Examining Surface-Related Degradation - An Emerging Issue for Commercial Silicon Solar Cells

Daniel Chen*, Chandany Sen*, Anastasia Soeriyadi, Moonyong Kim, Malcolm Abbott, Bram Hoex, Brett Hallam, and Phillip Hamer

[1] *School of Photovoltaic and Renewable Energy Engineering, University of New South Wales, Kensington, Australia*
*These authors contributed equally

Introduction

The stability of existing and emerging solar cell architectures under illumination has historically been an area of significant research – drawing upon the interests of manufacturers, researchers, and end-users alike. In the last decade, silicon solar cells have been plagued by various bulk electronic instabilities, including the boron-oxygen related light-induced degradation (BO-LID) in p-type Czochralski-grown silicon (Cz-Si) and light- and elevated temperature-induced degradation (LeTID) affecting all silicon materials [1]. More recently, long-term stability studies on industrial passivated-emitter and rear cell (PERC) solar cells have unveiled a form of surface-related degradation (SRD) known to cause up to a $50\%_{rel}$ reduction in energy conversion efficiency [2]. There have been some studies identifying the properties of SRD in silicon by Sperber *et al.* [3–5] and Chen *et al.* [6], leading to conclusions that hydrogen may play a role; either through migration towards and accumulating at the surface where it can form hydrogen-induced defects, or away from the interface leading to a reduction in interfacial chemical defect passivation. More importantly, Sperber *et al.* demonstrated that diffused surfaces with sufficiently heavy doping concentrations can help to attenuate SRD [5]. Industrial solar cells, however, have slowly shifted towards lightly doped emitters (LDE) to reduce emitter saturation current density (J_{0e}). Solar cells incorporating a homogenous phosphorus-diffused emitters commonly have sheet resistances, R_{SH} > 110 Ω/sq with expected increases up to 140 Ω/sq within the coming decade. Alternatively, solar cell architectures employing selective emitters are expected to increase from 130 Ω/sq to 180 Ω/sq for the unmetallised regions, leaving solar cells more susceptible to SRD [7]. In this work, we investigate the impact of various emitter diffusion profiles and thermal oxidation on the characteristics of SRD, demonstrating that a combination of lightly diffused layers and thermal oxides results in a significant worsening of SRD.

Experimental Methodology

For this study, symmetrical lifetime structures were fabricated on commercially available 6-inch, 1.9 Ω·cm boron-doped, p-type multicrystalline silicon (mc-Si) wafers.

Figure 1. Simplified process flow diagram for the fabrication of test structures

Wafers were chemically cleaned using an Radio Corporation of America (RCA) cleaning procedure prior emitter diffusion. The formation of n-doped emitters was done using a phosphoryl chloride ($POCl_3$) source in a quartz tube furnace. Several emitter concentrations were targeted, resulting in a range of sheet resistivities between 78 Ω/sq and >500 Ω/sq measured prior to thermal oxidation

(see Figure 1). Phosphosilicate glass (PSG) was removed using dilute hydrofluoric acid. After this, a 10-nm-thick silicon oxide was grown on half the wafers in each diffusion group using thermal oxidation at 980 °C for 10 min. Surface passivation was achieved through a deposition of 75-nm-thick hydrogenated silicon nitride (SiN_x:H) films on both sides of each wafer using plasma enhanced chemical vapour deposition (PECVD, Meyer Burger, MaiA). All wafers were then fired at a peak actual temperature of 786 °C using a conventional metallization firing furnace (Meyer Burger, Camini) to introduce hydrogen into the wafer bulk, both for the purpose of inducing degradation and defect passivation. All wafers were then laser cleaved into 52 mm by 52 mm tokens and sorted into adjacent "sistering" sets with similar electrical characteristics. Carrier-induced degradation of both groups was carried out at 130 °C under 1 kW/m^2 illumination by a halogen lamp. An accelerated test at a higher temperature of 175 °C both under illumination and in the dark was additionally carried out on thermal oxide passivated samples. The performance of all samples was monitored periodically using quasi-steady-state photoconductance (QSSPC, Sinton WCT-120).

