Silicon Solar Cell Passivation using Heterostructures

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Abstract

Standard surface passivation schemes for crystalline silicon solar cells use SiO₂ or SiNₓ. The c-Si surface passivation mechanisms related with these schemes have been elucidated within the framework of interface recombination modeled by an extended SRH formalism: interface recombination centers characteristic of the SiO₂ passivation have larger electron (e⁻) than hole (h⁺) capture cross sections and SiO₂ yields thus poorer passivation of lower resistivity p-type c-Si, while SiNₓ layers lead to the occurrence of a large fixed charge density leading, for instance, to parasitic leakage currents that adversely affect the performance of SiNₓ rear passivated p-type c-Si solar cells. An alternative to these two major schemes is hydrogenated amorphous silicon (a-Si:H). In this paper, we determine first differences between the natures of the electronic recombination centers. To understand the passivation properties of a-Si:H, we then introduce an interface recombination model based on the amphoteric nature of silicon dangling bonds. We show experimentally and theoretically that a-Si:H is a high performance and broad range surface passivation material as its e⁻ and h⁺ capture cross sections on neutral defects are similar, while additional field effect passivation can be tuned by further growth of doped a-Si:H layers. The quality of the passivation is illustrated with a lifetime of 7ms reached on lightly p-type doped c-Si passivated with intrinsic a-Si:H, which is to the best of our knowledge the highest ever measured value for a-Si:H passivated wafers. By using our modeling of the a-Si:H/c-Si interface recombination as a guidance for interface and solar cell improvement, we are able to fabricate full a-Si:H/c-Si heterojunction devices reaching a maximal open-circuit voltage of 713mV and a maximal efficiency of 19.1% on flat c-Si wafers, using very high frequency plasma enhanced chemical vapor deposition (VHF-PECVD).

1. Introduction

Within the actual trend towards thinner and more efficient silicon solar cells, surface passivation is becoming a more and more important issue. At the crystalline silicon (c-Si) surface, the abrupt discontinuity in the crystal structure results in a high density of dangling bonds, creating a large density of defects in the bandgap. Passivation schemes allow terminating these dangling bonds properly, and by consequence the number of recombination centers can be considerably decreased. Silicon dioxide (SiO₂) and silicon nitride (SiNₓ) are the standard surface passivation materials. An alternative to these two major surface passivation schemes is hydrogenated amorphous silicon (a-Si:H) [1], that attracted the photovoltaic community’s attention due to the success of Sanyo’s a-Si:H/c-Si heterojunction (HJ) solar cells. Using stacks of intrinsic plus doped a-Si:H layers to form both the emitter and the back surface field (BSF), Sanyo's HIT solar cells hold the world record open-circuit voltage (V_{oc}) of c-Si based solar cells [2].

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SiO\textsubscript{2}, SiN\textsubscript{x} and a-Si:H have all inherent advantages and drawbacks: SiO\textsubscript{2} yields the lowest interface state densities \cite{3} but only when grown at high temperatures (~1000°C) followed by a subsequent alneal and it suffers from long term stability issues. SiN\textsubscript{x} is an excellent antireflection coating and is grown at lower temperatures (≤400°C), but, because of the presence of a large fixed charge, the effectiveness of the passivation depends on the Si doping type and level. In particular, parasitic current flows through p-type BSFs can occur \cite{4}. a-Si:H provides excellent surface passivation \cite{5}, passivates all Si doping types and levels and can be used to form both the emitter and the BSF. It is grown at temperatures as low as 200°C, but it does not withstand temperatures higher than 400°C. Additionally, for solar cell front passivation, only ultra-thin a-Si:H layers can be tolerated due to their high blue light absorption. It becomes therefore obvious that the choice of the best passivation layer is strongly influenced by the device structure and by the fabrication process sequence.

The main experimental parameter used for the quantification of the c-Si surface passivation’s quality is the lifetime (LT) of the overall excess (photo-generated) carriers. Using high bulk LT c-Si substrates, the surface passivation properties of an overlaying material can be studied independently. The modeling of the injection level dependent passivation yields insight into the specific surface passivation mechanism provided by a material. Finally, the injection level dependent LT measurements allow the determination of upper limits for the \textit{V}_{OC} and the maximum power point of complete, contacted Si solar cells. Conversely, together with the measurements of the final solar cell’s current-voltage (\textit{IV}) curve, injection level dependent LT measurements allow for device diagnostic whenever the predicted upper performance limits are not reached.

