

# Acoustically driven degradation in single crystalline silicon solar cell

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## Abstract

The influence of ultrasound on current–voltage characteristics of crystalline silicon solar cell was investigated experimentally. The transverse and longitudinal acoustic waves were used over a temperature range of 290–340 K. It was found that the ultrasound loading leads to the reversible decrease in the photogenerated current, open–circuit voltage, fill factor, carrier lifetime, and shunt resistance as well as the increase in the ideality factor. The experimental results were described by using the models of coupled defect level recombination, Shockley–Read–Hall recombination, and dislocation–induced impedance. The contribution of the boron–oxygen related defects, iron–boron pairs, and oxide precipitates to both the carrier recombination and acousto–defect interaction was discussed. The experimentally observed phenomena are associated with the increase in the distance between coupled defects as well as the extension of the carrier capture coefficient of complex point defects and dislocations.

*Keywords:* silicon, solar cells, ultrasound influence

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## 1. Introduction

The silicon solar cells (SSCs) are still dominant in the photovoltaic field due to their high efficiency, low selling price and process maturity. The material properties driving is a top priority for most of manufacturers of SSC or another semiconductor devices. For example, the loss in the SSC efficiency is observed due to illumination (the light–induced degradation or LID in the c–Si case [1–4] and the carrier-induced degradation or CID in the mc–Si case [5, 6]), high voltage (the potential–induced degradation or PID [7–9]), or irradiation (the radiation–induced degradation or RID [10, 11]). The degradation reason is a changing of crystal defects. That is a transformation of the boron–oxygen or copper–contained complex (in LID case), a decoration of the stacking faults by the positive ions, predominantly sodium, (in PID case) or a creation of the radiation recombination centers (in RID case). The annealing at an elevated temperature is quite often required for efficiency recovery.

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At the same time, the ultrasound (US) can effectively interact with defects in silicon. It was experimentally observed that US can cause transformation of impurity and radiation defects [12–17], modification of spectrum [18] and density [19] of surface states, changing of carrier diffusion length [20, 21], variation of current in barrier structures [22–27]. Hence, it is expected that ultrasound-induced degradation (USID) can be originated by the acoustic wave (AW) action. After AW propagation had stopped, the full recovery of material properties was often observed without annealing [12, 20–22]. Therefore, the USID is expected to be a reversible at room temperature in contrast to rest of degradations.

The aim of our work is to investigate experimentally the acoustically induced (AI) variation of crystalline SSC photo-electrical parameters. Ultrasound was found to result in a decrease in the solar cell efficiency. The US intensity did not exceed  $0.5 \text{ W/cm}^2$  and the USID full recovery was observed at room temperature. The USID dependencies on the AW both type and intensity are presented. The experimentally observed phenomena are associated with the decrease in the carriers lifetime and in the shunt resistance as well as the increase in the ideality factor. To describe the processes in the space charge region (SCR) and in the diode base as well as to study shunt resistance, we used the models of coupled defect level recombination [28, 29], Shockley–Read–Hall (SRH) recombination and dislocation-induced impedance [30, 31], respectively. The observed AI phenomena are accounted for in terms of the defect interaction with the AW strain field [32, 33].

## 2. Experimental and calculation details

### 2.1. Samples

The SSC was fabricated from 2 in. ( $300 \mu\text{m}$  thick) p-type boron doped Czochralski silicon wafer with  $\langle 111 \rangle$  orientation and a doping level of  $1.4 \times 10^{15} \text{ cm}^{-3}$ . The  $n^+$  emitter with a carrier concentration of about  $10^{19} \text{ cm}^{-3}$  and a thickness of  $0.5 \mu\text{m}$  was formed by phosphorus implantation. The wafer surface was capped by the  $\text{TiO}_x$  antireflective coating. The front grid and rear full area aluminium electrodes were deposited by screen printing before rapid annealing.

The samples used in the experiment were cut from the wafer and mainly differed in the shunt resistance ( $R_{sh}$ ) value. The typical results for the samples with low ( $R_{sh} \simeq 10^4 \Omega \cdot \text{cm}^2$  at room temperature) and high ( $R_{sh} > 10^{15} \Omega \cdot \text{cm}^2$ ) values are only presented in the article. These samples is labeled “SC4” and “SC15”, respectively, from now on.

### 2.2. Ultrasound loading

In case of ultrasound loading (UL), the transverse or longitudinal AWs, which were excited by using  $\text{LiNbO}_3$  piezoelectric transducer, were applied to the samples in the  $[111]$ -direction. The transducer was attached to a full-area Al back contact. The acoustic contact was made by using the glue “BF-6”.

Table 1: The ultrasound loading parameters.

$f_{\text{US}}$ (MHz)	wave type	$W_{\text{US}}$ (W/cm <sup>2</sup> )	$\xi_{\text{US}}$ (10 <sup>-6</sup> )	$u_{\text{US}}$ (nm)	UL label	subjected samples
8.0	longitudinal	0.18	1.3	0.3	lUL	SC4, SC15
4.2	transverse	0.19	2.8	0.6	tULa	SC15
4.2	transverse	0.22	3.1	0.7	tULb	SC4
4.2	transverse	0.40	4.2	0.9	tULc	SC4, SC15

The US frequencies  $f_{\text{US}}$ , intensities  $W_{\text{US}}$ , amplitudes of lattice deformation  $\xi_{\text{US}} = \sqrt{2W_{\text{US}}/\rho_{\text{Si}}} \vartheta_{\text{US}}^3$ , and lattice atom displacements  $u_{\text{US}} = \sqrt{W_{\text{US}}/2\pi^2 f_{\text{US}}^2 \rho_{\text{Si}}} \vartheta_{\text{US}}$  are listed in Table 1.  $\rho_{\text{Si}} = 2.33 \text{ g/m}^3$  is the silicon density,  $\vartheta_{\text{US}}$  is the US velocity, 9850 m/s and 5840 m/s in cases of longitudinal and transverse AWs, respectively.

It was reported previously [13, 21, 27] that the characteristic time of change in silicon structure parameters under the US action did not exceed  $2 \times 10^3 \text{ s}$ . In order to wait until the AI transitional period is completed, the following experimental procedure was used. When UL started, the sample was first exposed to room temperature for 60 min and then the measurement and the sample heating were started. In order to avoid the effect of piezoelectric field on both the measurements and sample parameters, the transducer was shielded. The more details about the experimental setup are presented elsewhere [27].

### 2.3. Current–voltage measurements and SSC parameters determination

The dark and illuminated forward current–voltage ( $J$ – $V$ ) characteristics of the samples both with and without UL were measured over a temperature range of 290–340 K. The temperature was controlled by differential copper–constantan thermocouple. Some of the obtained curves are shown in Fig. 1.

The short–circuit current density  $J_{sc}$ , open–circuit voltage  $V_{oc}$  and the fill factor  $FF$  were estimated from the illuminated  $J$ – $V$  curve by the conventional mode.

The double–diode model of  $n^+$ – $p$  SSC  $J$ – $V$  characteristics is expressed in the following form:

$$J(V, T) = -J_{ph} + \frac{qn_i d}{2\tau_g} \left\{ \exp \left[ \frac{q(V - JR_s)}{n_{id} kT} \right] - 1 \right\} + \frac{qn_i^2}{p_p} \sqrt{\frac{\mu_n kT}{\tau_n}} \left\{ \exp \left[ \frac{q(V - JR_s)}{kT} \right] - 1 \right\} + \frac{V - JR_s}{R_{sh}}, \quad (1)$$

where  $J_{ph}$  is the photogenerated current density,  $n_i$  is the intrinsic carrier concentration,  $\tau_g$  is the SCR carrier lifetime,  $d$  is the SCR thickness:

$$d(V, T) = \sqrt{\frac{2\varepsilon\varepsilon_0(p_p + n_n)}{qp_p n_n} \left[ \frac{E_g}{q} - \frac{kT}{q} \ln \left( \frac{N_v N_c}{p_p n_n} \right) - \frac{2kT}{q} - V \right]}, \quad (2)$$

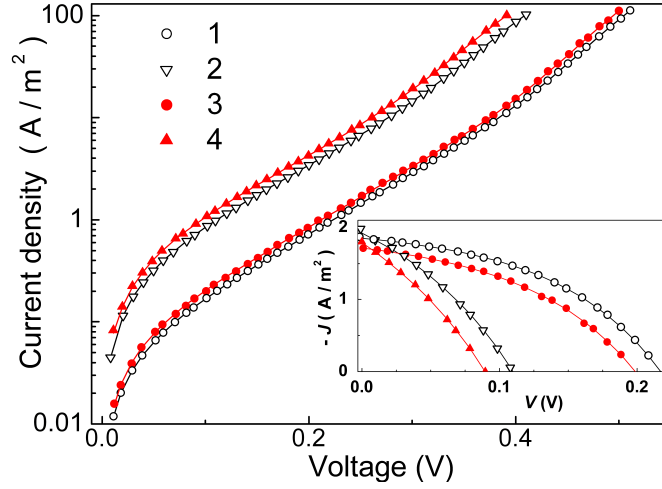


Figure 1: Dark  $J$ - $V$  characteristics measured at 301 K (curves 1, 3, circles) and 341 K (curves 2, 4, triangles) with (2, 4, filled marks, tULc) and without (1, 3, open marks) UL. Inset: Parts of illuminated  $J$ - $V$  characteristics over a voltage range of  $0-V_{oc}$ . The marks are the experimental results, and the lines are the curves fitted by Eqs. (1)–(2).

