INFLUENCE OF SHORT HIGH TEMPERATURE STEPS
ON THE REGENERATION OF BORON-OXYGEN RELATED DEFECTS

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ABSTRACT: Boron-oxygen related recombination active defects typically limit solar cell efficiency in boron-doped solar cells made from Czochralski grown silicon due to their detrimental effect on minority carrier lifetime. Lifetime can be recovered by applying a regeneration procedure. The kinetics of this recovery process has been found to depend considerably on the amount of hydrogen in the silicon bulk. Therefore, the influence of short high temperature steps, which may affect the hydrogen bulk content, on the regeneration process is investigated. We found that increasing peak temperature and increasing holding time at high temperatures results in a considerable acceleration of the regeneration process. This could be correlated with the amount of hydrogen released from an SiN_x:H layer at high temperatures supporting the theory that the regeneration of boron-oxygen related defects might in fact be a form of hydrogen defect passivation.
Keywords: silicon, boron-oxygen, hydrogen, defects, regeneration

1 MOTIVATION

Silicon solar cells made from high quality Czochralski grown silicon (Cz-Si) instead of cheaper multicrystalline materials have the advantage of a higher efficiency potential and also reduce module installation costs. However, the Czochralski process introduces high amounts of oxygen into the material and thus boron-doped Cz-Si suffers from recombination active boron-oxygen (BO) related defects. They limit minority carrier lifetime and consequently cell efficiency of solar cells made from this material [1,2,3]. Hence exploitation of the full efficiency potential requires avoiding or suppressing their deteriorative effect. These BO-defects are metastable and become recombination active under carrier injection, which is called BO-related degradation. BO-defects can be rendered inactive through thermal treatment (~200°C) but the resulting defect state is instable leading to renewed degradation under carrier injection. In 2006, Herguth et al. [4,5] presented a way to transform BO-defects into a stable and recombination inactive state by applying a combination of slightly elevated temperatures (typically in the range of 100-200°C) and carrier injection (by illumination or forward biasing of a solar cell). This so called regeneration procedure results in a recovery of the minority carrier lifetime.

It has been found that the kinetics of this regeneration process is negatively affected by different kinds of impurities like boron [6], interstitial oxygen [7], thermal donors [6] or metal impurities [8]. By contrast, the hydrogen content of the silicon bulk has been found to be crucial for successful regeneration [9,10,11,12]. As hydrogen found in silicon solar cells normally originates from hydrogenated passivation layers [13] the release conditions of hydrogen from those layers might play an important role in the kinetics of regeneration and in consequence for the industal applicability of the regeneration process to solar cells.

In this paper we will focus on lifetime samples coated with hydrogen rich amorphous silicon nitride (SiN_x:H) and evaluate the influence of peak sample temperature and the total firing time on the kinetics of the regeneration process. This is correlated with the amount of hydrogen a SiN_x:H layer releases during the firing process.

2 EXPERIMENTAL DETAILS

Cz-grown silicon wafers (boron doped, $2\,\Omega$cm, thickness 200 µm) were saw damage etched in hot NaOH and cleaned in HCl and HF, before receiving a $POCl_3$ gettering step at high temperatures (~840°C). Thereafter phosphorous glass and diffused layer were removed in diluted HF and in a chemical polishing solution, respectively. The samples were then RCA cleaned before being surface passivated on both sides by SiN_x:H layers (~ 75 nm) deposited using a Centrotherm direct plasma PECVD (Plasma Enhanced Chemical Vapor Deposition). The final short high temperature firing step was realized in an industrial belt furnace with IR heating and sample temperature was measured using thermocouples. The peak sample temperature was varied between ~650°C and ~850°C. A reference sample did not receive any firing step. A selection of used temperature/time profiles can be found in Fig. 1 for variable peak temperatures. For comparison, some samples were fired in a Rapid Thermal Processing (RTP) furnace instead (Solaris 150 from Surface Science Integration (SSI)) in order to allow an independent control of the duration at peak temperature while keeping heating/cooling rates constant. Details are given in Fig. 8.
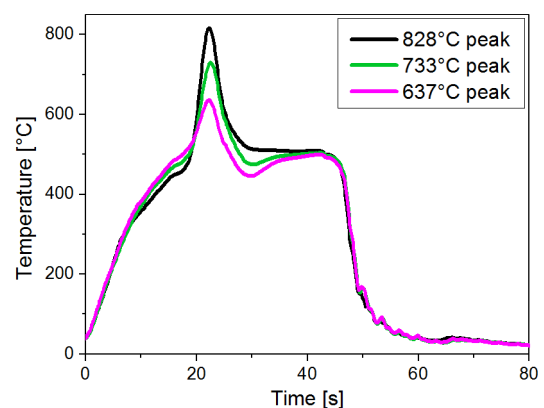

Figure 1: Selection of used temperature/time profiles for different peak sample temperatures.

