 3. It can be seen that the carrier lifetime of Ga-doped Cz-Si PERC structure samples will degrade rapidly once being illuminated and the degradation rate accelerates as the illumination intensity increases, similar trends are also found in B-doped multicrystalline silicon and cast-monocrystalline silicon wafers, which can be explained by the injection dependent reactions of LeTID defect [16,21]. In addition, Zerfaß et al. have reported the generation behavior of lifetime equivalent defect density in Ga-doped Cz-Si wafers coated with SiN$_x$:H layers during illumination with different injection level from 7.5×10^{14} to 3.6×10^{16}
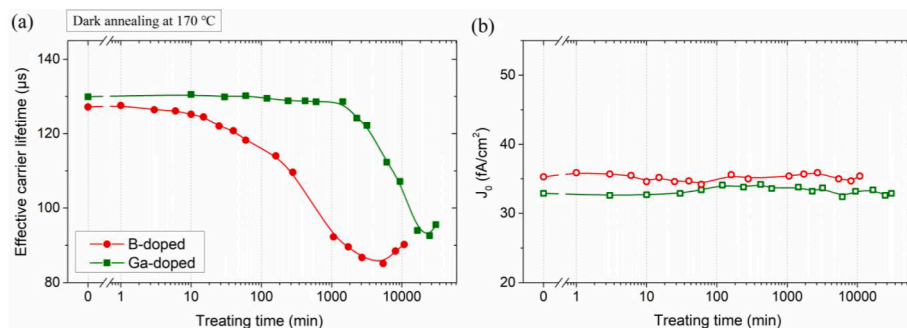

Fig. 2. Evolution of (a) effective carrier lifetime and (b) J_0 during 170 °C dark annealing in p-type Ga- and B-doped Cz-Si PERC structure samples. Lines are shown to serve as a guide to the eye.
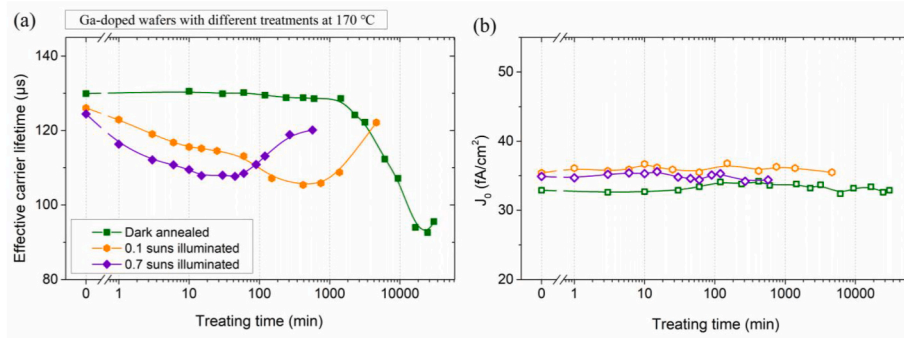
Fig. 3. Evolutions of (a) effective carrier lifetime and (b) J_0 of *p*-type Ga-doped Cz-Si PERC structure samples during dark annealing, 0.1 and 0.7 suns illumination at 170 °C. Lines are shown to serve as a guide to the eye.

cm^{-3} at 120 °C, and they have also noticed the slow degradation process during dark annealing [22]. In addition, as the variations of J_0 during each treatment plotted in Fig. 3(b), the surface passivation quality of the Ga-doped Cz-Si PERC structure samples stay stable during illumination as well. It can be inferred that the dark annealing generated defects should be the same as the illuminated annealing generated defects for Ga-doped Cz-Si wafers, although the activation process takes more time.

In order to further confirm the properties of generated defects upon different treating conditions in *p*-type Ga-doped Cz-Si PERC structure samples, the Shockley-Read-Hall (SRH) inverse lifetime $[\tau_{SRH}(\Delta n)]^{-1}$ of the generated defects are analyzed by the difference between the inverse lifetime after degradation $[\tau_{degraded}(\Delta n)]^{-1}$ (i.e. the maximum degradation point in Fig. 3) and firing $[(\tau_{fired}(\Delta n)]^{-1}$ (i.e. starting point in Fig. 3).

