



On the possibility of improving silicon solar cell efficiency through impurity photovoltaic effect and compensation

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ABSTRACT

The possibility of improving silicon (Si) solar cell efficiency through combined impact of impurity photovoltaic effect (IPV) and compensation is investigated. In the mechanism presented here, the IPV effect is produced by a *deep* level impurity, while the compensation is achieved through some other *shallow* level impurity. It has been pointed out that compared to the primary dopant, the deep level impurity concentration must be kept moderate, such that its presence does not deteriorate the carrier lifetime. In presence of moderate concentration of deep impurity, shallow level impurities can be effectively deployed to improve the carrier lifetime through compensation and this can lead to overall enhancement of solar cell efficiency. Results have been presented to validate the concept with a cell having a compensated boron (B) doped base, which also contains moderate concentration of chromium (Cr) that absorbs sub-bandgap photons.

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1. Introduction

The efficiency of a silicon (Si) solar cell is mainly limited by its inability to absorb photons with energies less than the band gap (E_g) and the recombination lifetime (τ) of the photo-generated carriers. However, a significant fraction of sub-bandgap photons can be absorbed by creating energy states within the band gap through deliberate inclusion of impurity atoms or defects. This mechanism, which is known as impurity photovoltaic (IPV) effect, has gained considerable research interest as a potential mean for improving solar cell efficiency [1–5]. Unfortunately, the energy states created within the band gap act as additional recombination centers which can have severe influence on lowering the carrier lifetime. To make the situation worse, depending on the position of these states, their influences on IPV effect and recombination lifetime is opposite to each other. In order to absorb maximum number of photons (through IPV effect) impurity states should be located near the center of the band gap. But such deep level energy states closer to the gap center are found to be very efficient recombination centers and therefore lifetime degrades severely in their presence. Therefore, non-mid-gap, yet deep level impurity atoms are more suitable, as they can provide some balance between the access to the sub-bandgap photons and lifetime deterioration. Moreover, choosing such a deep level impurity allows at least one of the two

transitions of the carriers (from the valence band to the impurity level and from there to the conduction band) to occur through strong thermal excitation rather than through weak optical absorption [1]. Based on this concept, incorporation of Indium (In), which introduces an energy level at around 157 meV above the Si valence band (VB), was suggested for improving the Si solar cell efficiency through the IPV effect [1]. Using a modified Shockley–Read–Hall (SRH) recombination model and assuming infinite mobility, a significant improvement in short circuit current (up to 5 mA/cm²) was predicted, provided that In concentration is sufficiently high (around 10¹⁷ cm^{−3}) to closely compensate the *n*-type base [1]. This was followed by the experimental demonstration of Keevers and Green [3], which confirmed that In incorporation increases the absorption coefficient of the films in the infrared region. However subsequent in depth theoretical analysis carried out by Karazhanov did not substantiate the idea as it showed that the IPV effect produced by In incorporation have negligible effect on improving efficiency [4]. Despite of increased absorption in presence of In, the fact that efficiency does not improve can be explained by the degradation of carrier lifetime.

In all these previously reported works In was deployed in high concentration to compensate the base material, as it is believed that compensation can improve lifetime by lowering the concentration of free carriers. It has been claimed that compensation, even achieved with deep level impurity can improve the overall lifetime [4,6]. However, careful investigation of the results presented therein [4,6] reveal that the lifetime archived through even full compensation remains lower compared to that of an

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uncompensated material. The reason is the following. The effective carrier lifetime in Si (or in any bulk semiconductor) containing multiple impurities of comparable concentration, is always dominated by the impurity atoms that introduce deeper energy state, and hence work as the most efficient recombination centers. As a result lifetime becomes lower in such material compared to the uncompensated one, which contains only shallow level dopant impurities. Nevertheless, lifetime degradation becomes less severe in a situation where deep level impurity tends to compensate the primary dopants. Therefore it was found that, although the lifetime of *In* incorporated Si solar cell improves when *In* tend to compensate the primary dopants of the cell [4], it remains lower than that of a uncompensated cell containing no *In*.

