



Minority carrier lifetime in silicon photovoltaics: The effect of oxygen precipitation [☆]



J.D. Murphy ^{a,*}, R.E. McGuire ^b, K. Bothe ^c, V.V. Voronkov ^d, R.J. Falster ^d

^a University of Warwick, WMG, International Manufacturing Centre, Coventry, CV4 7AL, UK

^b University of Oxford, Department of Materials, Parks Road, Oxford, OX1 3PH, UK

^c Institut für Solarenergieforschung Hameln/Emmerthal, Am Ohrberg 1, 31860 Emmerthal, Germany

^d SunEdison, viale Gherzi 31, 28100 Novara, Italy

ARTICLE INFO

Available online 15 July 2013

Keywords:

Silicon
Photovoltaic
Oxide precipitate
Lifetime
Recombination

ABSTRACT

Single-crystal Czochralski silicon used for photovoltaics is typically supersaturated with interstitial oxygen at temperatures just below the melting point. Oxide precipitates therefore can form during ingot cooling and cell processing, and nucleation sites are typically vacancy-rich regions. Oxygen precipitation gives rise to recombination centres, which can reduce cell efficiencies by as much as 4% (absolute). We have studied the recombination behaviour in p-type and n-type monocrystalline silicon with a range of doping levels intentionally processed to contain oxide precipitates with a range of densities, sizes and morphologies. We analyse injection-dependent minority carrier lifetime measurements to give a full parameterisation of the recombination activity in terms of Shockley–Read–Hall statistics. We intentionally contaminate specimens with iron, and show recombination activity arises from iron segregated to oxide precipitates and surrounding defects. We find that phosphorus diffusion gettering reduces the recombination activity of the precipitates to some extent. We also find that bulk iron is preferentially gettering to the phosphorus diffused layer rather than to oxide precipitates.

© 2013 The Authors. Published by Elsevier B.V. All rights reserved.

1. Introduction

At present the majority of solar cells are made from bulk crystalline silicon. Minority carrier lifetime is the main parameter used to assess the quality of wafers from which cells are produced. For a given generation rate, the minority carrier lifetime is largely determined by recombination processes. Some recombination is intrinsic (band-to-band and Auger), while other is determined by defects in the bulk or at surfaces. It is necessary to understand which defects are typically present in solar wafers before processing, and what effect processing has on those defects. Moreover, it is important to understand the mechanism by which the relevant defects give rise to recombination, as well as to quantify their recombination activity.

Monocrystalline Czochralski silicon (Cz-Si) typically contains $\sim 10^{18} \text{ cm}^{-3}$ of interstitial oxygen, which is mainly incorporated from the silica crucible which contains the melt. This level of oxygen is supersaturated below $\sim 1200 \text{ }^\circ\text{C}$, so the equilibrium state

is reached by the formation of SiO_2 particles (oxide precipitates) [1]. The morphology of such particles changes as they grow, from unstrained particles initially, to strained precipitates, which are eventually surrounded by dislocations and sometimes stacking faults [2,3]. The first stage in precipitation is nucleation, and the rate of this is strongly enhanced by the presence of crystal defects. In modern Cz-Si used for integrated circuits the grown-in defect concentration is insufficient for oxygen precipitation to occur unintentionally. However, even in the highest quality Cz-Si, oxide precipitates can nucleate upon prolonged annealing at $650 \text{ }^\circ\text{C}$ to $850 \text{ }^\circ\text{C}$ [1,4]. In silicon for microelectronics thermal processes are often used to force oxygen precipitation to provide gettering centres for harmful metallic contaminants [5,6]. For photovoltaics, the Cz-Si wafers used are often of lower crystal quality, and several studies have found concentric rings of oxide precipitates in wafers or cells after growth or processing [7–10]. It is also noted that oxygen precipitation occurs at dislocations in multicrystalline silicon (mc-Si) during ingot cooling [11–13].

The undesirable precipitation of oxygen in Cz-Si is not a new problem, having been widely studied (and essentially solved) in Cz-Si for integrated circuits. Oxide precipitates are known to form in vacancy-rich regions [14]. The formation of such regions can be essentially eliminated by carefully controlling the so-called v/G criterion (where v is the crystal growth rate and G is the near-interface temperature gradient) [15]. Although it is possible to

[☆]This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.

* Corresponding author. Tel.: +44 24 7657 5378.

E-mail address: john.d.murphy@warwick.ac.uk (J.D. Murphy).

reduce intrinsic point defect concentrations to levels which are essentially negligible, doing so requires slow growth rates and these are not always compatible with the commercial constraints of the silicon photovoltaics industry. Thus, although the problem can in principle be eliminated, the fact is many commercial Cz-Si solar wafers do contain vacancy-rich regions in which oxide precipitates form [7–9].

Oxide precipitates have been linked to a substantial detrimental impact on conversion efficiencies in silicon solar cells [7,16]. A study by Haunschild et al. associated oxide precipitates with a 4% (absolute) efficiency reduction [7]. Interestingly, they found that the recombination activity to be strongly affected by a 10 s anneal at 800 °C. This, and earlier studies on iron-contaminated samples [17,18], suggests that impurities might play a role in the recombination mechanism.

The aim of this paper is to answer some open questions regarding the effects of oxygen precipitation in silicon photovoltaics. These include:

- Can the impact of oxide precipitates on minority carrier lifetime be systematically quantified?
- What is the mechanism of recombination at oxide precipitates? Do impurities play a role?
- What happens to the recombination activity of oxide precipitates after phosphorus diffusion gettering used in solar cell processing? Which is the more effective gettering system for bulk iron: oxide precipitates or phosphorus diffusion?

