Influence of hydrogen effusion from hydrogenated silicon nitride layers on the regeneration of boron-oxygen related defects in crystalline silicon

S. Wilking, a) S. Ebert, A. Herguth, and G. Hahn
Department of Physics, University of Konstanz, 78457 Konstanz, Germany

(Received 30 September 2013; accepted 8 November 2013; published online 21 November 2013)

The degradation effect boron doped and oxygen-rich crystalline silicon materials suffer from under illumination can be neutralized in hydrogenated silicon by the application of a regeneration process consisting of a combination of slightly elevated temperature and carrier injection. In this paper, the influence of variations in short high temperature steps on the kinetics of the regeneration process is investigated. It is found that hotter and longer firing steps allowing an effective hydrogenation from a hydrogen-rich silicon nitride passivation layer result in an acceleration of the regeneration process. Additionally, a fast cool down from high temperature to around 550 °C seems to be crucial for a fast regeneration process. It is suggested that high cooling rates suppress hydrogen effusion from the silicon bulk in a temperature range where the hydrogenated passivation layer cannot release hydrogen in considerable amounts. Thus, the hydrogen content of the silicon bulk after the complete high temperature step can be increased resulting in a faster regeneration process. Hence, the data presented here back up the theory that the regeneration process might be a hydrogen passivation of boron-oxygen related defects.

I. INTRODUCTION

Crystalline silicon containing significant amounts of boron as well as oxygen typically suffers from severe degradation under carrier injection (e.g., under illumination).1–9 This degradation is due to so called boron-oxygen related defects that switch from a recombination inactive state to a recombination active state under carrier injection resulting in a degradation of minority carrier lifetime evolving with time until an asymptotic limit is reached.7–9 In 2006, Herguth et al. discovered that the defect can be converted to a new recombination inactive state by the so called regeneration process consisting of a combination of slightly elevated temperature (typically 60–200 °C) and carrier injection resulting in a recovery of lifetimes to the pre-degradation level.10,11 However, the necessary preconditions for the occurrence of this transformation process are not completely clear yet, but some influencing factors have been found: different impurities like boron,12 interstitial oxygen,13 thermal donors,12 or metal impurities14 have been found to slow down the process. In contrast, a high enough hydrogen concentration in the silicon bulk seems to be crucial15,16 with a higher concentration allowing a faster regeneration.17 It may be speculated at this point that the dependency on the aforementioned impurities might also trace back to the hydrogen dependency as the impurities tend to trap hydrogen permanently or at least reduce its effective mobility.

The hydrogen often originates from hydrogenated surface coatings, e.g., silicon nitride SiNₓ:H, and it is found that interlayers blocking the hydrogen diffusion into the silicon bulk from an external source, e.g., a SiNₓ:H layer or hydrogen plasma, are likely to slow down the regeneration process.18 Such a SiNₓ:H layer can release hydrogen during short high temperature steps (later referred to as firing steps) with the amount depending on the actual firing parameters19,20 being peak sample temperature, the holding time at temperatures exceeding 700 °C (referred to as peak width) and the cooling rate below 700 °C, which can be adjusted by the belt velocity in a belt furnace. The influence of these parameters on the hydrogen concentration in the SiNₓ:H layer, the maximum lifetime prior to degradation and regeneration kinetics is investigated.

II. EXPERIMENTAL DETAILS

Czochralski (Cz) grown silicon wafers (boron doped, 2 Ω cm, thickness 200 μm) were saw damage etched in hot NaOH solution, followed by cleaning in diluted HCl and HF, before receiving a gettering step realized in form of a POCl₃ diffusion at high temperatures (~1 h at ~840 °C). Thereafter phosphorous glass and diffused layer were removed in diluted HF and in a chemical polishing solution, respectively. After the following chemical cleaning, the samples were surface passivated on both sides by SiNₓ:H layers (~75 nm) deposited using the direct plasma, low frequency PECVD (Plasma Enhanced Chemical Vapor Deposition) technique of a Centrotherm system. The subsequent short high temperature step was realized in an industrial-type belt furnace from Centrotherm using optical heating, and sample temperature was continuously monitored using thermocouples and a tracker system. Measurement uncertainty is in the range of ±10 K for all temperatures but we refrained from giving error bars for the benefit of readability of the graphs. All firing temperatures given in this paper are measured sample temperatures, however, in order not to compromise the actual samples, parallel samples were used instead. A reference sample was not fired; firing conditions were systematically changed for all other samples. The set temperature was varied between ~650 °C and ~850 °C for high, medium, and...
low belt velocity. This leads automatically to variations in peak sample temperature, the total time a sample is held at high temperature ($>700\,^\circ\text{C}$, referred to as peak width), and cooling rate. Typical temperature/time profiles can be found in Fig. 1 for variable peak sample temperatures and for variable belt velocities. The corresponding average cooling rates in the range from $700\,^\circ\text{C}$ down to $550\,^\circ\text{C}$ (between peak temperature and $550\,^\circ\text{C}$ for the peak temperatures below $700\,^\circ\text{C}$) are given in Fig. 2. For comparison, the time a sample is held at peak temperature was modified independently from the heating/cooling phase using a Rapid Thermal Processing (RTP) furnace (Solaris 150 from Surface Science Integration).