In this work we have investigated a Si solar cell structure where the concentration of IPV producing deep level impurities is kept moderate compared to the primary dopants, such that it does not produce any appreciable compensation effect. This ensures that recombination lifetime is dominated by the primary dopants and is not significantly degraded by the presence of deep impurities. In such a structure compensation of primary dopants by other shallow impurity may enhance the overall lifetime. In fact recent experimental evidence shows that compensation of boron (B) doped base of a Si solar cell with shallow level phosphorus (P) atoms improve the overall lifetime, which is determined by some deep level metal impurities (like Cr or Fe) inevitably existing in solar-grade Si [7]. Following this, the compensation of the base material is proposed to be achieved with some shallow level impurities, which can reduce the recombination activity of both the primary dopants and deep impurities. It has been theoretically demonstrated that the deep level metal impurities, deployed in moderate concentration, can produce appreciable IPV effect, which along with even moderate improvement of carrier lifetime archived through compensation (with shallow impurities) can lead to increased efficiency.

The various effects of incorporating both deep and shallow level impurity atoms on different parameters like lifetime, mobility and resistivity have been quantified in the context of efficiency calculation. For example it has been shown that incorporation of additional impurities (both shallow and deep) reduces carrier mobility and hence put a constraint on deploying them in any large concentration. Increasing the compensation has another negative impact: increasing the resistivity. Taking all the above mentioned factors, insights are provided for choosing the deep level impurity and their concentration, along with the compensation level (CR) and base width (*W*) to maximize the efficiency.

2. Material choice and device modeling

2.1. Device structure and impurities

To illustrate the concept, we assume a 30 μm thick (*W*) solar cell operating under global AM 1.0 illumination ($\sim 135 \text{ mW}/\text{cm}^2$). The base region is made of boron (B) doped *p*-type Si, compensated by some shallow level donor species like phosphorus (P), which creates an energy state only 0.045 eV below the conduction band (E_C) [8]. The base region is also assumed to be containing Cr atoms that introduce a donor level at 0.22 eV below the conduction band (E_C) [7]. The concentration of Cr (N_{Cr}) is assumed to be several orders of magnitude lower than that of B (N_A), such that it does not produce any compensation effect. In fact N_{Cr} is kept much smaller than the net doping, [B–P], even at the highest compensation level considered here. Cr is an interstitial impurity that in thermal equilibrium generally forms pairs with substitutional B atoms (Cr_iB_s pairs), and inevitably exists in solar-grade (So-G) Si. These pairs introduce one major energy level at 0.28 eV above the valence

band (E_v) [7] and therefore Cr is a potential candidate for providing improved access to sub-gap photons compared to In atoms. Like Cr, Fe is another interstitial metal impurity that forms Fe_iB_s pairs which introduce energy level at $E_C - 0.26 \text{ eV}$ [7]. However, Fe_iB_s is not stable under illumination [9] and interstitial Fe atoms are more efficient recombination centers compared to Fe_iB_s pairs at low injection level. Moreover, Fe_i introduce an energy level at $E_v + 0.38 \text{ eV}$, which is in the lower half of the gap and therefore at higher compensation level probability of Fe_iB_s formation is considerably reduced. Cr_iB_s pairs on the other hand is stable even under very strong illumination [9,10] and due to the position of energy state of Cr_iB_s pair formation is not endangered even at the highest compensation level.

2.2. Minority carrier lifetime

The effective lifetime (τ) in the base containing both shallow compensating impurity and deep IPV producing impurity is calculated by treating different impurity levels as independent recombination centers and then adding the inverse lifetimes limited by each of them [11,12]:

$$\frac{1}{\tau} = \frac{1}{\tau_1} + \frac{1}{\tau_2} + \frac{1}{\tau_3} + \dots \quad (1)$$

where $\tau_{1,2,3,\dots}$ are recombination lifetime limited by different recombination centers or impurity levels that can be calculated using the following simplified Shockley–Read–Hall (SRH) statistics assuming negligible trapping of excess carriers such that excess electron and hole concentration can be considered equal ($\Delta n = \Delta p$) [12]:

$$\tau_{\text{SRH}} = \frac{\tau_{p0}(n_0 + n_1 + \Delta n) + \tau_{n0}(p_0 + p_1 + \Delta n)}{n_0 + p_0 + \Delta n} \quad (2)$$