A Bruker Optics Vertex 80 Fourier-Transformed InfraRed (FTIR) spectrometer was used to monitor changes in the hydrogen content of the SiN$_x$:H layers. Layer thickness was determined by ellipsometry measurements using a VASE system from J.A. Woollam.

The whole regeneration procedure consisted of five different steps shown in Fig. 2. All samples were first annealed at 200°C in the dark for 10 min, then completely degraded at 40°C, 0.1 suns and finally regenerated until saturation at 130 ± 2°C and 0.6 ± 0.1 suns. Minority charge carrier lifetime was measured at 30°C at constant injection level of 0.1 N$_A$ (doping concentration N$_A$) in each state and every few minutes during the regeneration process using a Sinton Instruments WCT-120 lifetime tester.
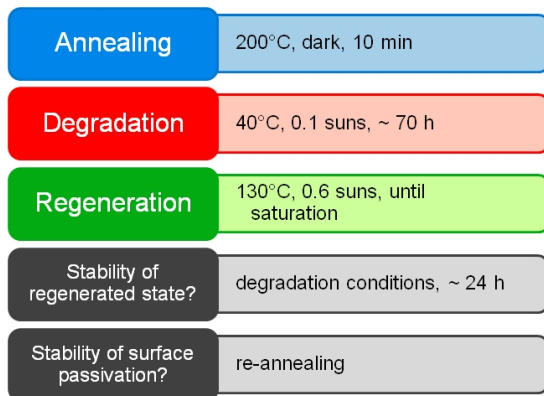
Figure 2: Course of one regeneration sequence.

Minority carrier lifetimes were converted into effective boron-oxygen related defect concentrations N*(t) according to

$$N^*(t) = 1/\tau(t) - 1/\tau_0 \qquad (1)$$

with $\tau(t)$ being the minority carrier lifetime at time t, and τ_0 being the lifetime in the annealed state where no BO defects are supposed to be recombination active.

3 RESULTS OF THE REGENERATION MEASUREMENTS

3.1 Pre-experiment

In a pre-experiment the regeneration behavior of two samples differing in their final heat treatment was investigated: only one of the samples received a short high temperature firing step (at around 800°C peak temperature). The results of the pre-experiment (see Fig. 3) show that the unfired reference sample could not be regenerated by applying the sequence presented in Fig. 2 in contrast to the fired sample which shows the characteristic lifetime recovery with time (see also [12]). Hence the question arises what temperatures are necessary to make the regeneration process possible in a fired sample.
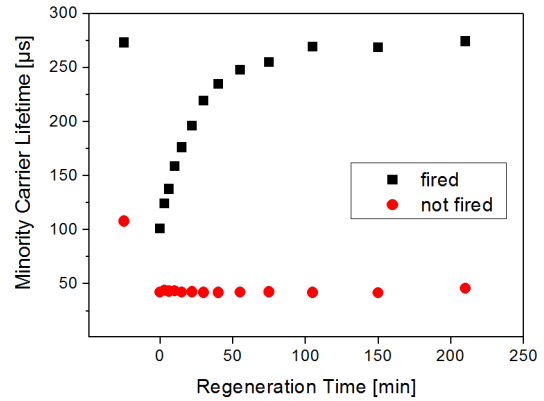
Figure 3: Comparison of the evolution of minority carrier lifetime during regeneration of samples coated with SiN$_x$:H. One sample received a high temperature firing step while the other did not. The first data point represents the annealed state featuring virtually no recombination active BO defects.

