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Superacid Passivation of Crystalline Silicon Surfaces

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ABSTRACT: The reduction of parasitic recombination processes commonly occurring within the silicon crystal and at its surfaces is of primary importance in crystalline silicon devices, particularly in photovoltaics. Here we explore a simple, room temperature treatment, involving a nonaqueous solution of the superacid bis(trifluoromethane)sulfonimide, to temporarily deactivate recombination centers at the surface. We show that this treatment leads to a significant enhancement in



optoelectronic properties of the silicon wafer, attaining a level of surface passivation in line with state-of-the-art dielectric passivation films. Finally, we demonstrate its advantage as a bulk lifetime and process cleanliness monitor, establishing its compatibility with large area photoluminescence imaging in the process.

KEYWORDS: silicon, surface passivation, bulk lifetime, photoluminescence imaging, photovoltaics

INTRODUCTION

A central aim in a number of crystalline silicon (c-Si) devices, most prominently the solar cell, is to lengthen the effective lifetime of the photoexcited carriers. A slower recombination rate allows a greater population of carriers to build up for a given carrier generation density, which is directly linked to the implied voltage of the solar cell. The upper limit of this carrier lifetime is defined by the intrinsic, or unavoidable, recombination mechanisms occurring within silicon: radiative and Auger recombination. In c-Si this intrinsic lifetime can be on the order of 0.1 s for lowly doped materials.¹ However, in most practical cases the carrier lifetime is significantly shorter than this, being instead dominated by defects in the wafer bulk and at the surfaces. These defects introduce energy states within c-Si's bandgap, providing a pathway for Shockley–Read–Hall (SRH) nonradiative recombination. The SRH recombination rate is extremely sensitive to both the defect characteristics and concentration, and hence the carrier lifetime is often utilized as a proxy for process cleanliness and material quality.²

Substantial progress over the past three decades in the understanding and development of surface passivation techniques has reduced the amount of SRH recombination at the *c*-Si surfaces. A growing family of thin dielectric films including $\text{SiO}_{x0}^{3,4} \text{SiN}_{x0}^{5} \text{AlO}_{x0}^{6,7} \text{GaO}_{x0}^{8} \text{TiO}_{x0}^{9,10}$ and HfO_{x}^{11} have been shown to provide permanent passivation of surface defects. This has placed a greater emphasis on the SRH recombination in the bulk of the wafer. Consequently, an increasing amount of work is being devoted to analyzing and reducing defects within the bulk, particularly for low-cost silicon growth methods, such as multicrystalline ingots, and for

solar-grade feedstocks such as upgraded metallurgical grade (UMG) silicon. Even for high quality float-zone growth, it has been shown that the bulk lifetime can be dramatically altered during thermal processing through the activation/deactivation of metastable defect centers.^{12–14}

To monitor the bulk lifetime, it is useful to have a technique which temporarily removes the surface recombination component, so the bulk component can be studied in isolation. Ideally this process would be fast, simple, and nondestructive while being conducted at room temperature. Such a technique would allow a modernization of wafer quality screening before or between processing steps in c-Si device fabrication procedures, a need for which has been recognized pre-viously.^{2,15,16} The above-mentioned dielectric passivation layers are often unsuitable for such application, as they are typically deposited at elevated temperatures (200–1000 °C), commonly requiring an additional postdeposition anneal to effectively passivate the surface, which can in many cases alter the recombination processes to be studied. Instead, a number of solution-based treatments have previously been developed after this cause, including inorganic molecules such as iodine or bromine (in ethanol/methanol), $^{17-19}$ organic molecules such as quinhydrone or benzoquinone (also in ethanol/methanol),²⁰⁻²² and aqueous alkalines and acids (most prominently hydrofluoric acid).^{17,23-25} More complex multistep solutionbased techniques have also been shown to provide reasonable

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Figure 1. (a) Schematic of superacid treatment procedure. (b) Chemical structure of the three trialed superacids. (c) Left-hand panel shows the excess carrier-dependent effective lifetime $\tau_{\text{eff}}(\Delta n)$ measured on moderately doped (5 × 10¹⁵ cm⁻³) n-type *c*-Si wafers treated on both sides with the three different superacids. The right-hand panel shows the decay in carrier lifetime (measured at $\Delta n = 10^{15}$ cm⁻³) for the above three wafers as a function of air exposure time. Error bars are based on the estimated uncertainty in measurement.



