Phys. Status Solidi RRL **7**, No. 9, 616–618 (2013) / **DOI** 10.1002/pssr.201308053

rrl solar

Thermal deactivation of lifetime-limiting grown-in point defects in n-type Czochralski silicon wafers

F. E. Rougieux*, N. E. Grant, and D. Macdonald

Research School of Engineering, College of Engineering and Computer Science, The Australian National University, Canberra ACT 0200, Australia

Received 4 July 2013, revised 23 July 2013, accepted 24 July 2013
Published online 1 August 2013

Keywords carrier lifetime, point defects, silicon, annealing

* Corresponding author: e-mail fiacre.rougieux@anu.edu.au

In this study, we uncover a recombination-active grown-in defect reducing the minority carrier lifetime of Czochralski grown n-type silicon from 5 ms to below 2 ms. We also demonstrate that the defect can be de-activated by annealing between 300 °C and 360 °C. Our experimental findings suggest that vacancy-related pairs incorporated during ingot growth may be responsible for the decreased minority carrier lifetime.

1 Introduction Common metallic-related impurities such as iron, and the boron–oxygen defect, which are critical in determining the performance of lower quality p-type solar cells, are of much less concern in high purity n-type monocrystalline silicon used for very high efficiency solar cells. However, in this material, the electronic quality may still be limited by the presence of grown-in defects, involving, for example, silicon vacancies or self-interstitials, and complexes formed with dopant atoms or light elements such as oxygen and carbon. These have been much less studied in terms of their impact on silicon solar cells.

Silicon self-interstitial and vacancy-related pairs have been studied extensively in the past using techniques such as deep level transient spectroscopy (DLTS) [1, 2], electron paramagnetic resonance (EPR) [3] and localized vibrational mode (LVM) spectroscopy [3]. The thermal stability and energy levels of vacancy–defect pairs and interstitial-related defects are well known [3]. In the microelectronics industry, reduction of the minority carrier lifetime has also been demonstrated using high concentrations of intrinsic-related defects created by high-energy electron, proton, alpha-particle or ion irradiation [2] to improve the switching characteristics of silicon power devices.

More recent studies have demonstrated that grown-in extended-defects such as oxygen precipitates [4–6], oxidation-induced stacking faults (OSF) [6, 7] and grown-in extrinsic point defects such as thermal donors [8, 9] can also significantly reduce the minority carrier lifetime in monocrystalline silicon.

However, the impact of grown-in intrinsic point defects [10] (which are in much lower concentrations than in high energy irradiated samples) on the minority carrier lifetime remains unclear. Such knowledge is fundamental to increase the efficiency of silicon solar cells processed at low temperature (such as heterojunction solar cells) beyond the 24.7% record efficiency recently reported [11], and to increase the yield of very high lifetime wafers from Cz ingots.

2 Experimental methods In this Letter, we investigate the thermal stability of grown-in defects using minority-carrier lifetime measurements with a room-temperature surface-passivation technique [12]. In this technique silicon wafers were immersed in a plastic container filled with 150 ml of 20 wt% HF and subsequently illuminated to activate the passivation, as outlined by Grant et al. [12]. Post illumination, the samples were measured by a transient photoconductance method using a WCT-120 Sinton lifetime tester [12, 13]. To achieve very high effective lifetimes, the samples were etched in a 25 wt% TMAH solution at 80–90 °C for 10 min prior to immersing the silicon wafers in the HF solution, in order to remove surface defects. The surface recombination velocity of the passiva-

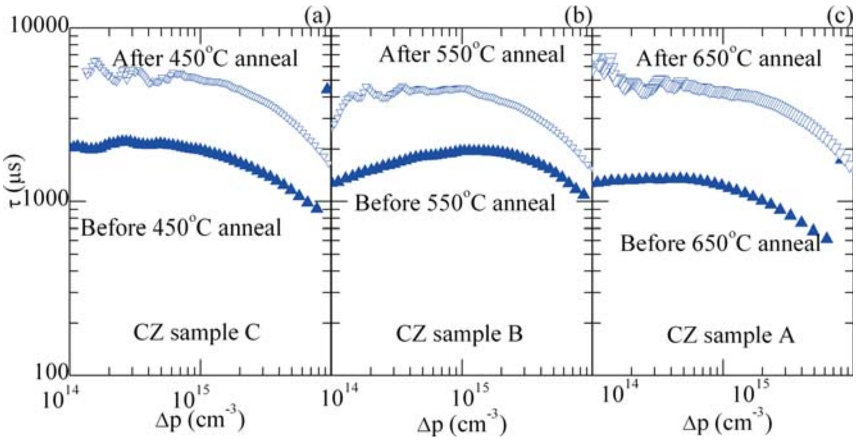

Figure 1 Measured injection dependence of the carrier lifetime in Czochralski grown n-type silicon samples before and after annealing for 30 minutes at (a) 450 °C, (b) 550 °C and (c) 650 °C. The lifetime increases similarly for all samples.

tion technique measured on n-type FZ samples with similar resistivity was found to be injection independent with a value of $S_{eff} = (1.1 \pm 0.2)$ cm s^{-1}. The silicon samples used in this work were sourced from two Czochralski (Cz) grown n-type silicon ingots grown for high efficiency solar cells, with resistivity ranging from 4.1 Ω cm to 3.6 Ω cm, and thicknesses ranging from 955 µm to 1022 µm. Considering the samples are thick and the surface recombination velocity is low, the lifetime measurements are dominated by bulk recombination. Additionally, the silicon wafers were not subject to any thermal processing after being sawn from the ingot.

