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RESEARCH ARTICLE

THEORETICAL STUDY OF DIFFUSION CAPACITY (CD) IN THE LIMITING CASE OF BULK RECOMBINATION IN SILICON SOLAR CELLS

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ABSTRACT

The electrical characterization of solar cells is essential to evaluate their performance and understand their behavior under different environmental conditions, including temperature. Charge carriers, under the influence of temperature, diffuse into the cell, a phenomenon quantified by the diffusion capacitance. These generated carriers do not contribute to the electric current; some recombine in specific areas, either on the surface or in the bulk. Bulk recombination mechanisms include Shockley-Read-Hall (SRH) recombination, radiative recombination, and Auger recombination. We analyzed the variation of diffusion capacitance as a function of temperature, neglecting surface recombinations to focus on bulk recombination mechanisms. Calculations, performed for three different bias voltages, show that diffusion capacitance due to Auger recombination predominates, followed by that associated with radiative recombination, while SRH recombination contributes the least. The study reveals that, although the open-circuit voltage decreases with increasing temperature, the diffusion capacitance increases, mainly due to carrier thermogeneration and the exponential variation of the diode current. These results demonstrate a lack of direct causal relationship between the decrease in open-circuit voltage and the increase in diffusion capacitance.

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INTRODUCTION

Photovoltaic solar cells are affected by environmental parameters such as temperature, sunlight, humidity, dust or wind speed. These parameters have an influence on the electrical quantities and other electrical parameters of the cell. It is therefore necessary to take into account the dependence of the electrical parameters on these environmental parameters. However, in the scientific literature, studies most often focus on the variation of temperature. The charge carriers in a photovoltaic solar cell tend to diffuse in the cell under the influence of an electric field or a concentration gradient [1]. The diffusion capacity is the measure of the capacity of the carriers to diffuse. This article makes the theoretical study of the diffusion capacity of a silicon solar cell. In a solar cell, during the carrier generation process, not all of them contribute to the electric current. Some of these carriers recombine. The main recombination zones are in volume or on the surface. For the volume recombination mechanisms, we distinguish three main recombination mechanisms which are: SRH, radiative and Auger recombination mechanisms. The diffusion capacity of a solar cell is in a certain way linked to the different recombination mechanisms.

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METHODS

Simpliflying Assumptions

To study the diffusion capacity, we consider the following hypotheses:

- The solar cell used is based on crystalline silicon: therefore all the parameters that will be used will be specific to silicon. However, we do not focus on the level and degree of doping of silicon because in practice solar cells can be weakly or strongly doped.
- The semiconductor is non-degenerate at thermodynamic equilibrium. The number of electrons and holes is given by the product of the density of states by the distribution function and that the Fermi level is located in the forbidden band so that the Boltzmann approximation is valid and the carrier densities can be written as follows:

$$n = N_c exp - \left[\frac{(E_c - E_F)}{kT}\right] \quad (1)$$

$$p = N_V exp - \left[\frac{(E_V - E_F)}{kT}\right] \quad (2)$$

Where n and p are the numbers of electrons and holes respectively, N_c and N_V are called the equivalent densities of states in the conduction band and the valence band respectively, E_c and E_V are the energies of the bottom of the conduction band and the valence band respectively, k is the Boltzmann constant, T is the temperature and E_F is the Fermi level, which is the energy level where the probability of a state being occupied by an electron is 50% at zero absolute temperature.

- The electric field is constant in the absorbing layer, so the energy band diagram does not depend on it. This allows us to rewrite equations (1) and (2) as follows:

$$n(x) = n_0 exp\left(-\frac{qEx}{kT}\right) \quad (3)$$

$$p(x) = p_0 exp\left(-\frac{qE(L-x)}{kT}\right) \quad (4)$$

Where n_0 and p_0 are the electron and hole densities at the photoanode and cathode, respectively, E is the electric field, and L is the thickness of the cell base.

These assumptions are intended to simplify the analysis by neglecting certain effects such as carrier transport currents. This allows us to focus on volume-limited recombination mechanisms.

