ON THE STABILITY OF DIELECTRIC PASSIVATION LAYERS UNDER ILLUMINATION AND TEMPERATURE TREATMENT

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ABSTRACT: Different dielectric layers were deposited onto boron doped floatzone silicon wafers and the stability of the effective lifetime was investigated at elevated temperatures ranging from 75°C to 250°C with and without illumination. It was found that samples fired in a belt furnace show an instable behavior on a timescale of minutes to months. The short term behavior of a sample is strongly influenced by the peak firing temperature whereas the long term behavior appears to be less influenced by this parameter. Different chemical cleaning procedures during sample preparation show no significant influence on stability. Via corona charging, the changes at 250°C in darkness could be associated with changes in chemical passivation quality. It could be shown that a non-fired sample shows a similar, but less pronounced instability whereas an annealed sample is stable under the given treatment conditions.
Keywords: Passivation, Stability, Degradation, Silicon-Nitride, Lifetime

1 MOTIVATION

Light induced degradation (LID) mechanisms [1] such as boron-oxygen related degradation [2] or mc-PERC (passivated emitter and rear cell) degradation [3,4,5] strongly affect the minority carrier lifetime of silicon solar cells. Additionally, the effective lifetime of minority carriers τ_{eff} is strongly influenced by the quality of surface passivation. To differentiate between effects happening in the bulk and at the surface of a lifetime sample, a detailed knowledge of the behavior of passivation layers during degradation treatments is necessary. This is especially important for long term experiments, examining, *e.g.*, the long term stability of the regenerated state of boron-oxygen related defects [6]. On the other hand, a significant degradation in surface passivation quality can itself lead to a decrease in the conversion efficiency of solar cells, especially in concepts like PERC that rely heavily on the long term stability of the rear side passivation.

To investigate the stability of dielectric passivation layers, differently processed lifetime samples were investigated at elevated temperature and illumination conditions. It is important to note that the samples used in this study were processed using silicon nitride deposition recipes that are also used for typical solar cells and received a fast firing step with sample temperatures similar to those reached in solar cell processes.

2 EXPERIMENTAL

2.1 Preparation of the samples

The base material used was p-type floatzone (FZ) material with a specific resistivity of 1 Ωcm. All samples received a chemical cleaning step in a cleanroom environment followed by a dip in hydrofluoric acid (HF). Some samples also received a thin chemically grown silicon oxide (SiO_x) layer after the HF dip. All samples were then coated with hydrogenated silicon nitride (SiN_x:H). For this purpose, three different plasma enhanced chemical vapor deposition (PECVD) systems were used, one using a remote plasma (type 1) and two using a direct plasma technique (type 2 and type 3). If not stated otherwise, the samples were then fired in a fast firing belt furnace with measured peak sample temperatures reaching temperatures between 730°C and 830°C. After the firing step, the samples were stored in darkness until measurement series were carried out.

2.2 Measurement setups

The samples were treated at temperatures of 75°C, 150°C or 250°C. Some samples were simultaneously illuminated using a tungsten halogen incandescent lamp while others were kept in the dark.

For the repeated measurement of the effective lifetime during a treatment, two types of photo conductance decay (PCD) setups were available: For some samples, a Sinton lifetime tester (WCT 120) was used and the degradation treatment was shortly paused while the measurement was carried out at room temperature (RT-PCD). On other samples, PCD measurements were carried out at elevated temperature, so that only a short break in illumination occurred during measurements (ET-PCD). Because of the elevated temperature during these measurements, the absolute values of the measured τ_{eff} differ from the ones measured by RT-PCD, but the curve shape of a sample's evolution over time shows the same qualitative behavior in both measurements. All PCD measurements were evaluated at an injection level of $\Delta n = 1 \cdot 10^{15}$ cm^{-3}.

For corona charging experiments, a setup comparable to the one described in [7] was used.

3 RESULTS

3.1 What is already known

As has already been shown earlier, SiN_x:H layers can show strong changes in passivation quality at elevated temperature and illumination [8]. An example is shown in Fig. 1 where it can be seen that τ_{eff} of two differently processed samples is far from stable during a treatment at 75°C under illumination. It is interesting to note that the effective lifetime curves start at rather different values but show a similar qualitative behavior in the short term and converge in the long term behavior. It was already concluded that differences in the short term behavior are mainly caused by different peak firing temperatures.

Another important observation is that the process under investigation can be significantly sped up by increasing the temperature or illumination intensity as can be seen in Fig. 2. Using a chemical repassivation, it was also shown that the loss in τ_{eff} of the blue sample in

Fig. 2 after around 500 h is probably caused by a decrease in surface passivation quality, as would be expected because of the FZ material with high minority carrier bulk lifetime.

