

PERMEABILITY OF TiO₂ ANTIREFLECTION COATINGS TO DAMP HEAT

Maria Colom Talló and Keith R. McIntosh

Centre for Sustainable Energy Systems, Australian National University, Canberra, ACT 0200, AUSTRALIA

ABSTRACT: As-deposited TiO₂ coatings are found permeable to water vapour under the “damp heat” conditions of 85 °C and 85% relative humidity. They do not, therefore, protect underlying films or interfaces from any detrimental effects of gaseous H₂O at elevated temperature. Consequently, high-efficiency solar cells with a TiO₂ antireflection coating and oxide passivation could fail the damp-heat reliability test due to H₂O diffusing through the TiO₂ and degrading the underlying Si–SiO₂ interface. The TiO₂ films, which were deposited at 400 °C by atmospheric pressure chemical vapour deposition, were also densified by an 800 °C anneal. While the anneal might have reduced the films’ permeability to water vapour, it degraded the underlying Si–SiO₂ interface or possibly the silicon itself; the samples could not be repaired by a subsequent forming-gas anneal.

Keywords: Antireflection coating, Degradation; Passivation.

1. INTRODUCTION

Oxide-passivated silicon degrades when exposed to the “damp-heat” reliability test [1–3]. The test is known to increase the density of Si–SiO₂ interface states [1] and surface recombination, whether the silicon is (100) planar or textured [2], n-type or p-type [3]. It is also known that the degradation is not due to significant changes in surface charge [3].

The most likely explanation for the damp-heat degradation is a diffusion of water vapour through the SiO₂ to react with the Si near the Si–SiO₂ interface to convert Si–Si bonds to Si–OH–Si structures [4]. The activation energies of the diffusion and reaction processes are $E_a = 0.79$ eV [5] and 1.1–1.5 eV [4], respectively, sufficiently low to permit water vapour to diffuse to the interface [2] and, possibly, to permit the reaction at the damp-heat temperature of 85 °C.

A second explanation of damp-heat degradation relates to a reaction between H₂O and SiO₂ that occurs at ambient temperatures [6, 7] to form silicic acid (H₄SiO₄ or H₈SiO₁₂). This is known to make SiO₂ less compressive (more tensile). The changing film stress might cause an increase in surface states and therefore an increase in surface recombination.

Damp-heat degradation of Si–SiO₂ interfaces is relevant to high-efficiency silicon solar cells that utilise oxide passivation [8–12]. The emitter saturation current density J_{0E} of a light phosphorus diffusion with 20 nm of SiO₂ on planar (100) silicon has been found to increase from 14 to 19 fA/cm² after 10,000 mins at 85 °C and 85% relative humidity [3]; these conditions constitute the damp-heat requirement of the UL and IEC humidity-freeze test, and the IEEE damp-heat test [13]. Such an increase in J_{0E} would slightly reduce a high-efficiency cell’s open-circuit voltage (by 1–3 mV) and, in the case of rear-contact cells, its short-circuit current density (by 0.2–0.6 mA/cm²). A greater increase in J_{0E} occurs for textured surfaces [2]. Consequently, high-efficiency solar cells might fail the damp-heat requirements of reliability tests unless their SiO₂ is protected from water vapour.

Since EVA is permeable to water vapour [14], modules must either be sealed (as employed by some thin-film modules [15, 16]) or the cells must be coated with an impermeable layer. Fortunately, the most common antireflection coating (amorphous PECVD SiN_x) is impermeable to water vapour—just one of its many beneficial properties—but given the expense associated with its deposition, it is worth assessing the permeability of alternative coatings.

A less expensive alternative to PECVD SiN_x is APCVD TiO₂ (as used on most silicon cells in the 1970s–1990s). Being atmospheric pressure (AP) rather than plasma-enhanced (PE), this method of chemical vapour deposition (CVD) does not require vacuum, plasma or belt processing. To provide the same electrical benefits as SiN_x, however, it must also contain significant fixed charge and atomic hydrogen, and it must be impermeable to water vapour. This paper explores the latter of these three properties.

Lifetime experiments are used to quantify the degradation of Si–SiO₂ with and without an overlying TiO₂ film. The permeability of TiO₂ is then examined after an anneal at 800 °C in both O₂ and N₂, which is known to densify TiO₂. Finally, the application of hexamethyldisilazane (HMDS) onto TiO₂ is investigated as a sealant to water vapour.

