

**Manuscript version: Author's Accepted Manuscript**

The version presented in WRAP is the author's accepted manuscript and may differ from the published version or Version of Record.

**Persistent WRAP URL:**

<http://wrap.warwick.ac.uk/118993>

**How to cite:**

Please refer to published version for the most recent bibliographic citation information. If a published version is known of, the repository item page linked to above, will contain details on accessing it.

**Copyright and reuse:**

The Warwick Research Archive Portal (WRAP) makes this work by researchers of the University of Warwick available open access under the following conditions.

Copyright © and all moral rights to the version of the paper presented here belong to the individual author(s) and/or other copyright owners. To the extent reasonable and practicable the material made available in WRAP has been checked for eligibility before being made available.

Copies of full items can be used for personal research or study, educational, or not-for-profit purposes without prior permission or charge. Provided that the authors, title and full bibliographic details are credited, a hyperlink and/or URL is given for the original metadata page and the content is not changed in any way.

**Publisher's statement:**

Please refer to the repository item page, publisher's statement section, for further information.

For more information, please contact the WRAP Team at: [wrap@warwick.ac.uk](mailto:wrap@warwick.ac.uk).

**Iodine-ethanol surface passivation for measurement of millisecond carrier lifetimes in silicon wafers with different crystallographic orientations**

*Mohammad Al-Amin, Nicholas E. Grant, Alex I. Pointon, John D. Murphy\**

Dr M. Al-Amin  
WMG, University of Warwick, Coventry, CV4 7AL, UK

Dr N.E. Grant, Mr Alex I. Pointon, Prof. J.D. Murphy  
School of Engineering, University of Warwick, Coventry, CV4 7AL, UK  
\*E-mail: john.d.murphy@warwick.ac.uk

Keywords: silicon, surface passivation, lifetime, recombination, superacid.

**Abstract**

To improve silicon device fabrication processes it is necessary to monitor bulk minority carrier lifetimes accurately, and this requires surface recombination to be well controlled and, ideally, minimized. Good surface passivation can result from thermal oxidation or by deposition of dielectrics (*e.g.* Al<sub>2</sub>O<sub>3</sub>, SiN<sub>x</sub>, amorphous Si), but these forms of passivation can modify the lifetime of the material under investigation. Various schemes can passivate surfaces on a temporary basis without modifying the bulk, and, in this paper, the virtues of the iodine-ethanol temporary surface passivation scheme are explored. A procedure for preparing the wafer surfaces prior to passivation is developed. For the optimised pre-treatment, a series of experiments on 3–5 Ωcm float-zone wafers cut from the same ingot with different thicknesses is conducted. This enables the material's bulk lifetime to be measured at 10<sup>15</sup> cm<sup>-3</sup> injection as ~ 46 ms, with the surface recombination velocity being 6.5 ± 0.3 cm/s. Iodine-ethanol passivation is then compared to a recently developed superacid-derived temporary passivation scheme. Although the latter is superior on (100)-orientation substrates, iodine-ethanol performs much better on (111)-orientation substrates, making it a better choice for (111)-orientation wafers, such as those used for power devices.

## 1. Introduction

Minority carrier lifetime is an important parameter to control in the fabrication of silicon-based electronic devices. Even in very high quality silicon wafers, the bulk lifetime can vary substantially from one process step to the next. This is shown, for example, in a recent study of lifetime during a passivated emitter and rear cell (PERC) solar cell fabrication process.<sup>[1]</sup> Without passivation, recombination of charge carriers at the wafer surfaces limits the lifetime, so to make reliable measurements it is necessary to passivate the surfaces. Dielectric passivation of surfaces (reviewed recently)<sup>[2]</sup>, can provide excellent, stable surface passivation. Unfortunately dielectric deposition and/ or its subsequent activation annealing can change the bulk lifetime and hence result in a false diagnosis of a bulk lifetime change which may occur during a given processing step. It has been shown that thermal processing at dielectric deposition and activation annealing temperatures can form recombination centres,<sup>[3, 4]</sup> hydrogenation from passivating films can modify bulk recombination centres,<sup>[5]</sup> and impurities can be externally gettered to the dielectric layer at the sample's surface.<sup>[6, 7]</sup>

To avoid artefacts associated with dielectric passivation, room temperature temporary passivation can instead be used for lifetime measurements. There are many possible forms of temporary passivation, as reviewed recently by Grant and Murphy.<sup>[8]</sup> Some of these, such as liquid hydrofluoric acid (HF)<sup>[9, 10]</sup> and superacid-derived<sup>[11-13]</sup> passivation, can have a passivation quality similar to some of the best dielectrics. However, the toxicity of HF restricts its use to specialist laboratories, and superacid-derived passivation tends to require a controlled atmosphere often achieved with a glovebox. A further consideration for any passivation scheme is the degree to which different orientation surfaces are passivated. While (100)-orientation wafers are the most common for integrated circuit fabrication and are widely used for photovoltaics, (111)-orientation wafers are often used for power devices, and multicrystalline (mc-Si) wafers with a range of orientation grains including (111) and (100)<sup>[14]</sup> are used for the majority of photovoltaics cells. HF passivation has been demonstrated to

work as well (or better) on (111)-orientation wafers compared to (100),<sup>[9]</sup> but from a preliminary study on mc-Si there are some concerns that superacid-derived passivation does not work as well on orientations other than (100).<sup>[11]</sup>

Given the practical considerations associated with HF and superacid-derived passivation, and the orientation limitation of the latter, there remains a need to develop alternative passivation schemes. Passivation of silicon surfaces by halogen-alcohol solutions including iodine-ethanol (I-E), has been studied by many groups.<sup>[15-23]</sup> I-E passivation has been used on (111)-orientation surfaces<sup>[15]</sup> and on mc-Si.<sup>[24]</sup> The passivation level provided by halogen-alcohol systems is not as good as HF and superacid-derived passivation,<sup>[8]</sup> but it is still sufficient for measuring high lifetimes if procedures are performed carefully.

An important parameter often used to describe the efficacy of a passivation scheme is the surface recombination velocity,  $S$ . For a symmetrically passivated sample with relatively low  $S$ ,  $S$  is defined as:

$$S = \frac{W}{2} \left( \frac{1}{\tau_{\text{effective}}} - \frac{1}{\tau_{\text{bulk}}} \right) \quad (1)$$

where  $W$  is the sample thickness,  $\tau_{\text{effective}}$  is the measured effective lifetime, and  $\tau_{\text{bulk}}$  is the bulk lifetime.  $S$ ,  $\tau_{\text{effective}}$  and  $\tau_{\text{bulk}}$  are dependent on the excess carrier concentration in the sample. Many researchers estimate  $S$  by assuming  $\tau_{\text{bulk}}$  to be infinite. In our experience, this assumption is often not valid, even in high quality float-zone silicon,<sup>[3, 4]</sup> so from a single measurement it is only possible to put an upper-limit on  $S$ . By varying the sample thickness with constant  $\tau_{\text{bulk}}$  it is, in principle, possible to determine the absolute value of  $S$ .

