DEGRADATIOIN OF OXIDE-PASSIVATED SILICON

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ABSTRACT: The surface recombination of light-boron diffused (~ 200 Ω/sq) and oxide-passivated n-type silicon was found to increase at room temperature for samples that did and did not receive a forming-gas anneal. This increasing recombination is manifested as a 45 fold increase in J_{0e} for the boron-diffused silicon and a doubling of S_{eff} for un-difffused silicon, taking 120 days to saturate at room temperature. Phosphorus-diffused oxide-passivated silicon does not degrade at room temperature over the same time period. PC-1D modelling shows the degradation is consistent with a defect formed at the Si-SiO_2 interface, independent of surface doping, where the defect has much larger capture-cross section area for electrons rather than holes, where the fully degraded interfaces imply the recombination is dominated by a defect with a σ_N/σ_P ratio greater than 100. The formation of this defect is possibly related to oxygen in the storage ambient.

1. INTRODUCTION

The highest efficiency single and multi-crystal silicon-solar cells utilise oxide-passivated silicon to reduce surface recombination at the front and rear surfaces [1-2]. Zhao *et al.* has fabricated high-efficiency-solar cells (HESC) with conversion efficiencies in excess of 24 % based on the single-crystal p-type passivated-emitter rear-locally diffused (PERL) and the passivated-emitter rear-totally diffused (PERT) solar cells on floatzone and magnetically-confined Czochralski silicon [2]. A modified version of the single-crystal processing has been used by Schultz *et al.* to fabricate multi-crystalline HESC, where low temperature wet-oxidations where used to passivate the "honeycomb" textured devices, achieving conversion efficiencies of 20.3 % [1]. Excellent oxide-passivation of their front and rear surfaces or these devices was essential to their performance for which they hold current efficiency records for silicon-solar cells [3].

Silicon-oxide passivation has been extensively studied in the context of solar cells. Kerr *et al.* optimised the oxidation and "alnealing" of n and p-type silicon, this processing resulted in the best recorded upper bound on SRV of 0.46 and 0.63 cm/s for n and p-type silicon 90 and 150 Ω·cm respectively [4]. Very low combined recombination at the surface and in the diffused layer of boron and phosphorus-diffused silicon has also been reported by Kane and Swanson *et al.*, Kerr *et al.* and King *et al.*, where these results are generally used for comparisons of optimised diffused surface recombination [5-9]. Although thermally-oxidised silicon affords excellent passivation, its use is limited commercially, the

