International Journal of Pure and Applied Physics
ISSN 0973-1776 Volume 5, Number 2 (2009), pp. 133–141

http://www.ripublication.com/ijpap.htm

Optimization of Recombination Parameters to Enhance Minority Carrier Lifetime

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Abstract

The study of recombination mechanism and its control parameters in multicrystalline silicon solar cell is very essential to achieve high cell efficiency for photovoltaic application. Recombination Statistics of various impurity elements in crystalline silicon solar cell is strongly determined by recombination parameters, i.e. the bulk carrier recombination lifetime τ_b, and the effective surface recombination velocity (SRV) at the rear of the cell. Study was performed using Shockley-Read-Hall (SRH) recombination and modeling is done by the simulation software PC1D to calculate output parameters of PVC. We have obtained larger recombination lifetime of 22.6 ms for an impurity (vanadium) at injection level of 4.498 x 10^{15} cm^{-3} for base resistivity 1 Ωcm & surface recombination velocity 10^3 cm s^{-1} and hence efficiency of PVC increased to the value 19.06% with respect to the chosen base model.

Keywords: Multicrystalline Silicon, SRH Recombination lifetime, Surface recombination velocity, Trap energy state, Capture cross section, Efficiency.

Introduction

High optical absorption and little carrier recombination are the two prerequisites for an efficient power conversion and the most relevant parameter for characterizing carrier recombination in semiconductors is the recombination lifetime. The equations describing recombination through impurity energy levels in the silicon bandgap were originally derived by Shockley and Read [1] and Hall [2]. In this paper, recombination within the bulk and at the surfaces of crystalline silicon has been studied to gain insight into the recombination mechanisms [3, 4]

Here a graphical study of injection level dependent bulk carrier lifetime of silicon using general mathematical formulation for recombination rates is reported and an attempt is made to show the dependence of recombination rates and minority carrier lifetimes on the injection level and trap energy level of some impurity elements with optimum base resistivity. Maximum recombination lifetime was obtained as 22.6 ms at injection level of 4.498 x 10^{15} cm^{-3} for base resistivity 1 Ωcm for an impurity element.

Recombination Statistics

The most relevant parameter for characterizing carrier recombination in semiconductors is the recombination lifetime, which, not surprisingly therefore, has powerful monitoring and predictive properties [3]. In practice, the total recombination lifetime is usually the result of a number of independent processes. This is referred to as the effective recombination lifetime, and may, for example, comprise mostly of Auger and Shockley-Read-Hall recombination lifetimes [3].

Auger recombination occurs when the energy released by the recombination of an electron-hole pair is carried off by a third free carrier. In lowly-injected p-type silicon, the third carrier is most likely to be a hole, and the corresponding recombination rate U_{Auger} is given by [4]:

$$U_{Au} = C_p \Delta n N_A^2$$

Where $C_p = 9.9\text{x}10^{-32}$ $cm^{-6}s^{-1}$ and $C_n = 2.8\text{x}10^{-31}$ $cm^{-6}s^{-1}$ [5]

The Auger lifetime for p-type silicon is

$$\tau_{Au} = \frac{1}{C_p N_A^2} \qquad \text{low injection}$$

$$\tau_{Au} = \frac{1}{(C_p + C_n)\Delta n^2} \text{ high injection}$$

$C_p + C_n = C_a = 1.66\text{x}10^{-30}$ $cm^{-6}s^{-1}$ [6].

Shockley-Read-Hall Recombination

For silicon (indirect semiconductor) devices it is sufficient to calculate the total recombination rate with Auger [5] and SRH only, neglecting the radiative component. The injection-level dependence of the SRH lifetime τ_{SRH} is a function of base resistivity, recombination center density N_t, defect energy level E_t and capture cross-sections, and for *p*-Si is given by [6,7,8]:

$$\tau_{SRH} = \frac{\tau_{n0}(N_A + p_1 + \Delta n) + \tau_{p0}(n_1 + \Delta n)}{N_A + \Delta n} \qquad (1)$$

Here, Δn = Δp is the excess carrier density, and τ_{n0} and τ_{p0} are the fundamental electron and hole lifetimes, which are related to the recombination center density, the thermal velocity and the capture cross-sections via $\tau_{n0}=1/(v_{th}\sigma_n N_t)$ and $\tau_{p0}=1/(v_{th}\sigma_p N_t)$ [9]. The values of electron and hole densities n_1 and p_1 can be calculated from defect energy level [10] when the Fermi energy coincides with the recombination center energy by:

$$p_1 = N_v \exp(\frac{E_c - E_G - E_t}{kT})$$

$$n_1 = N_C \exp(\frac{E_t - E_c}{kT})$$

Values for the effective densities of states at the conduction and valence band edges [11] are taken as N_C=2.86×10^{19} and N_V=1.02×$10^{19}$$cm^{-3}$.

