

ACCELERATING BORON-OXYGEN RELATED REGENERATION: LESSONS LEARNED FROM THE BORNEO PROJECT

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ABSTRACT: The boron-oxygen related defect is a well-known lifetime killer and in consequence seemed to be a show-stopper for the high efficiency solar cell development on boron-doped substrates. However, the related degradation may be overcome by the regeneration process eliminating the harmful defects. The recently finished research project BORNEO aimed at a more fundamental understanding of boron-oxygen related regeneration in order to answer the pending questions that impede industrial application so far. Some basic relations between macroscopic parameters (such as the manufacturing process of the solar cell and the regeneration conditions) and microscopic processes (such as the defect kinetics) are explained, and which lessons were learned to be able to realize a fast and reliable regeneration process not only on lifetime samples, but also on solar cell level, and why the chosen cell architecture matters.

Keywords: Degradation, boron, oxygen, hydrogen, crystalline silicon

1 INTRODUCTION

Even though a multiplicity of publications and technology roadmaps may give the impression that n-type substrates will be the first choice in the future for wafer based silicon solar cell mass production, the reality nowadays looks different. The main part of silicon solar cells are manufactured on p-type (almost always boron-doped) substrates with mc-Si dominating over Cz-Si as it features the better cost-benefit ratio for the classic full area Al-BSF (back surface field) architecture. However, currently almost all solar cell manufacturers are switching/have already switched from full area Al-BSF to PERC (passivated emitter and rear cell) architecture, or they are at least evaluating the cost structure.

In contrast to the full area Al-BSF architecture, where a high substrate quality is not that necessary as the relatively weak rear side passivation of the Al-BSF limits the effective lifetime (or diffusion length) anyway, the PERC architecture with its good rear side passivation can benefit significantly from a high minority carrier lifetime and may reach efficiencies even exceeding 22% [1]. With respect to this point, high quality Czochralski-grown silicon (Cz-Si) should be better suited than multicrystalline silicon (mc-Si). However, boron-oxygen related degradation changes the situation dramatically. Even for comparable boron concentration (around 10^{16} cm^{-3}), high quality mc-Si may feature higher lifetimes than Cz-Si after complete degradation due to its lower oxygen concentration (defect density scales approx. quadratically with interstitial oxygen [2]) even though both materials suffer from the effect.

The advantage of Cz-Si shows up only after the regeneration process [3,4] whereby the harmful defects are most likely passivated by hydrogen [5]. Then, and only then, stable substrate lifetimes exceeding even a millisecond in Cz-Si [6] and in consequence the desired efficiencies of about 22% on boron-doped substrates are achievable [1]. This potentially eliminates the need for n-type substrates and avoids any n-type process related issues such as a high temperature boron diffusion and contacting boron emitters with Ag/Al pastes without shunting by undesired Al spikes.

2 THE BORNEO PROJECT: UNDERSTANDING REGENERATION

Even though the regeneration reaction was discovered in 2006 [3,4,7,8], it failed to enter the industrial application quickly as too many industrially relevant questions remained unanswered in the first few years and the need for high lifetime material was not considered that critical as today.

In the past three years, two German research groups (University of Konstanz and Fraunhofer ISE), and company SolarWorld have joined their efforts in the publicly funded BORNEO project with the aim to better understand the boron-oxygen related (BO) degradation and especially regeneration and thus help to answer the still open questions regarding the industrial applicability of the regeneration process:

- What are the basic requirements for regeneration?
- Can it be accelerated (suited for production cycle times)?
- Is the effect stable for longer times?
- What does it mean for real solar cells, especially for the upcoming PERC architecture?

This contribution will sum up the known facts from recent publications within the BORNEO project and is dedicated especially to the last question.

3 THE REGENERATION PROCESS

3.1 Basic requirements for Regeneration

As of 2006 [3,4] it was known that excess charge carriers and temperature are two main requirements for the regeneration reaction to occur with both higher temperature and higher injection level accelerating the process [9,10]. There existed also a 3-state model of the BO defect explaining the experimental findings qualitatively [3,4] and quantitatively [11]. It seemed obvious at that point that there is an unknown component involved, however, it took some more time to identify hydrogen as a key component [12,5]. This extended the existing model to its actual form.

