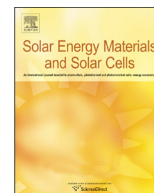
Solar Energy Materials and Solar Cells 183 (2018) 164–172

Contents lists available at ScienceDirect

Solar Energy Materials and Solar Cells

journal homepage: www.elsevier.com/locate/solmat



Superacid-derived surface passivation for measurement of ultra-long lifetimes in silicon photovoltaic materials

A.I. Pointon[a], N.E. Grant[a], E.C. Wheeler-Jones[b], P.P. Altermatt[c], J.D. Murphy[a,*]

[a] School of Engineering, University of Warwick, Coventry CV4 7AL, United Kingdom
[b] Department of Chemistry, University of Warwick, Coventry CV4 7AL, United Kingdom
[c] Trina Solar Limited, Changzhou 213031, China

ARTICLE INFO

Keywords:
Silicon
Surface
Passivation
Lifetime
Superacid

ABSTRACT

Accurate measurements of bulk minority carrier lifetime are essential in order to determine the true limit of silicon's performance and to improve solar cell production processes. The thin film which forms when silicon wafers are dipped in solutions containing superacids such as bis(trifluoromethane)sulfonimide (TFSI) has recently been found to be effective at electronically passivating the silicon surface. In this paper we first study the role of the solvent in which TFSI is dissolved for the passivation process. We study ten solvents with a wide range of relative polarities, finding TFSI dissolved in hexane provides improved temporal stability, marginally better passivation and improved solution longevity compared to dichloroethane which has been used previously. Sample storage conditions, particularly humidity, can strongly influence the passivation stability. The optimised TFSI-hexane passivation scheme is then applied to a set of 3 Ω cm *n*-type wafers cut from the same float-zone ingot to have different thicknesses. This enables the reproducibility of the scheme to be systematically evaluated. At 10^{15} cm^{-3} injection the best case effective surface recombination velocity is 0.69 ± 0.04 cm/s, with bulk lifetimes measured up to the intrinsic lifetime limit at high injection and > 43 ms at lower injection. Immersion of silicon in superacid-based ionic solutions therefore provides excellent surface passivation, and, as it is applied at room temperature, the effects on true bulk lifetime are minimal.

1. Introduction

The highest efficiency silicon solar cells require substrates with bulk minority carrier lifetimes well into the millisecond range. Recent advances in wafer production and processing technologies mean that the true lifetime limit is not known, with several recent studies [1–5] reporting lifetimes higher than the currently accepted intrinsic "limit" due to Auger and radiative recombination [6].

To measure high bulk lifetimes accurately, it is necessary to have excellent surface passivation to minimise recombination at the surface. Dielectric-based surface passivation (see Ref. [7] for a review) can provide excellent stable passivation, although the passivation process itself can affect the bulk lifetime due to bulk passivation, external gettering [8] or thermal effects. These artefacts can often be avoided if room temperature temporary surface passivation is used instead, and this has been recently reviewed by Grant and Murphy [9]. Temporary passivation has traditionally been achieved by immersion of samples in solutions of acids, halogen-alcohols or benzyl-alcohols, but such liquid-based methods are not easy to characterise using conventional approaches. Recently a new class of temporary passivation has been developed, whereby a thin film is formed when silicon samples are treated with a superacid-containing solution at room temperature [2,10]. When the surface pre-treatment and processing are optimised, it has been shown that the resulting effective surface recombination velocity is below 1 cm/s [2]. Thus, the level of passivation is similar to some of the best dielectric-schemes, but possible changes in bulk lifetime during the passivation step are avoided due to the low temperatures used. This passivation scheme can therefore be used to measure true bulk lifetimes resulting from cell processing, as recently done in the fabrication of interdigitated back contact (IBC) solar cells [11].

The initial work by Bullock et al. examined various superacid solutions finding bis(trifluoromethane)sulfonimide (TFSI) crystals dissolved in 1,2-dichloroethane (DCE) to give the best surface passivation [10]. This composition was taken forward by Grant et al., who optimised the surface pre-treatments, and demonstrated the measurement of extremely high lifetimes (up to 75 ms) in high resistivity silicon [2]. However, there are now good reasons to re-examine the composition of the ionic solution used in the passivation process. First, DCE is classified as "possibly carcinogenic to humans" by the World Health Organization [12] so may be best avoided. Second, by changing the composition of

* Corresponding author.
E-mail address: john.d.murphy@warwick.ac.uk (J.D. Murphy).

https://doi.org/10.1016/j.solmat.2018.03.028
Received 13 February 2018; Accepted 14 March 2018
0927-0248/ © 2018 The Author(s). Published by Elsevier B.V. This is an open access article under the CC BY license (http://creativecommons.org/licenses/BY/4.0/).

Table 1
Solvents for TFSI investigated in this study. All solvents are in anhydrous forms. Relative polarities are taken from Ref. [19].

