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The Influence of Surface Electric Fields on the Chemical Passivation of Si-SiO₂ Interfaces after Firing

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Abstract. In this work it is demonstrated that the presence of surface electric fields during a post-deposition anneal can impact the chemical passivation of SiO₂ + SiN_x double layer stacks. Although the surface passivation generated in such dielectrics is well known, we demonstrate that an electric field present in the dielectric not only modifies the surface carrier concentration but can also induce a chemical change in the interface properties upon annealing. By tailoring the surface electric field in the dielectric stack prior to annealing, it is shown that the capture rates at the Si-SiO₂ interface can be modified depending on the field polarity and magnitude. Planar FZ specimens are examined here. It is found that annealing in the presence of a field pointing into the Si surface, as intrinsically occurs in positively charged SiN_x, increases the dielectric charge density without any substantial changes in the chemical passivation. When an opposite electric field is established by negative charge on the dielectric, the chemical passivation worsens substantially where a fourfold increase in the capture rate of minority carriers is obtained via electrical characterisation. We hypothesise that the electric field may be driving atomic hydrogen away from the interface, thus damaging the passivation.

INTRODUCTION

Improving the surface passivation of silicon is an essential step to improving the performance of silicon solar cells. One method to minimise surface defects and surface carrier recombination is through chemical passivation via the deposition of a dielectric layer¹. Common dielectrics used in commercial solar cells are hydrogenated amorphous silicon (a-Si:H), silicon nitride (SiN_x) and aluminium oxide (AlO_x). These dielectrics are commonly grown via plasma enhanced chemical vapour deposition (PECVD). Annealing of the dielectric is known to induce hydrogen migration to the silicon-dielectric interface to saturate silicon dangling bonds^{2,3}. The second method is to use field effect passivation (FEP). FEP can be used to reduce the minority carrier concentration at the silicon surface via band bending. FEP can be generated either through the native charge that exists in dielectric layers, through the deposition of extrinsic charges^{4,5}, or through the migration of stable fixed ionic charges, such as potassium, to the interface^{6,7}.

There are three charge states that atomic hydrogen can exist in; positive (H⁺), negative (H⁻) and neutral (H⁰)^{8,9}. Given this, we propose that an extrinsic surface charge can control the migration of hydrogen within the dielectric since it establishes a metastable electric field across the dielectric. Here we examine the interface properties and the resultant changes in chemical passivation after charging a SiO₂ + SiN_x dielectric stack on planar FZ silicon. The interface passivation is evaluated via effective lifetimes and capacitance-voltage measurements, and determined to be heavily

influenced by the polarity and magnitude of the surface charge. It was found that a positive surface field followed by annealing increases the dielectric charge density without any substantial changes of the chemical passivation. When an opposite electric field is established by negative charge on the dielectric, the chemical passivation worsens substantially. A fourfold increase in the minority carrier capture rate is obtained via electrical characterisation. We hypothesize that the electric field may be driving atomic hydrogen away from the interface, thus damaging the passivation. When the conditions of a positive field are maintained or enhanced, optimal chemical passivation can be achieved, with SRV below 0.24 cm/s and a $J_{0s} < 0.35$ fA/cm² in n-type 1 Ω cm float zone silicon. We postulate that the hydrogen content of SiN_x is relevant and critical to explaining our results. These findings can have severe implications for surface passivation and hydrogenation processes during firing of industrial silicon solar cells.

SAMPLE PREPARATION AND METHODOLOGY

In this work, planar 200 μ m thick, n-type 1 Ω cm Float Zone (FZ) 4 inch wafers are used. These wafers had 100 nm thermal SiO₂ grown at 1050 °C in oxygen and dichloroethylene at Fraunhofer ISE, followed by a forming gas anneal in a tube furnace at 425 °C for 30 minutes. Following this, a single layer of 65 nm SiN_x with a refractive index n of 1.9 was deposited on top of the oxide via PECVD (Oxford Instrument PlasmaLab 80+) with silane and ammonia as precursor gases. The wafers were cleaved into quarters before further processing. Subsequently, either positive or negative corona charge was applied to both sides of the wafers immediately followed by annealing at 450 °C in air. This process is termed *corona anneal* from hereon and details of the apparatus can be found in references 10 and 11.