where $\tau_{n0,p0} = 1/(N\sigma_{n,p}v_{th})$, N is the impurity concentration, $\sigma_{n,p}$ are the capture cross sections for electrons and holes, n_0 and p_0 are the equilibrium electron and hole concentrations, n_1 and p_1 are the statistical factors representing equilibrium electron and hole concentrations respectively when the Fermi level (E_F) coincides with the energy of the impurity state. It is worth mentioning that by considering each recombination centers “independent”, various interactions among the centers are neglected. The validity of ignoring interaction between different recombination centers, in conjunction with the use of simplified SRH model requires that the concentrations of each type of recombination centers are considerably smaller than a critical value (N_{crit}), which ensures that amount of carrier trapping by the centers are negligible [12]. It should be noted here that for a recombination center concentration (N) below N_{crit} , the excess carrier concentrations are not noticeably perturbed through trapping and therefore it can be safely considered that $\Delta n = \Delta p$, which is a required condition to derive Eq. (2) from a more general form SRH lifetime equation [12]. It is also worth mentioning here that the derivation of Eq. (2) implicitly contains electroneutrality condition [12]. Therefore it can be shown that when recombination center concentration is kept below N_{crit} , $\Delta n = \Delta p$, implying $\tau_n = \tau_p$ at steady state. N_{crit} in the most restrictive case, depends on the equilibrium carrier concentration (p_0) and the ratio of σ_p and σ_n [7,12]. Using the similar values of $\sigma_{n,p}$ for B and CrB pairs used in Refs. [7,10] respectively (listed in Table 1), N_{crit} are found to be $4.5 \times 10^{18} \text{ cm}^{-3}$ and $5 \times 10^{16} \text{ cm}^{-3}$ for B and CrB pairs respectively, at $N_A = 10^{17} \text{ cm}^{-3}$. Since in the calculations presented here, N_{CrB} is the order of 10^{12} cm^{-3} , Eq. (2) is well applicable. The excess carrier concentration in Eq. (2) is calculated using the definition of generation rate (*G*) at steady state:

$$G = \frac{\Delta n}{\tau_n} = \frac{\Delta p}{\tau_p} \quad (3)$$

Table 1
Capture cross sections used for calculation.

σ_n (CrB)	$5 \times 10^{-15} \text{ cm}^2$, Ref. [10]
σ_p (CrB)	10^{-14} cm^2 , Ref. [10]
σ_p (B)	$7.65 \times 10^{-15} \text{ cm}^2$, Ref. [7]
σ_n (B)	10^{-18} cm^2 , Ref. [7]

The generation rate under AM 1.0 has been calculated using simulation software SILVACO according to the following equation [13]

$$G = \eta_o \frac{P\lambda}{hc} \alpha e^{-\alpha y} \quad (4)$$

where η_o is the internal quantum efficiency that represents the number of electron–hole pairs generated per photon, h is the Planck's constant, c is the velocity of light, α is the wavelength (λ) dependent attenuation constant, and y is the direction of propagation. P is a factor that takes into account the cumulative effect of reflection, transmission and attenuation loss depending on the structure geometry and material.

$\alpha(\lambda)$ has been computed considering all absorption processes in the cell, namely hole and electron photo emissions, band to band absorption and free carrier absorption. In case of electron photo-emission, sub-bandgap photons are absorbed by an electron at the deep impurity level, which is then excited to the conduction band. The coefficient associated with this process is proportional to electron photoemission cross section (σ_{on}) of the IPV impurity and the occupancy factor of the impurity level (f_i). Similarly absorption coefficient for hole photoemission, which takes a valence electron to the impurity energy level, is proportional to hole photoemission cross section (σ_{op}) times $(1 - f_i)$ [1]. The free carrier and, band to band absorption coefficients are also calculated as prescribed in Ref. [1]. In case of Si containing CrB pairs, $E_{CrB} = E_v + 0.28 \text{ eV}$, and therefore the sub-bandgap photons are mainly absorbed through electron photoemission where electrons from E_{CrB} are excited to E_c . Electron transition from E_v to E_{CrB} occurs thermally and hence absorption coefficient for hole photoemission is almost negligible. $\alpha(\lambda)$ thus calculated is passed onto the SILVACO to calculate G and lifetime.

