physica status solidi **rrl**

Temporary Surface Passivation for Characterisation of Bulk Defects in Silicon: A Review

Nicholas E. Grant* and John D. Murphy*

Accurate measurements of the bulk minority carrier lifetime in high-quality silicon materials is challenging due to the influence of surface recombination. Conventional surface passivation processes such as thermal oxidation or dielectric deposition often modify the bulk lifetime significantly before measurement. Temporary surface passivation processes at room or very low temperatures enable a more accurate measurement of the true bulk lifetime, as they limit thermal reconfiguration of bulk defects and minimize bulk hydrogenation. In this article we review the state-of-the-art for temporary passivation schemes, including liquid immersion passivation based upon acids, halogen-alcohols and benzyl-alcohols, and thin film passivation usually based on organic substances. We highlight how exceptional surface passivation (surface recombination velocity below $1\,\mathrm{cm\,s^{-1}}$) can be achieved by some types of temporary passivation. From an extensive review of available data in the literature, we find p-type silicon can be best passivated by hydrofluoric acid containing solutions, with superacid-based thin films showing a slight superiority in the n-type case. We review the practical considerations associated with temporary passivation, including sample cleaning, passivation activation, and stability. We highlight examples of how temporary passivation can assist in the development of improved silicon materials for photovoltaic applications, and provide an outlook for the future of the field.

1. Introduction

The minority carrier lifetime (henceforth referred to as just "lifetime") is a key figure of merit in the development of silicon wafers for use in photovoltaics or for integrated circuits (ICs). The highest efficiency silicon solar cells, for example, now require silicon substrates with lifetimes well into the millisecond range. To develop device processes it is necessary to measure

Dr. N.E. Grant, Dr. J.D. Murphy
School of Engineering, University of Warwick, Coventry, CV4 7AL, UK
E-mail: nicholas.e.grant@warwick.ac.uk; john.d.murphy@warwick.ac.uk

such high lifetimes reproducibility, with minimal influence from recombination at the sample surfaces. Thermal oxides and deposited dielectrics can provide excellent surface passivation, but their growth can modify the bulk properties of the material under investigation.

It has long been known that exceptional surface passivation can be achieved by immersing semiconductor samples in hydrofluoric acid (HF),[1] and techniques which used this, such as the electrolytic metal tracer (ELYMAT),[2] were invaluable in the development of high purity silicon for ICs in the late 1980s and early 1990s.[3] Since then a range of alternative liquid passivation schemes has emerged, and many of these are used in laboratories worldwide to characterize materials by what are now standard techniques including injection-dependent photoconductance lifetime measurements,[4] microwave photoconductance decay,[5] and photoluminescence (PL) imaging.[6] Recently a range of temporary thin film passivation schemes has been discovered and these offer improved compatibility with established characterisation methods. This article aims to review the literature on temporary surface passivation of silicon. The primary focus is on junction-less substrates for photovoltaic applications, but much of the article is equally applicable to IC wafers.

The effectiveness of passivation is usually measured by a surface recombination velocity (S) which depends on the doping type, doping level, and excess minority carrier density. McIntosh and Black have demonstrated that the surface saturation current density (J_{0s}) is often superior to S as a passivation metric,[7] but unfortunately it is often impossible to calculate J_{0s} retrospectively from reports of temporary passivation in the literature. In this review we therefore use the definition of S which assumes that both sides are equally well passivated and a relatively low S, which is:

$$S = \frac{W}{2}\left(\frac{1}{\tau_{\mathrm{eff}}} - \frac{1}{\tau_{\mathrm{bulk}}}\right) \qquad (1)$$

where W is the sample thickness, τ_{eff} is the measured effective lifetime, and τ_{bulk} is the true bulk lifetime. Some passivation

studies assume infinite bulk lifetime, in which cases the value of S should be regarded as an upper limit.

The motivation for high quality surface passivation in accurate bulk lifetime determination is illustrated by **Figure 1**, which shows the impact of varying S on τ_{eff} for given τ_{bulk} values. If τ_{eff} is to be within 10% of τ_{bulk}, S must be reduced below $1\,\mathrm{cm\,s^{-1}}$ for $\tau_{bulk} > 2\,\mathrm{ms}$ and if τ_{eff} is to be within 20% of τ_{bulk}, S must be reduced below $1\,\mathrm{cm\,s^{-1}}$ for $\tau_{bulk} > 3\,\mathrm{ms}$. Excellent surface passivation is therefore required for the accurate measurement of bulk lifetimes, particularly in the context of high efficiency solar cells which now require substrate lifetimes $>10\,\mathrm{ms}$ for optimum performance.

This review will first describe the motivation for temporary passivation schemes, before briefly describing the physics of surface passivation. A range of temporary passivation schemes will be reviewed, and processing and practical issues will be discussed for each. Applications of temporary surface passivation will be reviewed and the outlook for the field will be commented upon.

2. Motivation for Temporary Passivation

Very good surface passivation can be achieved by thermal oxidation, a process which usually takes place $\geq 800\,^\circ\mathrm{C}$. Advanced oxidation processes, such as "alnealing", can give S below $1\,\mathrm{cm\,s^{-1}}$.[8] Over the past decade or so there have been considerable advances in surface passivation by deposited dielectric films (such as SiN_x, Al_2O_3, and a-Si) by growth techniques such as plasma enhanced chemical vapor deposition (PECVD) or atomic layer deposition (ALD), which occur at much lower temperatures than thermal oxidation. Dielectric passivation has been reviewed previously (e.g., Ref.[9] for a general review, Ref.[10] for Al_2O_3, and Ref.[11] for SiN_x). Excellent surface recombination velocities (often of order $1\,\mathrm{cm\,s^{-1}}$ or better) can be achieved with single materials. Charge modification (e.g., by corona charging) can be used to

Nicholas E. Grant studied Physics at the University of Adelaide graduating with Honours in 2007. In 2008 he undertook a PhD in Photovoltaic Engineering at the Australian National University, graduating in 2012. In 2013, he was awarded a postdoctoral fellowship by the Australian Renewable Energy Agency, where he developed low temperature passivation methods to detect, quantify, and annihilate bulk silicon defects. In 2016, he moved to the UK and undertook a research fellow position at the University of Warwick where he is working toward improving silicon photovoltaic material performance, and developing novel organic thin films.

John D. Murphy studied Physics and Materials Science at the University of Oxford, UK, graduating with an MA and DPhil in 2006. He subsequently held a 5-year Royal Academy of Engineering/EPSRC Research Fellowship at Oxford, during which time he developed a programme of research into silicon materials for photovoltaics. In 2013, he moved to a faculty position at the University of Warwick, UK, where he is now an Associate Professor in the School of Engineering. He is currently Principal Investigator of the EPSRC SuperSilicon PV project which aims to unify the UK's silicon photovoltaic materials research activities and to extend the current limits of wafer performance.

improve the properties of as-deposited dielectrics. Even better passivation can be achieved with stacks of materials.[12,13]

Whilst improvements in passivation have resulted in better photovoltaic devices, use of state-of-the art passivation processes can cause confusion when trying to understand defect physics and the true bulk lifetime in device process development. The starting bulk lifetime can change (positively or negatively depending on details) during the passivation process, both due to defect re-configuration and because the wafer bulk is not a closed system. For example, high temperature treatments used for thermal oxidations can affect the distribution of bulk oxygen in Czochralski silicon, and may, depending on the details, create oxygen-containing precipitates (which reduce lifetime[14]) or dissolve nuclei. Lower temperature (≈ 250 to $450\,^\circ\mathrm{C}$) processes to deposit dielectric films can impact on the bulk lifetime in at least three ways. Firstly, annealing can activate bulk recombination centres – even in high purity float-zone silicon.[15,16]. Secondly, although not directly proven to our knowledge at these temperatures, various authors have provided evidence to suggest that hydrogen diffuses into the bulk from the dielectric layers,[17,18] and hydrogen has the potential to affect bulk
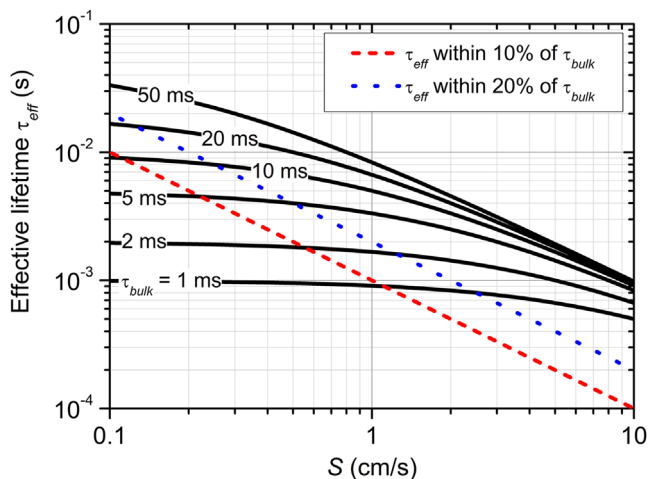

Figure 1. S versus effective lifetime (τ_{eff}) for material with a τ_{bulk} of 1–50 ms and wafer thickness of 200 μm. The red dashed line represents a τ_{eff} within 10% of τ_{bulk} and the blue dotted line represents a τ_{eff} within 20% of τ_{bulk}.

lifetime by interacting with other defects.[19] Thirdly, impurities such as iron have been shown to be highly soluble in dielectrics such as SiN_x[20,21] and can be gettered to the Al_2O_3–Si interface[22] and thus sufficiently mobile metallic impurities can be potentially removed from the bulk during the passivation step.

Temporary surface passivation helps fulfil a need to measure representative bulk lifetimes with reduced influence from recombination at the sample surfaces. It is also the case that systems to deposit state-of-the-art dielectrics are expensive, so temporary passivation can be used as a low cost alternative in companies and laboratories without access to such tools.

3. Energy Levels at the Silicon–Electrolyte Interface and the Influence of Illumination

In general, silicon–electrolyte interfaces behave similar to silicon–metal interfaces. Therefore, under thermal equilibrium, the Fermi levels E_F in each material must balance. For this to occur, electrons flow from the material with an energetically higher E_F to the material with a lower E_F. This results in band-bending at the silicon surface and, in general, a space charge region. For electrolytic solutions, the corresponding "Fermi level" is governed by the ions in the solution and is thus characterised by the redox potential E_{redox}, so $E_F \approx E_{redox}$. The redox potential can be described by a solution's (or a species') tendency to either accept or donate electrons, and can thus be varied depending on the composition of the solution and its pH.[23] **Figure 2** depicts the energetics when an *n*-type silicon wafer is brought into contact with an electrolyte. In this case, the redox potential of the solution is below the silicon Fermi level E_{FS} and therefore electrons are transferred from the silicon to the solution, resulting in upward bending of the bands at the silicon surface and the formation of a space charge region. On the solution side of the interface, the reciprocal charge is reflected by ions attracted to the interface, and is known as the Helmholtz layer, and is typically 3 Å thick (not shown).[23,24] If the electrolyte is relatively concentrated (>0.1 M), then all of the reciprocal charge is made up in the Helmholtz layer. In some cases however the charge distribution extends beyond the Helmholtz layer into the bulk solution which is made up of excess ions of one sign and is known as the Gouy-Chapman layer.[23]

E_{CS} and E_{VS} in Figure 2 correspond to the conduction and valence band edges in silicon, while E_{ox} and E_{red} correspond to
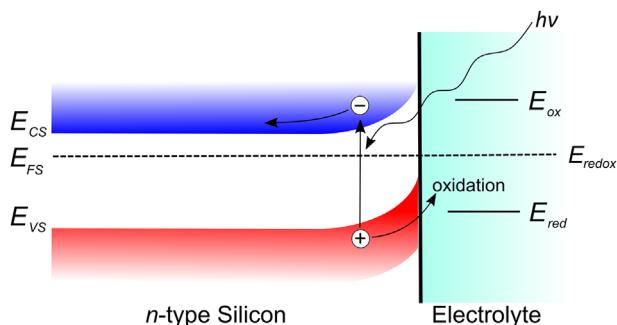
the most probable energy levels for the oxidizing and reducing species respectively. In this regard, oxidising refers to a species that donates or "gives up" electrons while reducing refers to a species which accepts or "gains" electrons. E_{redox} is thus given by $E_{redox} = \frac{1}{2}(E_{ox} + E_{red})$. In liquid electrolytes, these energy levels are often better represented by a Gaussian distribution because the energy of the ions tend to fluctuate because the dipoles of the molecules surrounding the ions move to/away and rotate around them causing thermal fluctuations in the polarisation.[23] For n- and p-type silicon immersed in the same electrolyte, the level of surface passivation may differ, as reactions which promote bonding with the silicon surface might be carrier selective.

When the silicon–electrolyte interface is illuminated, electron-hole pairs are generated in the silicon material when $h\nu \geq 1.12\,eV$ at room temperature. In the case of Figure 2, illumination will result in a hole diffusing to the silicon–electrolyte interface due to the space charge region, which can then oxidize a species at the surface (shown on diagram). For cases where the space charge region is replaced by an accumulation layer, an electron will diffuse to the surface and reduce a species at the surface. Thus it is clear that illumination can influence the chemical reactions at the silicon–electrolyte interface and this may aid or hinder surface passivation.