In this paper, we present results to optimise the I-E passivation process. A series of experiments is first performed to determine an effective surface preparation process for high quality I-E passivation. We then use a specially produced set of samples cut to different thicknesses from the same float-zone ingot to determine the absolute value of  $S$  for the I-E

passivation process. Finally, we demonstrate the superiority of I-E over superacid-derived passivation on (111)-orientation silicon.

## 2. Experimental methods

Three different sets of samples were used with the key properties given in Table 1. The samples were subjected to various surface pre-treatments, as specified in the corresponding results sections, with the chemicals and conditions for the pre-treatments defined in Table 2.

For I-E passivation, the silicon samples were placed in transparent sealable plastic bags immediately after any pre-treatment steps. A 0.1 M solution of iodine (Fisher Scientific,  $\geq 99.8\%$ ) in ethanol (Sigma-Aldrich,  $\geq 99.8\%$  purity) was poured into the bags. Excess solution and air bubbles were squeezed out to ensure a thin layer of I-E solution coated both sides of the sample. The bags were then sealed. The whole process was performed at room temperature. After measurements, the I-E solution was removed from the sample's surface using methanol.

For comparison purposes, some samples were passivated using a standard superacid-derived passivation approach using thin films formed from solutions of bis(trifluoromethane)sulfonimide (TFSI, Sigma-Aldrich, 95%) in anhydrous 1,2-dichloroethane (Sigma-Aldrich, 99.8%). The full details of this passivation scheme have been published previously<sup>[12, 13]</sup> and, for *n*-type (100)-orientation silicon, *S* has been measured to be  $< 1$  cm/s.<sup>[12]</sup>

Passivated samples were characterised by injection-dependent transient photoconductance lifetime measurements made using a Sinton WCT-120 lifetime tester. For the variable thickness experiment, the lifetime tester was recalibrated to account for the effects of particularly thick samples using a method developed by Black and Kessels.<sup>[25]</sup> Errors in lifetime are taken as  $\pm 5\%$ , guided by a reproducibility study.<sup>[26]</sup> Uncalibrated photoluminescence (PL) images were acquired using a BT Imaging LIS-L1 PL imaging

system at an illumination of  $\sim 0.4$  suns for an exposure time of 0.5 s. The surface of the pre-treated silicon was characterised by optical microscopy in some cases.

For one set of tests on (111)-orientation wafers, the standard superacid-derived passivation approach was modified so that the lifetime was measured with the sample immersed in a liquid solution of TFSI in hexane (Sigma-Aldrich, 95%). For these measurements a lifetime tester was located inside a sealed filtered MBRAUN UNIlab modular glovebox workstation with gas purification system and solvent filter with a controlled low humidity atmosphere ( $<0.1$  ppm  $O_2$ ;  $<0.1$  ppm  $H_2O$ ).

### 3. Results and analysis

#### 3.1 Surface preparation experiments

Experiments to investigate the optimal pre-treatment conditions for I-E passivation were first performed. As bulk lifetime can vary substantially from one float-zone wafer to another,<sup>[4]</sup> high lifetime Set A wafers were cleaved into quarters which can be assumed to have the same bulk lifetime distributions due to the radial symmetry of the crystal growth process. Samples were deliberately chosen to be *n*-type so to avoid lifetime instabilities associated with light-induced degradation<sup>[27]</sup> or metal-dopant pairing in *p*-type silicon. Each quarter sample underwent one of the following cleaning sequences:

1. HF dip only (labelled “HF”).
2. RCA 1 clean, and HF dip (labelled “RCA 1”).
3. RCA 2 clean, and HF dip (labelled “RCA 2”).
4. RCA 1 clean, HF dip, RCA 2 clean, and HF dip (labelled “RCA 1+2”).

Samples were then passivated with I-E solution prior to lifetime measurement and PL imaging. After passivation removal, the same sample set was subjected to RCA 1 and RCA 2 cleaning prior to a chemical polish by a 30 minute planar etch which removed  $\sim 40$   $\mu m$  from each side of the samples. Each of the four quarters was then subjected to one of the four pre-

treatment sequences listed above, prior to I-E passivation and characterisation. Finally, after passivation removal and more RCA 1 and RCA 2 cleaning, the same sample set was subjected to tetramethylammonium hydroxide (TMAH) etching (10 minutes). This removed a further  $\sim 5 \mu\text{m}$  of material from each side of the samples. Samples were again subjected to one of the four pre-treatment sequences listed above, followed by I-E passivation and characterisation.

Figure 1 shows the effective lifetime at an excess carrier density of  $10^{15} \text{ cm}^{-3}$  in Set A samples subjected to the different cleaning and etching processes. Lifetimes in the as-received states ranged from 3 ms to 4.9 ms, with higher lifetimes resulting from cleaning rather than HF dipping alone. The impact of the different cleaning sequences is not particularly conclusive, but it is clearly the case that as-received lifetimes were improved substantially by etching. In general, pre-cleaning with an RCA 1 or RCA 2 solution shows higher lifetime than a pre-cleaning process with HF dip only or an RCA 1+2. The best measured lifetime is  $\sim 7$  ms for a sample which was subjected to TMAH etching followed by the RCA 1 cleaning process. All results with I-E passivation are inferior to the lifetime of 8.5 ms measured with the optimised superacid-derived passivation process,<sup>[12]</sup> as expected for (100)-orientation substrates.

Figure 2 shows uncalibrated PL images after the different pre-surface treatment and cleaning procedures. The data shown were all acquired from a single Set A wafer, with each quarter being subjected to a different cleaning procedure each time. There is a slight reduction in thickness as the sample moves from column (a), to column (b), to column (c), and as the wafer becomes slightly thinner the effect of surface recombination becomes slightly stronger. The PL signal increases significantly after the planar etching process compared to the as-received states. The I-E passivation is not particularly uniform, with some regions of the samples giving a high PL signal and others relatively low. These differences are due to difference in passivation (and not bulk lifetime) as the good/ bad regions change location between the different process steps. The presence of dark regions occurs irrespective of the

choice of pre-cleaning process. The bottom row of Figure 2 shows optical micrographs of the sample surface at the given process stage. The samples initially have square features characteristic of (100)-orientation material subjected to an alkaline etch (*e.g.* KOH), likely to be as a consequence of etching performed by the manufacturer. The planar etch smoothens the surface, and the TMAH etch acts to texture the surface partially, providing small and rounded features.

### 3.2. Passivation time dependence

The level of surface passivation achieved with I-E is not initially stable. Figure 3 shows the results of a series of lifetime measurements on a Set A wafer passivated with I-E. The wafer shown in Figure 3 had been subjected to TMAH etching (10 minutes) and an RCA 1 clean, as this was found to give the highest lifetime in the earlier study (Figure 1). The lifetime increases with time over the period of about one minute before it stabilises. This is shown by the injection dependent data in Figure 3 (a) and the data at an excess carrier density of  $10^{15} \text{ cm}^{-3}$  in Figure 3 (b). After the I-E experiment, the same sample was subjected to our optimised superacid-derived surface passivation process<sup>[12]</sup> and the results are also shown in Figure 3. This shows the bulk lifetime is substantially higher than the effective lifetime measured with I-E passivation.