The BO defect exists as a latent species in a recombination inactive form. Under carrier injection the defect transforms to a different species now becoming a harmful lifetime killer. The regeneration reaction is then most likely a hydrogen passivation of the defect centre; however, it is yet unclear, why this only happens under carrier injection. There are two possible explanations: first, hydrogen changes its charge state for enhanced mobility and/or second, hydrogen and/or the BO defect changes its charge state to enable the attachment of hydrogen to the complex. Whatever the complex then looks like, it seems to be stable under typical operation condition (like up to 80°C under illumination), but may be dissolved at higher temperatures [5,13].

3.2 Accelerating the Regeneration process

In principle, the described model shows already the way to accelerate the regeneration process and concurrently also to test the model itself. If hydrogen plays a key role in the regeneration process, then every experiment influencing hydrogen in the silicon bulk should have an impact on the regeneration kinetics. A variety of comprehensive experiments were carried out within the BORNEO project.

The first question is, of course, where the hydrogen in the silicon bulk originates from. Fortunately, hydrogenated silicon nitride ($\text{SiN}_x\text{:H}$) deposited by PECVD (plasma-enhanced chemical vapor deposition) does not only passivate the surface, but also acts as hydrogen source releasing it during a high temperature (firing) step usually used for contact formation of screen-printed pastes. And this was one of the first lessons learned in the project: only fired $\text{SiN}_x\text{:H}$ coated samples do regenerate reliably [5,13]. Unfired samples do hardly show the regeneration effect [5,13], but it cannot be ruled out completely, as the $\text{SiN}_x\text{:H}$ deposition already injects a small amount of hydrogen into the bulk. In general, any hydrogen containing layer seems to work (PECVD $\text{SiN}_x\text{:H}$, ALD (atomic layer deposited) AlO_x [5,13]).

An obvious second question then is whether hydrogen may originate from other sources as well and still induces the regeneration reaction. The project answered that question as well. Hydrogen may, e.g., be introduced via a hydrogen plasma atmosphere and then the sample regenerates even without a hydrogen-rich dielectric layer and firing step [13].

Assuming hydrogen to be the key (and thus probably limiting) component in the regeneration process implies that increasing the hydrogen concentration in the silicon bulk should accelerate the regeneration process. And there are four logical ways to improve hydrogenation of the bulk from $\text{SiN}_x\text{:H}$ layers.

First, simply enlarge the reservoir of hydrogen by thickening the $\text{SiN}_x\text{:H}$ layer. And indeed it was shown that this approach works [14]. The same holds for the approach to use a hydrogen-enriched $\text{SiN}_x\text{:H}$ layer, meaning a different layer composition [5,15].

Second, do not hinder in-diffusion from a $\text{SiN}_x\text{:H}$ layer (or probably any hydrogen source) into the substrate by introducing a hydrogen diffusion barrier layer between the hydrogen source and the c-Si bulk. It could be shown that too thick AlO_x layers (at least 16 nm) slow down the regeneration process, whereas a thin AlO_x interlayer (at least up to 8 nm) does not influence the regeneration kinetics significantly, both compared to no AlO_x interlayer in between a $\text{SiN}_x\text{:H}$ layer and the crystalline substrate [5].

Third, increase the amount of hydrogen released from a $\text{SiN}_x\text{:H}$ layer (or probably any hydrogen releasing layer) by increasing peak temperature and duration of the firing step. Both methods have been proven to work separately [16].

Fourth, cool down the sample quickly enough so that hydrogen cannot effuse from the substrate anymore. This applies especially for the temperature range 700-550°C of the cool-down ramp where the release of hydrogen from the $\text{SiN}_x\text{:H}$ layer ceases and net hydrogen movement switches from in- to out-diffusion of the substrate [16].

3.3 Effect of tempering steps

In addition, it was shown that also the temperature regime 200-400°C has an influence on the regeneration kinetics. A tempering step prior to the regeneration process proved to be beneficial if the correct temperature/duration combination is chosen (e.g. 230°C, 15 min) [17]. However, treating the sample too long at a too high temperature (e.g. 350°C, 15 min) virtually switches off the regeneration reaction completely [16]. This behavior is interpreted in a way that hydrogen may be trapped in different bond states in silicon and only certain configurations may be pried open under regeneration conditions (carrier injection and temperature) to re-mobilize trapped hydrogen while others permanently retain hydrogen and thus reduce the hydrogen content available for the regeneration reaction [17].