To simplify, assuming the energy level of the generated defects is around the mid-gap, then the electron/hole capture cross section ratio (k) of the generated defects during each treating condition can be extracted [23], with the statistical fitting results shown in Fig. 4, noted that no data of dark annealing sample is shown before 3000 min due to almost no degradation in effective carrier lifetime. Evidently, the derived k values for each treating condition (dark annealing, 0.1 and 0.7 suns illumination) are similar and all in good agreement with that of LeTID-related defect which is in the range of 26–36 [24,25]. It is also demonstrated that the defects activated through both dark annealing

and illumination have identical recombination features in Ga-doped and B-doped Cz-Si wafers. Hence, the thermally generated excess carriers during dark annealing at elevated temperatures should play a similar role in lifetime degradation as the excess carriers generated during illumination, both causing the activation of LeTID defect inside silicon bulk. In addition, Lin et al. have also recently investigated the degradation behavior of LeTID defect in *p*-type Ga-doped Cz-Si wafers under illumination and found that the activation energies of degradation and regeneration processes are not much different from that of *p*-type B-doped Cz-Si, so they have concluded that the root cause of degradation and regeneration of lifetime under illumination in Ga-doped Cz-Si is the same as in B-doped Cz-Si [8]. In conclusion, the extremely slow degradation of minority carrier lifetime in Ga-doped Cz-Si wafer during dark annealing is the characteristic processes of LeTID defect activation.

3.3. Extreme slow reaction rate of LeTID defect in Ga-doped Cz-Si during dark annealing

Since the extreme slow degradation behavior in Ga-doped Cz-Si during dark annealing has been demonstrated to be induced by LeTID defect, it is worthy exploring the detailed mechanism which is responsible for its evidently slow reaction rate, i. e., why the generation of LeTID defect in Ga-doped Cz-Si is much slower than it in B-doped Cz-Si.

For ease of comparsion, Fig. 5 depicts the evolutions of normalized carrier lifetime and *NDD* of the Ga-doped Cz-Si samples during dark annealing at varied temperatures ranging from 170 to 260 °C. Notably, a similar trend can be observed in these curves depicting lifetime degradation: the degradation in carrier lifetime has all undergone two stages, an almost stable stage and then, a degradation stage. Interestingly, the durations of the almost stable stages would decrease with the increasing temperature of dark annealing. Thus, the almost stable stage can be labeled as 'precursor time' which is possible related to the pre-reaction for the generation of precursors of LeTID defect, according to the kinetic model proposed by Fung et al. [18]. In general, deriving the activation energies of both degradation and regeneration of the LeTID defect in Ga-doped Cz-Si is conducive to obtaining related understanding. However, the same analysis proposed before does not work out for these curves in Fig. 5, i. e., no good fit (both single and double exponential fits) can be obtained based on these curves. This may be related to different levels of regeneration of LeTID defect, or to multiple kinetic processes during the precursor time. It should be noted that the evident regeneration in carrier lifetime will take over 500 h when annealed at 170 °C, which may impact the surface quality of the samples since the experiment cannot be conducted in situ. Thus, we only focus on the degradation behavior herein.

The precursor time where the carrier lifetime of the Ga-doped Cz-Si samples is almost unchanged (within 1%$_{rel}$, considering the measurement error) at each temperature has been selected according to Fig. 5(a). Then, for simplify, we identified this period of precursor time as the
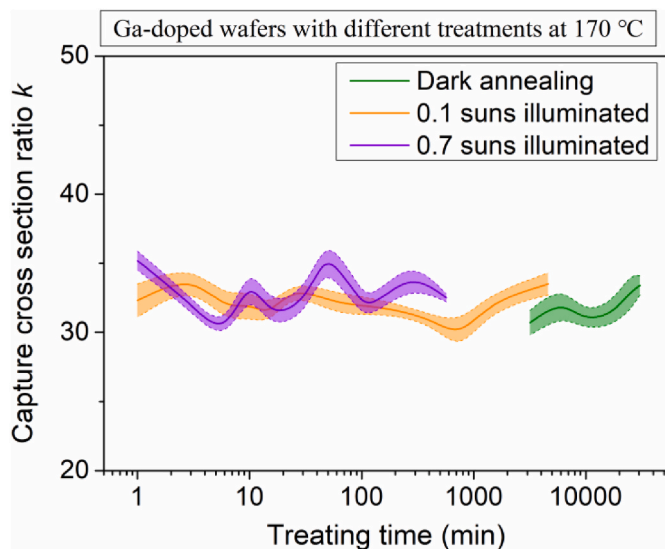