### 3.3. Surface recombination velocity extraction

As noted in the introduction, it is possible to use Equation 1 to extract an absolute value of the surface recombination velocity,  $S$ , by varying the wafer thickness,  $W$ , for a fixed bulk lifetime,  $\tau_{\text{bulk}}$ . The wafers in Set B were cut from the same float-zone ingot to have different thicknesses, and so can be assumed, to a reasonable approximation, to have the same  $\tau_{\text{bulk}}$ . The samples were first pre-cleaned with RCA 1 and RCA 2, and then were subjected to a

200 °C anneal for 30 minutes to deactivate recombination-active bulk defects.<sup>[28]</sup> Guided by the results in Figure 1, the samples were subjected to an extended TMAH etch (30 minutes), before cleaning with an RCA solution followed by an HF dip, and I-E passivation. Figure 4 (a) shows the effective lifetimes measured, with the intrinsic lifetime limit of Richter *et al.*<sup>[29]</sup> also plotted. As expected, the effective lifetime increases with wafer thickness due to the reducing impact of surface recombination due to a thickening bulk. The plot in Figure 4 (b), which uses lifetime data at an excess carrier density of  $10^{15} \text{ cm}^{-3}$ , is in accordance with Equation 1, and gives a linear relationship. At this level of injection, the surface recombination velocity is found to be  $6.5 \pm 0.3 \text{ cm/s}$  and the bulk lifetime is estimate as 46 ms. The uncertainty in the bulk lifetime is relatively large with the lower limit being 30 ms and the upper limit being 100 ms. Figure 4 (c) shows the injection dependence of the surface recombination velocity extracted from the lifetime curves in Figure 4 (a). The surface recombination velocity falls below 5 cm/s at relatively low injection and increases at higher injection. The lowest  $S$  determined in our measurement range is  $4.4 \pm 0.2 \text{ cm/s}$  at  $3.2 \times 10^{14} \text{ cm}^{-3}$  injection.

### 3.4. Orientation dependence

The final experiment was performed to assess the efficacy of I-E passivation on (111)-orientation silicon and to compare the results to superacid-derived passivation on the same material. A wafer from Set C was initially cleaned (RCA 1 and RCA 2) prior to a planar etch (30 minutes). The sample was then dipped in HF followed by an RCA 1 clean. The sample was the passivated with I-E solution and was characterised. The I-E passivation was removed in methanol, before the sample was re-cleaned (RCA 1 and RCA 2). The same sample was then passivated with the standard superacid-derived passivation, and then was re-characterised. Lifetime was also measured on another (111)-orientation sample from the same wafer by immersion in a superacid-based solution of TFSI-hexane for 390 minutes.

Figure 5 shows the injection-dependent lifetime results for the (111)-orientation silicon. Figure 5 (a) shows the lifetime is considerably higher with I-E passivation than with superacid-derived passivation, and for the latter better passivation is achieved when the sample is immersed in the solution rather than removed from the solution and dried. At an excess carrier density of  $10^{15} \text{ cm}^{-3}$  the effective lifetime is 12.6 ms with I-E, compared to 2.4 ms with the immersion method and 590  $\mu\text{s}$  with the standard drying method. Also shown on Figure 5 (a) is the manufacturer's estimate of bulk lifetime at ingot level. This was measured using a Napson photoconductance decay system with laser excitation to be in the range 30 ms to 50 ms.

Figure 5 (b) and 5 (c) show PL images of the same sample passivated with I-E and the standard superacid-derived method. The I-E method gives relatively uniform passivation, whereas the standard superacid-derived method is better passivated at the bottom than the top. We link this gradient in passivation results from the way in which the sample was removed from the superacid-containing solution, as shown by the arrow on Figure 5 (c). This is discussed later. It is not possible to perform PL experiments on samples immersed in superacid-based solutions as we are unable to perform PL measurements in the glovebox.

## 4. Discussion

### 4.1 Sample processing issues

Our surface preparation results (Figure 1 and Figure 2) highlight the need to pre-prepare the sample surface in order to achieve the highest possible levels of passivation with I-E. Our as-received samples had probably been subjected to some sort of alkaline etch by the manufacturer, as suggested by the optical micrograph in Figure 2. Better lifetimes were achieved when these samples were cleaned prior to an HF dip, as expected from earlier studies.<sup>[30, 31]</sup> Subjecting the samples to etching further improved the lifetimes. The choice of

specific cleaning process seems to be relatively unimportant, with all cleaning sequences improving the lifetime relative to the as-received state.

The time dependence of passivation we observe (Figure 3(b)) is consistent with established mechanisms for I-E passivation. Our understanding is the Si-H bonds on hydrogen-terminated silicon surface after the HF dip are broken, with iodine then forming Si-I bonds.<sup>[8, 32]</sup> In the I-E solution, the iodine exists as I<sub>2</sub>, so these dimers must be dissociated in order to passivate the surface. This dissociation is achieved by illumination<sup>[32, 33]</sup> and so the time dependence we observe is most likely due to the short flashes from the lifetime tester dissociating the iodine dimers to enable improved surface passivation.

#### 4.2 Surface recombination velocities

By using wafers with variable thickness (assumed to have the same bulk lifetime) and the latest calibration for thick wafers, we have obtained a robust measurement of the surface recombination velocity,  $S$ , as  $6.5 \pm 0.3$  cm/s in 3–5  $\Omega\text{cm}$   $n$ -type silicon at  $10^{15}$  cm<sup>-3</sup> injection (Figure 4 (b)). The lowest value we measure is  $4.4 \pm 0.2$  cm/s at  $3.2 \times 10^{14}$  cm<sup>-3</sup> injection (Figure 4 (c)). Thickness-variation studies such as ours are performed only rarely in the literature. Such a study by Chen *et al.* using microwave photoconductance decay found  $S$  to be 5.2 cm/s in 1.7–13  $\Omega\text{cm}$  (100)-orientation  $n$ -type silicon.<sup>[22]</sup> Many other studies assume an infinite bulk lifetime, and consequently can only provide an upper limit for  $S$ . Stephens and Green studied a range of polarities and resistivities and determined the lowest upper-limit of  $S$  as 5.6 cm/s for 100  $\Omega\text{cm}$   $p$ -type silicon, with 7.9 cm/s found for 100  $\Omega\text{cm}$   $n$ -type silicon.<sup>[18]</sup> Horányi *et al.* estimate  $S < 10$  cm/s for 25  $\Omega\text{cm}$   $n$ -type (111)-orientation silicon.<sup>[15]</sup> Maekawa and Shima fit a value of  $S$  in the wide range 0.3–5.5 cm/s for 6.7  $\Omega\text{cm}$   $n$ -type (100)-orientation silicon.<sup>[17]</sup> Our results are consistent with the findings of these other studies for which the injection dependence is usually not reported. We also note that the increase in  $S$

with injection level is consistent with that found for dielectric passivation schemes such as  $\text{Al}_2\text{O}_3$ <sup>[34]</sup>.