In general, it is possible to measure band-bending at the silicon–electrolyte interface using electrochemical based techniques.[25,26] By this method a potential difference is applied across a silicon wafer and counter electrode immersed in an electrolytic solution (e.g., HF). By varying the potential, information regarding space charge capacitance can be inferred, and the resulting band bending can be determined. In contrast, band-bending at the silicon–thin film interface can be measured using surface voltage and Kelvin probe techniques.[27]

4. Types of Temporary Surface Passivation

We have chosen to group all temporary passivation schemes into five types. The first three types (acids, halogen-alcohols and benzyl-alcohols) can be grouped together as "liquid immersion" passivation schemes as they involve placing the sample in a passivating solution. Notable liquid immersion passivation results are summarised in **Table 1**. We call the fourth type "thin film" passivation and summarize the key results for this type in **Table 2**. The fifth type we call "other" and the key results are summarised in **Table 3**. To enable a rapid comparison, **Figure 3** plots the upper limit surface recombination velocity of significant temporary surface passivation studies as a function of doping concentration for n- and p-type silicon. The colored ellipses are guides to the eye and represent the broad range of S achieved for that particular passivation scheme. The five passivation types are now discussed in turn.

4.1. Liquid Acids

4.1.1. Overview

Hydrofluoric acid (HF) is particularly effective at providing temporary surface passivation of silicon surfaces. A standard

Figure 2. Energy level diagram of an n-type silicon wafer in contact with an electrolytic solution under illumination.

Table 1. Summary of significant temporary "liquid immersion" passivation studies from the literature. Samples were (100)-orientation unless stated. Highlighted studies have $S \leq 1\,\mathrm{cm\,s^{-1}}$.

Type	Variant	Chemicals	Growth	Type	Resistivity [Ω cm]	τ_{eff} max [ms]	W [μm]	S_{max} [cm s^{-1}]	Ref.
Acid	HF	HF (20%)	FZ	n	1	2	400	2.7	[28]
		HF (20%)	FZ	n	5	10	700	2.8	[28]
		HF (20%)	FZ	p	1	0.222	400	≤10	[51]
		HF (20%)	FZ	p	>1000	50	500	0.7	[28]
		HF (40%)	FZ	p	0.8	0.8	300	4.8	[28]
		HF (48%)	FZ (111)	n	4000–6000	2.2	500	11	[35]
		HF (48%)	FZ	p	22	2.460	2700	1	[31]
		HF (48%)	FZ (111)		150	40	250	0.25	[1]
		HF (48%)	FZ		150	5	250	0.4	[1]
		HF (48%)	Cz	p		2.9	525	2.8[a]	[32]
		HF (48%)	FZ (textured)	p		1.8	300	1.9[a,b]	[32]
		BHF	FZ (111)	n	4000–6000	3	500	8.3	[35]
	HF-HCl	HF(15%)-HCl	FZ	n	1	3.09	137	0.6	[16]
		HF(15%)-HCl	FZ	n	1.5	5.874	200	1.7[a]	[15]
		HF(15%)-HCl	FZ	n	5	9.689	150	0.77[a]	[15]
		HF(15%)-HCl	FZ	n	100	17.45	400	1.15[a]	[16]
		HF(15%)-HCl	FZ	p	1	1.12	207	0.63	[16]
		HF(15%)-HCl	FZ	p	2	4.307	300	3.48[a]	[15]
		HF(15%)-HCl	FZ	p	>100	17.23	300	0.87[a]	[15]
Halogen-alcohol	I-E	I-E (0.03 M)	Cz	n	6.7	1.82	1190	<5.5	[42]
		I-E (0.08 M)	Cz	n	1.7–13	0.974	180	5.2	[44]
		I-E (0.08 M)		n	1–10	0.9	500	28[a]	[52]
		I-E (0.08 M)	FZ	n	100	2.72	430	7.9	[43]
		I-E (0.08 M)	FZ	p	0.5	0.02	16	40.4	[43]
		I-E (0.08 M)	FZ	p	1	0.293	290	49.5	[43]
		I-E (0.08 M)	Cz	p	1.7–13	0.363	180	15.8	[44]
		I-E (0.08 M)	FZ	p	2.5	0.555	194	17.5	[43]
		I-E (0.08 M)	FZ	p	10	1.55	298	9.6	[43]
		I-E (0.08 M)	FZ	p	100	1.70	279	8.2	[43]
		I-E (0.08 M)	FZ	p	200	6	220	1.8[a]	[53]
		I-E (0.08 M)	FZ	p	1000	2.50	280	5.6	[43]
		I-E	FZ (111)	n	25		200	<10	[41]
		I-E (0.1 M)	FZ	n	8–12	10	350	1.8[a]	[46]
		I-E (0.1 M)	FZ(111)	n	30	20	350	0.9[a]	[46]
	I-M	I-M (0.001 M)	FZ	n	1.2	1.53	300	10	[54]
		I-M (0.001 M)	FZ	p	3	2.08	300	7	[54]
		I-M (0.001 M)	FZ	p	22	3.245	2700	≤0.75	[31]
	Br	Br-M	FZ	n	2.6–3.4		200	20	[31]
	Br	Br-E (0.08 M)	FZ	p	5	0.170	650	>100	[45]
Benzyl-alcohol	QHY-E	QHY-E (0.01 M)	FZ	p	5	0.6	650	54[a]	[55]
		QHY-E (0.01 M)	FZ	p	150	4.1	400	4.6	[56]
	QHY-M	QHY-M (0.01 M)	Cz	n	1	0.673	170	12.6	[57]
		QHY-M (0.01 M)	Cz	n	3	1.36	280	10.2	[57]
		QHY-M (0.01 M)	FZ	n	100	3.3	460	7	[58]
		QHY-M (0.01 M)	FZ	p	2	1.1	280	13[a]	[58]
		QHY-M (0.01 M)	FZ	p	5	0.7	650	46[a]	[55]
		QHY-M (0.01 M)	FZ	p	150	4.5	380	4.2	[55]
		QHY-M (0.07 M)	FZ	p	200	8.5	220	1.3[a]	[53]
	BQ-M	BQ-M (0.1 M)	FZ	n	25	3.25	500	8[a]	[59]
		BQ-M (0.1 M)	FZ	p	10 000	1.9	525	14[a]	[59]
	HQ-M	HQ-M (0.1 M)	FZ	n	25	0.61	500	41[a]	[59]
		HQ-M (0.1 M)	FZ	p	10 000	0.85	525	31[a]	[59]

[a] Maximum S (assume infinite bulk) determined from lifetime data and material parameters.
[b] Surface area corrected S ($S_{max}/1.73$).

Table 2. Summary of significant temporary "thin film" passivation studies from the literature. Samples were (100)-orientation unless stated. Highlighted studies have $S \leq 1\,\mathrm{cm\,s}^{-1}$.

Variant	Chemicals	Growth	Type	Resistivity [Ω cm]	τ_{eff} max [ms]	W [μm]	S_{max} [cm s^{-1}]	Ref.
Superacid	TFSI-DCE (2 mg ml^{-1})	FZ	n	1	2.5	250	3	[61]
	TFSI-DCE (2 mg ml^{-1})	FZ	n	1	8	200	1	[62]
	TFSI-DCE (2 mg ml^{-1})	FZ	n	10	30	200	0.3	[62]
	TFSI-DCE (2 mg ml^{-1})	FZ	n	75	75	320	0.2	[62]
	TFSI-DCE (2 mg ml^{-1})	Cz	n	1270	65	720	0.6	[62]
	TFSI-DCE (2 mg ml^{-1})	FZ	p	0.8	0.7	300	13[a]	[61]
	TFSI-DCE (2 mg ml^{-1})	FZ	p	1	1.7	200	2.7	[62]
	TFSI-DCE (2 mg ml^{-1})	FZ	p	10	13	240	0.7	[62]
Organic	Polystyrenesulfonate	FZ	n	1–5	2.4	280	6[a]	[63]
	Polystyrenesulfonate	FZ	n	3000–5000	28.65	370	0.65[a]	[63]
	Polystyrenesulfonate	FZ	p	1–5	2.05	280	7[a]	[63]
	PEDOT:PSS	FZ	p	150	3.3	300	4.5[a]	[64]
	PEDOT:PSS	FZ	p	150	2.5	300	6[a]	[65]
	Methyl 10-undecenoate	FZ	p	1–2	0.13	375	125[b]	[66]
Polymer	poly(tetrafluoroethylene)	FZ	p	0.5		250	90	[67]
	poly(tetrafluoroethylene)	FZ	p	1.25		250	50	[67]
	poly(tetrafluoroethylene)	FZ	p	17		250	30	[67]

[a] Maximum S determined from lifetime data and material parameters.
[b] Not included in **Figure 3**.

Table 3. Summary of significant temporary "other" passivation studies from the literature. Samples were (100)-orientation unless stated. Highlighted studies have $S \leq 1\,\mathrm{cm\,s}^{-1}$.

Type	Variant	Chemicals/process	Growth	Type	Resistivity [Ω cm]	τ_{eff} max [ms]	W [μm]	S_{max} [cm s^{-1}]	Ref.
Other[a]	Photoresist	S1818 + Corona Charge	FZ	n	11	0.387	315	40	[82]
		S1818 + Corona Charge	FZ	p	1.3	0.2	295	69	[82]
		S1818 + Corona Charge	FZ	p	3.5	0.402	305	37	[82]
		S1818 + Corona Charge	FZ	p	21	0.353	380	54	[82]
	Alkylation	Chlorination/Methylated	FZ (111)		3800	0.29	190	21	[77]
		Chlorination/Octylated	FZ (111)		3800	0.30	190	21	[77]
		Chlorination/Methyl	FZ (111)	n	4000	0.23	250	44	[78]
		Chlorination/Ethyl	FZ (111)	n	4000	0.18	250	60	[78]
		Chlorination/Iso-propyl	FZ (111)	n	4000	0.20	250	60	[78]
		Chlorination/Tert-butyl	FZ (111)	n	4000	0.16	250	80	[78]
		Chlorination/Phenyl	FZ (111)	n	4000	0.20	250	60	[78]
		CH$_3$	FZ (111)		20 000-40 000		300	40	[79]
	Others	NH$_4$F (40%)	FZ (111)	n	4000–6000	2.5	500	10	[35]
		H$_2$SO$_4$ (96–100%)	FZ (111)		3800	0.80	190	12	[77]
		H$_2$SO$_4$ (96–100%)	FZ (111)					0.25	[1]
		HCl	FZ (111)					0.3	[1]
		H$_3$PO$_4$	FZ (111)					1.5	[1]

[a] Not included in **Figure 3**.

ADVANCED SCIENCE NEWS
www.advancedsciencenews.com

pssrrl
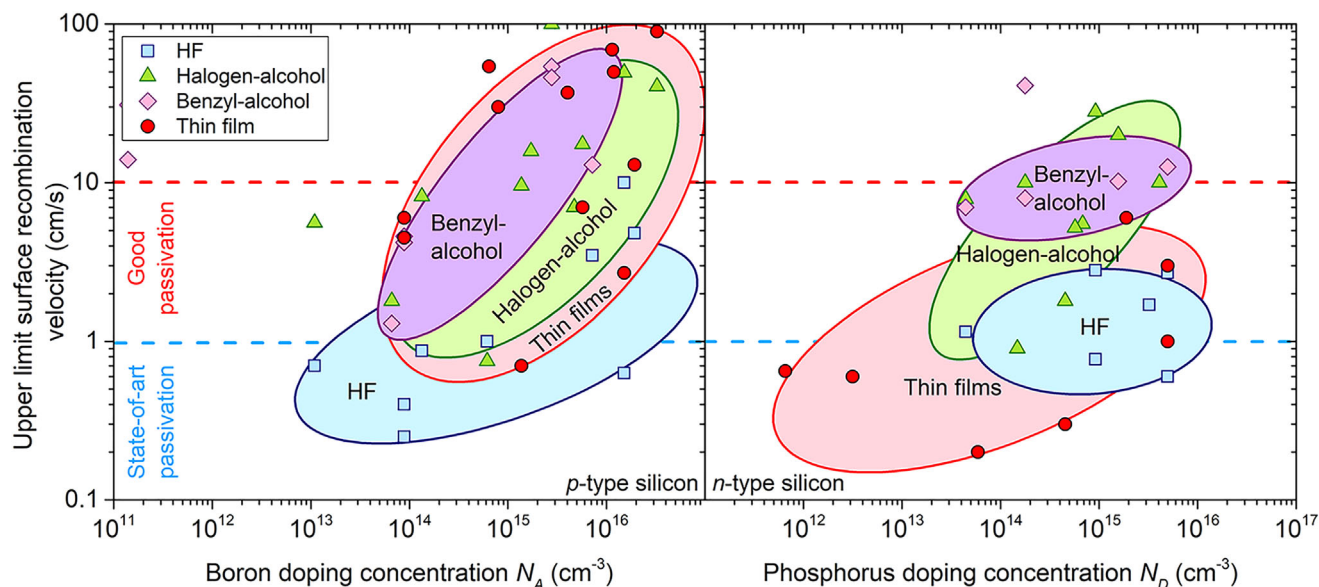physica status solidi
www.pss-rapid.com