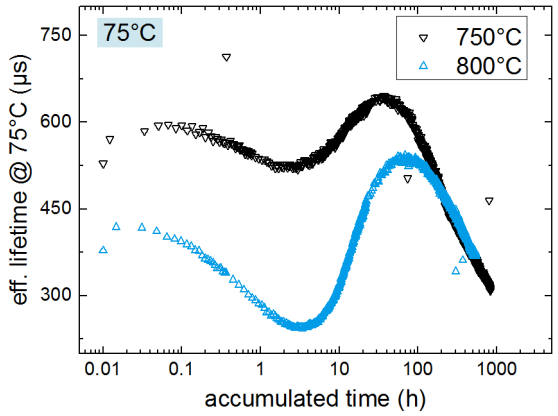

Figure 1: ET-PCD measurement of two differently processed samples coated with SiN_x:H and treated at 75°C and 0.65 suns illumination (after [8]). The peak sample temperatures during firing are given in the legend.

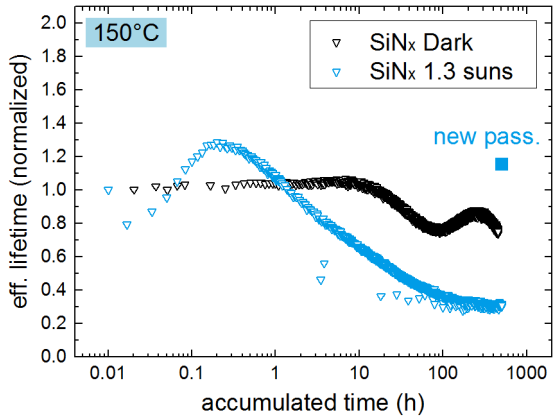

Figure 2: ET-PCD measurement of two identically processed samples coated with SiN_x:H, fired at 750°C peak sample temperature and treated at 150°C at different illumination conditions (after [8]). The blue sample was afterwards repassivated using quinhydrone (blue square).

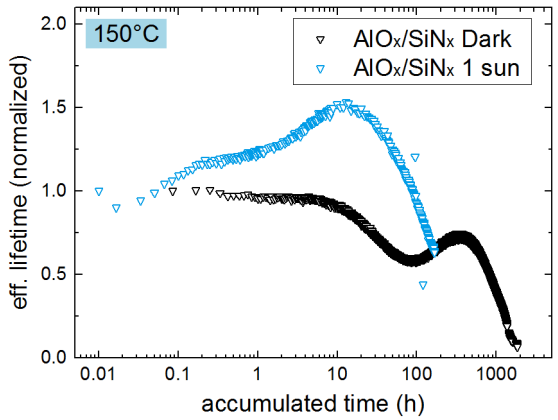

Figure 3: ET-PCD measurement of two identically processed samples coated with AlO_x:H/SiN_x:H, fired at 750°C peak sample temperature and treated at 150°C at different illumination conditions (after [8]).

Interestingly, also dielectric layer stacks consisting of a thin aluminum oxide (AlO_x:H) layer and a SiN_x:H layer show a similar characteristic curve shape as shown in Fig. 3. In darkness, the time scale of sample evolution is similar for both types of passivation. Under illumination, however, the AlO_x:H/SiN_x:H sample degrades much slower compared to the pure SiN_x:H passivated sample in Fig. 2. Still, illumination generally speeds up the process under investigation at 150°C.

This is different at 250°C where illumination only leads to a small acceleration of sample evolution compared to a treatment in darkness as can be seen in Fig. 4.

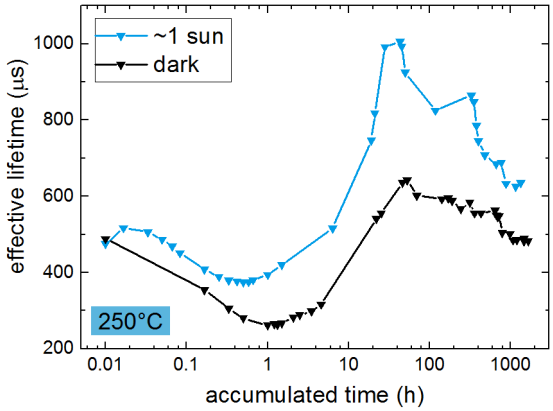

Figure 4: RT-PCD measurement of two identically processed samples coated with SiN_x:H, fired at 750°C peak sample temperature and treated at 250°C at different illumination conditions (after [8]). Lines only serve as a guide to the eye.