2.3. Efficiency

The performance of the cell has been quantified using SILVACO, to which calculated values of lifetime and absorption coefficient (as described in previous subsection) is provided as external input. The short circuit current density (J_{sc}) generated through absorbing photons is calculated by SILVACO using the following equation [13]:

$$J_{sc} = \frac{qB_n}{hc} \sum_{i=1}^{N_\lambda} P_i \lambda_i \sum_j^{N_j} L \int_0^W P_i \alpha_i e^{-\alpha_i y} dy \quad (5)$$

where q is the electronic charge, B_n is the light beam intensity (in this case defined by AM 1.0 spectrum), N_λ is the number of discrete wavelengths considered, N_j is the number of light rays traced through the cell, which is determined by the reflection at the back end, and W is the cell thickness in the direction of light propagation (y). L is the width associated with the light beam, P_i accounts for the attenuation before the start of the light beam, λ_i is the discrete wavelength within the spectrum.

The typical injection values (Δn) considered for studying solar cell performance is significantly smaller than N_A considered here, which is around 10^{17} cm^{-3} . This combined with the fact that N_{CrB} is also much smaller than N_A , ensures that the dependence of carrier lifetime on injection level is weak. Considering the fact that

compensation can increase the depletion region width considerably, recombination therein has been taken into account in the simulation. Since with increased doping density carrier mobility is known to deteriorate because of increased scattering, an impurity concentration based empirical low field mobility model available in SILVACO has been used [13].

3. Results and discussion

Table 1 lists the capture cross section ($\sigma_{n,p}$) values used for modeling the lifetime and simulating the efficiency of the proposed solar cell structure. Fig. 1 shows the computed effective carrier lifetime (τ_{eff}) along with the lifetimes limited by different impurities. Both CrB and B limited lifetimes improve with the compensation ratio, $CR = N_D/(N_A - N_D)$, where N_D is the compensating donor (P) density. The P atoms capture the holes and reduce the free carrier concentration. This shifts E_F towards the center of the band gap and changes the charging state of both B and CrB pairs in a way that reduces their recombination activity and improves the lifetime. Similar trend of improvement of τ_{eff} in B doped So-G Si compensated with P and containing metal impurities like Fe or Cr was recently experimentally demonstrated [7].

It should be noted that according to Eq. (1), τ_{eff} is always dominated by the impurity level having lower associated τ and therefore, to have improved τ_{eff} , the competing recombination centers must have comparable lifetimes. Since CrB pairs are more efficient recombination centers due to their larger $\sigma_{n,p}$ compared to B [7,10], N_{CrB} is kept considerably lower ($\sim 10^{12} \text{ cm}^{-3}$) than that of B (N_A). This ensures that the lifetime limited by CrB pairs is not significantly smaller than that limited by B atoms. Note that, N_{CrB} has been chosen in such a way that only with $CR \approx 10$, CrB limited lifetime becomes equal to that of the uncompensated material containing B only (see Fig. 1). It should be emphasized that with higher N_{CrB} , compensation would not be able to improve the CrB limited lifetime to the extent comparable to B limited lifetime and hence improving lifetime beyond that achievable with an uncompensated material would not be materialized. The influence of N_{CrB} on τ_{eff} for different CR and N_A is shown in the inset of Fig. 1. As expected, increasing N_{CrB} has severe negative impact on τ_{eff} and it is found that N_{CrB} should not exceed 10^{13} cm^{-3} to obtain appreciable lifetime improvement through compensation. B concentration (N_A) has been assumed to be 10^{17} cm^{-3} in calculating the cell performance that is presented in the following sections.

To reveal the impact of compensation and CrB pairs, short circuit current (J_{sc}) is calculated for different concentration of CrB pairs as a function of compensation ratio and is shown in Fig. 2. It clearly reveals that short circuit current improves with increased compensation ratio through its several positive impacts. First, through lifetime improvement and this is obvious. The second effect comes through the shifting of the Fermi level closer to E_{CrB} , which increases the occupancy factor (f_i) and in turn enhances the electron photoemission rate. However it should be noted that J_{sc} is reduced as N_{CrB} is increased, as CrB reduces the carrier lifetime severely even at high compensation ratio (see Fig. 1). The inset of Fig. 2 shows the short circuit current density as a function of compensation ratio in the absence of CrB pairs and hence any IPV effect. It is noted that the base (no CrB and negligible compensation) cell produces only $\sim 71.7 \text{ mA/cm}^2$ under AM 1.0 illumination. On the other hand, with CrB pairs IPV effect can push it above 80 mA/cm^2 with almost no compensation. This confirms the positive impact of CrB pairs in improving photon absorption. Another interesting point to be noted in Fig. 2 is that the trend of J_{sc} with CR is different in cells with and without CrB pairs. In the absence of CrB pairs compensation fails to improve J_{sc} despite of the improvement in carrier lifetime. In this case mobility degradation

