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Lifetime spectroscopy and hydrogenation of chromium in n- and p-type Cz silicon

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Abstract

The defect parameters of isolated Cr_i and chromium-boron (CrB) pairs are reassessed by conducting lifetime spectroscopy on both n- and p-type, Cr-doped silicon samples with different doping levels, and fitting the lifetimes with the Shockley-Read-Hall (SRH) model. The uncertainty ranges of the parameters are significantly tightened through a combined analysis of the two defects with the lifetime data measured on both n- and p-type samples. Both the experimental data and the modelling results suggest that Cr_i has a greater negative impact on lifetimes in p-Si than n-Si. The possible hydrogen passivation of Cr_i in n- and p-Si is then investigated both through charge state modelling and experimentally. A general occupancy factor is applied to predict the charge states of both monovalent Cr_i and multivalent H as a function of temperature and injection level. The modelling results suggest that above 800K, both the injection and the doping become unimportant as silicon becomes intrinsic. However, despite some positive hints, the experimental evidence for hydrogenation of Cr_i is inconclusive at this stage.

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Keywords: Lifetime spectroscopy; hydrogenation; chromium; silicon.

1. Introduction

Chromium is detrimental to silicon devices, yet it is a relatively common contaminant. [1] Previous studies have shown the concentration of chromium in photovoltaic-grade multicrystalline silicon wafers can be in the $10^{12} \sim 10^{13} \text{ cm}^{-3}$ range. [2, 3] The defect parameters of isolated Cr_i and CrB pairs (only in p-Si) are important in the detection[4]

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and imaging [5] of Cr_i in silicon. However, those parameters, especially the capture cross sections, vary across orders of magnitudes in the literature. [4-8]

Injection-Dependent Lifetime Spectroscopy (IDLS) offers a convenient method to determine the defect parameters, by fitting the injection-dependent lifetime with the Shockley-Read-Hall (SRH) model. To allow unambiguous measurement of the defect parameters, a method is to simultaneously fit the injection-dependent lifetime measured on several samples with different doping levels.[9, 10] In this work, we use this method to determine the defect parameters with several n- and p-type samples. The results also allow a direct experimental comparison of the recombination activity of chromium in both n- and p-type silicon.

Hydrogen can bind with and passivate a wide range of defects in crystalline silicon, which can often improve the electronic quality of the material.[11] The hydrogen passivation of Cr in silicon has not been investigated before. In this work the possible hydrogen passivation of Cr_i in n- and p-type Si is investigated both through charge state modelling and experimentally.

2. Lifetime spectroscopy

Several samples selected at different solidified fractions g of Cr-doped and control n- and p-type ingots were chosen for this study, which is described in more details elsewhere [12]. The doping levels are within the range of $0.9\sim 1.5\times 10^{16}\text{cm}^{-3}$. The injection-dependent lifetimes were measured using the Quasi-Steady State PhotoConductance method (QSSPC). For the p-type samples, we measure the lifetime at both the fully associated state and after quenching, where the fraction of isolated Cr_i is estimated to be above 85% [13].

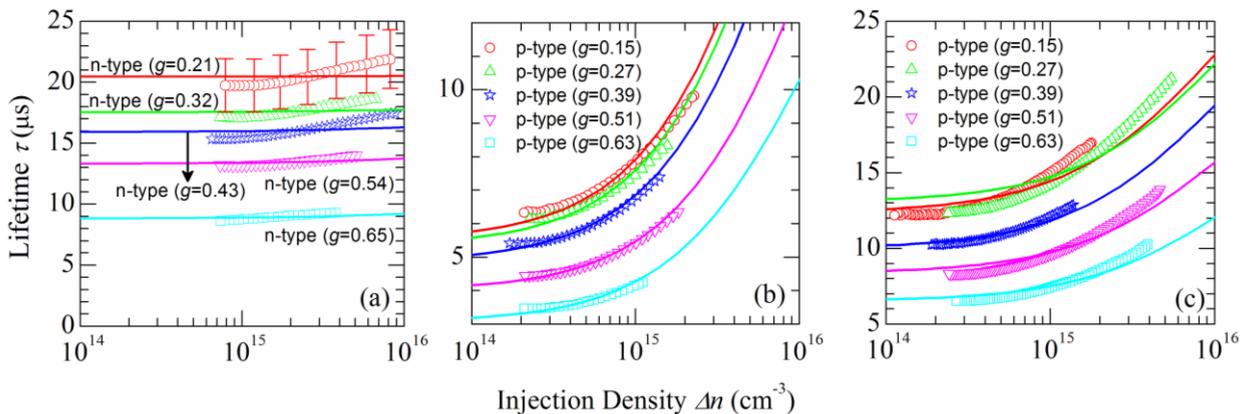


Fig. 1. Lifetime measurements (symbols) and SRH fits (solid lines) for (a) n-type samples, (b) p-type samples in the fully associated state, and (c) p-type samples after quenching. The 11% relative error is shown for sample n-type ($g=0.21$). Defect parameters found in this work are used in the fitting.