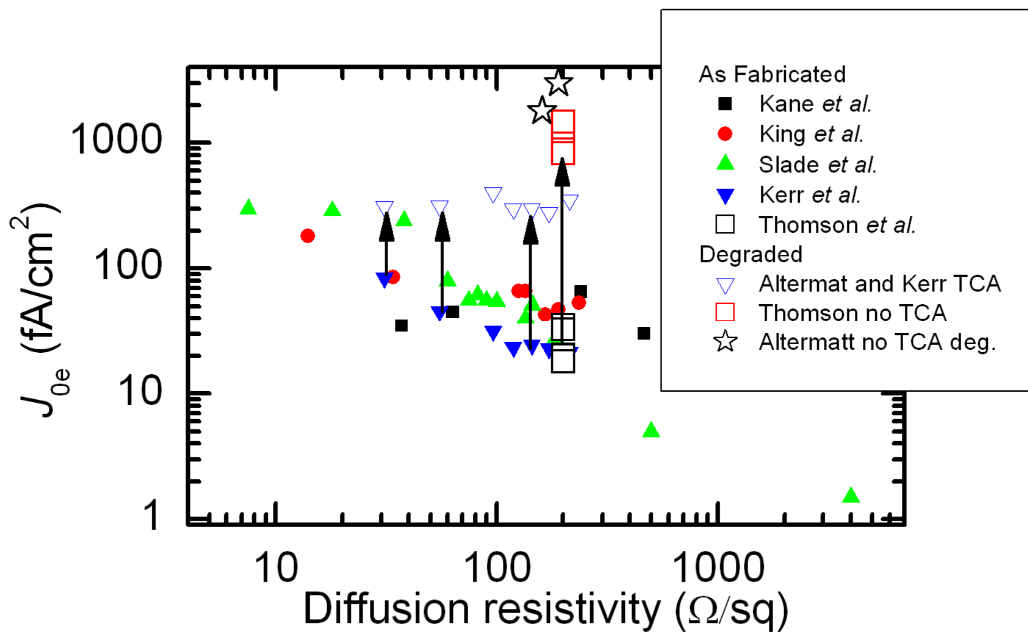

Figure 1: Summary of boron-diffusion passivation result, where J_{0e} is plotted as a function of diffused resistivity.

only example of which is the SunPower A-300 [10]; however chemical-oxides with short-high temperature anneals may become widely used in the industry [11-12].

Surface recombination in high-efficiency silicon-solar cells that utilise oxide-passivation, still significantly contributes to the preventable losses in the devices; hence any degradation in this passivation has a serious impact on the device performance [10, 13].Common degradation mechanisms reported in solar literature are, humidity, thermal treatment, and atomic hydrogen [14-17]. Exposing oxide interfaces to humidity at elevated temperatures has been found to increase the recombination in the oxide interface [15, 18-19]. Where oxide passivated, n and p-type and, phosphorus, and boron-diffused silicon have been found to degrade. These works showed that humidity degradation was not caused by changing oxide charge, or loss of hydrogen, but an increase of interface states. Until recently the stability of oxide passivation had not been studied at room temperature, with no degradation stimulus (humidity, thermal anneals, exposure to hydrogen plasma).

We found the passivation of boron-diffused oxide-passivated silicon severely degrades at room temperature [20]. Up to a 45 fold increase in J_{0e} is observed over the course of 120 days when the reaction is approximately saturated; this effect occurs irrespective of whether the samples receive a FGA after oxidisation. The reaction was observed for samples stored at 50, 75, and 100 °C; the degradation followed a second-order reaction where the time constant of one component of the reaction is 10–40 times shorter than the other, the activation energy of the fast reaction is 0.19±0.05 eV. Subsequent to degradation, annealing in air reduces the recombination with increasing anneal temperature saturating at ~300 °C to a value that is about four times higher than the pre-degradation value [20].

While our study of degrading boron-diffused silicon [20] was the first comprehensive study of the degradation reaction, it has been observed twice by other researchers. In 2003 Zhao *et al.* reported degradation of the n-type PERT solar cells created at UNSW, where the V_{oc} decreased by up to 100 mV [21]. This occurred after the cells had been stored for two years. Subsequent to this in 2006 Altermatt *et al.* reported serious degradation to oxide-passivated boron-diffused samples with a resistivity 31 – 213 Ω/sq [22], the samples that degraded were that of Kerr and had been stored in a draw for over two years. Altermatt found that Kerr's samples degraded to ~ 300 fA/cm^2 when oxidised with in-situ TCA and degraded to ~ 1200 fA/cm^2 when oxidised without [6, 22]. To provide a summary of current oxide-passivated boron-diffused result, and indicate the extent of the measured degradation Figure 1 provides a summary of the passivation results of boron emitters and the resultant degraded J_{0e} for the aforementioned studies, where J_{0e} is plotted as a function of diffusing resistivity. The arrows indicate the change in J_{0e} caused by the degradation reaction. These studies indicate that the degradation is not limited to light diffusions, and will drastically affect the efficiency of a solar cell.

