DEGRADATION OF AN UNDIFFUSED SI–SIO$_2$ INTERFACE DUE TO HUMIDITY

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ABSTRACT: The effect of humidity on undiffused oxide-passivated silicon is investigated. High resistivity *n*-type silicon wafers with 200 Å of SiO_2 were submitted to 100% relative humidity at 75 ºC for various periods of time. A significant increase in surface recombination was observed with increasing humidity exposure, irrespective of whether the sample was textured or planar, or whether the sample had received a forming-gas anneal, an Alneal, or a rapid-thermal anneal prior to exposure. These findings are relevant to modules of high-efficiency silicon solar cells that utilise SiO_2 passivation because EVA is permeable to water vapour, and therefore the encapsulation of a cell will not necessarily prevent a degradation of its Si–SiO_2 interface during humidity exposure. Three mechanisms that may have caused the degradation are discussed: the diffusion of H_2O through the SiO_2 to react with hydrogen molecules at the Si–SiO_2 interface; a reaction of H_2O with the SiO_2 creating silicic acid molecules that alters the film stress thereby increasing the density of states at the Si–SiO_2 interface; and the deposition of surface charge during exposure.
Keywords: Degradation, Passivation, Recombination

1 INTRODUCTION

"Humidity-Freeze" is one of many tests that photovoltaic modules must pass to gain approval by organisations such as the UL, IEC, and IEEE. In the case of the UL 1703 standard [1], humidity-freeze requires a module to satisfactorily survive ten 24-hour thermal cycles, where the temperature varies from –40 to 85 ºC, and where at least 20 hours of each cycle must be spent at 85 ºC in an atmosphere of 85% relative humidity. Not surprisingly, such tests can lead to mechanical faults [2].

Rather than mechanical degradation, this paper concerns the electrical degradation that might be incurred during the "damp heat" component of the humidity-freeze test. Smith observed that damp heat caused a significant increase in emitter saturation current of oxide-passivated silicon diffused with either boron or phosphorus [3]. This works investigates the influence of damp heat on undiffused oxide-passivated silicon and the role of hydrogen at the interface.

2 EXPERIMENTAL PROCEDURE

Six pairs of samples were prepared and labelled "planar FGA", "planar Alneal", "planar RTA", "textured FGA", "textured Alneal" and "textured RTA". The reason for these labels will be apparent once their fabrication is described.

The samples were fabricated from *n*-type <100> float-zone silicon wafers with a nominal resistivity of >1000 Ω-cm. After removing saw damage with a TMAH chemical etch, half the wafers were textured with KOH to form random pyramids, while the remainder were left planar. A 200 Å thermal SiO_2 was then grown and annealed at 1000 ºC for 30 minutes in N_2.

The samples were completed by giving them one of three anneals: (1) a simple forming-gas anneal (FGA), (2) an Alneal, or (3) a rapid-thermal anneal (RTA).

The FGA was performed at 400 ºC for 30 minutes; this procedure is known to result in low recombination at Si–SiO_2 interfaces [4]. The Alneal was performed by depositing 1000 Å of Al on each side of the wafer before submitting it to the FGA described above and removing the Al immediately after; an Alneal leads to a lower surface recombination rate than a simple FGA [4]. The RTA was performed in N_2 at 550 ºC for 3 minutes; this procedure removes hydrogen from the interface leading to poor surface passivation [5].

The total recombination rate—or equivalently, the effective lifetime—was measured with the WCT-100 photoconductance tool [6] by the transient method [7]. The effective lifetime was then monitored while one wafer from each pair was submitted to damp heat and the other was kept at room temperature in N_2 (as a control). The damp heat consisted of a relative humidity of 100% and a temperature of 75 ºC; at the time of the experiment, our humidity chamber was not capable of matching the exact conditions of the UL 1703 standard.

3 RESULTS

The samples were very sensitive to the quality of their surface passivation for two reasons: (i) the bulk recombination rate was very low due to the use of high-resistivity float-zone wafers and clean processing; and (ii) there were no diffusions at the surfaces. Thus, any degradation of the surface passivation is easily detected by measuring their effective lifetime before and after humidity exposure.

