Solid State Phenomena Vol. 242 (2016) pp 120-125
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doi:10.4028/www.scientific.net/SSP.242.120

Submitted: 2015-06-12
Accepted: 2015-06-15

Low temperature activation of grown-in defects limiting the lifetime of high purity n-type float-zone silicon wafers

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Keywords: Annealing, bulk lifetime, defects, float-zone, silicon, vacancy

Abstract

We investigate the recombination activity of a bulk silicon defect limiting the lifetime of high quality *n*-type float-zone (FZ) silicon wafers. By isochronal annealing between 200 and 1100 ˚C, a defect was found to become activated upon annealing at 450–700 ˚C, causing an order of magnitude reduction in the bulk lifetime. From photoluminescence imaging, it was evident that recombination active circular patterns were present in these low lifetime samples, suggesting the defect(s) originates from the growth conditions of the ingot. When the samples were passivated by SiN_x:H films, a substantial improvement in the bulk lifetime resulted, which we postulate occurred due to hydrogenation of the bulk defects. In contrast, when the samples were annealed at high temperatures (800–1100 ˚C), the circular recombination active patterns were removed, and the bulk lifetime improved, with the highest lifetime achieved at an annealing temperature of 1100 ˚C. The experimental results suggest that the defect limiting the lifetime in this FZ material is related to a lattice-impurity defect, which can be permanently annihilated upon annealing at >1100 ˚C.

Introduction

Understanding and mitigating the recombination activity of lifetime limiting bulk silicon defects is essential for producing high efficiency (>24%) solar cells. Currently the lifetime of multicrystalline and monocrystalline Czochralski (Cz) grown silicon is predominantly limited by oxygen and metal impurities [1],[2]. With higher feedstock quality and improved ingot growth processes, other defects involving grown-in vacancies and self-interstitials may become the next tier of defects which prevent the lifetime from reaching the intrinsic limit, especially if the concentration of lighter elements such as oxygen, carbon, nitrogen and hydrogen are not supressed during ingot growth.

The recombination lifetime of defects with low binding energies thought to be vacancy-oxygen (VO_x) and vacancy-phosphorus (VP) in Cz *n*-type silicon has recently been examined through low temperature isochronal annealing and photoconductance (PC) measurements [3],[4]. It was found that in the as-grown state, both defects are recombination active, and limit the bulk lifetime (τ_{bulk}) to ≤1 ms. However upon annealing at 200 ˚C, the VP defect can be annihilated, thus increasing the lifetime by hundreds of microseconds [4]. Although VP can inhibit the bulk lifetime, such a defect is only expected to significantly affect relatively highly doped silicon wafers (<1 Ω-cm). In contrast, the VO_x defect is not deactivated until the samples are annealed at ≥350 ˚C, which has been shown to increase the bulk lifetime from ~1 ms to 5 ms [3]. Interestingly, a similar defect has also been observed in *p*-type FZ silicon, where the 'as-grown' lifetime is limited to just hundreds of microseconds, however upon annealing at ≥250 ˚C the lifetime is found to improve by several milliseconds [5]. In this case however, the defect is not related to oxygen, phosphorus or metal impurities, but rather relates to another intrinsic defect which has yet to be identified.

At high annealing temperatures, intrinsic defects have been shown to either improve or degrade the bulk lifetime. For example, at high temperatures >700 ºC, vacancies can enhance interstitial oxygen diffusivity and act as nucleation sites for oxygen precipitation, which then become recombination active, and thus reduce the bulk lifetime [6]. In contrast, if vacancy rich silicon

(oxygen lean) is doped with nitrogen, as in the case of float-zone (FZ) silicon, vacancy-nitrogen pairs form, which can significantly limit the bulk lifetime in the as-grown state to hundreds of microseconds [7]. However, contrary to oxygen precipitation, when the defect is subject to high temperatures, vacancy-nitrogen (VN_x) pairs dissociate, which can then substantially improve the bulk lifetime into the multi-millisecond range [7].