The passivation stability of oxide-passivated n-type silicon and phosphorus-diffused silicon is measured, to

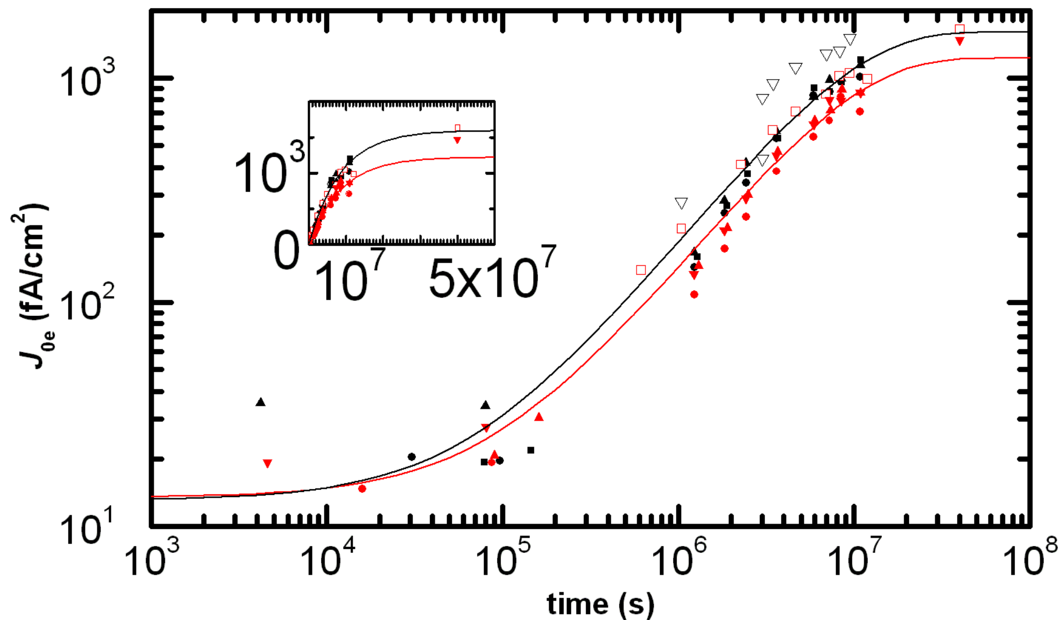

Figure 2: Emitter saturation current J_{0e} as a function of time for eight boron-diffused samples stored in air at room temperature. The red data represents samples fabricated on 5 and the black on 1000 cm n-type silicon, and samples that received a FGA are represented by filled markers, the samples that did not are represented by open markers. The lines are least squares fits of to the data of FGAed samples for each wafer resistivity.

further understand the cause of the boron-diffused silicon degradation reaction. Where we find that oxide-passivated n-type silicon degrades moderately, and phosphorus-diffused silicon, may degrade slightly, however any measured change in J_{0e} is within error limits of the measurement. These results combined with semiconductor modelling in PC-1D has show that it is likely this degradation is caused by the formation of a defect with highly uneven capture-cross section ratios. The mechanism for the formation is discussed, where we tentatively suggest the defect is created by room temperature oxidisation of the Si-SiO_2 interface.

This paper is set out as follows: firstly our experimental process is detailed, where wafer processing and PCD measurements are described; the degradation results are then presented; our results are discussed and summarised, and degradation of surfaces is modelled by altering S_N and S_P.

2. METHODOLOGY

All test structures for the following characterisations were fabricated on n-type, FZ, <1,0,0> silicon. To remove saw damage and prepare each wafer for high temperature furnace steps, each wafer was saw damage etched in HF:HNO_3 (1:10) solution for three minutes and RCA cleaned [23]. After RCA cleaning, all wafers were HF:H_2O deglazed in 1:10 solution until hydrophobic.

To passivate, wafers were either lightly diffused with BBr_3, $POCl_3$ or left undiffused and oxidised. Boron-diffusions were performed at 850 °C for 20 min with a 20 min drive-in followed by a 30 min 900 °C oxidation to allow for BSG deglazing. Phosphorus diffusions were performed at 760 °C for 20 min with a 10 min drive-in. All wafers were HF deglazed post-diffusion, and were dry-oxidised at 1100 °C for 6 min, followed by a 30 min N_2 anneals at the same temperature. Resulting in 200 Ω/sq diffusions post-oxidation. To improve passivation of the Si-SiO_2 interface, some samples received a forming-gas anneal (FGA) at 400 °C for 30 min; the forming gas was comprised of 95 % Ar and 5 % H_2, note this process is only a FGA not “alneal” which is considered to give unstable passivation.