Mathematical Model of Diffusion Capacity: The diffusion capacity depends on the total quantity of excess minority charges in the base of the solar cell; the derivative of this allows us to have the expression of the capacity as a function of the voltage:

$$C_d(V) = \frac{dQ_{nb}}{dV} \quad (5)$$

The total quantity of minority charges Q_{nb} is given by:

$$Q_{nb} = I_0\tau_n[exp(KV/T) - 1] \quad (6)$$

By deriving equation (4) with respect to voltage V, we obtain:

$$C_d(V) = (\frac{K}{T})I_0\tau_n \exp(\frac{KV}{T}) \quad (7)$$

It is clear from equation (7) that the diffusion capacity depends on the voltage applied to the terminals of the solar cell. It thus becomes interesting to express it in the case where the voltage is equal to the open-circuit voltage. To have this expression in open circuit, the following condition is required: KV/T≫1. We thus obtain:

$$C_d(V_{oc}) = K\tau_n\frac{I_{cc}}{T} \quad (8)$$

In this equation, I_{cc} is the short-circuit current.

The diode current (I_d), at the junction, is given by equation (9):

$$I_d = I_0 exp\left(\frac{KV}{T} - 1\right) \quad (9)$$

The saturation current of the diode is given by equation (10):

$$I_0 = I_{cc}\left[exp\left(\frac{KV_{oc}}{T} - 1\right)\right]^{-1} \quad (10)$$

For KV/T≫1, C_d can be expressed as a function of I_d. We obtain:

$$C_d = K\tau_n\frac{I_d}{T} \quad (11)$$

For solar cells whose relationship between base thickness (x) and diffusion length satisfies the condition $\frac{x}{L_n} \ll 1$, equations (6) and (11) must be multiplied by $\frac{x}{L_n}$.

The diffusion capacitance, mainly related to the diffusion process and expressed in Farad (F) is associated with the diffusion charge stored in the quasi-neutral region of the junction when forward biased. It plays a very important role and influences the dynamics of the cell under forward bias. Parameters such as the lifetime of minority carriers in the base and their diffusion length, influence the diffusion capacitance because these parameters determine how many carriers can be injected and stored in the quasi-neutral region under forward bias.

Mathematical model of open Circuit Voltage: The determination of the open circuit voltage implies a total absence of carrier flux. This implies a balance between the generation rate and the recombination rate of the photogenerated carriers, so that:

$$R(n,p) = G \quad (12)$$

From equations (3) and (4), the product np is independent of x as shown in equation (13).

$$np = n_0p_0 exp\left(-\frac{qEL}{kT}\right) \quad (13)$$

The open-circuit voltage depends on the product np. It is given by the following equation (14):

$$V_{oc} = \frac{E_g}{q} - \frac{kT}{q} ln\left(\frac{N_C N_V}{np}\right) \quad (14)$$

Where E_g represents the band gap energy.

We have established the hypothesis that, in open circuit operation, the recombination rate and the generation rate are related by the illumination level by the product np. The determination of this product requires having expressions for the recombination rate. For this, we consider the following three types of recombination: bulk trap-assisted Shockley-Read-Hall (SRH) recombination, radiative recombination, and Auger recombination, using models that can be found in [2]. These models are given by equations (15), (16) and (17):

$$R_{SRH} = 2A\frac{np}{n+p} \quad (15)$$

$$R_{rad} = Bnp \quad (16)$$

$$R_{Auger} = \frac{C}{2}np(n+p) \quad (17)$$

Equations (15), (16) and (17) give respectively the Shockley-Read-Hall (SRH), radiative and Auger recombination rates and A, B and C are the respective recombination constants. These recombination constants are given by the ABC model [3]. To obtain the expressions of the open-circuit voltage as a function of the three different types of bulk recombinations, the following hypothesis is required: the intrinsic absorbing layer is considered to be homogeneous with a constant illumination G and n = p. Under these conditions and on the basis of the Boltzmann approximation giving equations (1) and (2), the open-circuit voltage can be expressed as follows:

$$V_{oc(SRH)} = \frac{E_g}{q} - \frac{kT}{q}[ln(A^2N_CN_V) - 2\ln(G)] \quad (18)$$

$$V_{oc(rad)} = \frac{E_g}{q} - \frac{kT}{q}[ln(BN_CN_V) - \ln(G)] \quad (19)$$

$$V_{oc(Auger)} = \frac{E_g}{q} - \frac{kT}{q}\left[ln\left(C^{2/3}N_CN_V\right) - \frac{2}{3}\ln(G)\right] \quad (20)$$

The coefficients 2, 1 and 2/3 represent the slope S for the respective cases of SRH, radiative and Auger recombination. This slope is given by:

$$S = \frac{\partial[ln(np)]}{\partial[ln(G)]} \quad (21)$$

The expression for the slope S given by equation (21) only concerns the case where we assume that n=p.