Figure 3. Upper limit surface recombination velocity of significant temporary passivation techniques plotted against doping concentration for p- (left) and n-type (right) silicon. The various ellipses correspond to each passivation type and represent the broad range of S reported for that particular method. Results from our "other" category (Section 4.5) are excluded due to limited data.

procedure is to immerse silicon wafers in a plastic container in which the HF solution completely covers the silicon sample. For photoconductance decay (PCD) lifetime measurements this could involve placing an open plastic petri-dish over an induction coil in an extracted environment. Clearly this is not without safety risk and it is also possible that this approach will result in corrosion of components within the lifetime tester. In practice, both issues can be mitigated by replacing the petri-dish with a plastic air-tight container. In this case, the lid must be completely transparent for adequate illumination levels during the PCD measurement as demonstrated by Grant et al.[28,29] For low lifetime samples (<100 μs), Lago-Aurrekoetxea et al. have demonstrated the use of quasi steady-state photoconductance (QSSPC) measurements, which in contrast to PCD, requires an accurate measurement of the generation rate as the sample is continually illuminated during the measurement.[30]

The lowest reported S for HF passivation are $0.25\,cm\,s^{-1}$[1,31] but these are for (111)-orientation surfaces, which are of limited interest for photovoltaics. For (100)-orientation surfaces, the best reported S to our knowledge is $0.4\,cm\,s^{-1}$.[1] For conventionally doped silicon ($\approx 1\,\Omega\,cm$), Grant et al. have demonstrated a very low S of $0.6\,cm\,s^{-1}$ on (100) n- and p-type silicon by a light enhanced HF passivation method.[16,29] In this method 20 ml of 37% HCl is mixed with 150 ml of 15% HF, which is superior to the previous study on HF passivation.[28] Comparing the HF passivation results presented in Table 1, it is interesting to note that most authors report using concentrated HF (usually 48%), however results in Table 1 indicate there is no significant advantage or necessity to use such highly concentrated HF, as demonstrated by Grant et al.[16,28,29]

Textured silicon wafers are of significant interest to the PV community, as texturing greatly improves the light trapping properties of solar cells. In this regard, temporary passivation

techniques which can passivate such surfaces are of interest in terms of material properties and surface roughness/ability to passivate. The lowest reported S for textured silicon wafers is $1.9\,cm\,s^{-1}$, once accounting for the additional surface area (1.73).[32] Baker-Finch examined the dependence of S on the (111) surface area proportion, and found that S increased from $\approx 1\,cm\,s^{-1}$ to $4-5\,cm\,s^{-1}$ when the (111) proportion was increased from 0.4 to 1 respectively.[33] It was concluded that the vertices/edges are responsible for the increased surface recombination.

In general, HF passivation techniques provide the lowest S in p-type silicon compared to other temporary methods and this is shown clearly in Figure 3. HF passivation also gives excellent passivation in n-type silicon, however lower S have been reported using thin films (see Section 4.4). Compared to the best dielectric passivation films to date,[9,13] HF passivation has demonstrated equivalent passivation levels, which is astonishing considering the basic principles of the technique.

Figure 3 also demonstrates a doping dependence in the measured S for HF passivation (less pronounced/obvious for n-type), however this could simply be an artefact resulting from the formation of a space charge region (which occurs when silicon is immersed in HF as will be discussed below), as elucidated by McIntosh and Black.[7]

4.1.2. Passivation Mechanisms

When silicon wafers are immersed in HF solutions, band bending like that shown in Figure 2 occurs, where in general a space charge region is formed in n- and p-type silicon.[28,34,35] During this process, the HF etches any remaining oxide on the surface and passivates the dangling bonds with fluorine

ADVANCED
SCIENCE NEWS

www.advancedsciencenews.com

physica
status
solidi
pss rrl

www.pss-rapid.com

(Si—F).[34,36] Although this bond is energetically strong ($\approx$5 eV), its polarization makes it vulnerable to attack by HF.[36,37] This results in the separation of SiF_4 from the silicon surface resulting from the formation of Si—H back bonding, thus forming a stable hydrogen terminated silicon surface.[38] Interestingly, although the Si—H bond is energetically weaker ($\approx$3.5 eV) than Si—F bonds, the Si—H bond is nonpolar, and therefore it is no longer attacked by the HF solution,[23,38,39] thus providing exceptional passivation.[1]

In contrast, Grant et al. examined the passivation of the silicon–HF interface after illumination, and their results showed a temporary, but substantial improvement in the surface passivation. They concluded that the improvement in surface passivation was attributed to temporary (unstable) bonds with F and OH, which are highly polar and prone to attack by HF.[28,29,39,40] It was demonstrated that immediately after illumination, the passivation level degraded back down to a stable level (Si—H bonds), however could be recovered by further illumination, consistent with temporary bonding with F and OH.

4.2. Liquid Halogen-Alcohol

4.2.1. Overview

Solutions of halogens dissolved in alcohols have been found to provide reasonably low surface recombination and are considerably less hazardous than HF. In practice samples can be placed into transparent plastic bags filled with halogen-alcohol solutions and once sealed samples can be tested with a range of conventional laboratory techniques, such as PCD, QSSPC, and PL imaging. This is discussed later in Section 5.3.

To the best of our knowledge Horányi et al. performed the first study into iodine-ethanol (I-E) pasivation, achieving S of <10 cm s^{-1}.[41] Maekawa and Shima were later successful in reducing S to 0.36–5.5 cm s^{-1}.[42] M'Saad et al. diversified the field by using iodine-methanol (I-M) and bromine-methanol (Br-M) solutions and improved the surface passivation quality, reducing S to $\leq$0.75 cm s^{-1} on (100)-orientation silicon by using I-M.[31] This remains the lowest reported for halogen-alcohol passivation schemes, as summarised in Table 1. M'Saad et al. showed that both I-M and Br-M have strong passivating effects on (100)-orientation silicon wafers, with I-M being more effective than Br-M, and interestingly they achieved better surface passivation with I-E than with concentrated HF (48%).[31] Stephens and Green examined the doping dependence of I-E passivation and broadly found that S reduces with increasing substrate resistivity.[43] Chen et al. investigated the passivation dependence on the iodine concentration in the I-E solution.[44] Their results clearly demonstrated that 0.08 M iodine in ethanol (as used by Stephens and Green[43]) was the optimum concentration, achieving S of 5.2 and 15.8 cm s^{-1} on 1.7–13 Ω-cm n- and p-type Cz silicon, consistent with other reported S values for 0.08M I-E passivation.

Batra et al. compared I-E to Br-M and found I-E to be more effective.[45] Although in general iodine-based passivation appears to be initially more effective than bromine-based

passivation, Batra et al.'s study does suggest better stability in the bromine case.[45] Furthermore, in their study bromine-based passivation provided better surface passivation in the presence of a native oxide (compared to a HF dipped surface), contrary to iodine-based passivation schemes. Recently Sopori et al. reported very high effective lifetimes of 20 ms on n-type 30 Ω cm FZ (111) silicon using I-E passivation.[46] In this regard, the exceptionally high lifetime was attributed to the cleaning procedures, as outlined in Section 5.1.

In general, Figure 3 demonstrates that halogen-alcohol passivation schemes provide approximately even levels of passivation between n- and p-type silicon. The level of passivation is not necessarily high enough to assess accurately the bulk lifetime for material with a resistivity of <10 Ω cm. The strong doping dependence in S for halogen-based passivation shown in Figure 3 is consistent with the work of Stephens and Green.[43] At this time it is difficult to understand exactly why the doping dependence is so strong, but it could be a result of silicon band-bending (as discussed next) or a change in the interface defect density.

4.2.2. Passivation Mechanisms

Silicon wafers immersed in I-M or I-E solutions exhibit a band bending structure like that that shown in Figure 2.[47] In this case, depletion can result in both n- and p-type silicon if the Fermi levels are pinned near mid-gap at the silicon surface.[47] For iodine termination of the silicon surface, the Si—H bonds must be broken and then passivated by iodine. Iodine in methanol/ethanol solvents is naturally in the form of I_2, thus dissociation of the I_2 species must occur for effective I termination of the silicon dangling bonds. In this regard, illumination is necessary to dissociate I_2 into I$^-$ ions which can then remove the hydrogen from the silicon surface. The silicon surface can then "oxidise" another iodine atom, thus forming Si—I bonds.[48,49] The Si—I bonds are susceptible to nucleophilic attack by methanol/ethanol, meaning they are prone to attack by the methanol/ethanol solvents, this results in a silicon surface which is preferentially terminated by methoxy or ethoxy.

Illumination whilst silicon is immersed in I-E or I-M solutions has been shown to reduce the time required to reach maximum surface passivation dramatically.[42,49,50] In this regard, illumination plays two roles in I-E and I-M passivation (i) dissociation of I_2 molecules into I$^-$ atoms and (ii) generation of photoexcited carriers in the silicon material which can further enhance surface reactions. Cai et al. demonstrate that photoattachment reactions occur preferentially on n-type silicon because photogenerated holes are driven to the surface (due to the space charge region) which are readily available for oxidation of the silicon surface (i.e., Si–I formation).[47] In p-type silicon, the space charge region drives holes back into the bulk and electrons to the surface, thus reduction is predominant over oxidation reactions. It must be noted, that the effectiveness of illumination is dependent on the amount of band-bending and the minority carrier lifetime of the material in order to drive sufficient holes to the surface.

4.3. Liquid Benzyl-Alcohol

4.3.1. Overview

Various temporary passivation methodologies have emerged based on benzene-based chemicals (such as quinhydrone) dissolved in alcohols (including methanol and ethanol). Similar to halogen-alcohol passivation schemes, samples can be placed into transparent plastic bags filled with benzyl-alcohol solutions and once sealed, samples can be tested with a range of conventional laboratory techniques, such as PCD, QSSPC, and PL imaging.

Takato et al. provided an early report on the quinhydrone-ethanol/methanol based passivation scheme, achieving a very low S of $\approx 4\,cm\,s^{-1}$ on high resistivity p-type silicon, one of the lowest reported for this passivation scheme.[55,56] Only Pollock et al. have demonstrated a lower S of $1.3\,cm\,s^{-1}$, however this measurement was also performed on high resistivity p-type silicon.[53] Chhabra et al. demonstrated that a moderate level of surface passivation is retained when the silicon samples are taken out of the quinhydrone-methanol solution.[57,58] For 1 Ω cm n-type silicon they achieve S of $12.6\,cm\,s^{-1}$ (in solution) and $60.7\,cm\,s^{-1}$ (out of solution), however for 100 Ω cm n-type silicon they achieve S of $7\,cm\,s^{-1}$ (in solution) and $8.5\,cm\,s^{-1}$ (out of solution).

Kotulak et al. worked on benzoquinone- and hydroquinone-methanol passivation,[59] and demonstrated that benzoquinone provides a good level of surface passivation after a short 2–5 min incubation period, while hydroquinone-methanol requires an incubation period of ≈ 1 day for effective surface passivation.

From Table 1, it is evident that benzyl-based passivation schemes are yet to demonstrate $S < 1\,cm\,s^{-1}$. Either more work is required for benzyl-alcohol passivation to reach the state-of-art passivation level like that achieved with HF and halogen-alcohol passivation schemes, or there is a fundamental reason which prohibits this. From Figure 3, it appears that benzyl-alcohol passivation is more stable or less dependent on the doping concentration for n-type silicon, however in comparison to halogens, HF and thin films, benzyl-alcohol passivation shows higher surface recombination values. For p-type silicon, the same doping dependence is observed for benzyl-alcohol, halogens, and thin films, thus little can be concluded if benzyl-alcohol is superior/inferior to either of these passivation techniques on p-type silicon.

Benzyl-alcohol based passivation schemes are regarded as a viable alternative method to I-E and I-M methods and generally offer better stability.[53,55,56,59] In general, three benzyl species have been examined, hydroquinone (HQ), p-benzoquinone (BQ), and quinhydrone (QHY), where the latter is the combination of HQ and BQ. Of the three benzyl species, quinhydrone dissolved in methanol provides superior surface passivation when its concentration is 0.05 to 0.1 M.[58,59,60]

4.3.2. Passivation Mechanisms

When silicon is immersed in benzyl-alcohol based solutions, band bending like that shown in Figure 2 arises, that is, a space charge region is formed.[60] The reactions of charge carriers with species in the benzyl-alcohol solutions have not been extensively examined, however the role of oxidation/reduction reactions at the surface is likely to affect the level and speed of surface passivation.