Lifetime measurements were performed over 3-4 montsh, to quantify the increasing recombination. See reference [20] for details on boron-diffused PCD measurements.

3. RESULTS

Figure 2 plots the J_{0e} of boron diffusions stored at room temperature as a function of time. The J_{0e} of each sample increased from 30–80 to 1000–1400 fA/cm^2, saturating after 1.0×10^7 s or 120 days. The degradation was similar, irrespective of whether the samples received an FGA. The degradation of the samples stored at 25 °C followed a first-order exponential.

Surface recombination versus time results for passivated-silicon and phosphorus diffused silicon is plotted in Figure 3. Where the left graph plots the maximum SRV for un-diffused 5 Ω·cm n-type silicon, and the right graph plots the J_{0e} of phosphorus diffused 5 and 1000 Ω·cm silicon, both stored at room temperature measured over 200 days. There is a moderate first-order degradation of the of oxide-passivated silicon the SRV is seen to double, this has occurred irrespective of whether the samples receive an FGA. Phosphorus diffused samples show almost no degradation; when linear fits are performed we find there is a small increasing gradient of J_{0e} however the changes are within the uncertainty limits of the

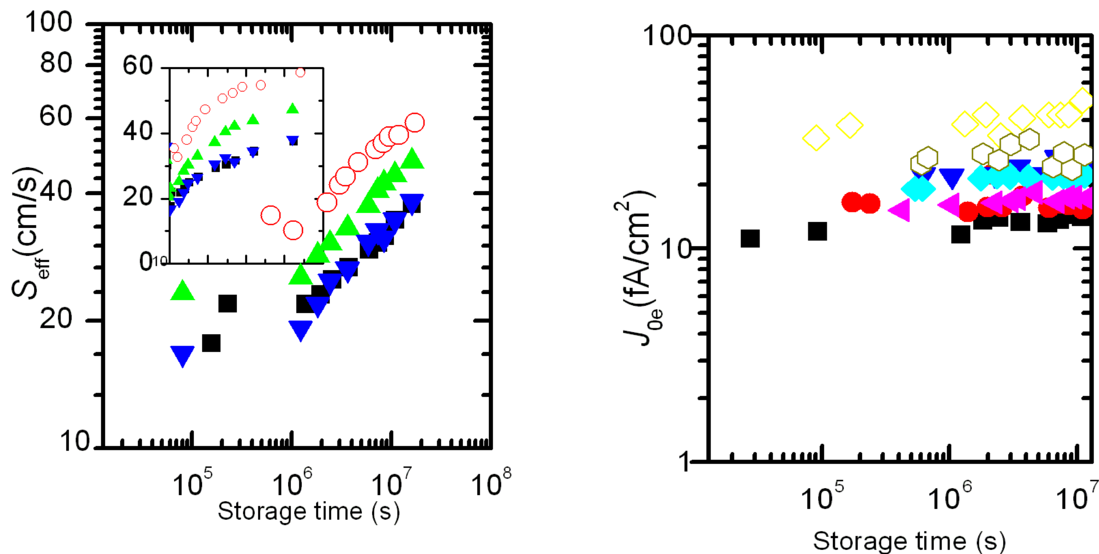

Figure 3: (Left) S_{eff} for un-diffused 5 Ω·cm, (right) J_{0e} of phosphorus-diffused oxide passivated silicon versus storage time at room temperature. In both plots filled markers represent samples that received an FGA and open markers represent samples that did not.

measurement.

4. DISCUSSION

We find that oxide passivation degrades at room temperature, slowly over a number of months. This degradation is pronounced for boron-diffused surfaces, and is hardly observable for phosphorus diffused surfaces. These results are consistent with the degradations observed by Zhao *et al.* and Altermatt *et al.*. We propose two potential modes of degradation: either the Si-SiO_2 interface is degrading and the defect created has a much larger cross-capture section area for electrons, or the degradation is linked specifically to the boron close to the surfaces. The first mode will be modelled to determine if it fits our results; the latter could be true if there is boron contamination of the oxide-passivated silicon interface, this has been observed by Widdershoven *et al.* when using the same clean and surface preparation processes [24], a potential degradation mode, we do not investigate it further here.