3.2 Effect of peak temperature on the regeneration

In a subsequent experiment several lifetime samples were fired using different peak temperature settings. The actual peak sample temperature was determined for each setting. As presented in Fig. 4, changing the peak sample temperature clearly affects the regeneration behavior: the samples fired at higher temperature regenerate faster than samples fired at lower temperature.
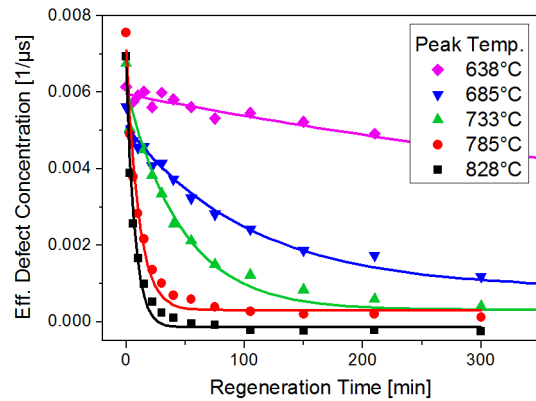
Figure 4: Influence of peak sample temperature on the regeneration process. The lines are single exponential fits to the data.

The single exponential fits to the data are used to extract characteristic time constants. The regeneration rates as shown in Figure 6 are the reciprocal values of these time constants. The rate of the unfired reference sample is zero.
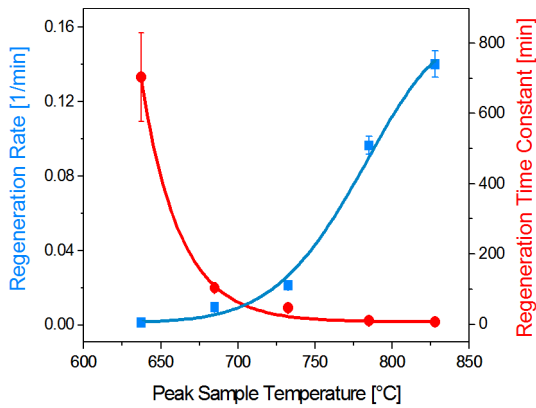
Figure 5: Regeneration rates extracted from the exponential fits in Fig. 4. The lines are guides to the eye.

Firing temperatures below 730°C only allow very slow regeneration corresponding to durations of more than 5 h until saturation under 0.6 suns illumination at 130°C, but for increasing firing temperatures the regeneration rate increases. For the highest firing temperatures the regeneration process can be completed within 1 h under the same conditions.

4 RESULTS OF HYDROGEN RELATED MEASUREMENTS

4.1 Effect of peak temperature on the hydrogen content of the SiN_x:H layer
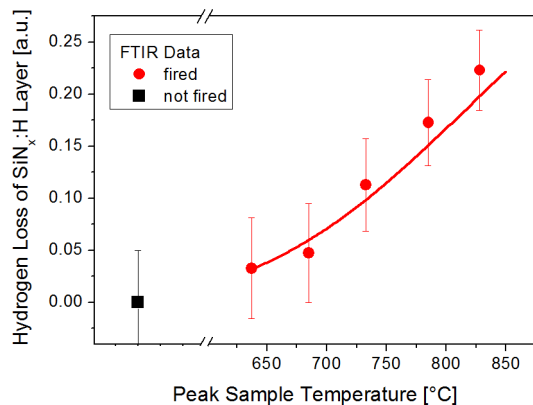

Figure 6: Changes in hydrogen content of the SiN_x:H passivation layers due to firing steps relative to the unfired sample. The line is a guide to the eye.

As the hydrogen being considered crucial for the regeneration process is released from the SiN_x:H layer during firing, changes in its hydrogen content can be a measure for the amount of hydrogen effusing from the layer – mostly into the ambient air (~99%) but also partly into the silicon bulk (~1%) [15]. Therefore the change in hydrogen content after firing steps at different peak sample temperatures was calculated from N-H and Si-H bond densities measured by FTIR.

As can be seen in Fig. 6 the loss increases with rising temperature (in accordance with literature [14]) meaning that higher firing temperatures are assumed to result in higher hydrogen concentrations in the silicon bulk.

