



Effects of oxygen related thermal donors on the performance of silicon heterojunction solar cells

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ABSTRACT

The influence of oxygen-related thermal donors (TDs) on the performance of silicon heterojunction (SHJ) solar cells was explored experimentally in this paper. It is found that a certain number of thermal donors could do much harm to the performance of SHJ solar cells. The efficiency of SHJ solar cells is usually reduced by a value of $\sim 1\%$ absolute in the case of thermal donors with a concentration of nearly 10^{15} cm^{-3} . The microwave photoconductance decay and Hall Effect studies have proved that the TDs can significantly reduce the carrier lifetime of n-type silicon substrate, but have no influence on the carrier mobility. Deep level transient spectroscopy (DLTS) measurements have further demonstrated that the TDs cause an energy level at $E_c - 0.13 \text{ eV}$ with carrier capture cross-section of 10^{-15} cm^2 , which is responsible for the reduction of carrier lifetime and solar cell efficiency.

1. Introduction

The first diffused p-n junction silicon solar cell was developed in the early 1950s with a conversion efficiency of around 4.5%. From then on, the efficiency of silicon solar cells has significantly improved [1]. So far, one of the highest efficiencies was at around 25.6%, achieved on the n-type silicon heterojunction with an intrinsic thin-layer interdigitated back contact (SHJ-IBC) structure [2]. Therefore, the heterojunction with intrinsic thin-layer has become one of the most promising solar cell structures, due to its high efficiency and potential low cost. The main features of SHJ solar cells are low temperature processes and little light-induced degradation [3–5].

Silicon materials made for SHJ solar cells are usually n-type single-crystalline Czochralski (CZ) silicon. It is well known that oxygen is one of the most important impurities in CZ silicon, with the concentration of about 10^{18} cm^{-3} . The effects of oxygen and related defects in CZ silicon on the performance of solar cells have been studied intensively [6,7]. During the cooling process of CZ silicon ingots or the annealing in the temperature range of 350–500 °C, oxygen impurities inevitably accumulate to form thermal donors (TDs) [8–10]. It has been known that the TDs are doubly ionized at room temperature in standard resistivity Si, which means that one TD can provide two free electrons. The double-donor character of TDs will cause a downward shift of resistivity in n-type phosphorus (P)-doped silicon. Especially, for the sample with high

concentration of oxygen impurities or subjected to a long-time heat treatment in the temperature range of 350 – 500 °C, the TD concentration could be high enough to cause the obvious doping effect. Based on the measurements of Hall effect, Fourier transform infrared spectrometry (FTIR) and deep level transient spectroscopy (DLTS), 16 families of TDs have been resolved [11–13], which usually introduce two donor levels, i.e., $E_1 = E_c - 0.05 \text{ eV}$ and $E_2 = E_c - 0.15 \text{ eV}$ [14,15].

The TDs can be generally eliminated in the high temperature courses of homo-junction cell processes, so their influence on the performance of wafers and solar cells does not get enough attention. With the developments of high efficiency and low temperature SHJ solar cell process, this issue starts to become more and more important [16–18]. Since the maximum temperature of SHJ processes remains below 300 °C, as mentioned above, the as-grown TDs are still retained in the bulk of silicon wafers. Recently, theoretical simulation results have pointed out that the TDs can significantly deteriorate the performance of SHJ cells [19]. However, few experimental data have ever been reported as of today [20].

In this paper, we have experimentally investigated the influence of oxygen-related TDs on the performance of SHJ solar cells. The evolution of SHJ solar cell performances with the TDs is explored. Meanwhile, DLTS measurements have been performed to reveal the energy levels associated with the recombination activity of TDs. The results are quite of significance for understanding the mechanism of the

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TDs influencing on the performances of SHJ solar cells.

