HUMIDITY DEGRADATION OF OXIDE-PASSIVATED DIFFUSED SILICON

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ABSTRACT: The effect of humidity on diffused oxide-passivated silicon was investigated. High resistivity *p*-type silicon wafers were diffused with either phosphorus or boron and then passivated with 1000 Å of SiO_2 before being submitted to 85% relative humidity at 85 ºC. The emitter saturation current density J_{0E} of the samples was measured as a function of humidity exposure time and surface charge, where the latter was varied by way of corona discharge. The J_{0E} of both *n*- and *p*-diffused samples was found to increase with humidity exposure at all levels of surface charge. The results indicate that the conditions inside the humidity chamber did not greatly alter the surface charge on the samples, and this cannot explain the increase in J_{0E}. Instead, the predominant cause of the increased in J_{0E} must be a degradation of the SiO_2–Si interface. These findings are relevant to high-efficiency silicon solar cells that utilise SiO_2 passivation on diffused silicon; and since EVA is permeable to water vapour, the encapsulation of a cell will not necessarily prevent a degradation of its SiO_2–Si interface during humidity exposure.
Keywords: Degradation, Passivation, Recombination

1 INTRODUCTION

The effect of humidity on oxide-passivated silicon diffused with either phosphorus or boron is investigated. The relevance of this work pertains to the “humidity-freeze” reliability test required by certification 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. It has been found that under the “damp heat” component of the test, the surface recombination of diffused [2] and undiffused [3, 4] oxide-passivated silicon can increase. Here, we investigate diffused oxide-passivated silicon before and after corona discharge to ascertain whether the cause of the degradation relates solely to surface charge.

2 SAMPLE PREPARATION

Samples were fabricated from <100> *p*-type float-zone silicon wafers with a resistivity of ~200 Ω-cm. After removing saw damage with a TMAH wet etch, the samples were diffused in one of four ways: “light phosphorus”, “heavy phosphorus”, “light boron” and “heavy boron”; the sheet resistance of each diffusion is listed in Table I. Following the diffusion, a 1000 Å thermal SiO_2 was grown and annealed in N_2 for 30 mins at 1000 ºC. The final processing step was to anneal the samples in forming gas at 400 ºC for 30 minutes to passivate the interface with hydrogen.

Six samples were fabricated for each diffusion: One sample was a control (stored in air) while the others were submitted to damp heat for various periods of time. The damp heat had a relative humidity of 85% and a temperature of 85 ºC, mimicking the damp-heat component of the UL 1703 standard. The longest exposure was 10,000 minutes (~167 hours), which is similar to the time spent under those conditions in the UL standard (200 hours).

The effect of damp-heat exposure was evaluated with the WCT-100 photoconductance tool [5] using the transient decay method [6]. 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 1×10^{15} cm^{-3}.

Table I lists the J_{0E} of each diffusion after the forming gas anneal but prior to damp-heat exposure. The range encompasses the maximum and minimum values of each diffusion. These J_{0E} are typical of their respective diffusion for oxide-passivated planar samples, except for the “light boron” diffusions, for which the J_{0E} is ten times higher than expected. Consequently, the “light boron” diffusions are not representative of a diffusion that might be incorporated into a high-efficiency solar cell. The high J_{0E} could be due to contamination introduced during high-temperature processing.

Table I: Sheet resistance and J_{0E} of the samples after forming gas anneal but before damp-heat exposure.

Diffusion name	Sheet res (Ω/sq)	J_{0E} (fA/cm^2)
Light phosphorus	155	14 ± 6
Heavy phosphorus	27	134 ± 12
Light boron	250	260 ± 20
Heavy boron	40	187 ± 27

3 RESULTS AND DISCUSSION

Figure 1 plots J_{0E} for all samples after exposure to damp heat. For each diffusion, J_{0E} tends to increase with the duration of exposure, which is consistent with observations on other oxide-passivated silicon samples [2–4]. The heavier diffusions appear to degrade more than the light diffusions.