Silicon immersed in 0.07–0.1 M QHY-M solutions, undergoes a reaction with QHY, which passivates the silicon surface. Analysis of the silicon/QHY-M interface has indicated that of the passivated silicon bonds, 50% are bound to QHY and the remaining 50% are bound to methoxy, similar to I–M based passivation methods.[59,60]

In order to examine the passivation mechanisms by QHY-M, the individual constituents of QHY (BQ and HQ) have been investigated.[59] For both constituents individually dissolved in methanol, BQ-M solutions were found to provide a similar level of passivation to those samples immersed in QHY-M, however samples immersed in HQ-M solutions showed very poor passivation levels, suggesting BQ is the active passivation component in QHY-M solutions.[59,60] In contrast, HQ-M solutions do begin to passivate after being immersed in the solution for ≈ 1 day.[59] Kotulak et al. have suggested that BQ and HQ convert back and forth in solution through an intermediate QHY species, which can then passivate the silicon surface, however this conversion requires both protons and photons to readily occur.[59] The availability of protons can be controlled by the solvent used (i.e., methanol), while photons can be controlled by external illumination sources. Under illumination, BQ-M solutions provided an immediately high level of surface passivation, indicating the transition from BQ to QHY is very fast, while for samples immersed in HQ-M solutions, the passivation level did increase faster under illumination, however was inferior to BQ-M based solutions, suggesting the transition from HQ to QHY is much slower.[59] While the role of illumination was not fully discussed, it is postulated that photogenerated carriers in the silicon material are aiding surface passivation through oxidation reactions at the surface. Therefore, the incubation period[55,56,59,60] required to achieve maximum surface passivation can be significantly reduced if the use of external illumination is applied.

4.4. Thin films

4.4.1. Overview

Temporary surface passivation of silicon can also be achieved by the formation of a thin passivating film at the sample surface(s). Temporary thin films include polymers and films arising from a superacid-based solution (a superacid has acidity greater than that of 100% H_2SO_4). It is noted that polymer-based processing sometimes requires a curing step above room temperature and it is possible that this may have an impact on bulk lifetime. In general thin film-passivated samples have good short-term stability and therefore can be characterised in a similar manner to those passivated with inorganic dielectric films (e.g., SiN_x, Al_2O_3). That is, the samples can be measured using PCD, QSSPC, and PL without being immersed in a liquid and without the instruments being kept in an extracted environment.

As part of the development of organic-silicon heterojunction solar cells, Schmidt et al. found spun-on poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) provides a surprisingly high level of surface passivation with emitter saturation current density (J_{oe}) values of 80 fA cm^{-2},[64] with Zielke et al. further improving the J_{oe} to 46 fA cm^{-2} by optimising the surface preparation prior to deposition. In terms of S, 4–6 cm s^{-1} has been estimated from the data reported by Schmidt et al. and Zielke et al.[65]

Yang et al. achieved an S of 100 cm s^{-1} for PEDOT:PSS passivation.[68] On textured surfaces they found the standard PEDOT:PSS film was not conformal (i.e., the film did not coat the troughs), however by reducing the viscosity of the organic film, conformal passivation of the textured surfaces could be achieved, as demonstrated by Schmidt et al.[64,69]

Following on from the PEDOT:PSS work, Chen et al. examined the passivation quality of PSS after a short 130 °-C heat-treatment.[63] Very low S values of 0.65–7 cm s^{-1} were attained when the PSS films were exposed to an oxygen ambient, however S increased dramatically when exposed to either nitrogen or ambient air conditions,[63] which is clearly problematic from a materials characterisation perspective.

Sieval et al. investigated organic mono-layers formed from methyl 10-undecenoate, which gave an S of 120 cm s^{-1}.[66] It is noted that the process of Sieval et al. had a 2 h step at 200 °C, which may be sufficient to impact on the bulk lifetime, so this combined with the relatively poor surface recombination velocity shows this is of limited use for characterisation of high bulk lifetimes. A similar high S was also reported for a spin coated oleylamine organic film, however the film was cured at room temperature.[70]

Rappich et al. have studied electrochemical deposition of ultra-thin benzene-type layers, which have shown stability up to 200 °C, although their work did not give values of S.[71] Biro et al. achieved low S of 30 cm s^{-1} by depositing a poly(tetrafluoroethylene) based polymer Nafion, whereby a 1 hr 90 °C curing process was necessary. The passivation was shown to stabilize after ≈20 min following the polymer coating (with bias illumination).[67]

Yang et al.[72] and Castillo et al.[73] have examined the passivation capabilities of room temperature deposited/formed multifunctional polymeric films using chemical vapor deposition (CVD). While good passivation ($S < 10$ cm s^{-1}) has been achieved by this method, the use of a CVD system is not attractive for low cost and straightforward passivation.

More recently, following on from successful results on the passivation of transition metal dichalcogenides,[74] Bullock et al.[61] and the authors of this review[62] have developed bis(trifluoromethane)sulfonimide (TFSI) passivation of silicon. The approach is to dissolve TFSI crystals in a solvent (typically anhydrous 1,2-dichloroethane) and to dip the wet chemically-cleaned and HF-dipped silicon sample into the solution for a short period of time (typically ≈60 s). Upon drying, a thin passivating film is left on the sample surfaces, which enables lifetime measurements by usual characterisation methods.[67] By this passivation scheme, Grant et al. have demonstrated very low S of <1 cm s^{-1} on n- and p-type silicon.[62]

From Table 2, it is clear that thin films (organic- and superacid-based) can provide a very high level of surface passivation. Superacid-based passivation in particular has demonstrated exceptional passivation ($S \leq 1$ cm s^{-1}), which makes it suitable for measuring very high lifetimes while being compatible with conventional techniques such as PCD, QSSPC, and PL. Turning to Figure 3, it is evident that the best thin films are better at passivating n-type silicon than any other temporary passivation scheme (including HF). On p-type silicon, the non-safety benefits of using thin films over other passivation schemes (excluding HF) is not obvious, however future developments in organic thin film passivation such as TFSI-based solutions, could see superior passivation on p-type also.

4.4.2. Passivation Mechanisms

PEDOT:PSS is currently used as a hole conducting layer in organic-silicon heterojunction solar cells.[75] The carrier selectivity of the film is attributed to the band offset, which on n-type silicon inverts/depletes the near surface region of electrons, while on p-type silicon the converse is true, whereby the silicon surface is under accumulation.[75] It is therefore postulated that a large part of the surface passivation is attributed to a field effect mechanism. Schmidt et al.[64] and others[65,75] have recently begun to use a thin native oxide in between the silicon surface and PEDOT:PSS, resulting in lower S, which could be due to a reduction in the interface defect density.

In contrast to PEDOT:PSS, Chen et al. investigated the passivation mechanisms of PSS when in contact with silicon.[63] The initial requirement for a high level of surface passivation is a H-terminated silicon surface. When the PSS film is deposited on the silicon surface, thermal equilibrium must be satisfied, in which case the bands bend downwards in n-type silicon, thus forming accumulation of electrons at the silicon surface.[63] Prior to exposing the PSS film to an oxygen ambient, the silicon surface is moderately passivated by the PSS film, however in the presence of oxygen, excellent surface passivation is attained. During exposure to an oxygen ambient, it is suggested that oxygen penetrates the PSS film and oxidises the surface through an electron transition from the silicon surface. The PSS monomer molecule then bonds to the oxygen. Therefore the very high level of surface passivation is attributed to an oxidation effect of the silicon surface in the presence of the PSS film. In contrast, when the oxygen ambient is replaced by nitrogen, the reverse occurs, whereby the surface undergoes de-oxidation leading to an increase in S.

The deposition of polymers has been examined however little information in the literature exists, therefore no explanation regarding their passivation mechanisms can be discussed at this time. In general, polymers, and organic films (PEDOT:PSS, PSS) require a 100–200 °C heat-treatment to activate and bake the films, which might be undesirable from a materials characterisation perspective due to possible effects on bulk lifetime.

Regarding the recently discovered superacid-based passivation, at present the exact passivant is unclear. Both Grant et al.[62] and Bullock et al.[61] have examined the injection-dependent lifetime for n- and p-type silicon and they find no evidence for substantial field-effect passivation and thus these schemes are not likely to give rise to strong band bending. While the superacid-based passivation procedure has demonstrated very low surface recombination, more work is required

**ADVANCED
SCIENCE NEWS**

www.advancedsciencenews.com

physica pss rrl
status solidi

www.pss-rapid.com

to understand the details of the film composition and its thickness.

4.5. Other Temporary Passivation Schemes

4.5.1. Overview

Beyond the scope of the more established temporary passivation schemes, there are many "other" schemes which provide adequate surface passivation for bulk material characterisation, however they have not been widely investigated like those schemes discussed previously in this review. Table 3 summarises the best S attained for each "other" passivation scheme discussed herein.

Immersion of silicon wafers in ammonium fluoride (NH$_4$F) solutions has demonstrated low S of $\approx 10\,cm\,s^{-1}$ on high resistivity FZ (111) silicon.[35] In contrast, much higher S result when FZ (100) silicon is immersed in NH$_4$F solutions.[76]

Yablonovitch et al. have demonstrated very low S in the range of 0.2–1.5 cm s^{-1} for highly acidic, concentrated solutions of HCl, HSO$_3$CF$_3$, H$_2$SO$_4$, and H$_3$PO$_4$ when Si (111) silicon wafers are immersed in the said solutions.[1] They also deduced that S is proportional to the acid molarity, whereby S increases as the concentration of the acid is reduced.[1]

Royea et al.[77] and Nemanick et al.[78] have examined the passivation quality of alkyl group termination of Si dangling bonds, and measured S in the range 20–60 cm s^{-1}, while Plymale et al. have achieved an S of 40 cm s^{-1} by a two-step halogenation/alkylation method forming a passivating coverage of CH$_3$.[79]

Solutions of potassium cyanide have been tried, but have not been found to passivate bare silicon surfaces particularly effectively.[80] In contrast, when a thin oxide on the silicon surface exists, a potassium cyanide treatment can reduce the surface recombination,[80] which could be attributed to a reduction of interface states at the Si–SiO$_2$ interface.[81]

Schmidt and Aberle deposited varnish (a photoresist) on the silicon surface by spin coating, and then deposited corona charges on its surfaces, achieving S of 30–70 cm s^{-1},[82] suitable for defect characterisation of lower purity silicon material such as p-type Cz and mc-Si.

4.5.2. Passivation Mechanisms

In contrast to HF solutions, NH$_4$F are highly buffered and thus have a much higher pH of 8.[83,84] The presence of OH$^-$ and other related species in NH$_4$F promote selective etching of silicon, where (111) surfaces are attacked more efficiently, leading to smooth monohydride-terminated Si(111) surface.[84,85] However on Si(100), the anisotropic etching nature of NH$_4$F leads to Si(111) facets, which prevents the formation of a smooth H-terminated surface.[83,86] The energy bands of n-type silicon while immersed in 40% NH$_4$F solutions have been shown to form accumulation (opposite to Figure 2), where the chemical reactions are facilitated by electrons from the conduction band (reduction).[35,84] No reports for p-type silicon could be found, and thus we cannot assume what the band bending would look like for p-type silicon in contact with NH$_4$F,

as Fermi level pinning could arise if sufficient surface states exist, which could result in accumulation or depletion/inversion.

Immersion of n- and p-type silicon wafers in highly acidic solutions such as sulfuric acid (H$_2$SO$_4$) and hydrochloric acid (HCl) result in depletion/inversion conditions, however they offer excellent passivation levels when their concentration is high.[1,35,77] At present little information is available regarding the passivation mechanisms of these acids.

Chlorination/alkylation of silicon surfaces has been investigated as a means to both passivate the silicon surface and prevent oxidation during storage.[77–79] In general H-terminated Si(111) surfaces using NH$_4$F are first chlorinated using chlorobenzene saturated with phosphorus pentachloride for $\approx$1 h at 100 °C, resulting in a Cl-terminated surface. After chlorination the surfaces are then treated by immersion in a tetrahydrofuran solution containing various Grignard reagents (alkyl groups) at 115 °C for $\approx$1 day. The alkylation of the Cl-terminated Si(111) surface results in complete removal of Cl, thus prior chlorination is vital for successful alkylation. The dissociation of Si—Cl bonds does not result from direct attack from the alky groups, but rather from the transfer of an electron to the silicon surface which undergoes a chemical reaction of the "reduced" Si—Cl, thereby dissociating this bond.[77–79] Based on the requirement for electrons to reduce the surface in order for sufficient alkyl surface passivation, suggests the silicon surface is under accumulation (in the case of n-type).[77–79]

Deposition of varnish followed by corona charging has led to some relatively low S on n- and p-type silicon.[87] In this case, the varnish does not provide any chemical passivation, meaning a very high interface defect density is present. However when negative corona charge is applied, the surfaces of n-type become inverted (repels electrons) resulting in upward band bending, while for p-type, the silicon is under accumulation, resulting in downward band bending. Thus the low S achieved by this passivation scheme is purely driven by a field effect mechanism.

5. Processing Issues

5.1. Cleaning

In this section we address the cleaning procedures for each liquid passivation type, and summarize the common procedures required to achieve consistent surface conditioning. From our experience, the chemicals used should be of high purity (impurity level of parts per billion) and the DI water have a very high resistivity (in our experience $\geq 18\,M\Omega$).

