

Video Article

Light Enhanced Hydrofluoric Acid Passivation: A Sensitive Technique for Detecting Bulk Silicon Defects

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Keywords: Engineering, Issue 107, Bulk lifetime, defects, hydrofluoric acid, illumination, passivation, photoconductance, recombination.

Date Published: 1/4/2016

Citation: Grant, N.E. Light Enhanced Hydrofluoric Acid Passivation: A Sensitive Technique for Detecting Bulk Silicon Defects. *J. Vis. Exp.* (107), e53614, doi:10.3791/53614 (2016).

Abstract

A procedure to measure the bulk lifetime ($>100 \mu\text{sec}$) of silicon wafers by temporarily attaining a very high level of surface passivation when immersing the wafers in hydrofluoric acid (HF) is presented. By this procedure three critical steps are required to attain the bulk lifetime. Firstly, prior to immersing silicon wafers into HF, they are chemically cleaned and subsequently etched in 25% tetramethylammonium hydroxide. Secondly, the chemically treated wafers are then placed into a large plastic container filled with a mixture of HF and hydrochloric acid, and then centered over an inductive coil for photoconductance (PC) measurements. Thirdly, to inhibit surface recombination and measure the bulk lifetime, the wafers are illuminated at 0.2 suns for 1 min using a halogen lamp, the illumination is switched off, and a PC measurement is immediately taken. By this procedure, the characteristics of bulk silicon defects can be accurately determined. Furthermore, it is anticipated that a sensitive RT surface passivation technique will be imperative for examining bulk silicon defects when their concentration is low ($<10^{12} \text{ cm}^{-3}$).

Video Link

The video component of this article can be found at <http://www.jove.com/video/53614/>

Introduction

High lifetime ($>1 \text{ msec}$) monocrystalline silicon is becoming ever more important for high efficiency solar cells. Understanding the recombination characteristics of embedded impurities has been, and remains an important topic. One of the most widely used techniques to examine the recombination activity of grown-in defects is by a photoconductance method¹. By this technique it is often difficult to completely separate surface from bulk recombination, thus making it difficult to examine the recombination characteristics of grown-in defects. Fortunately there exist several dielectric films which can achieve very low effective surface recombination velocities (S_{eff}) of $< 5 \text{ cm/sec}$, and thus effectively inhibit surface recombination. These are, silicon nitride ($\text{SiN}_x\text{:H}$)², aluminum oxide (Al_2O_3)³ and amorphous silicon (a-Si:H)⁴. The deposition and annealing temperatures ($\sim 400 \text{ }^\circ\text{C}$) of these dielectric films are considered to be low enough not to permanently deactivate the recombination activity of the grown-in defects. Examples of this are the iron-boron⁵ and boron oxygen⁶ defects. However, recently it was found that vacancy-oxygen and vacancy-phosphorus defects in *n*-type Czochralski (Cz) silicon can be completely deactivated at temperatures of $250\text{-}350 \text{ }^\circ\text{C}$ ^{7,8}. Similarly a defect in float-zone (FZ) *p*-type silicon was found to deactivate at $\sim 250 \text{ }^\circ\text{C}$ ⁹. Therefore, conventional passivation techniques such as plasma enhanced chemical vapor deposition (PECVD) and atomic layer deposition (ALD) may not be suitable for inhibiting surface recombination to examine grown-in bulk defects. Furthermore, $\text{SiN}_x\text{:H}$ and a-Si:H films have been shown to deactivate bulk silicon defects through hydrogenation^{10,11}. Therefore to examine the recombination activity of grown-in defects, a RT surface passivation technique would be ideal. Wet chemical surface passivation fulfils this requirement.

In the 1990s Horanyi *et al.* demonstrated that immersion of silicon wafers in iodine-ethanol (I-E) solutions provides a means to passivate silicon wafers, achieving $S_{\text{eff}} < 10 \text{ cm/sec}$ ¹². In 2007 Meier *et al.* showed that iodine-methanol (I-M) solutions can reduce the surface recombination to 7 cm/sec ¹³, while in 2009 Chhabra *et al.* demonstrated that S_{eff} of 5 cm/sec can be attained by immersing silicon wafers in quinuhydrone-methanol (Q-M) solutions^{14,15}. Despite the excellent surface passivation achieved by I-E, I-M and Q-M solutions, they do not provide adequate surface passivation ($S_{\text{eff}} < 5 \text{ cm/sec}$) to measure the bulk lifetime of high purity silicon wafers.

Another means to achieve a high level of surface passivation is by immersing silicon wafers in HF acid. The notion of using HF to passivate silicon wafers was first introduced by Yablonavitch *et al.* in 1986, who demonstrated a record low S_{eff} of $0.25 \pm 0.5 \text{ cm/sec}$ ¹⁶. Although excellent surface passivation was attained on high resistivity wafers, we have found the technique to be non-repeatable, thus adding a large uncertainty to the lifetime measurement. Therefore to limit the uncertainty by consistently achieving a very low S_{eff} ($\sim 1 \text{ cm/sec}$), we have developed a new HF passivation technique that incorporates three critical steps, (i) chemically cleaning and etching of silicon wafers, (ii) immersion in a 15% HF solution and (iii) illumination for 1 min^{17,18}. This procedure is both simple and time efficient in comparison to the traditional PECVD and ALD deposition techniques listed above.