Mathematical Model of Short-Circuit Current: The short-circuit current density does not depend on the different recombination cases. This is demonstrated by the assumptions that have been established.

However, in short-circuit conditions, the different recombination mechanisms are neglected compared to open-circuit operation. Under these conditions and taking into account the small variation of the short-circuit current compared to the temperature variation, the short-circuit current density can be expressed as follows [4]:

$$I_{sc} = qGL\left[1 + \alpha I_{sc}\frac{(T-T_r)}{100}\right] \quad (22)$$

Where αI_{sc} represents the temperature coefficient in short-circuit operation and T_r is the reference temperature.

Mathematical model of the Band Gap Energy: Currently, the models presented in the literature and dealing with the band gap are made on the basis of the works of Bludau and Macfarlane. However, three models are most often used. His models are the works of Thurmond, Alex and Pässler [5][6][7][8].The models of Thurmond and Alex follow the following equation:

$$E_g^0(T) = E_g^0(0) - \frac{\propto T^2}{T+\beta} \quad (23)$$

Where α is expressed in $eV.K^{-1}$ and β in K.

The two assumptions of equation (23) are that the energy gap must be inversely proportional to T at high temperature and proportional to T^2 at low temperature. The use of this equation is justified by the fact that it adequately represents the experimental results of M. B. Panish et al [9].

The Pässler model follows the following equation:

$$E_g^0(T) = E_g^0(0) - \propto\theta\left[\gamma + \frac{3\Delta^2}{2}\left(1 + \frac{\pi^2}{3(1+\Delta^2)}\chi^2 + \frac{3\Delta^2-1}{4}\chi^3 + \frac{8}{3}\chi^4 + \chi^6 - 1\right)^{\frac{1}{6}}\right] \quad (24)$$

Where α represents the limit at the slope level when T tends to infinity, θ is the average temperature of the phonons, Δ is the degree of dispersion of the phonons, specific to the material, γ depends on Δ, θ and T. Its expression is given by the following equation:

$$\gamma = \frac{1-3\Delta^2}{exp\left(\frac{\theta}{T}\right)-1} \quad (25)$$

The following table (Tab 1) gives the values of the different coefficients for different materials and table (Tab 2) gives the parameter values for the models of equations (23) and (24).

The following table (Tab 2) gives the parameter values for the models of equations (23) and (24).

Although the gap between the parameters of the three models is small, there is a difference between these three models. In Fig. 1, the deviation does not exceed unity and is of the order of 0.7 at low temperature and 0.8 at high temperature. These observations can be misleading because the intrinsic charge carrier density depends on the band gap but, it may well not follow the same trends given by the models of this band. Let us analyze more closely the implication of the band gap models on the model of the intrinsic charge carrier density. The unrealism of the extremely wide dispersion regime implied by the Varshni model and which has never been observed experimentally is the proof of the greater accuracy of the Pässler model. For high temperatures, we observe a tendency of E_g^0(T) towards the asymptote $E_{lim}(0) - \alpha T$, where α is the slope of this asymptote and $E_{lim}(0)$ is the intersection of this asymptote with the y-axis at 0K. According to the Pässler model, the renormalization energy is defined as $E_{lim}(0) - E_g^0(0)$ and is equal to αΘ/2 in the Varshni model [10]. This means that the parameter α and the renormalization energy are overestimated in the Thurmond and Alex models. In the further development of the different models, taking into account the band gap, the Passler model will be used.