This work aims to detect and characterise the recombination activity of grown-in defects which limit the lifetime of high purity FZ silicon. We examine the activation and deactivation kinetics of the defect(s) by isochronal annealing the samples between 200–1100 ˚C. We perform photoluminescence imaging to detect spatial non-uniformities in the bulk lifetime when the defect(s) is activated. Finally we subject the samples to a plasma enhanced chemical vapour deposition (PECVD) silicon nitride (SiN_x:H) process to determine if hydrogen can passivate (and thus deactivate) the defect(s). Ultimately the intention is to develop thermal (or hydrogenation) processes which permanently deactivate intrinsic defects (vacancy and self-interstitial related), thus achieving very high lifetimes for very high efficiency solar cells.

Experimental methods

The samples under investigation were phosphorus doped FZ silicon wafers from three different ingots with resistivities of approximately 1 Ω-cm, 10 Ω-cm and 100 Ω-cm. The thickness of the wafers was 200 μm (1 and 10 Ω-cm) and 400 μm (100 Ω-cm) respectively and their diameter was 100 mm.

The wafers were cleaved into quarters and then RCA cleaned. Following the clean, the samples were loaded into a quartz tube furnace and annealed at the set temperature for 30 mins in oxygen. For temperatures higher than 700 ºC, there was an additional ramp up and cool down period.

To examine the impact of annealing temperature on the bulk lifetime, minority carrier lifetime measurements were performed using a room temperature surface passivation technique [8]. By this technique, silicon wafers were immersed into a container filled with 170 mL of 15 wt% hydrofluoric acid-hydrochloric acid (HF-HCl) solution (100ml of H_2O, 50ml of 48% HF and 20ml of 37% HCl) and centred over an inductive coil for transient photoconductance (PC) measurements (using a WCT-120 system from Sinton Instruments) [9]. To activate the surface passivation, the wafers were subsequently illuminated at 0.2 suns for 1 minute using a halogen lamp, the light source was switched off, and a transient measurement was immediately performed. To achieve a very low S of less than 1 cm/s on n-type silicon, the wafers were chemically treated prior to immersing the wafers into the HF-HCl solution. The chemical treatment involved two steps, (1) the wafers were cleaned by the standard RCA procedure, and (2) subsequently etched in 25 wt% tetramethylammonium hydroxide (TMAH) at 80–90 °C for 5 minutes (removing about 2.5 microns of silicon per side). This chemical treatment ensures the silicon surface is defect and contaminant lean prior to surface passivation.

To investigate the spatial non-uniformity of the bulk lifetime, some samples were also passivated with a 20 nm atomic layer deposited (ALD) aluminium oxide (Al_2O_3) film. Prior to the depositions, all samples received a damage etch in 25 wt% TMAH at 80–90 °C for 10 minutes followed by a standard RCA clean. The Al_2O_3 films were deposited at 200 °C using a Beneq TFS200 ALD system. Post deposition, the Al_2O_3 films were annealed in forming gas at 400 °C for 30 minutes to activate the surface passivation.

To examine the effect of hydrogenation on the bulk lifetime, samples were passivated with an 80 nm PECVD SiN_x:H film. Prior to the depositions, all samples received a damage etch in 25 wt% TMAH at 80–90 °C for 10 minutes followed by a standard RCA clean. The SiN_x:H films were deposited at 235 °C using an AK400 Roth and Rau PECVD. Post deposition, no subsequent anneals were performed.