$\varepsilon$  is the permittivity (11.7 for Si),  $p_p$  and  $n_n$  are the majority carrier concentration in the  $p$ - and  $n$ -type regions,  $E_g$  is the semiconductor band gap,  $N_c$  and  $N_v$  are the effective density of states in the conduction and valence bands;  $n_{id}$  is the ideality factor,  $R_s$  is the series resistances, and  $\mu_n$  and  $\tau_n$  are the mobility and lifetime of the electron (minority carrier) in the diode base. The current-voltage equation that models the solar cell by an equivalent electrical circuit contains several parameters related to physical phenomena occurring in the device. It is commonly believed that  $J_{0base} = (qn_i^2/n_n)\sqrt{\mu_n kT/\tau_n}$  is closely related to the recombination in the quasi-neutral region, while  $J_{0SCR} = (qdn_i/2\tau_g)$  describes the overall SCR recombination.

We used Eqs. (1)–(2) to fit the experimental data taking  $\tau_g$ ,  $\tau_n$ ,  $n_{id}$ ,  $R_{sh}$ ,  $R_s$ , and  $J_{ph}$  (for illuminated  $J$ - $V$  curves only) as the fitting parameters. Also, we used the known [34–36] temperature dependences of  $n_i$ ,  $E_g$ , and  $\mu_n$ . As a result, we obtained extremely good fit to the experimental data — see Fig. 1. The parameters values, obtained from the dark and illuminated measurement at the same temperature and UL option, were identical practically. This concordance is quite expected at low illumination intensity [37].

It is known that  $J_{sc} \approx J_{ph}R_{sh}/(R_{sh} + R_s)$ . Typical values for SSC  $R_s$  are between 0.5 and 2  $\Omega\cdot\text{cm}^2$  [38, 39]. The value of  $R_s$  was found to be about 1.5  $\Omega\cdot\text{cm}^2$ , whereas  $R_{sh}$  exceeded 4  $\text{k}\Omega\cdot\text{cm}^2$ . Therefore it is expected that  $J_{sc} \approx J_{ph}$ . In fact, this relation was observed for the  $J_{ph}$ , which was obtained by fitting of whole of  $J$ - $V$  curve, and the  $J_{sc}$ , which was obtained as a point of intersection of a  $J$ - $V$  curve with a current axis.

To evaluate the US influence the relative change of parameters were used:

$\varepsilon_P = (P_{in} - P_{us})/P_{in}$ , where  $P$  is one of the set  $\{J_{sc}, V_{oc}, FF, \tau_g, \tau_n, R_{sh}\}$ , subscripts “US” and “in” indicate the values obtained at the same temperature with and without UL, respectively. The AI change of the ideality factor was characterized by the absolute value  $\Delta n_{id} = n_{id,in} - n_{id,us}$ .

#### 2.4. Illumination

The monochromatic ( $\lambda = 900$  nm) and low-intensity light was used for the SSCs illumination. It is known [40] that illumination with intensity of above 0.01 suns can leads to defect formation in p-type silicon. The our work was devoted to investigation of AI effects and the light intensity of  $W_{ph} = (8 \pm 4)$  W/m<sup>2</sup> was chosen to avoid any current induced degradation processes. The light monochromatism allowed to simplify the short-current dependence. In case of used wavelength, the photocurrent defined by the electron-hole pairs generation in the  $p$ -region mainly. If the base is several minority carrier diffusion lengths  $L_n = \sqrt{\mu_n kT \tau_n / q}$ , the  $J_{sc}$  can be written as [36, 41]

$$J_{sc} = \frac{W_{ph}(1 - M)q\beta\lambda}{hc} \frac{\alpha L_n}{1 + \alpha L_n}, \quad (3)$$

where  $\alpha$  is the absorption coefficient,  $M$  is the reflection coefficient,  $\beta$  is the quantum yield coefficient. We used Eq. (3) to fit the experimental  $J_{sc}(T)$  data taking  $L_n$  as the fitting parameter. Also, we used the known [36] temperature dependence of  $\alpha$  and supposed that  $\beta$  and  $M$  were temperature independent,  $L_n \propto T^{0.5}$ . The last relation was obtained from  $J$ - $V$  curves fitting — see Sec. 3.3. Thus,  $L_n$  and  $\tau_n$  can be obtained from the both single  $J$ - $V$  curve and  $J_{sc}$  temperature dependence. To to separate the second case values, the subscript “ $ph$ ” was used:  $L_n^{ph}$ ,  $\tau_n^{ph}$ ,  $\varepsilon_{\tau_n}^{ph}$  etc.

#### 2.5. Defect structure modification

To determine the major recombination centers in the investigated samples, the following experimental procedure was used after the AI effects investigation. The samples were light soaked under intensive illumination by a halogen lamp (2 Suns) at approximately 305 K. The illumination time varied from 1 h to 8 h. After illumination was terminated, the sample was exposed to room temperature in the darkness. Over 5 h period, dark  $J$ - $V$  characteristics were measured with the interval of 10–15 min in order to determine the kinetics of the parameters at room temperature. To estimate the permanent light-induced change, the measurements of dark  $J$ - $V$  characteristics were performed in 48 h after illumination. After the total time under intensive illumination ran up to 15 h, the samples were annealed at 200 °C for 10 min in darkness, after which the measurements were carried out at room temperature. Then, the illumination and measurements were repeated.

#### 2.6. Fitting procedure

All non-linear fittings were done by using the differential evolution method [42–44]. The least-squares method was used to linear fitting.

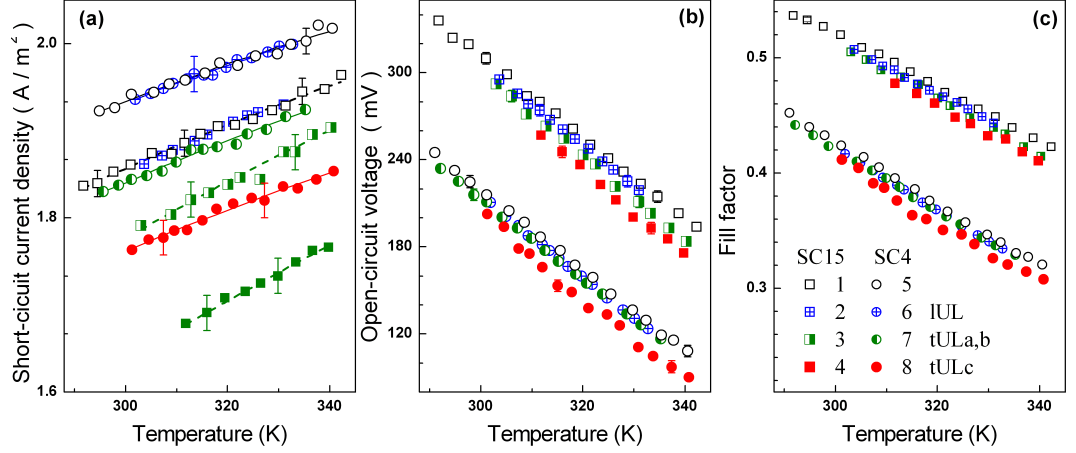


Figure 2: Temperature dependences of short-circuit (a), open-circuit voltage (b) and fill factor (c) for SC15 (squares) and SC4 (circles). The curves 1 and 5 (open marks) are obtained without UL, curves 2 and 6 correspond to IUL, curve 3 corresponds to tULa, curve 7 corresponds to tULb, curves 4 and 8 correspond to tULc. The marks are the experimental results, and the lines are the curves fitted by Eq. (3).