2. Injection level dependent surface passivation

The injection level dependent LT of extra charge carriers photo-generated in the c-Si bulk is most easily evaluated by measuring the excess carrier density (\textit{ECD}) decay, during or after a short light pulse with the quasi-steady-state photo-conductance (QSSPC) and the photo-conductance decay (PCD) techniques \cite{6}. The measured effective LT \(\tau_{\text{eff}}\) results from excess carrier recombination within c-Si and at its surface and is therefore given by \(\tau_{\text{eff}}^{-1} = \tau_{c}\text{-Si}^{-1} + \tau_{\text{surface}}^{-1}\). Bulk c-Si recombination is composed of intrinsic radiative, intrinsic Auger and extrinsic SRH recombination, hence \(\tau_{c}\text{-Si}^{-1} = \tau_{\text{rad}}^{-1} + \tau_{\text{Aug}}^{-1} + \tau_{\text{SRHbulk}}^{-1}\). Lightly doped (intrinsic recombination is only limiting at high injection levels) FZ (few bulk defects, high \(\tau_{\text{SRHbulk}}\)) wafers are the most appropriate to explore the upper LT limits imposed by various surface passivation schemes.

![State of the art surface passivation of lightly doped p- (left) and n-type (right) FZ c-Si.](image)

**Figure 1.** State of the art surface passivation of lightly doped p- (left) and n-type (right) FZ c-Si.
Figure 1 compares the passivation performances of SiO$_2$, SiN$_x$ and a-Si:H on such lightly doped FZ wafers. The c-Si bulk LT is parameterized according to Kerr et al. [7]. The results for a-Si:H have been obtained at the University of Neuchâtel. Before loading wafers into the PECVD chamber, we just take them out of box, as received from the commercial supplier, and dip them into diluted HF.

Annealed SiO$_2$ such as grown by Kerr et al. yield the highest LTs ever measured on c-Si wafers [3]. Record passivating SiN layers (stoichiometric) achieve slightly lower passivation performances [7]. Our VHF-PECVD intrinsic a-Si:H passivation scheme results in almost the same passivation quality as Kerr’s SiN on lightly doped $p$-type c-Si. For the lightly doped $n$-type wafers, we intentionally show a curve with a poorer passivation of a-Si:H than SiN. Such results are obtained when using HF of low purity (frequent re-use or poor DI water quality – however, VLSI grade is not required). With freshly prepared diluted HF, the outstanding a-Si:H passivation LT of 7ms on 130$\Omega$cm $p$-type c-Si is repeatedly reached.

Our best surface passivating intrinsic a-Si:H ($i$ a-Si:H) layers are 50nm thick. To be used in stack with doped a-Si:H layers to form a-Si:H/c-Si HJ solar cells, the $i$ a-Si:H thickness has to be reduced to avoid undesired blue light absorption and/or increase in device series resistance. Figure 2 shows thus the passivation performance of HJ solar cell precursors. These are structures consisting of asymmetrical stacks of 4nm intrinsic plus 25nm doped $p^+$ and $n^+$ a-Si:H layers. In this example, $n$-type 1$\Omega$cm and $p$-type 0.5$\Omega$cm c-Si wafers are used. The implied $V_{OC}$ of the full solar cell is extracted from the injection level dependent LT curves [8] and its value is above 700mV for $n$- and close to 700mV for $p$-type c-Si. The complete HJ device is obtained after contact formation by ITO sputtering on the front and ITO/Ag(Al) on the back of the precursor. The real $V_{OCS}$ as measured by 1-sun $IV$ curves amount to 713mV on 1$\Omega$cm $n$-type, and 695mV on 0.5$\Omega$cm $p$-type c-Si, close to the implied values.