Results and Discussion

The changes in effective minority carrier lifetime (τ_{eff}) as a function of illuminated annealing time at 130 °C for samples with and without oxidation are depicted in Figure 2. All samples exhibit an initial distinct degradation followed by a recovery phase which is again succeeded by a secondary deterioration. The injection-dependent lifetime plots depicted in Figure 3 indicate that the initial degradation was associated with a bulk defect, identified to be LeTID with a capture-cross-section ratio (k) of 37.3, consistent with those reported within the literature [8]. This would be expected for mc-Si materials coated in a hydrogen-containing dielectric film during firing, irrespective of the presence of SiO_2 passivation [9]. The secondary decline can be seen as a decrease in the carrier lifetime at high injection, which we also observe as an increase in J_{0e} (not shown), usually associated with surface degradation. On non-oxidized samples [Figure 2(a)], the surface appears to be stable at low R_{SH} (78 Ω/s). Although SRD becomes apparent at R_{SH} > 230 Ω/sq, the lifetime appears to stabilize and recover beyond 10^5 min. On samples with thermal oxide layer [Figure 2(b)], the severity of SRD is significantly increased with up to 90%$_{rel}$ degradation in lifetime on samples with a R_{SH} >500 Ω/sq [Figure 3(c)] whereas those with R_{SH} ≤ 110 Ω/sq [Figure 3(a)] remain stable, in agreement with the conclusions of Sperber *et al.* [5].

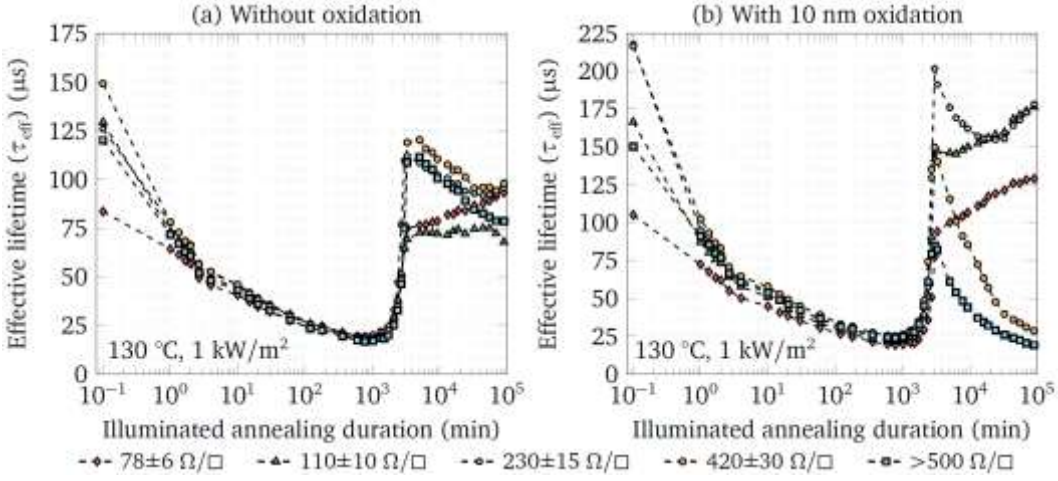

Figure 2. Change in τ_{eff} as a function of illuminated annealing duration at 130 °C and ~1 kW/m^2 for diffused samples (a) with and (b) without oxidation. τ_{eff} is extracted at $\Delta n = 1\times10^{15}$ /cm^3. The legend refers to R_{SH} measured prior to oxidation.