Protocol

1. Experimental Setup

1. Locate a suitable fume hood for the measurement technique, and remove any irrelevant equipment to allow better air flow and reduce cluttering. **Do not use any chemicals** other than hydrofluoric acid (HF) in the fume hood.
2. Test the quality of the deionized (DI) water from the tap within the fume hood using a conductivity meter. Ensure that the DI water has a conductance of at most $0.055 \mu\text{S}/\text{cm}$ at a temperature of 20°C .
3. Place a minority carrier lifetime tester into the fume hood. Connect the cables to a computer, which is situated on a table outside of the fume hood.
4. Switch on the computer and lifetime tester. Open the lifetime tester file on the computer and click the 'measure' button to ensure correct communication between computer and the lifetime tester. The light source on the lifetime tester should flash if the computer and tester have been connected correctly.
5. Place a halogen lamp inside the fume hood. Position the lamp such that it can illuminate the lifetime tester stage where the sample will be located.
6. Connect the halogen lamp to a power source which should be situated outside of the fume hood. When the halogen lamp is switched on, its intensity should be at least $0.02 \text{ W}/\text{cm}^2$ on the lifetime tester stage.

2. Preparing the 15% HF Solution

Note: HF is a dangerous chemical and must be treated with care. It causes slow, sustained, and deep damage to the body following exposure. HF does not readily burn the skin like other acids - rather it absorbs quickly into the skin and causes deep blistering and damage to bones. This means that bones become brittle and blistered as the fluorine reacts with calcium. HF also binds with free calcium which is used in nerve regulation and osmotic cell balance, so binding of free calcium in the body can be fatal. **It is paramount that the user follows laboratory safety protocols when using HF, and ensures they know the location of the HF first aid kit and hexafluorine (or calcium gluconate gel).**

1. Place a **chemically cleaned** round plastic container (H: 55 mm, D: 170 mm) into the fume hood (same as in Section 1). The container **must** have a clear plastic lid. See Section 6 on how to chemically clean the container prior to use.
2. Clear the area around the plastic container in the fume hood so the HF solution can be prepared without any obstructions nearby.
3. Apply all personal protection equipment (PPE).
4. CAUTION: Add 50 ml of HF to 100 ml DI water (H_2O) in the container.
5. CAUTION: Add 20 ml of hydrochloric acid (HCl) to the container and mix the $\text{H}_2\text{O} : \text{HF} : \text{HCl}$ solution using plastic tweezers. Rinse the tweezers thoroughly afterwards.
6. CAUTION: Place the lid on the plastic container and allow the solution to settle for 1 hr. During this time, HF fumes will condense on the lid.
7. Adequately label the container, and make it clear that it contains HF.
Note: The HF solution will last 1-2 months with heavy usage. Therefore there is no need to replace the solution each time a measurement is to be performed.

3. Calibration of the Lifetime Tester

1. Locate at least 6 silicon wafers of known resistivity and conductance. Ideally the resistivity range should span $0.1\text{-}100 \Omega\text{-cm}$.
2. On the computer, open the lifetime tester calibration file. Enter the resistivity of each wafer in the table and then click 'Update # of wafers'.
3. Click the 'Get data' button in the calibration file and enter the details of the lifetime tester.
4. Apply all necessary PPE.
5. CAUTION: Place the plastic container filled with the HF solution on the lifetime tester stage and position it over the inductive coil (blue circle region).
6. When prompted to measure the 'air voltage' on the computer, measure the voltage of the HF solution by clicking the 'Ok' button. In this case, the air has been replaced by the conductance of the HF solution.
7. CAUTION: Carefully remove the container filled with HF from the stage and place it on the fume hood bench. Carefully remove the lid.
8. CAUTION: When the lid has been removed from the container, immerse the first silicon wafer into the HF solution using plastic tweezers. Place the lid back on the container.
9. CAUTION: Place the plastic container back onto the lifetime tester stage and position it over the inductive coil. Ensure the silicon wafer is centered over the coil (blue circle region).
10. When prompted to measure the 'sample voltage' on the computer, click the 'Ok' button once again. Remove the container from the stage and place it on the fume hood bench.
11. CAUTION: Carefully remove the silicon wafer from the HF solution using plastic tweezers and rinse the wafer in the dedicated rinse beakers. Do a final rinse under the tap in the fume hood.
12. CAUTION: Place the lid back onto the container, and position the container back onto the lifetime tester stage.
13. Repeat steps 3.6 to 3.12 until all samples have been measured.
14. Once all of the samples have been measured, click the 'Fit data' button in the calibration file. This will fit a parabolic curve to the measured data and provide calibration coefficients A, B and C which are specific to this setup.
15. On the computer, open the lifetime tester file and click on the 'settings' tab. Enter in the new calibration coefficients A, B and C for the HF setup. Save the file under a new name.
Note: The HF setup only requires a calibration every 6 months. Therefore there is no need to calibrate the setup each time a measurement is to be performed.