Figure 2. (a) Excess carrier density-dependent carrier lifetime $\tau_{\text{eff}}(\Delta n)$ measured on a moderately doped (5 × 10¹⁵ cm⁻³) n-type *c*-Si wafer treated by dip coating in a 2 mg/mL TFSI solution in a range of solvents. The chemical structure of the solvents are shown on the left-hand side. (b) The measured $\tau_{\text{eff}}(\Delta n)$ of n-type (5 × 10¹⁵ cm⁻³) *c*-Si wafers after spin coating (purple triangle) and dip coating (green circle) in a 2 mg/mL TFSI in DCE solution.

levels of surface passivation,^{26–28} as have techniques involving corona-deposited charges on polymer films.²⁹ However, as it currently stands, all of these treatments either require prohibitively long processing times, provide only moderate quality surface passivation, or are not sufficiently stable in air to take measurements (and hence measurements have to be taken while submerged in solution).

In this work we study the surface passivation of *c*-Si using superacids. In particular, we identify a nonaqueous hydrophobic solution of bis(trifluoromethane)sulfonimide (TFSI) in 1,2-dichloroethene (DCE) as an excellent candidate to provide fast, high quality, room temperature passivation of the *c*-Si surface with sufficient air stability to allow photoluminescence- and photoconductance-based characterization. A similar treatment has recently been demonstrated by our group to yield near unity internal quantum efficiency when treating sulfurcontaining transition metal dichalcogenides.^{30,31} In addition,

we demonstrate the potential of this technique to slow the surface oxidation process, suggesting its potential use to preserve the surface between fabrication steps for a *c*-Si-based device.

RESULTS AND DISCUSSION

The simple procedure utilized for superacid passivation of the *c*-Si surface is shown in Figure 1a. Following an initial dilute hydrofluoric acid (HF) immersion to remove the native oxide at the *c*-Si surface, the samples were dipped into one of the three superacids (as described below), which were held at room temperature. After removal from solution, samples were allowed to dry before being characterized using photoconductance decay (PCD) or photoluminescence (PL) techniques. In a previous study, the nonaqueous superacid trifluoromethanesulfonic acid (TFMS) was shown to provide excellent passivation of the *c*-Si surface.²⁴ Figure 1c compares



Figure 3. (a) Comparison of effective lifetime (measured at $\Delta n = 10^{15} \text{ cm}^{-3}$) between concentrated HF treatment (hollow bars) and TFSI treatment (filled bars) for a number of wafers with different surface doping types and concentrations. The left- and right-hand panels show the measured lifetime while samples are immersed in the treatment solution and ~1 min after being removed from the solution, respectively. (b) The effect that water addition to the TFSI solution has on both the starting SRV value (measured on an n-type 5 × 10¹⁵ cm⁻³ wafer at $\Delta n = 10^{15} \text{ cm}^{-3}$) and the rate of SRV increase. Error bars are based on the estimated uncertainty in measurement.