5.1.1. HF Based Passivation

Yablonovitch et al. emphasize the importance of a pre-treatment method for exceptional surface passivation.[1] Their method consisted of 2-steps: (i) the oxidation of the silicon surface (thermal or chemical); and (ii) dissolution of the oxide layer by HF (this can be done in the passivating HF solution).

Luke and Cheng investigate the level of passivation attained after extensive cleaning using a boiling solution of trichlorethylene, acetone, and methanol.[51] After rinsing and HF

ADVANCED
SCIENCE NEWS

www.advancedsciencenews.com

physica
status
solidi
rrl

www.pss-rapid.com

dipping the sample, they were chemically oxidised in boiling 90 °C concentrated sulphuric acid (H_2SO_4) for 10 min. Without removing the chemical oxide, the final treatment involved cleaning the samples in a boiling solution of $HCl:H_2O_2:H_2O$ (1:1:1) for 6 min. Notably, the chemical oxide was not etched away prior to immersing the samples in the passivating HF solution, similar to that reported in Ref.[29].

Tian et al. examined the difference in passivation of H-terminated silicon (111) surfaces treated by either an RCA clean and NH_4F or a pirhana etch and 10% HF dip. It was demonstrated the latter gave the highest lifetime.[88]

Grant et al. demonstrated that not only does chemical cleaning and oxidation provide good surface conditioning prior to immersion in HF, etching the silicon surface in 25% tetramethylammonium hydroxide (TMAH) prior to immersion in the HF solution provides a superior surface condition for HF passivation.[28,29] It was postulated that higher hydrogen coverage occurs on these surfaces due to the micro-roughness present after the TMAH etch.[89,86,28]

Summary to Achieve the Best Results

It is clear from the literature that the silicon surface must be cleaned prior to immersion in HF. The most common cleaning procedure is the RCA developed by Kern,[90] however this process does not necessarily provide the best surface condition. To improve the surface condition, it is apparent that RCA cleaning should be followed by etching silicon in TMAH or $HF:HNO_3$ followed by a chemical oxidation (RCA 1 or H_2SO_4). The chemical oxide is then removed once immersed in the passivating HF solution.

5.1.2. Halogen-Alcohol Passivation

I-E and I-M chemical passivation solutions are very attractive for temporary liquid passivation applications, however the chemical pre-treatment has not been the subject of many detailed reports. Stephens and Green demonstrate $S < 10 \, \mathrm{cm \, s^{-1}}$ following a single dilute HF dip.[43] Although this simple pre-treatment is desirable, it is susceptible to inconsistent surface passivation by the halogen-alcohol treatment due to surface contamination, and varying surface conditions.

In general, the standard RCA clean and HF dip prior to I-E or I-M passivation has proved to be a good surface pre-treatment, where in one case a very low S of $0.75 \, \mathrm{cm \, s^{-1}}$ was attained.[31] In contrast there have been reports that indicate a piranha etch ($H_2SO_4:H_2O_2$) or silicon etch ($HF:HNO_3$) prior to halogen-alcohol passivation provide clean/smooth silicon surface, resulting in S of 1 to $10 \, \mathrm{cm \, s^{-1}}$.[41,42,46,49,91]

In contrast to HF based passivation, the silicon surface must be free of any oxide prior to halogen-alcohol passivation. In this regard, the final oxide "removal" step is critical for good and reliable surface passivation. While dilute HF solutions are the most common way to remove a native or chemical oxide layer, several authors have examined replacing dilute HF with ammonium fluoride (NH_4F) on Si(111) surfaces.[47] NH_4F is a highly buffered HF solution and has been shown to minimize surface roughness (compared to dilute HF solutions) during the final oxide removal step, thereby yielding lower S after halogen-alcohol passivation.

Angermann et al. demonstrated that NH_4F treated Si(111) surfaces attained a much higher hydrogen coverage (lower interface defect density) compared to a simple dilute HF dip, and concluded this be attributed to the anisotropic etching behavior of NH_4F.[86,89] In contrast, the same treatment on Si(100) surfaces results in a much rougher silicon surface (higher interface defect density) compared to a simple dilute HF treatment.[86,89]

Summary to Achieve the Best Results

Halogen-alcohol based passivation techniques do not show a strong correlation with wet chemical pre-treatment steps, however the examined literature indicates that wafer cleaning by either the standard RCA process or piranha etch is required to achieve a clean silicon surface. Furthermore, in cases where silicon etching is required, a standard $HF:HNO_3$ etch provides a good surface condition for the passivation treatment. Perhaps the most critical step prior to halogen-alcohol passivation is the final oxide removal and the termination of Si bonds with hydrogen. For Si(100), dilute HF is deemed the best solution, while for Si(111), NH_4F is superior to dilute HF.

5.1.3. Benzyl-Alcohol Passivation

In the surveyed literature for benzyl-alcohol passivation, the favored wet chemical pre-treatment is the piranha etch followed by a dilute HF dip [46,53,57–59]. In contrast to halogen-alcohol passivation, an S below $1 \, \mathrm{cm \, s^{-1}}$ has not been reported for benzyl-alcohol passivation, which could be a consequence of the relatively unexplored wet chemical pre-treatment processes. It is therefore possible that $S < 1 \, \mathrm{cm \, s^{-1}}$ could be attained by benzyl-alcohol passivation if the pre-treatment is optimised.

5.1.4. Thin Film Passivation

Biro et al.[67] deposited a polymer film on silicon without any pre-treatment, yielding similar S values to Schmidt et al. whom deposited varnish (photoresist) on "as-received" (native oxide coated) silicon wafers, which were subsequently corona charged to give S of 30–70.[87] While no pre-treatment is attractive for process simplicity, the high S values would indicate the native oxide is potentially limiting the minimum surface recombination which otherwise might be lower for these methods if the surface pre-treatment were optimised.

In contrast, there have been a number of trialled wet chemical pre-treatment processes, however the favored treatment to-date is a simple HF dip to remove any native oxide prior to deposition. This simple treatment prior to thin film passivation has led to some very low S values of $3–10 \, \mathrm{cm \, s^{-1}}$,[61,63,72] and in one case a very low S of $0.65 \, \mathrm{cm \, s^{-1}}$,[63] however the later was achieved on near intrinsic silicon. While low S have been achieved without substantial wet chemical pre-treatment processing, a simple HF dip is susceptible to an unreliable surface condition by either surface contamination from previous wet chemical processing or the surface morphology (etched versus polished). Thus, for materials characterisation, a consistent surface condition is vital for reliable surface passivation, and a simple HF dip process is not likely to satisfy this condition.

ADVANCED SCIENCE NEWS
www.advancedsciencenews.com

pss rrl
physica status solidi
www.pss-rapid.com

Recently, Grant et al. demonstrated the significance of a surface pre-treatment process on the level of passivation attained when silicon wafers are treated with a superacid-containing solution.[62] In that work, it was demonstrated that a simple HF dip provided inferior surface passivation to a sample which was chemically cleaned or etched in either HF:HNO₃ or 25% TMAH. The work demonstrated that a sample subjected to an RCA 1 clean and HF dip degraded the surface condition, while a sample subjected to an RCA 2 clean and HF dip (no RCA 1) provided the best surface condition for superacid-based passivation, achieving $S < 1\,\mathrm{cm\,s^{-1}}$ on various silicon material, much lower than any other thin film reported in the literature. Grant et al. also demonstrated that etching the silicon samples in 25% TMAH prior to a RCA 2 clean and HF dip achieved a reliably high level of surface passivation using the superacid method.[62] In this regard, the etching process was considered desirable, as it would remove any differences in as-received or previously processed silicon wafers, thereby minimising variations in S from one sample to the another.

Summary to Achieve the Best Results

Although a high level of surface passivation has been achieved by simply treating the silicon wafers with dilute HF prior to thin film deposition, Grant et al. have demonstrated that a superior level of passivation results if the silicon surface is etched, cleaned, and HF dipped. The best pre-treatment processes may have some dependence on the film being deposited and the chemical reactions that occur at the interface during passivation, and therefore variations of the etch and clean procedures compared to Grant et al. may be required for the best results.

5.2. Stability Issues

Measurements of the degradation kinetics and accurate extraction of bulk silicon defects relies on the stability of the surface passivation during such measurements. Therefore the stability of the temporary passivation scheme needs to be addressed in order to understand which films are best suited for quick high bulk lifetime measurements (minutes) or longer light induced degradation experiments (hours). The following section outlines the stability of each passivation strategy.

5.2.1. HF Based Passivation

While HF based techniques in general provide the highest level of surface passivation (see Figure 3), the instability of the passivation whilst silicon wafers are immersed in HF is undesirable for long term measurements. Recently, Razera et al.[32] examined the time dependence of silicon wafers immersed in 48% HF, and demonstrated that for planar (100) silicon wafers, the lifetime decays steadily for the first 6 min and then stabilises beyond this time. It was proposed that the initial high lifetime at $t = 0\,\mathrm{min}$ represents a fluorine passivated surface, while for $t > 6\,\mathrm{min}$ the passivation is attributed to hydrogen termination of silicon surface states, resulting in a lower, but stable surface lifetime.[32] In contrast, when textured

silicon wafers are immersed in 48% HF, the initial lifetime is low, but quickly increases, reaching its peak lifetime after ≈3 min of immersion, and then drops again where it finally stabilises for $t > 8\,\mathrm{min}$. The different behavior in the time dependent lifetime measurements, suggests formation of Si—F bonds is slower on textured wafers, which has been attributed to a delay in the reaction that substitutes the OH (formed during chemical oxidation) group with F.[32]

For silicon wafers immersed in lower concentrated HF solutions (15–20%), Grant et al. have demonstrated that immediately following illumination (to active the surface passivation), the lifetime degrades substantially from 10 to 6 ms after 1 min in the dark (a change in S of ≈3 cm s⁻¹), at which point the passivation begins to stabilise.[28] Fortunately the lifetime (and surface passivation) can be recovered by subjecting the sample to illumination, which then degrades once the illumination source is terminated. This degradation and recovery mechanism is said to involve temporary passivation with F and hydroxyl goups during illumination, which are subsequently attacked by the HF solution post illumination, resulting in a decay in the surface passivation, stabilising at a level where Si—H bonds are the predominant passivating species.[28] Although Grant et al. only demonstrated 3–4 cycles of this passivation mechanism, it is anticipated, many more cycles could be performed before any permanent reduction in the lifetime is observed. In this regard, it is possible to measure the same sample many times in order to achieve an accurate measurement of the measured lifetime and its injection dependence regarding any bulk defects in the material.

In contrast, if the bulk lifetime of the material is low (<1 ms), then any degradation resulting from changes in the surface passivation while immersed in HF (dilute or concentrated) would be negligible because bulk recombination mechanisms are dominant over changes in surface mechanisms, as demonstrated by Sugimoto et al.[92]

5.2.2. Halogen-Alcohol Passivation

Although I-E or I-M is the most utilised liquid passivation technique, there have been numerous reports regarding the stability of the passivation scheme.[31,44,45,49,53,56,91] In all cases, iodine based passivation steadily degrades within minutes after reaching its peak passivation level and then stabilises at a much lower level after ≈4 h of immersion. On high lifetime samples (FZ wafers), Pollock et al. examined the time dependence of I-E passivation, and found the scheme degraded steadily from ≈6 ms (initial) to ≈3 ms after 4 h in solution.[53] For lower lifetime samples (Cz wafers), a similar reduction in lifetime was observed, that is a 50% reduction in the effective lifetime after ≈4 h in solution. In contrast, when the I-E passivated silicon sample is removed from the solution and exposed to ambient air, the degradation rate is much faster, where a 60–70% reduction in the effective lifetime is observed after ≈5 min out of solution. In this regard, it is evident that I-E passivation is susceptible to oxidation, similar to that for H-terminated silicon surfaces following a HF dip.[91]

The degradation of I-E or I-M passivation while silicon is immersed in solution has been attributed to oxidation of the silicon

surface.[31,44,57] Chhabra et al.[57] performed X-ray photoelectron spectroscopy of a I-E passivated silicon sample after 1 h immersion, and observed a small SiO_x peak, indicating the sample had become oxidized whilst immersed in solution, consistent with other reports.[31,44,45] In order to mitigate oxidation of the silicon surface by dissolved oxygen in the I-E solution, M'saad et al.[31] bubbled nitrogen through the methanol solution before and during the time dependent lifetime measurements, which did improve the stability of the surface passivation. In this regard, future experiments regarding the stability of iodine-solvent passivation might be carried out in a glovebox whereby the humidity and oxygen levels are better controlled.