4. Wet Chemical Treatment of Silicon Wafers Prior to Measuring

1. Prepare standard clean 1 (SC 1).
 1. CAUTION: In an alkaline allocated fume hood, add 185 ml of ammonium hydroxide (NH_4OH) to 1,295 ml of DI water in a 2 L glass beaker.
 2. CAUTION: Place the beaker onto a hot plate and heat the $\text{H}_2\text{O} : \text{NH}_4\text{OH}$ solution to a temperature of $\sim 50^\circ\text{C}$. Use a watch glass to cover the beaker.
 3. CAUTION: Once the $\text{H}_2\text{O} : \text{NH}_4\text{OH}$ solution has reached a temperature of $\sim 50^\circ\text{C}$, add 185 ml of hydrogen peroxide (H_2O_2) and continue to heat until the temperature reaches $\sim 75^\circ\text{C}$. This $\text{H}_2\text{O} : \text{NH}_4\text{OH} : \text{H}_2\text{O}_2$ solution is known as **SC 1**.
Note: SC 1 should be changed daily to effectively clean silicon wafers.
2. Prepare standard clean 2 (SC 2).
 1. CAUTION: In an acid allocated fume hood, add 185 ml of HCl to 1,295 ml of DI water in a 2 L glass beaker.
 2. CAUTION: Place the beaker onto a hot plate and heat the $\text{H}_2\text{O} : \text{HCl}$ solution to a temperature of $\sim 50^\circ\text{C}$. Use a watch glass to cover the beaker.
 3. CAUTION: Once the $\text{H}_2\text{O} : \text{HCl}$ solution has reached a temperature of $\sim 50^\circ\text{C}$, add 185 ml of H_2O_2 and continue to heat until the temperature reaches $\sim 75^\circ\text{C}$. This $\text{H}_2\text{O} : \text{HCl} : \text{H}_2\text{O}_2$ solution is known as **SC 2**.
Note: Change SC 2 daily to effectively clean silicon wafers.
3. Prepare the silicon etching solution.
 1. In an alkaline allocated fume hood, add 1,600 ml of tetramethylammonium hydroxide (TMAH) to a **chemically clean** 2 L glass beaker. Please see Section 6 on how to chemically clean the beaker prior to use.
 2. Place the beaker onto a hot plate and heat the TMAH solution to a temperature of $\sim 85^\circ\text{C}$. Use a watch glass to cover the beaker.
Note: The TMAH solution will not need changing until it starts to crystallize, *i.e.*, after 1 month.
4. Perform the wet chemical treatment.
 1. Load samples into a quartz cradle and place them in a communal HF solution in the lab. The concentration is not critical.
 2. After ~ 10 sec or once the samples become hydrophobic (pull dry), remove the cradle from the HF solution and rinse using 3 beakers filled with DI water.
 3. Transport the cradle of wafers to the fume hood where SC 1 has been prepared. When SC 1 has stabilized at $\sim 75^\circ\text{C}$, slowly immerse the cradle of wafers into SC 1.
 4. Clean the wafers in SC 1 for 10 min.
 5. After 10 min has elapsed, remove the cradle of wafers from SC 1 and rinse them using three 2 L glass beakers filled with DI water. **Chemically clean** these glass beakers prior to filling them with DI water. Please see Section 6 on how to chemically clean the beakers.
 6. After rinsing, place the samples into a HF solution which is dedicated only for post SC 1 processing. The concentration is not critical.
 7. After ~ 10 sec or once the samples become hydrophobic (pull dry), remove the cradle from the HF solution and rinse using 3 beakers filled with DI water. Use the same beakers as in step 4.4.5.
 8. Transport the cradle of wafers to the fume hood where SC 2 has been prepared. When SC 2 has stabilized at $\sim 75^\circ\text{C}$, slowly immerse the cradle of wafers into SC 2.
 9. Clean the wafers in SC 2 for 10 min.
 10. After 10 min has elapsed, remove the cradle of wafers from SC 2 and rinse them using 3 beakers filled with DI water. Use the same beakers as in step 4.4.5.
Note: The cradle of wafers could be stored in one of the rinse beakers filled with DI water until the following day.
 11. After rinsing, place the samples into a HF solution which is dedicated only for post SC 2 processing. The concentration is not critical.
 12. After ~ 10 sec or once the samples become hydrophobic (pull dry), remove the cradle from the HF solution and rinse using 3 beakers filled with DI water. Use the same beakers as in step 4.4.5.
 13. Transport the cradle of wafers to the fume hood where the TMAH solution has been prepared. When the TMAH solution has stabilized at $\sim 85^\circ\text{C}$, slowly immerse the cradle of wafers into the TMAH solution.
 14. Etch the wafers in TMAH for 5 min. This will remove $\sim 5 \mu\text{m}$ of silicon.
 15. After 5 min has elapsed, remove the cradle of wafers from the TMAH solution and rinse them using 3 beakers filled with DI water. Use the same beakers as in step 4.4.5. More than 3 rinses might be required as TMAH is quite 'sticky'.
 16. Transport the cradle of wafers in DI water to the fume hood where the experiment has been setup. See section 1.1.
 17. Measure the prepared silicon wafers within 2 hr after step 4.4.16.