### 3. Results and Discussion

#### 3.1. Photo-electric conversion

The obtained temperature dependences of the short-circuit current density, open-circuit voltage and the fill factor are shown in Fig. 2. The parameters values at 320 K are listed in Table 2. It should be noted that not only  $I_{sc}$  and  $V_{oc}$  but also SSC efficiency,  $FF$ , and minority carrier lifetime decreases under low-intensity light conditions [38, 45–47]. Hence, data in Fig. 2 and Table 2 are not equivalent to the standard test condition (AM1.5, 25°C, 1000 W/m<sup>2</sup>) results, but illustrate the AI effects. Note that the yearly averaged energy yield of a solar panel, especially if operated in the middle Europe, strongly depends on its low light-level performance.

Fig. 2 shows an acoustically driven degradation of the short-circuit current, open-circuit voltage, and fill factor. The parameters relative changes are listed in Table 3. We would like to stress that, firstly, all found AI effects are reversible. In other word, the  $J_{sc}$ ,  $V_{oc}$ ,  $FF$ , and another parameters, which are described above, revert to the initial value after the UL termination and sample storage for about 24 h at room temperature. The reversibility testifies that ultrasound neither causes defect diffusion nor changes defect concentration. Secondly, the AI relative changes are weakly depend on temperature over the explored range.

The US intensities of IUL, tULa, and tULb are close. But it is shown by  $J_{sc}$  and  $V_{oc}$  data that the tULa,b result in the more prominent AI parameter changes. At the same time, IUL and tULa,b differ in the both  $f_{US}$  and  $u_{US}$  ( $\xi_{US}$ ). It was previously shown [23, 48] that US influence on the silicon structures

Table 2: The determined SSC parameters (at 320 K).

Parameter	SC15				SC4			
	Ultrasound loading				Ultrasound loading			
	non	IUL	tULa	tULc	non	IUL	tULb	tULc
$J_{sc}$ (0.01A/m <sup>2</sup> )	191±2	191±2	184±2	171±2	198±2	198±2	189±2	181±2
$V_{oc}$ (mV)	256±4	250±4	243±4	233±4	164±4	159±4	157±4	141±4
$FF$ (10 <sup>-3</sup> )	475±2	468±2	463±2	458±2	372±2	366±2	366±2	353±2
$L_n^{ph}$ (μm)*	99±5	92±5	67±4	55±3	125±6	124±6	103±5	98±5
$L_n$ (μm)	93±5	82±4	47±3	34±2	106±5	99±5	80±4	69±4
$\tau_n^{ph}$ (10 <sup>-7</sup> s)*	31±3	26±3	14±2	9±1	49±5	48±5	33±4	30±3
$\tau_n$ (10 <sup>-7</sup> s)	26±3	21±3	7±2	3.5±0.7	35±3	31±3	20±3	15±2
$\tau_g$ (10 <sup>-9</sup> s)	70±4	66±3	57±3	48±2	35±2	31±2	30±2	29±2
$E_{\tau g}$ (meV)*	242±7	237±5	234±5	234±5	246±6	234±5	241±5	243±5
$n_{id}$ (±0.01)	2.59	2.60	2.61	2.63	2.51	2.52	2.54	2.54
$T_{id}$ (K)*	226±8	215±10	243±15	233±15	327±10	319±15	308±20	358±25
$K_{us}$ (m <sup>-2</sup> s <sup>-1</sup> )		(3.3±0.5)×10 <sup>24</sup>				(5.0±0.2)×10 <sup>23</sup>		
$R_{sh}$ (kΩ·cm <sup>2</sup> )	> 10 <sup>12</sup>	> 10 <sup>12</sup>	> 10 <sup>12</sup>	> 10 <sup>12</sup>	12±1	13±1	10±1	8±1

\* determined by using the whole temperature range

Table 3: The acoustically induced change of SSC parameters.

Parameter	SC15			SC4		
	IUL	tULa	tULc	IUL	tULb	tULc
$\varepsilon_{J_{sc}}$ (%)	0±1	4±1	10±1	0±1	5±1	9±1
$\varepsilon_{V_{oc}}$ (%)	2±2	5±2	9±2	3±2	4±2	14±2
$\varepsilon_{FF}$ (%)	2±1	3±1	4±1	2±1	2±1	5±1
$\varepsilon_{L_n^{ph}}$ (%)	7±7	32±7	44±7	1±7	18±7	22±7
$\varepsilon_{L_n}$ (%)	12±6	49±6	63±6	6±6	25±6	35±6
$\varepsilon_{\tau_n^{ph}}$ (%)	16±15	55±15	70±15	2±15	33±15	39±15
$\varepsilon_{\tau_n}$ (%)	19±12	73±12	87±12	11±12	43±12	57±12
$\varepsilon_{\tau_g}$ (%)	6±5	19±5	31±5	9±5	14±5	17±5
$\Delta n_{id}$ (10 <sup>-2</sup> )	1±1	2±1	4±1	1±1	3±1	3±1
$\varepsilon_{R_{sh}}$ (%)				-8±10	17±10	33±10

should arise with the  $f_{\text{US}}$  increase. Therefore the efficiency of US action on the SSC is determined by the atom displacement (lattice deformation) mainly and the transverse AWs are more effective influence tool.

Eq. (3) shows that  $J_{sc}$  strongly depends on a carrier diffusion length. The determined by fitting  $L_n^{ph}$ , calculated  $\tau_n^{ph}$  values, and its changes are given in Tables 2 and 3. The fitting results are shown on Fig. 2(a) by curves. Thus the US effects the minority carrier lifetime.

Unfortunately the analytical expressions for  $V_{oc}$  and  $FF$  are absent in the double-diode model case. But Eq. (1) shows that the open-circuit voltage and fill factor depend on  $\tau_n$ ,  $n$ ,  $\tau_g$ , and  $R_{sh}$ . The next three Sections are devoted to the consideration of US influence on these parameters. The reasons of  $V_{oc}$  and  $FF$  change are discussed in Section 3.5.

### 3.2. Space charge region

The parameters of  $I$ - $V$  characteristics associated with SCR phenomena are  $n_{id}$  and  $\tau_g$ . The temperature dependences of the SCR carrier lifetime and ideality factor are shown in 3(a) and 3(b), respectively. The thermoactivated growth of SCR lifetime is observed over the explored temperature range — see 3(a). The measured temperature dependence of  $\tau_g$  is well described by the following equation

$$\tau_g(T) = \tau_{g0} \exp\left(-\frac{E_{\tau_g}}{kT}\right). \quad (4)$$

As shown in Fig. 3(b), the ideality factor decreases with the increase in temperature, and the dependence of  $n_{id}$  on  $1/T$  is close to linear. Thus, dependence  $n_{id}(T)$  can be expressed as

$$n_{id}(T) = n_{id,\infty} + T_{id}/T. \quad (5)$$

The values of  $T_{id}$  and  $E_{\tau_g}$  found for samples under UL as well as without UL are listed in Table 2.

As seen from Fig. 3 and Table 2,

- (i) UL leads to the increase in  $n_{id}$  and decrease in  $\tau_g$ ; the AI changes are listed in Table 3;
- (ii)  $\tau_g$  and  $n_{id}$  are varied by tUL more effectively;  $\varepsilon_{\tau_g}$  and  $\Delta n_{id}$  increase with  $W_{\text{US}}$  enhancement;
- (iii) UL does not affect  $E_{\tau_g}$  and  $T_{id}$  values;  $E_{\tau_g}$  is equal to  $0.24 \pm 0.01$  eV;  $T_{id}$  depends on sample and is equal to  $330 \pm 30$  K (in the SC4 case) or  $230 \pm 20$  K (in the SC15 case).