Fig. 4. The extracted capture cross section ratio k values of the generated defect in Ga-doped Cz-Si wafers based on the mid-gap assumption during each degradation process under dark annealing, 0.1 and 0.7 suns illumination at 170 °C. The marked gray range represents the reported typical k value of LeTID-related defect in literature [24,25].
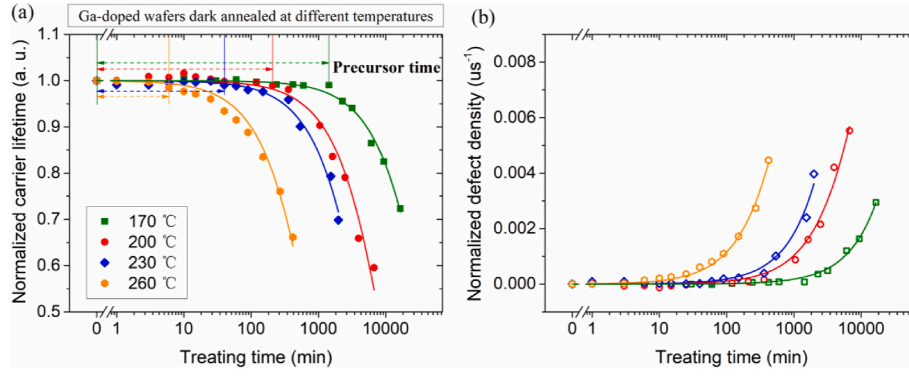
Fig. 5. Evolutions of (a) normalized carrier lifetime and (b) normalized defect density of *p*-type Ga-doped Cz-Si PERC structure samples during dark annealing at different temperatures. Lines are shown to serve as a guide to the eye.

generation of the precursor of LeTID defect which is considered to be recombination inactive (may be accompanied by the transition of a small number of LeTID defect precursors to the active defect state, which is negligible considering that the lifetime remains evidently stable) and take its reciprocal as the reaction rate constant (R_{rt}) to carry out Arrhenius fitting, as given in Fig. 6. Notably, an equivalent activation energy of $E_A = 1.05 \pm 0.05$ eV can be derived from it according to Eq. (1):

$$R_{rt} = k_0 \times exp\left(-\frac{E_A}{k_B T}\right) \qquad \text{Eq. (1)}$$

where k_0 denotes the temperature-independent pre-factor, E_A denotes the equivalent activation energy, k_B and T denote the Boltzmann constant and the absolute temperature [21]. Please noted that the error in each data point represents the uncertainty of precursor time selection.

Noted that the derived equivalent E_A here is quite higher than the reported activation energies for the activation of LeTID defect under illumination at elevated temperature, for instance, in Ga-doped Cz-Si of $E_{fast} = 0.96 \pm 0.04$ eV, $E_{slow} = 0.90 \pm 0.05$ eV, while in B-doped multicrystalline and cast-mono silicon of $E_{fast} = 0.89 \pm 0.04$ eV, $E_{slow} = 0.93 \pm 0.06$ eV and 0.83 ± 0.01 eV [8,16,21]. However, the derived equivalent E_A is close to the activation energy of degradation in B-doped multicrystalline under dark annealing is demonstrated to be 1.08 ± 0.05 eV [20]. Therefore, more exploration is needed to figure it out, the precursor time, i. e., whether the extreme slow reaction process in

Fig. 6. Reaction rate constants of the precursor time plotted versus the inverse temperature 1/T with Arrhenius fit, the different precursor times at each temperature are given inside.

