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## RESEARCH ARTICLE

### GENERATION AND DIFFUSION OF EXCITONS IN SILICON SOLAR CELLS

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#### ABSTRACT

We studied the phenomena of exciton generation and diffusion in a monocrystalline silicon solar cell. This study revealed two types of exciton generation: an exciton generation associated with the generation rate  $G_{ex}$  of the excitons and a generation rate  $C_{ex/eh}$  related to the coupling between the electron and the hole and representing the number of holes and electrons which are bonded per unit volume and per unit time to form an exciton. We have studied the exciton fraction generated as a function of the wavelength, which shows that the exciton generation is more important in the infrared. The rate of coupled exciton generation increases as a function of the coupling coefficient. Indeed, the strong coupling between the electron and the hole, synonymous with a strong bond between these two particles, favors the formation of coupled excitons. We also noted a decrease in the effective diffusion lengths as a function of the coupling coefficient. The strong bond between the electron and the hole reduces the mobility of the latter.

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#### INTRODUCTION

The production of the electric current passes through the generation of excitons which diffuse into the material before dissociating into free electron-hole pairs. Two types of exciton generation are defined: The generation of excitons associated with the generation rate  $G_{ex}$  of the excitons (Barrau et al., 1973; Burgelman and Minnaert, 2006; Corkish et al., 1998; Kane and Swanson, 1993; Kane and Swanson, 1993; Zhang et al., 1998) and the generation of excitons linked to the coupling between the electron and the hole (Lin et al., 2001). This second generation, defined by the magnitude  $C_{ex/eh}$  ( $cm^{-3}s^{-1}$ ), represents the number of electrons and holes that bind per unit volume and per unit time to form excitons. According to Burgelman, the opposite of this size corresponds to a volumic dissociation of excitons in free electron-hole pairs (Lin et al., 2001). We call these excitons, coupled excitons because their formation is related to electron - hole coupling. Moreover, the mutual influence between the electrons and the excitons results in an effective diffusion of these charge carriers, which is characterized by the two diffusion lengths  $L_1$  and  $L_2$ . The aim of this article is to study the variations of the two types of generation as a function of the wavelength and the exciton binding coefficient. This article studies also the diffusion lengths of electrons and excitons as a function of the coupling coefficient.

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We consider a model of solar cell silicon n+p simplified. The contribution of the emitter is neglected and the excitation is low.

#### Theoretical model

We will denote electrons, holes and excitons with the subscript e, h and ex, respectively. We will limit ourselves to a one-dimensional analysis.

#### Excitons generation

Our study model reveals two types of excitons generation  $G_{ex}$  and  $C_{ex/eh}$  involved in the distribution of charge carriers, translated by the following equations system (Corkish et al., 1998; Niassé et al., 2009; Zhang et al., 1998):

$$D_e d^2 \frac{\Delta n_e}{dx^2} = \frac{\Delta n_e}{\tau_e} + b(\Delta n_e N_A - \Delta n_{ex} n^*) - G_{e0} \exp[-\alpha x] \quad (1)$$

$$D_{ex} d^2 \frac{\Delta n_{ex}}{dx^2} = \frac{\Delta n_{ex}}{\tau_{ex}} - b(\Delta n_e N_A - \Delta n_{ex} n^*) - G_{ex0} \exp[-\alpha x] \quad (2)$$

$$G_{ex} = G_{ex0} \exp[-\alpha x] \quad (cm^{-3}s^{-1}) \quad (3)$$

$$C_{ex/eh} = b(\Delta n_e N_A - \Delta n_{ex} n^*) \quad (cm^{-3}s^{-1}) \quad (4)$$

### Excitons generation associated to $G_{ex}$

The total generation of the carriers depends on the fraction of the generated free electron-hole pairs  $f_{eh}$  and the exciton fraction  $f_{ex}$  generated. Thus, the generation rates of free electron-hole pairs  $G_e$  and excitons  $G_{ex}$  are defined by the following relations (Corkish *et al.*, 1998).

$$G_e = f_{eh}G(\lambda) \quad \text{and} \quad G_{ex} = f_{ex}G(\lambda) \quad (5)$$

$$f_{ex} + f_{eh} = 1 \quad (6)$$

The expression of  $G(\lambda)$  is given by:

$$G(\lambda) = \alpha(\lambda)F(\lambda)[1-R(\lambda)]\exp[-\alpha(\lambda)x] \quad (7)$$

### $G(\lambda)$ : Total generation rate of free electron-hole pairs and excitons.

$f_{eh}$ : Fraction of electron-hole pairs generated.