![Figure 2. HJ solar cell precursor’s passivation.](image)

To enhance photo-generation within the c-Si by minimizing optical reflection losses, c-Si solar cell surfaces are not flat but textured – at least on the front side. Using textured c-Si, the above mentioned cleanliness issue is of much more importance: purchased, random pyramidal textured 1$\Omega$cm $n$-type wafers preconditioned the same way as the flat polished c-Si wafers – out of box, HF-dip – are limited to LTs of 0.1ms when passivated with the same $i$ a-Si:H layers. Textured wafers with a high quality 100nm thermal oxide, removed with the same HF-dip treatment, perform slightly better when passivated the same way, but LTs of only 0.2ms are reached. In contrast, Fig. 3 shows that the optimal surface preconditioned textured wafers prepared at the Hahn-Meitner Institute [9] (only HF-dipped before VHF-PECVD deposition) are
well passivated by the i a-Si:H layers leading to implied $V_{OC}$ of 725mV on 1Ωcm n-type and 720mV on 1Ωcm p-type c-Si. The LT of the 1Ωcm p-type c-Si drops to 0.1ms at an injection level of $10^{14}\text{cm}^{-3}$, but nevertheless a solar cell having such an injection level dependence could reach a fill factor (FF) of 79%. However, up to now, in contrast to the case of flat c-Si wafers, we did not succeed to maintain the quality of passivation obtained with thick i a-Si:H by the subsequent deposition of doped a-Si:H for emitter and BSF formation on thinner i a-Si:H layers.

3. Surface recombination modeling

The injection level dependent LT curves such as measured on c-Si FZ wafers passivated with SiO$_2$ and SiN have noticeably different shapes for different doping types, as can be seen by comparing the left and right of Fig. 1. By modeling the injection level dependence of the c-Si surface recombination in various configurations (e.g. c-Si doping type and level) and comparing to experiment, the mechanism of a specific surface passivation scheme can be elucidated. There are in fact two mechanisms for reducing interface recombination: On one hand, the density of interface states is reduced by e.g. hydrogen passivation of interface dangling bonds, on the other hand, the c-Si surface density of either electrons or holes is reduced by field effect. The latter is achieved by the presence of (fixed) charges within the passivating layer, at the interface with c-Si or on the passivating layer’s outer surface. The resulting c-Si surface band bending – and thus the surface carrier densities of electrons and holes $n_S$ and $p_S$ – is usually calculated by the extended SRH surface recombination model [10]. In analogy to bulk SRH recombination, the surface recombination rate $U_{SRH}$ for single level surface states is given by

$$U_{SRH} = \frac{n_S p_S - n_i^2}{(n_S + n_i)\sigma_p + (p_S + p_i)\sigma_n} \nu_{th} N_S \text{ [cm}^{-2}\text{s}^{-1}].$$

Real surface states are distributed throughout the whole bandgap, with energy dependent capture cross sections for electrons and holes. The measurement of these energy dependent surface parameters is sophisticated, but the single level case considering only the midgap capture cross sections holds in first approximation.

Experimentally measured injection dependence of effective LT data fitted with this formalism by Aberle et al. [11], indicate that the injection level dependence of SiO$_2$ is mainly governed by the larger capture cross section for electrons than for holes. The left of Fig. 4 shows the surface plot of $U_{SRH}(n_S,p_S)$ with the capture cross section ratio $\sigma_n/\sigma_p = 100$. As $\tau_{eff} \sim ECD/U_{SRH}$, the trajectories on the surface plot (zero surface band bending assumed) reproduce the main tendencies observed on the injection level dependent LT curves for SiO$_2$ on lightly doped c-Si shown in Fig. 1: The LT decrease at low $ECD$s observed for SiO$_2$ passivating 150Ωcm p-type c-Si corresponds to the flattening of the equivalent trajectory curve in Fig. 4.

**Figure 4.** $U_{SRH}(n_S,p_S)$ with $\sigma_n > \sigma_p$ (left), $\sigma_n < \sigma_p$ (right).

**Figure 5.** Amphoteric $U_{DB}(n_S,p_S)$. 
Aberle et al. [12] identified too that the passivation effect of SiN$_x$ is mostly due to large fixed positive charges within the SiN$_x$ layers. Schmidt et al. [13] identified three different interface defects with extremely different electron to hole capture cross section ratios – 1000, 10 and 0.01 – supposed to be Si dangling bonds with different back bond configurations. Which defect dominates, depends on the SiN$_x$ deposition method. The right of Fig. 4 shows the surface plot of $U_{SRH}(n_S,p_S)$ for low frequency direct PECVD deposited SiN$_x$ – supposed to damage the c-Si surface – where the defect with $\sigma_n/\sigma_p = 0.01$ dominates [14].