It is well known that J_{0E} depends on recombination at the Si–SiO_2 interface and recombination in the diffusion [7]. We discount the possibility that recombination in the diffusion could change with damp-heat exposure because at 85 ºC, it is highly unlikely that H_2O or any other contaminant could have diffused through the SiO_2 and into the silicon. Thus, we attribute all changes in J_{0E} to changes in interface recombination

The interface recombination itself depends on the interface-state density, the capture cross section of electrons and holes, the dopant diffusion profile, charge

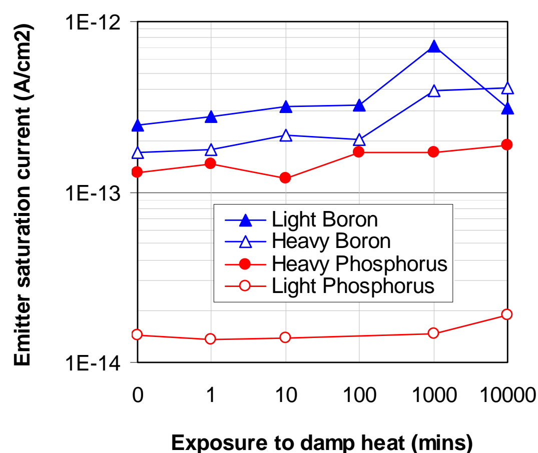

Figure 1: Emitter saturation current J_{0E} vs duration of damp-heat exposure prior to corona charging.

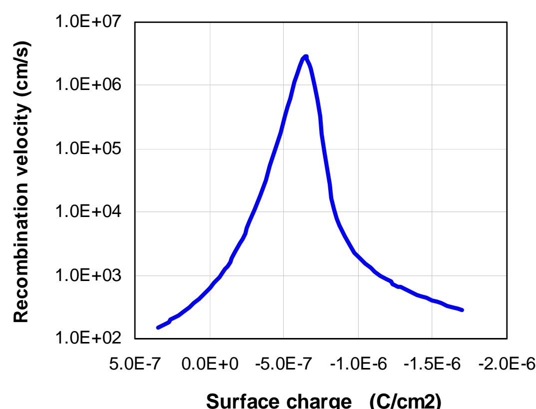

Figure 2: Interface recombination velocity vs surface charge, calculated for an oxide-passivated *n*-type surface with a 3×10^{18} cm^{-3} donor concentration; see text for further detail.

at the interface, charge in the SiO_2, and charge on the surface of the SiO_2 [7]. Apart from the dopant profile, any of these parameters may have changed during damp-heat exposure. The possibility that surface charge is the sole culprit is now explored.

Figure 2 shows how charge on the external surface of the SiO_2 can affect the interface recombination velocity *S*. The data was calculated following the procedure of Ref. 8, using the interface-state density from Figure 5 and the capture cross sections from Figure 7 of the same reference. The calculations assume a fixed charge density of 10^{11} cm^{-2} within the first 200 Å of the SiO_2, a total SiO_2 thickness of 1000 Å, a constant donor atom concentration of 3×10^{18} cm^{-3}, and an excess carrier concentration of 10^8 cm^{-3}. There are clearly some assumptions in this calculation that are not entirely representative of our experimental samples, but the trend in the curve of Figure 2 is reasonable. It shows that a low recombination rate arises from a sufficiently negative or positive surface, which results from the surface charge limiting the concentration of either electrons (for negative charge) or holes (for positive charge) from the interface. The recombination rate is a maximum when the charge is such that the concentrations of holes and electrons are similar. In this *n*-type example, the peak occurs at a negative surface charge because a significant concentration of holes must be attracted before it is similar to the concentration of electrons; for *p*-type silicon, the peak occurs for positive surface charge. Such plots are described in more detail in Refs. 8–11.

The purpose of our investigation was to determine whether the damp-heat exposure caused an increase in *S* (and therefore J_{0E}) solely due to a change in surface charge. While often neglected, changes in surface charge can play a significant role in the quality of oxide passivation—even for diffused samples [12]. If the conditions within the humidity chamber were such that charged particles were either deposited or removed from the external surface of the samples, the J0E would be altered, as illustrated by Figure 2.