Figure 1 (a) shows the lifetime measurements for the n-type Cr-doped samples. We simultaneously fit this group of lifetime data with the SRH model and obtain the defect parameters for Cr_i . When taking the 11% relative error [14] of the measured lifetime data into account, the fitting gives the uncertainty ranges of the defect parameters. Similarly, we obtain the uncertainty ranges of the defect parameters of CrB pairs using the lifetime measured on the p-type Cr-doped samples in the fully associated state (Figure 1 (b)). In addition, we found that fitting the third group of lifetime data, which are measured on the p-type samples after quenching (Figure 1(c)), helps tighten the uncertainty ranges of the two defects significantly. As this combines the lifetime measured on both n- and p-type samples, we regard the values generated by this fitting as the most accurate. The results are listed in Table 1, in comparison with the literature [4-8].

Table 1. Defect parameter of Cr_i and CrB pairs found in this work, in comparison with the literature.

Cr _i	E _c -E _i (eV)	σ _n (cm ²)	σ _p (cm ²)	k
Literature	0.22~0.24	(0.73, 25)×10 ⁻¹⁴	(0.91, 12.5)×10 ⁻¹⁴	2~5
This work	0.24	2.4 (-1.0, +0.3)×10 ⁻¹⁴	0.8 (-0.3, +0.2)×10 ⁻¹⁴	3.2 (-0.6, +0)

CrB	E _c -E _v (eV)	σ _n (cm ²)	σ _p (cm ²)	k
Literature	0.27~0.29	(0.5, 15)×10 ⁻¹⁴	(0.15, 8.4)×10 ⁻¹⁴	0.5~60
This work	0.27	3.8 (-1.6, +0.5)×10 ⁻¹⁴	0.7(-0.3,+0.6)×10 ⁻¹⁴	5.8 (-3.4, +0.6)

Our samples allow a direct comparison of the recombination behaviour of Cr_i in n- and p-Si. Shown by both modelling and experiments, CrB pairs are always more recombination active than isolated Cr_i in p-Si, and isolated Cr_i is always more recombination active in p-Si than in n-Si with the same doping level. We can therefore conclude that Cr has a greater negative impact on carrier lifetimes in p-Si than n-Si.

3. Hydrogenation of chromium

3.1. Charge states of monatomic hydrogen and Cr_i

As Cr_i introduces a donor level (0/+) in the band gap of silicon, the Cr_i atoms should be mostly hydrogenated by the negative hydrogen H⁻ through the reaction Cr_i⁺+H⁻→CrH. Thus the prediction of the charge states of monatomic hydrogen and Cr_i is important for understanding the hydrogenation reaction. In this work we predict the charge states of Cr_i and H applying a general charge occupancy factor for the defects. We have demonstrated that this occupancy factor can be applied to predicting the charge states of both monovalent defects such as Cr_i and multivalent defects like monatomic hydrogen, as a function of both temperature and injection level in another work. [15] Figure 2 shows the results of $f(\text{H}^-):f(\text{Cr}_i^+)$ in both n- and p-Si, which determines the reaction rate at a fixed temperature if the concentration of monatomic hydrogen and isolated Cr_i are regarded as invariant, according to the law of mass action. From the results we can see that at the lower temperature range, carrier injection has a significant effect on $f(\text{H}^-):f(\text{Cr}_i^+)$; however, at temperatures above 800K, both carrier injection and the doping become unimportant as silicon becomes intrinsic.