5.2.3. Benzyl-Alcohol Passivation

This relatively new passivation scheme has demonstrated some very low S values as shown in Table 1 and Figure 3, however is generally inferior to the best halogen-alcohol, HF and thin film based passivation schemes. When considering the stability of the passivation scheme however, QHY is by far the most stable temporary passivation scheme when silicon wafers are immersed in solution.[53,55,56,59] Pollock et al. demonstrated that even on high lifetime silicon wafers (sensitive to surface recombination), the passivation (≈8 ms) remains stable for at least 5 h, and only slightly degrades thereafter. On lower lifetime samples (≈500 μs) Takato et al. demonstrated stability of the surface passivation up to 72 h of immersion in a QHY-E solution, while Kotulak et al.[59] demonstrated stable passivation (3.2 ms) under constant illumination (ambient laboratory light) for up to 13 h, however on average, there were no signs of degradation, consistent with Takato et al.[56]

When the QHY passivated samples are removed from the solution and exposed to ambient air, the passivation does degrade relatively quickly, that is a 50–60% drop in the effective lifetime after 30 min in air, however this rate is still much slower than that for I-E and H-terminated surfaces under the same conditions.[91]

The degradation (or lack thereof) when silicon wafers are immersed in QHY-M or QHY-E has been investigated by Chhabra et al.[57] In contrast to an I-E treated silicon wafer, where the surface becomes prone to oxidation, XPS measurements of QHY treated surfaces did not show any indication of oxidation following a 1 h immersion in QHY-M solution, suggesting QHY passivation is far more resistant to oxidation than I-E, hence the passivation is also very stable.

5.2.4. Thin-Film Passivation

The hole-conducting transparent polymer PEDOT:PSS provides a reasonable level of surface passivation, as demonstrated in Table 2. However under ambient conditions, significant degradation in the surface passivation by PEDOT:PSS has been observed.[64] Schmidt et al.[64] measured the degradation rate of a n-type silicon solar cell featuring the PEDOT:PSS film on the front surface, and demonstrated substantial degradation of the cell efficiency after being stored in air (≈4% absolute drop) for ≈100 h. In contrast, when a sister cell was stored in

dehumidified air (desiccator), no degradation was observed, and the front passivation provided by the PEDOT:PSS film remained stable for 3,000 h. From these findings, Schmidt et al. concluded that the observed degradation is caused by the interaction of the PEDOT:PSS junction with water molecules in the atmosphere.[64] In contrast, Walter et al.[93] examined the passivation properties of the PEDOT:PSS layer under intense illumination (200 mW cm^{-2}) for 11 h at 130 °C, and observed no degradation, however the lifetime level was restricted to ≤100 μs.

Chen et al.[63] examined the stability of 800 nm thick PSS films, and demonstrated that degradation was unavoidable under low relative humidity (RH: 10–20%) levels, whereby the measured lifetime decreased by 50% over a 1 h period and this was exacerbated when the film was exposed to ambient conditions (RH: 40–60%), leading to much stronger degradation. PL imaging of a passivated sample demonstrated the degradation was relatively uniform across the wafer surface. In contrast, poly(tetrafluoroethylene) based polymers have demonstrated excellent stability over a 4 h period in ambient conditions under constant illumination (50 mW cm^{-2}),[67] however the surface recombination is much higher (30–90 cm s^{-1}), which limits this film to low bulk lifetime samples.

More recently, the stability of superacid-treated silicon surfaces (under ambient conditions) has been examined by Bullock et al.[61] and the authors of this review.[62] In both cases the "film" remained relatively stable over the first 60 min following the treatment, but degradation was more prominent over a 2–3 h period, where a lifetime drop of ≈30% was observed. Grant et al. reported an average degradation rate in S of 0.0052 cm s^{-1} min^{-1}, determined from three separate experiments in order to improve the accuracy. The source of degradation is still unclear, however it is speculated that moisture from the ambient air is reacting with the "film".[62]

5.2.5. "Other" Passivation

Although acid-based passivation schemes such as NH_4F, HCl, and H_2SO_4 have demonstrated excellent levels of surface passivation, as evident in Table 3, their passivation stability has not been examined while silicon wafers are immersed in solutions, however, the passivation degrades immediately once the silicon wafers are taken out of the solution, as demonstrated by Michalak et al.[35]

Chlorination/alkylation of silicon surfaces have led to some moderately low S of 20–60 cm s^{-1}, however the passivation has demonstrated excellent stability over hundreds of hours exposed to ambient air conditions.[77–79] The excellent stability of alkylated silicon surfaces is attributed to prevention of surface oxidation, as demonstrated by Refs.[77–79]. Such films could find use on lower quality silicon materials whereby bulk recombination is dominant over that occurring at the surfaces.

Corona charged films (charge deposited on the surfaces of a film/dielectric layer) have shown steady degradation immediately following the deposition of charge when exposed to ambient conditions, whereby Schmidt and Aberle demonstrated a 60% reduction in lifetime 20 min post charge deposition.[87] In contrast, Bonilla et al.[94] have shown that corona charges can be stabilised (on the timescale of days) by depositing hexamethyl-disilazane (HMDS) on the corona charged surface at 120 °C for

ADVANCED
SCIENCE NEWS
www.advancedsciencenews.com

physica **pss** rrl
status solidi
www.pss-rapid.com

30 min. Such passivation techniques could thus find use in long term degradation experiments, such as light induced degradation (LID).

5.3. Compatibility With Characterisation Methods

Practical constraints due to safety and stability issues mean some approaches work better than others under certain conditions. In **Table 4** we summarize the practical issues associated with the five categories of temporary surface passivation.

One of the first commercial techniques to measure the spatial distribution of the minority carrier lifetime was ELYMAT.[2] The basic operation of the system consisted of immersing a defined area of silicon (front and back surface) in dilute HF (1–5%), applying a potential difference across the front and rear HF contacts of the silicon wafer, illuminating the front surface with a laser beam and then measuring the corresponding current and voltage, which could be converted to a minority carrier lifetime (or diffusion length). Although this system was essential for detecting metal contamination and wafer inhomogeneity, the system was too slow and not practical compared to current techniques such as PCD and PL imaging.[2] In contrast, Sugimoto and Tajima performed PL imaging of mc-Si immersed in dilute 5% HF.[92] Whilst it is noted that HF passivation has been used in PL imaging[92] this was with a custom laboratory set-up and not a commercial tool, thus in general HF passivation might not be suitable for PL imaging (in terms of safety). Grant et al. have successfully demonstrated a light enhanced HF passivation method which is conducted inside a fume-hood, as shown in **Figure 4**.[28,29]

In comparison to HF passivation setups, halogen- and benzyl-alcohol passivation schemes do not possess the same safety concerns and thus surface passivation of silicon samples can be achieved by immersing them in a sealable plastic bag containing a small amount of halogen- or benzyl-alcohol solution, as shown in **Figure 5**.[95] By this method, samples can be characterised using commercial PCD and PL set-ups such as those from Sinton Instruments and BT imaging, respectively.[96]

Recently, Al-Amin and Murphy have demonstrated the effectiveness of the sealable bag approach for passivating mc-Si to measure the increase in bulk lifetime after sequential low temperature annealing to getter interstitial iron internally,[96] as shown in **Figure 6**. Other benefits of this approach include room temperature passivation conditions, a reliable level of
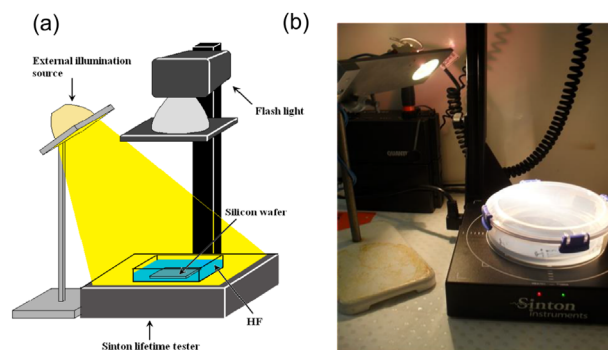

Figure 4. (a) Schematic of the HF passivation method and (b) a photograph of the setup in a fume-hood Reproduced with permission[29].

passivation and more importantly, I-E does not provide a source of hydrogen which can deactivate bulk defects, therefore shielding true bulk recombination mechanisms.

For high lifetime silicon samples (>1 ms), the requirement for a spatially uniform, high level of surface passivation is necessary in order to accurately characterize bulk silicon defects using PL-based techniques. While halogen- and benzyl-alcohol based passivation schemes have demonstrated a high level of passivation, their spatial uniformity is limited.[41,46,97] In this regard, thin film passivation schemes have demonstrated exceptional uniformity. Chen et al.[63] have shown that spun-on PSS films exhibit excellent uniformity, however the films degrade rapidly under ambient conditions. In contrast, Bullock et al.[61] and the authors of this review,[62] have demonstrated by dipping a silicon sample into a TFSI based solution for a short period of time (typically ≈60 s) and drying (see **Figure 7**(a)), a thin passivating film is left on the sample surfaces, which enables lifetime measurements by PCD and PL. The uniformity of the superacid-based passivation scheme can be seen in Figure 7(b).

In comparison to HF based passivation, thin films such as those derived from superacid-based solutions are more attractive

Table 4. Practical issues associated with temporary passivation.

Type	Preparation	Usage	Safety risk	PCD/PL
Acid	Fume-hood	Fume-hood	High	Yes/Possible (Fume-hood)
Halogen-alcohol	Fume-hood	Sealed bags	Medium	Yes/Yes
Benzyl-alcohol	Fume-hood	Sealed bags	Medium	Yes/Yes
Thin film	Glovebox	Ambient	Medium	Yes/Yes
Other	Fume-hood	Ambient	Medium	Yes/Yes
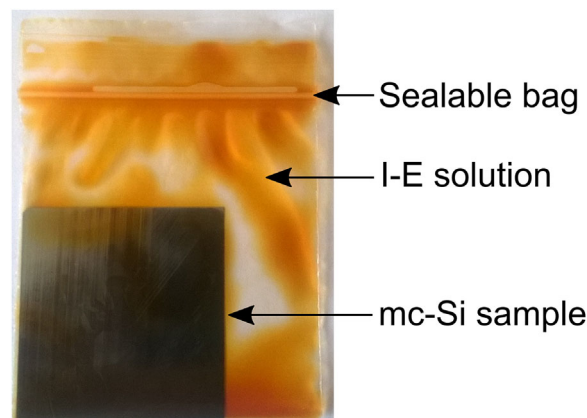
Figure 5. A mc-Si sample in a plastic sealable bag containing I-E solution (photograph from M. Al-Amin [95]).

ADVANCED
SCIENCE NEWS
www.advancedsciencenews.com

pssrrl
physica status solidi

www.pss-rapid.com
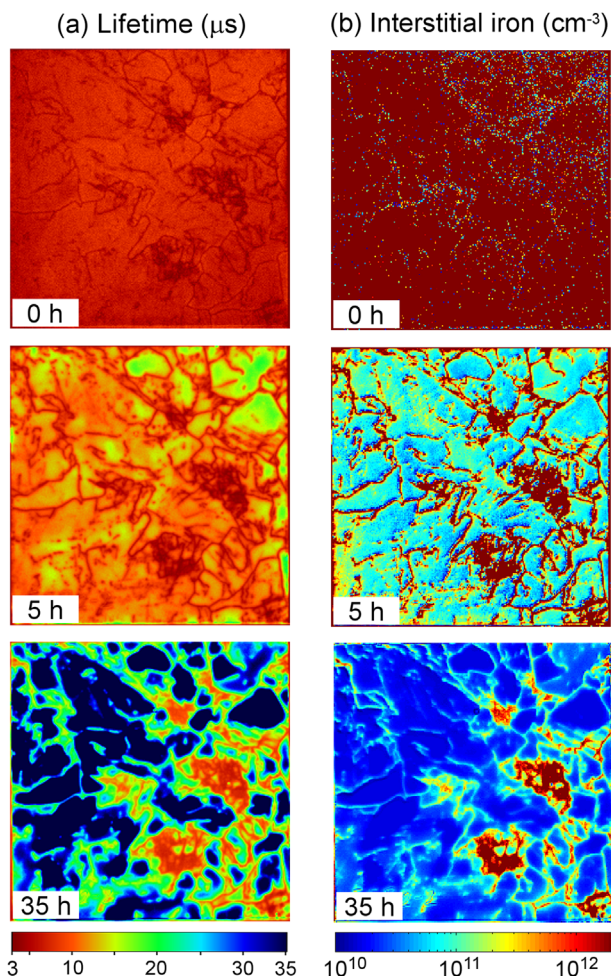
(a) Lifetime (μs)   (b) Interstitial iron (cm⁻³)

Figure 6. (a) PL lifetime images of a 3.9 cm by 3.9 cm mc-Si bottom ingot sample after annealing at 400 °C for 0, 5, and 35 h, with (b) corresponding interstitial iron concentration maps. Data were acquired using I-E passivation with the sealable bag approach (adapted from [96]).

for PL-based lifetime imaging, however rapid throughput with such techniques is unlikely.

6. Applications of Temporary Passivation for Silicon Materials and Device Development

Temporary passivation can have advantages over conventional passivation techniques which enables cleaner experiments to be designed with fewer variables. Specific ways in which temporary passivation has been used are briefly outlined in this section.