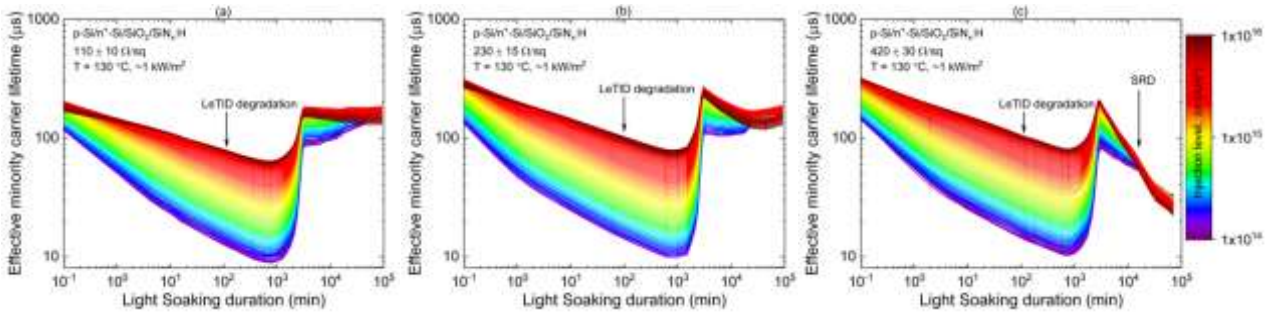

Figure 3. Injection-dependent τ_{eff} as a function of illuminated annealing duration for samples with thermal oxidation and emitter resistivity of (a) 110 Ω/sq, (b) 230 Ω/sq and (c) 420 Ω/sq.

To further understand whether the extensive degradation experienced by samples with lightly doped emitters and thermal oxide is also reversible, an accelerated testing condition of 175 °C was used. Under illumination [Figure 4(a)], the onset of SRD occurred within 100 min for the lightest emitter without signs of recovery beyond 10^5 min. The J_{0e} on the worst impacted sample is observed to increase from 32 fA/cm^2 to beyond 230 fA/cm^2, confirming the deteoriation of the surface. All samples, aside from the heavily diffused (78 Ω/sq) experience severe long-duration degradation. Alternatively, in the dark [Figure 4(b)], degradation occurs rapidly for emitters with R_{SH} > 420 Ω/sq, with all other samples experiencing a decline in τ_{eff} after 10^5 min.

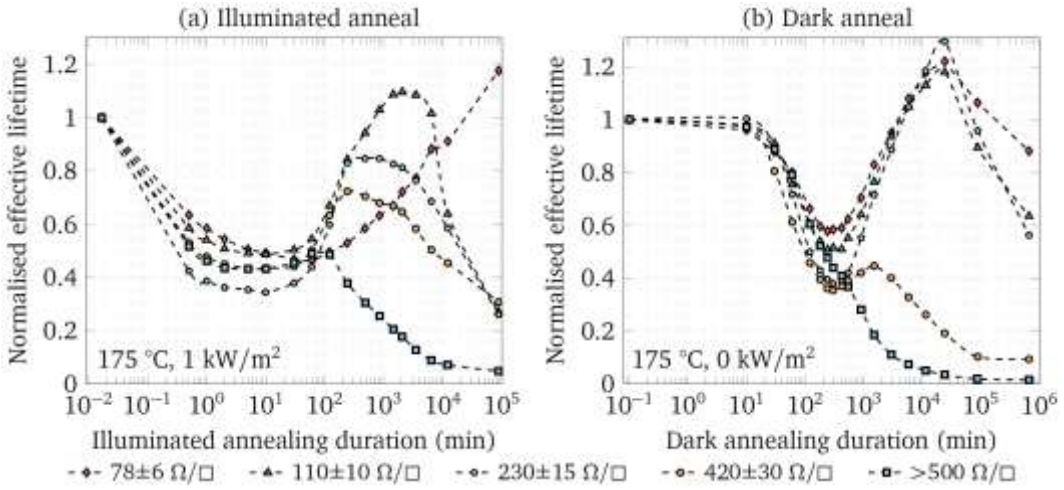

Figure 4. Change in normlised τ_{eff} as a function of (a) illuminated annealing duration at 175 °C and ~1 kW/m^2 and (b) dark annealing 175 °C. τ_{eff} was extracted at an injection level of $\Delta n=1\times10^{15}$ /cm^3 and normalised to the initial carrier lifetime obtained after firing.

Conclusion, Implications and Further Work

The results in this work demonstrates the impact of lightly doped emitters and thermal oxide layers on the formation of SRD in silicon. We highlight that lightly doped emitters (>110 Ω/sq) and thermal oxide layers can increase the susceptibility of p-type silicon wafers to performance-limiting long-term degradation mechanisms. These results have significant implications on commercial PERC solar cell technologies which are transitioning towards lightly doped emitters and commonly incorporate thermal oxides for surface passivation, bringing into question the long-term stability of these emerging products. Further investigation of the degradation kinetics both at lower temperatures and carrier injections will be carried out to represent and predict degradation under field conditions. To investigate the link between hydrogen and the formation of SRD, extended hydrogen charge state modelling incorporating measured diffusion profiles will be presented at the time of the conference.

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