Figure 4., (a) FTIR spectra of DCE (bottom) and a 2 mg/mL TFSI in DCE solution (top) with labeled characteristic peaks. (b) ATR-FTIR spectra of TFSI-treated 100-oriented (bottom) and 111-oriented (top) *c*-Si surfaces. (c) XPS Si 2p (left) and O 1s (right) spectra of HF-treated (black lines) and (HF + TFSI)-treated (orange lines) 100-oriented *c*-Si surface. The two sets of spectra in each plot are measured shortly after treatment and then again 3 days later. The oxide thickness is estimated from the peak area. (d) Carbon 1s XPS core levels of a 2 mg/mL TFSI in DCE solution-treated (111) silicon surface showing the presence of a higher binding energy carbon oxidation state suggestive of the CF₃ species.

this previously trialed superacid with two others: (1) neat perfluorobutanesulfonic acid (PFBS) and (2) an optimized solution of 2 mg/mL TFSI in DCE. TFSI is a solid at room temperature and hence must be dissolved in a solvent for treatment. The chemical structures of these three superacids are shown in Figure 1b. As can be seen from the excess carrierdependent lifetime $\tau_{\text{eff}}(\Delta n)$ in the left panel of Figure 1c, all three superacids produce millisecond scale carrier lifetimes. These values were measured by transient PCD, on moderately doped ($\sim 5 \times 10^{15}$ cm⁻³), n-type *c*-Si wafers (relevant to contemporary *c*-Si solar cells). The uncertainty in carrier lifetimes measured using this setup has previously been estimated as less than 10%.³² Among the alternatives, the nonaqueous TFSI solution produces the highest lifetime, with a corresponding upper-limit surface recombination velocity (SRV) of ~3 cm/s (calculated using the approach for a

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double-side passivated wafer³³), in line with results obtained for conventional dielectric passivating films.^{3–6,8–11} We emphasize that this is an *upper-limit* SRV; that is, no allowance for a bulk contribution to recombination is made, and therefore the actual SRV is slower. Importantly, the nonaqueous TFSI solution also exhibits the greatest air stability, as highlighted in the timedependent carrier lifetime plot on the right panel of Figure 1c. Consequently, the nonaqueous TFSI solution was made the focus of this study.

In optimizing the TFSI solution it was found that a broad range of solvents, as shown in Figure 2a, and TFSI concentrations (down to 0.002 mg/mL) could be used to achieve effective surface passivation, with a 2 mg/mL TFSI in DCE solution producing the best results. In addition, as presented in Figure 2b, an equivalent level of surface passivation could be achieved by spin coating the nonaqueous TFSI solution on both sides of the wafer, indicating that this treatment may be compatible with high throughput approaches, such as spray coating.

To further highlight the versatility of the TFSI treatment, it was trialed on a range of *c*-Si wafers with n, p, n⁺, and p⁺ dopant surface concentrations relevant to a number of c-Si-based devices. The results of this study were compared to a more established procedure utilizing HF-based solutions,²⁵ which is known to effectively measure the bulk lifetime of wafers by almost completely deactivating recombination at the c-Si surface. As shown in the left-hand panel of Figure 3a, similar surface passivation can be achieved when immersing the wafers in the HF and TFSI solutions, the equivalence of the two in situ measurements indicating that the TFSI treatment is equally suitable for bulk lifetime determination. Compared to the undiffused surfaces, the n⁺ and p⁺ heavily doped regions reduce the surface minority carrier concentration and hence surface recombination (which is good), while at the same time increasing the surface region majority carrier concentration and hence Auger recombination (which is bad).³⁴ Therefore, the measured lifetime of the passivated n⁺ and p⁺ samples is partially reduced by Auger recombination. Interestingly, when the wafers were removed from the solution, the surface passivation performance of the two treatments was dramatically different, as shown in the right-hand panel of Figure 3a. The concentrated HF surface passivation rapidly decays in <1 min to an effective lifetime value approaching the "diffusivity limit". Under this scenario, the surface recombination rate is limited by the rate of carrier diffusion to the surface rather than the surface defect concentration.³⁵ It should be noted that the 100-200 μ s lifetimes measured for the HF-treated n⁺ and p⁺ samples are due to the reduced minority carrier concentration, as discussed above, rather than residual surface passivation and are in line with values measured for unpassivated wafers. The TFSI solution, however, affords quasi-stable passivation, in some cases providing slightly higher lifetimes than those measured while in solution. The surface passivation of the TFSI-treated sample was found to be strongly related to the concentration of water contamination in the TFSI solution. Figure 3b shows that higher water concentration within the TFSI solution increases both the starting SRV and its rate of surface decay. Extending from this result, further refinement of this technique may lead to permanent surface passivation suitable for use in operating devices.

