

LETID IN P-TYPE AND N-TYPE MONO-LIKE AND FLOAT-ZONE SILICON, AND THEIR DEPENDENCE ON SiN_x FILM PROPERTIES

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ABSTRACT: We compare light-and-elevated-temperature-induced-degradation (LeTID) activities in both p- and n-type lifetime samples made from mono-like silicon (ML-Si) and float-zone silicon (FZ-Si) materials, and investigate their dependence on SiN_x film properties. All four materials show degradation behaviour upon illumination at elevated temperature. We observe a smaller, but still noticeable lifetime degradation in the studied n-type ML-Si and FZ-Si samples when comparing with the p-type samples. A similar capture cross section ratio of 20 ± 7 is determined from injection dependent lifetime spectroscopy (IDLS) for the p-type ML-Si and FZ-Si samples, assuming a mid-gap defect. The studied n-type samples, on the other hand, show significantly less injection dependent lifetime behaviours. Moreover, it is found that LeTID phenomena is strongly related to the SiN_x film properties. Samples coated with SiN_x films deposited at higher temperature suffer more severe lifetime degradation, despite containing less amount of hydrogen in the films.

Keywords: degradation, mono-like silicon, Float-Zone silicon, silicon nitride

1 INTRODUCTION

Light and elevated temperature induced degradation (LeTID) leads to significant performance loss in solar cells and modules [1]. While there are many reports of LeTID in p-type silicon materials, there are inconsistent reports on whether n-type silicon materials are stable under illumination at elevated temperature [2, 3]. In this work, we compare degradation activities in p- and n-type ML-Si and FZ-Si. ML-Si contains similar amount of metal impurities compared to multicrystalline silicon (mc-Si), but features uniform lifetime distribution as monocrystalline silicon, making it a suitable candidate for investigating the origins of LeTID. On the other hand, FZ-Si wafers, in principle, contain much lower defect and impurity concentrations, which allows us to investigate the role of defects and impurities in LeTID, and potentially correlate LeTID behaviours with SiN_x film properties.

2 EXPERIMENTS

ML-Si wafers used in this work were provided by Jinko Solar, and they were cut from the bottom of p-type boron doped and n-type phosphorus doped ML-Si ingots, with a resistivity of around 1.5Ω·cm for both types. Wafers from the ingot bottom were chosen as they do not contain any grain boundaries nor dislocation clusters, exhibiting a uniform lifetime distribution. In addition to ML-Si wafers, p-type and n-type FZ-Si wafers were also used in this work. After saw damage etch, p-type samples (including both ML-Si and FZ-Si) were subjected to a 40 min POCl₃ diffusion at 815°C. The gettered p-type wafers and as-grown n-type wafers were then divided into three different groups, and received PECVD SiN_x films deposited at 100°C, 300°C and 650°C respectively, while keeping other deposition parameters such as gas ratio (GR), pressure and radio frequency (RF) power constant. After SiN_x deposition, the samples were fired at 750°C in an RTA furnace and then re-passivated with fresh SiN_x before lifetime degradation measurement. The light soaking was performed at one-sun illumination condition at 140°C. The lifetime values were measured using QSSPC with an injection level of $1 \times 10^{15} \text{ cm}^{-3}$. Fourier

transform infrared spectroscopy (FTIR) was applied to the samples to measure the bonding densities in the deposited SiN_x films before and after firing.

3 RESULTS AND DISCUSSION

3.1 Dependence on material types

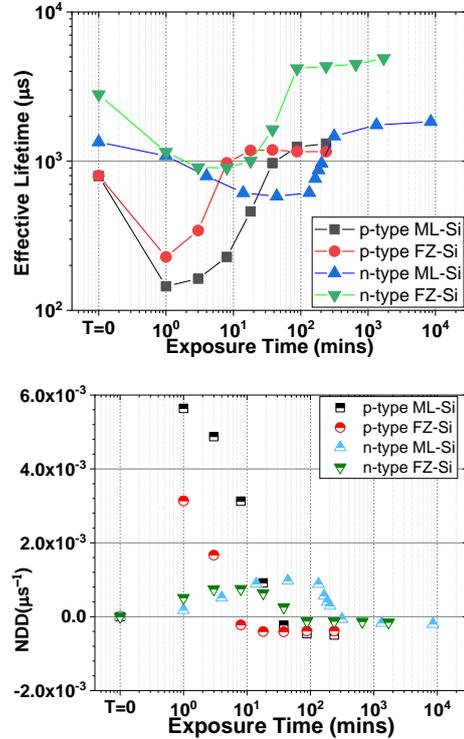


Figure 1: (a) Effective lifetime (measured by QSSPC at injection level of $1 \times 10^{15} \text{ cm}^{-3}$) and (b) NDD as a function of degradation time for p- and n-type ML-Si and FZ-Si wafers. All studied samples were deposited with a SiN_x layer under same deposition conditions.