2. SAMPLE PREPARATION

All samples were fabricated from (111) float-zoned n-type silicon wafers with a nominal resistivity of 800–1200 Ω-cm and thickness of 400 μm. The surfaces were first prepared with a 4 minute polishing etch in 1:10 HF:HNO₃ at room temperature, after which the wafers were RCA cleaned and submitted to a 20 minute POCl₃ deposition and a 10 minute N₂ drive-in at 780 °C. The resultant phosphorus glass was removed with HF, before driving in the phosphorus further and growing an oxide with a 40 minute dry oxidation at 950 °C. Finally, the Si–SiO₂ interface was improved and hydrogenated with a 30 minute N₂ anneal at 1100 °C and a 30 minute forming-gas anneal at 400 °C.

This procedure produced 24–28 nm of thermal oxide on a 100–160 Ω/sq phosphorus surface diffusion on (111) silicon. It represents the diffusion, oxide and orientation that is used on many high-efficiency solar cells [8–12]. Note, however, that cells have textured surfaces where their exposed planes have a (111) orientation, whereas these samples are planar; we therefore expect a smaller J_{0E} than would occur for equivalently passivated textured wafers because the planar samples have a smaller surface area and lack film stress associated with the peaks and troughs [17].

On some samples, TiO_2 was deposited by APCVD using a SierraTherm pilot-line reactor. The reactants were H_2O and tetraisopropyl titanate (TPT) (held at 100 °C), where the gases were transported into the chamber by N_2 carrier gas such that the $\text{H}_2\text{O}:\text{TPT}$ ratio was 1:6. During deposition, the sample temperature was 400 °C.

Some samples were submitted to damp heat for increasing durations, while equivalent samples were stored at room temperature in air to provide a control. The damp heat had a relative humidity of 85% and a temperature of 85 °C, mimicking the damp-heat component of the UL 1703, IEC 61215, and IEEE 1262 standards. The longest exposure was 69,560 minutes (1160 h), which exceeds the IEEE’s damp heat test (1000 h), and the time spent under damp-heat conditions in the UL and IEC humidity–freeze tests (200 h).

The effect of damp-heat exposure was evaluated with the WCT-100 photoconductance tool [18] using a transient analysis [19]. The parameter best suited to compare the samples was the emitter saturation current density J_{0E} , which was calculated at an excess carrier concentration of $1 \times 10^{15} \text{ cm}^{-3}$.

3. RESULTS: AS-DEPOSITED TiO_2

Figure 1 presents the measurements of J_{0E} against time, comparing samples that were exposed to damp heat with the controls that were stored in air, and comparing samples with and without TiO_2 . Several conclusions can be drawn:

Firstly, all samples commenced with a similar J_{0E} of 30–40 fA/cm^2 . This is typical of a well-passivated phosphorus diffused (111) surface. It shows that the deposition of TiO_2 did not degrade the underlying Si– SiO_2 interface, as has been previously observed due to hydrogen out-diffusing from the interface or to texture-related defects [20].

Secondly, the J_{0E} of the control samples remained relatively constant, indicating that there was little or no degradation due to factors other than damp-heat exposure.

Thirdly, the J_{0E} of the samples exposed to damp heat began to degrade after ~30 minutes and continued to degrade for as long as the exposure continued (1159 hours). That is, further degradation is expected if the exposure continued.

Fourthly, the rate of damp-heat degradation was the same whether the sample was coated with TiO_2 or not. Thus the TiO_2 did not hinder the diffusion of water vapour into the SiO_2 . This is likely due to the films being porous, as is known to occur for evaporated and CVD TiO_2 deposited at low temperature [21, 22].

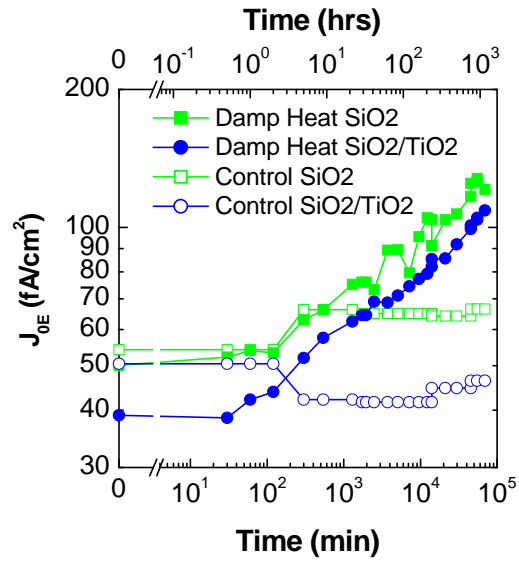


Figure 1: J_{0E} vs time, comparing sample exposed to damp heat (solid) to controls (open), and samples with TiO_2 (blue) and without TiO_2 (green).