Label	Solvent name used	Chemical name	Formula	Relative polarity	Supplier (product number)	Purity
A	Acetone	2-propanone	C_3H_6O	0.355	VWR (83683)	99.9%
B	Chlorobenzene	Chlorobenzene	C_6H_5Cl	0.188	Sigma Aldrich (284513)	99.8%
C	Cyclohexane	Cyclohexane	C_6H_{12}	0.006	Sigma Aldrich (227048)	99.5%
D	Dichloroethane (DCE)	1,2-dichloroethane	$C_2H_4Cl_2$	0.327	Sigma Aldrich (284505)	99.8%
E	Dioxane	1,4-dioxane	$C_4H_8O_2$	0.164	Sigma Aldrich (296309)	99.8%
F	Dichloromethane (DCM)	Dichloromethane	CH_2Cl_2	0.309	Alfa Aesar (41835)	99.7%
G	Hexane	*n*-hexane	C_6H_{14}	0.009	Sigma Aldrich (296090)	95%
H	Isopropanol (IPA)	2-propanol	C_3H_8O	0.546	Sigma Aldrich (278475)	99.5%
I	Octane	*n*-octane	C_8H_{18}	0.012	Sigma Aldrich (296988)	$>$ 99%
J	Toluene	Toluene	C_7H_8	0.099	Sigma Aldrich (244511)	99.8%

the solution it may be possible to improve its long-term stability, and this may be important in converting what is currently a temporary passivation scheme into a more permanent one. Third, the mechanism by which the thin film passivates the silicon surface is not currently clear, and understanding the effect of varying the solvent may improve fundamental understanding. This has implications beyond silicon-based photovoltaics, as TFSI-containing electrolytes are being studied as a potential way to stabilise silicon-based anodes for lithium ion batteries [13].

This paper reports the results of an investigation to develop alternative ionic solutions for surface passivation, which do not rely on DCE. A series of experiments is performed to passivate silicon wafer surfaces with TFSI dissolved in different solvents which have a wide range of relative polarities. The passivation effects are quantified using carrier lifetime measurements and the temporal stability is studied taking into account variables such as solution age and the humidity of sample storage between measurements. The effective surface recombination velocity and bulk lifetime are extracted by using a robust method involving variable thickness samples cut from the same high purity ingot. Finally, we report the results of a series of tests to assess the reproducibility of the optimal process.

2. Experimental methods

2.1. Samples and surface preparation

Most experiments were performed on quarters of 5 Ω cm *n*-type (100) orientation 100 mm diameter float-zone (FZ) silicon wafers with an initial thickness of 750 µm. Some experiments were performed on whole 3 Ω cm *n*-type (100) orientation 100 mm diameter FZ silicon wafers cut with a wide range of thicknesses from the same ingot. Prior to starting the passivation processes, these 3 Ω cm wafers were subjected to a 200 °C anneal for 30 min, as this has previously been found to deactivate bulk defects in FZ silicon [14–16] and for the relevant part of the study the absolute – rather than relative – lifetime is of interest. We use relatively large pieces of silicon to minimise edge effects. These can occur if the passivation film induces an inversion layer in the silicon so both carrier types can easily travel laterally to the sample's edge as majority carriers and recombine there [17,18].

All samples were subjected to a rigorous cleaning and surface preparation procedure which was developed in our previous work [2]. For all processes very high purity (18.2 MΩ) deionized (DI) water was used. Our standard procedure comprised seven stages, as follows:

1. A dip in 1% HF to remove the native oxide.
2. Standard clean 2 (SC 2), which is sometimes called RCA 2, consisting of H_2O, H_2O_2 (30%), HCl (37%) (5:1:1) for 5 min at ~75 °C.
3. A dip in 1% HF to remove the chemical oxide formed during SC 2.
4. An etch in 25% tetramethylammonium hydroxide (TMAH) for 10 min at ~80 °C.
5. A dip in 1% HF.
6. An SC 2 clean using the same chemicals as above for 10 min at ~75 °C.
7. Immersion in 2% HF for 5 s followed by air drying (no DI water rinse).

Later in this paper we conduct a series of reproducibility tests on the variable thickness 3 Ωcm wafers. After the initial complete passivation cycle and lifetime characterisation, the passivation was removed by rinsing in DI water then performing steps 1–3 above. The samples were then subjected to another 200 °C anneal for 30 min followed by steps 1–7 above again, with a slight modification so that step 4 is a 30 min TMAH etch instead.

2.2. Preparation and application of surface passivating solutions

Chemicals for passivation were measured and mixed in nitrogen (N_2) purged gloveboxes. To prepare the passivating solution, 100 mg of bis(trifluoromethane)sulfonimide (Sigma-Aldrich, 95%) crystals were measured out and then dissolved in 50 ml of an anhydrous solvent. The solvents used in this work are given in Table 1. Solvents chosen have a wide range of relative polarities with values obtained from Ref. [19]. The TFSI crystals generally dissolved in the solvents fairly rapidly, with the exception of chlorobenzene, hexane, and octane in which the crystals took several hours or even days to dissolve fully. Solutions were stored in air-tight glass bottles.

Immediately following their surface pre-treatment, as described above, silicon samples were transferred into the glovebox which was purged with N_2 to give a relative humidity below 25%. For a given treatment, a pre-prepared passivating solution was poured into a glass beaker and a silicon sample was immersed in the solution for about 60 s. The silicon sample was then removed from the passivating solution and was dried in the N_2 ambient of the glovebox. Passivated samples were then placed in plastic petri dishes and removed from the glovebox for characterisation.

2.3. Lifetime measurements

Excess carrier lifetime measurements were made using a Sinton WCT-120 photoconductance (PC) lifetime tester with an 2 cm diameter coil under transient PC mode. Care was taken always to site samples in the same place relative to the coil, and lifetimes in full wafer samples were measured at the wafer centre. Photoluminescence (PL) images were acquired with a BT Imaging LIS-L1 system to check the homogeneity of passivation. PL images were acquired with excitation by LEDs with a wavelength of 650 nm. To preserve the structural integrity of the passivating films, lifetime and PL measurements were made with the samples in the plastic petri dishes. This prevented damage occurring to the films during handling, and required recalibration of the lifetime tester to mitigate the effects of the plastic petri dish immediately above the coil. Unless otherwise stated, samples were subsequently stored in their petri dishes in the dark with their lids loosely in place between

Download English Version:

https://daneshyari.com/en/article/6534103

Download Persian Version:

https://daneshyari.com/article/6534103

Daneshyari.com