For the (111)-orientation silicon results, we can use Equation 1 to determine  $S$  at an excess carrier concentration of  $10^{15} \text{ cm}^{-3}$ , with the known value of thickness (360  $\mu\text{m}$ ), manufacturer's bulk lifetime (30–50 ms), and effective lifetime (12.6 ms). This gives  $S$  in the range 0.8–1.1 cm/s, without correcting for possible surface area effects. Even if the manufacturer's bulk lifetime were an underestimate, we note that  $S$  would only be 1.4 cm/s if the bulk lifetime were infinite. Thus, I-E passivation is extremely effective at passivating (111)-orientation silicon surfaces. This is particularly impressive given the relatively higher recombination centre densities of (111)-orientation surfaces compared to (100)-orientations.<sup>[35]</sup>

### 4.3 Limitations of superacid-derived passivation

Our results, such as those in Figure 3 (a), clearly demonstrate that superacid-derived passivation is superior to I-E on (100)-orientation surfaces. It is therefore surprising that it is considerably less effective than I-E on (111)-orientation surfaces (Figure 5). With superacid-derived passivation on (111)-orientation surfaces, the level of passivation depends on how the sample was removed from the passivating solution with side of the sample removed first being less well passivated. It appears that the superacid-derived passivation solution does not wet the (111)-orientation particularly well. To overcome this, we tried immersing the sample in a superacid-based solution. This improved the passivation, but the level of passivation achieved was still well below that of I-E. With the superacid-derived immersion passivation, the 410  $\mu\text{m}$  thick sample gave an effective lifetime of 2.4 ms at an excess carrier density of  $10^{15} \text{ cm}^{-3}$ , which implies an  $S$  of 7.8–8.2 cm/s based on the manufacturer's bulk lifetime range, or 8.5 cm/s based on infinite bulk lifetime. For standard superacid-derived passivation,

$S$  is considerably higher than this, but given the lack of uniformity in the passivation it is not possible to calculate this accurately.

It is noted that passivation schemes other than the superacid-derived one are more, rather than less, effective on (111)- compared to (100)-orientations. As far as we are aware, for HF passivation, the lowest reported  $S$  is 0.25 cm/s.<sup>[9]</sup> This is for a (111)-orientation surface, with the same study reporting recombination at (100) surfaces to be 50% faster.<sup>[9]</sup> Our analysis in this paper for (111)-orientation silicon also shows I-E to be more effective on (111)-orientations. It is not currently clear to us why superacid-derived passivation performs differently to other passivation schemes in this respect. Confirming the work by Bullock *et al.*,<sup>[11]</sup> superacid-derived passivation in its current form is not suitable for reliable lifetime measurements on mc-Si wafers used for photovoltaics.

## 5. Conclusions

We have studied the temporary passivation of  $n$ -type float-zone silicon surfaces by I-E solutions. By using a thorough surface preparation and cleaning procedure it is possible to measure effective lifetimes of several milliseconds, with up to ~8 ms measured in ~640  $\mu\text{m}$  thick 5  $\Omega\text{cm}$  (100)-orientation silicon, and up to ~17 ms measured in 360  $\mu\text{m}$  thick 60  $\Omega\text{cm}$  (111)-orientation silicon. Using variable thickness 3–5  $\Omega\text{cm}$  (100)-orientation wafers with a bulk lifetime of ~46 ms, we determine the surface recombination velocity for the I-E scheme as  $6.5 \pm 0.3$  cm/s at the commonly used  $10^{15}$   $\text{cm}^{-3}$  injection level, with a lower value of  $4.4 \pm 0.2$  cm/s measured at  $3.2 \times 10^{14}$   $\text{cm}^{-3}$  injection. I-E passivation is demonstrated to be superior to superacid-derived passivation on (111)-orientation substrates, even when lifetimes are measured with the samples fully immersed in the superacid-based solutions. I-E passivation therefore provides a practical way of measuring fairly high carrier lifetimes in silicon wafers, and is particularly good for (111)-orientation substrates.

## Supporting Information

Data published in this article can be freely downloaded from <https://wrap.warwick.ac.uk> (full link to be provided upon article's acceptance).

## Acknowledgements

The work was supported by the EPSRC SuperSilicon PV project (EP/M024911/1), the EPSRC Impact Acceleration Account (EP/R511808/1), and an EPSRC First Grant (EP/J01768X/2). A.I. Pointon is the recipient of an EPSRC studentship (EP/N509796/1). Sune Bro Duun of Topsil Semiconductor Materials is gratefully acknowledged for provision of the FZ-Si wafers with variable thickness from the same ingot and with (111)-orientation. Lachlan Black of the Australian National University is thanked for recalibrating our lifetime tester for measurements of thick samples.

Received: 2<sup>nd</sup> April 2019

Revised: 31<sup>st</sup> May 2019

Published online: ((will be filled in by the editorial staff))

## References

1. M. Müller, F. Wolny, G. Fischer, A. Krause, P. Palinginis, H. Neuhaus, "Change of the bulk carrier lifetime of high quality silicon wafers during PERC solar cell processing". *35th European Photovoltaic Solar Energy Conference and Exhibition* (Brussels, Belgium, 2018), pp. 366, doi: 10.4229/35thEUPVSEC20182018-2BO.3.3.
2. R. S. Bonilla, B. Hoex, P. Hamer, P. R. Wilshaw, *Physica Status Solidi A* **2017**, *214*, 1700293.
3. N. E. Grant, V. P. Markevich, J. Mullins, A. R. Peaker, F. Rougieux, D. Macdonald, *Physica Status Solidi Rapid Research Letters* **2016**, *10*, 443.
4. N. E. Grant, V. P. Markevich, J. Mullins, A. R. Peaker, F. Rougieux, D. Macdonald, J. D. Murphy, *Physica Status Solidi A* **2016**, *213*, 2844.
5. M. Al-Amin, J. D. Murphy, *IEEE Journal of Photovoltaics* **2017**, *7*, 68.
6. A. Y. Liu, C. Sun, V. P. Markevich, A. R. Peaker, J. D. Murphy, D. Macdonald, *Journal of Applied Physics* **2016**, *120*, 193103.
7. A. Liu, Z. Hameiri, Y. Wan, C. Sun, D. Macdonald, *IEEE Journal of Photovoltaics* **2019**, *9*, 78.