Passivating low doped c-Si with i a-Si:H results in interface dangling bonds that are neutral. However, the amphoteric nature of these defects makes that the SRH model is no more sufficient to describe the results obtained on various wafers. Thus, in the aim of disposing of a suitable model to describe interface recombination at the a-Si:H/c-Si HJ, we extended the model previously established for bulk a-Si:H recombination based on amphoteric defects [15,16] to c-Si/a-Si:H interface recombination [17]. This gives a direct access to the interface recombination center density and to the charges creating the field effect passivation. These charges depend on the capping doped layers, microdoping of the i-layer and on band discontinuities at the interfaces.

Figure 6 shows the distribution of recombination centers in the bulk a-Si:H bandgap. In first approximation, recombination in band tails is neglected, leading (as sketched in Fig. 7) to two parallel co-existing recombination paths, both consisting of two successive capture events.

![Figure 6. a-Si:H density of states. Figure 7. a-Si:H recombination steps (successive, parallel).](image)

With the further hypothesis of medium illumination level [16], the calculation of the recombination rate can be reduced to the case of a discrete recombination level possessing three charge conditions. In analogy to the resulting bulk recombination rate, the surface recombination rate $U_{DB}$ can be written as:

$$U_{DB} = \frac{n_S \sigma_n^0 + p_S \sigma_p^0}{n_S \sigma_n^0 + p_S \sigma_p^0 + 1 + \frac{n_S \sigma_n^0}{p_S \sigma_p^0}} v_{th} N_S \text{ [cm}^{-2}\text{s}^{-1}]$$

The four capture cross sections depend on the carrier type and on the state of charge of the defect. By analyzing recombination curves on a wide variety of configurations [17], we found best accordance between theory and experiment with $\sigma_n^0/\sigma_p^0 = 0.05$ and $\sigma^+/-/\sigma^0 = 500$. Figure 5 shows the surface plot of $U_{DB}(n_S,p_S)$ given above. In contrast to SRH recombination, there exists a local minimum in the DB recombination rate. Its position is determined by the value of $\sigma_n^0/\sigma_p^0$ while its width depends on the value of $\sigma^+/-/\sigma^0$. In this minimum, recombination is limited by the larger free carrier density, which is opposite to the SRH case. When the density of one carrier type becomes much higher than the other, $U_{DB}$ reduces to $U_{SRH}$ as denoted by the empty surface in Fig. 5. The trajectories on the surface plot in Fig. 5 show $U_{DB}(n_S,p_S)$ for three different lightly doped c-Si wafers as resulting from surface passivation with 5nm i a-Si:H. In general, surface
recombination is examined in terms of the effective surface recombination velocity $S_{\text{eff}} = U/ECD = (W/2) \cdot \left( \tau_{\text{eff}}^{-1} - \tau_{\text{c-Si}}^{-1} \right)$ to get rid off the dependence on the c-Si wafer thickness $W$. Figure 8 shows the translation of the trajectories on the surface plot in Fig. 5 into $S_{\text{eff}}(ECD)$ curves together with the measured surface recombination velocities of these three different lightly doped c-Si wafers passivated with 5nm $i$ a-Si:H. Figure 8 additionally shows that – without further capping layer – these ultra-thin passivation layers are not stable with respect to ambient air storage due to their outer surface potential modification. Plagwitz et al. [18] use them in stack with SiN layers as a good illustration of benefiting from advantages while eliminating drawbacks by combining several single layer passivation schemes: thicker a-Si:H layers would absorb too much light and a-Si:H can not act as antireflection coating, while SiN layers with optimum refractive indexes for antireflection coating have no passivating effect on $p^+$ emitters.

Figure 8. 5nm $i$ a-Si:H on different c-Si.