For the purpose of our analysis, it is important to discuss the recombination mechanism in SCR of the investigated samples. At first, the large  $n_{id}$  value and small  $\tau_g$  value should be accentuated. According to classical SRH theory, the ideality factor must be smaller than 2, and  $\tau_g$  temperature dependence is expected [49, 50] to be described by the relation

$$\tau_g \simeq 2\tau_n \sqrt{\sigma_n/\sigma_p} \cosh[(E_t - E_i)/kT] \quad (6)$$



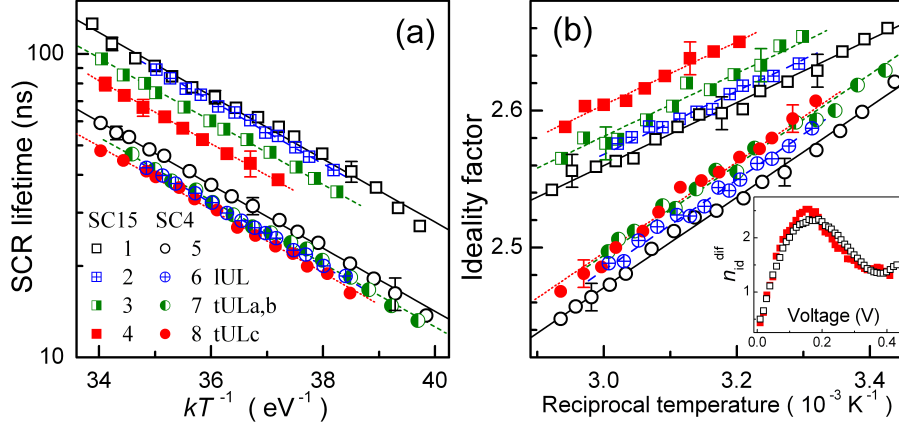


Figure 3: Temperature dependences of SCR carrier lifetime (a) and ideality factor (b) for SC15 (curves 1–4, squares) and SC4 (5–8, circles). The curves 1 and 5 (open marks) are obtained without UL, and curves 2 and 6 correspond to IUL, curve 3 corresponds to tULa, curve 7 corresponds to tULb, curves 4 and 8 correspond to tULc. The marks are the experimental results, and the lines are the fitted curves using Eq. (4) and  $E_{rg} = 0.24$  eV (a) or Eq. (5) and  $T_{id} = 330$  or  $230$  K (b). Inset: Two examples of voltage dependences of differential ideality factor for SC15. The open marks are obtained without UL, full mark correspond to tULc.  $T = 335$  K.

where  $\sigma_n$ ,  $\sigma_p$ , and  $E_t$  are the electron and hole capture cross sections (CCSs) and the energy level of the recombination center, and  $E_i$  is the intrinsic energy level. In our case,  $n_{id}$  is greater than 2, and  $\tau_g$  increases with temperature. Therefore, SRH theory cannot be applied in our case.

Several attempts to account for large  $n_{id}$  value have been made by using different models. According to van der Heide *et al.* [51], the nonuniform contact resistance of the front side metallisation leads to a high  $n_{id}$  value. However, this theory predicts the dependence of ideality factor on light intensity, whereas  $n_{id}$  change with  $W_{ph}$  is not observed in our case. Beier and Voss [52] explain the large  $n_{id}$  by the saturation effects within the SRH-model. However, this theory is unable to explain the  $J_{0SCR}$  magnitude, which is much greater than expected for a silicon. The large ideality factor is attributed to the deep-level-assisted tunneling [53, 54] too. But according to this model, the  $n_{id}$  does not depend on temperature.

At the same time, all the observed features of SCR recombination can be explained by the model of coupled defect level recombination (CDLR) [28, 29, 38, 55, 56]. According to the CDLR model, the recombination is the result of carrier exchange between two defect levels and crystal bands; and the high ideality factor is due to saturation of the inter-level recombination channel, leading to a hump in the  $n_{id}^{dif} = \frac{1}{kT} \frac{dV}{d(\ln I)} = f(V)$  characteristics. Such hump is observed in the our case — see inset in Fig. 3(b). It was found that the magnitude and the position of this hump strongly depends on the energy positions and on the

capture and inter-level recombination parameters of the two levels involved [29, 38]. In particular, it is supposed [29] that the recombination rate is dominant at the sites where acceptor-like defect is coupled with donor-like defect. In a simplified case, when there is no carrier exchange between the donor level  $E_t^D$  and valence band, as well as between the acceptor level  $E_t^A$  and conduction band, the recombination rate  $R$  can be expressed [28] as

$$R = \frac{R_{12} - \sqrt{R_{12}^2 - 4\tau_n^D \tau_p^A (np - n_i^2)(1 - \epsilon)}}{2\tau_n^D \tau_p^A (1 - \epsilon)}, \quad (7)$$

$$R_{12} = \frac{(n + n_D)(p + p_A)}{R_{DA}} + \tau_n^D (p + p_D) + \tau_p^A (n + n_A), \quad (8)$$

$$\tau_n^D = (N_D \sigma_n^D v_{th,n})^{-1}, \quad \tau_p^A = (N_A \sigma_p^A v_{th,p})^{-1}, \quad (9)$$

where  $R_{DA}$  is the coupling parameter,  $N_D$  and  $N_A$  are the densities of donor and acceptor-like defects,  $\sigma_n^D$  and  $\sigma_p^A$  are the electron CCS of the donor and hole CCS of the acceptor,  $v_{th,n}$  and  $v_{th,p}$  are the thermal electron and hole velocities,  $n_{D,A}$ ,  $p_{D,A}$ , and  $\epsilon$  depend on  $E_t^D$ ,  $E_t^A$ , and level degeneracy factors.

According to Steingrube *et al.* [29], CCS for defect in a pair differs from that for an isolated defect and depends on the distance  $r$  between the donor and the acceptor:

$$\sigma_{n,p}^{D,A}(r) \propto r^2, \quad (10)$$

$R_{DA}$  is proportional to the overlap integral of the defect wave functions as well. If both defects are characterized by the H-like radial-symmetric wave function and equal Bohr radius  $a_0$ , the following expression can be used: [29]

$$R_{DA}(r) \propto N_D N_A \left[ 1 + \frac{r}{a_0} + \frac{1}{3} \left( \frac{r}{a_0} \right)^2 \right] e^{-r/a_0}. \quad (11)$$

Unfortunately, the equation does not account for the functional relation between  $J$ - $V$  characteristics parameters and attributes of defects taking part in CDLR. However, it is shown [28, 55] that  $n_{id}$  increases with the decrement in  $R_{DA}$ . Since  $\tau_g \propto R^{-1}$ , the  $n_{D,A}$ ,  $p_{D,A}$ , and  $\epsilon$  are expected to provide a thermoactivated behavior of SCR lifetime. In our opinion, the value of  $E_{\tau_g}$  is mainly determined by couple component energy levels, whereas the value of  $T_{id}$  is affected by  $N_D$  and  $N_A$  too. Hence, (i) same defects are take part in the SCR recombination in both SC15 and SC4 because the  $E_{\tau_g}$  values are identical; (ii) the defect concentrations in SC15 and SC4 are different because the  $T_{id}$ ,  $\tau_{g,in}$ , and  $n_{id,in}$  values are different; (iii) UL does not result in the modification of the level position as well as defect concentration because the  $E_{\tau_g}$  and  $T_{id}$  values are not affected.

In our opinion, the observed reversible AI modifications of  $n_{id}$  and  $\tau_g$  are induced by donor-acceptor distance alteration in the samples under UL. In fact, according to the data [32, 33], the force acting on a point defect during UL can be expressed as

$$F_d = \chi \Delta \Omega_d \frac{\partial \xi(x, t)}{\partial x}, \quad (12)$$

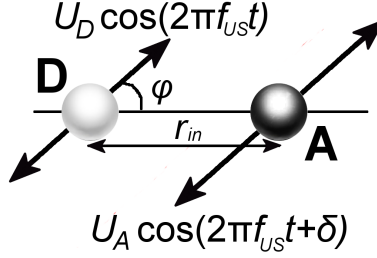


Figure 4: Model of CDLR center behavior under US action.

where  $\chi$  is the bulk elasticity modulus,  $\Delta\Omega_d$  is the crystal volume change per defect (e.g.  $\Delta\Omega_d < 0$  and  $\Delta\Omega_d > 0$  for the vacancy and interstitial atom, respectively),  $\xi$  is the crystal lattice deformation, and AW propagates along  $x$  axis,  $\partial\xi(x,t)/\partial x \propto \xi_{US}$ . Therefore, a point defect vibrates under UL, so oscillation amplitude and phase are determined by both the defect character and AW intensity.