Changes in the hydrogen content of the SiNx:H layers were measured directly on the actual samples using a Bruker Optics Vertex 80 Fourier-Transformed Infrared spectrometer (FTIR). Hydrogen content was calculated from the normalized areas under the hydrogen related infrared absorption peaks at around $2200\,\text{cm}^{-1}$ and at around $3350\,\text{cm}^{-1}$ using the calibration factors published by Lanford et al.\textsuperscript{21} Layer thickness was determined by standard spectral ellipsometry measurements using a VASE system from J. A. Woollam.

For measuring the regeneration behavior subsequent to the firing process, the samples were first annealed at $200\,^\circ\text{C}$ in the dark for 10 min, then completely degraded at $40\,^\circ\text{C}$, 0.1 suns, and finally regenerated until lifetime saturation at $130\pm 2\,^\circ\text{C}$ and 0.6 ± 0.1 suns. The stability of the regenerated state was checked at $40\,^\circ\text{C}$, 0.1 suns, as well as the stability of the surface passivation by repeating the annealing step. Minority carrier lifetime was measured at $30\,^\circ\text{C}$ at a constant injection level of 0.1 $N_A$ (doping concentration $N_A$) after each intermediate step and every few minutes during the regeneration process using a WCT-120 lifetime tester from Sinton Instruments. Minority carrier lifetimes were then converted into normalized boron-oxygen related defect concentrations $N^*(t)$ using

$$N^*(t) = \frac{1}{\tau(t)} - \frac{1}{\tau_0}$$  \hspace{1cm} (1)

with $\tau(t)$ being the minority carrier lifetime at time $t$ and $\tau_0$ being the lifetime in the annealed state, where the lifetime is not affected by boron-oxygen related defects.

III. INFLUENCE OF PEAK TEMPERATURE AND HIGH TEMPERATURE PEAK WIDTH ON REGENERATION

A. Effect of peak temperature on the hydrogen content of the SiN$_x$:H layer

Since hydrogen seems to affect the required duration of the regeneration process\textsuperscript{17} and it is known that SiN$_x$:H layers can release hydrogen into the silicon bulk during high temperature firing steps,\textsuperscript{19} the question of how much hydrogen can effuse from the layer at a certain firing temperature may be a clue to explaining possible differences in the regeneration behavior of differently fired samples.

FTIR measurements reveal that with increasing peak temperature, hydrogen concentration in the SiN$_x$:H layer decreases considerably meaning that the layer loses more hydrogen with increasing temperatures (see Fig. 3). This is in accordance with literature\textsuperscript{20} and means that at higher temperature, more hydrogen atoms can overcome their binding energy and either effuse from the SiN$_x$:H layer into the ambient ($\sim 99\%$) or into the silicon bulk ($\sim 1\%$).\textsuperscript{22} Therefore, we assume that higher hydrogen concentrations in the silicon bulk can be expected when the SiN$_x$:H layer releases more hydrogen due to higher firing temperatures.

B. Effect of peak temperature on regeneration

The ability of SiN$_x$:H layers to release hydrogen being dependent on peak sample temperature during firing, a variation in this temperature can be expected to affect regeneration kinetics. The results of the regeneration measurement of samples fired at different temperatures but constant belt velocity is shown exemplarily in Fig. 4. All samples show the regeneration effect recognizable by a decrease of the
effective boron-oxygen related defect concentration with
time. A clear influence of peak sample temperature on the
regeneration behavior can be seen, with the samples fired at
higher temperature regenerating faster than samples fired at
lower temperature.