$f_{ex}$ : Generated exciton fraction.

$F(\lambda)$ : Incident flow

$\alpha(\lambda)$ : absorption coefficient of the material

$R(\lambda)$ : reflection coefficient of the material

Depending on the values of  $f_{eh}$  and  $f_{ex}$ , which depend on the exciting wavelength and the type of semiconductor (organic or inorganic), we can have two distinct situations:

$$- \quad f_{eh} \approx 1 \quad \text{and} \quad f_{ex} \approx 0$$

The total generation of carriers corresponds to the generation of free electron-hole pairs. In this case, the excitons arise only from the relaxation of the free electron-hole pairs.

$$- \quad f_{eh} \approx 0 \quad \text{and} \quad f_{ex} \approx 1$$

This situation is obtained in organic semiconductors.

The fraction of excitons is almost equal to the total generation of carriers.

### Exciton generation associated to $C_{ex/eh}$

By observing the continuity equations (1) and (2),  $C_{ex/eh}$  corresponds to an exciton generation rate and a recombination rate of electrons. Indeed, a continuity equation governs the phenomena of generation, diffusion and generation of charge carriers.  $C_{ex/eh}$  is related to the coupling between the electron and the hole. This generation of excitons represents the number of electrons and holes that bind per unit volume and per unit time to form excitons (Corkish *et al.*, 1998; Zhang *et al.*, 1998). We call these excitons coupled excitons because their formation is related to electron - hole coupling. This generation is zero when the electron exciton system is in equilibrium.

This equilibrium is translated by the following equality:

$\Delta n_e N_A = \Delta n_{ex} n^*$ . With  $n^*$ , the equilibrium constant. One thus notes the disappearance of the mutual influence between the electrons and the excitons in the material. This leads to the equations of continuity peculiar to electrons and excitons.

$$D_e d^2 \frac{\Delta n_e}{dx^2} = \frac{\Delta n_e}{\tau_e} - G_{e0} \exp[-\alpha x] \quad (8)$$

$$D_{ex} d^2 \frac{\Delta n_{ex}}{dx^2} = \frac{\Delta n_{ex}}{\tau_{ex}} - G_{ex0} \exp[-\alpha x] \quad (9)$$

### Excitons diffusion

The phenomena of generation are followed by an effective diffusion of the charge carriers. This diffusion is characterized by two effective diffusion lengths  $L_1$  and  $L_2$  which depend on the mutual influence between the electrons and the excitons. When this influence disappears, the effective diffusion lengths tend to the own diffusion lengths  $L_e$  and  $L_{ex}$ . The excitons have a very low diffusion length ( $L_{ex} < L_e$ ). The expressions of the diffusion lengths are given in the papers of Zhang and Corkish (Corkish *et al.*, 1998; Zhang *et al.*, 1998).

## RESULTS AND DISCUSSION

### Variation of the exciton generation fraction as a function of wavelength

We consider a monocrystalline silicon solar cell which has a depth  $H = 1000 \mu\text{m}$  and a doping level  $N_A = 10^{15} \text{cm}^{-3}$ . We have plotted in Figure 1, the variation of the fraction of excitons generated as a function of the excitation wavelength. We find that low wavelengths do not generate excitons. However, there is a strong generation of excitons for wavelengths between 1110 and 1200 nm, the largest at a wavelength equal to 1130 nm. The strong generation of excitons is thus obtained in the infrared. Indeed, for the wavelengths that are higher but close to the wavelength gap of the silicon ( $\lambda_g \approx 1108 \text{nm}$ ) the generated electron does not reach the conduction band, it is in an intermediate state and thus forms with the hole of the valence band an exciton. The silicon atoms are then in an excited state. For wavelengths less than  $\lambda_g$ , the electron has enough energy to cross the gap and become free in the material. This electron is weakly bound to the valence band hole.