The Cz n-type samples were annealed for 30 minutes at different temperatures ranging from 150 °C to 650 °C in a quartz tube furnace using a nitrogen ambient. To determine the remaining defect density after annealing at any given temperature, the effective defect concentration was first calculated by $N^*_{t,initial} = 1/\tau_{asgrown} - 1/\tau_{max}$ and $N^*_{t,anneal} = 1/\tau_{anneal} - 1/\tau_{max}$, where $\tau_{asgrown}$ is the measured lifetime in the as-grown state, $\tau_{annealed}$ refers to the annealed lifetime after a given annealing time, and τ_{max} is the maximum life time measured at a given temperature. The remaining normalised defect density after annealing was then determined by $N_{t,anneal}/N_{t,initial}$. In this work, the normalised defect concentration was determined at an injection level of 10% of the net doping $\Delta p = 0.1 \times n_0$.

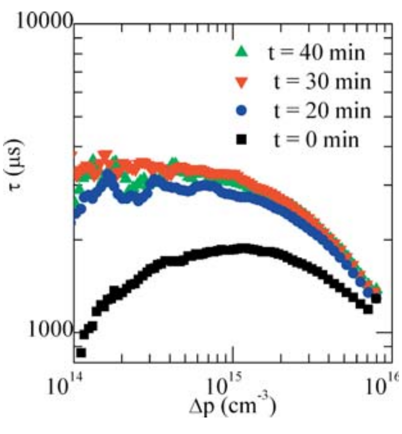

Figure 2 Measured injection dependence of the carrier lifetime in Czochralski grown n-type silicon samples after annealing at 360 °C for different lengths of time.

3 Results and discussion Figure 1 shows the minority carrier lifetime in the as-grown and annealed state for temperatures ranging between 450 °C and 650 °C. The samples came from the same wafer at the bottom of the CZ ingot with a resistivity of 4.1 Ω cm. For the three samples investigated, the minority carrier lifetime increases from (1.6 ± 0.4) ms to (4.7 ± 0.4) ms (at $\Delta p = 1 \times 10^{15}$ cm^{-3}) after annealing. The fact that the lifetime increases similarly for all samples – even at 450 °C – suggests that thermal donors are not responsible for the reduced lifetime, because thermal donors are created at 450 °C (and removed at 650 °C) [14, 15]. This is further confirmed by the constant resistivity measured before and after the annealing at 650 °C, suggesting that if thermal donors are present they exist in relatively low concentrations. Note that the only dopant species in the samples is phosphorus (no boron or gallium), hence the observed defect is also not related to the well-studied boron-oxygen defect. Figure 2 shows the injection dependence of the minority carrier lifetime after annealing at 360 °C for different lengths of time. After a 30 min anneal at 360 °C, the defect is completely deactivated. Additionally we observe no significant lifetime degradation of the deactivated samples after 8 months of storage.

Figure 3a shows the remaining defect density after isochronal annealing of 30 minutes for temperatures ranging from 150 °C to 650 °C. The samples came from two different ingots and had resistivities of 4.4 Ω cm (black square), 4.7 Ω cm (blue upward triangle) and 6.3 Ω cm (red downward triangle). This graph clearly shows that for temperatures above 360 °C, the defect is annealed, while the defect remains recombination-active for temperatures below 300 °C. In a similar fashion, Fig. 3b shows the remaining defect density after isochronal annealing from Watkins et al. measured using electron paramagnetic resonance (EPR) [3]. One can see that the annealing tempera-

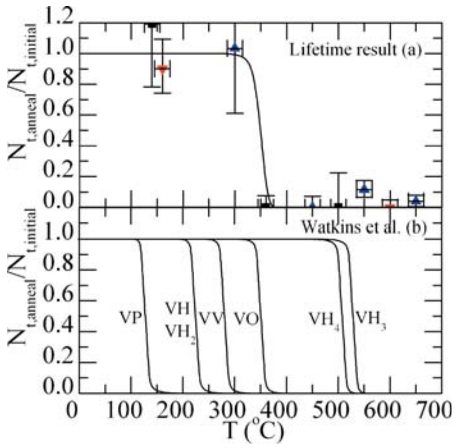

Figure 3 (a) Remaining defect density after 30 min isochronal anneal for temperature ranging from 150 °C to 650 °C measured by lifetime measurements. The line is a guide to the eye. For temperatures above 360 °C, the defect is annealed, while the defect remains recombination-active for temperatures below 300 °C. (b) Remaining defect density after 30 min isochronal anneal for temperatures ranging from 0 °C to 600 °C measured by EPR from Watkins et al. [3].

ture of the recombination-active defect in our sample is similar to the vacancy–oxygen pairs from Watkins et al. [3].