Combined with the results shown in Fig. 3, these meas-
urements suggest that higher firing temperatures making the
SiNx:H layer release more hydrogen result in faster regenera-
tion processes.

C. Effect of high temperature peak width on
regeneration

If firing conditions especially higher temperatures that
lead to higher hydrogen losses in the SiNx:H layer can be
made responsible for an accelerated regeneration process,
longer holding times at high temperature should cause the
same effect since the probability of a bound hydrogen atom
to be released into a mobile state and to diffuse into the Si
bulk increases with time and temperature. In a belt furnace,
peak width can only be varied by changing the belt velocity,
which at the same time leads to changes in the heating and
cooling phase. In order to clearly separate those effects, an
RTP furnace was used to create two temperature profiles
with the same peak temperature (difference < 10 K) only dif-
fering in peak width as depicted in Fig. 5.

Indeed, the difference in peak width (Fig. 5) results, as
expected, in a difference in regeneration rate of a factor three
(Fig. 6) not explainable by the peak temperature difference
(<10 K) in Fig. 5.

We emphasize that the higher hydrogen effusion probabil-
ity from the SiNx:H layer for hotter or longer high temperature
phases will probably only lead to higher bulk concentrations if
the SiNx:H layer acting as hydrogen source contains a high
enough amount of hydrogen and is not significantly depleted
as it could be expected after long tempering steps at high tem-
peratures. Hence, considerably longer or hotter firing steps
would rather result in lower hydrogen bulk concentrations due
to effusion from the silicon bulk at those high temperatures
and thus lead to lower regeneration rates according to the
hydrogen-based model of regeneration underlying this paper.
IV. INFLUENCE OF COOLING RATES ON REGENERATION

A. Results of regeneration measurements

In addition to the variation of peak sample temperature, the belt velocity is an important parameter of firing processes in a belt furnace. It was found that variation of the belt velocity indeed significantly affects regeneration kinetics as shown exemplarily for high peak temperatures in Fig. 7.

Fig. 7 reveals a tendency that samples fired at higher belt velocities regenerate faster than other samples. The single exponential fits to the data are used to extract characteristic time constants of which the reciprocal value corresponds to the regeneration rate as given in Fig. 8 for all combinations of firing parameters (belt velocity and peak sample temperature). The inset zooms into the regions around 650 °C. The unfired reference sample is not included in the graph, but has a regeneration rate of zero.

For temperatures below 700 °C, only very slow regeneration occurs for any of the three belt velocities. Assuming the need for hydrogen as a basis of the regeneration effect, this can be explained considering the results presented in Fig. 3; because for those temperatures, the SiNx:H layer releases only small amounts of hydrogen and presumably does even less for the narrow high temperature peaks resulting from high belt velocities. Thus, an increase in belt velocity results in decreasing regeneration rates (see Fig. 8, inset).

For high enough peak temperatures, an increase in belt velocity results in increasing regeneration rates by up to a factor of six. The variation of the total peak sample temperature (±30 °C compared to medium velocity) due to differing belt velocities is nowhere near enough to explain these differences as can be concluded, e.g., from a comparison of regeneration rates with different peak temperature but constant belt velocity (see Fig. 8). In addition to that, the higher temperatures and wider peaks resulting from slower belt velocities would lead to a contrary tendency (see Figs. 4 and 6). Furthermore, plotting the regeneration rates over the relative hydrogen loss from the SiNx:H layer (corresponding to different peak temperatures) of the respective samples leads to a tendency of increasing regeneration rates for increasing hydrogen loss, as can be seen in Fig. 9.

However, for constant hydrogen loss from the SiNx:H layer, a slower firing process results in lower regeneration rates. The reason for this might not be found in slight differences in peak temperature or peak width (that would affect the hydrogen loss of the SiNx:H layer) but rather in the third factor influenced by belt velocity—the cooling rate after the high temperature peak. The cooling rate should not affect the

![FIG. 7. Influence of belt velocity (peak temperature 850 ± 30 °C) during high temperature firing on the regeneration process. Even though a high peak temperature (blue) should yield a faster regeneration process than a low peak temperature (black), the differing belt velocity reverses the order. The lines are single exponential fits to the data.](image)

![FIG. 8. Regeneration rates of all measured samples after firing at different peak temperatures and belt velocities (black: fast, orange: medium, blue: slow). The lines are guides to the eye. The inset zooms into the low temperature region.](image)

![FIG. 9. Correlation of the amount of hydrogen released from the SiNx:H layer and regeneration rates for different belt velocities. Note the different scales on the regeneration rate axis. The lines and their slopes are added for comparison only. Measurement uncertainty concerning hydrogen loss from the SiNx:H layer is in the range of ±0.05.](image)
hydrogen loss of the layer but might influence the hydrogen content of the silicon bulk, anyway.