5. Measurement Procedure

1. Apply all necessary PPE.
2. Fill two 2 L plastic beakers with DI water and place them in the fume hood. These will be used for rinsing the silicon samples post measurement.
3. Place plastic tweezers into an empty 500 ml plastic beaker and place inside the fume hood near the rinse beakers. These tweezers will be used to handle the silicon samples.
4. On the computer, open the lifetime tester file. Make sure the file contains the correct calibration coefficients for the HF measurement setup. See section 3.
5. In the lifetime tester file, select the 'Transient' mode. Enter the details of the silicon wafer to be measured, for example, thickness, resistivity and dopant type.
6. CAUTION: Place the container (lid on) filled with HF onto the stage of the lifetime tester and center it over the inductive coil (blue circle region). Let the solution settle for 1 min.
7. On the computer, click on the 'Zero instrument' button in the lifetime tester file. This will measure the voltage of the solution.

Note: Over time, the solution voltage will decrease because the composition of the solution changes with time. Irrespective of this, the HF solution does not show any degradation in its passivating quality, which is why the solution can be used for 1-2 months without being changed.

8. CAUTION: Carefully remove the container from the lifetime tester stage and place it on the fume hood bench.
9. CAUTION: Carefully remove the lid from the container filled with the HF solution. If there is some condensation on the lid, carefully rinse the lid in DI water using the tap in the fume hood.
10. CAUTION: Carefully immerse the first silicon wafer into the HF solution. Using the plastic tweezers, lightly press down on the silicon wafer to ensure it is sitting on the bottom of the container.
11. Rinse the tweezers and place them back into the empty 500 ml plastic beaker.
12. CAUTION: Carefully place the lid back on the container and then place the container on the lifetime tester stage. Ensure the silicon wafer is positioned over the inductive coil (blue circle region).
13. Rinse and dry your gloves. **Remove them before operating the computer.**
14. If the fluorescent light in the fume hood is on, it must be switched off before a measurement is to be conducted. Minimum light is required during the measurement.
15. Switch the halogen lamp on, and ensure it is illuminating the silicon wafer through the lid of the plastic container. Time for 1 min (the exact time is not critical).
16. During the illumination period, click the 'Measure' button in the lifetime file on the computer. A small window labeled 'Taking data' will appear.
17. In the 'Taking data' window, type in a name for the file. Under 'sample averaging' select 10.
18. When the silicon wafer has been illuminated for 1 min, switch the halogen lamp off and **immediately** click the 'Average' button in the 'Taking data' window. The lifetime tester will flash 10 times and average the lifetime measurements.
Note: Once the halogen lamp is switched off, the passivation of the silicon wafer will start to degrade, and thus it is important to measure immediately after illumination to achieve the best results.
19. When the averaging is complete, click the 'Ok' button in the 'Taking data' window.
20. If another measurement is required, repeat steps 5.15-5.18.
21. CAUTION: Once the measurement is complete, remove the container from the lifetime tester stage and place it on the fume hood bench.
22. CAUTION: Carefully remove the lid from the container filled with the HF solution. If there is some condensation on the lid, carefully rinse the lid in DI water using the tap in the fume hood.
23. CAUTION: Carefully remove the silicon wafer from the HF solution using plastic tweezers and rinse the wafer in the dedicated rinse beakers. Do a final rinse under the tap in the fume hood.
24. If more samples are to be measured, repeat steps 5.10-5.23.
25. Once all samples have been measured, ensure the lid is placed on the container and store the HF solution in the fume hood. Make sure the container is adequately labeled.
26. Rinse all beakers and tweezers and store them in their allocated spots in the laboratory.
27. Allow the lifetime tester to remain in the fume hood for 1 hr after use and then remove it from the fume hood.