8. N. E. Grant, J. D. Murphy, *Physica Status Solidi Rapid Research Letters* **2017**, *11*, 1700243.
9. E. Yablonovitch, D. L. Allara, C. C. Chang, T. Gmitter, T. B. Bright, *Physical Review Letters* **1986**, *57*, 249.
10. N. E. Grant, *Journal of Visualized Experiments* **2016**, *107*, e53614.
11. J. Bullock, D. Kiriya, N. Grant, A. Azcatl, M. Hettick, T. Kho, P. Phang, H. C. Sio, D. Yan, D. Macdonald, M. A. Quevedo-Lopez, R. M. Wallace, A. Cuevas, A. Javey, *ACS Applied Materials & Interfaces* **2016**, *8*, 24205.
12. N. E. Grant, T. Niewelt, N. R. Wilson, E. C. Wheeler-Jones, J. Bullock, M. Al-Amin, M. C. Schubert, A. C. van Veen, A. Javey, J. D. Murphy, *IEEE Journal of Photovoltaics* **2017**, *7*, 1574.
13. A. I. Pointon, N. E. Grant, E. C. Wheeler-Jones, P. P. Altermatt, J. D. Murphy, *Solar Energy Materials & Solar Cells* **2018**, *183*, 164.
14. Y. Wang, J. D. Murphy, P. R. Wilshaw, *Journal of the Electrochemical Society* **2010**, *157*, H884.
15. T. S. Horányi, T. Pavelka, P. Tüttö, *Applied Surface Science* **1993**, *63*, 306.
16. H. M'saad, J. Michel, J. J. Lappe, L. C. Kimerling, *Journal of Electronic Materials* **1994**, *23*, 487.
17. T. Maekawa, Y. Shima, *Japanese Journal of Applied Physics* **1996**, *35*, L133.
18. A. W. Stephens, M. A. Green, *Solar Energy Materials & Solar Cells* **1997**, *45*, 255.
19. N. Batra, Vandana, S. Kumar, M. Sharma, S. K. Srivastava, P. Sharma, P. K. Singh, *Solar Energy Materials & Solar Cells* **2012**, *100*, 43.
20. M. Ju, Y. Lee, K. Lee, C. Han, Y. Jo, J. Yi, *Japanese Journal of Applied Physics* **2012**, *51*, 09MA03.
21. K. L. Pollock, J. Junge, G. Hahn, *IEEE Journal of Photovoltaics* **2012**, *2*, 1.
22. J. Chen, L. Zhao, H. Diao, B. Yan, S. Zhou, Y. Tang, W. Wang, *Advanced Materials Research* **2013**, *652-654*, 901.
23. B. Sopori, S. Devayajanam, P. Basnyat, V. Mehta, H. Moutinho, B. Nemeth, V. LaSalvia, S. Johnston, N. M. Ravindra, J. Binns, J. Appel, *MRS Proceedings* **2014**, *1670*, mrss14.
24. M. Al-Amin, J. D. Murphy, *Journal of Applied Physics* **2016**, *119*, 235704.
25. L. E. Black, W. M. M. Kessels, paper presented at the Silicon PV 2019, Leuven, Belgium, 8th April 2019.
26. A. L. Blum, J. S. Swirhun, R. A. Sinton, F. Yan, S. Herasimenka, T. Roth, K. Lauer, J. Haunschild, B. Lim, K. Bothe, Z. Hameiri, B. Seipel, R. Xiong, M. Dhamrin, J. D. Murphy, *IEEE Journal of Photovoltaics* **2014**, *4*, 525.
27. T. Niewelt, M. Selinger, N. E. Grant, W. M. Kwapil, J. D. Murphy, M. C. Schubert, *Journal of Applied Physics* **2017**, *121*, 185702.
28. N. E. Grant, F. E. Rougieux, D. Macdonald, J. Bullock, Y. Wan, *Journal of Applied Physics* **2015**, *117*, 055711.
29. A. Richter, S. W. Glunz, F. Werner, J. Schmidt, A. Cuevas, *Physical Review B* **2012**, *86*, 165202.
30. H. M'saad, J. Michel, A. Reddy, L. C. Kimerling, *Journal of the Electrochemical Society* **1995**, *142*, 2833.
31. B. Sopori, P. Rupnowski, J. Appel, V. Mehta, C. Li, S. Johnston, "Wafer preparation and iodine-ethanol passivation procedure for reproducible minority-carrier lifetime measurement". *33rd IEEE Photovoltaic Specialists Conference* (San Diego, CA, USA, 2008), doi: 10.1109/PVSC.2008.4922688.
32. R. T. Mo, T. A. Burr, G. T. Merklin, F. Machuca, P. A. Pianetta, L. C. Kimerling, R. P. Chiarello, C. E. D. Chidsey, "Atomic-Scale Mechanistic Study of Iodine/Alcohol Passivated Si(100)". *196th Meeting of the Electrochemical Society* (Honolulu, HI, USA, 1999), doi: not available.

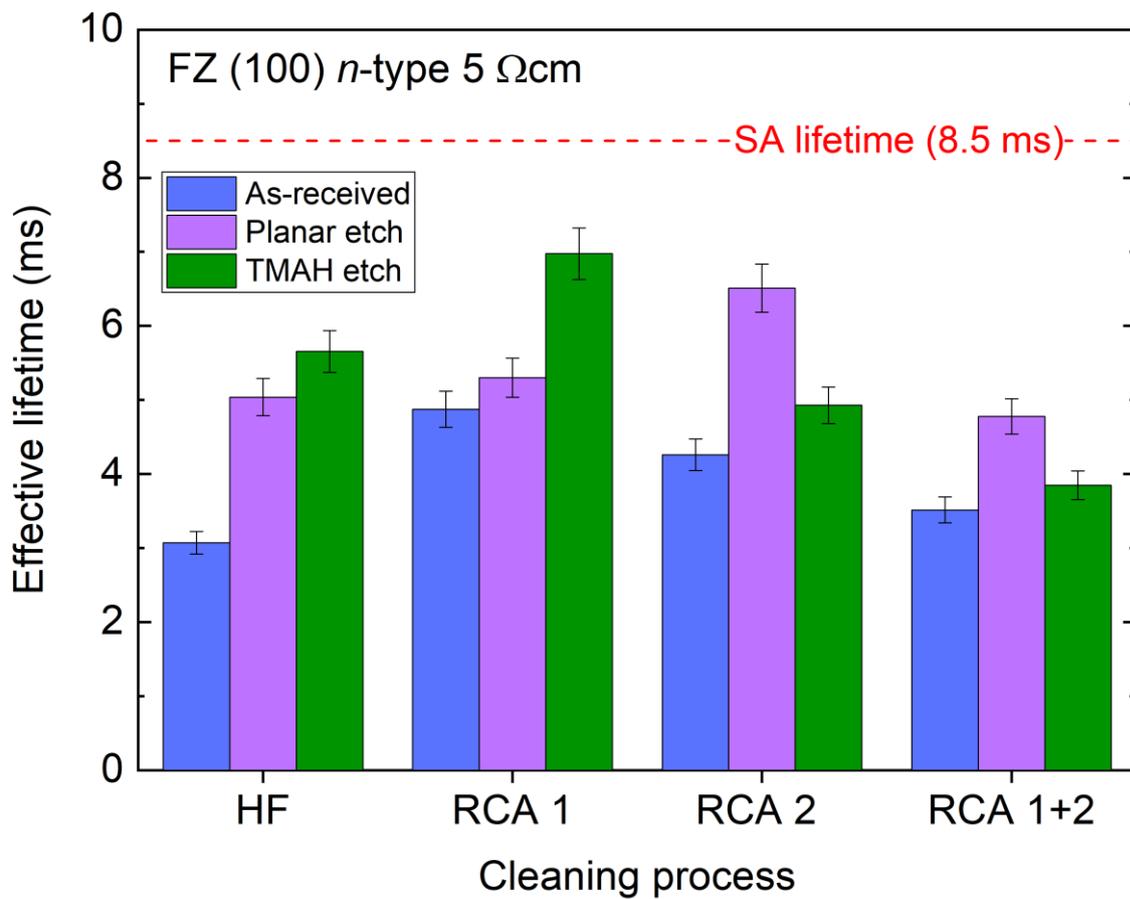
33. W. Cai, Z. Lin, T. Strother, L. M. Smith, R. J. Hamers, *Journal of Physical Chemistry B* **2002**, *106*, 2656.
34. K. R. McIntosh, L. E. Black, *Journal of Applied Physics* **2014**, *116*, 014503.
35. S. C. Baker-Finch, K. R. McIntosh, *IEEE Journal of Photovoltaics* **2011**, *1*, 59.

