Extremely low surface recombination in 1 Ω cm n-type monocrystalline silicon

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A key requirement in the recent development of highly efficient silicon solar cells is the outstanding passivation of their surfaces. In this work, plasma enhanced chemical vapour deposition of a triple layer dielectric consisting of amorphous silicon, silicon oxide and silicon nitride, charged extrinsically using corona, has been used to demonstrate extremely low surface recombination. Assuming Richter’s parametrisation for bulk lifetime, an effective surface recombination velocity $S_{\text{eff}} = 0.1$ cm/s at $\Delta n = 10^{15}$ cm$^{-3}$ has been obtained for planar, float zone, n-type, 1 Ω cm silicon. This equates to a saturation current density $J_{\text{sat}} = 0.3$ fA/cm$^2$, and a 1-sun implied open-circuit voltage of 738 mV. These surface recombination parameters are among the lowest reported for 1 Ω cm c-Si. A combination of impedance spectroscopy and corona-lifetime measurements shows that the outstanding chemical passivation is due to the small hole capture cross section for states at the interface between the Si and a-Si layer which are hydrogenated during nitride deposition.
probe technique on a 3 × 20 mm² sample with four 0.5 mm wide by 3 mm long InGa contacts separated by 5 mm. Resistivity was also measured using the Van der Pauw technique [12] in a rectangular 5 × 5 mm² sample. These measurements resulted in a resistivity of 1.01 Ω cm ± 2%. A dopant concentration of 4.9 × 10¹⁵ cm⁻³ was assumed for all the analysis performed here. It is noted here that an accurate estimation of surface recombination parameters depends on precise values for the wafer bulk characteristics, as reported above.

A triple layer dielectric coating consisting of hydrogenated amorphous silicon (a-Si), silicon oxide (SiO₂), and silicon nitride (SiNₓ) was deposited using plasma enhanced chemical vapour deposition (PECVD). a-Si was deposited in a Plasmatron 100 system from Oxford Instruments at a temperature of 200 °C, using silane SiH₄ and hydrogen H₂ as precursor gases. SiO₂ and SiNₓ were deposited in an industrial-type in-line PECVD system (Roth & Rau SiNA XS), at a temperature of 250 °C. Silane SiH₄, nitrous oxide N₂O and ammonia NH₃ were used as precursor gases, and the gas-flux ratio was optimised to achieve a refractive index of n_SiO₂ = 1.45 in the oxide, and n_SiNₓ = 2.15 in the nitride at λ = 632 nm, as described in reference [13]. The a-Si/SiO₂/SiNₓ film thicknesses were 8 ± 1 nm/13 ± 2 nm/60 ± 1 nm as measured using spectroscopic ellipsometry. After deposition, corona charge was deposited on both sides of the wafer by placing it under a point electrode held at 30 kV, 20 cm above the sample, in laboratory conditions. Further details on this process can be found in [14]. Surface charge concentration was assessed using Kelvin Probe (KP) surface potential measurements [15].

The interface electrical characteristics were measured using frequency dependent capacitance-conductance-voltage (CGV) measurements using a Keysight E4980A precision LCR meter. The top contact was created by thermally evaporating ~100 nm of Al through a contact mask, with the area of the contact measured using an optical microscope to within 5% accuracy. The back contact was created using a gallium–indium eutectic. Interface trap density D_{it} was determined using the Nicollian and Goetzberger conductance method [16] without any surface potential fluctuations. The insulator capacitance was determined using the McNeutt–Sah method [17] with the extension in [18], and used to calculate the effective oxide thickness as EOT = ε₀K_{SiO₂}Area/C_{inv}. The flatband voltage V_{fb} was found by correcting the measured gate voltage V_G to account for the stretching produced by interface states D_{it} and fitting the corrected curve with a theoretical model as proposed in [19].

Surface passivation was quantified using several parameters. Firstly, the effective surface recombination velocity S_{eff} = W/(2/τ_{eff} − 1/τ_{sat}), with τ_{sat} defined by Richter’s parameterisation (Eq. (18) in [20] using B_{Sat} from [21] and B_{low} from [22]) and τ_{eff} measured experimentally using a Sinton photoconductance decay (PCD) instrument. A WCT 120 instrument was used with an accuracy of 8% as reported in [23]. This accuracy was the main source of error and was used here to quantify the error bars in the reported data. Secondly, an upper limit to the surface recombination velocity (SRV) was calculated by assuming τ_{Sat} → ∞ such that S_{sat} < W/(2τ_{Sat}). This removes the dependence of the inferred value on the empirical relation for bulk lifetime. Thirdly, the surface recombination current J_{sb} [24], calculated here using approximation (5) in [25], since for high lifetimes Kane and Swanson’s method produces nonphysical negative recombination currents. Lastly, the implied open-circuit voltage V_{oc} from the measured photoconductance decay curve was determined as described by Kerr in [26].