4.2 Effect of peak temperature on the maximum lifetime

Hydrogen can passivate different recombination active defects in the silicon bulk as well as at the interface between crystalline silicon and SiN_x:H coating [16]. Less recombination active defects result in higher effective minority carrier lifetimes. Hence there should be a correlation between the amount of hydrogen that leaves the SiN_x:H passivation layer at high temperatures towards the silicon bulk and/or interface and the effective carrier lifetime. In the case of samples possibly affected by boron-oxygen related degradation the effect of other defects can best be seen in the fully annealed state (as defined in section 2) when the lifetime is not affected by boron-oxygen defects.
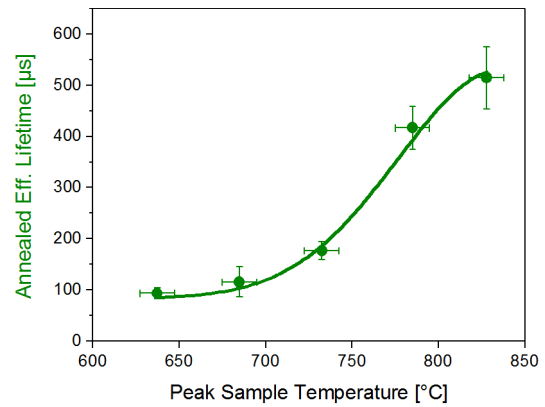

Figure 7: Maximal effective lifetime in the annealed state for different peak temperatures. The line is a guide to the eye.

Fig. 7 shows higher effective lifetimes for higher firing temperatures. This is in accordance with what we expected supposing the maximum lifetime is limited by defects that can partly be passivated by hydrogen atoms and assuming that the hydrogen atoms needed for this are released by the SiN_x:H layer. Higher temperatures can free more hydrogen atoms from their bonds inside the SiN_x:H layer, as indicated in Fig. 6, and thus higher lifetime values are rendered possible. In order to verify this expected correlation, the maximal lifetime (Fig. 7) is plotted versus the hydrogen loss of the SiN_x:H layer (Fig. 6) in Fig. 8. A clear correlation can be seen between increasing maximal lifetimes and rising hydrogen losses, supporting the argumentation above.
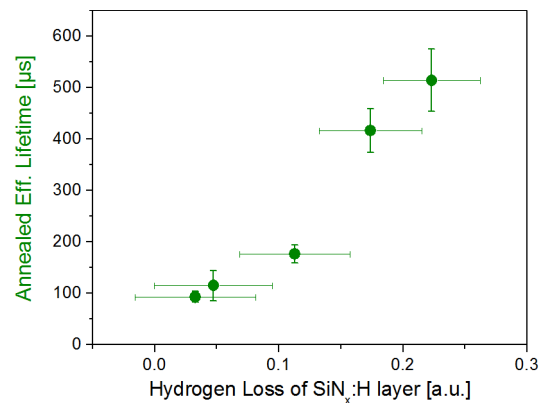

Figure 8: Lifetime in the annealed state for different amounts of hydrogen lost from the SiN_x:H layer as derived from the data presented in Fig. 6 and Fig. 7.

Assuming that hydrogen is also involved in the regeneration process, an increase of the hydrogen concentration in the silicon bulk (derivable from Fig. 6) should also lead to an acceleration of the process quantified by the regeneration rate (Fig. 5). Combining both data sets results in Fig. 9, also verifying the expected correlation of accelerated regeneration with rising hydrogen losses.
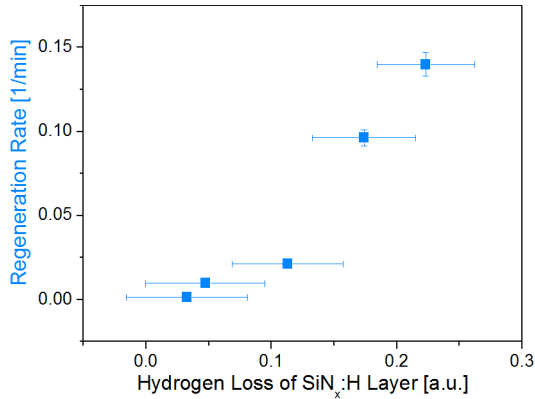

Figure 9: Regeneration rate of samples with different amounts of hydrogen released from the SiN$_x$:H layer during firing.

Based on these results one would predict higher regeneration rates when either the peak temperature during a firing step is further increased or when the time the sample is held at high temperatures is increased because both variations would result in the SiN$_x$:H layers releasing more hydrogen.

5 CONSEQUENCES FOR LONGER HOLDING TIMES AT HIGH TEMPERATURE

In order to investigate the influence of the duration of the high temperature phase within the firing process further experiments were performed using a RTP furnace.