Ga-doped Cz-Si wafers during dark annealing involves LeTID defect activation or other kinetic process.

3.4. Underlying mechanisms behind the LeTID defect reaction in Ga-doped Cz-Si

After years of studies, it is widely accepted that hydrogen is directly involved in the formation and/or activation of LeTID defect [11]. After fast firing, the majority of hydrogen injected into silicon bulk exists in molecular form (H_2A), especially at tetrahedral interstitial sites, leaving only a small fraction of acceptor-hydrogen complexes [26–28]. It has been demonstrated by McQuaid et al. that the annealing at 175–200 °C will result in the formation of B-H complex in silicon wafer pre-treated with high-temperature annealing and rapid quenching to room temperature [29]. In general, annealing at the elevated temperature, for instance, > 170 °C, induces the re-distribution of hydrogen with the binding behavior depending on the applied temperature and treating duration. Meanwhile, dopants also participate in this process, by the means of formation and dissociation of acceptor-hydrogen complexes, and then, affect the subsequent degradation and degeneration behavior of the minority carrier lifetime, by the means of LeTID defect reaction [26,30]. According to the four-state model proposed by Fung et al. [18], the most possible explanation for the precursor time in Ga-doped Cz-Si wafers during dark annealing displayed above can be the low transition rate from reservoir state (metastable H_2A) to precursor state (acceptor-hydrogen complex) [26,31]. Walter et al. have detailed studied the formation and subsequent dissociation behaviors of B-H complex during dark annealing at 140–270 °C in float-zone silicon (FZ-Si) wafers covered with hydrogen-rich SiN$_x$ films, they indicate the formation of B-H complex at the beginning of the annealing is related to the transition from weakly bound H_{2A} [32]. The results from Simon et al. have showed that Ga-H complexes will be formed during dark annealing at 180 °C in hydrogenated Ga-doped Cz-Si wafers while LeTID defect will barely not even for over 3 h [33]. In addition, Winter et al. have also demonstrated the slower increasing behavior of resistivity in fast fired Ga-doped Cz-Si as compared to B-doped FZ-Si with two orders of magnitude [34]. These results indicate that the formation of acceptor-hydrogen complex that is supposed as the precursor of LeTID defect in *p*-type Cz-Si wafers during dark annealing may need to overcome a larger barrier, which is one of the reasons for the presence of precursor time.

To verify these possibilities, the formation energies of the acceptor-hydrogen complexes, B-H and Ga-H complexes, are calculated through DFT, respectively. Fig. 7 shows the optimized configuration of interstitial H, B-H and Ga-H complexes in a supercell containing 216 silicon atoms. It is well accepted that when a B/Ga atom takes a substitutional site in the silicon lattice, it will form covalent bonds with four surrounding silicon atoms. Pankove et al. proposed a bonding configuration that H atom is more inclined to take the position between the acceptor
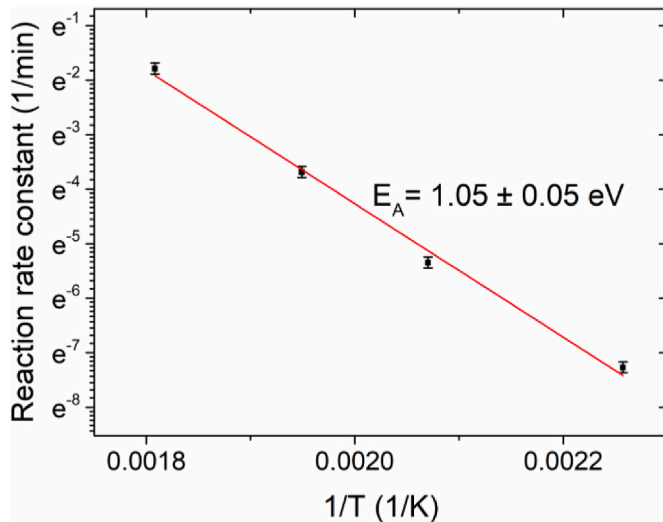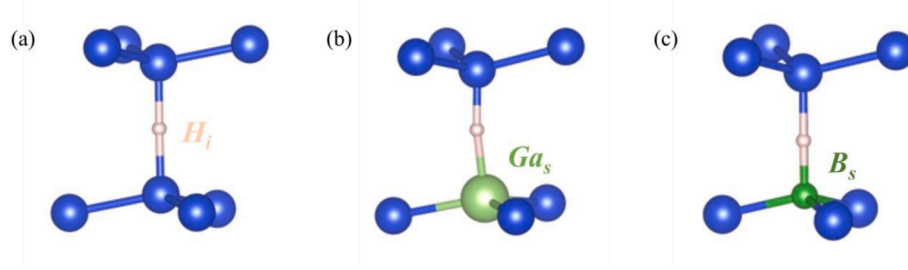
Fig. 7. The optimized configuration of (a) interstitial H, (b) Ga-H and (c) B-H complexes.