To determine if the first degradation mode would show similar changes in recombination for the three types of oxidised surfaces, the affect of changing the surface-recombination velocity of electrons and holes, S_N and S_P on J_{0e} was modelled in PC-1D for boron and phosphorus diffused surfaces. Figure 4 plots modelled J_{0e} versus diffusion resistivity for increasing S_N, to highlight the observability of the degradation for different resistivity diffusions. PC-1D was used to model the changing conductivity of silicon structures, and from this the J_{0e} was calculated [5]. Modelled Gaussian diffusions profiles were used, that returned similar boron diffusions created in our labs, here the diffusion depth parameter was set to 0.25 and the surface concentration was adjusted.

We find for boron-diffused surfaces, that J_{0e} increases with S_N but it remains virtually unaltered for phosphorus-diffused surfaces. Increasing S_N and keeping S_P constant is effectively increasing the density-of-interface states D_{it} at the Si-SiO_2 interface, where the defect created has a much larger capture-cross section areas for electrons. High capture-cross section ratios, greater than 100 are know to exist at the oxide interface [25], and silicon-SiN_X interfaces [26]. When increasing S_N to 1×10^5 cm/s we find similar changes in J_{0e} as that measured by the above experiment for boron and phosphorus diffused surfaces.

To ascertain how similar changes S_N would affect the SRV of an un-diffused surface, the same modelling process was performed for 5 Ω·cm n-type silicon. The results of this are plotted in Figure 5 where, S_{eff} is plotted versus excess carrier concentration Δn, to identify the injection dependence of the surface recombination. If S_P is kept constant and S_N is increased from 10 to 1×10^5 cm/s increases in, S_{eff} at $\Delta n = 1 \times 10^{15}$ to that of the measured results (see Figure 3) are modelled. This modelling indicates that the first degradation mode is a likely caused of the degradation.

We do not know the mechanisms causing this defect to form at room temperature; however we can identify a number of possible culprits. Initially it was assumed that this reaction was a form of humidity degradation, similar to the degradations observed by Bellet *et al.*, Johnson *et al.* and Klamphas *et al.* [15, 18-19], but we have found that boron-diffused and un-diffused oxide-passivated samples degrade in zero humidity ovens [20]. We have found some evidence that the atmospheric storage gas