2. Experimental details

One n-type phosphorus-doped CZ silicon crystal ingot with a diameter of 6-in. is grown by the magnetic field application and thermal field modification. Two kinds of wafers with a thickness of 190- μm cutting from different parts of the ingot were used in our experiments, which were labeled as A and B here. The interstitial oxygen concentrations in the wafer A and B were 2.5×10^{17} and $5.5 \times 10^{17} \text{ cm}^{-3}$, respectively, determined by means of FTIR after polishing at room temperature with a calibration factor of $3.14 \times 10^{17} \text{ cm}^{-2}$, with an error less than 10% through repeated experiments. After etching in an alkaline KOH solution to remove the sawing damaged layer, some wafers were subjected to 450 °C heat treatments [21] in a clean furnace for 0–50 h with argon protection to intentionally generate TDs. The resistivities of the wafers were measured by a four point-probe measurement at room temperature before and after different thermal treatments. The initial TD concentration can be derived from the resistivity variation of the samples ($n_0 = [P] + 2[\text{TD}]$) before and after a 650 °C thermal treatment in a clean furnace with argon protection for 30 min. Here n_0 is the majority carrier concentration calculated from the value of resistivity, $[P]$ is the doping concentration of phosphorus, and $[\text{TD}]$ is the concentration of TDs. As the influence of TDs on the majority carrier mobility is negligible, standard mobility models have been used for the conversion from resistivity into $[\text{TD}]$ data. For further measurements, some silicon wafers were cut into several $1 \text{ cm} \times 1 \text{ cm}$ sized samples prepared from the wafer center. The carrier mobility in the samples were measured by a Hall effect system (Lakeshore 7700 A) after four Ohmic contacts by employing Al electrodes with a diameter of 1-mm and thickness of 200-nm were fabricated on top of the samples. Detailed parameters and measurement data of the wafers are shown in Table 1.

Meanwhile, the far-infrared absorption bands related to the TDs were inspected by FTIR (Bruker Vertex 70 v) at 10 K at a resolution of 1.0 cm^{-1} . The IR-spectra were accumulated 200 times. In order to further reveal the parameters of the TD-induced energy levels, the DLTS (Phys Tech FT1030, 1 MHz) measurements were performed. Schottky diodes by employing Au electrodes with a diameter of 1-mm and thickness of 80-nm were fabricated on top of the samples, an In/Ga layer was pasted on the backside surface to form Ohmic contact. The reverse voltage (U_R) of -2 V was kept and the filling-pulse voltage (U_p) of 0 V was applied with the period (T_p) of 100 ms and duration (T_w) of 50 ms.

The SHJ solar cells were fabricated using a standard process, i.e., an intrinsic α -Si:H layer followed by a p-type α -Si:H layer was deposited on the $15.6 \text{ cm} \times 15.6 \text{ cm}$ textured n-type CZ Si wafer to form a p-n heterojunction. Subsequently, the intrinsic and n-type α -Si:H layers were deposited to obtain a back surface field (BSF) structure. In the meantime, the effective lifetime (τ_{eff}) was inspected by the Sinton lifetime tester (WCT-120) with an excess carrier density of $1 \times 10^{15} \text{ cm}^{-3}$. Next, the transparent conducting oxide (TCO) layers were deposited on the top of the doped α -Si:H layers. Finally, metal grid electrodes of 4 busbars were formed using a screen-printing method. The solar cell performances were measured under the standard conditions (one sun, AM 1.5 Global spectrum, $25 \pm 1 \text{ }^\circ\text{C}$), using a Berger Flasher PSS 10 solar

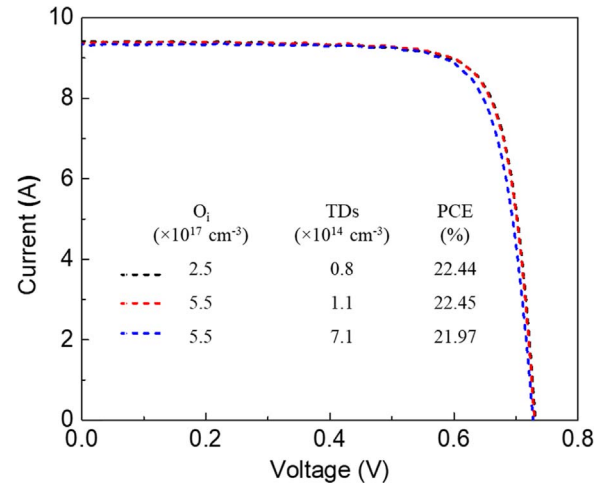


Fig. 1. Experimental I-V curves of SHJ solar cells with different TD and oxygen concentrations.

simulator. The illumination intensity was calibrated using a reference cell obtained from FISE (Fraunhofer Institute for Solar Energy Systems), Germany. The leakage current (J_0) values of solar cell are extracted through plotting the inverse τ_{eff} reduced by the inverse intrinsic lifetime (τ_{intr}) versus the excess carrier density (Δn), based on the following formulas:

$$\frac{1}{\tau_{\text{eff}}} - \frac{1}{\tau_{\text{intr}}} = \frac{1}{\tau_{\text{SRH}}} + \frac{J_0(N_d + \Delta n)}{qn_i^2 W} \quad (1)$$

where τ_{intr} is resulting from Auger and radiative recombination, τ_{SRH} is the lifetime determined by SRH defect recombination, W is the substrate thickness, q is the elementary charge, N_d is the base doping density, and n_i is the intrinsic carrier density.