The simplest model, which is shown in Fig. 4, gives the following qualitative conclusion. Initially, the donor (D) and the acceptor (A) are separated by the distance  $r_{in}$ . Under UL, the defects would vibrate with amplitudes  $u_D$  and  $u_A$ . Depending on  $\xi_{US}$ , defect elastic strain ( $\Delta\Omega_d^D$  and  $\Delta\Omega_d^A$ ), and defect coupling the defect vibration amplitudes can have different values. The vibration axis coincides with AW displacement direction and forms angle  $\varphi$  with the line, which passes through the defect initial positions.  $\delta$  is the phase shift between donor and acceptor vibration.

We use Eqs. (10) and (11) to estimate AI relative changes of CCS  $\varepsilon_\sigma = [\sigma_{US} - \sigma(r_{in})]/\sigma(r_{in})$  and coupling parameters  $\varepsilon_{RDA} = [R_{DA,US} - R_{DA}(r_{in})]/R_{DA}(r_{in})$ , where  $\sigma_{US}$  and  $R_{DA,US}$  are averaged over the AW period. The results of simulation are shown in Figs. 5 and 6. In this estimation, the relaxation time in the CDLR sub-system is assumed to be considerably shorter than  $f_{US}^{-1}$ , and we apply the previously used [29] value  $a_0 = 3.23$  nm. In addition, the chosen  $u_D$  and  $u_A$  values are commensurate with  $u_{US}$ . However, it should be taken into account that the displacement of the point defect without the covalent bond could exceed a matrix atom displacement.

Fig. 5(a) show that the UL leads to the increase in SSC. The AI alteration of coupling parameter is more complicated — see Fig. 5(b). In particular, the decrease in  $R_{DA}$  is expected in case of  $\varphi \approx 90^\circ$  [the couple axis is perpendicular to the AW displacement direction, see Fig. 6(b)] or in case of low  $r_{in}/a_0$  value [see Fig. 6(a)]. In the lat case, the intensive CDLR is expected [28, 29].

Thus, according to the our model estimation, UL causes the donor-acceptor distance change and results in  $\varepsilon_\sigma$  and  $\varepsilon_{RDA}$ , which mainly depend on lattice deformation. According to the CDLR theory, the increase in the SSC and decrease in the coupling parameters should lead to the decrease in the carrier

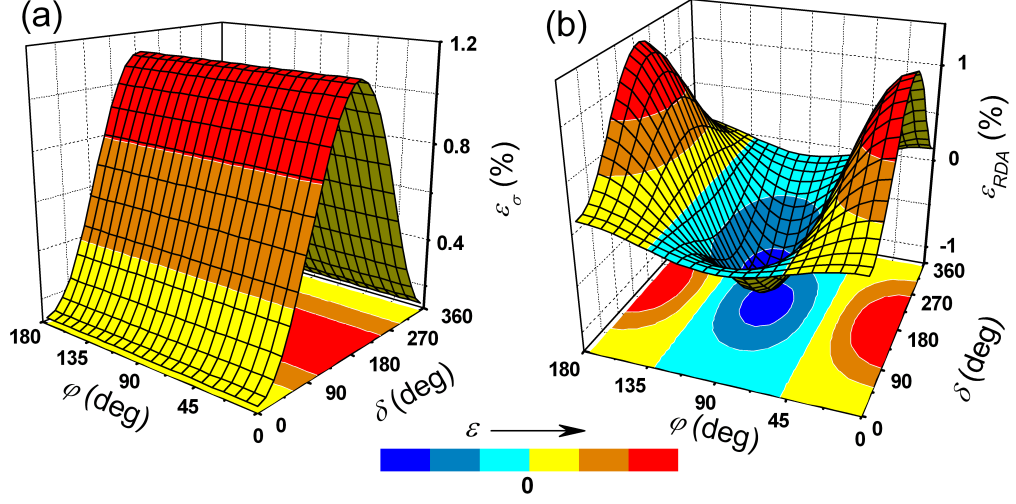


Figure 5: Simulated dependencies of AI changes of capture cross section (a) and coupling parameter (b) on the vibration phase shift and AW displacement direction. The parameters are set to  $a_0 = 3.23$  nm,  $r_{in} = 10$  nm,  $u_A = 1$  nm, and  $u_D = 0.5$  nm.

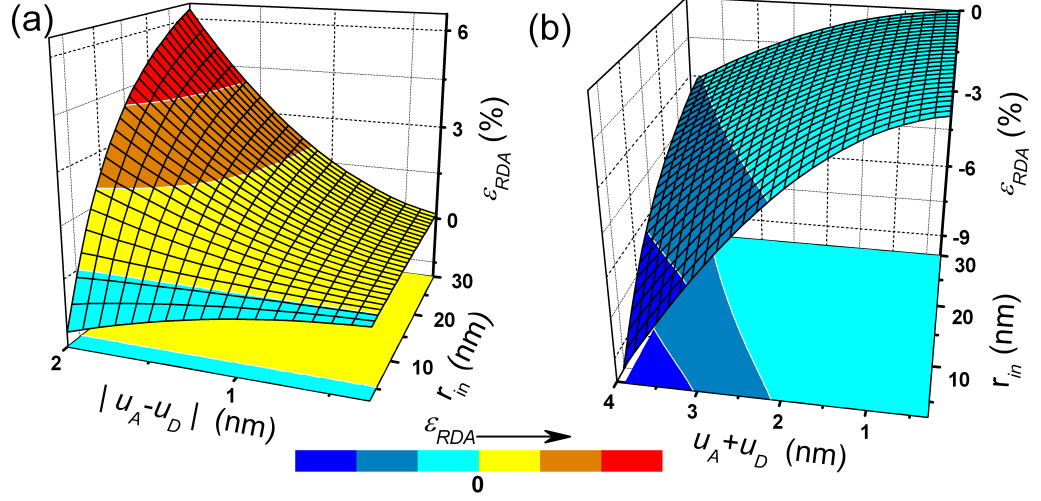


Figure 6: Simulated dependencies of AI changes of coupling parameter on the vibration amplitudes and initial donor-acceptor distance. The parameters are set to  $\varphi = 0^\circ$ ,  $\delta = 0^\circ$  (a), and  $\varphi = 90^\circ$ ,  $\delta = 180^\circ$  (b).

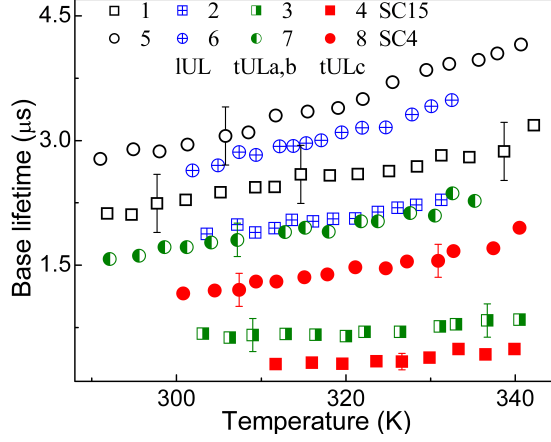


Figure 7: Temperature dependences of base lifetime for SC15 (curves 1–4, squares) and SC4 (5–8, circles). The curves 1 and 5 (open marks) are obtained without UL, and curves 2 and 6 correspond to IUL, curve 3 corresponds to tULa, curve 7 corresponds to tULb, curves 4 and 8 correspond to tULc.

lifetime and increase in the ideality factor. It was observed in the experiment.

### 3.3. Quasi-neutral region

Base lifetime describes the processes which occur in the quasi-neutral region of the solar cell. Fig. 7 shows  $\tau_n$  behaviour in the explored temperature range. As expected, minority carrier lifetime increases as the temperature increases. The determined by fitting  $\tau_n$ , calculated  $L_n$  values, and its changes are given in Tables 2 and 3. The obtained values of  $L_{n,in}$  are comparable with the  $L_{n,in}^{ph}$  values. The small quantitative difference between the  $\varepsilon_{Ln}^{ph}$  and  $\varepsilon_{Ln}$  values, in our opinion, deals with the AI change of the  $L_n$  temperature dependence, which is not taken into account during the  $J_{sc}(T)$  fitting.