Results and discussion

Activation and deactivation of bulk silicon defects by isochronal annealing

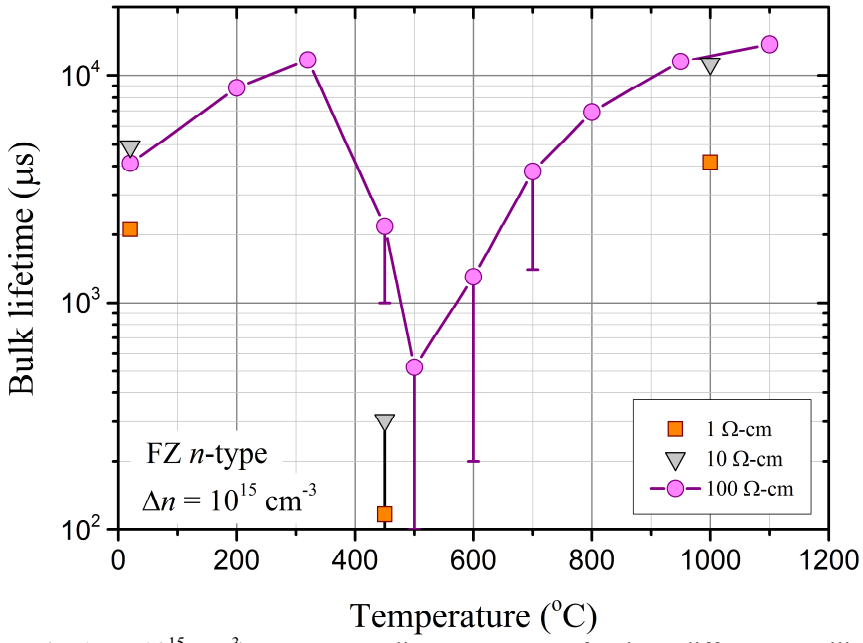

Figure 1: Bulk lifetime (at $\Delta n = 10^{15}$ cm^{-3}) versus annealing temperature for three different FZ silicon wafers, 1 Ω-cm, 10 Ω-cm and 100 Ω-cm. Annealing was performed in oxygen for 30 mins. For each annealing temperature, new samples were used. The bulk lifetime was measured using HF passivation [8].

Figure 1 plots the bulk lifetime (at $\Delta n = 10^{15}$ cm^{-3}) versus annealing temperature of three FZ *n*-type silicon wafers, 1 Ω-cm, 10 Ω-cm and 100 Ω-cm. In this case, all three silicon ingots were produced by the same manufacturer. For each annealing temperature, new samples were used.

Prior to any thermal treatment, all samples show lifetimes in the millisecond range. For the 100 Ω-cm sample, an increase in lifetime is observed for annealing temperatures up to ~300 °C, where τ_{bulk} increased from ~4 ms in the as-grown state to ~13 ms after annealing at 300 °C. This increase in lifetime is consistent with our previous work on deactivation of defects at low annealing temperatures [5], and thus the increase in lifetime as seen in Figure 1 is not related to surface passivation instabilities. From the figure, it is evident that a defect is being deactivated over this temperature range, but at this point in time identification of the defect is difficult to ascertain, however based on the literature we can rule out boron-oxygen [1], iron-boron [2] and vacancy-oxygen [10] pairs.

When the silicon samples were annealed at 450 °C, the lifetime was found to decrease significantly. For the 100 Ω-cm sample, the lifetime remained low even when samples were annealed between 450 °C and 600 °C. In contrast, control Cz silicon samples (not shown) showed no decrease in lifetime over this temperature range, and thus we do not attribute the reduction in τ_{bulk} to external contamination. The large error bars for the samples annealed at 450, 500, 600 and 700 °C represent the uncertainty in the true bulk lifetime, as the PC lifetime measurement of these samples were affected by a spatially non-uniform bulk lifetime, as will be shown in the following section.

When the samples were subject to a ≥1000 °C anneal in oxygen for 30 mins, the bulk lifetime not only recovered, but substantially improved relative to the as-grown lifetime. Furthermore, when the samples annealed at 1000 °C were subject to another 450 °C anneal, the lifetime did not decrease, indicating the defect(s) can be permanently deactivated after a high temperature (≥1000 °C) anneal. Such an improvement in the bulk lifetime after high temperature annealing is consistent with dissociation of VN_x pairs, as demonstrated in Ref. [7]. To further strengthen this finding, the nitrogen concentration was determined from secondary ion mass spectroscopy (SIMS) measurements. From SIMS, it was determined that all three silicon wafers contain detectible

quantities of nitrogen, where the concentration varies from 3 x10^{14} cm^{-3} to 5x10^{14} cm^{-3}, similar to that reported in Ref. [7]. This suggests that VN_x could be one defect limiting the lifetime in these FZ silicon wafers.