Finally, after 200 hours (12,000 minutes), the J_{0E} of the sample with TiO_2 had degraded from 40 to 80 fA/cm^2 , and the J_{0E} of the sample without TiO_2 had degraded from 50 to 100 fA/cm^2 . This degradation is very significant, far more so than has been found for (100) silicon diffused lightly with phosphorus and coated with a 20 nm SiO_2 [3]. High-efficiency solar cells with equivalent surfaces would certainly not pass the damp-heat component of any reliability test!

4. RESULTS: ANNEALED TiO_2

Four samples, identical to those described above, were annealed in both O_2 and N_2 at 800 °C for 30 minutes. Such an anneal densifies TiO_2 , making it less porous and less conductive [21–23]. This anneal caused irreparable damage to the samples with TiO_2 , however, resulting in very short lifetimes.

Figure 2 and Table I present the results of all four samples, where the figure plots the effective lifetime τ_{eff} against the excess carrier concentration Δn and the table lists the emitter saturation current J_{0E} and high-injection bulk lifetime τ_{bulk} extracted from the curves. The samples were measured before and after the 800 °C anneal, as well as after a subsequent 400 °C forming-gas (FG) anneal for 30 minutes. The table only lists J_{0E} and τ_{bulk} when they can be reliably determined.

The results of the samples without TiO_2 indicate that the N_2 anneal makes little difference to recombination whereas the O_2 anneal increases recombination substantially. The latter is due to the recommencement of oxide growth at the Si– SiO_2 interface, which then leads to a high density of interface defects; this is evidenced by an almost doubling of the J_{0E} . After the FG anneal, the O_2 -annealed sample improves, presumably due to annealing and hydrogenation of the newly grown interface, while the N_2 -annealed sample decays a little more. Despite their differences, both samples remain

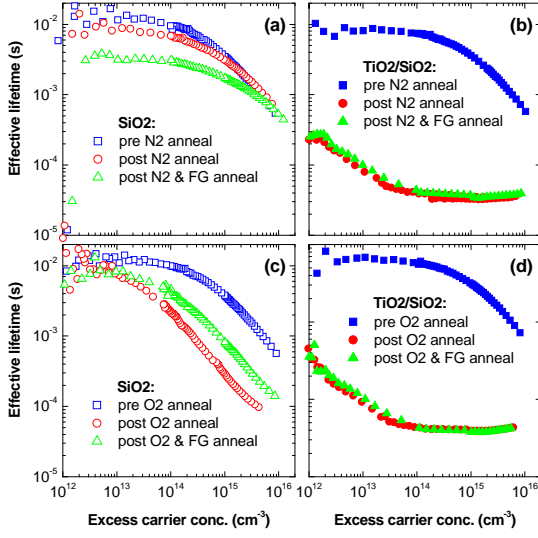


Figure 2: Effective lifetime τ_{eff} as a function of excess carrier concentration Δn of (a) SiO_2 and (b) $\text{TiO}_2/\text{SiO}_2$ samples submitted to an 800 °C N_2 anneal; and (c) SiO_2 and (d) $\text{TiO}_2/\text{SiO}_2$ samples submitted to an 800 °C dry O_2 anneal.

relatively well passivated, with the final τ_{eff} being >1 ms at $\Delta n < 10^{15} \text{ cm}^{-3}$. This is in marked contrast to the samples with TiO_2 .

The samples with TiO_2 exhibit a drastic increase in recombination after either an N_2 or O_2 anneal, and neither are affected by the subsequent FG anneal. We treat the absolute values of the low τ_{eff} data with caution, however, as the measurements were made by a transient analysis whilst the decaying illumination of the flash lamp was not completed. Thus, if anything, the measured τ_{eff} is an overestimate of the true τ_{eff} (probably just at high Δn) and consequently, we cannot extract a meaningful J_{0E} or τ_{bulk} from the data. Nevertheless, we can conclude that the TiO_2 led to a catastrophic increase in recombination that could not be reversed by an FG anneal. The most likely explanation is that impurities out-diffused from the TiO_2 films at 800 °C and contaminated the samples.

Following the FG anneal, the samples with TiO_2 were exposed to damp heat. They did not exhibit further decay but since their starting τ_{bulk} was so short, it cannot be concluded whether (i) the TiO_2 had become impermeable to water vapour and prevented further degradation of the Si– SiO_2 interface, (ii) the Si– SiO_2 interface was degraded by the 800 °C anneal to such an extent that no damp-heat degradation was possible, or (iii) the bulk lifetime was so low that any degradation at the Si– SiO_2 interface was comparably negligible.