The calculation shows that the both band-to-band recombination and Auger recombination can be neglected in the investigated samples. Therefore, the SRH recombination should be only under consideration. In case of the low injection level, SRH lifetime is described by the following equation

$$\tau_n^{-1} = \sum_i \tau_{n,i}^{-1} = \sum_i N_{d,i} \sigma_{n,i} v_{th,n}, \quad (13)$$

where  $\tau_{n,i}$  characterizes lifetime due to recombination by  $i$ -th defect, and  $N_{d,i}$  and  $\sigma_{n,i}$  are the concentration and electron CCS of  $i$ -th defect, respectively.

Fig. 7 shows that UL results in a decrease in  $\tau_n$ . As AI changes are reversible, the lifetime alteration, in our opinion, deals with the increase in  $\sigma_n$  under US action. The majority of recombination center in the silicon are known to be a complex point defect and a complex components are not the same. Following the empirical relation proposed in [57], we assume that Eq. (10) is valid for a

complex point defect as well. In this case, however,  $r$  is the distance which separates the components of a complex. According to the model suggested in Sec. 3.2, UL leads to  $r$  variation. In the case of CDLR, AI change of the capture cross section of donor (or/and acceptor) is supplemental to the variation of both the coupling parameter and the couple distance, but only CCS change determines the AI variation of base lifetime. If no US absorption by the defect is assumed,  $\delta$  is equal to  $0^\circ$  if  $(\Delta\Omega_d^D \cdot \Delta\Omega_d^A) > 0$  or to  $180^\circ$  if  $(\Delta\Omega_d^D \cdot \Delta\Omega_d^A) < 0$ . In this simple case, relative changes of CCS depend on oscillation amplitudes and do not depend on  $\varphi$ :

$$\varepsilon_\sigma = (u_D \pm u_A)^2 / 2 r_{in}^2, \quad (14)$$

where “+” and “−” correspond to  $\delta = 180^\circ$  and  $\delta = 0^\circ$ , respectively.

The defects in silicon structures are not all acoustically active (AA) and can remain unmodified under the action of ultrasound. The acoustodeflect interaction efficiency depends on the defect type and structure. [15, 16]. If only one AA center with  $N_d^{AA}$  and  $\sigma_n^{AA}$  is present in the sample, Eq. (13) for  $\tau_n^{-1}$  under UL takes the following shape:

$$\tau_{n,US}^{-1} = \tau_{n,in}^{-1} + \varepsilon_\sigma N_d^{AA} \sigma_n^{AA} v_{th,n} = \tau_{n,in}^{-1} + K_{US} u_{US}^2, \quad (15)$$

where  $K_{US}$  characterizes the complex-ultrasound interaction and depends on properties defects as well as crystal matrix; in particular,  $K_{US} \propto N_d^{AA}$ . Equation (15) takes into account that  $u_D, u_A \propto \xi_{US} \propto u_{US}$ . Eq. (15) is similar to the well-known Messenger-Spratt equation [36], which describes the irradiation-induced decrease in the lifetime.

The obtained dependences of the reciprocal base lifetime versus the AI atom displacements are shown in Fig. 8. The linearity of these dependences proves the correctness of our assumptions. The obtained  $K_{US}$  values are listed in Table 2. The greater  $K_{US}$  value in SC15 is evident that the AA defect concentration is greater as well.

It should be noted that an initial distance between the recombination complex components is much less than the donor-acceptor distance in CDLR. Therefore, according to Eq. (14), the more effective US influence is expected in the first case and  $\varepsilon_{\tau n} > \varepsilon_{\tau g}$  is observed experimentally.

### 3.4. Shunt resistance

Fig. 9 shows the shunt resistance over the explored temperature range. As seen from the figure, the tUS results in a decrease in  $R_{sh}$  whereas the lUL does not change shunt resistance practically. The calculated data are listed in Tables 2 and 3.

The shunt resistance is known[38, 58] to occur in  $p$ - $n$  structure due to several non-mechanical reasons. It can be caused by aluminum particles, macroscopic  $\text{Si}_3\text{N}_4$  inclusions, filaments consisting from cubic SiC, or inversion layers at precipitates. In the course of firing, the Al particle can penetrate into the sample creating  $p^+$ -doped region around it, which compensates the emitter and remains

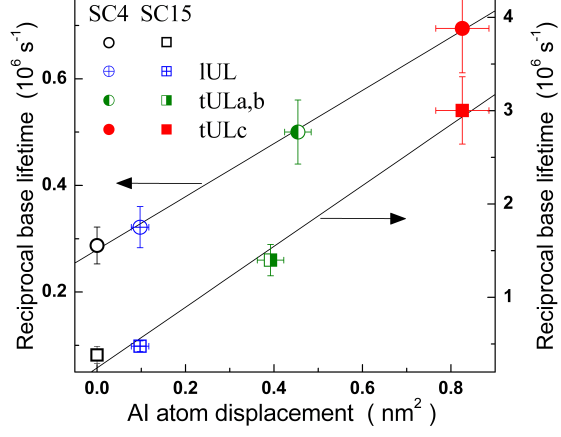


Figure 8: Dependencies of reciprocal base lifetime on AI lattice atom displacement for SC15 (squares, right axis) and SC4 (circles, left axis) at 320 K. Symbol filling is determined by the AW intensity and type and coincides with Fig. 7 notation. Lines are linear fitting.

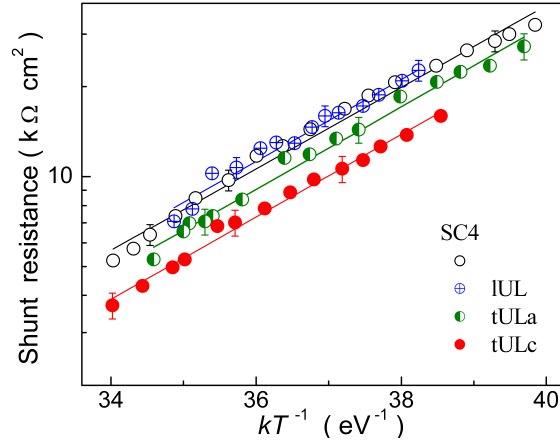


Figure 9: Temperature dependences of shunt resistance for SC4, obtained with and without (open marks) UL. The marks are the experimental results, and the lines are the fitted curves using Eq. (16)

in ohmic contact with the base. Subsequent annealing should decrease  $R_{sh}$ , but this expected behavior conflicts with data, which are presented therein after, in Sec. 3.6. SiC filaments, inversion layers, and  $\text{Si}_3\text{N}_4$  inclusions occur mainly in multicrystalline silicon cells [38, 58] and cannot cause shunt resistance in the investigated samples. Dislocations, however, which intersect the junction, are generally held responsible as a possible source of ohmic current [58–60]. Dislocations should be strongly recombinative, its recombination current may become strong enough for it to act as a shunt. For this reason they should be decorated by impurities [58].

According to the model of dislocation-induced impedance of photovoltaic detector suggested by Gopal and Gupta,[30, 31]  $R_{sh}$  can be given by:

$$R_{sh} = \frac{T}{\sigma_{\text{dis}}} \left[ \cosh \left( \frac{E_{\text{dis}} - E_i}{kT} \right) + \cosh \left( \frac{U_s}{kT} \right) \right], \quad (16)$$

with

$$\sigma_{\text{dis}} = \rho_{\text{dis}} A^2 q^2 A_{\text{dis}} \sqrt{K_n K_p} N_{\text{dis}} (n_p + p_p) / k, \quad (17)$$

where  $E_{\text{dis}}$  is the energy level which significantly contributes to the dislocation recombination current,  $U_s$  is the potential at the surface of the dislocation core,  $A$  is the sample area,  $\rho_{\text{dis}}$  and  $A_{\text{dis}}$  are the dislocation density and surface area, respectively,  $K_n$  and  $K_p$  are the probabilities for electrons and holes capture by the dislocation states, and  $N_{\text{dis}}$  is the density of surface states at each dislocation. Equation (16) is true for the simplified case of  $K_p = K_n$ . It should be noted that a similar temperature dependence of a SSC shunt resistance is used elsewhere [61] too.