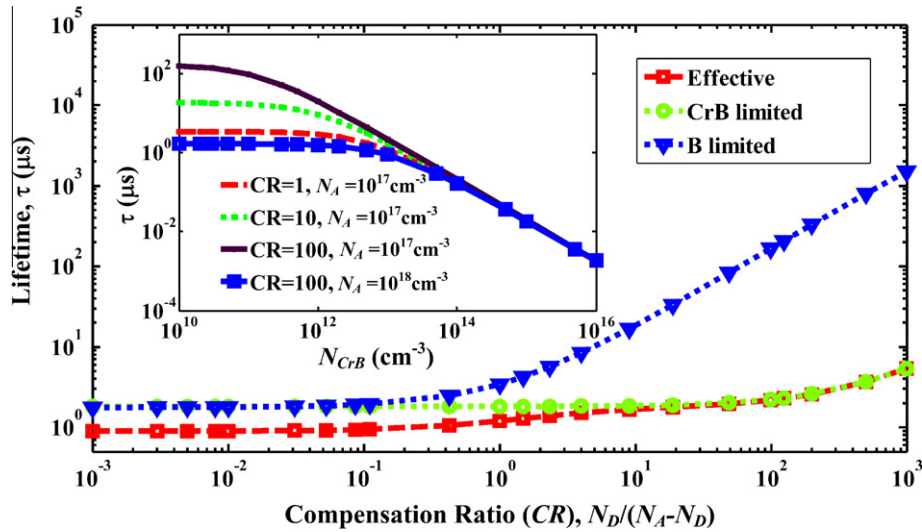


Fig. 1. Computed τ as function of CR for $N_A = 10^{17} \text{ cm}^{-3}$ and $N_{CrB} = 10^{13} \text{ cm}^{-3}$ and in inset, as a function of N_{CrB} for different CRs and N_A .

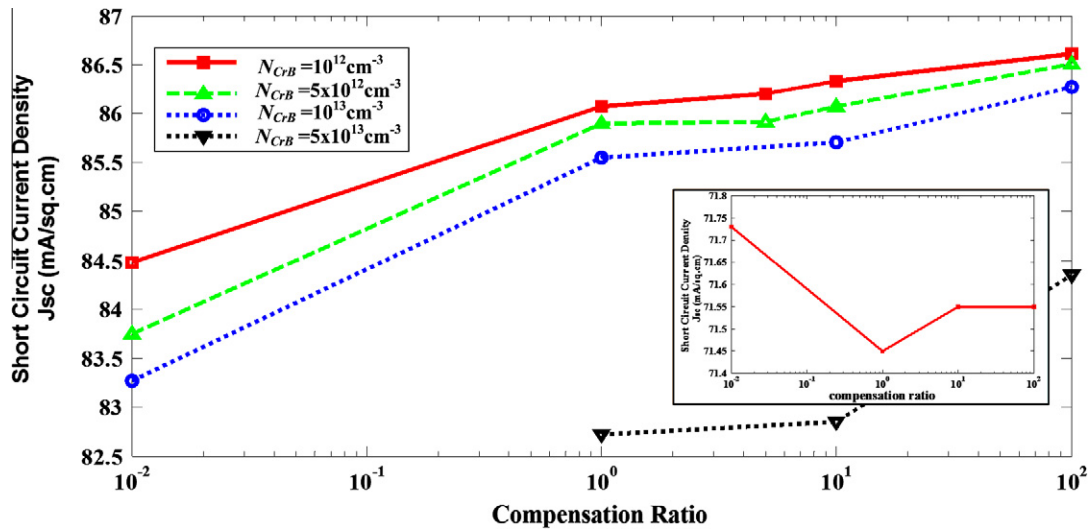


Fig. 2. J_{sc} calculated as a function of compensation ratio for different N_{CrB} . In the inset result is shown for the cell with no Cr impurity.

with increased CR dominates over the lifetime improvement. However, for cells with CrB pairs, combined effect of sub-gap photon absorption and lifetime improvement pacifies the mobility degradation. To illustrate these facts more clearly J_{sc} has been plotted as a function of N_{CrB} for different CRs in Fig. 3. From these two figures it can be concluded that compensation can improve J_{sc} through lifetime improvement with the compliment of IPV effect in presence of CrB pairs. But to achieve this, N_{CrB} must not exceed a certain value, in this case 10^{12} cm^{-3} , to avoid its detrimental impact on lifetime.