The investigation employed a corona discharge unit in a similar manner to Schöfthaler *et al.* [9] and Dauwe *et al.* [10]. Both sides of the samples were first saturated with positive charge (150 s), and then gradually made more negative by submitting them to short periods (~10 s) of negative corona discharge. We could therefore determine a relationship between J_{0E} and surface charge. We did not, however, have the capacity to measure absolute surface charge (such as with a Kelvin probe [9, 10]), and therefore the results are presented as a function of time under a negative corona discharge. To our knowledge, J_{0E} has not previously been plotted as a function of surface charge for diffused silicon.

Figure 3 presents results for “heavy phosphorus” and “heavy boron”, plotting J_{0E} and bulk lifetime τ_{bulk} as a function of time for damp-heat exposure and negative corona discharge (after an initial 150 s of positive discharge). The feature of most relevance is the increase in J_{0E} with increasing humidity exposure. This trend occurs at all levels of surface charge, indicating that humidity degrades the interface and does not simply alter the surface charge. If the latter were the case, the curves would overlap.

The dependence of J_{0E} on surface charge does not, however, follow the trend shown in Figure 2. We believe this is because after a certain duration of corona discharge, the deposition of surface charge saturates. Thus, once the charge saturates, any additional corona discharge will not alter J_{0E}. The dotted lines in Figure 3 provide the J_{0E} we might expect had charge saturation not occurred. This explanation is speculative and has not yet been tested.

Figure 3 also shows that τ_{bulk} has no dependence on damp-heat exposure or surface charge. This indicates that the influence of water vapour and surface charge does not extend to the base.

The results for “light phosphorus” and “light boron” samples are plotted in Figure 4. Like the heavy diffusions, J_{0E} tends to increase with humidity exposure for all charge. As for the heavy diffusions, this indicates that the damp heat degraded the interface.

For both light diffusions, the dependence of J_{0E} on surface charge follows the trend shown in Figure 2—if somewhat loosely—whereby the J_{0E} peaks at some surface charge. Were it possible to plot J_{0E} against the absolute surface charge, it is expected that the peaks for each humidity exposure would occur at the same charge.

The bulk lifetime for the “light boron” samples remains constant with surface charge, similar to the heavy diffusions. Curiously, however, there is a step-like