Sample Set	Orientation	Resistivity [ $\Omega\text{cm}$ ]	As-received thickness [ $\mu\text{m}$ ]	Etched thickness [ $\mu\text{m}$ ]
A	(100)	5	740	630–650
B	(100)	3–5	240–1,510	230–1,490
C	(111)	60	440	360–410

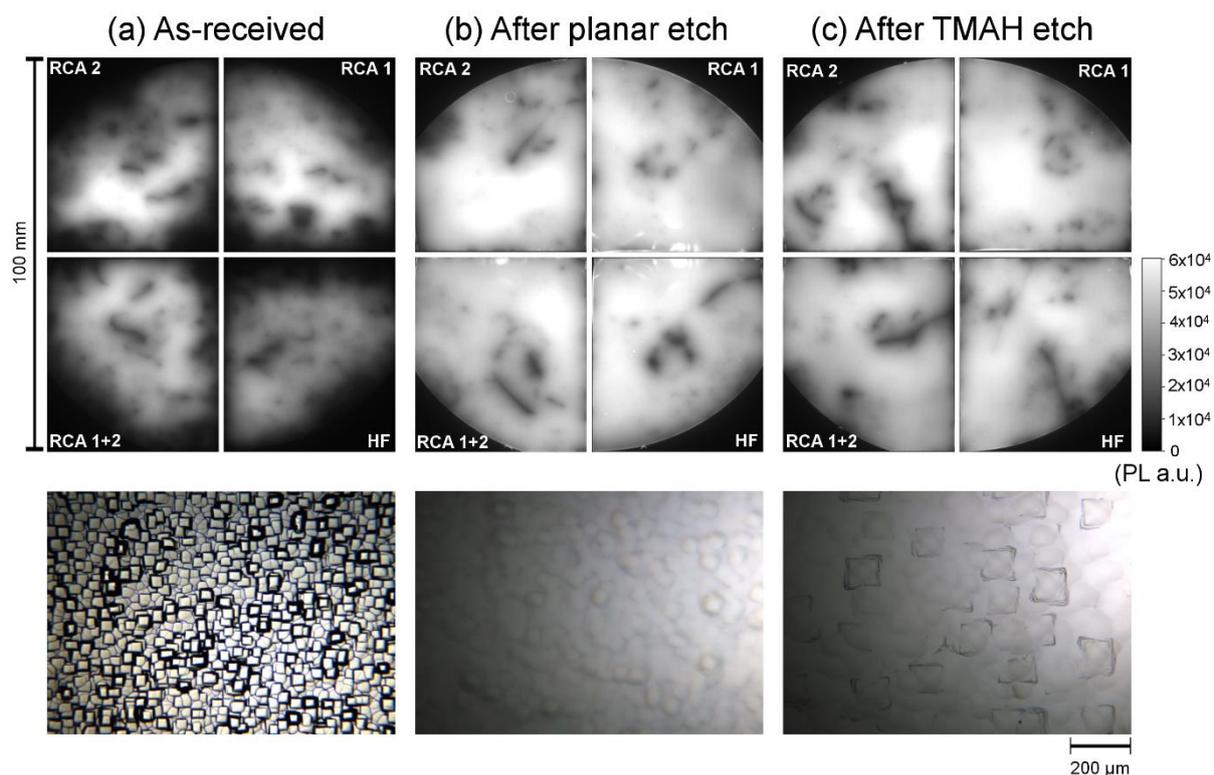
**Table 1.** Details of the three samples sets studied. All samples were *n*-type and were grown by the float-zone method.

Process	Chemicals	Conditions
HF dip	HF (10%)	Room temperature for 1 minute.
RCA 1 clean	H <sub>2</sub> O, H <sub>2</sub> O <sub>2</sub> (30% aq.), NH <sub>4</sub> OH (30% aq.) (5:1:1)	~80 °C for 10 minutes.
RCA 2 clean	H <sub>2</sub> O, H <sub>2</sub> O <sub>2</sub> (30% aq.), HCl (37% aq.) (5:1:1)	~80 °C for 10 minutes.
Planar etch	HF (50% aq.), HNO <sub>3</sub> (69% aq.), CH <sub>3</sub> COOH (100%) (8:75:17)	Room temperature.
TMAH etch	N(CH <sub>3</sub> ) <sub>4</sub> <sup>+</sup> OH <sup>-</sup> (25% aq.)	~80 °C.