The finely tunable heating/cooling facilitates decoupling the time the sample is held at high temperature from the heating and cooling phase to a large extent as shown in Fig. 10.
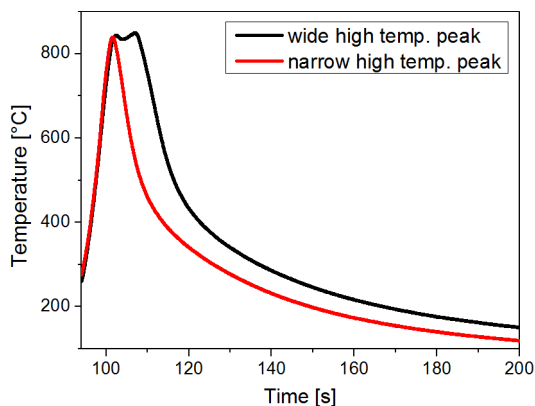

Figure 10: Temperature/time profiles created using an RTP furnace. Both profiles show comparable peak temperatures and the same heating and cooling phase, but different high temperature peak width.
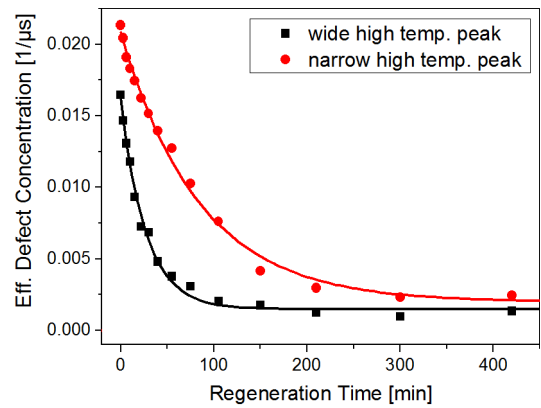

Figure 11: Regeneration behavior of samples fired in the RTP furnace with a narrow and a wider high temperature peak (see Fig. 10).

Keeping the peak temperature nearly constant, a difference of a factor three in the regeneration rate can be observed (Fig. 11) which is considerably more than the slightly different peak temperatures (difference < 10 K) could cause (see also Fig. 5). As expected, faster regeneration for a wider peak suggests the same tendency for increasing peak width than for increasing peak temperature (see Fig. 5).

We emphasize the short duration of all investigated firing steps because for considerably longer or hotter high temperature steps a depletion of the SiN$_x$:H layer can be expected [14]. In this case the layer would no longer act as a steady hydrogen source providing sufficient amounts of hydrogen and longer holding times would rather result in lower hydrogen concentrations in the silicon bulk due to permanent effusion from the bulk at those high temperatures. In consequence, a long high temperature step might result in a slower regeneration process according to the hydrogen-based model of regeneration assumed in this paper.

6 SUMMARY

In order to investigate the influence of the peak temperature during a high temperature firing process on the regeneration kinetics of boron-oxygen related defects, SiN$_x$:H coated lifetime samples were prepared. The regeneration behavior of the so-processed samples was measured, as well as the hydrogen content of the SiN$_x$:H layer and the maximum effective minority carrier lifetime.

Within the investigated parameter range we found that a higher peak sample temperature and longer holding time at high temperature result in a faster regeneration process. This observation is attributed to a higher amount of hydrogen that can be released by the hydrogen-rich SiN$_x$:H layer under these conditions – as proved by FTIR measurements. Thus, the data presented here support the assumption that a high enough concentration of hydrogen in the silicon bulk is crucial for the regeneration process to occur [9,10] and that more hydrogen permits higher regeneration rates [12] and thus the whole regeneration process takes less time. Hence our results support the theory that the regeneration of boron-oxygen related defects might in fact be a form of hydrogen defect passivation [12]. Considering this, firing parameters will

have to be chosen carefully if silicon samples are supposed to (1) have high maximum lifetime values and, more importantly for this material, (2) regenerate quickly in order to get rid of the detrimental effect of boron-oxygen related defects in industrially feasible durations of the regeneration process. Hence all processes in solar cell manufacturing affecting the hydrogen concentration in the bulk presumably have direct influence on the regeneration behavior of solar cells made from material suffering from boron-oxygen related degradation.

To fully exploit the efficiency potential provided by this material – especially to avoid any boron-oxygen related limitation – the here presented influence of the peak temperature chosen for high temperature firing steps should be considered.

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