To determine the interface recombination parameters, surface recombination at the oxide-silicon interface was varied by regulating the carrier density using a biased transparent gate. A method similar to that reported in ref. 12 was used to record effective lifetime as a function of surface bias. In this procedure, a PEDOT:PSS electrode is produced on top of the dielectric to simultaneously control surface potential and measure effective lifetime on the Sinton Lifetime Tester.

CHANGES IN EFFECTIVE LIFETIME AS A FUNCTION OF SURFACE FIELD POLARITY

As shown in Fig. 1 the effective lifetime (τ_{eff}) of symmetrically passivated SiO₂ + SiN_x samples is recorded for each processing step. The samples underwent a corona-anneal process that consisted of depositing between 10-40 seconds of positive or negative surface corona charge, followed by annealing at 450 °C for 20 seconds. A second identical corona-anneal was then performed to evaluate the maximum passivation that can be achieved when the field effect is further optimised. All samples treated with positive charge recorded improvements in τ_{eff} . A maximum τ_{eff} of 6.4 ms was recorded, equivalent to an SRV < 0.24 cm s⁻¹. In contrast, negative charge on the dielectric prior to annealing results in lower lifetimes of ~ 300 μ s.

Since surface passivation can be both chemical and field effect in origin, the results in Fig. 1 could imply that the hydrogen, which exists in the dielectric in H⁺ form, is migrating and chemically passivating the interface. Alternatively, corona charge remaining after the anneal can vary the surface charge concentration, which for positive (negative) charge would lead to lower (higher) recombination. To determine if these field dependent changes in lifetime are due to field effect or chemical passivation, a study of the interface electrical characterisation was then performed.

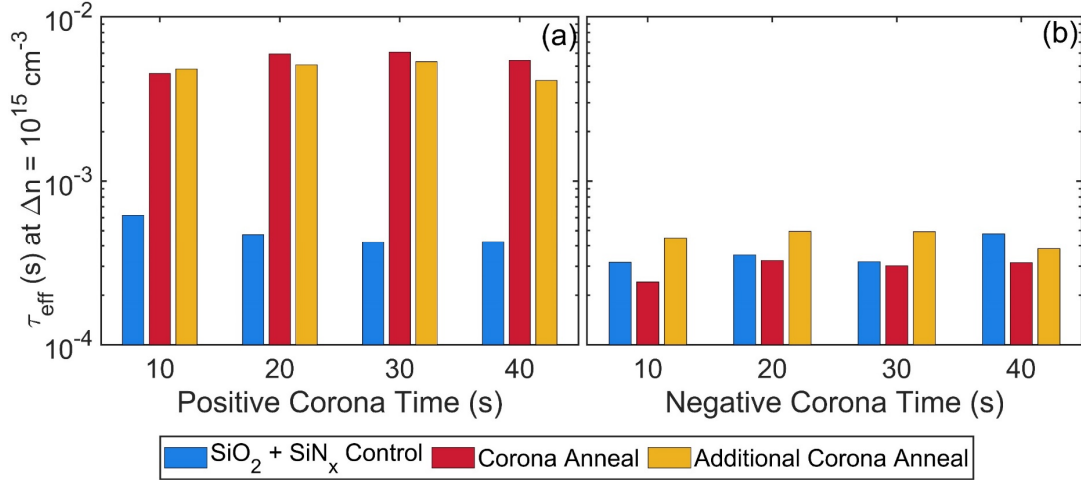


FIGURE 1. Effective lifetime of specimens before and after corona annealing using increasing concentrations of (a) positive and (b) negative corona charge