B. Influence of cooling rates on the regeneration process

In Fig. 10, the regeneration rate is shown in dependence of the mean cooling rate in the temperature range from 700 to 550°C (between peak temperature and 550°C for the peak temperatures below 700°C) resulting from different belt velocities.

A tendency can be seen in Fig. 10 that for a given peak temperature range above 700°C, higher cooling rates result in higher regeneration rates. For lower peak temperatures, the cooling rate does not seem to have an influence on the regeneration kinetics.

C. Discussion

The upper limit for the definition of the cooling rate was chosen to 700°C for the reason that, according to Fig. 3, below this temperature and for the relatively short times involved no considerable amount of hydrogen is released from the SiNx:H layer anymore, but it is still hot enough for hydrogen redistribution within and effusion from the silicon bulk for temperatures above \(~\sim 550\)°C. This means that the height and width of the high temperature peak above \(~\sim 700\)°C during firing determines how much hydrogen can diffuse from the hydrogen-rich SiNx:H layer into the silicon bulk. The duration the sample stays between \(~\sim 700\)°C and \(~\sim 550\)°C, or in other words the cooling rate in this temperature range, determines what percentage of the hydrogen that had been introduced into the bulk at high temperature stays there until the end of the whole firing process. Hence, high cooling rates allow high regeneration rates, provided that the peak temperature was high enough to make the hydrogenated passivation layer release a significant amount of hydrogen into the silicon bulk. This can also explain why the regeneration of samples fired at lower peak temperatures (Fig. 10: red, green) cannot be accelerated by higher cooling rates: in this temperature range, the positive effect of a high cooling rate, meaning a weaker depletion of hydrogen in the silicon bulk, is balanced out by the negative effect of a short and slightly colder high temperature peak, meaning a reduced hydrogen diffusion into the bulk. It may be speculated that the hydrogen content of the samples fired at around 750°C might be limited by in-effusion from the SiNx:H layer for high belt velocity and by effusion from the silicon bulk for slow belt velocity giving an optimum in between. But more data would be necessary to confirm this observation.

Another possible explanation would have been a depletion of the SiNx:H layer caused by slower firing steps. But as can be seen from Fig. 3, this does not seem to be the case after these very short high temperature steps.

V. INFLUENCE OF FIRING PARAMETERS ON THE MINORITY CARRIER LIFETIME IN THE ANNEALED STATE

A. Results of lifetime measurements

Since hydrogen is known to passivate a multitude of different recombination active defects in the silicon bulk as well as dangling bonds causing recombination at the silicon surface, more hydrogen in the silicon bulk and at the surface is likely to result in higher effective minority carrier lifetimes. Therefore, changes in the firing parameters should affect the effective lifetime due to passivation of other crystal defects apart from boron-oxygen related ones, and this effect would be expected to be comparable with the effect on the regeneration rate as discussed before. In the case of samples suffering from boron-oxygen related degradation, the effect of other defects can best be seen in the annealed state (prior to degradation) when the lifetime is not affected by boron-oxygen defects. Therefore, the effect of the different firing parameters on the maximal carrier lifetime measured in the annealed state (as defined in Sec. II) is shown in Fig. 11.

Indeed, it can be seen that the effective lifetime in the annealed state increases steadily with rising peak sample temperature. However, a comparison of different belt velocities also shows that besides peak temperature the belt velocity has a significant influence on the effective lifetime.
velocity plays a role. In particular, a cross-over of the different belt velocity curves at around 750 °C occurs.