and its adjacent silicon atom [35], which is consistent with the optimized molecular structure shown in Fig. 7. The energy of each supercell is listed in Table 2. It can be seen that the bridge H_i ensures lower structure energy, so the H_i atoms will tend to be at the bridge position rather than the gap position in the silicon lattice.

According to the energy of each supercell in Table 2, combined with Eq. (2), the formation energies of B-H and Ga-H complexes can be calculated.

$$E_f = E_{Si_{215}+X-H} + E_{Si_{216}} - E_{Si_{215}+X} - E_{H_i} \qquad \text{Eq. (2)}$$

Among them, X represents B/Ga atom, the left term of Eq. (2) represents the formation energy E_f, and the right term represents the energy of each supercell respectively. It is calculated that when the H atom is at the bridge site, the formation energy of B-H complex is - 0.96 eV while the one of Ga-H complex is - 1.09 eV. The similar value of equivalent activation energy $E_A = 1.05 \pm 0.05$ eV indicates that the dissociation of Ga-H complex may take the main role in precursor time as shown in Fig. 5. Pritchard et al. have also reported that the dissociation energy of the Ga-H complex of 1.40 eV is slightly larger than that of the B-H complex of 1.28 eV [36]. Noted that the variations in previously extracted formation energies of Ga-H complex can be caused by defect in sample or experimental errors. Furthermore, according to the results from Pritchard et al., the dissociation rate of molecular hydrogen is quite slow within a time scale of hours when annealed at 160 °C [30], so, at the beginning several minutes of dark annealing treatment, the degradation of lifetime should be mostly contributed by the initial hydrogen atoms dissociated from the as-fired acceptor-hydrogen complexes.

Thus, in addition to the higher stability of Ga-H complex which ensures its slower dissociation rate, the as-fired acceptor-hydrogen complexes in Cz-Si wafers may also contribute to the activation of LeTID defect. However, although the B-doped and Ga-doped Cz-Si samples underwent the same high-temperature fast firing and rapid cooling process, due to the lower formation energy of Ga-H complex, its initial concentration should be relatively lower in Cz-Si bulk, which contributes less to the initial activation of LeTID defect as compared to B-H complex, i. e., appearing as an extremely slow degradation process in initial stage (precursor time) since the acceptor-hydrogen complexes are regarded to be recombination inactive [18,26]. Consequently, the lower formation energy of Ga-H complex may be one of the root causes of the extreme slow reaction rates of LeTID defect in *p*-type Ga-doped Cz-Si wafers during dark annealing.