To fit the experimental data for  $R_{sh}$ , we used Eq. (16). As the fitting parameters,  $(E_{\text{dis}} - E_i)$ ,  $U_s$ , and  $\sigma_{\text{dis}}$  were taken. It has been found that the experimental data are in good agreement with the fitting curves (see Fig. 9) for values  $(E_{\text{dis}} - E_i) = (0.34 \pm 0.02)$  eV and  $U_s = (5 \pm 4) \times 10^{-8}$  eV, which were independent of UL. The obtained value of  $(E_{\text{dis}} - E_i)$  corresponds to the carrier activation energy  $0.22 \pm 0.02$  eV and is comparable with the  $0.22 \div 0.25$  eV [62], 0.28 eV [63], 0.19 eV [64], and 0.23 eV [65], which was earlier reported for an impurity at the dislocation or with an intrinsic dislocation level.

tUL causes  $\sigma_{\text{dis}}$  increase. In our opinion, this is caused by an  $A_{\text{dis}}$  augmentation. Namely, the dislocation core atom displacement is parallel or normal to the current direction in case of lUL or tUL, respectively. As a result, the carriers are captured by dislocation levels from enlarged volume in the tUL case. Therefore, the effective surface area increases and  $R_{sh}$  decreases due to US action.

### 3.5. Open-circuit voltage and fill factor simulation

In order to visualize dependencies of the open-circuit voltage and fill factor on  $\tau_n$ ,  $n_{\text{id}}$ ,  $\tau_g$ , and  $R_{sh}$ , the following procedure was used. Firstly, we used Eqs. (1)–(3) to simulated  $J$ – $V$  characteristics taking the various values of  $\tau_g$ ,  $\tau_n$ ,  $n_{\text{id}}$ , and  $R_{sh}$ . The parameters values, which are close to those of investigated SSCs, are used in simulation. Secondly,  $V_{oc}$  and  $FF$  were estimated from the



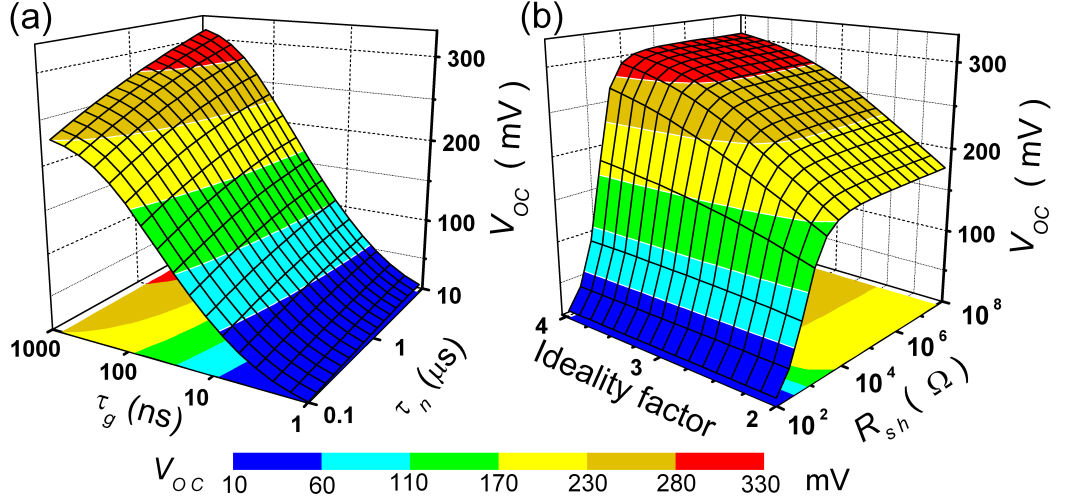


Figure 10: Simulated open-circuit voltage dependencies on the SCR lifetime and base lifetime (a), and on the ideality factor and shunt resistance (b). The constant values  $n = 2.55$  (a),  $R_{sh} = 5 \times 10^3 \Omega$  (a),  $\tau_n = 3 \times 10^{-6} \text{ s}$  (b),  $\tau_g = 5 \times 10^{-8} \text{ s}$  (b), and  $T = 320 \text{ K}$  were used.

obtained  $J$ - $V$  curves by the conventional mode. The results are shown in Figures 10 and 11.

As seen from the Figures 10(a) and 11(a), the  $\tau_g$  decrease leads to the decrease in both  $V_{oc}$  and  $FF$ . At the same time, the open-circuit voltage and fill factor dependencies on the base lifetime are weak for the investigated SSCs. It should be noted that the  $W_{ph}$  value from experiment was used in simulation. If the cell is operated at reduced illumination intensity, then the open-circuit voltage and maximum power point voltage become lower. Hence the recombination current essentially influences  $V_{oc}$  and fill factor in contrast to diffusion current [38]. Figs. 10(b) and 11(b) show that  $V_{oc}$  and  $FF$  are affected by the both  $n_{id}$  and  $R_{sh}$ , and the effect value considerably depends on shunt resistance value. For instance,  $V_{oc}$  increases with the increase in the ideality factor and both  $V_{oc}$  and  $FF$  does not almost depend on the shunt resistance value if  $R_{sh} > 10^5 \Omega$  (in the SC15 case). At the same time, the open-circuit voltage and fill factor decrease with decrease in the shunt resistance, and only  $FF$  weakly depends on  $n_{id}$  if  $R_{sh} \leq 10^4 \Omega$  (in the SCR4 case).

Therefore the discussed above decrease in  $\tau_g$  leads to AI degradation of the both open-circuit voltage and fill factor. This effect is enhanced by the AI decrease in  $R_{sh}$  and partially recovered by the AI increase in  $n_{id}$  for SC4 and SC15, respectively.

### 3.6. Defect type discussions

It is known that main lifetime killers in boron-doped Czochralski-grown Si are boron-oxygen related (BO) defects [2, 3], iron-boron pairs [66–68], and oxide

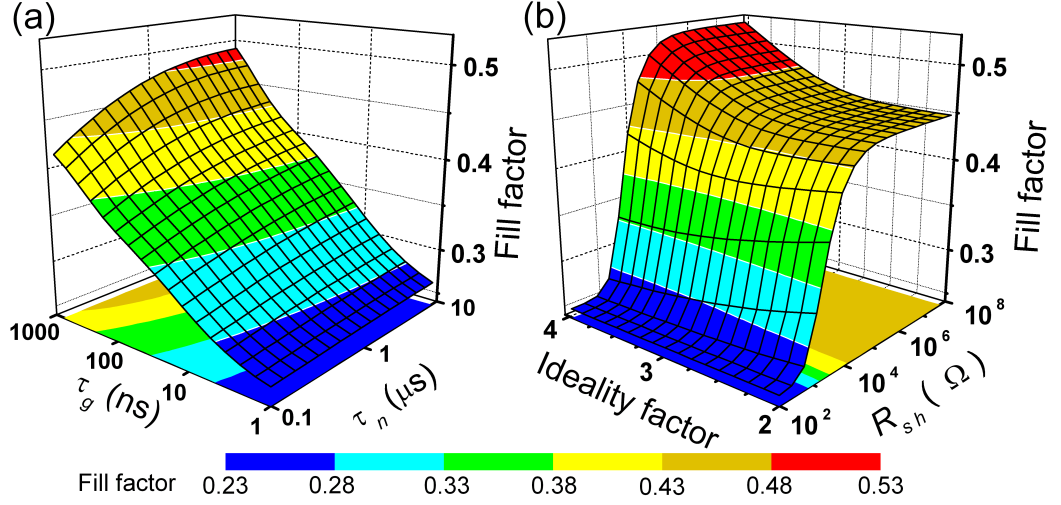


Figure 11: Simulated fill factor dependencies on the SCR carrier lifetime and base carrier lifetime (a), and on the ideality factor and shunt resistance (b). The constant values  $n = 2.55$  (a),  $R_{sh} = 5 \times 10^3 \Omega$  (a),  $\tau_n = 3 \times 10^{-6} \text{ s}$  (b),  $\tau_g = 5 \times 10^{-8} \text{ s}$  (b), and  $T = 320 \text{ K}$  were used.

precipitates [66, 69–73]. The first two defects are sensitive to intensive illumination at room temperature. Intensive light is known [2, 3] to cause permanent transformation of BO defects and considerable decrease of minority-carrier lifetime. Annealing at 200 °C for 10 min in the darkness results in both recovery of state and readiness to light-induced degradation of BO defects. At the same time, the vast majority of impurity iron exists in iron–boron pairs.  $\text{Fe}_i\text{B}_s$  can be readily dissociated under intense illumination to release interstitial iron, which results in lifetime changes. In the darkness,  $\text{Fe}_i\text{B}_s$  is repaired and  $\text{Fe}_i$  concentration decreases according to [66, 74]

$$N_{Fe}(t) = (N_{Fe,0} - N_{Fe,eq}) \exp \left[ -1.3 \cdot 10^{-3} p_p^{2/3} \exp \left( -\frac{0.68}{kT} \right) t \right] + N_{Fe,eq}, \quad (18)$$

where  $N_{Fe,0}$  is the concentration immediately after illumination, and  $N_{Fe,eq}$  is the equilibrium concentration which remains for a long time after dissociation.