Table I: Emitter saturation current density J_{0E} in fA/cm^2 and high-injection bulk lifetime τ_{bulk} in ms extracted from the curves of Figure 2.

Coating	Anneal	Pre-anneal		Post-anneal		Post-FG	
		J_{0E}	τ_{bulk}	J_{0E}	τ_{bulk}	J_{0E}	τ_{bulk}
SiO_2	N_2	47	12.2	40	6.5	50	2.8
SiO_2	O_2	43	12.2	79	5.9	25	6.6
$\text{TiO}_2/\text{SiO}_2$	N_2	35	8.0	?	?	?	?
$\text{TiO}_2/\text{SiO}_2$	O_2	35	5.9	?	?	?	?

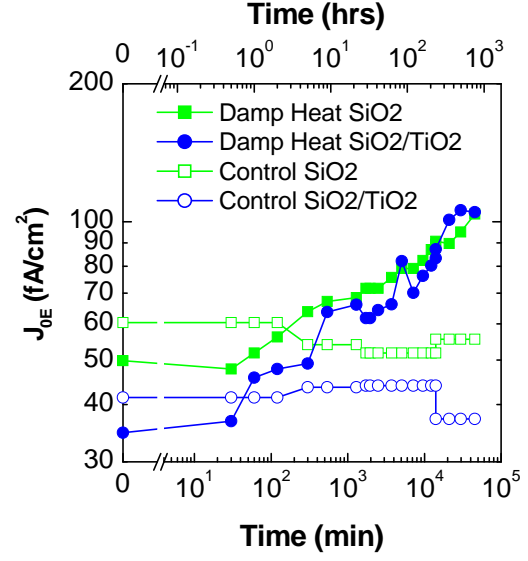


Figure 3: J_{0E} vs time of samples coated with HMDS, comparing those that were exposed to damp heat (solid) to controls (open), and samples with TiO_2 (blue) and without TiO_2 (green).

5. APPLICATION OF HMDS

HMDS is used to convert SiO_2 from being hydrophilic to hydrophobic [24]. It was applied to the samples to test whether it also reduced their permeability to water vapour. The results are shown in Figure 3, which plots J_{0E} against time of exposure. A comparison of Figures 1 and 3 illustrates that there is no significant difference in the degradation of the samples with and without HMDS. It is concluded that the HMDS did not alter the permeability of the TiO_2 , nor did it act as a sealant on the SiO_2 .

6. CONCLUSION

Exposure to damp heat significantly degraded oxide-passivated (111) silicon. The J_{0E} was found to increase from 50 to $\sim 100 \text{ fA}/\text{cm}^2$ after 200 hours, which would cause any high-efficiency cell with such a surface to fail the UL and IEC humidity-freeze test. The degradation continued for another 859 hours until the experiment was ended.

A coating of as-deposited APCVD TiO_2 did not affect the damp-heat degradation of the underlying surface, probably because the coating was porous. Densification of the film by an 800 °C anneal led to catastrophic damage of the samples, possibly due to contamination, and the permeability of the densified films could not be assessed. Finally, a coating of HMDS did not reduce the permeability of either the SiO_2 or the TiO_2 . Fortunately for the industry concerned with high-efficiency silicon solar cells, PECVD Si_nX can be made impermeable to water vapour. Evidence to this effect will be presented in a future publication [25].