6. Chemical Cleaning of Beakers and Containers

1. In an alkaline allocated fume hood, prepare an SC 1 solution as outlined in sections 4.1.1-4.1.4.
2. To chemically clean beakers and containers, pour the SC 1 solution into the beakers/containers. The beakers can only be cleaned one at a time.
3. Let the solution clean the beaker/container for 10 min. If the beaker/container is plastic, it cannot be placed on a hot plate, and therefore the SC 1 solution will cool during the clean. This will not affect the cleaning process.
4. After 10 min, pour the SC 1 solution into another beaker/container if they require cleaning also. Otherwise let the SC 1 solution cool in a large beaker. Once cooled, SC 1 can be poured down the sink with running water.
5. Rinse SC 1 cleaned beaker/container in DI water.
6. In an acid allocated fume hood, prepare an SC 2 solution as outlined in sections 4.2.1-4.2.4.
7. Pour the SC 2 solution into beaker/container from step 6.5. Allow the solution to clean the beaker/container for 10 min.
8. After 10 min, pour the SC 2 solution into another beaker/container if they require cleaning also. Otherwise let the SC 2 solution cool in a large beaker. Once cooled, SC 2 can be poured down the sink with running water.
9. Rinse SC 2 cleaned beaker/container in DI water. The beaker/container is now chemically cleaned.

Representative Results

Figure 1a shows a schematic and **Figure 1b** shows a photograph of the experimental setup. When a silicon wafer is immersed into the HF solution, subsequently placed onto the lifetime tester stage and a measurement is performed (before illumination), a lifetime curve which is limited by surface recombination will result, as shown by the blue triangles in **Figure 2**. However, when the sample is illuminated for 1 min (while immersed in HF), as shown in **Figure 1**, and a measurement is performed immediately after illumination, an increase in the lifetime will occur, as shown by the red circles in **Figure 2**. This increase in lifetime after illumination results due to a reduction in surface recombination, and thus the red circles in **Figure 2** represent the lifetime which is now limited by bulk recombination and not surface. The increase in lifetime post illumination will vary from sample to sample, however if the technique is working correctly, an increase in lifetime should always occur provided the bulk lifetime is not low ($<100 \mu\text{sec}$), whereby any reduction in surface recombination by illumination will not improve the lifetime because bulk recombination becomes dominant.

Although the bulk lifetime is attained after illuminating the silicon wafer for 1 min¹⁹, the surface passivation is temporary and will start to degrade within seconds of the halogen lamp being switched off. Thus it is important for the measurement to be performed directly after the illumination period to achieve the lowest surface recombination, as demonstrated in **Figure 3**. The red circles in **Figure 3** correspond to the lifetime when the sample is measured directly after the lamp is switched off, and the blue circles correspond to the lifetime when the sample is measured 1 min after the illumination period. From the figure, it is evident that the high level of surface passivation is temporary and degrades within seconds

of the illumination source being terminated. Therefore it is imperative that a measurement is performed directly after illumination to attain the bulk lifetime of the silicon wafer. In contrast, **Figure 3** also demonstrates that even when the lifetime degrades (blue circles), it can be completely recovered by illuminating the silicon wafer once again. This process can be repeated many times without any permanent increase in surface recombination as shown in **Figure 3**.

To ensure the technique is working correctly each time a measurement is conducted, control silicon wafers should be used. The control silicon wafers represent samples that have been measured by the technique multiple times and have produced the same lifetime each time. The control samples should always undergo the same wet chemical pretreatment as the samples to be measured. Prior to measuring the bulk lifetime of silicon wafers, the control samples should be measured first. Thus if their lifetime is not within $\pm 20\%$ of their previous lifetime measurement, a problem has occurred and the measurement should be aborted until the issue is resolved. On the contrary, if the control samples produce lifetimes within $\pm 20\%$ of their previously measured lifetime, the measurements can proceed. In some cases, the bulk lifetime of the samples will be low, and thus the measured lifetime before and after illumination will be the same, contrary to **Figure 2**. In this case, even though illumination will still reduce surface recombination, no improvement in the lifetime post illumination will be observed because bulk recombination is much higher than surface. When measuring a sample such as this, comparison to a control wafer can elucidate whether there is a problem with the measurement setup or the measured wafer simply has a very high bulk recombination.

To demonstrate that HF passivation does achieve measurements of the bulk lifetime, FZ 1 Ω -cm *n*- and *p*-type silicon wafers were passivated with ALD Al_2O_3 and PECVD SiN_x , as shown in **Figure 4**. **Figure 4** shows that for both doping types, HF passivation can attain the same lifetime as achieved with Al_2O_3 and SiN_x films. The lower lifetime achieved by the SiN_x film on the *p*-type sample is due to depletion region recombination caused by the positive charge contained within the SiN_x film. In contrast, depletion region recombination, if present, does not appear to significantly affect the lifetime measurement of either *n*- or *p*-type silicon when using the HF passivation technique^{9,17,18}. This also makes the technique desirable for analyzing bulk defects, because any injection dependence observed from the lifetime measurement can be attributed to bulk recombination and not surface.