Tab 1. Dispersion-related parameters from numerical fits of experimental band gap Eg(T), data available for various materials of the groups

Divice	Tmin-Tmax (K)	$\alpha/10^{-4}$ (eV/K)	Θ (K)	Δ	$\alpha\Theta/2$ (MeV)
Si	2 - 415	3,23	446	0,51	72

Tab 2. Parameters for the E_g^0 band gap models of Thurmond, Alex and Pässler

Parameters	$E_g^0(0)$ (eV)	α (eV/K)	β (K)	Θ (K)	Δ	γ	χ
Thurmond	1,17	$4{,}73.10^{-4}$	636	-	-	-	-
Alex	1,1692	$4{,}9.10^{-4}$	655	-	-	-	-
Pässler	1,17	$3{,}23.10^{-4}$	-	446	0,51	$\frac{1-3\Delta^2}{exp\left(\frac{\theta}{T}\right)-1}$	$\frac{2T}{\Theta}$

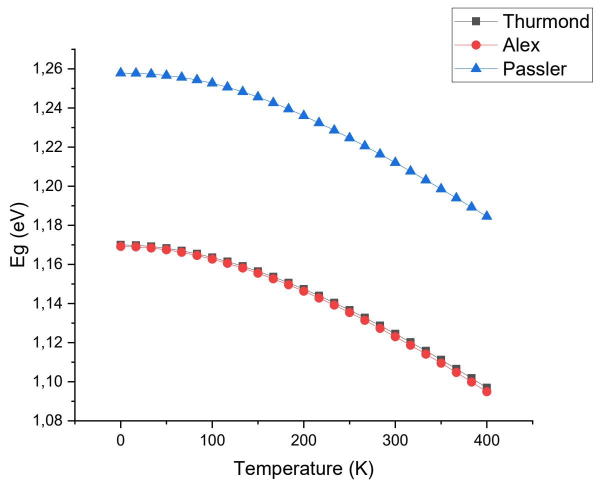

Fig. 1. Band gap model as a function of temperature

Mathematical Model of Carrier Lifetime: The minority carrier lifetime model mainly characterizes carrier recombinations. Taking into account the three recombination mechanisms considered: Shockley-Read-Hall (SRH), radiative and Auger. The lifetime is a measure of the average time during which a charge carrier (electron or hole) remains mobile in a semiconductor material before recombining. It is modeled as follows:

$$\frac{1}{\tau} = \frac{1}{\tau_{SRH}} + \frac{1}{\tau_{radiative}} + \frac{1}{\tau_{Auger}} \quad (26)$$

The carrier lifetime related to the SRH recombination mechanism is given by:

$$\tau_{SRH}(T) = \tau_{SRH}(300)\left(\frac{300}{T}\right)^{\alpha} \quad (27)$$

In this model, the value of α varies depending on the type of defect in question, but allows for a qualitative analysis. In the context of this present study, a value of α=1.5 was taken.

The carrier lifetime related to the radiative recombination mechanism is given by:

$$\tau_{rad} = \frac{1}{B(N_d+\Delta p)} \quad (28)$$

The carrier lifetime model associated with the radiative recombination mechanism given by equation (28), implies two situations: (i) for a low injection level, equivalent to ($\Delta p < N_d$), the lifetime associated with radiative recombination depends only on the doping level N_d, (ii) for a high injection level, this lifetime is inversely proportional to the concentration of excess carriers in the base of the cell. According to some authors, under classical illumination conditions, equivalent to AM 1.5G, the concentration of excess carriers and the doping are of the same order of magnitude. The experimentally measured radiative recombination coefficient B for c-Si which has an indirect band gap is $5.10^{-15}cm^{-3}.s^{-1}$at 300K [11]. In theory, this coefficient depends on the temperature. Some authors have proposed mathematical models for the radiative recombination coefficient. However, among these authors, some found that the radiative recombination coefficient increases with temperature and others obtained the opposite. Among those who obtained an increase in the radiative recombination coefficient with temperature, we can cite the work of Van Roosbroeck and Shockley [12], who obtained a slight increase in the radiative recombination coefficient with temperature. Among the authors who found a decrease in the recombination coefficient with temperature, we can cite: (i) T. Trupke et al., who determined the absorption coefficient of intrinsic crystalline silicon over the temperature range from 77K to 300K. They calculated the radiative absorption coefficient from the absorption coefficient for band-to-band transitions that they determined at different temperatures from the photoluminescence spectrum measured on silicon wafers. They observed that B(T) decreases as a function of temperature [13]. (ii) H. Schlangenotto et al., who experimentally determined the radiative recombination coefficient for silicon. By injecting carriers (electrons-holes) into the base of the cell, they measured the intensity of the emitted radiation as a function of the concentration of the injected carriers at different temperatures. In their studies, they took into account the effect of excitons. They found that the radiative recombination coefficient decreases by a factor of about 30 between 100K and 400K [11]. In this present study, we will use the model proposed by H. T. The expression of the coefficient B(T) is obtained using the theory of Van Roosbroech and Shockley:

