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Influence of hydrogenated passivation layers on the regeneration of boron-oxygen related defects

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Abstract

When exposed to light, boron-doped monocrystalline Czochralski grown silicon suffers from degradation of the minority carrier lifetime due to formation of recombination active boron-oxygen related defects. The so called regeneration procedure is often able to convert these recombination active defects into a new less recombination active state characterized by the higher original minority carrier lifetime and being stable under illumination.

The regeneration behavior of silicon wafers passivated with different dielectric layers is investigated in this work. We found that the characteristic regeneration time constant is subject to variation depending on the surface passivation layers used and the temperature steps applied prior to the regeneration procedure. Namely, a positive effect of a short high temperature (800-900°C) firing step is shown as well as the influence of SiN_x:H layer density. In addition to that, results are presented that suggest a negative effect of Al_2O_3/SiN_x:H stacks depending on the thickness of the Al_2O_3 interlayer. All three effects are attributed to the influence of the respective processes on the hydrogen content in the silicon bulk. A hypothesis to explain the effect of the regeneration of boron-oxygen related defect centers including a possible role of hydrogen is presented. This includes the assumption of regeneration actually being hydrogen passivation of boron-oxygen related defects, triggered by carrier injection in combination with slightly elevated temperatures.

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Keywords: Silicon; Boron-Oxygen; Regeneration; Hydrogen

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1. Motivation

The efficiency of solar cells produced from high quality boron-doped but oxygen-rich silicon is often limited by a low minority carrier lifetime due to recombination active boron-oxygen related defect centers [1]. This limitation develops under illumination and becomes noticeable in a severe degradation of device performance. Herguth *et al*. have shown that a so called regeneration procedure can cause the degraded material to permanently recover its bulk lifetime [2]. Therefore, the regeneration step is an excellent way to improve the efficiency of solar cells based on boron-doped Czochralski (Cz) grown material.

Münzer has shown that no regeneration could be seen on samples coated with LPCVD (Low Pressure Chemical Vapor Deposition)-SiN_x having very low hydrogen content [3]. Comparable results were published by Krugel *et al.* who had used sputtered SiN_x passivation layers with different hydrogen contents [4]. This leads to the assumption that hydrogen may have a major influence on whether the regeneration effect can occur or not. Nevertheless, no time-dependent measurements on the evolution of the boron-oxygen related defect concentration regarding a possible influence of hydrogen have been published yet. Experimental results and a new hypothesis to explain the regeneration effect is provided in this work.

2. General experimental setup

For all investigations presented here we used 2 Ωcm boron-doped Cz-grown silicon wafers with interstitial oxygen concentrations around $6\cdot10^{17}\,cm^{-3}$ (see Fig. 1 for details). After saw damage etching all wafers received a gettering step realized in form of a standard $POCl_3$ diffusion. Phosphorous glass and emitter were removed thereafter, and passivation layers were deposited on both sides in order to produce lifetime samples. The used SiN_x:H layers were fabricated via PECVD (plasma enhanced chemical vapour deposition), and the Al_2O_3 layers were produced via ALD (atomic layer deposition). Finally, all samples received a short high temperature firing step in a belt furnace at about 820°C peak sample temperature, except for some reference samples of which the thermal treatment is described later for all experiments separately.

For evaluating the regeneration behavior, the samples were first annealed, then completely degraded and finally regenerated at 130 ± 2°C, 0.6 suns (see Fig. 2 for details). After every step and every few minutes during regeneration, minority carrier lifetime was measured at an injection level of 10% of the doping level using a Sinton Instruments WCT-120 lifetime tester. Lifetime values were then converted into equivalent boron-oxygen related defect concentrations $N^*(t)$ according to

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

with $\tau(t)$ being the minority carrier lifetime at time t and τ_0 being the lifetime of the annealed state (measured after the completion of the regeneration cycle). Finally, the stability of the regenerated state was checked, as well as the stability of the surface passivation.