Figure 1 (a) and (b) respectively illustrate the effective lifetime and normalised defect density (NDD) of the

studied samples as a function of illumination time at 140°C. NDD is calculated based on QSSPC measured lifetime at $1 \times 15 \text{ cm}^{-3}$, according to

$$NDD(t) = \left(\frac{1}{\tau_{eff}(t)} - \frac{1}{\tau_{eff}(t=0)} \right)$$

where $\tau_{eff}(t)$ and $\tau_{eff}(t=0)$ are the effective lifetime at different illumination times. Comparing the LeTID behaviours in p- and n-type Si materials, the degradation is considerably slower and less severe in both n-type ML-Si and FZ-Si samples. This is consistent with our previous study on p- and n-type mc-Si [4]. To the best of our knowledge, this is the first work to report potential LeTID behaviour in n-type ML-Si and FZ-Si materials. Owing to the smaller extent of the lifetime degradation, the efficiency degradation on n-type ML-Si and FZ-Si solar cells may be not as obvious as that on p-type cells. In comparison with the ML-Si samples, FZ-Si materials experience lower extent of lifetime degradation, suggesting that defects and impurities in ML-Si materials might play a role in LeTID.

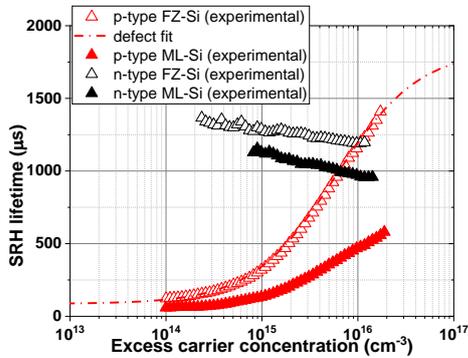


Figure 2: Fitting of measured defect lifetimes to the Shockley-Read-Hall (SRH) equation, assuming a mid-gap defect. SRH lifetime is obtained by the following equation: $\tau_{defects(\Delta)} = 1 / NDD(\Delta)$.

Figure 2 shows the injection dependent lifetime of the defects and their Shockley-Read-Hall (SRH) parameter fitting. Similar capture cross-section ratios (σ_n / σ_p) of 20 ± 7 were obtained for both p-type FZ- and ML-Si, assuming a mid-gap defect. The result is consistent with the reported value for p-type mc-Si from Bredemeier *et al.* [5]. It may imply that the LeTID activities in p-type FZ-Si, ML-Si, and mc-Si materials can be originated from the same defect. On the other hand, both n-type FZ- and ML-Si materials show relatively small injection dependence of lifetimes at low injection, which is consistent for a defect with capture cross-section ratio much larger than 1.

3.2 Dependence on SiN_x

Figure 3 shows that samples (p-type ML-Si) fired with different SiN_x films feature drastically different lifetime degradation behaviours, consistent with the work by Vargas *et al.* [6, 7]. SiN_x-I was deposited in an industrial production line, whereas SiN_x-II and SiN_x-IV were deposited using an AK400 and an Oxford instrument PECVD system at ANU. It can be seen that samples coated with SiN_x-II and SiN_x-IV show less lifetime degradation when compared to the samples coated with SiN_x-I. SiN_x-III films were deposited using an Oxford Instrument PECVD system at ANU, but with a similar deposition condition as SiN_x-I. We observe a similar extent of lifetime degradation in samples coated with

SiN_x-I and SiN_x-III. The distinct behaviours in the studied samples imply that the lifetime degradation and recovery is strongly sensitive to the SiN_x film properties. Therefore, we performed a study to investigate the correlation between LeTID activities and SiN_x film properties. The dependence of LeTID phenomena on SiN_x also implies that optimising SiN_x deposition conditions may potentially mitigate LeTID.

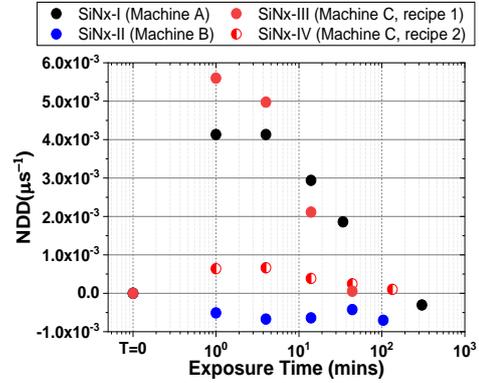


Figure 3: NDD as a function of degradation time for p-type ML-Si wafers, and each wafer was deposited with a different SiN_x film. SiN_x-I illustrates the LeTID behaviour in a p-type ML-Si wafer with industrially deposited SiN_x film, and the samples SiN_x-II, III and IV were deposited with laboratory tools at ANU.