$$B(T) = \frac{1}{n_i^2} \times \frac{1}{\pi^2 \hbar^3 c_0^2} \int_0^{\infty} \left[n^2 \times (\hbar\omega)^2 \times \alpha_{BB}(\hbar\omega, T) \times exp\left(\frac{-\hbar\omega}{kT}\right) \times d(\hbar\omega) \right] \quad (29)$$

Nguyen et al., who made a polynomial approximation of the logarithm to base 10 of the radiative recombination coefficient [15]. From equation (29), we derive the product $B(T) \times n_i^2$, given by equation (30):

$$B(T) \times n_i^2 = \frac{1}{\pi^2 \hbar^3 c_0^2} \int_0^{\infty} \left[n^2 \times (\hbar\omega)^2 \times \alpha_{BB}(\hbar\omega, T) \times exp\left(\frac{-\hbar\omega}{kT}\right) \times d(\hbar\omega) \right] \quad (30)$$

To solve the integration of equation (30) the authors Nguyen et al., carried out measurements of the interband absorption coefficient for the following temperatures: 170 K, 195 K, 249 K, 291 K, 310 K and 363 K [16]. With the data on the interband coefficient, they expressed the product B(T) × n_i^2 as a function of the temperature by plotting the corresponding graph (Fig 2). However, let us recall that the intrinsic concentration of the ni carriers also depends on the temperature. Therefore, we replace the expression $B(T) \times n_i^2$ by $B(T) \times n_i^2(T)$ in order to take into account the dependence of $n_i^2(T)$ on the temperature. It thus becomes necessary to choose a mathematical model for the intrinsic concentration of the ni carriers. In another publication that we had to do, we discussed the different ni models existing in the literature. We chose to use the Sproul model for the intrinsic charge carrier concentration as recommended in [17]. Details of the Sproul model can be found in [18].

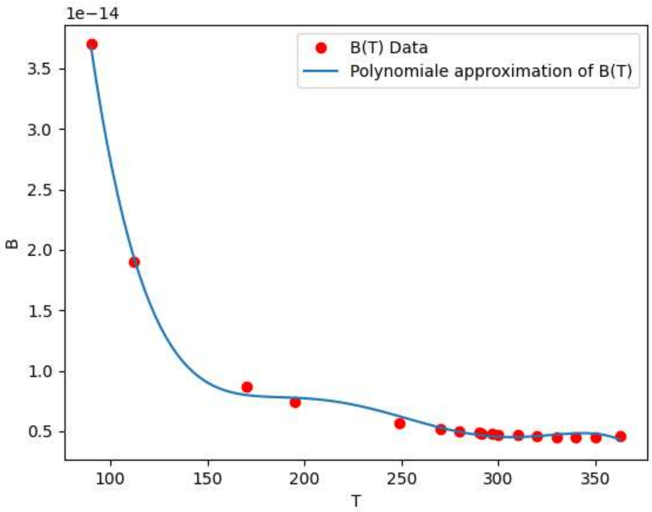

Fig. 2. B(T) versus Temperature and the 5th order Polynomial fit

The 5th order polynomial approximation allowed us to obtain the following expression:

$$B(T) = -4{,}14475658 \times 10^{-25}T^5 + 5{,}30654026 \times 10^{-22}T^4 - 2.65011535 \times 10^{-19}T^3 + 6.44719006 \times 10^{-17}T^2 - 7.66261708 \times 10^{-15}T + 3.65040697 \times 10^{-1} \quad (31)$$