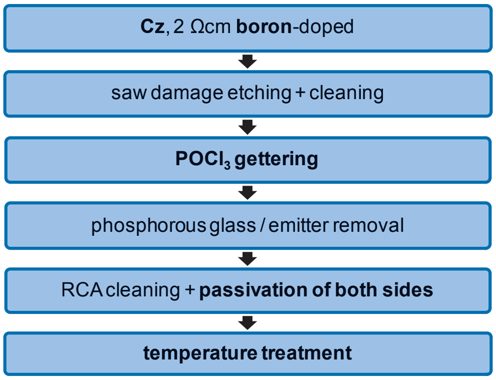

Fig. 1: Processing sequence of lifetime samples.

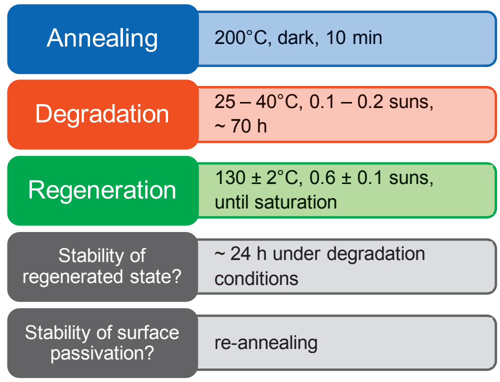

Fig. 2: Complete regeneration test sequence.

3. Results and discussion

3.1. Influence of short high temperature firing steps

In a first experiment the regeneration behavior of samples that received a high temperature firing step at 820°C peak sample temperature is compared to equivalently processed samples that did not receive that step (in the case of the SiN_x:H coated samples) or were alternatively tempered at a medium temperature (in the case of the Al_2O_3 coated samples). For the latter samples a typical 15 min, 390°C tempering step in nitrogen atmosphere was chosen in order to activate the Al_2O_3 passivation layer. The results for SiN_x:H and for Al_2O_3 coated samples are given in Fig. 3 and Fig. 4, respectively.

One can see that no (in the case of SiN_x:H) or only an extremely slow regeneration can be observed in samples that had not seen any high temperature firing step. The data collected from the Al_2O_3 sample tempered at 390°C is not sufficient to decide whether a very slow regeneration effect occurs or not, but in any case the significant difference to the fired sample can be clearly seen.

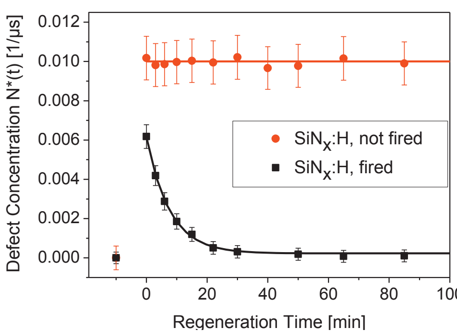

Fig. 3: Evolution of the boron-oxygen related defect concentration during the regeneration procedure for samples coated with SiN_x:H. Typical samples that did (black squares) or did not (red round symbols) receive any high temperature firing step are shown. The first data point represents the annealed state. The lines are exponential fits to the data.

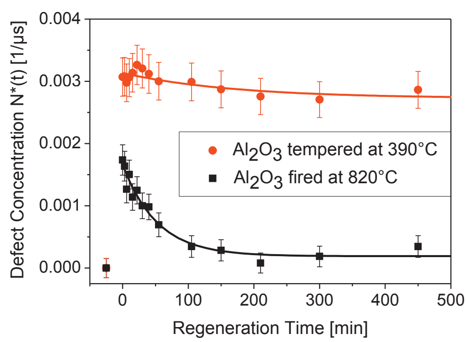

Fig. 4: Regeneration behavior of Al_2O_3 coated lifetime samples with the passivation activated at 390°C (red round symbols) or using a typical high temperature firing step (black squares), respectively. The first data point represents the annealed state. The lines are exponential fits to the data.

Considering the well documented fact, that both SiN_x:H passivation layers [5] and Al_2O_3 layers [6] are able to release hydrogen during a high temperature step, those first findings provoke the question whether the hydrogen released by these layers is necessary for the regeneration effect to occur.