Spatial distribution of active defects by photoluminescence imaging

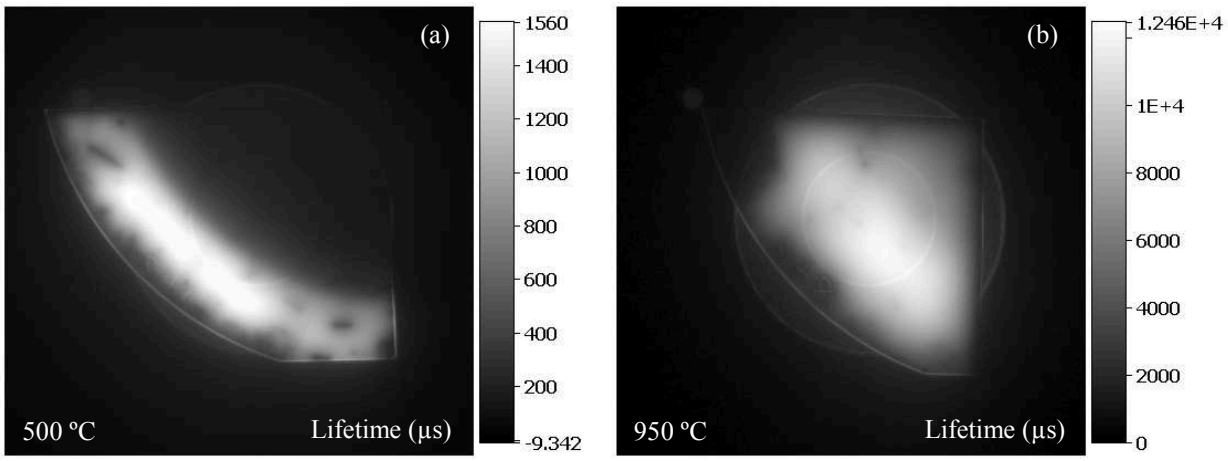

Figure 2: Calibrated photoluminescence images of Al_2O_3 passivated 100 Ω-cm silicon samples which were previously annealed at (a) 500 °C and (b) 950 °C in oxygen for 30 mins. Note the different lifetime scales.

Vacancy and self-interstitials tend to be distributed non-uniformly, with vacancies dominant in the central region and self-interstitials dominant in the peripheral region of silicon wafers grown under mixed growth conditions [11]. To investigate the potential presence of such revealing circular patterns, the 100 Ω-cm samples were passivated with ALD Al_2O_3 and subsequently measured using photoluminescence imaging, as shown in Figure 2. Figure 2a shows an image of a sample annealed at 500 °C. Interestingly, the image shows a highly recombination active central disk (black area), surrounded by a lower recombination active peripheral region (white area). While it cannot be concluded definitively, it is likely that the recombination active central core in Figure 2a corresponds to a vacancy related defect, such as VN_x pairs as previously seen in Ref. [7]. In contrast, it is difficult to assign the peripheral region to a silicon interstitial defect as the recombination activity of such defects are very rarely reported. However, it is evident from Figure 2a that the lifetime in the peripheral region is also limited by a bulk defect, where the lifetime is restricted to <2 ms.

When the silicon samples were annealed at high temperatures (>950 °C), the lifetime in both the central and peripheral regions improve, however the improvement in the central region is substantially greater, as evidenced by the PL image shown in Figure 2b. Thus while the very distinctive regions shown in Figure 2a likely correspond to dissimilar intrinsic defects, both can be annihilated by annealing the silicon wafers at high temperatures.

Deactivation of bulk silicon defects by PECVD SiN_x:H

Figure 3 plots the bulk lifetime of FZ *n*-type samples after annealing at 450 °C in O_2 for 30 mins (a) followed by a HF passivation measurement, (b) after a subsequent PECVD SiN_x:H deposition and (c) after stripping the SiN_x:H film and subsequently annealing the samples at 1000 °C in O_2 for 30 mins. Following the high temperature anneal, the samples were measured with HF passivation and then coated with PECVD SiN_x:H once again.

From Figure 3a, it is evident that a 450 °C anneal activates a bulk defect(s), where an order of magnitude reduction in lifetime (compared to as-grown lifetimes) is observed for each sample (1, 10 and 100 Ω-cm). While the 1 Ω-cm sample shown in Figure 3a exhibits typical lifetime injection dependence, the 10 and 100 Ω-cm samples do not. The most likely cause of this erroneous injection dependence is due to a spatial non-uniformity in the bulk lifetime, as seen in Figure 2a. Such an artefact has been previously investigated by Cuevas *et al*, who demonstrated that when there are regions of substantially different lifetimes in close proximity, the high lifetime region (peripheral