In the following, we consider a high level of doping. In this case, the dependence of the concentration of excess carriers in the base varies slightly as a function of temperature. To simplify the study, we then consider that this concentration does not vary as a function of temperature. The carrier lifetime linked to the Auger recombination mechanism depends on the injection level. For a low injection level, this lifetime is independent of the injection level Δp:

$$\tau_{Auger} = \frac{1}{C_n N_d^2} \quad (32)$$

For a high injection level, this lifetime becomes:

$$\tau_{Auger} = \frac{1}{C_a \Delta p^2} \quad (33)$$

In equations (32) and (33), the coefficients C_a and C_n are the ambipolar and electron-related Auger recombination coefficients, respectively. For a semiconductor material with a decreasing band gap, the Auger recombination coefficient increases with temperature. On the one hand, for silicon, the temperature dependence of the radiative recombination coefficient is given by equation (34):

$$C_a(T) = C_{a,300K} \times \left(\frac{T}{300}\right)^{\alpha} \tag{34}$$

On the other hand, the ambipolar Auger recombination coefficient depends on the Auger recombination coefficient linked to electrons C_n and that linked to holes C_p.

$$C_a(T) = C_n(T) + C_p(T) \tag{35}$$

For silicon, at 300K the coefficients C_n and C_p are respectively equal to $1 \times 10^{-31} cm^6/s$ et $2{,}28 \times 10^{-31} cm^6/s$.

From the point of view of the variation of the Auger lifetime with respect to the injection level, it is low in the low injection regime and decreases sharply in the high injection regime [19][20].

RESULTS

The variation of the diffusion capacity as a function of temperature has been represented in Fig. 4, 5 and 6. In the analysis of these graphs, we will take into account the parameters on which the diffusion capacity depends, such as the lifetime of the charge carriers and the diode current. Let us recall that the diode current (I_d) is directly linked to the short-circuit current and the open-circuit voltage via the reverse saturation current (I_0). The recombination mechanisms affect in particular the open-circuit voltage. For all three recombination mechanisms, the open-circuit voltage varies in the same way as shown in Fig. 3, but we still note that the open-circuit voltage for the SRH recombination mechanism is lower than that for the other two recombination mechanisms which are very close in terms of values with a small predominance of the open-circuit voltage for the radiative recombination mechanism [21].