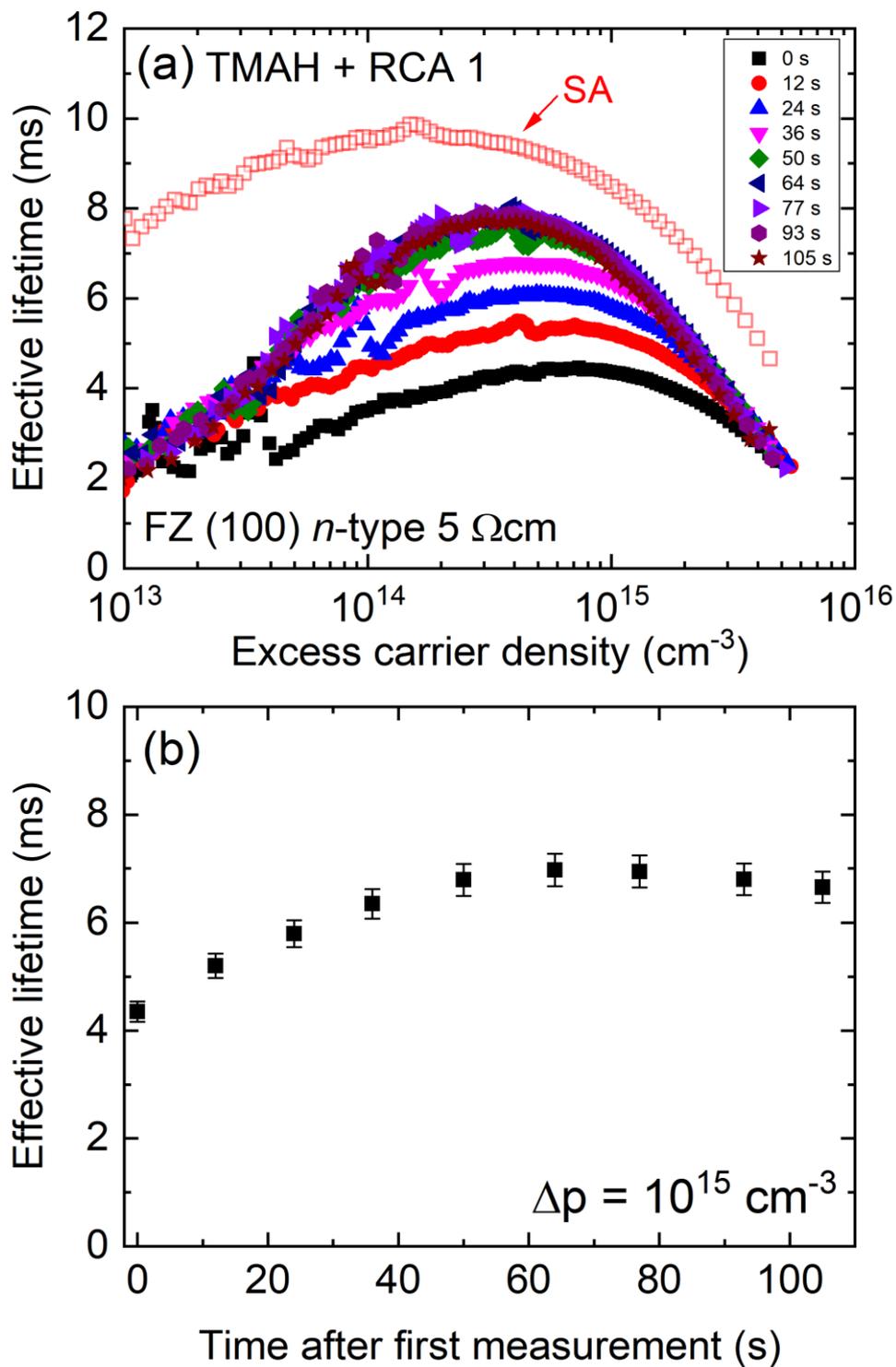
**Table 2.** Chemical pre-treatments used to prepare the samples for I-E passivation.



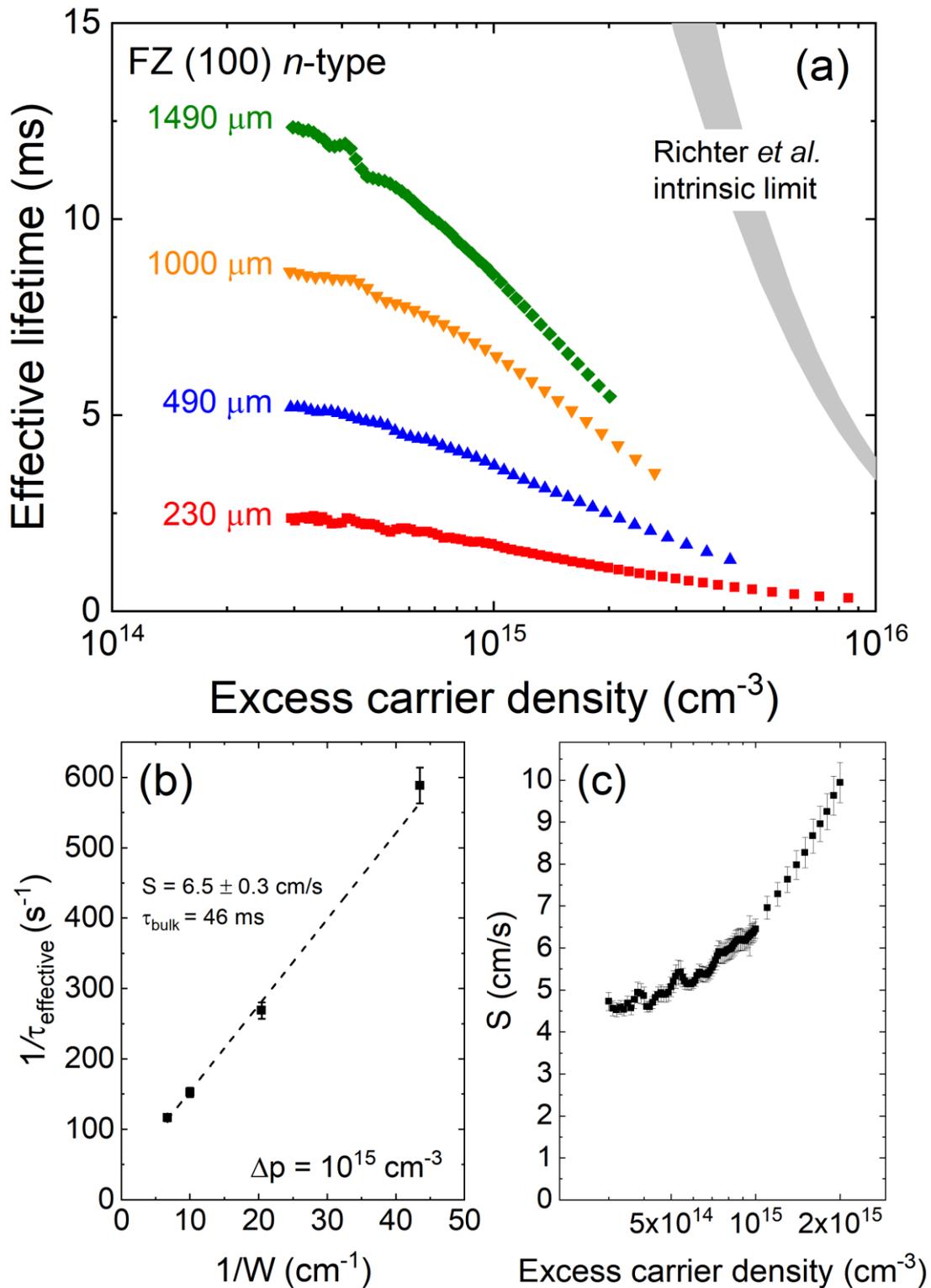
**Figure 1.** Effective lifetime of 5 Ωcm *n*-type (100)-orientation float-zone silicon samples (Set A) at an excess carrier density of  $10^{15} \text{ cm}^{-3}$  subjected to I-E passivation after different cleaning processes. For each cleaning process lifetimes were measured in the as-received state, after a planar silicon etch, and after a TMAH etch. The lifetime measured with standard superacid-derived passivation (“SA lifetime”) is shown as a horizontal dashed line.