This paper builds upon our previously published work in this area [19–23] by assimilating the key ideas in one article, adding new experimental data, and focussing specifically on photovoltaics. After presenting a general methodology for parameterising injection-dependent minority carrier lifetime in semiconductors, we apply this methodology to determine the recombination parameters of oxide precipitates in silicon.

2. Parameterisation of carrier lifetimes

2.1. Linear formulation of Shockley–Read–Hall statistics

Shockley–Read–Hall (SRH) statistics [24,25] are frequently used to quantify the bulk minority carrier lifetime in semiconductor materials. SRH statistics enable the recombination activity of states associated with point-like defects to be quantified by using just three parameters: the energy position of the defect in the bandgap (E_T), its capture coefficient for electrons (α_n) and its capture coefficient for holes (α_p). (Alternatively capture cross-sections for electrons (σ_n) and holes (σ_p) can be used instead of capture coefficients. The capture coefficient is the product of the capture cross-section and the thermal velocity). Capture coefficients (or cross-sections) are temperature-dependent empirically-determined parameters which quantify the propensity of the states to capture carriers. In some circumstances the use of simple SRH statistics is an oversimplification (see for example [26]), but for the most part the SRH approach is invaluable.

The most commonly used formation of SRH statistics describes the minority carrier lifetime in terms of the excess concentration of minority carriers (Δn for electrons; Δp for holes) (see Ref. [27] for example). In our work we use a different form which we have derived in an earlier paper [21]. We express the minority carrier lifetime as a *linear* function of the ratio of the total carrier concentrations. In p-type material, for example, the electron lifetime (τ_n) is expressed as a linear function of the ratio of the total electron concentration ($n=n_0+\Delta n$) to the total hole concentration

($p=p_0+\Delta p$) according to:

$$\tau_n = \frac{1}{\alpha_n N} \left[1 + \frac{Qn_1}{p_0} + \frac{p_1}{p_0} + X \left(Q - \frac{Qn_1}{p_0} - \frac{p_1}{p_0} \right) \right] \quad (1)$$

where $X=(n/p)=(1/p_0+n)$, where p_0 is the equilibrium hole concentration, n_0 is the equilibrium electron concentration, $Q=(\alpha_n/\alpha_p)=(\sigma_n/\sigma_p)$, and N is the concentration of the defect. The so-called SRH densities for electrons (n_1) and holes (p_1) are given by:

$$n_1 = N_C \exp\left(-\frac{E_C-E_T}{kT}\right) \quad (2)$$

$$p_1 = N_V \exp\left(-\frac{E_T-E_V}{kT}\right) \quad (3)$$

where E_C and E_V are the energies of the conduction band and valence band edge, respectively, and N_C and N_V are the densities of states in the conduction band and valence band, respectively. An equation analogous to Eq. (1) for the hole lifetime (τ_p) in n-type material can be derived as [21]:

$$\tau_p = \frac{1}{\alpha_p N} \left[1 + \frac{n_1}{n_0} + \frac{p_1}{n_0 Q} + Y \left(\frac{1}{Q} - \frac{n_1}{n_0} - \frac{p_1}{Qn_0} \right) \right] \quad (4)$$

where $Y=(p/n)=(p/n_0+p)$.

2.2. Extracting defect parameters from injection-dependent lifetime data

The linear formulation of SRH statistics provides an elegant route to parameterise recombination due to specific defects. The key feature of Eqs. (1) and (4) is that all the injection-dependence of the minority carrier lifetime is consumed into X or Y . All other terms in the Equations depend upon the properties of the defect, material or temperature. In the p-type case, information on the key SRH parameters can be extracted by taking the derivative of Eq. (1) with respect to X and dividing this by the high injection limit of lifetime (τ_n as $X \rightarrow 1$), which gives:

$$\frac{d\tau_n}{dX} / \tau_{nX \rightarrow 1} = \frac{Q}{1+Q} - \frac{1}{p_0} \left(\frac{Qn_1+p_1}{1+Q} \right) \quad (5)$$

By studying material with different values of p_0 , Eq. (5) can be used to deduce values of Q and Qn_1+p_1 , and an example to show this is given in Section 2.3 below. Information can also be gained from inspecting the low injection limit of Eq. (1) (τ_n as $X \rightarrow 0$), which gives:

$$\tau_{nX \rightarrow 0} = \frac{1}{\alpha_n N} \left[1 + \frac{1}{p_0} (Qn_1+p_1) \right] \quad (6)$$

If Qn_1+p_1 is known it is thus possible to use Eq. (6) to extract $\alpha_n N$, which is useful as, for constant α_n , it is proportional to the state density.

It is important to note that from single temperature injection-dependent lifetime measurements alone it is not possible to extract unique values for α_n , α_p , or E_T . Such measurements on samples with different doping levels enable the deduction of $Q=(\alpha_n/\alpha_p)$ and Qn_1+p_1 (which depends upon E_T via Eqs. (2) and (3)). To isolate separate values of α_n and α_p it is necessary to determine the state density, N , by another technique. Temperature-dependent lifetime measurements can be used to determine whether Qn_1 or p_1 dominates, and hence can allow E_T to be uniquely found.

In principle the linear SRH formulation is valid at all injection levels. However, it is important to note that care must be taken when using the approach over a wide range of injection levels. Under typical conditions, $X=0.01$ corresponds to $\Delta n \approx 0.011p_0$. Thus processes which manifest themselves at low injection, such as

Download English Version:

<https://daneshyari.com/en/article/10248766>

Download Persian Version:

<https://daneshyari.com/article/10248766>

[Daneshyari.com](https://daneshyari.com)