A possible scenario for the observed lifetime increase upon annealing is as follows. During ingot cooling (assuming it is a vacancy-rich ingot, which most ingots are today), vacancies pair with a range of available impurities in the crystal. Upon reaching 360 °C, many of the vacancies will therefore pair with oxygen interstitials, creating the recombination active vacancy–oxygen defect observed. The remaining free vacancies, if any, will then pair with, for example, other vacancies at 270 °C, and potentially phosphorus at 140 °C. Upon annealing above 360 °C, all of these pairs are dissociated. However, as the sample is subsequently rapidly cooled, vacancies not only pair with oxygen, but also with other vacancies to form divacancies VV, and phosphorus to form vacancy–phosphorus pairs VP [16], and other possible compounds. Thus, the proportion of vacancies paired with point defects other than oxygen may increase. Provided that these other vacancy-related complexes are less recombination active than VO pairs, the lifetime would therefore increase upon such annealing.

4 Conclusion In summary, we have uncovered a lifetime limiting defect in n-type Czochralski silicon, created during ingot growth. Our results indicate that the defect can be thermally deactivated by annealing above 360 °C. Note that this defect is unlikely to have been observed before through lifetime measurements due to the fact that typical surface passivation steps, which are generally performed at around 400 °C, would already de-activate it. This underlines the potential of HF passivation as a powerful tool to study the recombination activity of grown-in defects in high-lifetime silicon. The low de-activation temperature excludes most extended defects (stacking faults and oxygen precipitates) as well as thermal donors as responsible for the lower lifetime in the as-grown state. On the other hand, silicon self-interstitials and vacancy-related defect pairs have much lower binding energies and are therefore more likely to be responsible for the observed lifetime recovery upon annealing. A potential candidate showing a de-activation energy between 300 °C and 360 °C is the vacancy–oxygen pair VO, however, further independent results are needed to confirm this conjecture. Our result also has implications for studies showing an apparent improvement of surface passivation with annealing above 360 °C. In such studies, the implicit assumption that the bulk lifetime remains constant before and after annealing may be invalid. The net gain observed in our samples is a threefold increase of the minority carrier lifetime from (1.6 ± 0.4) ms to (4.7 ± 0.4) ms (at $\Delta p = 1 \times 10^{15}$ cm^{-3}), demonstrating the need to mitigate this defect for solar cells processes, especially heterojunction solar cells processed at low temperatures.

Acknowledements This work was supported by the Australian Solar Institute (ASI), the Australian Renewable Energy Agency (ARENA), and the Australian Research Council (ARC).

References

[1] J. H. Evans-Freeman, A. R. Peaker, I. D. Hawkins, P. Y. Y. Kan, J. Terry, L. Rubaldo, M. Ahmed, S. Watts, and L. Dobaczewski, Mater. Sci. Semicond. Process. **3**, 237–241 (2000).

[2] F. D. Auret and P. N. K. Deenapanray, Crit. Rev. Solid State Mater. Sci. **29**, 1–44 (2004).

[3] G. D. Watkins, Mater. Sci. Semicond. Process. **3**, 227–235 (2000).

[4] J. D. Murphy, K. Bothe, R. Krain, V. V. Voronkov, and R. J. Falster, J. Appl. Phys. **111**, 113709 (2012).

[5] J. D. Murphy, K. Bothe, M. Olmo, V. V. Voronkov, and R. J. Falster, J. Appl. Phys. **110**, 053713 (2011).

[6] J. Haunschild, I. E. Reis, J. Geilker, and S. Rein, Phys. Status Solidi RRL **5**, 199–201 (2011).

[7] H. Angelskar, R. Sondena, M. S. Wiig, and E. S. Marstein, Energy Procedia **27**, 160–166 (2012).

[8] Y. Hu, H. Schon, E. J. Ovrelid, O. Nielsen, and L. Arnberg, AIP Advances **2**, 032169 (2012).

[9] Y. Hu, H. Schon, O. Nielsen, E. J. Ovrelid, and L. Arnberg, J. Appl. Phys. **111**, 053101 (2012).

[10] V. V. Voronkov and R. Falster, J. Cryst. Growth **204**, 462–474 (1999).

[11] J. Gifford, PV magazine: Market & Trends, Research & Development (2013).

[12] N. E. Grant, K. E. McIntosh, and J. T. Tan, ECS J. Solid State Sci. Technol. **1**, 55–61 (2012).

[13] R. A. Sinton and A. Cuevas, Appl. Phys. Lett. **69**, 2510–2512 (1996).

[14] D. Aberg, B. G. Svensson, T. Hallberg, and J. L. Lindström, Phys. Rev. B **58**, 12944–12951 (1998).

[15] W. Wijaranakula, Appl. Phys. Lett. **59**, 1608–1610 (1991).

[16] S. Coffa and S. Libertino, Appl. Phys. Lett. **73**, 3369–3371 (1998).