While corona surface charging of SiO$_2$ passivation layers permits the tuning of field effect passivation for examination purpose [19], the deposition of a doped a-Si:H overlayer can produce such a field effect passivation permanently. This is illustrated in Fig. 9, which shows the injection level dependence of the surface recombination velocities of symmetrically grown stacks consisting of 10nm $i$ a-Si:H plus 30nm doped a-Si:H passivating 60Ωcm $n$-type c-Si. A second possibility of shifting the Fermi level (i.e. modifying the average state of charge of the recombination centers) in the passivating a-Si:H layers without increasing the defect density consists of microdoping the $i$ a-Si:H layers. Figure 9 shows well the equivalent effect of stack deposition and microdoping. The low injection level discrepancies are due to the simplifying assumptions made to obtain the analytical function for $U_{DB}$.

4. On lifetime measurements and final solar cell performances

A full description of the electrical properties of HJ devices would require, in addition to the parameters extracted from the LT measurement, a precise knowledge of the band positions and band discontinuities which have been shown to be critical [20]. However, the injection level dependence of the effective LT can be transformed into an illumination vs. implied $V_{OC}$ curve and further on into a predicted $IV$ curve. This allows a useful determination of the limits on $V_{OC}$ and $FF$ solely imposed by recombination. Comparing this $IV$ curve with the one measured on the complete contacted device permits to diagnostic any effect of the ITO deposition on the a-Si:H/c-Si HJ precursors. The Suns$V_{OC}$ [8] data of complete solar cells comprises further losses due to shunting, whereas the 1-sun $IV$ curve finally includes series resistance effects.
Figure 10 shows Si HJ solar cells formed on 2.8Ωcm n-type c-Si. The $V_{OC}$ of the solar cell on the left is limited by surface recombination. The final ITO deposition does not enhance recombination and introduces only small series resistance losses. The precursor on the right should result in a solar cell with a $V_{OC}$ exceeding 700mV. But as seen from the Suns$V_{OC}$ curve, the ITO deposition is detrimental as it causes increased recombination and consequently diminishes the $V_{OC}$. The final comparison of the Suns$V_{OC}$ and the 1-sun IV curves indicates appreciable "series resistance" losses.

To investigate the reason of the low measured LTs limiting the left cell’s $V_{OC}$ to around 680mV, we first checked the c-Si surface preconditioning by fabricating a 50nm thick $i$ a-Si:H passivation LT test sample. As Fig. 11 shows, its passivation would have implied a $V_{OC}$ of 715mV. Thus, the preconditioning is appropriate. Suspecting then that the $p$-layer deposition deteriorates the overall LT as observed by De Wolf et al. [21], the passivation performance of the $i/p$ stack was tested. But the implied $V_{OC}$ falls only down to 690mV. Surprisingly it was – as clearly shown in Fig. 11 – the remaining $i/n$ stack, which was the dominating recombination source limiting the $V_{OC}$ of the solar cell on the left of Fig. 10. Improving the growth conditions of the $n$-layer ($n^2$ stack) resulted in the same implied $V_{OC}$ as achieved by the $i/p$ stack. Using after an additional chamber cleaning this $i/n$ stack for a-Si:H/c-Si HJ solar cell formation yields the LT curve of the cell shown on the right of Fig. 10.

Figure 11. a-Si:H passivation of n-type 2.8Ωcm c-Si.

5. Conclusions

SiO$_2$ and SiN$_x$ are the most widely spread crystalline silicon surface passivation schemes. Intrinsic hydrogenated amorphous silicon is also a highly performing surface passivation material due to its broad range applicability on all kind of c-Si substrates – including all doping types,
levels and surface texture. By modeling the injection level dependence of surface recombination, the surface passivation mechanisms of a specific material can be determined. SiN\textsubscript{x} is for example characterized by its high fixed positive charge density. In contrast, with intrinsic amorphous silicon, the magnitude of the field effect passivation can be tuned by fixing its outer surface potential when capping it with doped amorphous silicon layers. Such stacks form the emitter and back surface field of amorphous/crystalline silicon heterojunction solar cells. A key point to our approach, which resulted in the fabrication of high open-circuit voltage heterojunction solar cells, is the interpretation of lifetime measurements on heterojunction test structures that allowed a rapid development by a fast device diagnostic procedure. In particular, by VHF-PECVD, full heterojunction devices with open-circuit voltages higher than 700mV and efficiency up to 19.1% can be fabricated on flat wafers.

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**References**