6.1. Minimising Hydrogenation and External Gettering Effects

There is evidence to suggest that hydrogenation of silicon occurs after passivation by dielectric films, particularly in the case of SiN_x. For example, platinum-hydrogen complexes form when SiN_x-coated samples are annealed at 750 °C[98] and deuterium is
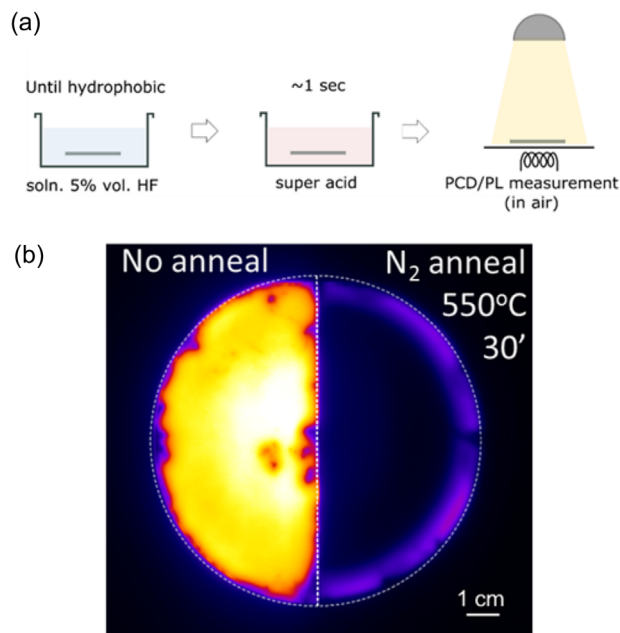

Figure 7. (a) Schematic of the superacid treatment procedure. (b) PL image of two halves of a low doped (5×10^{13} cm⁻³) n-type silicon wafer treated with the superacid solution, with a bulk silicon defect activated in the right half by annealing. Reprinted with permission.[61] Copyright 2016, American Chemical Society.

detected at oxide precipitates in samples with deuterated SiN_x films annealed at 800 °C.[99] Although not explicitly proven, it is often assumed that hydrogen enters the bulk from as-deposited SiN_x films or those annealed at low temperatures. Impurities can also be gettered to dielectrics or their interface with the silicon bulk.[20,22] Temporary passivation is performed at room or low temperature so even if external gettering were possible (e.g., to a temporary thin film) kinetic limitations would mean effective external gettering were impossible for key impurities such as iron.

Temporary passivation has enabled improved understanding of silicon PV which would be more difficult to achieve with dielectric-based passivation. For example, one of the biggest recent materials challenges has been LID (see Ref.[100] for a review) in which the mechanism of permanent deactivation of the boron-oxygen-related recombination centre is the subject of debate. Walter et al. used spin-coated organic passivation in a LID paper which they claim passivates the surfaces without bulk hydrogenation.[93] They found effective deactivation with this temporary passivation scheme, which they state is clear evidence that hydrogen is not involved in the process, contrary to conclusions of others.[101,102]

We are not aware of any specific direct studies into hydrogenation arising from temporary passivation processes. Wet chemical etching as used as a temporary passivation pre-treatment is however known to result in hydrogenation to a depth of a few microns, with subsequent annealing able to drive the hydrogen deeper into the material.[103] Whilst room temperature hydrogenation from etching is an important consideration for near-surface measurement techniques such as deep-level transient spectroscopy (DLTS), the effects on bulk lifetime measurements are likely to be small.

ADVANCED
SCIENCE NEWS
www.advancedsciencenews.com

pss rrl
physica status solidi
www.pss-rapid.com

Liquid-based temporary surface passivation, particularly of the halogen- or benzyl-alcohol class, is particularly valuable for understanding impurity behavior in mc-Si for solar cells.[17,21,53,96,104] Any difference in S between the various passivation types (Table 1) is largely insignificant in mc-Si due to the relatively short bulk lifetimes, and this means the safety risk associated with HF passivation is rarely worth taking. A study by Pollock et al. has shown QHY-M passivation has better stability than I-E,[53] but both give similar starting lifetimes and so I-E passivation gives reliable results if used relatively quickly. Karzel et al. used QHY-M passivation to study the fundamental behavior of iron in silicon.[17] Their conclusion was that QHY-M passivation enabled a much more reliable measure of interstitial iron concentrations than SiN_x passivation. Liquid passivation has also been invaluable in the development of low temperature gettering processes where again conventional dielectric passivation provides ambiguity due to possible hydrogenation, external gettering and thermal reconfiguration of impurities during passivation. Recently, Al-Amin and Murphy have used I-E passivation to measure lifetime changes during low temperature processing.[21,96,104] Their methodology has unambiguously shown lifetime improvements to arise from gettering and not due to bulk passivation. Recently, I-E passivation has also been used to demonstrate the effectiveness of saw damage at the wafer surfaces to getter impurities at $\leq 700\,°C$.[105] In summary, whilst the side-effects of dielectric passivation are usually beneficial to PV device performance, it is usually better to use temporary passivation to study defect behavior in the material as the variables of interest are easier to isolate.

6.2. Process Optimisation

Temporary surface passivation has important applications in the development of device processes. In a diagnostic context, for example, if a dielectric-passivated sample is measured to have a reduced effective lifetime after a process stage the origin of the lifetime change could be degradation of the passivation layer (i.e., an increased S) or degradation of the bulk. Temporary surface passivation can enable separation of the cases.

Grant et al. utilised the light enhanced HF passivation method to highlight the thermal instability in commercially available FZ silicon over the temperature range 80–1100 °C, which has led to an improved understanding of FZ silicon and how to thermally treat it.[15,16,106,107] In a recent study, effective lifetime degradation was measured in illuminated FZ silicon passivated with an Al_2O_3-SiN_x stack.[108] This stack was etched away and the sample was then re-passivated with a superacid thin film at room temperature with a similar S to the original passivation. The injection-dependent lifetime measured in the re-passivated was very similar to the degraded lifetime, and thus the authors were reliably able to link the degradation to increased bulk recombination and not a decrease in surface passivation quality.

Temporary passivation can also be used to study the thermal effects of solar cell processing, such as in the recent study of interdigitated back contact (IBC) cells by Rahman et al.[109] In this study, solar cell performance was improved by eliminating a bulk defect which formed during the boron diffusion process.

Room temperature superacid thin film passivation was applied after removal of the boron-diffused layer in the knowledge that as a room temperature process it would enable a measurement of the true bulk lifetime after cell processing without influence from the thermal effects and hydrogenation from dielectric-based passivation. The study then used knowledge of thermal-induced degradation of float-zone material obtained with liquid HF passivation[15,16] to develop a pre-annealing routine to minimize the degradation. In summary, temporary passivation schemes when correctly applied are able to provide state-of-the-art passivation without changing the bulk lifetime of the material and this is extremely valuable in the device and materials development in a silicon PV context.

7. Future Developments in Temporary Passivation

One future development could be exploratory research to stabilize what are currently temporary surface passivation schemes to enable their use in devices. This is only likely to be of interest in the cases which give S better than stable dielectric films grown by conventional methods. The idea of encapsulating HF-passivated silicon inside an organic coating was patented in 1986,[110] but there are clear safety risks with this. Superacid-based passivation such as that based on TFSI[61,62] may prove to be a more suitable future candidate for encapsulation in photovoltaic devices. Recent work has integrated polymer thin films into an IBC cell structure,[111] although their long-term stability has not been proven.

Temporary surface passivation is not restricted to silicon. HF passivation has been successfully used on germanium to provide an S of $2\,cm\,s^{-1}$.[1] Quinhydrone-methanol passivation has been shown to passivate germanium surfaces with an $S < 20\,cm\,s^{-1}$.[112] It seems likely that temporary passivation could be useful in the study of a range of semiconductor materials other than silicon, and this area is relatively unexplored.

A future possible application of temporary surface passivation could be in the development of a revised parameterisation of the intrinsic lifetime limit of silicon. Although the intrinsic lifetime limited has recently been revised,[113] there is evidence to suggest it is in need of further revision as some studies are reporting lifetimes in excess of the so-called limit.[62,114]

Conflict of Interest

The authors declare no conflict of interest.

Keywords

bulk defects, charge carrier lifetime, silicon, surface passivation

[1] E. Yablonovitch, D. L. Allara, C. C. Chang, T. Gmitter, T. B. Bright, *Phys. Rev. Lett.* **1986**, *57*, 249.

[2] V. Lehmann, H. Föll, *J. Electrochem. Soc.* **1988**, *135*, 2831.

[3] R. J. Falster, *Microelectron. Eng.* **1992**, *17*, 463.

[4] R. A. Sinton, A. Cuevas, *Appl. Phys. Lett.* **1996**, *69*, 2510.

[5] P. A. Basore, B. R. Hansen, Microwave-detected photoconductance decay. Conference Record of the 21st IEEE Photovoltaic Specialists Conference, **1990**, p. 374.

[6] T. Trupke, R. A. Bardos, M. C. Schubert, W. Warta, *Appl. Phys. Lett.* **2006**, *89*, 044107.

[7] K. R. McIntosh, L. E. Black, *J. Appl. Phys.* **2014**, *116*, 014503.

[8] M. J. Kerr, A. Cuevas, *Semicond. Sci. Technol.* **2002**, *17*, 35.

[9] R. S. Bonilla, B. Hoex, P. Hamer, P. R. Wilshaw, *Phys. Status Solidi A* **2017**, *214*, 1700293.

[10] G. Dingemans, W. M. M. Kessels, *J. Vac. Sci. Technol. A* **2012**, *30*, 040802.

[11] A. G. Aberle, *Sol. Energy Mater. Sol. Cells* **2001**, *65*, 239.

[12] N. E. Grant, T. C. Kho, K. Weber, *IEEE J. Photovolt.* **2015**, *5*, 1047.

[13] R. S. Bonilla, C. Reichel, M. Hermle, P. R. Wilshaw, *Phys. Status Solidi RRL* **2017**, *11*, 1600307.

[14] J. D. Murphy, R. E. McGuire, K. Bothe, V. V. Voronkov, R. J. Falster, *Sol. Energy Mater. Sol. Cells* **2014**, *120*, 402.

[15] N. E. Grant, V. P. Markevich, J. Mullins, A. R. Peaker, F. Rougieux, D. Macdonald, *Phys. Status Solidi RRL* **2016**, *10*, 443.

[16] N. E. Grant, V. P. Markevich, J. Mullins, A. R. Peaker, F. Rougieux, D. Macdonald, J. D. Murphy, *Phys. Status Solidi A* **2016**, *213*, 2844.

[17] P. Karzel, P. Frey, S. Fritz, G. Hahn, *J. Appl. Phys.* **2013**, *113*, 114903.

[18] A. Liu, C. Sun, D. Macdonald, *J. Appl. Phys.* **2014**, *116*, 194902.

[19] J. Mullins, S. Leonard, V. P. Markevich, I. D. Hawkins, P. Santos, J. Coutinho, A. Marinopoulos, J. D. Murphy, M. P. Halsall, A. R. Peaker, *Phys. Status Solidi A* **2017**, *214*, 1700304.

[20] A. Y. Liu, C. Sun, V. P. Markevich, A. R. Peaker, J. D. Murphy, D. Macdonald, *J. Appl. Phys.* **2016**, *120*, 193103.

[21] M. Al-Amin, J. D. Murphy, *IEEE J. Photovolt.* **2017**, *7*, 68.

[22] A. Y. Liu, D. Macdonald, *Appl. Phys. Lett.* **2017**, *110*, 191604.

[23] X. G. Zhang, *Electrochemistry of Silicon and Its Oxide*, Springer, New York, Boston, Dordrecht, London, Moscow, **2001**.

[24] A. W. Bott, *Current Separations* **1998**, *17*, 87.

[25] R. Memming, G. Schwandt, *Surf. Sci.* **1966**, *5*, 97.

[26] V. Bartagna, C. Plougonven, F. Rouelle, M. Chemla, *J. Electrochem. Soc.* **1996**, *143*, 3532.

[27] D. K. Schroder, *Meas. Sci. Technol.* **2001**, *12*, R16.

[28] N. E. Grant, K. R. McIntosh, J. T. Tan, *ECS J. Solid State Sci. Technol.* **2012**, *1*, P55.

[29] N. E. Grant, *J. Vis. Exper.* **2016**, *107*, e53614.

[30] R. Lago-Aurrekoetxea, I. Tobías, C. del Cañizo, A. Luque, *J. Electrochem. Soc.* **2001**, *148*, G200.

[31] H. M'saad, J. Michel, J. J. Lappe, L. C. Kimerling, *J. Electron. Mater.* **1994**, *23*, 487.

[32] R. A. Razera, A. Moehlecke, I. Zanesco, *IEEE J. Photovolt.* in press, **2017**, *7*, 1004.

[33] S. C. Baker-Finch, PhD Thesis, Australian National University, Australia, **2012**.

[34] M. Niwano, T. Miura, Y. Kimura, R. Tajima, N. Miyamoto, *J. Appl. Phys.* **1996**, *79*, 3708.

[35] D. J. Michalak, F. Gstrein, N. S. Lewis, *J. Phys. Chem. C* **2008**, *112*, 5911.

[36] W. Peng, S. M. Rupich, N. Shafiq, Y. N. Gartstein, A. V. Malko, Y. J. Chabal, *Chem. Rev.* **2015**, *115*, 12764.

[37] H. Ubara, T. Imura, A. Hiraki, *Solid State Commun.* **1984**, *50*, 673.