3.2 Combined treatment at 75°C and 150°C

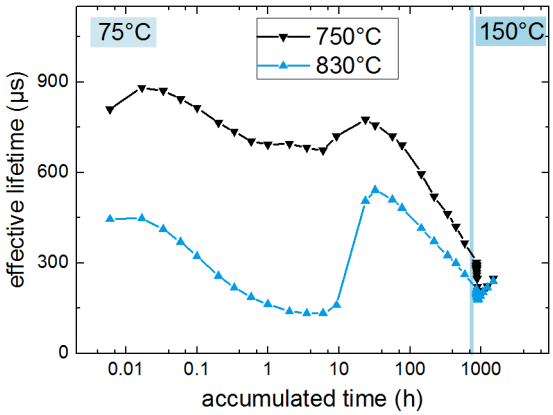

Figure 5: RT-PCD measurement of two samples first treated at 75°C and 1 sun illumination intensity (after [8] with additional new data points). Later, the temperature was increased to 150°C as indicated by the blue line. Both samples were processed identically: they first received an RCA clean and a thin chemically grown SiO_x layer before a type 2 SiN_x:H was deposited. Only the measured peak sample temperature of the firing step was varied as indicated in the legend. Lines only serve as a guide to the eye.

Using a measurement of two identically processed but differently fired samples, it was already concluded that the peak firing temperature has a strong influence on the short term behavior of a lifetime sample exposed to elevated temperature and illumination conditions [8]. But

independent of the peak firing temperature, the samples show a drastic decline in measured τ_{eff} after around 30 h of treatment time that is further investigated in this study (Fig. 5).

After around 860 h of treatment time, the temperature was increased to 150°C. The further sample evolution is again shown in more detail in Fig. 6. It seems that increasing the treatment temperature leads to a faster sample evolution as the decline in τ_{eff} gets much steeper immediately after the temperature change.

Interestingly though, the samples do not reach a saturation value but again traverse a second minimum in τ_{eff}. This gives rise to the idea that the minimum observed at 250°C after 1 h (Fig. 4) might in fact be associated with the minimum after around 900 h in Fig. 6. This assignment will be investigated more closely in a future publication. After passing this second minimum, the τ_{eff} curves converge and show a very similar behavior. This again promotes the idea that especially the first part of sample evolution is strongly influenced by the firing conditions while in the long run the peak firing temperature is of minor importance.

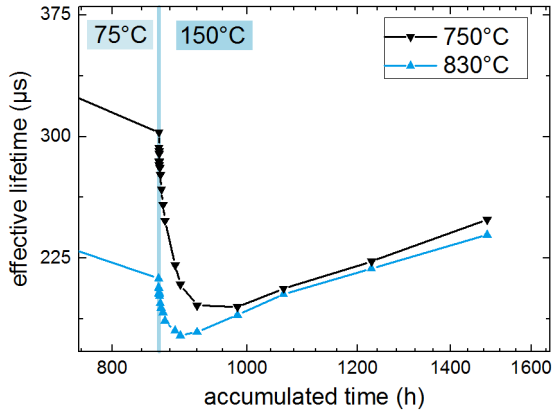

Figure 6: The right most part of the measurement shown in Fig. 2 in close up view. The blue line again indicates the switch from 75°C treatment temperature to 150°C while illumination intensity was kept constant at 1 sun. Lines only serve as a guide to the eye.

3.3 Influence of cleaning steps on stability

To investigate a possible influence of the chemical cleaning step on sample stability, three samples were processed using different cleaning steps because these might have a strong influence on the chemical passivation behavior of a sample. However, in Fig. 7 it can be seen that the qualitative curve shape at 250°C remains the same independent of the cleaning type used.

The Piranha cleaned sample (black) was also investigated with the corona charging technique and it could already be shown that also the chemical passivation quality shows a minimum after around 1 h of treatment [8]. For a further comparison of the different cleaning types, also the HCl+HF cleaned sample was investigated by corona charging and the result is shown in Fig. 8. Like the Piranha cleaned sample, also the HCl+HF cleaned sample shows a clear minimum in chemical passivation quality during the degradation treatment as indicated by τ_{eff} after corona charging of the surface. It can also be seen that the chemical passivation quality still increases after long treatment times while the overall τ_{eff} drops, suggesting a loss in charge of the silicon nitride layer.

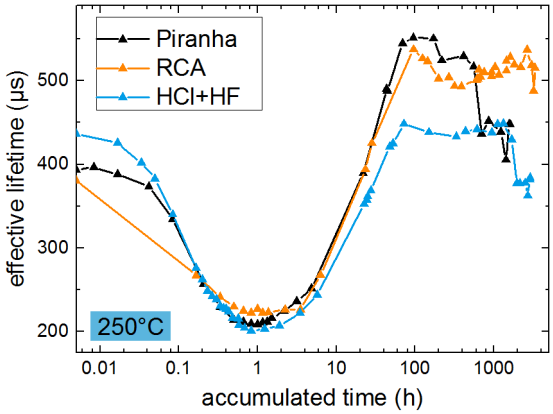

Figure 7: RT-PCD measurements of three samples at 250°C in darkness (black data after [8]). The samples received different chemical cleaning steps as given in the legend. All samples received a type 2 SiN_x:H deposition after the cleaning step and were fired at 800°C peak sample temperature. Lines only serve as a guide to the eye.