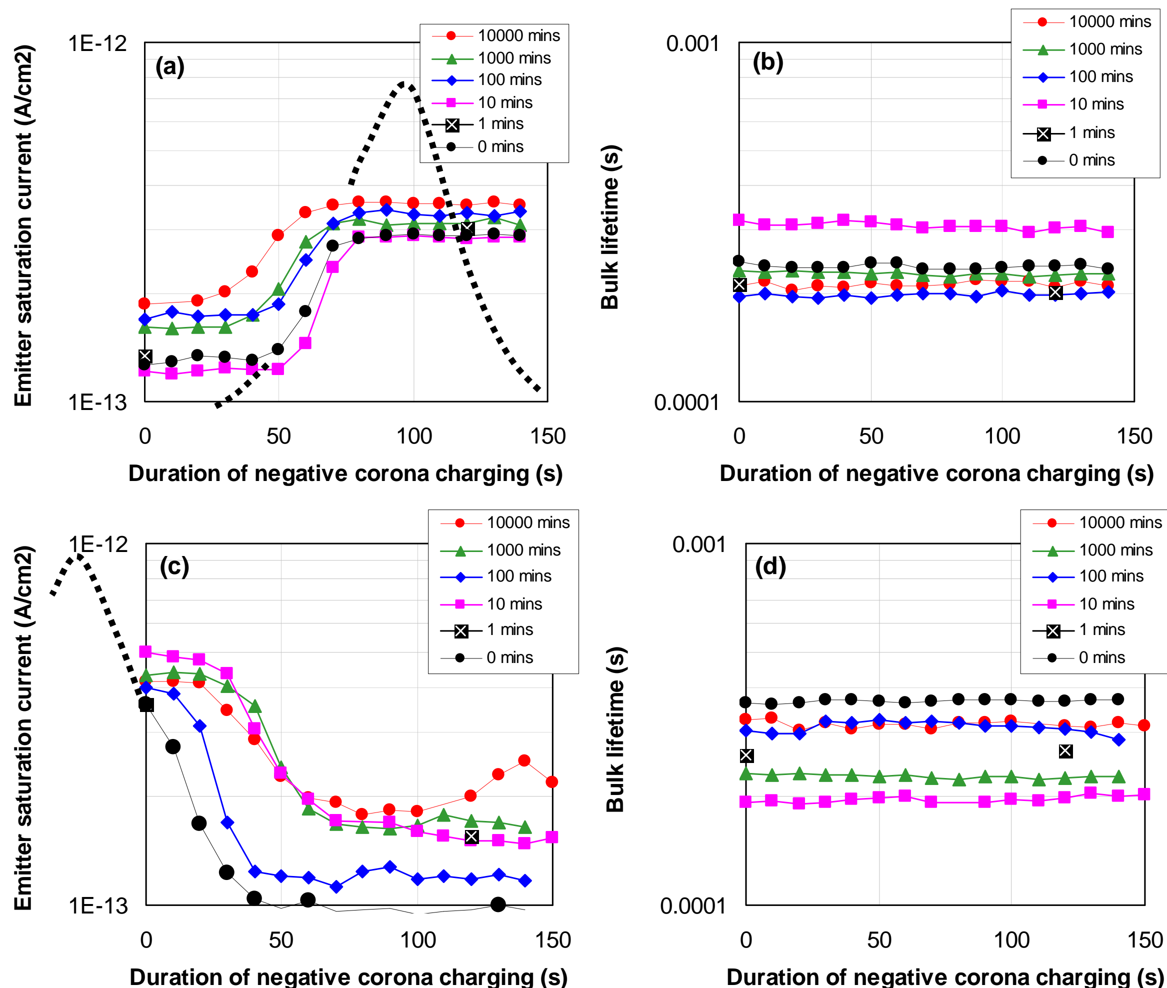

Figure 3: Results from photoconductance measurements as a function of damp-heat exposure and time under negative corona discharge after an initial 150 s of positive corona discharge. The graphs plot (a) J_{0E} and (b) τ_{bulk} for "heavy phosophorus" and (c) J_{0E} and (d) τ_{bulk} for "heavy boron".

decrease in the bulk lifetime of the "light phosphorus" samples, once the negative discharge exceeds ~50 s, corresponding to the peak of the J_{0E}. Furthermore, the J_{0E} on the negative side of this peak is significantly higher than on the positive side. This indicates that the total recombination in the light-phosphorus samples suddenly increases once the peak of the J_{0E} curve is passed. This unexpected result may have been due to damage caused by the corona discharge (as observed elsewhere [13]).

Finally, it is noted that for all but the "light boron" diffusion, which is particularly sporadic, the pre-charged J_{0E} (Figure 1) is similar to the post-charged J_{0E} after ~30 s of negative charging (following 150 s of positive charging) for all humidity exposures. This gives no indication of the absolute surface charge but does suggest that varying degrees of humidity exposure did not greatly alter the surface charge.

4 CONCLUSION

Interface recombination has been found to increase with damp-heat exposure for oxide-passivated silicon with either an *n*- or *p*-type surface diffusion. This result is consistent with unpublished data on diffused silicon [2] and has also been observed for undiffused *n*-type [3] and *p*-type [4] silicon.

By depositing charge on the surface of the wafers with a corona discharge unit, it was found that the increase in interface recombination cannot be solely attributed to either the deposition or removal of surface charge within the humidity chamber. Instead, the predominant mechanism must relate to a degradation of the interface itself. This is consistent with CV measurements on non-diffused samples, which showed an increase in the interface-state density after humidity exposure [4]. Discussion on the cause of the interface degradation can be found in Ref. 3, also presented at this conference. Since EVA is permeable to water vapour [14], cells encapsulated in modules are not necessarily exempt from the degrading effects of humidity.