To inspect a role of BO defects and iron–boron pairs in the investigated samples, the procedure, which is described in Section 2.5, was used. Fig. 12 shows the permanent changes of SSC parameters as a result of the intensive illumination and annealing. In contrast to other, Fig. 12 shows sample SC3 data as well. The SC3 features are the low  $R_{sh}$  value and the first 10 min 200 °C annealing before intensive illumination. As seen from the figure, illumination does not result in a considerable permanent change of  $\tau_g$ ,  $\tau_n$ , and  $n_{id}$  before as well as after annealing. Therefore, the BO influence on recombination can be neglected in both the SCR and the base.

The parameter evolutions after intensive illumination are shown in Fig. 13.

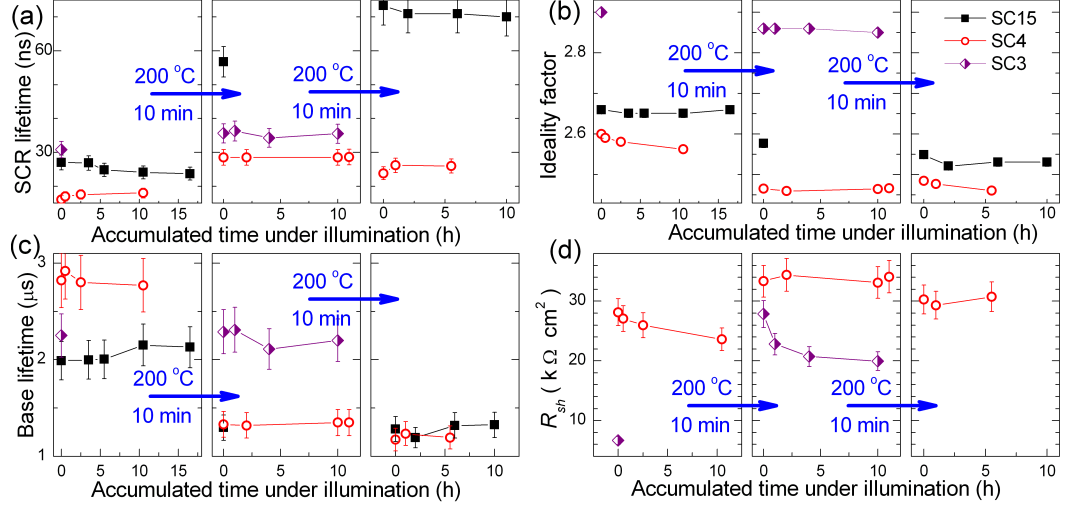


Figure 12: Dependencies of SCR lifetime (a), ideality factor (b), base lifetime (c), and shunt resistance (d) on accumulated illumination time and annealing. Lines only serve as guide to the eye.

Since  $\tau_n$  does not depend on illumination [see Fig. 13(c)],  $\text{Fe}_i\text{B}_s$  does not influence the base lifetime. It was found that  $n_{id}$  increased (by about 0.03) and  $\tau_g$  decreased (by about 10 %) immediately after illumination — see Fig. 13(a, b). These changes vanished gradually. We supposed that  $\tau_g$  and  $n_{id}$  evolutions could be described by expressions similar to Eq. (18). The expected characteristic time  $2.53 \times 10^4$  s was used, and the fitting lines are presented on Fig. 13(a, b). The fittings are in good agreement with the experimental data. Hence, it is evident that iron–boron pairs take part in SCR recombination and the acceptor level  $E_C - 0.23$  eV is involved in the CDLR. On the one hand, pair  $\text{Fe}_i\text{B}_s$  is a good candidate for an AA center: the B is substitutional impurities whose ionic radius is smaller than that of matrix atoms  $\Delta\Omega_d(\text{B}_s) < 0$  whereas the interstitial Fe leads to  $\Delta\Omega_d(\text{Fe}_i) > 0$ . On the second hand, electron and hole CCS of  $\text{Fe}_i$  are 1.7 and 0.04 times [66] as much as those of  $\text{Fe}_i\text{B}_s$ . A small  $\tau_g$  alteration (by about 10 %) caused by light is the evidence of the supporting role of iron–boron pair in SCR recombination.

Thus, a conclusion can be made that oxide precipitates are number one agents in SCR and base recombinations. According to Murphy *et al.* [69, 71] there exist at least two independent oxide precipitate related defects. These defects have  $\sigma_n/\sigma_p = 157$  and  $\sigma_p/\sigma_n = 1200$ , respectively, [71] which is suitable for CDLR. These facts allow us to conclude that the defect responsible for AI phenomena in iSC is mainly oxide precipitate. Dislocations and stacking faults surround the oxide precipitates and lead to capture coefficient change as well as to increase the concentrations of two defects, without introducing additional states into the bandgap [66, 69, 71] and assist to defects acousto-activity. The

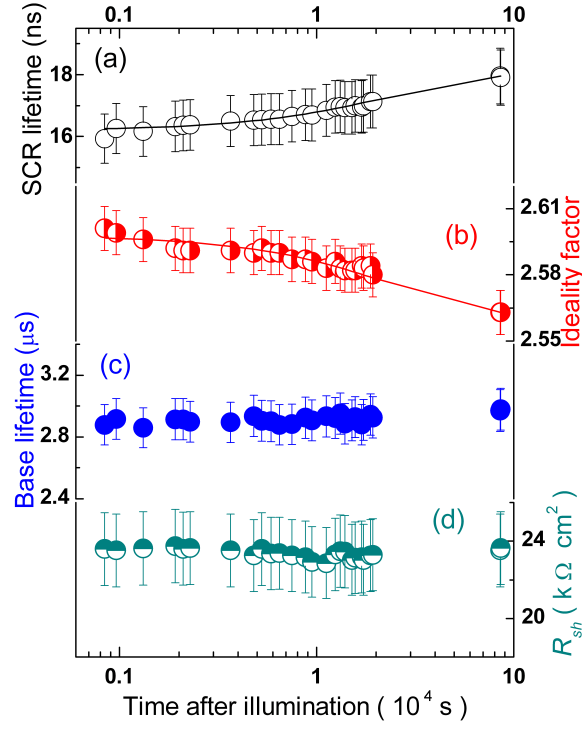


Figure 13: SCR lifetime (a), ideality factor (b), base lifetime (c), and shunt resistance (d) as a function of time since illumination has stopped. Sample SC4. Lines are plotted by using Eq. (18) and characteristic time  $2.53 \times 10^4$  s.

nonuniform distribution of oxide precipitates is observed in the Cz-Si wafer [70] and solar cell [72] and can be a reason of the investigated parameter variation. On the basis of mentioned above, we conclude that the defects, involved in the both recombination and acousto-defect interaction are oxide precipitates mainly.

#### 4. Conclusion

The influence of ultrasound on the silicon solar cell has been investigated experimentally over a temperature range of 290–340 K. The investigation has revealed an acoustically driven reversible degradation in SSC parameters. The effect is intensified in the case of the transverse acoustic waves using. The analysis has shown that degradation is caused by the acoustically induced increase in the carrier capture coefficient for point or extended defects. The qualitative model of the observed phenomenon, which is based on the increase in the distance between coupled defects or between complex defect components due to ultrasound action, has been considered. It has been shown that the oxide precipitates are most likely defects, which take part in the acousto-defect interaction. Thus, ultrasound can be an effective tool for controlling silicon structure characteristics.

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