3. Results and discussions

We first investigated the influence of interstitial oxygen concentration on the performance of solar cells. The I-V curves of SHJ solar cells based on two kinds of wafers with different oxygen concentration are shown by the black and red lines in Fig. 1. Note that the concentration of TDs for both kinds of samples are almost the same, about $1 \times 10^{14} \text{ cm}^{-3}$, but the oxygen concentrations are 2.5×10^{17} and $5.5 \times 10^{17} \text{ cm}^{-3}$, respectively. It can be seen that the I-V characteristics are coincident with each other. This suggests that the interstitial oxygen impurities themselves are not harmful for the solar cell performances when the oxygen concentration is not very high. However, for the samples with different TD concentration, the I-V curves of solar cells are obviously different even though the oxygen concentrations are the same, as revealed by the red and blue lines in Fig. 1. The TDs with a higher concentration of $7.1 \times 10^{14} \text{ cm}^{-3}$ give an obviously harmful influence on the performance of solar cells. Based on this result, we can conclude that the TDs instead of interstitial oxygen should be responsible for the deterioration of the SHJ solar cell performances. However, it should be mentioned here that the formation of TDs is strongly dependent on both the initial oxygen concentrations and the thermal history of sample. For the conventional production of CZ

Table 1
Description of silicon wafers.

Sample	A ₁	A ₂	B ₁	B ₂	B ₃	B ₄
Heat treatment	As-grown	450 °C/50 h	As-grown	450 °C/15 h	450 °C/35 h	450 °C/50 h
ρ ($\Omega\text{-cm}$)	4.50	4.31	4.10	3.19	2.02	1.98
TDs ($\times 10^{14} \text{ cm}^{-3}$)	0.1	0.8	1.1	2.7	7.1	7.5
Hall mobility (cm^2/Vs)	1450	1440	1435	1415	1385	1370

Table 2
Detailed data of SHJ cells of different wafers.

Sample	J_{SC} (mA/cm ²)	V_{OC} (mV)	FF (%)	PCE (%)	τ (μs)	R_{SH} (ohm)	R_S (ohm)
A ₁	38.65	731.1	79.48	22.46	3893	394	1.50
A ₂	38.60	731.2	79.51	22.44	2358	350	1.56
B ₁	38.49	729.7	79.92	22.45	2431	205	1.57
B ₂	38.77	730.2	78.78	22.30	2200	120	1.67
B ₃	38.39	727.5	78.67	21.97	978	90	1.93
B ₄	38.24	723.9	78.01	21.59	738	50	2.04

silicon crystal in photovoltaic industry without magnetic field application or/and thermal field modification, the crystal usually contains a much higher concentration of oxygen impurities ($\sim 1 \times 10^{18} \text{ cm}^{-3}$), and meanwhile suffers a long thermal history due to the low-cost continuous growth technology. The TD concentration could be high enough ($\sim 10^{15} \text{ cm}^{-3}$), which must be considered in the fabrication of SHJ solar cells.

In order to systematically investigate the effect of the oxygen-related TDs on the performances of SHJ cells, we have intentionally introduced the TDs with various concentrations in the samples by 450 °C for different time. The detailed parameters of SHJ cells are shown in Table 2. Note that for this part there were several wafers of each treatment, the data listed below were the average values of 4 samples for each treatment. Fig. 2 shows the variations of different SHJ cell parameters with the concentration of TDs. One can see that the effective minority carrier lifetime in the samples is monotonously reduced with an increase of TDs. It is strongly evident that the TDs can act as the effective recombination centers for minority carriers in our sample. The reduction of lifetime in our experiments can be attributed to two causes, i.e. Auger recombination due to increase of major carrier concentration and the SRH recombination through the TDs. However, it should be noted that Auger recombination plays an important role only in the case of high major carrier concentration above 10^{16} cm^{-3} . The variation of carrier concentration at the order of 10^{15} cm^{-3} has very limited effect on the carrier lifetime [22]. Since the carrier variation due to the TD generation is below 10^{15} cm^{-3} in this work, the Auger recombination can be neglected. Thus, it can be inferred that the reduction of lifetime is mainly caused by the recombination of TDs in our experiments.