Although in presence of Cr impurity in a compensated cell, J_{sc} is improved over what can be achieved in the base cell, open circuit voltage (V_{oc}) decreases steadily with CR due to mobility degradation. The open circuit voltage and minority carrier (electron) mobility both calculated as functions of compensation ratio is shown in Fig. 4. With the increment of CR, specifically at higher values, fill factor (FF) is found to be decreased. For example in the cell with $N_{Cr} = 10^{12} \text{ cm}^{-3}$, the FFs are found to be ~ 0.81 , 0.808 and 0.79 for CR = 1, 10 and 100 respectively. This can be attributed to increased voltage drop with compensation, as the series resistance becomes significant at higher values of CR. Please

note that increasing N_{CrB} also has some negative impact, though not very profound, on the open circuit voltage. V_{oc} of the base cell is found to be 0.571 V, with considerably high mobility ($\sim 800 \text{ cm}^2/\text{V}\cdot\text{s}$). The calculated values of open circuit voltage may appear somewhat smaller. But noting the fact that the cell thickness has been restricted to $30 \mu\text{m}$ to reduce the series voltage drop at higher compensation ratios, the low V_{oc} can be understood. At reduced cell thickness surface recombination becomes significant and hence the dark saturation current is increased, which results in low V_{oc} .

Finally, Fig. 5 shows the calculated efficiency (η) as a function of CR. The efficiency achieved with the base cell containing neither deep level (IPV effect producing) nor shallow level (compensating) impurities, were found to be 25.2%. Hence it is clear from Fig. 5 that efficiency can be improved with CrB pairs through IPV effect up to CR = 10. However without compensation, IPV effect from CrB pairs is not very effective in improving the efficiency. In fact the efficiency improvement in this case is small enough to be considered within the uncertainty limit. The reason is clearly the deterioration of lifetime with CrB pairs. To make IPV effect significant without compensation, one needs very high N_{CrB} , which deteriorates lifetime so severely that overall efficiency goes down. For example

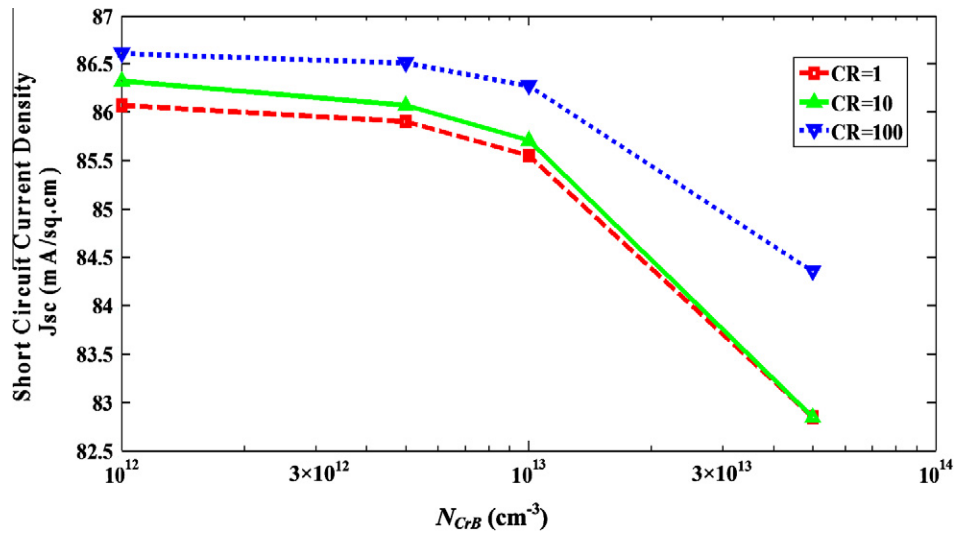


Fig. 3. J_{sc} calculated as a function of CrB concentration for different CRs.