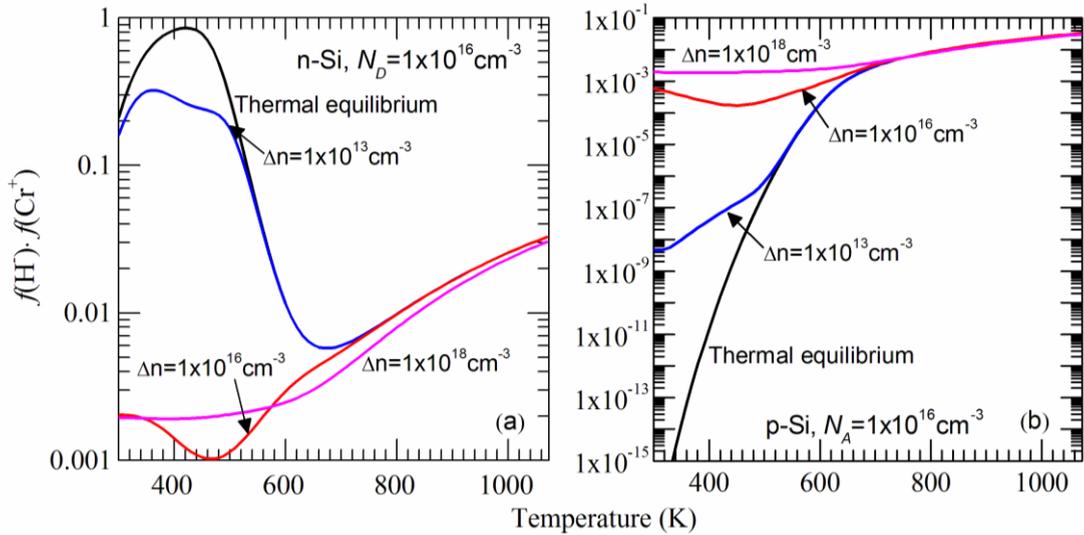


Fig. 2. The product of the fractions of H⁻ and Cr⁺ as a function of temperature at injection levels of $1 \times 10^{13} \text{ cm}^{-3}$, $1 \times 10^{16} \text{ cm}^{-3}$, and $1 \times 10^{18} \text{ cm}^{-3}$ in (a) n- and (b) p-Si with a doping level of $1 \times 10^{16} \text{ cm}^{-3}$.

3.2. Experiments on hydrogenation of Cr_i

One n-type sample and three p-type samples are chosen for the initial hydrogenation experiments, as listed in the first four rows in Table 2. The samples were annealed with a silicon nitride layer on the surface, which serves as a source of hydrogen upon annealing. After annealing, we stripped the nitride layer off and put a new nitride layer on the samples for characterisation. The remaining fraction of Cr_i in the n-type sample is determined by the ratio of the effective lifetime before and after annealing. The [Cr_i] in the p-type samples is determined by the CrB pairing reaction via $[\text{Cr}_i] = C(1/\tau_{\text{assoc}} - 1/\tau_{\text{diss}})$ [4]. Table 2 lists the preliminary experimental details and results. These experiments were performed without additional carrier injection during the hydrogenation step.

Table 2. Preliminary experimental details and results for the hydrogenation study

Samples	Initial [Cr _i] (cm ⁻³)	Temperature (°C)	Annealing time (min)	Annealing gas	Coating	Remaining [Cr _i] (%)
n-type (g=0.54)	1.1×10^{12}	600	30	N ₂	SiN _x	41
p-type (g=0.27)	4.9×10^{11}	750	15	N ₂	SiN _x	35
p-type (g=0.39)	5.3×10^{11}	600	40	N ₂	SiN _x	48
p-type (g=0.63)	8.3×10^{11}	900	30	N ₂	SiN _x	1
p-type (g=0.15)	4.7×10^{11}	900	30	O ₂	bare	5
n-type (g=0.21)	7.6×10^{11}	600	30	O ₂	bare	58
n-type (g=0.32)	8.7×10^{11}	600	30	N ₂	bare	40

A significant decrease of [Cr_i] after annealing is observed for all the samples. However, to check that the decrease is caused by hydrogenation, rather than by some other Cr-loss mechanism, three control samples were annealed without nitride layer in O₂ or N₂ at 600°C or 900°C for 30min, which ensures no hydrogen source during annealing, as listed in the last three rows in Table 2. However, they show similar [Cr_i] reductions with the experimental samples. This indicates that the observed decrease of [Cr_i] may not be caused by hydrogenation, but by some segregation gettering mechanism, possibly at the oxidised surfaces. This was not expected, since the precipitation of metals at surfaces would normally occur via a relaxation gettering mechanism, which should not occur at 900°C as Cr_i is not super-saturated [1]. Further studies should enable us to clarify these results.

4. Conclusions

Defect parameters of Cr_i and CrB pairs have been determined by lifetime spectroscopy of several n- and p-type Cr-doped samples. With a combined analysis of the two defects with the lifetime data measured on both n- and p-type samples, the uncertainty ranges of the defect parameters are significantly tightened in comparison with the literature. Through an experimental comparison of n- and p-type samples as well as modelling, we conclude that Cr has a greater negative impact on carrier lifetimes in p-type silicon than n-type silicon with similar doping levels.

The possible hydrogen passivation of Cr_i in n- and p-Si is investigated both through charge state modelling and experimentally. The charge states of Cr_i and monatomic H as a function of both temperature and injection level are predicted, applying a general occupancy factor. The modelling results show that at the lower temperature range, carrier injection has a significant effect on the charge distributions; however, at temperatures above 800K, both carrier injection and the doping become unimportant as silicon becomes intrinsic. However, despite some positive hints, the experimental evidence for hydrogenation of Cr_i is inconclusive at this stage.

Acknowledgements

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