Surface Recombination

Surface recombination is a special case of SRH recombination in which the localised states occur at the surface. Unlike bulk SRH centres however, these states do not usually occupy a single energy level, but rather form a set of states distributed across the band-gap. The large number of partially bonded silicon atoms give rise to many dangling bonds, and therefore a large density of defect levels are found within the bandgap near the semiconductor surface Surface recombination analysis is performed in terms of surface recombination velocities (SRV) instead of lifetimes, however, the principles are identical to bulk SRH recombination.

A detailed description of the analysis of the general case in which the SRV's have arbitrary magnitude and may be injection-level dependent can be found in Aberle[11]. In the simpler case of a sample with a constant bulk lifetime τb and a small constant SRV S that is the same on each surface, the effective lifetime is:

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_b} + \frac{2S}{W} \tag{2}$$

Here, S is recombination velocity and W is wafer thickness.

Dependence of SRH Recombination Lifetime on Various Parameters

From Eq. 1 it is evident that SRH recombination lifetime is dependent on base resistivity, defect concentration, trap energy level of impurities in BG with carrier injection level. However the recombination strength of a given impurity is determined by three parameters: the energy level and the capture cross sections for both electrons and holes [12]. In the SRH model the recombination rate will either be constant or increase with decreasing base resistivity, depending on the energy level and capture cross- sections of the dominant defect. An increase in recombination rate for a decrease of the resistivity of course counteracts any beneficial effects and shifts the optimum towards higher resistivity. High-efficiency laboratory cells use a base resistivity of 1 Ω cm [13].

Metallic impurities are common in photovoltaic grade crystalline silicon. They can sometimes limit the electronic properties of the material, and hence affect cell performance, for example, multicrystalline silicon there is significant quantities of Fe, Cr, Cu, Mo and Co [14,15] exist, even after the beneficial phosphorus gettering inherent in standard cell processing. These contaminants are known to have a damaging effect on the carrier lifetime, especially when occurring at interstitial or substitutional lattice sites, rather than as precipitates (although these are also detrimental). The purpose of this work is to explore how the recombination activity of these point-like impurities differs in n- and p type silicon. To do this, the Shockley-Read-Hall model is used in conjunction with values for the energy levels and capture cross sections from the literature.

The parameter (defect energy level and capture cross section for electron & hole) which controls the recombination strength of impurities is collected in the **Table 1** for Ti, V, Cr, Mo, Fe, Au and Zn [12]. Under low-injection ($\Delta n \ll N_A$) and high-injection ($\Delta n \gg N_A$) conditions, Eq. 1 can be simplified for a given recombination center for base resistivity of 1 Ω cm and defect densities of 10^{11} cm^{-3}. The graph shown in **Fig. 1** represents wide range of impurities.

The effects described in this paper are intrinsic properties of deep SRH centers with smaller cross-sections for majority carriers than minority carriers. Many other transition metal contaminants in silicon have capture cross-sections similar to Fe. For deep levels such as Fe, the low injection lifetime is limited by the capture of minority carriers, or electrons in p-Si. In high injection, however, the lifetime is controlled by both the electron and hole capture rates. If the hole capture cross section is much smaller, it will dominate the high injection lifetime, making it relatively large. Consequently, the lifetime will increase dramatically with injection level, as shown in **Fig. 1.** The highest effective lifetime (τ_{eff}), which incorporates all the bulk and surface recombination processes, previously reported for crystalline silicon appears to be 22 ms [16, 17].

Table 1 : Calculated bulk recombination lifetime at carrier injection level from graph in Fig.1.

Impurity Elements	Energy (eV)	SRH Recombination lifetime (from graph)	Carrier injection level (from graph)
Ti	$E_c - 0.27$	2.8×10^{-4}	2.94×10^{16}
	$E_v + 0.26$	6.1×10^{-3}	9.1×10^{15}
V	$E_v + 0.36$	2.26×10^{-2}	4.49×10^{15}
Cr	$E_c - 0.22$	7.33×10^{-6}	9.54×10^{16}
Mo	$E_v + 0.28$	5.8×10^{-4}	2.33×10^{16}
Fe	$E_v + 0.38$	3.1×10^{-3}	1.15×10^{16}
Au	$E_c - 0.55$	3.9×10^{-3}	1.099×10^{15}
Zn	$E_v + 0.33$	4.4×10^{-4}	1.45×10^{16}