The open circuit voltage (V_{OC}) of solar cell shows a decrease tendency from Table 2. When the TD concentration is lower than $4 \times 10^{14} \text{ cm}^{-3}$, the V_{OC} value nearly keeps constant (seeing Fig. 2a). However, the V_{OC} value of solar cell significantly decreases when the TD concentration exceeds $7 \times 10^{14} \text{ cm}^{-3}$. The reason will be explained later.

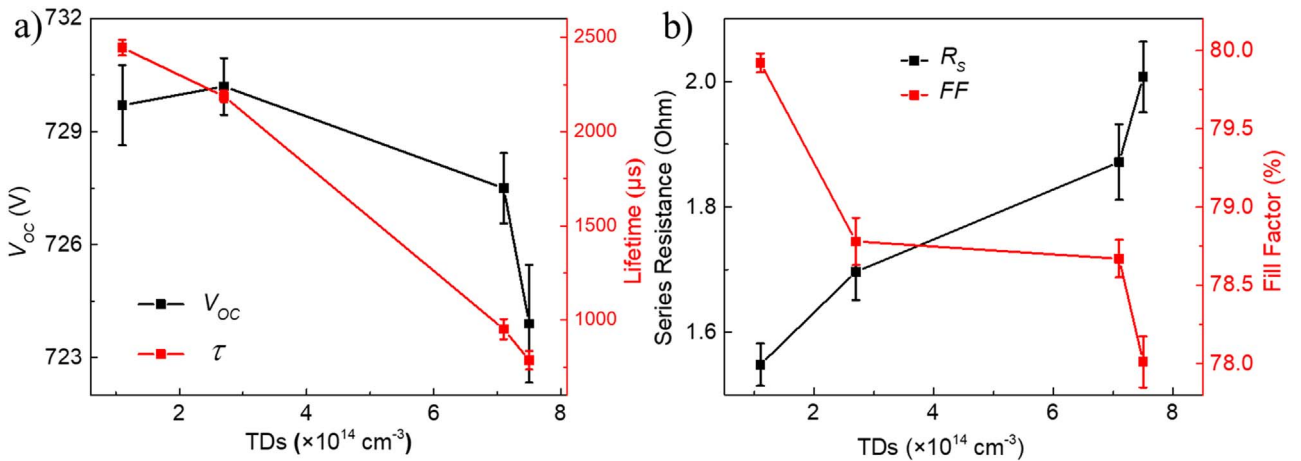


Fig. 2. a) Experimental results showing the variations of the open circuit voltage of SHJ solar cells and minority lifetime of silicon wafers with TDs. b) The variations of fill factor and series resistance with TDs.

The FF value of solar cell decreases with the increase of TD concentration (seeing Table 2 and Fig. 2b). Since the TDs can cause recombination current as the recombination centers, the shunt resistance of solar cell must be decreased, which is responsible for the reduction of FF. However, it is interestingly found that the reduction of FF is also partially attributed to the increase of series resistance of solar cell, due to the generation of TDs. As for the increase of R_S with the generation of TDs, it is not clear to understand the physical basis by now. One possible reason could be that the increase of TDs shifts the Fermi level upward. As a result, the interface barrier at the amorphous silicon and n-type bulk silicon might get increased and make the carrier transportation more difficult than before.

Since the J_{SC} values could be affected by errors in active area evaluation that reflect into efficiency values, our discussion will focus on V_{OC} values that are more related to the recombination than J_{SC} values and of course less affected by device area errors. Under the ideal conditions, it is well known that the open circuit voltage and the saturation current density can be written as