To provide insight into the mechanism of the quasi-stable passivation, attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy is performed on the nonaqueous TFSI solution. The FTIR spectra, shown in Figure 4a, suggest that the TFSI molecule remains intact in solution. This TFSI molecule also remains on the surface of the c-Si wafer following treatment and drying, regardless of the c-Si surface orientation. This is shown in the difference FTIR spectra of Figure 4b, calculated by subtracting the reference signal of a HF-treated silicon wafer from that of a TSFI-treated silicon wafer. The Hammett number of TFSI in DCE solvent is known to be extremely high ($\sim 10^{10}$ times higher than nitric and sulfuric acid³⁶), meaning the TFSI molecule acts as an excellent proton source. Therefore, the primary means of surface passivation could be the protonation of the c-Si surface, similar to that suggested for HF.^{24,37,38} An additional factor that could contribute to a lower surface recombination is the formation of inversion or accumulation conditions, that is, a localized high concentration of either electrons or holes, at the c-Si surface. This can occur under the influence of a significant surface charge from the conjugate TFSI anion or a chemical potential difference. To investigate the possibility of such a contributing factor, colloquially referred to as "field effect passivation", fourpoint probe dark measurements (not shown) were taken of surface sheet resistance on lowly doped p- and n-type wafers treated with the nonaqueous TFSI solution. These measurements revealed that no strong accumulation or inversion layers were present and hence that surface charge or chemical potential difference is unlikely to be a significant contributor to the very low rate of surface recombination.

While the TFSI anion may not play a direct role in surface passivation, the increased longevity of the surface passivation compared to HF could be associated with the TFSI anions protecting the surface from oxidation. Room temperature oxidation of the c-Si surface, resulting in a self-terminating nanometre scale SiO_x layer, is known to provide poor surface passivation. To investigate this effect, X-ray photoelectron spectroscopy (XPS) measurements of the O 1s and Si 2p core levels were taken, the spectra of which are provided in Figure 4c for samples treated with either just HF or the procedure outlined in Figure 1a. Two sets of spectra are shown: (i) shortly after treatments (less than 2 min of air exposure) and (ii) after 3 days storage in air. The appearance of a higher binding energy peak in the Si 2p core levels and the formation of a peak in the O 1s region clearly indicate the growth of a surface oxide shortly after the treatment. Importantly, it can also be clearly seen that the TFSI-treated surface has a lower rate of surface oxidation, with an extracted oxide thickness of ~ 1.7 Å after 3 days, approximately 3 times thinner than the HF-treated surface. These thicknesses were obtained from the Si 2p core level using an approach described elsewhere.^{39,40} One possible mechanism for this reduced surface oxidation rate is the contribution of the hydrophobic CF₃ moieties to the TFSI molecule which would protect the surface from H₂O molecules in the ambient air, preventing the formation of Si-O bonds at the c-Si surface. The presence of CF₃ moieties on the c-Si surface after treatment is also confirmed via XPS measurements presented in Figure 4d of the C 1s core level, which show a carbon oxidation state indicative of CF₃ species. Furthermore, the TFSI treatment uses the hydrophobic DCE solvent, which could play a similar role in restricting the access of water vapor to the c-Si surface. Regardless of the mechanism, the above results highlight the possibility of using the TFSI treatment to preserve a near pristine surface, potentially useful before the crucial surface passivation and contacting steps in the fabrication procedures of c-Si devices.