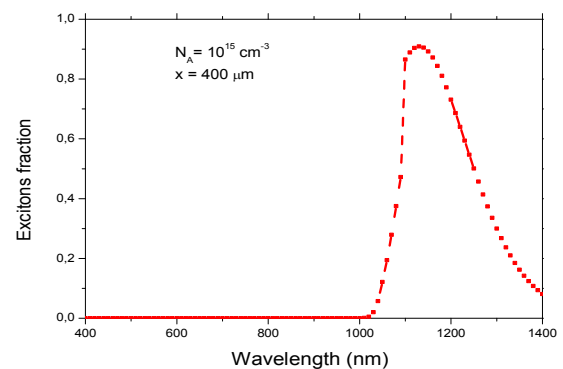
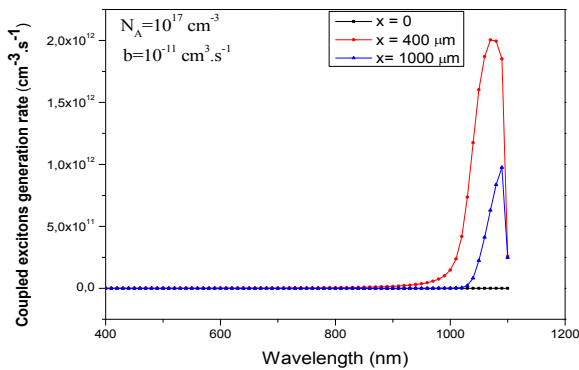


Figure 1. Fraction of excitons generated as a function of the excitation wavelength at a depth in the base  $x = 400 \mu\text{m}$

### Variation of the coupled excitons generation rate as a function of the wavelength

For a better study, we considered three positions in the photopile: the junction ( $x = 0 \mu\text{m}$ ), the inside of the base ( $x = 400 \mu\text{m}$ ) and the rear face ( $x = 1000 \mu\text{m}$ ). We have also

chosen an average coupling coefficient  $b = 10^{-11} \text{ cm}^3 \cdot \text{s}^{-1}$  and a doping rate  $N_A = 10^{17} \text{ cm}^{-3}$ . We study the influences of  $N_A$  and  $b$  on the resulting profile. Figure 2 represents this generation rate as a function of the wavelength for the three positions in the photovoltaic cell.

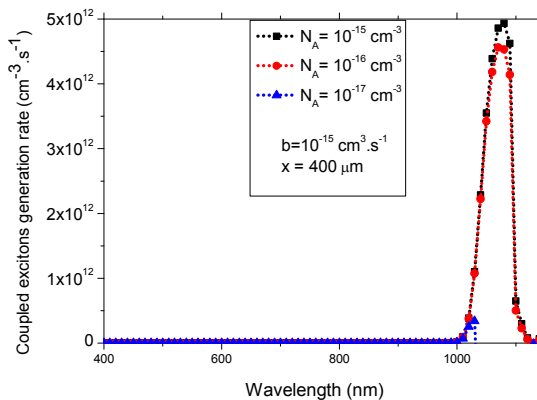


**Figure 2 :** Variation of the coupled excitons generation rate as a function of the wavelength for various positions in the solar cell.  $N_A = 10^{17} \text{ cm}^{-3}$  et  $b = 10^{-11} \text{ cm}^3 \cdot \text{s}^{-1}$

This figure shows that the generation of coupled excitons is more visible in the range of lengths in the vicinity of  $\lambda_g$ . The low wavelengths generate an insignificant number of coupled excitons. It is also noted that the amount of coupled excitons is zero at the junction and very low on the back side because of the electric field that prevails in the space charge zone and phenomena of recombination and excitonic conversion to the surface back

### Effect of the doping rate in acceptor atoms

Figure 3 shows the variations in the coupled excitons generation rate for given values of the doping rate.