$$V_{OC} = \frac{KT}{q} \ln \left(\frac{J_{SC}}{J_0} + 1 \right) \quad (2)$$

$$J_0 = \frac{qD_e n_i^2}{L_e N_A} + \frac{qD_h n_i^2}{L_h N_D} \quad (3)$$

where k is Boltzmann's constant, q is electronic charge, T is the absolute temperature and J_0 is the saturation current density, D is the diffusion coefficient, N_A/N_D is the base doping density, L is the diffusion length, and n_i is the intrinsic carrier density. Fig. 3 shows the saturation current density J_0 of the solar cells as a function of TD concentration. It can be seen that the saturation current density of the solar cells rapidly increases when TD concentration exceeds $7 \times 10^{14} \text{ cm}^{-3}$. The rapid increase of J_0 is attributed to the recombination activity of TDs. According to Eq. (2), V_{OC} is logarithmically proportional to the reciprocal of J_0 , indicating that reducing the saturation current will increase the open circuit voltage of solar cell. In Eq. (3), all the parameters are irrelevant with J_0 but the diffusion length L and the diffusion coefficient D . It is known that L has a positive correlation with D and τ . Note that the value of D is in direct proportion to the carrier mobility μ according to Einstein's relation. Thus, it can be induced that the influence of TDs on the J_0 of solar cell could be primarily attributed to the variations of μ and/or τ . It has been previously reported that high concentration of TDs can strongly reduce the carrier mobility [5,23]. However, for the sample with the TD concentration of $7.5 \times 10^{14} \text{ cm}^{-3}$, there is only a slight drop by $\sim 6\%$ of the carrier mobility (seeing Table 1), which could be ignored in our cases. Thus, the increase of J_0 originates from the decrease of carrier lifetime, due to the TD recombination centers.

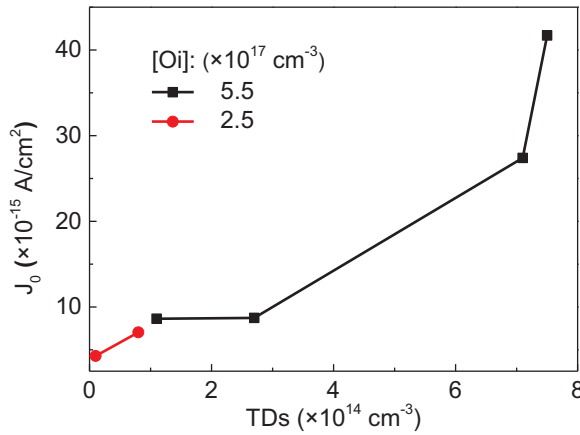


Fig. 3. Variation of J_0 of samples with different concentrations of oxygen and TDs.

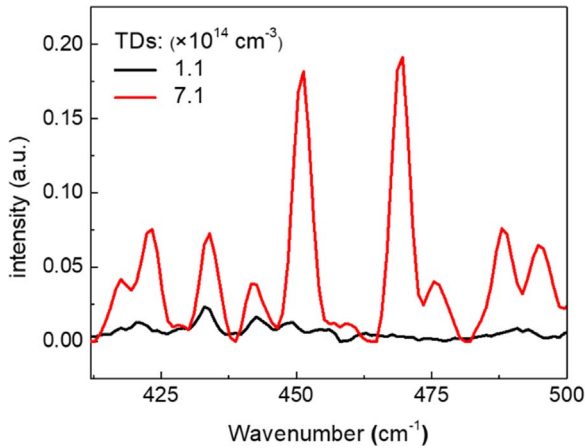


Fig. 4. Low temperature (10 K) FTIR spectra showing the absorption intensity of different concentrations of TDs.

Low temperature FTIR is one of the effective methods to detect TDs-related energy levels. TDs consist of a family of oxygen related defects that could be transformed to each other. As mentioned above, 16 families of TDs have been identified by nowadays, and several of them can be observed in our samples, seeing Fig. 4. These signals in FTIR spectra with different intensities can be observed in all the samples with 450 °C heat treatments. These peaks are quite similar with those reported before [24]. TDs are shown to give rise to IR electronic transitions showing ionization levels at about 0.04–0.07 eV, which could be identified as a superposition of absorption lines belonging to transitions from ground state to bound state [12]. However, the energy levels resolved by FTIR absorption band lines are too shallow to have enough recombination activity to reduce the carrier lifetime. The deeper levels could be detected by other methods like DLTS.

DLTS is dedicated to detecting the relatively deep energy levels induced by defects or impurities. Fig. 5 shows the DLTS spectra of samples with different concentrations of TDs. For the sake of contrastive analysis, the sample without TDs was also measured as a reference (seeing the black line in Fig. 5). It can be seen that the DLTS signals show significant enhancement with the increase of TDs, and the signal position remains unchanged, without any other energy levels being generated. More interestingly, the minor carrier capture cross-section (σ) and the state density (N_t) of TD-related energy level increase with the increase of TD concentration. Similar conclusion has been reported before [19]. So far, this phenomenon is quite beyond our understanding because of the complicity and various families of TDs. One possible reason may be that different families of TDs generate subsequently during the heat treatment at 450 °C, which have different