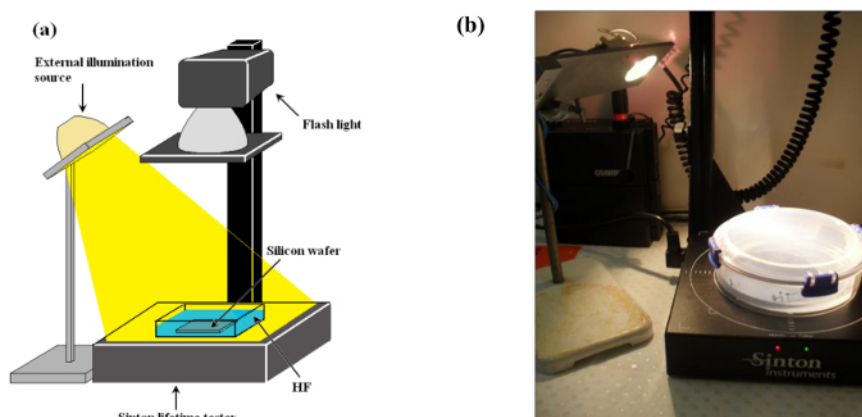


Figure 1. HF passivation setup. (A) schematic of the light-enhanced HF passivation and measurement setup¹⁷. Reproduced with permission from *J. Solid State Sci. Technol.*, 1(2), P55 (2012). Copyright 2012, The Electrochemical Society. (B) photograph of the setup. [Please click here to view a larger version of this figure.](#)

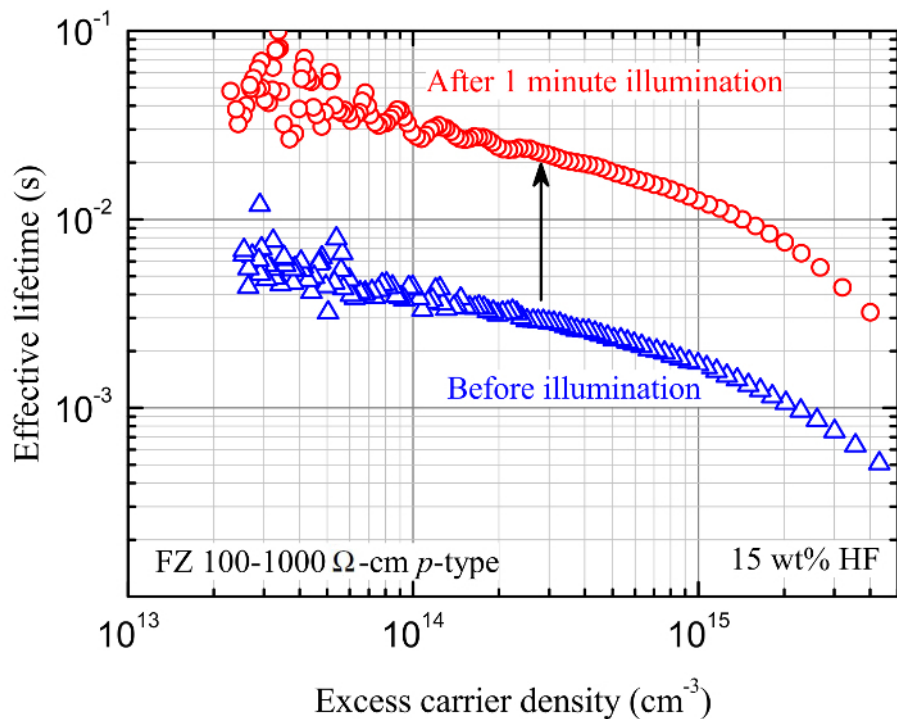


Figure 2. Enhancement of the surface passivation by illumination. Effective lifetime of a high resistivity silicon wafer immersed in 15% HF, before (blue triangles) and directly after (red circles) illumination. [Please click here to view a larger version of this figure.](#)