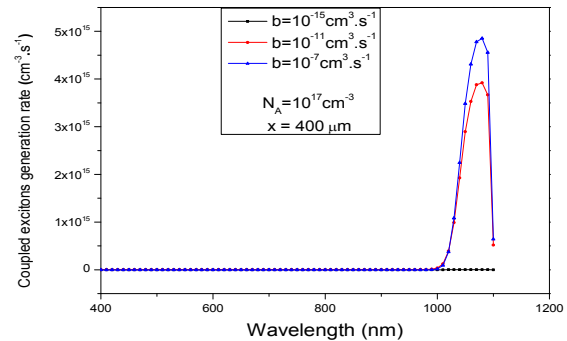


**Figure 3 :** Variation of the coupled excitons generation rate as a function of the wavelength for three values of the doping level :  $N_A = 10^{15} \text{ cm}^{-3}$ ,  $N_A = 10^{16} \text{ cm}^{-3}$  et  $N_A = 10^{17} \text{ cm}^{-3}$

We note that coupled excitons generation rate decreases as a function of the doping rate in acceptor atoms. Indeed, the increase of the doping rate favors the recombination phenomena of excitons through the formation of stable exciton-acceptor complexes ( $A^0X$ ) which are stable for any value of the capture cross-section  $\sigma$  (Karazhanov. S. Zh *et al.*, 2000 ; Lin. C.F *et al.*, 2001).

### Effect of the coupling coefficient

We consider three values of the coupling coefficient:  $b = 10^{-13} \text{ cm}^3 \cdot \text{s}^{-1}$ ,  $b = 10^{-11} \text{ cm}^3 \cdot \text{s}^{-1}$  and  $b = 10^{-8} \text{ cm}^3 \cdot \text{s}^{-1}$ . In figure 4, we have the coupling effect on the coupled excitons generation rate.

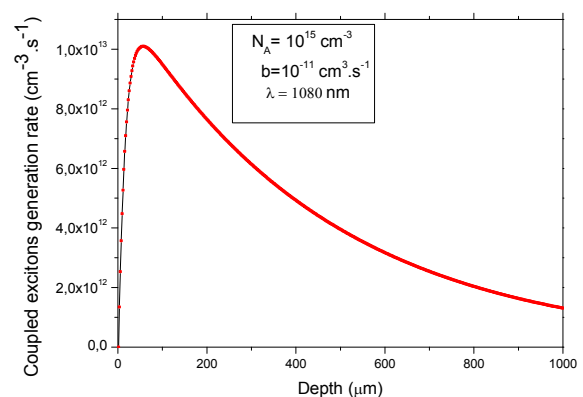


**Figure 4 :** Variation of the coupled excitons generation rate as a function of the wavelength for three values of the coupling coefficient :  $b = 10^{-13} \text{ cm}^3 \cdot \text{s}^{-1}$ ,  $b = 10^{-11} \text{ cm}^3 \cdot \text{s}^{-1}$  and  $b = 10^{-7} \text{ cm}^3 \cdot \text{s}^{-1}$

This rate increases as a function of the coupling coefficient. The strong coupling between the electron and the hole, synonymous with a strong bond between these two particles, favors the formation of coupled excitons.

### Variation of the coupled excitons generation rate as a function of the depth in the base

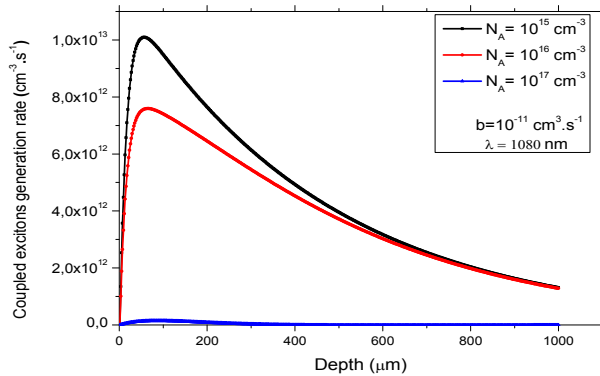
When the solar cell is illuminated with suitable light, the excitons are generated in the base. It follows the phenomena of diffusion and recombination in depth. We first approach the mechanisms of exciton generation in volume before going on to the influence of the doping rate and the coupling coefficient  $b$ . For this, we considered a wavelength  $\lambda = 1080 \text{ nm}$ , capable of generating excitons. The results obtained are represented by figure 5. We note that the generation rate, zero at the junction, is maximum at a given depth in the base and decreases considerably in depth. Indeed, the generation of the carriers in volume depends on the phenomena of recombination of the electrons and the catches of excitons.