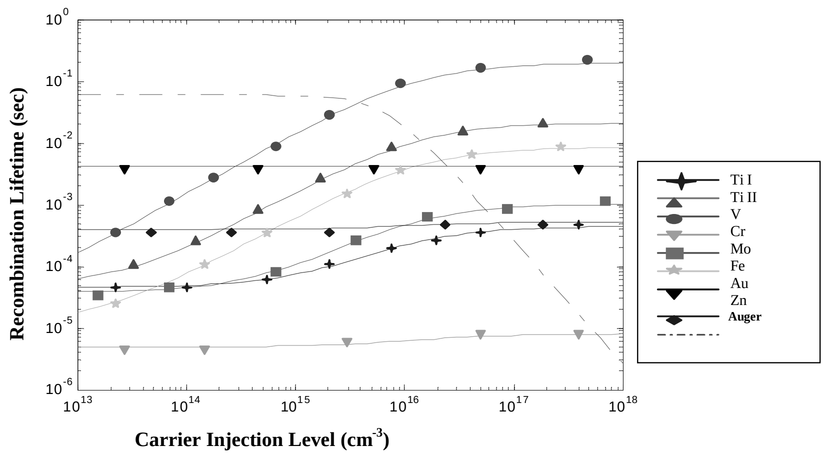

Figure 1: Recombination lifetime calculated as a function of carrier injection level for different impurities having asymmetric capture cross section and trap state in band gap.

From **Fig.** 1 it is clear that, out of a wide range of impurities maximum bulk carrier lifetime is obtained for vanadium which is 22.6 ms at an injection level 4.498 x 10^{15} cm^{-3}.

The effect of surface recombination is important when bulk recombination is low i.e., when minority carrier diffusion lengths are long. For electrons in p-type silicon, the surface recombination velocity at untreated surfaces, and at interface with metallic contacts, is in the range of 10^3 -10^5 cm s^{-1} [18] when the surface is passivated with a layer of silicon dioxide, the oxide shields minority carriers from defects at the surface and reduces S to less than 100 cm s^{-1} [19].

For modeling by PC1D first we have chosen a base model of output parameters P_{max} 2.575 watts, I_{sc} 5.780 amps and V_{oc} 610.9 mV. The other device parameters are given in the following table:-

Table 2: Parameters of the base model

Device Parameters	**Values**
Area	156.25 cm^2 [20]
Thickness	190 μm
Emitter contact	4.5 x10^{-3} Ω
Base contact	7.2 x10^{-3} Ω
Base doping P-type	1.5 x 10^{16} cm^{-3}
Emitter doping N-type	3.81 x 10^{20} cm^{-3}
Bulk recombination	10 μs
Surface recombination velocity	S_n = 4.5 x 10^5 cm/s S_p = 1000 cm/s
Primary light source Intensity Spectrum	 0.1 W cm^{-2} AM 1.5

The simulation results from PC1D for different impurities at different surface recombination velocities are given in table a, b, c & d.

Table a: Cell result for surface recombination velocity S 10^6 cm/s.

Impurity	**Max. Lifetime µs (Fig.1)**	**V_{oc} (mV)**	**I_{sc} (amp)**	**P_{max} (watt)**
Ti	280	619.7	5.927	2.702
	6100	620.4	5.94	2.712
V	22600	620.4	5.942	2.713
Cr	7.33	603.3	5.559	2.438
Mo	580	620.1	5.934	2.707
Fe	3100	620.4	5.93	2.712
Au	3900	620.4	5.93	2.712
Zn	440	620	5.932	2.706

Table b: Cell result for surface recombination velocity S 10^5 cm/s.

Impurity	**Max. Lifetime µs (Fig.1)**	**V_{oc} (mV)**	**I_{sc} (amp)**	**P_{max} (watt)**
Ti	280	625.7	6.053	2.791
	6100	626.6	6.067	2.803
V	22600	626.7	6.068	2.803
Cr	7.33	606.4	5.672	2.511
Mo	580	626.2	6.061	2.797
Fe	3100	626.6	6.0675	2.802
Au	3900	626.6	6.06	2.802
Zn	440	626.0	6.058	2.796

Table c: Cell result for surface recombination velocity S 10^4 cm/s.