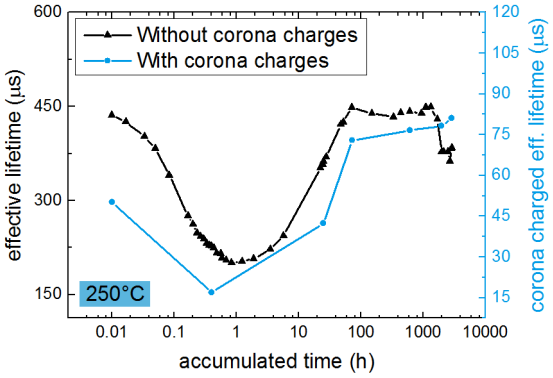

Figure 8: RT-PCD measurements of the HCl+HF cleaned sample of Fig. 4 before and after corona charging during a treatment at 250°C in darkness. For each corona charging measurement point, corona charges were deposited on the sample surface in small consecutive charging steps until a minimum in τ_{eff} was reached, which corresponds to a compensation of the field effect passivation mechanism. Therefore, the τ_{eff} values after charging (blue) correspond to the chemical passivation quality.

3.4 Influence of different high temperature steps

As it was found out that the firing step exerts a strong influence on the sample stability, some samples were identically processed and only the high temperature step after the SiN_x:H deposition was varied. Of the samples shown in Fig. 9, one did not receive a high temperature step at all, while another one was fired at 730°C peak sample temperature. A third sample was instead annealed at 420°C for 30 min in a nitrogen atmosphere.

As can be seen, the annealed sample shows a very stable behavior compared to all samples previously seen. This does not change when the temperature is increased to 150°C. The fired sample on the other hand shows a very instable behavior starting with a strong increase in effective lifetime already after 1 min of treatment time. This is probably related to the light induced curing (LIC) effect already observed in [9]. Afterwards, the sample shows only a very weak first minimum, probably because of the rather low firing temperature. The decrease in τ_{eff} after around

100 h of treatment is very pronounced and gets accelerated when the temperature is increased to 150°C.

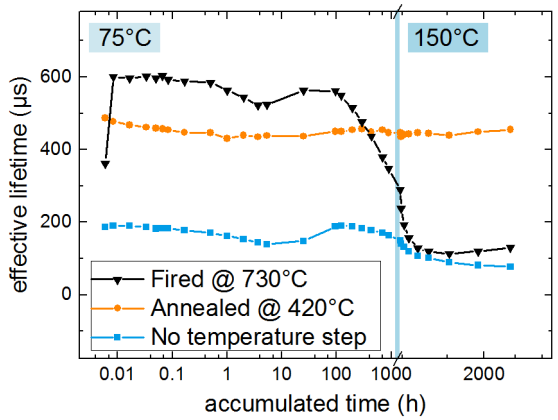

Figure 9: RT-PCD measurements of three samples treated at 75°C and 150°C with illumination between 0.6 and 1 suns. The samples differed in high temperature steps and were otherwise identically processed. After an RCA clean they received a thin chemical oxide before deposition of a type 3 SiN_x:H.

Interestingly, the sample without high temperature step (besides the PECVD step) also shows a similar qualitative curve shape as the fired sample but in a much less pronounced way. Still, it is remarkable that also a non-fired sample expresses some degree of instability under the given treatment conditions. Since it could be shown that the peak firing temperature mainly has an influence on the short term behavior but a fired sample shows a different long term behavior compared to a non-fired sample, it is assumed that other parameters of the firing process besides peak temperature influence the stability of the investigated dielectric layers.

4 SUMMARY

In summary, it could be shown that fired lifetime samples show strong instabilities in τ_{eff} when subjected to elevated temperature and illumination treatments. Because of the used FZ material and differences in the behavior of different passivation layers, it is assumed that these changes are caused by changes in dielectric passivation quality.

More evidence was found for the hypothesis that the peak firing temperature has a strong influence on the short term behavior of a sample whereas in the long run, the peak firing temperature is of less importance. Nevertheless, the firing step itself amplifies the instable long term behavior as could be seen in a comparison of a fired and a non-fired sample. It is therefore assumed that other details of the firing profile besides peak temperature may have an influence on the long term behavior. Finally, a non-fired but tempered sample shows a very stable behavior at elevated temperature and illumination.

Because the observed changes in passivation quality can be strongly pronounced, it is definitely advised to check for these effects when performing degradation experiments targeted on effects happening in the silicon bulk.

ACKNOWLEDGEMENTS

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