B. Discussion

With respect to the correlation of hydrogen release from a SiNx:H layer and firing temperature (Fig. 3), the behavior of these lifetime values can be explained consistently for firing temperatures up to 750 °C: hotter and slower (thus longer) firing steps result in better defect passivation because hydrogen atoms are released at a higher rate and for a longer duration from the SiNx:H layer leading to a higher concentration of hydrogen atoms in the silicon bulk and at its surface. For temperatures above 750 °C, the tendency changes: now fast firing steps are advantageous compared to slower firing steps. Assuming that less defects can now be passivated by hydrogen atoms, one has to ask the question why slower firing steps result in a less effective hydrogenation, even though the SiNx:H layer provides more hydrogen in the first case than in the latter. The influence of the cooling rate between ~700 °C and ~550 °C is a probable explanation, as suggested by the similarity between the temperature dependence of the annealed lifetimes (Fig. 11) and of the regeneration rates (Fig. 8). The existence of a cross-over point marking the firing temperature where low belt velocities become disadvantageous can be explained consistently: for lower temperatures, the positive effect of the SiNx:H layer releasing more hydrogen for slower belt velocity overcompensates the negative effect of more hydrogen effusion from the silicon bulk during the longer cooling phase. This reverses for temperatures above the cross-over point (at ~700 °C for the regeneration rates and at ~750 °C for the effective lifetimes in the annealed state). It may be speculated that the discrepancy in cross-over temperature could be caused by the fact that contrarily to the regeneration rates, the effective lifetimes in the annealed state should be affected by hydrogen concentration in the silicon bulk as well as at the silicon/SiNx:H interface which might not necessarily be affected by temperature to exactly the same extent.

VI. SUMMARY AND CONCLUSIONS

Hydrogenated silicon nitride (SiNx:H) coated lifetime samples were prepared in order to investigate the influence of peak temperature and belt velocity during a high temperature firing process in a belt furnace on the regeneration kinetics of boron-oxygen related defects in silicon. Time-resolved lifetime measurements were carried out to monitor the regeneration behavior of the samples fired under different conditions. Additionally, changes in the hydrogen content of the SiNx:H layer and the maximum effective minority carrier lifetime not affected by boron-oxygen related defects were measured.

We found that for the short high temperature steps investigated here, the same conditions leading to stronger hydrogen depletion of the SiNx:H layer, namely higher peak sample temperatures and holding times at high temperature, also result in a faster regeneration process. Therefore, it is assumed that a stronger hydrogenation of the silicon bulk is generally beneficial to the regeneration process and accelerates the transformation of the detrimental boron-oxygen related defects from their recombination active state to the inactive regenerated state.

However, peak temperature and holding time cannot consistently explain all findings. It could be shown that the cooling rate in the range ~700 °C down to ~550 °C has a non-negligible influence on the kinetics of the regeneration process, too: For high enough firing temperatures, the regeneration rate increases with higher cooling rates. A possible explanation for this observation could be the more efficient suppression of net hydrogen effusion from the silicon bulk during a very fast cooling phase in the temperature range in which hydrogen release of the SiNx:H ceases but hydrogen effusion from the silicon bulk still occurs. Assuming that a certain hydrogen concentration was achieved during the high temperature phase, higher cooling rates would diminish effusion losses and result in a higher hydrogen bulk concentration after the firing process compared to slower cooling rates.

It is also found that a higher peak temperature is generally beneficial for the minority carrier lifetime in the non degraded state when lifetime is not limited by boron-oxygen related defects but by various background defects in the bulk and at the surface as well. Analogue to the findings for the regeneration process, the results indicate that the cooling rate also plays a role in this context.

In summary, it can be stated that two aspects need to be considered concerning high temperature firing steps in order to allow a fast regeneration process: First, the combination of firing temperature and peak width at high temperatures needs to be chosen in such a way to allow significant hydrogen release from the hydrogenated passivation layer. Second, a fast cool down process down to temperatures around 550 °C should follow the high temperature peak in order to avoid significant net effusion from the silicon bulk in a temperature range where effusing hydrogen cannot be replaced by hydrogen originating from the SiNx:H layer anymore. This is valid when hydrogenated silicon nitride layers in particular or most probably any hydrogenated passivation layers are used as hydrogen source.

Thus, firing parameters will have to be chosen carefully if silicon samples are supposed to regenerate reliably and quickly in order to avoid the detrimental effect of boron-oxygen related defects.

ACKNOWLEDGMENTS

The authors would like to thank L. Mahlstaedt and T. Wiedenmann for technical support during sample preparation. Part of this work was supported by the German Federal Ministry for the Environment, Nature Conservation, and Nuclear Safety.