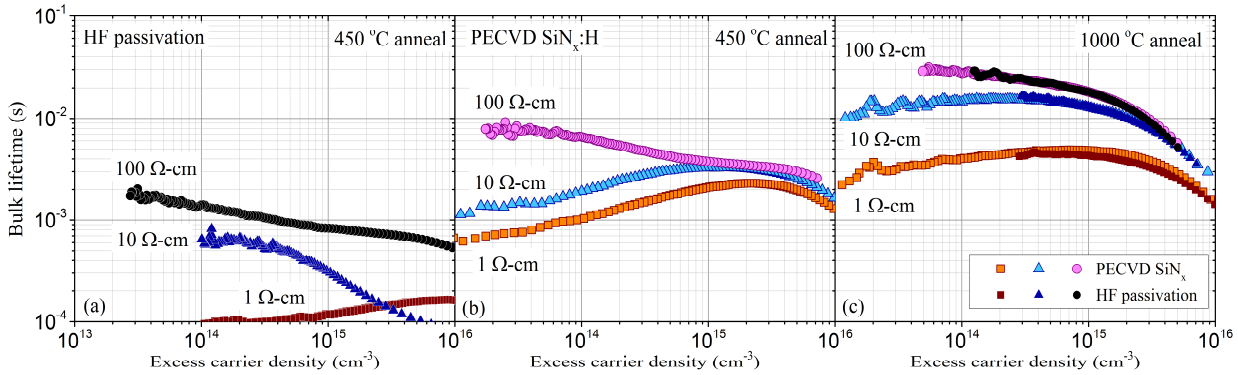

Figure 3: plots the bulk lifetime of FZ *n*-type samples after annealing at 450 °C in O_2 for 30 mins (a) followed by a HF passivation measurement, (b) after a subsequent PECVD SiN_x:H deposition and (c) after stripping the SiN_x:H film and subsequently annealing the samples at 1000 °C in O_2 for 30 mins. Following the high temperature anneal, the samples were measured with HF passivation and then coated with PECVD SiN_x:H once again.

region) will dominate a transient photoconductance measurement [12]. Therefore it is likely that the lifetime curves of the 10 and 100 Ω-cm samples shown in Figure 3a also suffer from a spatially non-uniform bulk lifetime like that shown in Figure 2a.

When the samples were subsequently passivated by PECVD SiN_x:H, a significant improvement in the bulk lifetime was observed, as seen in Figure 3b. This increase in lifetime is not due to variations in the surface passivation by HF and SiN_x:H, as evident by Figure 3c, but rather represents a true deactivation process. While it cannot be definitively concluded, we postulate that hydrogen from the SiN_x:H deposition has reduced the recombination activity of bulk silicon defects, which improves the bulk lifetime as demonstrated in [7],[13].

The injection dependent lifetime curves for the 1 and 10 Ω-cm samples shown in Figure 3b reveal the presence of a bulk defect(s) through the reduction in lifetime at low injection. Therefore, even though the SiN_x:H deposition has resulted in an improvement of τ_{bulk}, some defects remain partially activated. We do not assign this injection dependence to surface passivation as SiN_x:H contains a net positive charge of $>10^{11}$ cm^{-2} [14], which would form accumulation at the surfaces of *n*-type silicon.

Without knowing the defect energy level within the bandgap, we can infer from the injection dependent lifetime curves that the capture cross-section ratio ($\sigma_n/\ \sigma_p$) for the defect is <1, and therefore is most likely an acceptor level. In contrast, no information regarding the $\sigma_n/\ \sigma_p$ ratio can be determined from the lifetime curve of the 100 Ω-cm sample because its injection dependence is partly affected by circular patterns (similar to Figure 2a), as confirmed by PL imaging (not shown). Irrespective of this, the bulk lifetime has still improved after the SiN_x:H deposition.

When the SiN_x:H films were stripped and the samples subsequently annealed at very high temperatures (1000 °C), a further improvement in the bulk lifetime for each wafer was obtained, as seen in Figure 3c. The two sets of lifetime measurements shown in Figure 3c were obtained by first measuring the samples with HF passivation and then subsequently depositing PECVD SiN_x:H. Thus after high temperature annealing, the SiN_x:H deposition does not appear to have an impact on the bulk lifetime as seen in Figure 3b.