Impurity	**Max. Lifetime µs (Fig.1)**	**V_{oc} (mV)**	**I_{sc} (amp)**	**P_{max} (watt)**
Ti	280	632.7	6.186	2.887
	6100	634.1	6.204	2.903
V	22600	634.6	6.205	2.903
Cr	7.33	608.3	5.74	2.554
Mo	580	633.4	6.196	2.895
Fe	3100	634.0	6.203	2.902
Au	3900	634.1	6.204	2.902
Zn	440	633.2	6.193	2.893

Table d: Cell result for surface recombination velocity S 10^3 cm/s.

Impurity	**Max. Lifetime µs (Fig.1)**	**V_{oc} (mV)**	**I_{sc} (amp)**	**P_{max} (watt)**
Ti	280	638.6	6.280	2.958
	6100	640.0	6.301	2.970
V	22600	640.6	6.302	2.979
Cr	7.33	609.1	5.773	2.574
Mo	580	639.6	6.291	2.969
Fe	3100	640.5	6.300	2.978
Au	3900	640.5	6.300	2.978
Zn	440	639.3	6.288	2.966

The graph shown in **Fig. 2** represent the variation of maximum output power of photovoltaic cell with carrier lifetime at constant surface recombination velocity.

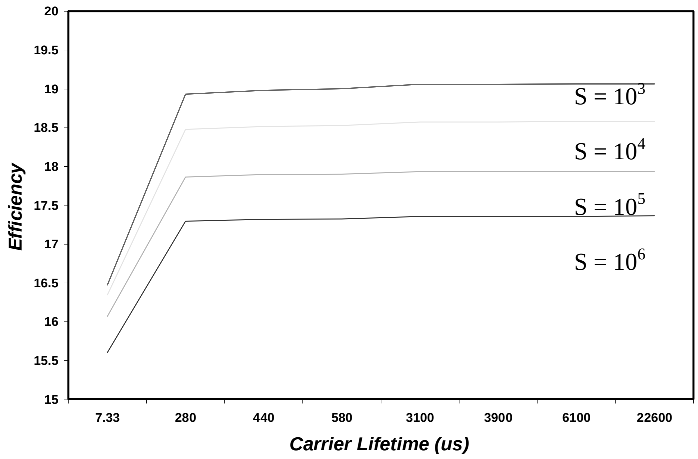

Figure 2: Maximum output power calculated with PC1D simulation software for different surface recombination velocity range 10^3- 10^6 cm s^{-1}.

Table e: Comparison of output parameter of base model and with impurity.

	P_{max} watt	I_{sc} amp	V_{oc} mV	Efficiency
Base model	2.575	5.780	610.9	16.48
With impurity	2.979	6.302	640.6	19.06

In this paper we report calculated maximum recombination lifetime is 22.6 ms (as shown in **Fig. 1**) at injection level 4.498 x 10^{15} cm^{-3} for base resistivity 1 Ωcm for V impurity. By modeling with PC1D it was found that with recombination velocity 10^3 cm s^{-1} (**Fig. 2**), maximum output power of the base model is increased by 15.69% (2.979 watt), I_{SC} by 9.03% (6.302 amp) V_{OC} by 4.86% (640.6 mV) and hence efficiency of PVC is 19.06%

Conclusion

Theoretical analysis of SRH recombination process was performed to study the impact of recombination strength parameter of different impurities on the bulk minority carrier lifetime. As shown in **Fig. 1**, we have obtained larger recombination lifetime of 22.6 ms for an impurity (vanadium) at injection level of 4.498 x 10^{15} cm-3 for base resistivity 1 Ωcm. Therefore it is also concluded here that the presence of vanadium impurity at reported injection level improves the recombination lifetime for silicon photovoltaic cell. It is also confirmed by modeling with PC1D that with recombination velocity 10^3 cm s^{-1} (**Fig. 2**), maximum output power of the base model is increased by 15.69% (2.979 watt), I_{SC} by 9.03% (6.302 amp) V_{OC} by 4.86% (640.6 mV) and hence efficiency of PVC is 19.06%.

For the development of vanadium doped thin film silicon photovoltaic cell sputtering process may be used. Vanadium doped silicon target may be used as sputtering material. The deposition of p–i–n sequence for the development of photovoltaic cell may then be done in the presence of diborane, argon and phosphine gases. Another method to develop this is by ion implantation, samples may be implanted with vanadium ions of high energy after they might be annealed in an N_2 atmosphere. Surface of silicon is also passivated by SiO_2 to reduce dagling bonds. Other parameters, e.g. base resistivity are dependent on dopant density which is controlled by deposition parameters within the vacuum chamber during the process.

Acknowledgement

One of the authors (SG) is grateful to UGC for providing financial help in the form of Junior Research Fellowship.

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