As mentioned, the dissociation of acceptor-hydrogen complexes is actually the decomposition of B-H or Ga-H complex into B or Ga atom and H atom, which is the reverse process of forming acceptor-hydrogen complexes. Essentially, the formation and dissociation of B-H or Ga-H complex are two reversible processes, as can be expressed below,

$$B - H \leftrightarrow B_s + H_i \qquad \text{Eq. (3)}$$

$$Ga - H \leftrightarrow Ga_s + H_i \qquad \text{Eq. (4)}$$

Herein, B-H or Ga-H represents the B-H or Ga-H complex, B_s, Ga_s and H_i represent the substitutional B, substitutional Ga and interstitial H atoms, respectively. Then, the Gibbs free energy change (ΔG) for the decomposition of B-H or Ga-H complex is written as

$$\Delta G = \Delta H - T \times \Delta S \qquad \text{Eq. (5)}$$

Where ΔH and ΔS are the enthalpy change and entropy change due to the decomposition of B-H or Ga-H complex, which can be obtained by DFT calculations. To ensure the decomposition of acceptor-hydrogen complexes at a certain temperature (T_1), we should have

$$\Delta G(T_1) < 0 \qquad \text{Eq. (6)}$$

Based on Eq. (5), the temperature dependence of ΔG for the reactions expressed as Eqs. (3) and (4), can be calculated, as shown in Fig. 8. Therein, the crossover temperature according to $\Delta G = 0$ is ~97 °C and ~177 °C for B-H and Ga-H complex, respectively, indicating a higher equilibrium temperature of reaction of acceptor-hydrogen formation and dissociation for Ga-doped Cz-Si wafers. Noted that since the crossover temperature ($\Delta G = 0$) of Ga-H complex is ~177 °C, exactly corresponding to the applied dark annealing temperature (170 °C) which leads to longest precursor time in Fig. 5, while the increasing treating temperature will shorten the precursor time exponentially, which also
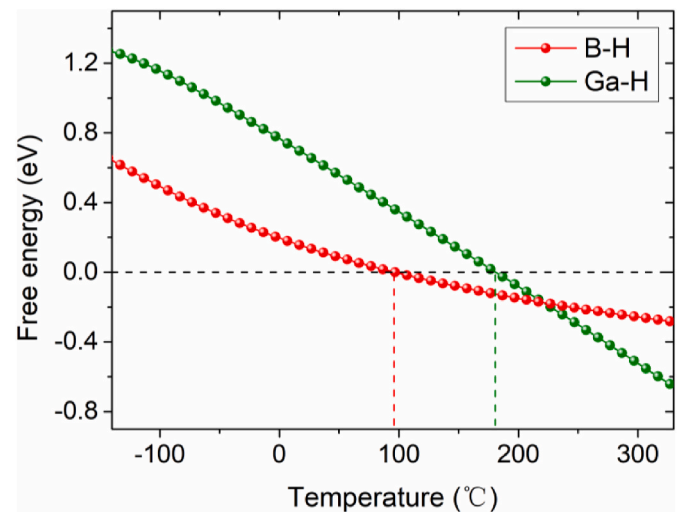
Table 2
Listed energies of different supercells.

Structure of supercells	Energy (eV)
Si_{216}	−1168.8100
$Si_{215}+B_s$	−1169.3601
$Si_{215}+Ga_s$	−1165.5714
$Si_{216}+H_i$ (bridge H)	−1170.8063
$Si_{216}+H_i$ (hexagonal interstitial H)	−1170.4731
$Si_{215}+B-H$	−1172.3181
$Si_{215}+Ga-H$	−1168.6549

Fig. 8. The change in Gibbs free energy as a function of temperature for the reactions expressed as Eqs. (3) and (4).

confirms the higher threshold temperature for the decomposition of the Ga-H complex. Considering that most of hydrogen will exist as H_{2A} in as-fired silicon wafers, and the acceptor-hydrogen complexes will form at the beginning of dark annealing through the capture of H^+ which is dissociated from H_{2A} by acceptor atoms [26]. According to the four-state model proposed by Fung et al., these acceptor-hydrogen complexes are ready for releasing H_i as the precursors of LeTID defect during prolonged treatment [18]. The key point is, since Ga-H obtains a lower formation energy than B-H, higher concentration Ga-H complex will be formed in Ga-doped silicon wafers with the same doping concentration due to the dissociation of H_{2A} during dark annealing, which reduces the existence of free H_i. In addition, the energy barrier for Ga-H decomposition is also higher, with a dissociation-trend temperature of above 170 °C, which corresponds to the long-term platform of stable carrier lifetime — precursor time in Fig. 5.