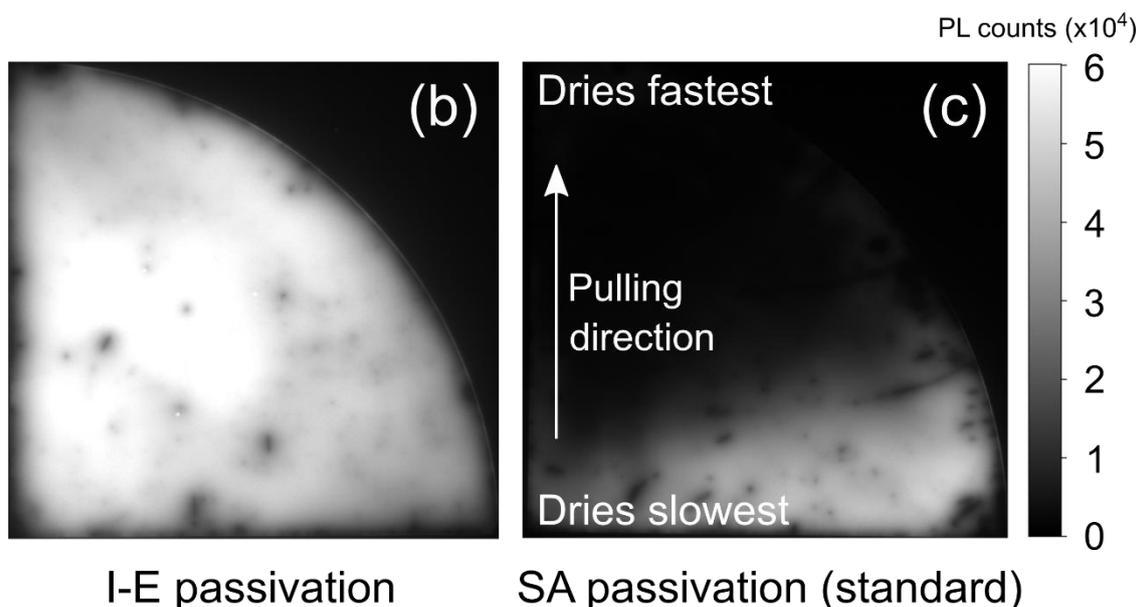
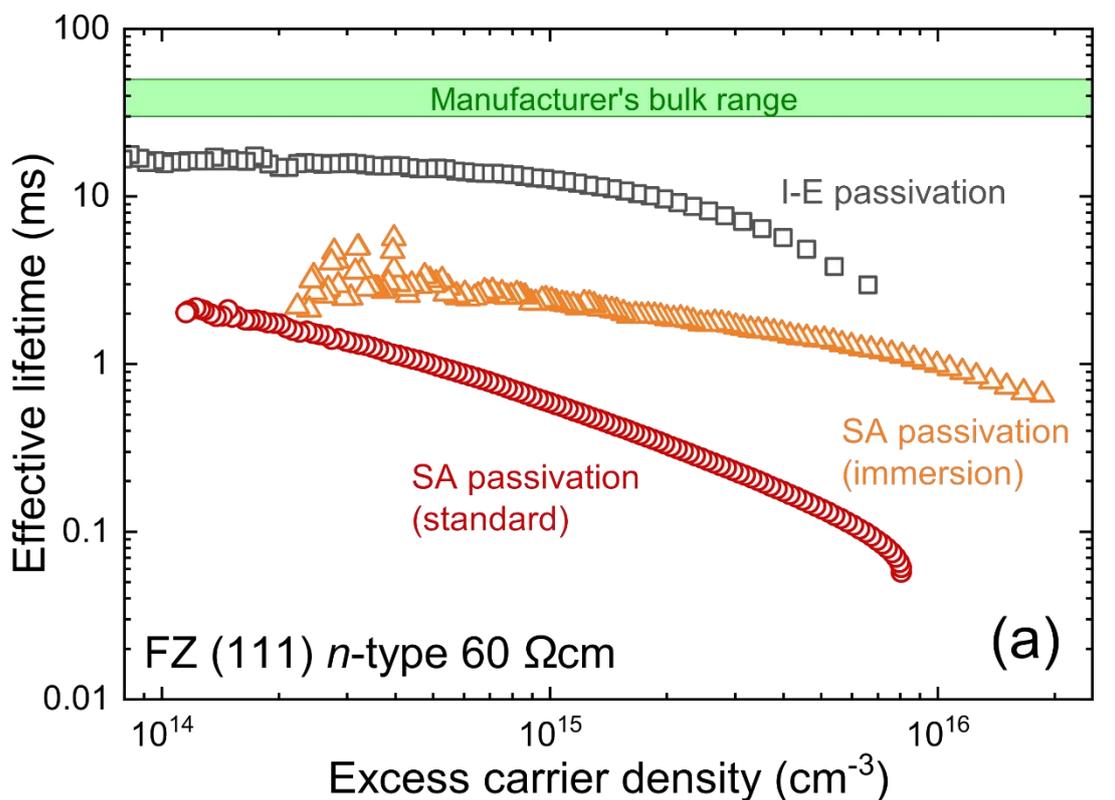
**Figure 2.** Uncalibrated photoluminescence images and optical micrographs for different sample preparation and pre-cleaning processes. All the results in this figure come from the same (100)-orientation silicon wafer from Set A.



**Figure 3.** (a) Injection-dependent lifetime measurement in *n*-type float-zone (100)-orientation silicon from Set A passivated with I-E after TMAH etching and an RCA 1 cleaning sequence. The lifetime was measured at different times after the first measurement. Also shown is the lifetime on the same sample with superacid-derived passivation (“SA”). (b) Effective lifetime at an excess carrier density of  $10^{15} \text{ cm}^{-3}$  for I-E passivated results plotted in (a).



**Figure 4.** (a) Injection-dependent effective lifetime in variable thickness *n*-type float-zone (100)-orientation silicon from Set B passivated with I-E. The intrinsic lifetime limit according to Richter *et al.*<sup>[29]</sup> is also shown. (b) A plot in accordance with Equation 1 to determine the surface recombination velocity and bulk residual lifetime from the data in (a) at an excess carrier concentration of  $10^{15}$  cm<sup>-3</sup>. (c) A plot to show the variation of surface recombination velocity with excess carrier concentration from the data in (a).



**Figure 5.** (a) Injection-dependent effective lifetime for *n*-type float-zone (111)-orientation silicon from Set C passivated with I-E and the superacid-derived (SA) scheme. Two curves are shown for SA passivation: one with the standard method and the other in which the lifetime was measured with the sample immersed in the superacid-based solution. The bulk lifetime range from the manufacturer is also shown as a horizontal band. (b) Uncalibrated PL image for an I-E passivated wafer quarter with a radius of 50 mm. (c) Uncalibrated PL image for the same wafer quarter as in (b) subjected to the standard superacid-derived passivation scheme. The approximate direction in which the sample was removed from the passivating solution is indicated.

**Table of contents entry (50 to 60 words)**

Keyword: Silicon

M. Al-Amin, N.E. Grant, A.I. Pointon, J.D. Murphy\*

**Title:** Iodine-ethanol surface passivation for measurement of millisecond carrier lifetimes in silicon wafers with different crystallographic orientations

Excellent passivation of silicon surfaces is achieved via optimization of an iodine-ethanol scheme. A robust method based on samples with different thicknesses cut from the same float-zone ingot is used to determine a lowest surface recombination velocity of 4.4 cm/s for (100)-orientation silicon. Iodine-ethanol is demonstrated to be superior to superacid-derived passivation for (111)-orientation silicon surfaces.

ToC figure (55 mm broad × 50 mm high):