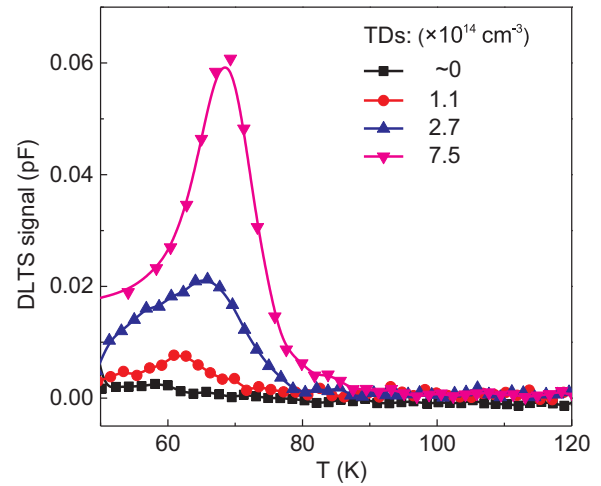


Fig. 5. DLTS spectra of different TDs. The measurement parameters are that $U_R = -2$ V, $U_P = 0$ V, $T_P = 100$ ms and $T_W = 50$ ms.

Table 3

Trap level, cross-section and state density of the DLTS levels.

TDs ($\times 10^{14} \text{ cm}^{-3}$)	~ 0	1.1	2.7	7.5
$E_C - E_t$ (eV)	–	0.12	0.12	0.13
Sigma ($\times 10^{-17} \text{ cm}^2$)	–	6.4	37	118
N_t ($\times 10^{12} \text{ cm}^{-3}$)	–	1.62	8.16	30.9

capture cross sections. This will result in the increase of the capture cross section of TDs with N_t . This issue cannot be fully resolved in this work and is worth further research (Table 3).

According to the SRH theory, recombination activity is positively correlated with state density and capture cross-section. In another word, the influence of TDs on the minority carrier lifetime becomes more and more important with the increase of TDs. As previously observed in the literatures [24,25], three TD-related energy levels (0.05, 0.12 and 0.21 eV below E_C) have been revealed in the samples subjected to heat treatment at 450 °C. The deepest one $E_C - 0.21$ eV, as reported before [19], is predicted to be responsible for the limitation of lifetime. However, the DLTS signal of this level is comparatively too weak to be detected in our measurements as the TD concentration is not very high. It is believed that in our case, the energy level of $E_C - 0.12$ – 0.13 eV associated with TDs, is responsible for the limitation of lifetime.

According to the SRH theory, it is well known that the recombination probability (U) of TDs for minority carriers can be written as

$$U \propto \sigma N_t \exp\left(\frac{E_C - E_t}{k_0 T}\right) \quad (4)$$

where k_0 is Boltzmann constant. It is simply understood that a deeper level should have stronger recombination activity for minority carriers. However, one must notice that the cross-section and state density also play an important role in the recombination activity of the energy level. The state density of TDs is usually dependent on the TD concentration, but their capture cross-section for minority carriers are significantly different in previous reports [19,24]. In our case, when the TD concentration in the sample is $1.1 \times 10^{14} \text{ cm}^{-3}$, the minority carrier capture cross-section of $E_C - 0.12$ – 0.13 eV is in the magnitude order of $\sim 10^{-17} \text{ cm}^2$. However, this value gets increased with the increase of TD concentration. When the TD concentration in the sample is $7.5 \times 10^{14} \text{ cm}^{-3}$, the minority carrier capture cross-section of $E_C - 0.12$ – 0.13 eV becomes in the magnitude order of $\sim 10^{15} \text{ cm}^2$. This situation is quite similar with the FeB pairs in silicon. The FeB pairs, with an energy level at $E_V + 0.1$ eV [26], can act as an effective recombination centers due to its large capture cross-section.

4. Conclusions

In this paper, it is experimentally clarified that the TDs have negative influences on the performance of SHJ solar cells. The decrease of minority carrier lifetime is the uppermost factor responsible for the deterioration of efficiency. By means of DLTS, the energy levels related to the TDs in band gap have been detected, which significantly reduce the fill factor and open circuit voltage to a certain extent. The results indicate that the solar cell manufacturers should choose the wafer with the concentrations of TDs as low as possible to limit their detrimental effect on the cell efficiency. Furthermore, it is of great importance for the silicon crystal growers to manage to reduce the contamination of oxygen during the crystal growth, and make the ingot cooling time as short as possible or develop appropriate methods to decrease the oxygen concentration and suppress the formation of thermal donors.

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