Figure 1 plots the effective lifetime τ_{eff} for the "planar FGA" sample as a function of excess carrier concentration Δn after various periods of humidity exposure. Figure 1(a) shows $\tau_{eff}(\Delta n)$ when calculated in the conventional manner, which assumes that the output voltage from the WCT-100 has a linear response to sample conductance. The lifetime curves contain an unusual peak but there is a clear decrease τ_{eff} at all Δn.

A recent study has shown that the peak in the lifetime curves is an artefact of the measurement and is not the actual lifetime curve [8]. The deviation results from the WCT-100 having a non-linear response at very low conductance, and it is evident here because the silicon is undiffused and lightly doped. Figure 1(b) plots $\tau_{eff}(\Delta n)$ when it is calculated using the calibration curve in [8] shifted on the voltage axis so that the resultant $\tau_{eff}(\Delta n)$ curves are relatively peak free. This shift in voltage axis

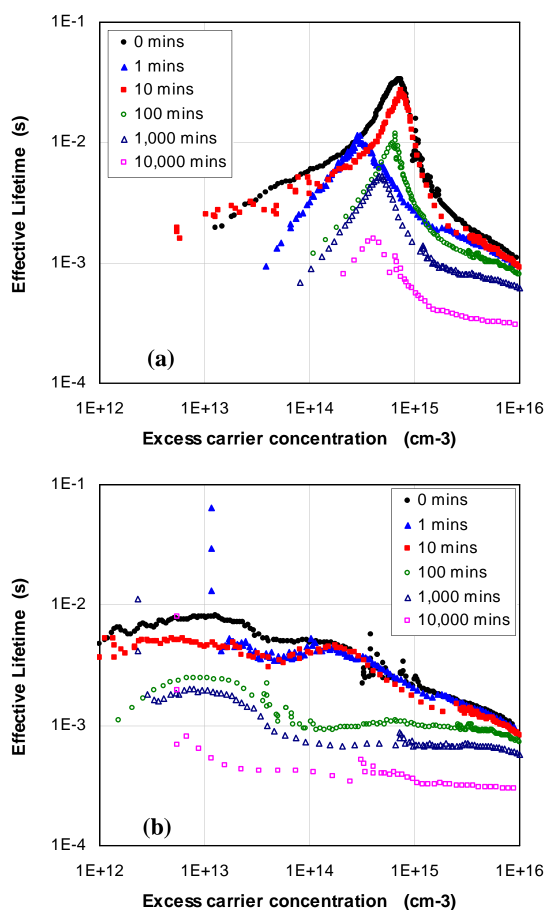

Figure 1: Effective lifetime τ_{eff} vs excess carrier concentration Δn of the "planar FGA" sample after damp heat exposure, where $\tau_{\mathrm{eff}}(\Delta n)$ is **(a)** determined with the conventional linear calibration and **(b)** corrected for the WCT-100's non-linear response at low conductance.

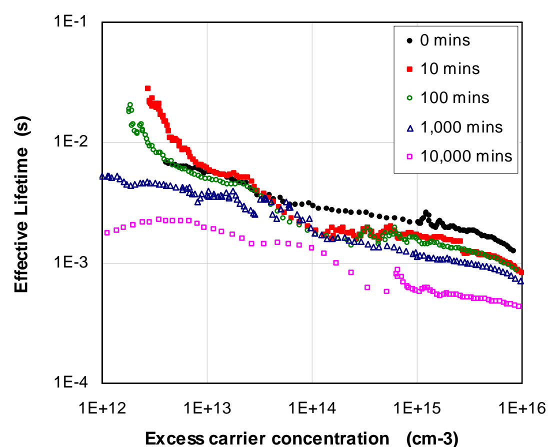

Figure 2: $\tau_{\mathrm{eff}}(\Delta n)$ of the "planar Alneal" sample after damp heat exposure, corrected for non-linear calibration.