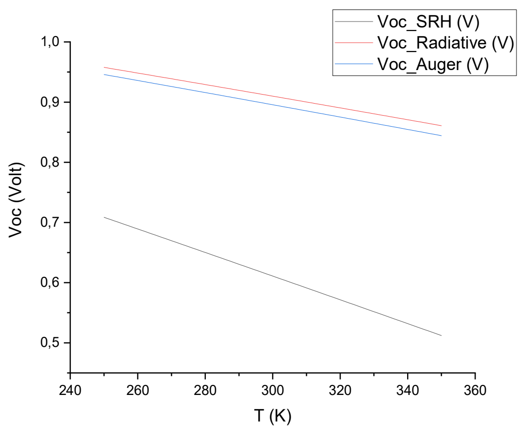

Fig. 3. Open circuit voltage versus temperature

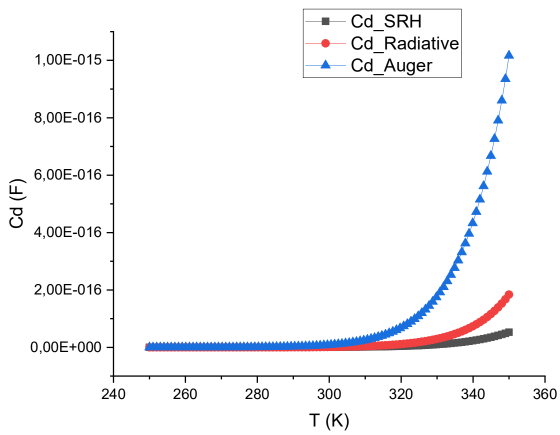

Fig. 4. Dynamic capacitance versus temperature for Vd = 0.3 Volt

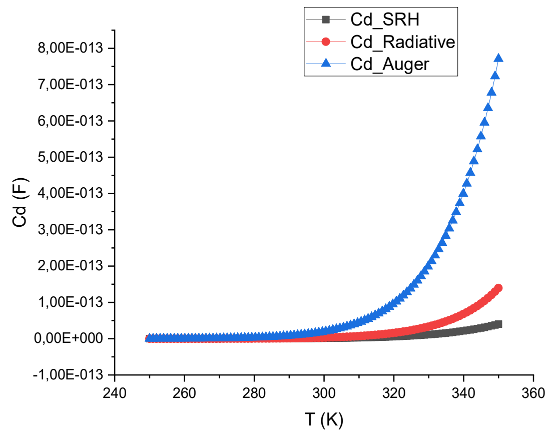

Fig. 5. Dynamic capacitance versus temperature for Vd = 0.5 Volt

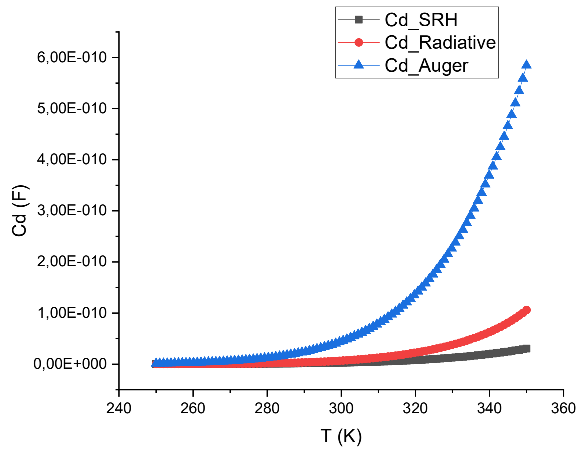

Fig. 6. Dynamic capacitance versus temperature for Vd = 0.7 Volt

DISCUSSION

The diffusion capacity follows the same trend for all applied voltage values. For all voltages, the diffusion capacity increases as the temperature increases. In Figs 4, 5 and 6, we notice that the diffusion capacity due to the Auger recombination mechanism takes over the other two recombination mechanisms. This is followed by the diffusion capacity due to the radiative recombination mechanism. The lowest capacity is that due to the SRH recombination mechanism. These results are in agreement with the open circuit voltages in Fig 3. Note however that these results are valid in the absence of an electric field [21]. However, to be able to interpret these results, we will first base ourselves on the internal physical quantities and then consider the diode current of the cell because the diffusion capacity is proportional to the lifetime of the charge carriers and the diode current of the cell. Compared to the carrier lifetime, the increase in diffusion capacity with increasing temperature cannot be attributed to the carrier lifetime because their mathematical models are not related to an exponential variation. Compared to the diode current, the increase in diffusion capacity with increasing temperature can be attributed to it. To make the analysis, let us consider the diode current in open circuit and at the maximum power point, equation (9) changes if we replace the reverse saturation current by its expression given by:

$$I_d \simeq I_{cc}\{exp[K(V_d - V_{oc})/T]\} \tag{36}$$

Equation (36) shows that for open-circuit operation, the diode current is approximately equal to the short-circuit current because the exponential function becomes equal to unity. This implies that the diode behaves like a short circuit [22]. The diode current depends exponentially on the temperature. According to some authors, when the applied voltage is equal to Vmp, the diode enters an operating mode corresponding to the (knee region), which does not make it completely conductive [22]. This thus leads to an increase in the forward current of the diode. Since the diffusion capacitance is proportional to the diode current and inversely proportional to T, its increase is therefore due to the increase in the diode current when the temperature increases.

CONCLUSION

In this paper, we have expressed the transition capacitance as a function of the charge carrier lifetime, the cell diode current and the temperature. Considering the three bulk recombination mechanisms namely SRH, radiative and Auger recombination, we have made a representation of the cell capacitance for each of these recombination mechanisms as a function of temperature. These latter influence the open circuit voltage of the cell and this open circuit voltage is related to the cell diode current. We found that the diffusion capacitance related to the Auger recombination mechanism predominates, followed by that related to the radiative recombination mechanism and the lowest capacitance is that related to the SRH recombination mechanism

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