**Figure 5.** Variation of the coupled excitons generation rate as a function of the depth in the base.  $b = 10^{-11} \text{ cm}^3 \cdot \text{s}^{-1}$  and  $N_A = 10^{15} \text{ cm}^{-3}$

### Effect of the doping level

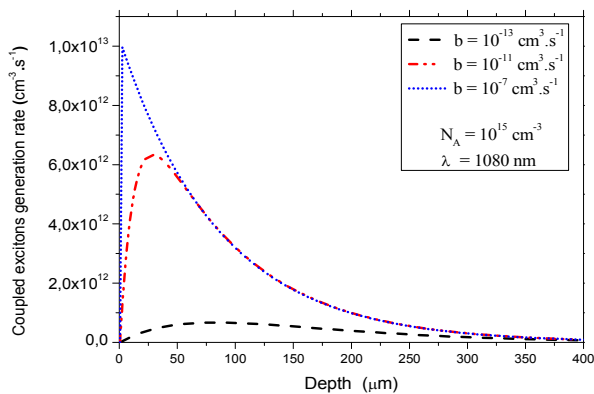
In order to better study the influence of the doping rate, we considered three values of  $N_A$  :  $N_A = 10^{15} \text{ cm}^{-3}$ ,  $N_A = 10^{16} \text{ cm}^{-3}$  et  $N_A = 10^{17} \text{ cm}^{-3}$ . Thus, we obtain the results given by figure 6. The doping of the solar cell reduces the formation of excitons coupled in any part of the solar cell. The increase of the doping rate reinforces the sites of capture of excitons by the impurities thus leading to the formation of exciton-impurity complex.



**Figure 6.** Variation of the coupled excitons generation rate as a function of the depth in the base for three values of the doping level :  $N_A = 10^{15} \text{ cm}^{-3}$ ,  $N_A = 10^{16} \text{ cm}^{-3}$  and  $N_A = 10^{17} \text{ cm}^{-3}$

### Effect of the coupling coefficient

We have plotted in Figure 7 the variations of coupled exciton formation under the influence of the exciton binding coefficient.



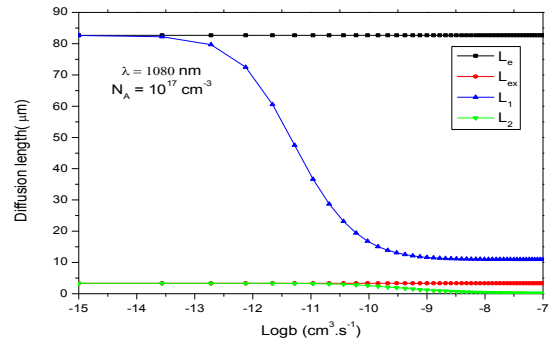
**Figure 7.** Variation of the coupled excitons generation rate as a function of the depth in the base for three values of the coupling coefficient :  $b = 10^{13} \text{ cm}^3 \cdot \text{s}^{-1}$ ,  $b = 10^{11} \text{ cm}^3 \cdot \text{s}^{-1}$  and  $b = 10^7 \text{ cm}^3 \cdot \text{s}^{-1}$

We find that there is a strong generation of coupled excitons if the coupling is strong. It is also important to note that the maximum of these profiles approximates the space charge area as a function of the increasing values of  $b$ .

### Effective diffusion lengths as a function of the exciton binding coefficient

We have plotted in Figure 8 the profiles of the effective diffusion lengths  $L_1$  and  $L_2$  as a function of the exciton

bonding coefficient. By way of comparison, we have represented the own diffusion lengths  $L_e$  and  $L_{ex}$ . The doping rate is  $N_A = 10^{17} \text{ cm}^{-3}$ .