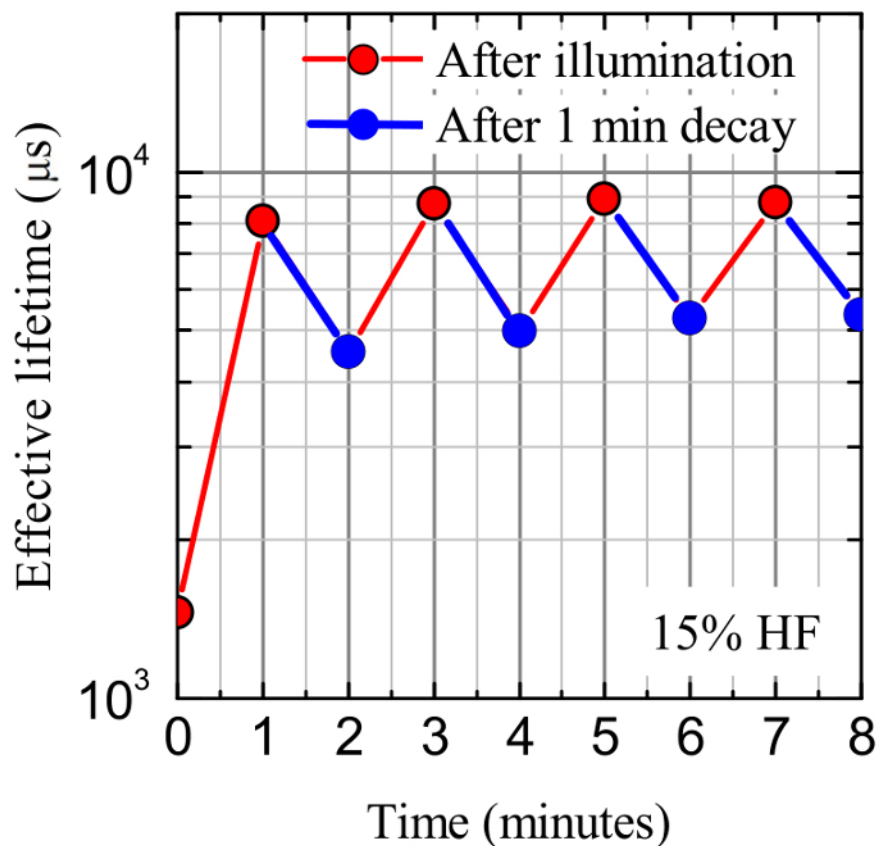


Figure 3. Degradation of the surface passivation post illumination. Effective lifetime of a 5 $\Omega\text{-cm}$ n-type silicon wafer immersed in HF directly after illumination (red circles) and 1 min after illumination (blue circles). The figure demonstrates how the passivation can be recovered by subsequent illumination steps. [Please click here to view a larger version of this figure.](#)

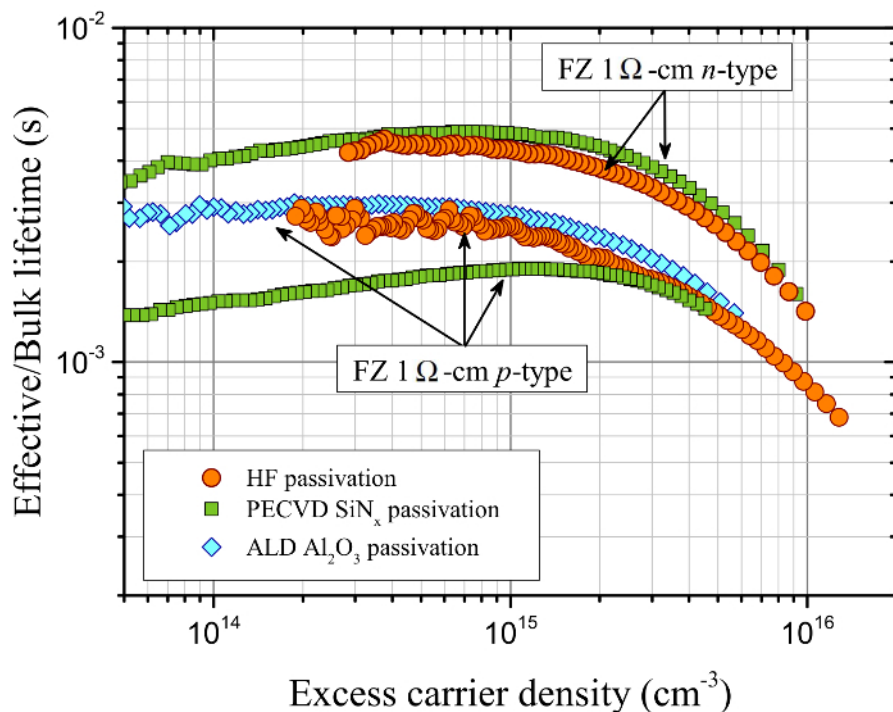


Figure 4. Comparison with other dielectric films. Effective/bulk lifetime of FZ 1 Ω-cm *n*- and *p*-type silicon wafers passivated with HF (orange circles), PECVD SiN_x (green squares) and ALD Al₂O₃ (blue diamonds). [Please click here to view a larger version of this figure.](#)

Discussion

The successful implementation of the bulk silicon lifetime measurement technique described above is based on three critical steps, (i) chemically cleaning and etching the silicon wafers, (ii) immersion in a 15% HF solution and (iii) illumination for 1 min^{17,18,19}. Without these steps, the bulk lifetime cannot be measured with any certainty.