5 ACKNOWLEDGEMENTS

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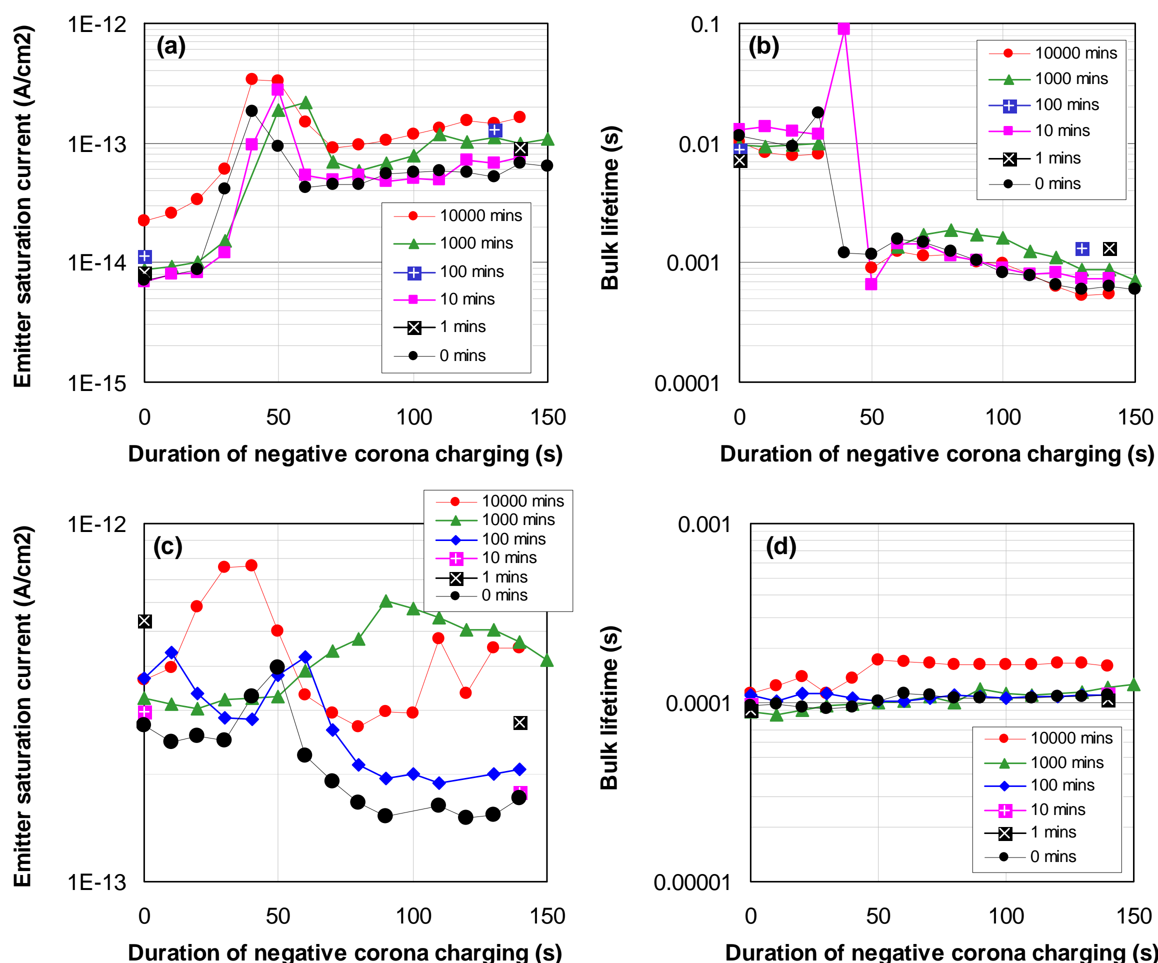

Figure 4: Results from photoconductance measurements as a function of damp-heat exposure and time under negative corona discharge after an inital 150 s of positive corona discharge. The graphs plot (a) J_{0E} and (b) τ_{bulk} for "light phosphorus" and (c) J_{0E} and (d) τ_{bulk} for "light boron".

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