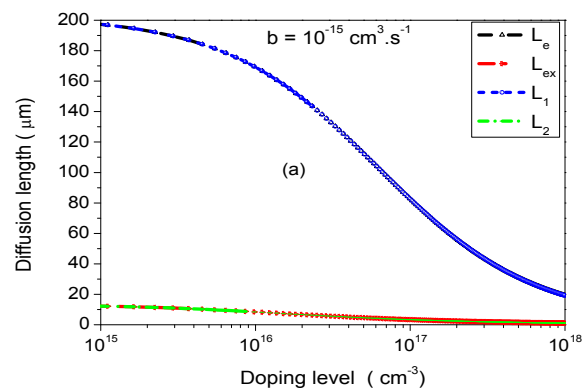
**Figure 8.** Variation of the effective diffusion lengths  $L_1$  and  $L_2$  compared to own diffusion lengths  $L_e$  et  $L_{ex}$  for a doping level  $N_A = 10^{17} \text{ cm}^{-3}$

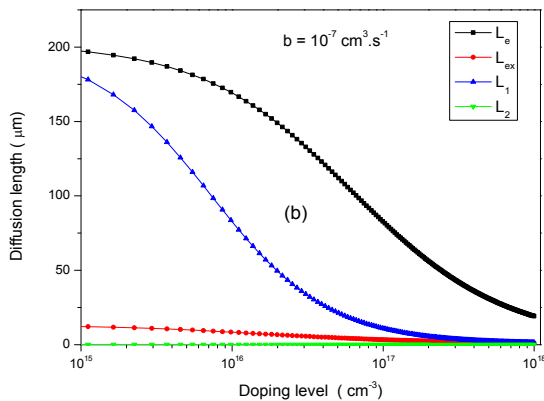
This figure, which shows three types of coupling according to the values of  $b$ , shows a decrease in the effective diffusion lengths as a function of the coupling coefficient.

- $10^{-15} \text{ cm}^3 \cdot \text{s}^{-1} \leq b \leq 10^{-13} \text{ cm}^3 \cdot \text{s}^{-1}$ , coupling is low. The effective diffusion lengths remain equal to the own diffusion lengths:  $L_1 \approx L_e$  and  $L_2 \approx L_{ex}$ . The electron and the exciton diffuse independently with their own diffusion length.
- $10^{-9} \text{ cm}^3 \cdot \text{s}^{-1} \leq b \leq 10^{-7} \text{ cm}^3 \cdot \text{s}^{-1}$ , we have a strong coupling. The electron and the hole are strongly bonded. This strong bond reduces the mobility of the electron and the hole of the exciton, which results in a reduction in the effective scattering lengths.
- Between these two types of coupling, there is an intermediate coupling: the average coupling moyen ( $10^{-13} \text{ cm}^3 \cdot \text{s}^{-1} < b \leq 10^{-10} \text{ cm}^3 \cdot \text{s}^{-1}$ ). The electron and the exciton do not diffuse independently, but each of water has its own effective diffusion length  $L_1$  and  $L_2$ , respectively.

### Diffusion lengths as a function of the doping level

Figure 9 shows the variations of the effective and own diffusion lengths as a function of the doping rate in acceptor atoms for each type of coupling.





**Figure 9. Variation of the diffusion lengths as a function of the doping rate in acceptor atoms for weak coupling (a) and for strong coupling (b)**

Increasing the doping rate reduces the diffusion of electrons and excitons regardless of the type of coupling. Indeed impurities favor the formation of particle-impurity complex of lower mobility. It is also observed that when the electron and the hole of the exciton are weakly bonded, the effective diffusion lengths are equal to the own diffusion lengths whatever the value of the doping rate.

### Conclusion

In this article we studied the phenomena of exciton generation and diffusion in a monocrystalline silicon solar cell. This study revealed that the notion of electron - exciton coupling developed in the articles of Zhang and Corkish is in fact related to the mutual influence between the electron and the hole which in some cases binds to form an exciton. This phenomenon disappears at equilibrium terminating the coupling. Our article has thus revealed a new exciton generation mechanism associated with  $C_{ex/eh}$ . We also find

that the strong bond between the holes and the electrons decreases the mobility of these carriers in the material thus causing a lower diffusion length of the excitons than that of the electrons.

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