Determining the charge states and capture mechanisms of defects in silicon through accurate recombination analyses: A review

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A R T I C L E   I N F O

A B S T R A C T

A key strategy for further reducing the cost of solar electricity is through the development and production of very-high efficiency silicon solar cells (> 25%). The challenge in achieving this goal lies in overcoming limitations imposed by the electronic quality of the silicon wafers themselves. To overcome this challenge, it is necessary to understand the defects limiting the electronic quality of silicon wafers. In this review, we critically assess recent progress in understanding the recombination properties of defects in silicon and provide a nuanced and detailed picture of what constitutes accurate recombination parameters for such defects. Here we show that lifetime spectroscopy and capacitance spectroscopy analyses contain significant limitations, namely disregard of multivalent defect recombination in lifetime spectroscopy analyses, lack of exciton capture mechanisms in some deep level capacitance spectroscopy measurements and limitations in using detailed balance to extract capture parameters in capacitance spectroscopy. We demonstrate that combining multiple analyses leads to a more robust determination of recombination parameters. We use such combined analyses to review recombination pathways and parameters for technology relevant defects with the goal of enabling robust simulation of the lifetime in silicon for solar cell applications.

1. Introduction

The original Westinghouse study reported the normalized efficiency of silicon solar cells as a function of impurity concentration for a wide range of transition metals [1]. Since then, device architectures have dramatically improved and evidently the impact of impurities is felt at even lower concentrations, as shown by the recent studies of Riepe et al., Coletti et al., and Schmidt et al. [2–4]. The work of Graff and more recently Peaker et al. are excellent reviews of the energy levels and majority capture cross sections of metallic point defects in silicon [5,6]. For solar cell modelling and defect identification, accurate data on minority capture cross sections of defects are also required to allow modelling of their impacts on silicon solar cells, as well as a more nuanced approach to modelling the impact of defects, taking into account the limitations of the current literature. Three major sources of uncertainties currently exist as follows:

1) Temperature and Injection Dependent Lifetime Spectroscopy (TIDL [7] S) analyses are sometimes conducted using two or more independent energy levels (as is the case for Ti, Co and sometimes for Zn and Au) whereas they should be conducted using two or more dependent energy levels using the Sah and Shockley formalism [8].

2) Deep Level Transient Spectroscopy (DLTS) measurements are conducted with injection of only one type of carrier. As such, capture mechanisms operating via exciton enhanced Auger phenomena cannot take place, as exciton, are not present in significant concentrations when only one carrier is injected. This means the capture mechanism measured by DLTS may not be representative of the real capture mechanism in a device with both minority and majority carrier injection.

3) Determination of capture cross sections from DLTS emission data using detailed balance can yield capture cross sections with values orders magnitude higher or smaller than the actual capture cross section.

In this review, we apply the above three considerations to critically assess existing experimental data of defect recombination activity. We bring together a consistent set of values extracted from the literature for the modelling of point and extended defects in silicon. When necessary, the reported values are also corrected for different assumed values of the thermal velocities. We also review the temperature dependence of the majority and minority capture cross sections as well as more complex parameterizations of defect recombination such as via thermal donors, metal precipitates and dislocations.

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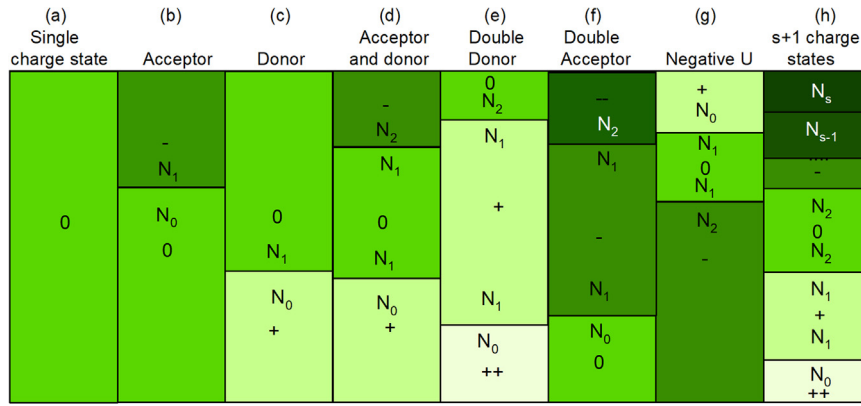| (a) Single charge state	(b) Acceptor	(c) Donor	(d) Acceptor and donor	(e) Double Donor	(f) Double Acceptor	(g) Negative U	(h) s+1 charge states
				$\begin{matrix}0\\N_2\end{matrix}$		$\begin{matrix}+\\N_0\end{matrix}$	N_s
	$\begin{matrix}-\\N_1\end{matrix}$		$\begin{matrix}-\\N_2\end{matrix}$	N_1	$\begin{matrix}--\\N_2\end{matrix}$	N_1	N_{s-1}
			N_1		N_1	$\begin{matrix}0\\N_1\end{matrix}$	---
0	$\begin{matrix}N_0\\0\end{matrix}$	$\begin{matrix}0\\N_1\end{matrix}$	$\begin{matrix}0\\N_1\end{matrix}$	$+$		N_2	$\begin{matrix}N_2\\0\\N_2\end{matrix}$
		N_0	N_0	N_1	$\begin{matrix}-\\N_1\end{matrix}$	$-$	$\begin{matrix}N_1\\+\\N_1\end{matrix}$
		$+$	$+$	$\begin{matrix}N_0\\++\end{matrix}$	$\begin{matrix}N_0\\0\end{matrix}$		$\begin{matrix}N_0\\++\end{matrix}$

Fig. 1. Possible defect charge states and energy level associated with transitions between charge states.