[38] V. A. Burrows, Y. J. Chabal, G. S. Higashi, K. Raghavachari, S. B. Christman, *Appl. Phys. Lett.* **1988**, *53*, 998.

[39] G. W. Trucks, K. Raghavachari, G. S. Higashi, Y. J. Chabal, *Phys. Rev. Lett.* **1990**, *65*, 504.

[40] K. W. Kolasinski, *Phys. Chem. Chem. Phys.* **2003**, *5*, 1270.

[41] T. S. Horányi, T. Pavelka, P. Tüttö, *Appl. Surf. Sci.* **1993**, *63*, 306.

[42] T. Maekawa, Y. Shima, *Jpn. J. Appl. Phys.* **1996**, *35*, L133.

[43] A. W. Stephens, M. A. Green, *Sol. Energy Mater. Sol. Cells* **1997**, *45*, 255.

[44] J. Chen, L. Zhao, H. Diao, B. Yan, S. Zhou, Y. Tang, W. Wang, *Adv. Mater. Res.* **2013**, *652-654*, 5.

[45] N. Batra, Vandana, S. Kumar, M. Sharma, S. K. Srivastava, P. Sharma, P. K. Singh, *Sol. Energy Mater. Sol. Cells* **2012**, *100*, 43.

[46] B. Sopori, S. Devayajanam, P. Basnyat, V. Mehta, H. Moutinho, B. Nemeth, V. LaSalvia, S. Johnston, N. M. Ravindra, J. Binns, J. Appel, *MRS Proc.* **2014**, *1670*, mrss14.

[47] W. Cai, Z. Lin, T. Strother, L. M. Smith, R. J. Hamers, *J. Phys. Chem. B* **2002**, *106*, 2656.

[48] 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**.

[49] B. Sopori, P. Rupnowski, J. Appel, D. Guhabiswas, L. Anderson-Jackson, *MRS Proc.* **2008**, *1123*, 1123.

[50] W. Cai, Z. Lin, T. Strother, L. M. Smith, R. J. Hamers, *J. Phys. Chem. B* **2002**, *106*, 9.

[51] K. L. Luke, L.-J. Cheng, *J. Electrochem. Soc.* **1988**, *135*, 957.

[52] M. Ju, Y. Lee, K. Lee, C. Han, Y. Jo, J. Yi, *Jpn. J. Appl. Phys.* **2012**, *51*, 09MA03.

[53] K. L. Pollock, J. Junge, G. Hahn, *IEEE J. Photovolt.* **2012**, *2*, 1.

[54] D. L. Meier, M. R. Page, E. Iwaniczko, Y. Xu, Q. Wang, H. M. Branz, Determination of Surface Recombination Velocities for Thermal Oxide and Amorphous Silicon on Float Zone Silicon. 17th NREL Crystalline Silicon Workshop, **2007**.

[55] H. Takato, I. Sakata, R. Shimokawa, *Jpn. J. Appl. Phys.* **2002**, *41*, L870.

[56] H. Takato, I. Sakata, R. Shimokawa, *Jpn. J. Appl. Phys.* **2001**, *40*, L1003.

[57] B. Chhabra, C. Weiland, R. L. Opila, C. B. Honsberg, *Phys. Status Solidi A* **2011**, *208*, 86.

[58] B. Chhabra, S. Bowden, R. L. Opila, C. B. Honsberg, *Appl. Phys. Lett.* **2010**, *96*, 063502.

[59] N. A. Kotulak, M. Chen, N. Schreiber, K. Jones, R. L. Opila, *Appl. Surf. Sci.* **2015**, *354*, 469.

[60] R. Har-Lavan, R. Schreiber, O. Yaffe, D. Cahen, *J. Appl. Phys.* **2013**, *113*, 084909.

[61] 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 Appl. Mater. Interfaces* **2016**, *8*, 24205.

[62] 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 J. Photovolt.* published online **2017**, https://doi.org/10.1109/JPHOTOV.2017.2751511

[63] J. Chen, Y. Shen, J. Guo, B. Chen, J. Fan, F. Li, H. Liu, Y. Xu, Y. Mai, *Appl. Phys. Lett.* **2017**, *110*, 083904.

[64] J. Schmidt, V. Titova, D. Zielke, *Appl. Phys. Lett.* **2013**, *103*, 183901.

[65] D. Zielke, C. Niehaves, W. Lovenich, A. Elschner, M. Horteis, J. Schmidt, *Energy Proc.* **2015**, *77*, 9.

[66] A. B. Sieval, C. L. Huisman, A. Schönecker, F. M. Schuurmans, A. S. H. van der Heide, A. Goossens, W. C. Sinke, H. Zuilhof, E. J. R. Sudhölter, *J. Phys. Chem. B* **2003**, *107*, 6846.

[67] D. Biro, W. Warta, *Sol. Energy Mater. Sol. Cells* **2002**, *71*, 6.

[68] Z. Yang, P. Gao, J. He, W. Chen, W. Yin, Y. Zeng, W. Guo, J. Ye, Y. Cui, *ACS Energy Lett.* **2017**, *2*, 556.

[69] Z. Yang, P. Gao, J. He, W. Chen, W. Yin, Y. Zeng, W. Guo, J. Ye, Y. Cui, *ACS Energy Lett.* **2017**, *2*, 7.

[70] O. S. Shinde, A. M. Funde, M. Agarwal, S. R. Jadkar, S. R. Mahamuni, R. O. Dusane, N. G. Dhere, S. V. Ghaisas, *J. Mater. Sci.: Mater. Electron.* **2016**, *27*, 12459.

[71] J. Rappich, P. Hartig, N. H. Nickel, I. Sieber, S. Schulze, T. Dittrich, *Microelectron. Eng.* **2005**, *80*, 62.

[72] R. Yang, T. Buonassisi, K. K. Gleason, *Adv. Mater.* **2013**, *25*, 2078.

[73] M. L. Castillo, A. Ugur, H. Sojoudi, N. Nakamura, Z. Liu, F. Lin, R. E. Brandt, T. Buonassisi, B. Reeja-Jayan, K. K. Gleason, *Sol. Energy Mater. Sol. Cells* **2017**, *160*, 470.

[74] M. Amani, P. Taheri, R. Addou, G. H. Ahn, D. Kiriya, D.-H. Lien, J. W. Ager, R. M. Wallace, A. Javey, *Nano Lett.* **2016**, *16*, 2786.

[75] S. Jäckle, M. Liebhaber, C. Gersmann, M. Mews, K. Jäger, S. Christiansen, K. Lips, *Sci. Rep.* **2017**, *7*, 2170.

[76] H. Angermann, W. Henrion, A. Roseler, M. Rebien, *Mater. Sci. Eng. B* **2000**, *73*, 6.

[77] W. J. Royea, A. Juang, N. S. Lewis, *Appl. Phys. Lett.* **2000**, *77*, 1988.

[78] E. J. Nemanick, P. T. Hurley, B. S. Brunschwig, N. S. Lewis, *J. Phys. Chem. B* **2006**, *110*, 14800.

[79] N. T. Plymale, Y.-G. Kim, M. P. Soriaga, B. S. Brunschwig, N. S. Lewis, *J. Phys. Chem. C* **2015**, *119*, 19847.

[80] S. Devayajanam, P. Rupnowski, S. Shet, B. L. Sopori, N. M. Ravindra, D. Caskey, J. Chang, J. Covington, Studies on the use of liquid surface passivation for lifetime measurements on good-quality silicon wafers. Conference Record of the 37th IEEE Photovoltaic Specialists Conference, **2011**, p. 001647.

[81] H. Kobayashi, A. Asano, M. Takahashi, K. Yoneda, Y. Todokoro, *Appl. Phys. Lett.* **2000**, *77*, 4392.

[82] J. Schmidt, A. G. Aberle, *Prog. Photovolt.: Res. Appl.* **1998**, *6*, 259.

[83] G. S. Higashi, Y. J. Chabal, G. W. Trucks, K. Raghavachari, *Appl. Phys. Lett.* **1989**, *56*, 656.

[84] P. Allongue, C. H. de Villeneuve, S. Morin, R. Boukherroub, D. D. M. Wayner, *Electrochim. Acta* **2000**, *45*, 4591.

[85] W. Peng, S. M. Rupich, N. Shafiq, Y. N. Gartstein, A. V. Malko, Y. J. Chabal, *ACS Chem. Rev.* **2015**, *115*, 12764.

[86] H. Angermann, J. Rappich, L. Korte, I. Sieber, E. Conrad, M. Schmidt, K. Hubener, J. Polte, J. Hauschild, *Appl. Surf. Sci.* **2008**, *254*, 3615.

[87] J. Schmidt, A. G. Aberle, *Prog. Photovolt.: Res. Appl.* **1998**, *6*, 5.

[88] F. Tian, D. Yang, R. L. Opila, A. V. Teplyakov, *Appl. Surf. Sci.* **2012**, *258*, 3019.

[89] H. Angermann, W. Henrion, A. Roseler, M. Rebien, *Mater. Sci. Eng. B* **2000**, *73*, 178.

[90] W. Kern, *J. Electrochem. Soc.* **1990**, *137*, 1887.

[91] H. M'saad, J. Michel, A. Reddy, L. C. Kimerling, *J. Electrochem. Soc.* **1995**, *142*, 2833.

[92] H. Sugimoto, M. Tajima, *Jpn. J. Appl. Phys.* **2007**, *46*, L339.

[93] D. C. Walter, J. Schmidt, *Sol. Energy Mater. Sol. Cells* **2016**, *158*, 91.

[94] R. S. Bonilla, C. Reichel, M. Hermle, P. Hamer, P. R. Wilshaw, *Appl. Surf. Sci.* **2017**, *412*, 11.

[95] M. Al-Amin, PhD Thesis, University of Warwick, UK, **2017**.

[96] M. Al-Amin, J. D. Murphy, *J. Appl. Phys.* **2016**, *119*, 235704.

[97] A. Laades, J. Brauer, U. Stürzebecher, K. Neckermann, K. Klimm, M. Blech, K. Lauer, A. Lawerenz, H. Angermann, Wet-Chemical Treatment of Solar Grade CZ Silicon Prior to Surface Passivation. 24th European Photovoltaic Solar Energy Conference, Hamburg, Germany, **2009**.

[98] S. Kleekajai, L. Wen, C. Peng, M. Stavola, V. Yelundur, K. Nakayashiki, A. Rohatgi, J. Kalejs, *J. Appl. Phys.* **2009**, *106*, 123510.

[99] G. Hahn, M. Käs, B. Herzog, *Solid State Phenom.* **2010**, *156-158*, 343.

[100] T. Niewelt, J. Schön, W. Warta, S. W. Glunz, M. C. Schubert, *IEEE J. Photovolt.* **2017**, *7*, 383.

[101] S. Wilking, A. Herguth, G. Hahn, *J. Appl. Phys.* **2013**, *113*, 194503.

[102] N. Nampalli, B. Hallam, C. Chan, M. Abbott, S. Wenham, *Appl. Phys. Lett.* **2015**, *106*, 173501.

[103] O. V. Feklisova, N. A. Yarykin, *Semicond. Sci. Technol.* **1997**, *12*, 742.

[104] M. Al-Amin, J. D. Murphy, *IEEE J. Photovolt.* published online, **2017**, https://doi.org/ 10.1109/JPHOTOV.2017.2741100

[105] M. Al-Amin, N. E. Grant, J. D. Murphy, *Phys. Status Solidi RRL* published online, **2017**, https://doi.org/10.1002/pssr.201700268

[106] N. E. Grant, F. E. Rougieux, D. Macdonald, J. Bullock, Y. Wan, *J. Appl. Phys.* **2015**, *117*, 055711.

[107] N. E. Grant, F. E. Rougieux, D. Macdonald, *Solid State Phenom.* **2016**, *242*, 6.

[108] T. Niewelt, M. Selinger, N. E. Grant, W. M. Kwapil, J. D. Murphy, M. C. Schubert, *J. Appl. Phys.* **2017**, *121*, 185702.

[109] T. Rahman, A. To, M. E. Pollard, N. E. Grant, J. Colwell, D. N. R. Payne, J. D. Murphy, D. M. Bagnall, B. Hoex, S. A. Boden, *Prog. Photovolt.: Res. Appl.* published online **2017**, https://doi.org/10.1002/pip.2928

[110] B. R. Weinberger, H. W. Deckman, E. Yablonovitch, Method for producing an electronically passivated surface on crystalline silicon using a fluorination treatment and an organic overlayer, US Patent No 4,608,097 (**1986**).

[111] J. Chen, Y. Shen, B. Chen, K. Ge, J. Guo, Z. Wang, F. Li, Y. Xu, Y. Mai, *Solar RRL* **2017**, *1*, 1700079.

[112] B. P. Swain, H. Takato, I. Sakata, *Appl. Phys. Express* **2009**, *2*, 105501.

[113] A. Richter, S. W. Glunz, F. Werner, J. Schmidt, A. Cuevas, *Phys. Rev. B* **2012**, *86*, 165202.

[114] T. Niewelt, W. Kwapil, M. Selinger, A. Richter, M. C. Schubert, *IEEE J. Photovolt.* **2017**, *7*, 1197.