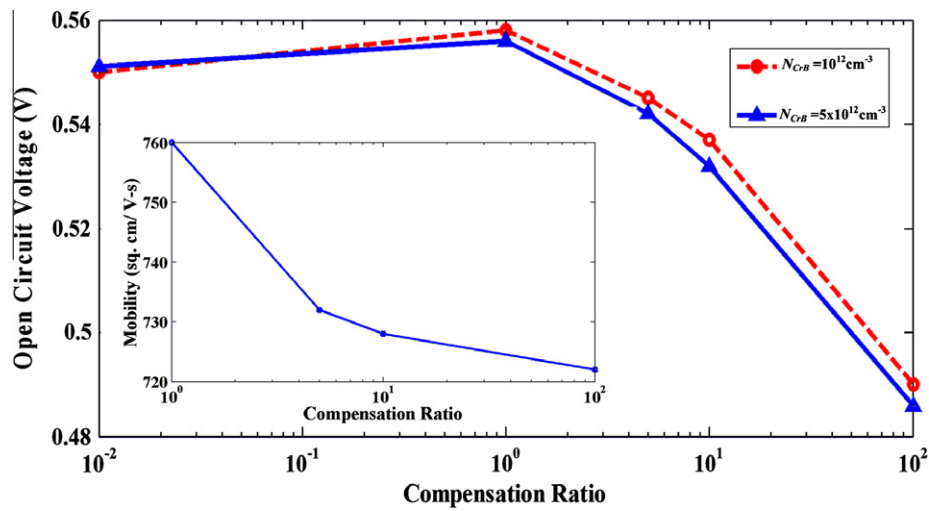


Fig. 4. Open circuit voltage and electron mobility (in inset), both calculated as functions of compensation ratio.

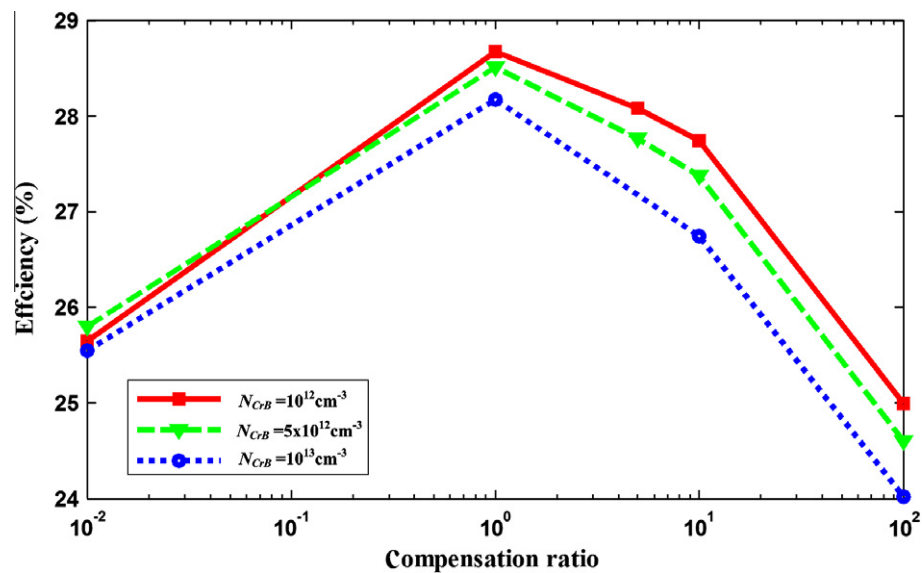


Fig. 5. Efficiency, calculated as a function of CRs for different CrB pair concentrations. Note that the base cell efficiency is 25.2%.