3.4 Effect of injection level

Besides influencing the hydrogen concentration in the silicon bulk, increasing the injection level (quasi-Fermi level shifting) by light or external biasing during the regeneration process is a powerful tool to accelerate the regeneration reaction [9,10,11] even if this means using a laser [14]. However, it should be kept in mind that not only illumination intensity or external biasing determine the actual injection level, but also the operation conditions of a cell (e.g. open or short circuited) [9,10] and the effective substrate minority carrier lifetime (mix of actual bulk lifetime and effectiveness of passivation on both sides). This implicates that a well passivated lifetime sample, featuring a higher injection level than a poorly passivated one under constant generation, is expected to show an accelerated regeneration reaction and this effect could be proven as well [14].

This argumentation not only holds for passivation layers but also for emitter layers. A dielectrically passivated emitter layer typically provides inferior passivation as compared to a well passivating dielectric layer alone. Charge carriers get lost in the emitter region (emitter saturation current) meaning the overall injection level in the substrate drops and it could be shown that, as a result, the regeneration reaction slows down [14].

3.5 Effect of temperature

Last but not least, temperature during the regeneration process is maybe the most important parameter. Increasing the temperature generally speeds up the regeneration reaction as it is a thermally activated process, however, it should be kept in mind that other reactions are also boosted and it can be shown that the regenerated state of the BO related defect becomes increasingly unstable with rising temperature and converts back to the degraded or annealed state [7,11,17].

In consequence, the collective of BO related defects ends up in a mixed macroscopic state (mixture of defects in annealed, degraded and regenerated states) instead of all defects being in the desired regenerated state.

Not reaching a perfectly regenerated state is most probably not the aim of the regeneration process, but, perhaps even worse, the defects ending up in the annealed state begin again to switch to the degraded state under operation conditions of solar cells and the sample seems to degrade again even though it should be perfectly stable in the regenerated state. The above mentioned mechanism should never be confused with a general instability of the regenerated state itself leading to the next question.

4 LONG TIME STABILITY

The perhaps most frequently asked question (maybe the key question for industrial application) is whether the regeneration effect persists permanently (or at least for the module lifetime).

It is pretty hard to answer this question because obviously no one has tested it since 2006 for 25 years under real outdoor conditions and there exists no suitable and meaningful accelerated ‘aging’ test yet. On the contrary, one should keep in mind that the BO-related defect generally reacts to illumination and temperature and thus simply increasing light intensity and/or temperature will not yield a reasonable result.

Mid-term testing was done under illumination and slightly elevated temperature for a few days [3,4] to months [17] and instability of the regenerated BO species seems at least not to be a remarkable phenomenon. On the contrary, what was observed is that also passivation layers seem to suffer in the cause of time and it is still an unsolved issue to clearly separate where changes in lifetime (or electrical parameters) originate from [17].

5 BORON CO-DOPED P- AND N-TYPE SILICON

Even if it might seem contradictive at a first glance that n-type silicon suffers from boron-oxygen related degradation, there are two material classes which exhibit a certain boron content: n-type material which is co-doped with boron to compensate for segregation issues of phosphorous and UMG silicon exhibiting a multitude of dopant species. Furthermore, research in co-doped and compensated silicon grants another point of view on the boron-oxygen related degradation and regeneration as it allows, e.g., to decouple hole and dopant concentration.

It was found that regeneration occurs in co-doped n-type silicon as well and, if adequate process parameters are chosen, can lead to a stable regenerated state with virtually no BO related degradation even in n-type silicon [18,19]. However, compared to purely boron-doped material, regeneration kinetics is slower in n-type and also in compensated p-type silicon [18,19].

6 REGENERATION OF SOLAR CELLS

Studying a bulk lifetime effect in a complex system such as a solar cell does not seem to be reasonable if it can be done in a simpler system such as a lifetime sample. That is the reason why most publications

concerning fundamental issues deal with lifetime rather than electric parameters of solar cells. Then, however, the question is, to what extent the results are transferable to real solar cells and where adoptions have to be made.