3.2. Influence of SiN_x:H passivation layer composition

For a second set of samples, we kept constant the high temperature treatment, but used SiN_x:H passivation layers with different refractive indices (evaluated at 630 nm), n = 2.05 and n = 2.15. The samples show a different regeneration behavior as presented in Fig. 5. In order to find out what difference between the two layers might affect the regeneration rate of the respective samples, Fourier Transformed Infrared (FTIR) absorption spectra were measured using a Bruker Optics Vertex 80 spectrometer. The resulting spectra reveal a difference in the thickness normalized absorption of the Si-N bonds (see Fig. 6), which is proportional to the Si-N bond density in the layer. Van Erven [7] has shown, that the mass density of a SiN_x:H layer correlates with this bond density, with higher bond densities corresponding to higher layer mass densities. Therefore, the comparison of the FTIR results and the measured regeneration behavior leads to the idea that a higher SiN_x:H mass density (at least up to a certain density) might accelerate the regeneration process.

A possible explanation for this can be found in the work presented by Dekkers *et al.* [8], who showed that even though low density SiN_x:H layers release a lot of hydrogen during a high temperature firing step, only few hydrogen atoms can diffuse from the layer into the silicon bulk because hydrogen is mainly released in its molecular, slowly diffusing, form. In contrast, SiN_x:H layers with higher mass density mainly release atomic hydrogen that can easily diffuse into the silicon bulk. Hence, after firing one can expect a higher bulk hydrogen content in the samples coated with high density SiN_x:H . This corresponds to the lower refractive index n = 2.05 which are exactly those samples showing a faster regeneration of boron-oxygen related defects. We therefore observe: passivation layers releasing more atomic hydrogen during the firing step seem to allow a faster regeneration.

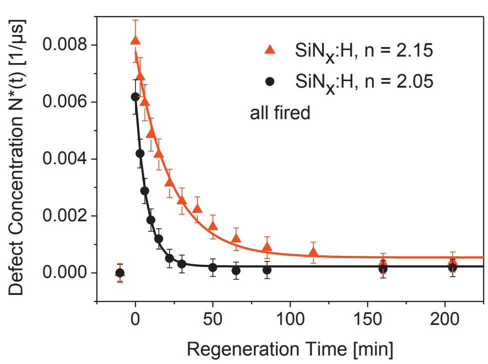

Fig. 5: Regeneration behavior of samples coated with SiN_x:H layers with different refractive indices. The first data point represents the annealed state. The lines are exponential fits to the data.

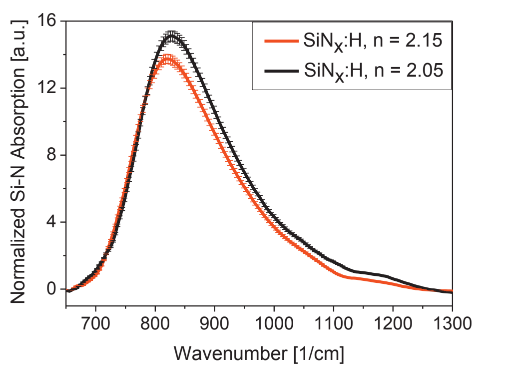

Fig. 6: Thickness normalized absorption of Si-N bonds in two SiN_x:H layers of different refractive indices, measured before the high temperature firing step. Higher Si-N absorption peaks imply a higher mass density of the SiN_x:H layer.

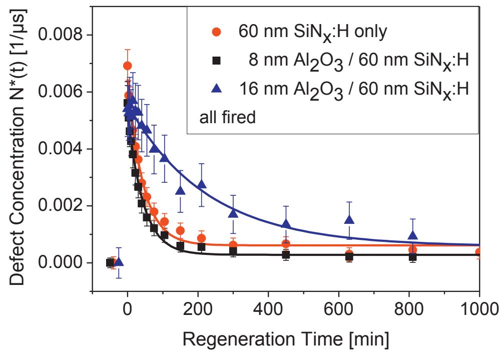

Fig. 7: Evolution of the regeneration of samples coated with stacks of Al_2O_3 and SiN_x:H compared with a single SiN_x:H layer coating. For the stacks, two different thicknesses of the Al_2O_3 interlayer are used. The first data point represents the annealed state. The lines are exponential fits to the data.