In fact, the specific responses of Ga-doped Cz-Si wafers towards different injection conditions have also been studied. Kwapil et al. have found the temporary recovery of carrier lifetime in Ga-doped Cz-Si wafers during and regarded this kind of temporary behavior to be related to hydrogen reactions [37]. Further, Thome et al. have determined the dependence of temporary recovery in Ga-doped Cz-Si wafers on injection conditions, showing that Ga doping can delay the formation of LeTID defect at the temperature up to 80 °C which also suggests the potential relation to Ga doping [38]. Although the degradation kinetics of *p*-type multicrystalline silicon solar cells under current injection condition at elevated temperature have been confirmed to depend on the excess carrier concentration, indicating the involvement of one electron in the ratelimiting step of LeTID defect formation [39], which is also supported by the varied current injection treatments on *p*-type B-doped cast-mono silicon PERC solar cells [21]. At present, Ga-doping cannot completely solve the problem of LeTID, but can only change the sensitivity of LeTID, or reduce the influence of LeTID to a certain extent, as the results shown in Fig. 1(b). Therefore, further studies on Ga and H reactions under injection conditions are still needed in the future to completely solve LeTID. In general, this work provides some hints for this purpose.

4. Conclusions

In this work, we presented the statistical electrical results of industrial *p*-type Ga- and B-doped Cz-Si PERC solar cells and their responses to light and elevated-temperature, showing that Ga-doped Cz-Si with higher LeTID stability possesses evident potential in PV application. In order to investigate the underlying mechanism of it, several groups of experiments focusing on the degradation behaviors of *p*-type Ga- and B-doped Cz-Si wafers with PERC structure upon elevated temperature during dark or illuminated were conducted. Notably, an extreme slow degradation stage in *p*-type Ga-doped Cz-Si wafers during 170 °C dark annealing was observed and labeled as precursor time, with its minority carrier lifetime staying almost unchanged. By using IDLS, the electron/hole capture cross-section ratios of defects generated during dark annealing, 0.1 and 0.7 suns illumination at 170 °C are extracted and are all in agreement with the characteristics of LeTID defect. In addition, it is demonstrated that the precursor time in Ga-doped Cz-Si wafers during dark annealing is highly temperature-dependent, which leads to an equivalent activation energy for this process of $E_A = 1.05 \pm 0.05$ eV. At last, through DFT calculations, the molecular structures of the possible LeTID defect precursors Ga-H and B-H complexes are optimized, the formation energies of Ga-H and B-H complexes are calculated to be -1.09 and -0.96 eV, respectively. Noted that the absolute value of formation energies of Ga-H complex of 1.09 eV is similar to the derived equivalent activation energy of 1.05 ± 0.05 eV, also indicating a correlation to the precursor time. Further calculation also confirms a higher equilibrium temperature of reaction of Ga-H complex of ~177 °C formation and dissociation than B-H complex of ~97 °C. Consequently, the lower formation energy of Ga-H complex can be one of the fundamental reasons for the better LeTID stability of *p*-type Ga-doped Cz-Si wafers, further regulation on acceptor and acceptor-hydrogen binding behavior may be one of the promising approaches to control LeTID defect. The understanding about the reaction of LeTID defect in *p*-type Ga-doped Cz-Si may be valuable for the development of mitigation strategies of LeTID defect.

CRediT authorship contribution statement

Zechen Hu: Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Data curation. **Lei Yang:** Methodology, Investigation, Formal analysis. **Tong Zhao:** Investigation, Formal analysis, Data curation. **Lihui Song:** Resources, Methodology. **Alex Hsu:** Resources. **Darren He:** Visualization, Resources. **Yongmei Cai:** Resources. **Hao Yu:** Data curation. **Deren Yang:** Writing – review & editing, Supervision. **Xuegong Yu:** Writing – review & editing, Supervision, Resources, Project administration, Funding acquisition.

Data availability statements

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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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Data availability

Data will be made available on request.

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