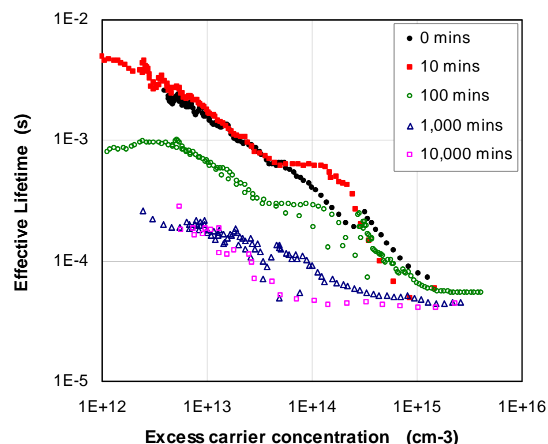

Figure 3: $\tau_{\mathrm{eff}}(\Delta n)$ of the "planar RTA" sample after damp heat exposure, corrected for non-linear calibration.

may have been required because the calibration curve of [8] was performed on a different WCT-100 instrument and on samples with a thicker oxide, and because the balance voltage and room-light illumination were not strictly controlled in this experiment. Thus, the adjustment of the curves is somewhat manufactured and the absolute lifetime should be considered approximate; the data becomes increasingly uncertain for decreasing Δn. The correction has been included to provide more accurate data and to illustrate the importance of the WCT-100 calibration at very low conductance.

It is evident from Figure 1 that the "planar FGA" sample degrades significantly during humidity exposure. The same is true of the "planar Alneal" (Figure 2) and "planar RTA" (Figure 3) samples, as well as all textured samples (not shown).

To summarise these results, Figure 4 plots τ_{eff} at $\Delta n = 10^{15}$ cm^{-3} for the six samples submitted to damp heat as function of exposure time, and Figure 5 plots the equivalent data for the control samples. This value of Δn was chosen to represent a high-efficiency solar cell under operating conditions. At this Δn, the uncertainty introduced by the non-linear calibration is small and represented by the error bars in Figures 4 and 5.

The following can be construed from Figures 4 and 5: The control samples had a stable τ_{eff} while the samples submitted to damp heat had a decreasing τ_{eff}. For the latter, the relative change in τ_{eff} was similar for planar and textured surfaces. After 10,000 minutes, τ_{eff} at $\Delta n = 10^{15}$ cm^{-3} decreased by a factor of 3–5 for samples that had received an FGA or an Alneal prior to damp-heat exposure, and by a factor of 1.2–1.4 for samples that had received an RTA. (For these RTA samples, the relative reduction in τ_{eff} was larger at smaller Δn, as evident in Figure 3.) After 10,000 minutes of damp-heat exposure, the degradation of τ_{eff} is not complete; if anything, it is increasing at a faster rate.

4 DISCUSSION

The above results show that τ_{eff} of oxide-passivated undiffused *n*-type silicon decreases with increasing periods of damp-heat exposure. Similar results have been attained for undiffused *p*-type silicon [9] and diffused silicon of both types [3, 10].

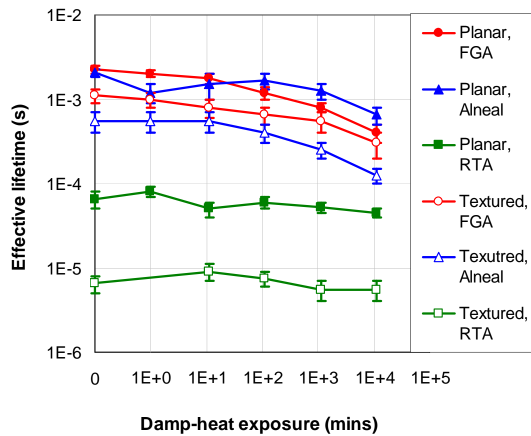

Figure 4: τ_{eff} at $\Delta n = 10^{15}$ cm^{-3} for the samples submitted to damp heat, corrected for non-linear calibration.

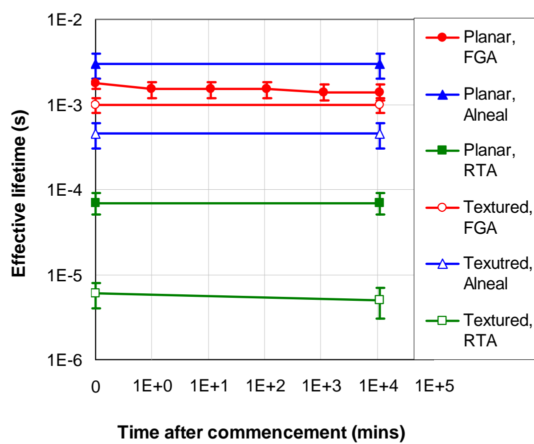

Figure 5: τ_{eff} at $\Delta n = 10^{15}$ cm^{-3} for the control samples (stored at room temperature in N_2), corrected for non-linear calibration.