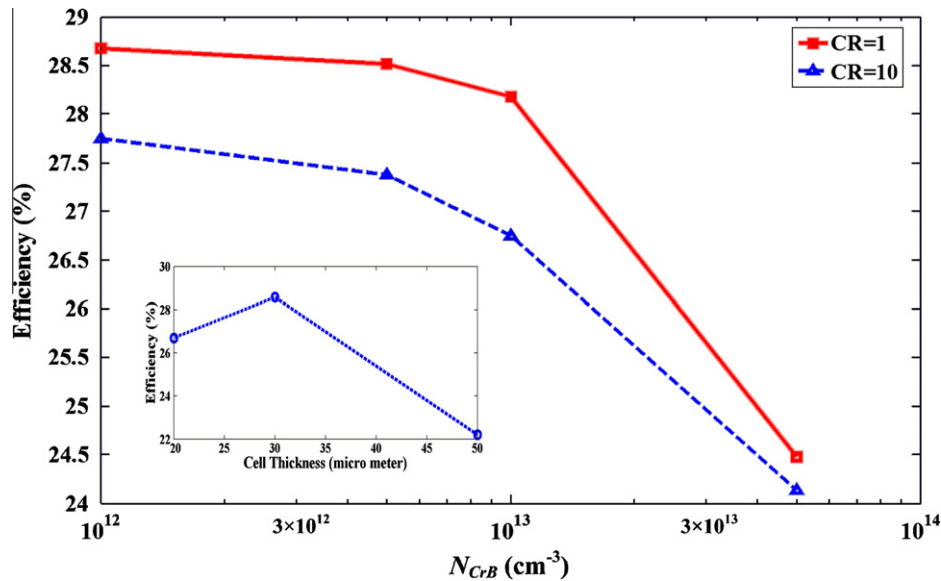


Fig. 6. Efficiency calculated as functions of N_{CrB} and cell thickness (inset).

with $N_{CrB} = 5 \times 10^{13} \text{ cm}^{-3}$ without compensation, efficiency falls below 23%. On the other hand, for cells with compensation, η starts to fall after $CR = 1$. This is due to the competition between improved lifetime and deteriorated mobility. It appears that at higher CR the deterioration of mobility is more dominant and therefore efficiency goes down. The maximum efficiency is predicted to be $\sim 28.7\%$ with $N_{CrB} = 10^{12} \text{ cm}^{-3}$ and $CR = 1$.

In order to make the impact of N_{CrB} on efficiency more vivid, it has been plotted as a function of N_{CrB} in Fig. 6. With $CR = 1$, the efficiency achieved with almost the entire range of N_{CrB} is found higher than that achievable with the base cell. The influence of cell thickness on the efficiency is shown in the inset of Fig. 6, for the cell with $N_{CrB} = 10^{12} \text{ cm}^{-3}$ and $CR = 10$. As the base material is compensated, the resistivity is increased due to the reduction of free carriers. Such increased resistivity would cause additional voltage drop across the cell and bring the FF and efficiency down. Obviously this effect becomes more prominent as the cell thickness is increased. The voltage drop in fact cancels out the positive impact of additional photon absorbed by a thicker cell. The inset of Fig. 6 represents this idea, as it shows that the efficiency is peaked at $W = 30 \mu\text{m}$.

4. Conclusion

This paper proposes and investigates a mechanism, which exploits IPV and compensation effect in a complimentary way for improving silicon solar cell efficiency. In this mechanism the base layer is assumed to contain, apart from the primary dopants, two distinct types of impurity atoms for producing the desired effects. It has been shown through simulation that efficiency can be improved when the concentration of the impurities are carefully chosen based on several constraints. First, the concentration of the deep level impurities included for absorbing sub-bandgap photons through IPV effect must be kept moderate compared to the primary dopants, such that the deep level impurities do not cause the lifetime to deteriorate. In the presented investigation, CrB pairs are assumed to produce the IPV effect in a solar cell having a B doped base layer. It is found that N_{CrB} should be $\sim 10^{12} \text{ cm}^{-3}$ (for $N_A = 10^{17} \text{ cm}^{-3}$) to ensure that effective lifetime is determined by B concentration and hence can be improved through compensa-

tion. Second, the compensating impurity (which is P in this case) concentration needs to be limited considering its two fold impact on the cell performance. The positive impact is that compensation improves lifetime (provided that N_{CrB} is moderate enough). However, with compensation, mobility decreases due to increased scattering and resistivity increases because of drastic reduction of free carriers. The resistivity increment puts an additional constraint on the thickness of the cell. Using these understanding the optimized cell ($N_{CrB} = 10^{12} \text{ cm}^{-3}$, $CR = 1$, and $W = 30 \mu\text{m}$) is predicted to achieve $\sim 28.7\%$ efficiency, which is significantly higher than that of the base cell (25.2%). An impurity that creates non mid-gap yet deep energy level within the gap (like CrB pairs in Si) therefore seems to be a very suitable candidate for improving the efficiency of a Si cell, which is then needs to be carefully compensated to ensure reasonably high carrier lifetime.

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