3.3. Influence of Al_2O_3 as hydrogen diffusion barrier layer

In a third experiment lifetime samples were passivated using Al_2O_3 layers of different thickness (8 nm and 16 nm, respectively), capped by a 60 nm SiN_x:H layer. For reference, a sample coated only with 60 nm of SiN_x:H was fabricated, too. All samples were fired at 820°C peak sample temperature and the whole regeneration procedure was applied as described in section 2. Results from the regeneration measurement are presented in Fig. 7.

Obviously, the thin 8 nm Al_2O_3 layer does not affect the regeneration: an exponential fit to the data yields a time constant of 44 ± 3 min which is the same as for the SiN_x:H single layer coated samples. This is in contrast to the thicker 16 nm Al_2O_3 layer clearly slowing down the regeneration (resulting time constant: 225 ± 28 min).

Dameron *et al.* have shown that depending on their thickness, Al_2O_3 layers can act as diffusion barriers for atomic hydrogen with hydrogen diffusivity decreasing by more than one order of magnitude between 5 and 10 nm layer thickness [9]. This means that a 16 nm Al_2O_3 layer can considerably impede the hydrogen diffusion from an overlying SiN_x:H capping layer during the firing step, contrary to a thinner one. Concerning a possible regeneration ability resulting from the Al_2O_3 interlayer, Dingemans *et al*. have shown, that at about 400°C for 10 min (typical SiN_x:H deposition conditions) hydrogen already effuses from Al_2O_3 layers leaving behind a depleted layer [6]. Thus, this layer cannot provide much hydrogen anymore that could diffuse into the silicon bulk during a following firing step. Therefore, we suppose that the amount of hydrogen provided by the presumably depleted Al_2O_3 interlayer can be neglected compared to the hydrogen provided by the SiN_x:H capping layer. As a result, the Al_2O_3 interlayer cannot act as a hydrogen source by itself, but represses hydrogen diffusion and hence has a negative effect on the regeneration of boron-oxygen related defects.

4. Model on the working principle of regeneration

All effects that the different process parameters presented here have on the regeneration of boron-oxygen related defect concentration seem to be explainable by how the atomic hydrogen content in the silicon bulk is affected by those process steps: short high temperature firing steps of hydrogenated passivation layers are able to accelerate regeneration as well as using a SiN_x:H layer releasing a lot of atomic hydrogen. In contrast, regeneration seems to be slowed down by using a SiN_x:H layer releasing less atomic hydrogen or by depositing an Al_2O_3 hydrogen diffusion barrier layer underneath a hydrogen providing SiN_x:H layer. We therefore come to the conclusion that a certain content of atomic hydrogen in the silicon bulk is necessary for the regeneration effect to occur with more hydrogen allowing a faster regeneration.

Considering those findings, there are three necessary conditions of regeneration: the presence of hydrogen, slightly elevated temperatures and carrier injection. Based on those criteria we propose the following model for the regeneration effect: The need for hydrogen suggests that regeneration actually might be hydrogen passivation of boron-oxygen related defects. Carrier injection might be necessary in order to free hydrogen atoms from bond states (e.g. from impurities or hydrogen molecules) or to change the charge state of hydrogen atoms in order to make a hydrogen passivation of boron-oxygen defects possible. Once being in its atomic form, slightly elevated temperatures might enable hydrogen diffusion and hence facilitate the regeneration process. Further research is necessary to clarify the interaction of these conditions.

5. Conclusions

It has been shown that no or at least only an extremely slow regeneration is possible, unless there is a considerable amount of hydrogen available in a SiN_x:H passivation layer which is subsequently released into the bulk as atomic hydrogen during a high temperature firing step. In addition to that, the characteristic time constant of the regeneration process might depend on the actual concentration of hydrogen in the silicon bulk. We therefore conclude that the presence of hydrogen is crucial for the regeneration effect to occur with more hydrogen allowing a faster regeneration. As a consequence of these results, we propose that regeneration might in fact be a process of hydrogen passivation of boron-oxygen related defects. A model about how the three necessary conditions hydrogen, carrier injection and elevated temperature might interact has been presented: the regeneration effect seems to rely on the presence of mobile atomic hydrogen, which can be realized by a combination of carrier injection and elevated temperatures, all applied to a hydrogen-rich silicon bulk.

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