INTERFACE RECOMBINATION PARAMETERS AFTER FIRING IN THE PRESENCE OF A SURFACE ELECTRIC FIELD

To determine the interface recombination parameters of the specimens, surface recombination at the oxide-silicon interface was varied by regulating the surface carrier density, as described in the experimental section. The solid lines in Fig. 2 indicate an analytical model used to explain the observed behaviour. The values for the fitting parameters are given in Table I. For the surface biased lifetime experiment, the Girisch and Aberle modelling formalism¹³ was followed, but accounting for charge fluctuations by introducing a distribution with deviation σ_q ¹⁴. The mid-gap density of interface states (D_{it}) were obtained from CV measurements using Nicollian and Goetzenberg MOS theory¹⁵. The remaining fitting parameters were varied to model effective lifetime as a function of the gate bias. It was found that annealing under a positive electric field only increased the built-in charge and its inhomogeneity in the dielectric stack. No substantial reduction in the electron and hole capture rates (S_{n0}, S_{p0}) values could be attributed. On the other hand, applying a negative field on the surface was seen to have a strong effect on the passivation quality after annealing, with a 1 order of magnitude increase in D_{it} from 10^{10} to 10^{11} cm⁻²eV⁻¹ and an increase in S_{n0} and S_{p0} by two to fourfold respectively. Such interface characteristics are not unaffected by surface carrier concentration and therefore are independent of field effect passivation. Our results determine that surface fields influence the chemical passivation of the Si-SiO₂ interface. Hydrogen is known to exist in charged forms in dielectric films¹⁶ and to respond strongly to applied electric fields¹⁷. We hypothesise that such loss in chemical passivation is related to de-hydrogenation of the interface under negative fields.

In previous work, Jin *et al.*¹⁸ utilized a comparable experimental approach and revealed analogous surface biased lifetime dependencies of Si-SiO₂ structures. They reported interface degradation under both low positive and negative surface field conditions, which is attributed to the presence of atomic hydrogen within the dielectric. Contrary to the observations of Jin *et al.*, we do not find evidence of interface degradation for positive surface fields. We similarly conjecture that hydrogen plays a significant role in the observed mechanics.

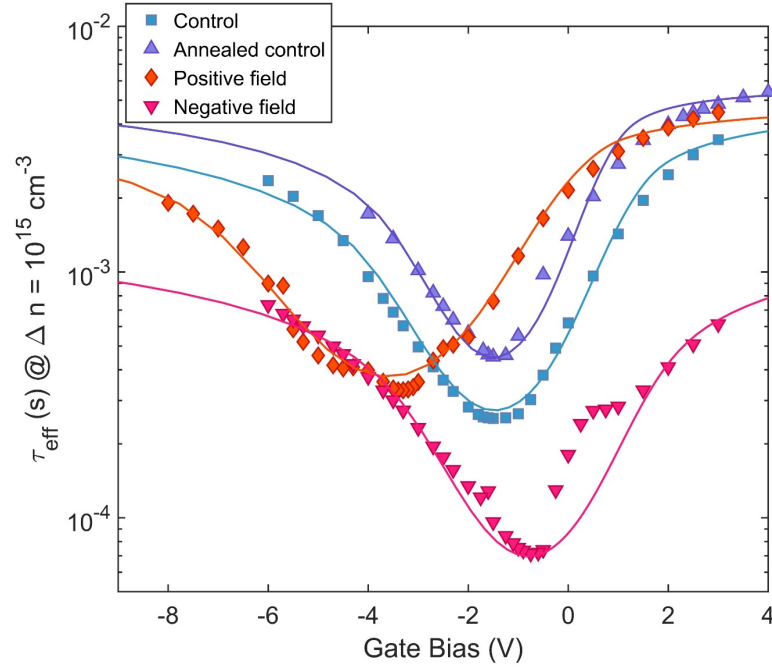


FIGURE 2. Effective lifetime as a function of gate bias as measured on planar FZ specimens using a PEDOT:PSS transparent gate

TABLE 1. Summary of modelling parameters used to fit lifetime vs surface potential in Fig. 2. EOT is the equivalent oxide thickness.