Figure 5. (a) PL image of a lowly doped $(5 \times 10^{13} \text{ cm}^{-3})$ n-type wafer treated with the TFSI solution in a select region (bright region) to form a *Cal* pattern. (b) PL image of two halves of a lowly doped $(5 \times 10^{13} \text{ cm}^{-3})$ n-type wafer treated with TFSI solution. The left half was treated out of the box and the right half received a 30 min N₂ anneal at 550 °C before treatment. (c) Excess carrier-dependent lifetime plots, measured via PCD, for the two halves shown in b.



Figure 6. (a and b) PL images of a multicrystalline wafer treated on both surfaces with the TFSI solution and standard SiN_x films, respectively. Both samples were excited with a photon flux of ~0.65 suns at 809 nm but were scaled separately to enhance contrast. The orange circles in panel a indicate twinning defects within larger grains, identified by the TFSI treatment. (c) EBSD mapping (top) and a magnified PL image (bottom) of the region indicated by the blue rectangle in panel a.

As mentioned in Introduction, a significant advantage of the quasi-stable surface passivation is the ability to characterize the carrier lifetime behavior of the sample out of solution, thus allowing the use of photoluminescence imaging. Figure 5a confirms the expected large increase in PL emission after TFSI treatment. The figure shows a large area PL image of a 4 in. wafer treated selectively in a patterned region, resulting in a very high PL contrast between TFSI-treated (bright) and untreated (dark) regions. An immediately relevant example of this utility can be seen in Figure 5b, which shows a PL image of two halves of a TFSI-treated, float zone c-Si wafer. The left half underwent no processing prior to TFSI treatment whereas the right half was subjected to standard RCA cleaning and a 550 °C, 30 min N₂ annealing step before TFSI treatment. This annealing step, which is not unusual for the fabrication of many c-Si devices, is thought to activate a metastable lattice-impurity bulk defect,¹⁴ leading to a dramatic reduction in bulk lifetime. To quantify this change, $\tau_{\rm eff}(\Delta n)$ curves measured from the two halves of the wafer in Figure 5b are shown in Figure 5c. A reduction by almost 2 orders of magnitude in carrier lifetime is seen, agreeing well with the strong decrease in PL intensity. As both surfaces can be assumed to have identical surface passivation, the difference can be attributed to changes in the bulk of the wafer.

Finally, another variant of this PL application is the measurement of multicrystalline silicon (mc-Si), a material

which dominates today's photovoltaic industry.⁴¹ The centimeter-scale grains found in this material result in a range of different crystal orientations across a wafer surface, all of which have different atomic densities and orbital arrangements. This variation in surface characteristics can give rise to different surface defect densities and hence different recombination rates at these surfaces.^{42,43} As shown in Figure 6a, the TFSI-treated mc-Si wafer shows a large variation in PL intensity from grain to grain, suggesting that the passivation is orientation dependent. Conversely, the adjacent PL image (Figure 6b) of the same wafer passivated using a standard PECVD SiN_x film shows only minimal grain to grain variation. This difference is attributable to the large positive fixed charge density present in the SiN, film which encourages strong field effect passivation.⁵ As discussed above, this mechanism is not expected to play a large role in the TFSI passivation treatment, and hence orientation dependence is seen. To further confirm this, Figure 6c shows an electron back scatter diffraction (EBSD) mapping of the local crystal orientation beside a PL image of the same regions after TFSI treatment. The chosen region is a close cluster of different orientation grains indicated by the blue box in Figure 6a. A clear correlation between surface orientation and PL intensity can be seen, with the highest PL intensity consistently originating from (100)-oriented surfaces and lower intensities coming from (111) surfaces, in line with other surface passivation techniques,⁴⁴ suggesting its suitability as a rapid

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alternative to EBSD and X-ray diffraction-based crystal orientation analysis. Also evident in Figure 6a is the identification of high recombination grain boundaries and twinning defects (as indicated by the orange circles) across the wafer. This highlights the possibility of using the TFSI treatment to test the efficacy of specialized grain boundary/ defect passivation procedures.