2. Background

2.1. Charge states, energy levels and occupation fraction

A defect with a single charge state (Fig. 1a) does not allow recombination and trapping events since capture or emission of carriers are not allowed. This is the case of some light elements in silicon.

DLTS and Electron Paramagnetic Resonance (EPR) studies indicate that defects such as interstitial chromium, molybdenum, tungsten and iron can have two charge states (a single level within the bandgap). For a defect with two charge states (Fig. 1b and c) in non-equilibrium steady state both charge states remain at constant concentrations. On average, from a positive charge-state for a + /0 defect the following events can happen:

1) capture an electron and then capture a hole: $D^+ + e^- \rightarrow D^0$ followed by $D^0 + h^+ \rightarrow D^+$
2) capture an electron and then emit an electron: $D^+ + e^- \rightarrow D^0$ followed by $D^0 \rightarrow D^+ + e^-$
3) emit a hole and then capture a hole: $D^+ \rightarrow D^0 + h^+$ followed by $D^0 + h^+ \rightarrow D^+$

Thus, for a defect with two charge states, there is a single possible recombination event with:

1) capture an electron and then capture a hole: $D^+ + e^- \rightarrow D^0$ followed by $D^0 + h^+ \rightarrow D^+$

Modelling the impact of single level defects on the minority carrier lifetime can be simply performed using the full [9,10] or the simplified SRH formalism [11] provided that both capture mechanisms involve a single carrier (eg they are not defect-related Auger capture processes [12–16]).

Most defects are multivalent defects including titanium, vanadium, manganese, cobalt, nickel, palladium, platinum, cobalt, gold and zinc [6]. While often modelled with two or more independent levels in the IDLS and TIDLS literature, such defects should in principle be modelled with dependent levels according to the formalism derived by Sah and Shockley and others [8,17]. In contrast to assuming independent levels, the relative population of dependent levels depends on the position of the fermi level, and as such on the doping and injection level. Fig. 1 illustrates different types of defects with more than two charge states .

For a defect with three charge states (two levels, Fig. 1d, e, f and g) in non-equilibrium steady state, again all charge states remain at constant concentrations. On average, from a positive charge-state for a + + / + /0 defect we can:

1) capture an electron and then capture a hole: $D^+ + e^- \rightarrow D^0$ followed by $D^0 + h^+ \rightarrow D^+$
2) capture an electron and then emit an electron: $D^+ + e^- \rightarrow D^0$ followed by $D^0 \rightarrow D^+ + e^-$

3) emit a hole and then capture a hole: $D^+ \rightarrow D^0 + h^+$ followed by $D^0 + h^+ \rightarrow D^+$
4) capture a hole and then capture an electron: $D^+ + h^+ \rightarrow D^{++}$ followed by $D^{++} + e^- \rightarrow D^+$
5) capture a hole and then emit a hole: $D^+ + h^+ \rightarrow D^{++}$ followed by $D^{++} \rightarrow D^+ + h^+$
6) emit an electron and then capture an electron: $D^+ \rightarrow D^{++} + e^-$ followed by $D^{++} + e^- \rightarrow D^+$

Thus, for a defect with three charge states there are, two possible recombination events with:

1) capture an electron and then capture a hole: $D^+ + e^- \rightarrow D^0$ followed by $D^0 + h^+ \rightarrow D^+$

4) capture a hole and then capture an electron: $D^+ + h^+ \rightarrow D^{++}$ followed by $D^{++} + e^- \rightarrow D^+$

Essentially, a three charge states defect (or two-level defects) allows for two recombination pathways instead of one. As the injection level changes, the relative strength of these two recombination pathway changes reflecting the change in the different charge state density. Capacitance transient spectroscopy typically sees process 2, 3, 5 and 6 and thus can clearly identify multivalent defects provided the emission rate are different. Lifetime spectroscopy only sees recombination processes 1 and 4 lumped together and on its own cannot distinguish between multivalent and monovalent levels. However, a combination of both techniques allows such identification.

Note that the defect energy level represents the energy associated with a charge state transition, the intrinsic properties of individual defects being their charge states (the defect energy level is not the energy of a defect, in fact such quantity does not exist and does not make sense).

For a defect with s + 1 charge states (s levels, Fig. 1h) in non-equilibrium steady state, again all charge states remain at constant concentrations. The sum of the occupation of the charge states of the defect center is equal to:

$$N_0 + N_1 + ... + N_s = N_t \tag{1}$$

where the index represents the number of electrons on the defect center. The occupation ratio α for an energy level $E(1/2)$ represents the occupation fraction of two consecutive charge states [18]:

$$\alpha_{1/2} = \frac{N_0}{N_1} = \frac{k_{1/2}n_{1/2} + p}{k_{1/2}n + p_{1/2}} \tag{2}$$

$$\alpha_{3/2} = \frac{N_1}{N_2} = \frac{k_{3/2}n_{3/2} + p}{k_{3/2}n + p_{3/2}} \tag{3}$$

More generally:

$$\alpha_{(2s-1)/2} = \frac{N_{s-1}}{N_s} = \frac{k_{(2s-1)/2}n_{(2s-1)/2} + p}{k_{(2s-1)/2}n + p_{(2s-1)/2}} \tag{4}$$

where $n_{(2s-1)/2}$ and $p_{(2s-1)/2}$ represent the ratio of the electron and hole