	Control	Annealed Control	Positive Field	Negative Field
τ_{bulk}	Richter's Parametrisation ¹⁹			
EOT (nm)	137.3			
Q_f (10^{11} q cm ⁻²)	2.4	2.4	5.6	1.6
σ_q (10^{11} q cm ⁻²)	1.4	1.2	2	1.3
S_{n0} (cm s ⁻¹)	305	172	293	607
S_{p0} (cm s ⁻¹)	34	17	29	137
$D_{it, Q, mg}$ (10^{10} cm ⁻² eV ⁻¹)	1	1	1	10
$D_{it, Q, VB}, D_{it, Q, CB}$ (10^{10} cm ⁻² eV ⁻¹)	1, 3	1, 1	1, 3	2.5, 8

CONCLUSIONS

This work demonstrates that a surface electric field can induce changes in the interface properties of $\text{SiO}_2 + \text{SiN}_x$ double layers, and that such changes could be related to the hydrogen content of the films. Our results show that for the specimens discussed here the presence of positive surface fields during annealing does not affect the density of interface states nor their capture rates. It only increases the film charge density, at the cost of inhomogeneity. Upon negative corona annealing, we observe a deterioration in chemical passivation as the hole capture rates increase fourfold, and the D_{it} by one order of magnitude. We hypothesise that hydrogen could play an important role in our observations. The ability to control hydrogenation has become a key requirement in improving the passivation quality of recombinative sites at the silicon interface, and in bulk defects. We have shown that it may be possible to use surface electric fields as a means of regulating hydrogen migration.

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REFERENCES

1. A.G. Aberle, [Prog. Photovoltaics Res. Appl.](#) 8, 473 (2000).
2. J. Schmidt, M. Kerr, and A. Cuevas, [Semicond. Sci. Technol.](#) 16, 164 (2001).
3. K. Kim, N. Borojevic, S. Winderbaum, S. Duttagupta, X. Zhang, J. Park, and Z. Hameiri, [Sol. Energy](#) 186, 94 (2019).
4. S.W. Glunz, D. Biro, S. Rein, and W. Warta, [J. Appl. Phys.](#) 86, 683 (1999).
5. M. Schoffhale, R. Brendel, G. Langguth, and J.H. Werner, [Proc. 1994 IEEE 1st World Conf. Photovolt. Energy Convers.](#) 2, 1509 (1994).
6. R.S. Bonilla and P.R. Wilshaw, [J. Phys. D: Appl. Phys.](#) 51, 25101 (2017).
7. K.A. Collett, S. Du, G. Bourret-Sicotte, Z. Luo, P. Hamer, B. Hallam, R.S. Bonilla, and P.R. Wilshaw, [IEEE J. Photovoltaics](#) 9, 26 (2018).
8. S.T. Pantelides, S.N. Rashkeev, R. Buczko, D.M. Fleetwood, and R.D. Schrimpf, [IEEE Trans. Nucl. Sci.](#) 47, 2262 (2000).
9. L.E. Black and K.R. McIntosh, [IEEE Trans. Electron Devices](#) 57, 1996 (2010).
10. R.S. Bonilla, N. Jennison, D. Clayton-Warwick, K.A. Collett, L. Rands, and P.R. Wilshaw, [Energy Procedia](#) 92, 326 (2016).
11. R.S. Bonilla, K. Collett, L. Rands, G. Martins, R. Lobo, and P.R. Wilshaw, [Solid State Phenom.](#) 242, 67 (2015).
12. R.S. Bonilla, [Sol. RRL](#) 2, 1800172 (2018).
13. R.B.M. Girisch, R.P. Mertens, and R.F. De Keersmaecker, [IEEE Trans. Electron Devices](#) 35, 203 (1988).
14. R.S. Bonilla, I. Al-Dhahir, M. Yu, P. Hamer, and P.P. Altermatt, [Sol. Energy Mater. Sol. Cells](#) 215, 110649 (2020).
15. E.H. Nicollian and J.R. Brews, *MOS (Metal Oxide Semiconductor) — Physics and Technology* (Wiley, New York, 1982).
16. C.G. de Walle and J. Neugebauer, [Nature](#) 423, 626 (2003).
17. P. Hamer, C. Chan, R.S. Bonilla, B. Hallam, G. Bourret-Sicotte, K.A. Collett, S. Wenham, and P.R. Wilshaw, [Sol. Energy Mater. Sol. Cells](#) 184, 91 (2018).
18. H. Jin, K.J. Weber, N.C. Dang, and W.E. Jellett, [Appl. Phys. Lett.](#) 90, 262109 (2007).
19. A. Richter, S.W. Glunz, F. Werner, J. Schmidt, and A. Cuevas, [Phys. Rev. B](#) 86, 165202 (2012).