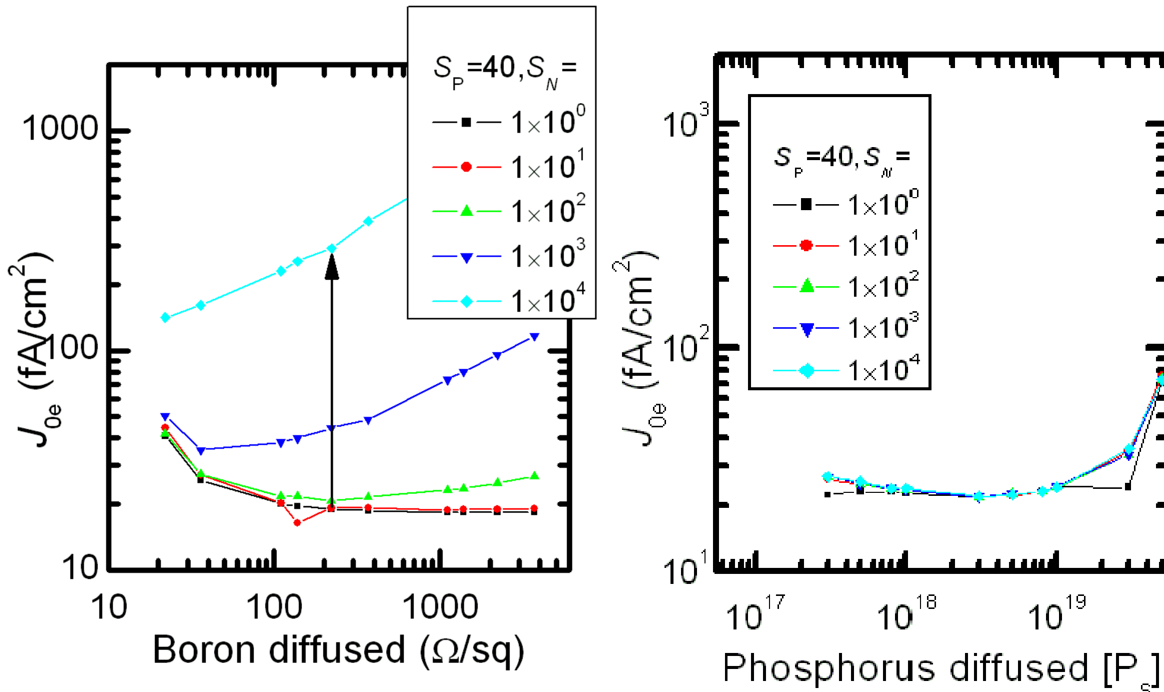

Figure 4: Modelled J_{0e} versus diffusions resistivity concentration using PC-1D for fixed S_P and increasing S_N, where the diffusions had a depth factor of 0.25 m, the left graph was boron diffused and the right graph was phosphorus diffused.

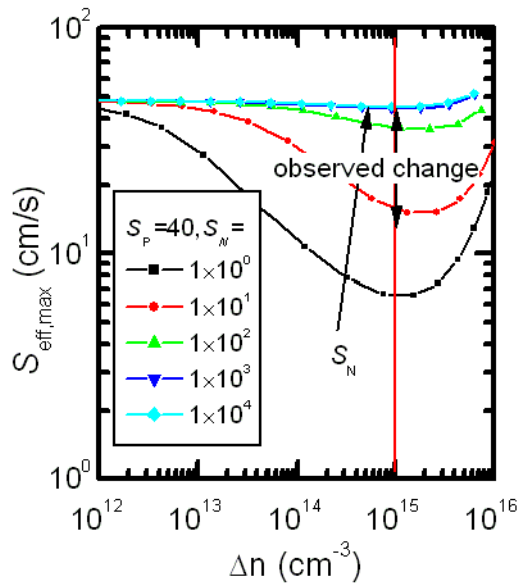

Figure 5: S_{eff} plotted versus Δn for a 5 Ω·cm un-diffused sample, where S_{eff} is plotted for increasing S_N and a fixed S_P of 40.

does alter the degradation, storage in nitrogen cabinets retards the degradation, this was noted by Zhao *et al.* to be the case [21], and since coating with PECVD SiN_x also seems to stop or retard this degradation, we tentatively suggest that diffusion of oxygen into the Si-SiO_2 interface forming defects with this very low activation energy, slowly returning the interface to its un-annealed state.

5. CONCLUSIONS

It appears that the first mode of degradation, that a defect is being created at all silicon-oxide interfaces at room temperature that had a cross-capture section area with a much larger capture-cross section for electrons, fits well with our results. We believe this is the most likely mode, however we do not discount the second; that the degradation is caused by the presence of boron. To determine if this is the case we are performing ion beam measurements to these samples, to ascertain if boron contamination is occurring, and if we can model the degradation reaction.

From our investigations of thermal-oxide passivated silicon the Si-SiO_2 interface on boron-diffused and un-diffused surfaces degrades slowly over three months at room temperature. The defect that is formed has a highly uneven cross-capture section ratio, and hence has a much larger recombining effect on boron-diffused surfaces. Defect formation appears to be enhanced or caused by the presence of oxygen in the ambient, hence proper encapsulation, or coating with impermeable layers may prevent this. If this is not the case, and no method for prevention of this degradation are ascertained then oxide-passivation is not suitable for used in high-efficiency solar cells on diffused p-type or undiffused surfaces.

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