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8. REFERENCES

- [1] L.P. Johnson, K.R. McIntosh, B.S. Richards, H. Jin, B. Paudyal, E. Klampaftis, "Si-SiO₂ interface characterisation from exposure to an accelerated humidity environment", *44th ANZSES conference*, 2006.
- [2] E. Klampaftis, K.R. McIntosh and B.S. Richards, "Degradation of an undiffused Si-SiO₂ interface due to humidity", *22nd EU PVSEC*, Milan, pp. 889–892, 2007.
- [3] J.C. Bellet and K.R. McIntosh, "Humidity degradation of oxide-passivated diffused silicon", *22nd EU PVSEC*, Milan, pp. 1318–1321, 2007.
- [4] S.T. Pantelides, L. Tsetseris, S.N. Rashkeev, X.J. Zhou, D.M. Fleetwood and R.D. Schrimpf, "Hydrogen in MOSFETs — A primary agent of reliability issues", *Microelectronics Reliability*, 47, pp. 903–911, 2007.
- [5] S.K. Ghandhi, *VLSI Fabrication Principles*, Wiley, New York, p. 375, 1983.
- [6] H. Leplan, J. Y. Robic, B. Geenen and Y. Pauleau, "Residual Stresses in Evaporated Silicon Dioxide Thin Films: Correlation with Deposition Parameters and Aging Behaviour", *Journal of Applied Physics*, 78, pp. 962–968, 1995.
- [7] H. Leplan, J. Y. Robic and Y. Pauleau, "Kinetics of Residual Stress Evolution in Evaporated Silicon Dioxide Films Exposed to Room Air", *Journal of Applied Physics*, 79 pp. 6926–6931, 1996.
- [8] R.A. Sinton, P.J. Verlinden, R.A. Crane, R.M. Swanson, C. Tilford, J. Perkins, and K. Garrison, "Large-area 21% efficient Si solar cells" *23rd IEEE PVSC*, Louisville, pp. 157–161, (1993).
- [9] J. Zhao, A. Wang, P.P. Altermatt and M. A. Green, "Twenty-four percent efficient silicon solar cells with double layer antireflection coatings and reduced resistance loss", *Applied Physics Letters*, 66, p.p. 3636–3638, 1995.
- [10] S.W. Glunz, J. Knobloch, C. Hebling and W. Wettling, "The range of high-efficiency silicon solar cells fabricated at Fraunhofer ISE", *26th IEEE PVSC*, Anaheim, pp. 231–234, 1997.
- [11] W.P. Mulligan, M.J. Cudzinovic, D.M. de Ceuster, K.R. McIntosh, D.H. Rose, D.D. Smith and R.M. Swanson, "Manufacture of solar cells with 21% efficiency", *19th EU PVSEC*, Paris, pp. 387–390, 2004.
- [12] K.J. Weber, A.W. Blakers, M.J. Stocks, J. H. Babaei, V.A. Everett, A.J. Neuendorf and P.J. Verlinden, "A novel low-cost, high-efficiency micromachined silicon solar cell", *IEEE Electron Device Letters*, 25, pp. 37–39, 2004.
- [13] IEEE 1262, "IEEE Recommended Practice for Qualification of Photovoltaic (PV) Modules", The Institute of Electrical and Electronics Engineers, New York, NY, USA; UL 1703, "Flat-plate photovoltaic modules and panels", Underwriters Laboratory Inc., Northbrook, IL, U.S.A; and IEC 61215, "Crystalline silicon terrestrial photovoltaic (PV) modules—Design qualification and type approval".
- [14] S.C. Agro and R.T. Tucker, "Development of new low-cost, high-performance, PV module encapsulant/packaging materials: Annual Technical Progress Report", NREL Report No. SR-520-35683, 2004.
- [15] G.R. Mon, L.C. Wen, R.S. Sugimura, and R.G. Ross, "Reliability studies of photovoltaic module insulation systems", *Electrical Electronics Insulation Conference*, pp. 324–329, Chicago, September 1989.
- [16] L.C. Olsen LC, M.E. Gross, G.L. Graff and S.N. Kundu, "Approaches to encapsulation of flexible CIGS cells", *Proc. SPIE*, 7048, pp. O480–O480, (2008).
- [17] K.R. McIntosh and L.P. Johnson, "Recombination at textured silicon surfaces passivated with silicon dioxide", *Journal of Applied Physics*, 105, 124520, 2009.
- [18] www.sintonconsulting.com
- [19] D.E. Kane and R.M. Swanson, "Measurement of the emitter saturation current by a contactless photoconductivity decay method", *Proc. 18th IEEE PVSC*, pp. 578–583, 1985.
- [20] A.F. Thomson, K.R. McIntosh and B.S. Richards, "Surface recombination in oxide-passivated Si after the deposition of APCVD TiO₂", *Proc. 22nd EU PVSEC*, pp. 1305–1308, 2007.
- [21] H. Sankur and W. Gunning, "Sorbed water and intrinsic stress in composite TiO₂-SiO₂ films", *Journal of Applied Physics*, 66 (2), pp. 807–812, 1989.
- [22] E.T. Fitzgibbons, K.J. Sladek and W.H. Hartwig, "TiO₂ film properties as a function of processing temperature", *Journal of the Electrochemical Society*, 119, pp. 735–739, 1972.
- [23] V. Mikhelashvili and G. Eisenstein, "Effects of annealing conditions on optical and electrical characteristics of titanium dioxide films deposited by electron beam evaporation", *Journal of Applied Physics*, 89, pp. 3256–3269, 2001.
- [24] J. Voorthuyzen, K. Keskin, and P. Bergveld, "Investigations of the surface conductivity of silicon dioxide and methods to reduce it", *Surface Science*, 187, pp. 201–211, 1987.
- [25] X. Dai and K.R. McIntosh, "Permeability of silicon nitride antireflection coatings to damp-heat exposure", in preparation.