Similar to the lifetime curves in Figure 3b, the injection dependence for the 1 and 10 Ω-cm samples in Figure 3c still show a slight reduction in lifetime at low injection, indicating some bulk defects are still active with a higher capture cross-section for holes than electrons, $\sigma_n/\ \sigma_p$ <1. Therefore to completely annihilate the bulk silicon defects and attain very high lifetimes, very high temperature annealing such as 1100–1300 °C may be required, or a more sophisticated hydrogenation step employed [13].

Conclusion

In this work we have uncovered a defect in high purity FZ silicon through isochronal annealing and a room temperature liquid surface passivation technique. When the samples were annealed at temperatures between 200–300 ˚C, the bulk lifetime was found to increase, however upon annealing at 450–700 ˚C, the lifetime was found to degrade by more than an order of magnitude. Photoluminescence imaging of these samples revealed the presence of circular patterns, with higher recombination occurring in the centre of the wafer, and far less around the periphery. The circular patterns suggest the defect originates from the growth conditions of the ingot, where the core of the ingot primarily consists of a vacancy related defect, such as VN_x. When these samples were passivated by PECVD SiN_x:H, a substantial improvement in the bulk lifetime resulted, which we postulate occurred due to hydrogenation of the bulk defects during the SiN_x:H deposition. From the injection dependent lifetime curves however, it was evident that a defect was still partly active, where $\sigma_n/\ \sigma_p$ of <1 was determined (irrespective of the trap energy level). In contrast, when the samples were annealed at high temperatures (800–1100 ˚C), the circular recombination active patterns were removed, and the bulk lifetime improved, with the highest lifetime achieved at an annealing temperature of 1100 ˚C. Therefore in order to attain defect lean high lifetime silicon wafers, very high temperature annealing such as 1100–1300 °C may be required, or a more sophisticated hydrogenation step be employed.

Acknowledgements

This work has been supported by the Australian Renewable Energy Agency (ARENA) fellowships program and the Australian Research Council (ARC) Future Fellowships program. Responsibility for the views, information or advice expressed herein is not accepted by the Australian Government.

References

[1] J. Schmidt and K. Bothe, *Physical Review B*, **69**, 024107 (2004).
[2] D. Macdonald, A. Cuevas, A. Kinomura, Y. Nakano and L. J. Geerligs, *Journal of Applied Physics*, **97**, 033523 (2005).
[3] F. E. Rougieux, N. E. Grant and D. Macdonald, *Physica status solidi*, **7**, 616–618, (2013).
[4] P. Zheng, F. Rougieux, N. Grant and D. Macdonald, *IEEE Journal of Photovoltaics*, **5**, 183–188, (2015).
[5] N. E. Grant, F. Rougieux, D. Macdonald, J. Bullock and Y. Wan, *Journal of Applied Physics*, **117**, 055711, (2015).
[6] J. D. Murphy, K. Bothe, R. Krain, V. V. Voronkov, and R. J. Falster, *Journal of Applied Physics*, **111**, 113709, (2012).
[7] F. E. Rougieux, N. E. Grant, C. Barugkin, D. Macdonald and J. Murphy, *IEEE Journal of Photovoltaics*, **5**, 496, (2015).
[8] N. E. Grant, K. R. McIntosh and J. T. Tan, *Journal of solid state science and technology*, **1**, (2012).
[9] R. A. Sinton and A. Cuevas, *Applied Physics Letters*, 69, 2510, (1996).
[10] V. Quemener, B. Raeissi, F. Herklotz, L. I. Murin, E. V. Monakhov, and B. G. Svensson, Physics Status Solidi B, **251**, 1, (2014).
[11] V. V. Voronkov, *Journal of Crystal Growth*, **59**, 625, (1982).
[12] A. Cuevas, M. Stocks, D. Macdonald and R. Sinton, *2nd World PVSEC*, (1998).
[13] B. J. Hallam, P. G. Hamer, S. R. Wenham, M. D. Abbott, A. Sugianto, A. M. Wenham, C. E. Chan, G. Xu, J. Kraiem, J. Degoulange, and R. Einhaus, *IEEE J. Photovoltaics*, **4**, 88–95, (2014).
[14] Y. Wan, K. R. McIntosh, A. F. Thomson and A. Cuevas, *IEEE J. Photovoltaics*, **3**, 554–559, (2013).