Since it is very unlikely that water vapour at 75 ºC can have any affect on the bulk of a silicon wafer, we conclude that the reduction in τ_{eff} must be due to an increase in surface recombination rate; this conclusion is supported by CV measurements on undiffused silicon that show an increase in $D_{it}(E)$ [9] and PC measurements on diffused silicon that show an increase in J_{0e} but not τ_{bulk} [10].

We postulate three ways for water vapour to influence recombination at the Si–SiO_2 interface. They relate to (i) diffusion of H_2O through the SiO_2 to the interface, (ii) a reaction between H_2O and SiO_2, and (iii) surface charge.

Regarding the first way, the diffusion of H_2O through SiO_2 at 75 °C is slow but by no means negligible in the context of the damp-heat test. The density of water vapour in air at 75 °C and 100% relative humidity is 305.3 g/m^3 [11], which correlates to an external concentration of $C_{ext} = 1.02 \times 10^{19}$ cm^{-3}. Assuming that the diffusion of H_2O through thermal SiO_2 has an effective activation energy of E_a = 0.79 eV [12] and a diffusivity constant of D_0 = 1.1 × 10^{-6} cm^2/s [12], its diffusivity at 75 °c is $D = D_0\exp(-E_a/kT) = 4.1 \times 10^{-18}$ cm^{2}s^{-1}. C_{ext} and D can be used to determine the final concentration of H_2O atoms at the interface C_{int} if the reaction rate between H_2O and the interface is understood. While this is not the case, we can examine two extremes cases: (a) the interface behaves as an infinite sink in steady state and (b) the oxide is a semi-infinite slab. In case (a), the interface concentration is zero and the steady-state flux of H_2O at the interface ($D*C_{ext}/W_{SiO2}$) is 2.1 × 10^7 cm^{-2}s^{-1}; over 10,000 minutes, that amounts to a reaction of ~10^{13} H_2O molecules per cm^2 of interface. This figure is only ~100 smaller than the density of interface atoms [13] and ~100 times greater than the defect density. In case (b) the H_2O concentration at a depth of 200 Å after 10,000 mins is C_{ext}*ERFC[W_{SiO2}/2*sqrt($D*t$)] = 3.8 × 10^{18} cm^{-3} for W_{SiO2} = 200 Å, which is not much smaller than C_{ext}. While we have ignored the activation energy associated with H_2O adsorption to the SiO_2 and the interface reaction, and the time taken to reach steady state (case (a)), these extreme cases suggest that 200 Å of thermal SiO_2 might not offer an adequate moisture barrier to 10,000 minutes of damp heat. If the H_2O molecules react with the interface at 75 °C to remove passivating H atoms (for example) a degradation of the oxide passivation would ensue. We note that he removal of passivating H molecules from the interface cannot be the sole mechanism of degradation in our experiment, since the RTA samples were observed to degrade in damp heat, albeit less than the FGA and Alneal samples.

A second way for water vapour to influence the surface passivation relates to a reaction between H_2O and SiO_2. Leplan *et al.* [14, 15] found that at ambient temperatures, a reaction between SiO_2 and water vapour can form silicic acid (H_4SiO_4 or H_8SiO_{12}), causing the intrinsic stress of the SiO_2 to be become less compressive (more tensile). The change in film stress might cause an increase in surface states and therefore an increase in surface recombination.

A third mechanism that might have influenced the surface recombination is the deposition of surface charge during the damp-heat exposure. We doubt this mechanism accounts for much of degradation, however, because in a related study, it was found that a degradation of diffused surfaces still occurred at all degrees of surface charge [10].

The relevance of this work pertains to silicon solar cells that utilise SiO_2 passivation. Such cells are generally of a high efficiency, such as SunPower's A-300 [16], UNSW's PERL cell [17], and ANU's Sliver cell [18]. Our results suggest that without a moisture barrier, these cells would exhibit electrical degradation when submitted to the humidity-freeze test. The standard encapsulation procedure may not offer a sufficient moisture barrier since EVA is permeable to water vapour [19]. Nevertheless, SunPower must circumvent this issue since their A-300 modules pass the UL standard.

5 ACKNOWLEDGEMENTS

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