CONCLUSION

In this study we have demonstrated the use of a nonaqueous TFSI solution as an effective means to passivate the *c*-Si surface. While it is believed that the underlying mechanism of surface passivation is the protonation of the c-Si surface, similar to other acid-based treatments, the TFSI treatment displays superior passivation longevity, potentially via a layer of protective TFSI anions on the c-Si surface which slow surface oxidation. As such, this treatment is of interest as an excellent process monitoring tool for a number of c-Si devices, particularly the photovoltaic industry-dominating c-Si solar cell. Multiple relevant applications are demonstrated including bulk lifetime measurement via PCD and PL measurements, c-Si surface preservation for a number of days, identification of crystal orientation, and grain boundary and defect studies. These applications combined with the simplicity of the procedure suggest that the TFSI treatment is a promising tool to further reduce losses in c-Si-based devices and test structures.

EXPERIMENTAL DETAILS

The three superacids, trifluoromethanesulfonic acid (TFMS), perfluorobutanesulfonic acid (PFBS), and bis(trifluoromethane)-sulfonimide (TFSI), as well as the solvents used to dissolve the solid TFSI superacid, were sourced from Sigma-Aldrich.

Superacid-treated n and p lifetime samples are prepared using (100), float-zone, n-type $(5 \times 10^{15} \text{ cm}^{-3})$ and p-type $(2 \times 10^{16} \text{ cm}^{-3})$ c-Si wafers. The n^+ and p^+ lifetime samples were prepared on (100), float-zone, lowly doped n- and p-type wafers. Opposite polarity heavily doped surface regions were achieved by high temperature diffusion using BBr3 and POCl3 gases, respectively. Prior to superacid treatment, samples were subjected to a dilute HF dip (5% vol) to remove any native oxide or dopant glass. Immediately after, superacid treatment was either achieved via immersion and measurement in solution or via a rapid dip (\sim 1 s) followed by measurement in air, as indicated in the text. The TFSM and PFBS treatments were conducted in a nitrogen glovebox due to the moisture sensitivity of these materials. The concentrated HF passivation treatment, used as a benchmark comparison in this study, was conducted using a 15% solution of HF-HCl solution following a literature procedure.²⁵ The SiN_x passivation layers, also utilized as a reference for high quality surface passivation, were deposited using a Roth and Rau AK400 PECVD via literature procedure.4

PCD and PL measurements were conducted using a Sinton WCT(100 and 120) photoconductance tester in the transient mode and a BT Imaging LIS-RI PL imager (excitation: 809 nm, detection: Si CCD), respectively. The pattered *Cal* symbol was achieved by growing a low quality, thin (less than 20 nm) thermal oxide and removing this oxide selectively so that the exposed surface could be treated with the TFSI solution.

ATR-FTIR measurements were taken on TFSI-treated, mechanically polished, (100)- and (111)-oriented, n-type silicon pieces using a Thermo Scientific Nicolet iSFO FT-IR spectrometer equipped with a Ge crystal-ATR accessory. Freshly prepared HF-treated Si with the corresponding orientation was used as reference. Dry N₂ purging was employed for these measurements. XPS measurements were performed on chemically polished n-type (100) wafers using a monochromated Al K α source ($\hbar\nu$ = 1486.7 eV) and an Omicron EA125 hemispherical seven-channel analyzer. The XPS scans were acquired at a pass energy of 15 eV and takeoff angle of 45°. For XPS peak deconvolution and data analysis, the software AAnalyzer was employed, where Voigt line shapes and an active Shirley background were used for peak fitting.⁴⁶ EBSD measurements of the multicrystal-line silicon wafer were conducted using a Zeiss UltraPlus analytical FESEM.

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Notes

The authors declare no competing financial interest.

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