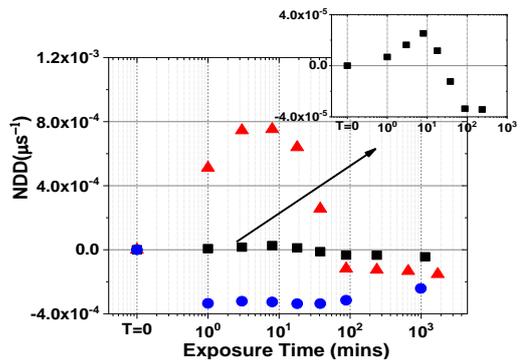
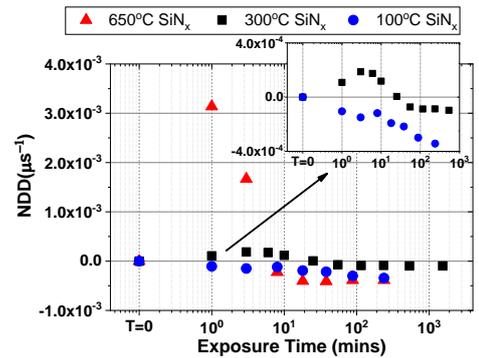


Figure 4: NDD as a function of degradation time for p-type (a), and n-type FZ-Si (b) samples. The SiN_x depositions were performed at 100°C, 300°C and 650°C temperatures, respectively. The other deposition parameters were set as 650mT (pressure), 30W (RF power) and 1:1.1 (NH₃:SiH₄ Gas ratio). Note that the scale of the two diagrams are different.

Figure 5 shows FTIR characterisation results for the three studied SiN_x films before firing, and also the change in the bonding densities after firing. We observe that the

SiN_x film deposited at a lower temperature contains a higher density of H bond (defined as [H] = [Si-H] + [N-H]). This agrees with the research by Fouad *et al.* [8] who reported that, using an Oxford Instrument PECVD system, the fraction of hydrogen in SiN_x layer increases as the deposition temperature drops. The maximum NDD, however, does not increase with the bond density of H in the SiN_x film, suggesting that the extent of degradation is not necessarily dependent on the hydrogen content in the SiN_x film. The change of hydrogen content ($[H]_{\text{change}} = ([H]_{\text{dep}} - [H]_{\text{fired}}) / [H]_{\text{dep}} \times 100\%$) defined by Vargas *et al.* [6], was also calculated for the studied samples in this work. We observe a negative correlation between the maximum NDD and the change of hydrogen fraction in the films.

As suggested by various works [3, 5-7], hydrogen can be the root cause for LeTID behaviours. Our results here show that SiN_x deposited at high temperature contains less hydrogen in the films, but yields larger degradation. It is suggested that SiN_x films deposited at high temperature [9, 10] feature higher mass density and thermal stability, allowing more hydrogen to be injected into the Si bulk during firing rather than out-diffusing into the ambient, comparing to SiN_x films deposited at low temperature where most hydrogen content in the films is lost during firing. The extent of degradation may not be directly related to the hydrogen concentration in the SiN_x films, but rather depends more on the amount of hydrogen injected into the Si bulk during the thermal treatment. The high amount of hydrogen diffused into the bulk may be the origin of the lifetime degradation associated with LeTID. Overall, we observe a positive correlation between the deposition temperature and the maximum NDD value. This could suggest that the degradation effect associated with LeTID can be alleviated by decreasing the SiN_x deposition temperature.

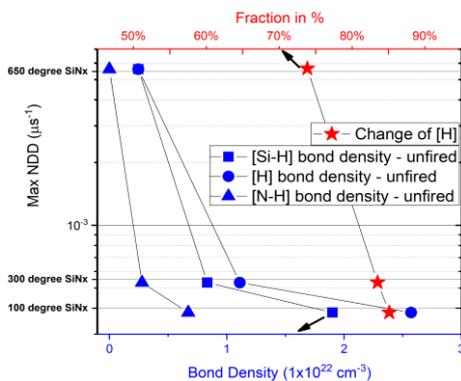


Figure 5: Correlation between degradation magnitude (maximum NDD) and FTIR measured data. Total hydrogen content is defined by total $[H] = [Si-H] + [N-H]$. The measurements were taken on the as-deposited SiN_x films processed at 100°C, 300°C and 650°C. The calculated data for the change of hydrogen content defined by $[H]_{\text{change}} = ([H]_{\text{dep}} - [H]_{\text{fired}}) / [H]_{\text{dep}} \times 100\%$ in literature [3]).

4 CONCLUSIONS

We have observed LeTID phenomena on all studied materials, including p-type and n-type ML- and FZ-Si. P-type samples suffer more severe degradation than their n-type counterparts. The degradation is also more significant

on ML-Si samples than on FZ-Si samples. SRH parameter fitting of the defect lifetimes reveal similar capture cross section ratio for the p-type ML-Si and FZ-Si samples. Additionally, the degradation behaviours in both p- and n-type samples vary significantly with the deposition conditions of SiN_x, and SiN_x deposited at a higher temperature shows more severe degradation, highlighting the possibility to reduce LeTID by modifying SiN_x deposition conditions. It is found that SiN_x deposited at high temperature contains lower hydrogen concentration in the film, but yields stronger degradation behaviours. This suggests that hydrogen may be related to LeTID and degradation severity might not be dependent on hydrogen content in SiN_x but on the amount of hydrogen injected into the bulk.

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