3 Results and discussion The chemical and field effect components of passivation in the a-Si/SiO₂/SiNₓ stack were studied by producing specimens without the SiO₂ and/or the SiNₓ layers. In a single layer of a-Si, CGV measurements were not possible due to the conductivity of the film leading to large leakage current errors. Samples with a double layer of 8 nm a-Si/100 nm SiO₂, and a triple layer of 8 nm a-Si/13 nm SiO₂/60 nm SiNₓ showed lower leakage and allowed CGV measurements. Figure 1a shows a subset of the CGV spectra for the triple and double layer systems, while Fig. 1b illustrates the resulting D_{it} calculated therefrom, in three samples. The solid lines in Fig. 1a show the theoretical model fitted to the conductance to angular frequency functions measured. No Gaussian dispersion was included here to account for fluctuations in the semiconductor surface potential. Despite this, the good fits obtained near the peak indicate good accuracy in the determination of D_{it} since it is the magnitude and frequency of the peak the parameters that relate to D_{it} [27, 28]. Figure 1b shows that the a-Si/SiO₂ presents a higher concentration of interface states than the a-Si/SiO₂/SiNₓ film. In both cases the D_{it} has been found to exceed 10¹¹ cm⁻² eV⁻¹ suggesting that substantial recombination activity could arise at these interfaces. It is, however, possible that the trap states sampled using the CGV method are at the a-Si/SiO₂ interface, or even the a-Si bulk. The flatband voltages obtained for the double a-Si/SiO₂, and triple a-Si/SiO₂/SiNₓ layers are −0.506 V, and −0.71 V, respectively. Such low V_{fb} indicates a minimal concentration of charge inside the film. The KP surface potential for these two structures was −0.31 V and −0.53 V, respectively, thus indicating very small charge concentrations at the surface of the film. The V_{fb} can be used to estimate an intrinsic charge of −5 × 10¹⁰ q/cm² and −2.1 × 10¹¹ q/cm² respectively, assuming all charge resides at the dielectric/silicon interface. These values are the average of three measurements taken in different specimens. It is noted that contrary to previous reports [29], the oxide/nitride interface in this work did not reveal a large concentration of positive charge.

The minority carrier lifetime in all three coatings has been measured using transient photoconductance. Figure 2a. The surface passivation provided by a single a-Si layer increases the lifetime to over 1 ms. Large leakage cur-
When the third nitride layer is deposited to form the a-
Si/SiO$_2$ system, the passivation is largely improved as
inferred from CGV measurements. This suggests that,
when compared to a Si/SiO$_2$ interface [34], the passivation
provided by the a-Si film, and its subsequent hydrogenation,
related to a strong reduction in the capture rate of holes at
the interface states, rather than a reduction in the number of
states. This is equivalent to a reduction in the capture cross
section of holes since the fundamental hole capture rate is
given by $\nu_{th}\sigma_D$. The intrinsic bulk lifetime limit $\tau_{\text{m}}$, as calculated from
Richter’s parameterisation [20], is included in the red solid
line in Fig. 2a. In the high injection regime the measured
effective lifetimes exceeded this assumed intrinsic limit.

The work of Wan et al. [35] is the only other report where
lifetimes exceeding the intrinsic limit are observed, yet in
their work 0.47 $\Omega$ cm Si was studied instead. Both in Wan
et al. and in this study, experimental effective lifetime is
seen to exceed the assumed radiative and Auger limit. Er-
ror bars for the effective lifetime measured here were cal-
culated considering the accuracy reported in [23] and in-
cluded in Fig. 2a. The intrinsic limit deduced from Rich-
ter’s parameterisation falls within these error bars. How-
ever, for the $\Delta n > 10^{15}$ cm$^{-3}$ regime, the lifetimes measured
fall in the top 50% percentile, suggesting that lifetimes sur-
passing the assumed intrinsic limit are likely.

The surface recombination parameters of these speci-
mens were calculated as described in Section 2. Figure 3 il-
ustrates the calculated SRV and currents, including the er-
rors from both lifetimes and thickness measurements. Here

d respectively. The best passivation achieved is shown by the red
and blue solid traces in Fig. 2a.

The solid lines in Fig. 2b illustrate a theoretical model
effective lifetime using an extended Shockley–Read–
Hall formalism with the parameterisations in Ref. [33].
The values for the parameters are included in the figure.
These show that a concentration of $10^{12}$ cm$^{-3}$ eV$^{-1}$ charged
donor and acceptor interface states is necessary to explain
the observed dependence. This is in agreement with the
substantial concentration of interface states measured using
CGV, Fig. 1. A combination of CGV and corona-lifetime
measurements thus suggests that, when compared to a
Si/SiO$_2$ interface [34], the passivation provided by the a-Si
film, and its subsequent hydrogenation, is related to a
strong reduction in the capture rate of holes at the interface
states, rather than a reduction in the number of states.
This is equivalent to a reduction in the capture cross section
of holes since the fundamental hole capture rate is given by
$S_0 = \nu_{th}\sigma_D$.