As the measurement technique is conducted at RT, the surface passivation quality is highly susceptible to surface contamination (metals, organic films). Thus to effectively remove surface contaminants, an SC 1 solution is used (H₂O : NH₄OH : H₂O₂)²⁰. When the silicon wafers are immersed in SC 1, the solution removes organic surface films by oxidative breakdown and dissolution, along with metal contaminants such as, gold, silver, copper, nickel, cadmium, zinc, cobalt and chromium²⁰. Post SC 1 cleaning, it is possible that some trace elements remain trapped in the hydrous oxide film resulting from the clean, and therefore an HF dip is required to remove the film. Following an HF dip, the silicon surfaces are then cleaned in SC 2 (H₂O : HCl : H₂O₂)²⁰. While SC 1 effectively removes most impurities, SC 2 is designed to remove alkali ions and cations such as aluminum, iron and magnesium. Furthermore, SC 2 will also remove any other metallic contaminants that weren't removed in SC 1. Following an SC 2 clean, the wafers can be HF dipped to remove the hydrous oxide film. Once the silicon wafers have been cleaned of surface contaminants by SC 1 and SC 2, they require a short surface etch in TMAH. TMAH is an anisotropic etch solution, meaning it only etches along (111) crystal plains. Therefore during the chemical etch, small silicon pyramids are formed on the surfaces, exposing (111) plains, which roughens the surfaces and helps improve the hydrogen coverage when immersed in HF^{21,22}. Therefore, with an optimized surface condition, surface recombination can be inhibited when the treated silicon wafers are immersed in HF and subsequently illuminated.

Optimization of the HF solution was examined in our previous publication¹⁷. It was found that when silicon wafers are immersed in 15%-30% HF, the lowest surface recombination is attained. This occurs because the HF concentration is high enough to passivate most of the silicon dangling bonds with hydrogen, and provides a field effect passivation mechanism by retaining a high surface charge caused by a difference in the silicon Fermi level and reduction potential of the HF solution²³. The choice of 15% HF was for safety reasons. Another important addition to the HF solution was the inclusion of HCl. By adding a small amount of HCl in the 15% HF solution, the hydrogen concentration in the HF solution is increased, which in turn increases the amount of hydrogen available for the surface passivation of silicon wafers, allowing the bulk silicon lifetime to be obtained post illumination²³.

Illumination of silicon wafers immersed in HF can significantly improve the surface passivation by creating additional bonds with chemical species in the solution through electron and hole transfer across the silicon/HF interface^{23,24}. There are a number of chemical bonds that can form at the silicon/HF interface, such as Si-H, Si-OH and Si-F²³⁻²⁷. Passivation of silicon immersed in HF has been shown to primarily come from the creation of Si-H bonds, which is considered to be one of the most stable bonds when silicon is immersed in HF^{26,27}. However, while the surface passivation is enhanced post illumination, as shown in **Figure 3**, the passivation is known to degrade within seconds after the illumination source has been terminated. Therefore it is unlikely the enhanced passivation post illumination is primarily due to the creation of stable Si-H bonds, as the passivation should not degrade if this were the case. Rather it is hypothesized that the enhanced surface passivation comes from the creation of unstable bonds with hydroxyl groups (Si-OH) and fluorine (Si-F)²⁶.

While the three critical steps listed above are designed to give the best results, there are circumstances where the measurement can produce erroneous results. In most cases, the likely source of error is surface contamination, which can come from contaminated chemical solutions

or a poorly filtered DI system. Under these conditions, it is best to test the DI water system using a conductance meter. If the DI water is not filtered correctly, the system requires changing before any measurements are to be performed. This will also affect other lab processes and thus a compromised DI water system will affect everyone. On the contrary, if the DI water is giving a sensible reading on the conductivity meter, the possible sources of contamination are the TMAH solution or the 15% HF solution (SC 1 and SC 2 will not be compromised). In this case, it is best to decant the solutions, chemically clean (SC 1 and 2) the containers and prepare new solutions. Furthermore, if the silicon wafers have been contaminated by a solution, they will require SC 1 and SC 2 cleaning multiple times before the surfaces are clean. To avoid solution contamination and thus erroneous lifetime measurements, it is best to prepare TMAH and HF solutions which are only used for this technique (and not by other processes in the laboratory). Another source of surface contamination could come from dielectric or metal films previously deposited on the silicon wafer. Thus if the wafers have undergone a dielectric or metal deposition, the surfaces require chemical cleaning and silicon etching prior to the three step process of the bulk lifetime measurement technique.

Although the technique is both simple and time efficient, the use of HF acid restricts the technique to a fume hood. Irrespective of this, the technique provides equivalent surface passivation to the best passivating dielectric films in the world ($\text{SiN}_x\text{:H}$, Al_2O_3 and $a\text{-Si:H}$), furthermore this technique does not require any complex machinery, nor does it require elevated temperatures. As the purity of silicon wafers improves, in a drive to improve solar cell efficiencies, defect concentrations will decline and thus their recombination activity will become difficult to measure using techniques such as deep level transient spectroscopy and Fourier transform infrared spectroscopy. Therefore it is anticipated that minority carrier lifetime measurements which incorporate a RT liquid surface passivation technique will be imperative for examining bulk silicon defects when their concentration is low ($<10^{12} \text{ cm}^{-3}$).

Disclosures

The authors have nothing to disclose.

Acknowledgements

This program has been supported by the Australian Government through the Australian Renewable Energy Agency (ARENA). Responsibility for the views, information or advice expressed herein is not accepted by the Australian Government.

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