For that purpose, two approaches have been followed. On the one hand, a comprehensive experiment was carried out, in which solar cells of different architecture are used: Al-BSF and PERC-type (the current industrial standards) [20]. On the other hand, simulations are used to explain and interpret the experimental findings [18].

Full area Al-BSF and PERC architecture differ mainly in one detail. In the PERC structure a dielectric passivation/reflector layer is inserted between the full area printed Al-paste and opened only locally to facilitate contact formation there. In practice, often layer stacks of thin oxide topped by thick $\text{SiN}_x\text{:H}$ are applied on the rear side featuring excellent passivation, and only contact area fractions of less than 10% are used.

This ‘small’ detail implicates a different firing behavior as compared to full area Al-BSF cells. The passivation of the full area Al-BSF cells results from the well known back surface (electrical) field due to the step in p-doping between the lowly B-doped substrate and the strongly Al-doped re-crystallized region formed during the alloying process of the Al-contact. The effectiveness of the BSF corresponds to the height of the step being determined by the solubility of Al in silicon. As the solubility increases with rising temperature, a higher peak temperature yields a better passivating BSF region and therefore full area Al-BSF cells tend to be fired at comparably high temperature (of course within the limits of the front side metallization).

Fortunately, this matches perfectly the suggestions for fast regeneration, and indeed these cells show the expected trend. Higher peak temperatures in the firing step result not only in a better electrical performance of full area Al-BSF cells, but also speed up their regeneration process [16,20].

The firing behavior of PERC-type cells depends on the used (rear side) passivation layer. It is known that thin AlO_x layers even ‘stabilized’ by a thicker $\text{SiN}_x\text{:H}$ layer tend to degrade by a too high peak temperature. Thus, this kind of PERC-type cells might better be fired at comparably lower temperatures to exploit its full potential. This trend opposes suggestions for a fast and reliable regeneration, and a trade-off between electrical performance and regeneration speed is necessary.

Nevertheless, experiments show that this kind of PERC cell regenerates more quickly than full area Al-BSF cells [20]. This is attributed to three main reasons: First, the substrate in a PERC structure with both sided $\text{SiN}_x\text{:H}$ layer is flooded by hydrogen from both sides thus hydrogen has to diffuse only half the distance. However, the lower peak temperature also reduces the amount of hydrogen released from the $\text{SiN}_x\text{:H}$ layers. From the experimental findings one can conclude that the eased hydrogen flooding seems to dominate. Second, the better passivation of the PERC structure implicates a higher injection level (under constant generation) speeding up the regeneration process.

This rather non-palpable higher injection level can be seen from the typically higher V_{oc} of PERC cells and the non-equilibrium mass action law

$$n \cdot p \approx \Delta n(p_0 + \Delta n) \approx n_i \cdot \exp\left(\frac{qV_{oc}}{kT}\right).$$

Third, as the regeneration process requires elevated temperatures, not V_{oc} at room temperature is relevant but V_{oc} at regeneration temperature T_{reg} (150 to 250°C). An extrapolation can be made according to the formula

$$V_{oc}(T_{reg}) = V_{oc}(25^\circ\text{C}) + \int_{25^\circ\text{C}}^{T_{reg}} \frac{dV_{oc}}{dT} dT$$

and thus not only $V_{oc}(25^\circ\text{C})$ but also the temperature coefficient dV_{oc}/dT is of importance. Therefore, it is also important to note that a higher V_{oc} at room temperature typically also implies a lower absolute temperature coefficient which can be seen from the formula

$$\frac{\partial V_{oc}}{\partial T} \approx -\frac{1}{T} \left(\frac{E_g}{q} - V_{oc}(T) \right)$$

Even though this argument is from a physics point of view already included in the second point, it is often forgotten when comparing cell structures.

6 CONCLUSIONS

In this contribution the current state of knowledge on the boron-oxygen related regeneration as it was investigated within the German BORNEO project is summarized. Conclusions are drawn regarding the application of the regeneration process to real solar cells, and not only lifetime samples as often used in fundamental experiments. It is found that, even though the basic properties of the regeneration process remain valid, real solar cells underlie different constraints due to their architecture and manufacturing process and have to be treated slightly differently. It is found and explained why PERC-type solar cells are better suited than full area Al-BSF cells.

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