The field effect passivation in these films was modified
extrinsically using corona discharge. In a single a-Si layer
the high conductivity led to a rapid leakage of the corona
deposited charge, thus no change in lifetime was observed
when attempting to charge this film. On the a-Si/SiO$_x$ and
a-Si/SiO$_x$SiN$_y$ systems, on the other hand, corona charge
modified strongly the field effect passivation as illustrated
in Fig. 2b. When the field effect component of passivation
was maximised, effective lifetimes as high as 3 ms and
7 ms were recorded in the double and triple layers, respec-

The field effect passivation is expected to passivate
the a-Si/Si interface is hydrogenated during the PECVD
nitride deposition reducing its recombination activity.

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tively.
it is evident that a-Si provides an outstanding base chemical interface to the underlying Si. The SiO2 provided negligible field effect passivation and affected the chemical passivation achieved from the a-Si alone, yet it was necessary to avoid the leakage of extrinsic corona charge later deposited on the three-layer film. Deposition of the final SiN layer provided additional chemical passivation from hydrogenation taking place during deposition, with a minor contribution from field effect. Once the chemical and the field effect components of passivation are exploited jointly, \( S_{\text{eff}} \) and \( J_0 \) of 0.1 cm/s and 0.3 fA/cm\(^2\) are observed at an injection level of \( 10^{15} \) cm\(^{-3}\). The calculated 1 sun \( V_{oc} \) for such specimen was 738 mV. It is noted that for such low recombination, these parameters are strongly dependent on the Auger and radiative lifetime models used. It is clear that if the parametrisation of Auger recombination is modified these surface recombination parameters will change substantially. In other reports this has been avoided by assuming zero bulk recombination and quoting an SRV upper limit. Such calculation has been here included in Table 1 for \( \Delta n = 10^{15} \) cm\(^{-3}\). Here the recombination parameters, calculated as stated in Section 2, are listed for state-of-the-art passivation methods reported in the literature. The values achieved in this work have been included for comparison. It is clear that this results in the work are the among lowest recombination observed for a 1 n-type FZ Si surface. Similarly low surface recombination was reported by Herasimenka in 2013 [36] yet their work was primarily due to the reduced hole capture rate provided by the a-Si layer and its hydrogenation during nitride deposition. Further improvement in passivation is demonstrated using corona charge field effect which leads to an effective SRV of 0.1 cm/s, a saturation current density of 0.3 fA/cm\(^2\), and a 1 sun implied open circuit voltage of 738 mV. Lastly, effective lifetimes exceeding the Auger intrinsic limit parametrised by Richter were observed for the \( \Delta n > 2 \times 10^{15} \) cm\(^{-3}\) regime.

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4 Conclusions This letter reports one of the lowest surface recombination parameters recorded using PCD lifetimes. In a float zone n-type 1 Ω cm silicon specimen, a triple layer dielectric of low temperature PECVD a-Si/SiO2/SiN\(_x\) provides outstanding chemical passivation, mainly due to the reduced hole capture rate provided by the a-Si layer and its hydrogenation during nitride deposition. Further improvement in passivation is demonstrated using corona charge field effect which leads to an effective SRV of 0.1 cm/s, a saturation current density of 0.3 fA/cm\(^2\), and a 1 sun implied open circuit voltage of 738 mV. Lastly, effective lifetimes exceeding the Auger intrinsic limit parametrised by Richter were observed for the \( \Delta n > 2 \times 10^{15} \) cm\(^{-3}\) regime.

Table 1 State of the art surface passivation methods on ~1 Ωcm n-type FZ Si. Values reported at \( \Delta n = 10^{15} \) cm\(^{-3}\).

| method                        | \( \rho \) [Ωcm] | \( \tau_{\text{eff}} \) [ms] | \( S_{\text{eff}} \) [cm/s] | \( S_{\text{RL}} \) [cm/s] | \( J_0 \) [fA/cm\(^2\)] |
|-------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| annealed SiO2 [37]            | 1.5             | 6               | 1.36            | 2.37            | 4.95            |
| charged SiO2 [6]              | 1               | 5.2             | 0.65            | 1.92            | 1.5             |
| PA-ALD AlO\(_x\) [20]        | 1               | 6.8             | 0.14            | 1.33            | 0.37            |
| r-PECVD SiN [20]              | 1               | 6.3             | 0.27            | 1.58            | 0.71            |
| a-Si/SiO2/SiN\(_x\) [36]     | 1.7             | 15              | 0.114           | 1               | 0.29            |
| SiO2/PECVD SiN\(_x\) [8]     | 1               | 6.7             | 0.14            | 1.49            | 0.36            |
| this work:                    | 1               | 7.2             | 0.1             | 1.38            | 0.21            |
| a-Si/SiO2/SiN\(_x\)          |                 |                 |                 |                 |                 |

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