PROPERTIES OF N-TYPE MULTICRYSTALLINE SILICON:

LIFETIME, GETTERING AND H-PASSIVATION

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ABSTRACT: This paper presents the characterisation of casted n-type mc-Si material using microwave detected photocurrent decay (µW-PCD) measurements of the minority charge carriers and other characterisation methods. The as-received material shows a very high average lifetime of the minority charge carriers (>100 µs), which confirms recent results on n-type mc-Si reported in the literature [1]. In particular, this paper focuses on material improvement by various gettering-techniques and by hydrogen-passivation. Application of these processes leads to effective charge carrier lifetimes of up to 220 µs averaged over the whole wafer. After testing different surface passivation methods for lifetime measurements, we found the PECVD SiN_x used at our laboratory to be bulk-passivating even without firing, therefore we chose iodine/ethanol-solution (I/E) for surface passivation in order to measure the real properties of the bulk. Boron-diffusion is considered to be the most destructive step during n-type cell-processing. We show that BBr_3-emitter diffusion is possible without degrading the carrier lifetime of the mc-Si material (and that the degradation occurring when using a spin-on-dopant with belt-furnace diffusion can be partially repaired by a subsequent phosphorous-diffusion.)
Keywords: n-type, multicrystalline Si, lifetime

1 INTRODUCTION

n-type mc-Si may become an important base material for solar cells in the near future. The supply of p-type Si feedstock for Si-photovoltaics partly originates from the off-spec material of the Electronic Industry (EI) and partly from idle capacity in expensive Si production plants developed for the EI. The continuous boom in the PV sector, a 44% growth between 2001 (391 MW_p) and 2002 (562 MW_p) [2], makes the introduction of new feedstock sources for the PV industry unavoidable to guarantee further unhindered growth.

The development of cost effective concepts for p^+nn^+-type solar cells on n-type substrates is an important issue as there is an additional amount of n-type off-spec Si material with the same abundance as the p-type material (approx. 2000 t/a) [3]. In addition, p^+nn^+-type solar cells have advantages compared to p-type technology, such as absence of boron-oxygen complexes and lower recombination activity of transition metal impurities (e.g. Fe) [4] . This is one reason for the very high carrier diffusion lengths occuring in n-type multicrystalline material, allowing the fabrication of highly efficient solar cells - even rear junction cells using thin substrates.

A part of the activities on n-type solar cell development by partners in the EC-supported NESSI-project is presented in this paper. The focus is on characterisation and material improvement in terms of charge carrier lifetimes by various gettering techniques and by H-passivation. Boron-diffusion plays an important role for n-type solar cell processing, as it is needed for emitter-diffusion. The effect of open-tube furnace diffusion using BBr_3 and belt furnace diffusion using spin-on dopant on effective minority charge carrier lifetime is tested.

2 EXPERIMENTAL TECHNIQUES

2.1 Material, lifetime measurements and gettering techniques

One column of an experimental 30 × 30 cm^2 phosphorus-doped ingot has been characterised at several positions from bottom to top. The specific resistivity ranges from 3.0 Ωcm to 0.5 Ωcm. While the carbon concentration – determined by FTIR spectroscopy – remains less than 10 ppma throughout almost the whole column, the interstitial oxygen-concentration does not drop below this level until the middle of the column, which is often characteristic for cast ingots.

The emphasis of the characterisation was on lifetime mapping (µW-PCD) of the minority charge carriers. The initial effective lifetimes were measured on the as-grown wafers after saw-damage removal using an acidic etch. A 0.1 molar I/E-solution was used for surface passivation for all lifetime measurements and, unless otherwise indicated, all lifetimes were averaged over a wafer area of 7×10 cm^2 and measured at a low injection level of 30×10^{12} photons × $(cm\ s)^{-1}$. 3 cm of the edge was not taken into consideration in these experiments because that area was affected by side effects from the crucible.

For our gettering- and passivation-experiments we chose neighbouring wafers located at 70% of the wap up the ingot. This region of the column has properties that are realistic and convenient for solar cell fabrication:

- specific resistivity around 1 Ωcm,
- oxygen concentration below 10 ppma.

We applied the following passivation- and gettering techniques to these wafers:

- passivation by microwave-induced remote hydrogen plasma (MIRHP),
- phosphorous-gettering,
- phosphorous gettering and subsequent MIRHP-passivation,
- aluminium-gettering.

The MIRHP-passivation was performed at 350°C for 1 h. The phosphorous-gettering consisted in a 50 Ω/sq $POCl_3$-diffusion and subsequent removal of the doped region by an acidic etch. For the aluminium-gettering, 2µm of Al was evaporated on one side and alloyed at 800°C during 30 minutes in a N_2-ambient. Afterwards the aluminium and the Si-Al-eutectic were etched away.

2.2. Selection of proper surface passivation

For a systematic lifetime determination, it was important to have a reliable surface passivation without changing the properties of the bulk. In preliminary examinations, the deposition of remote PECVD- SiN_x turned out to partly passivate the bulk at deposition temperatures of approximately 450°C, leading to about 40% higher effective lifetimes after removal of the SiN_x-layer.

For this reason, we used the I/E-solution to passivate the wafer-surfaces. On an I/E-passivated p-type FZ-Si reference wafer it was possible to measure effective lifetimes of τ_{eff} = 850 µs. This allows to estimate the surface recombination velocity, *S,* obtained using the I/E-solution.

If $S << D/W$, with W = wafer thickness = 300 µm, and $D \approx 30\ cm^2/s$ (diffusion constant of the minority carriers in p-type Si), we can use

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_{bulk}} + 2\frac{S}{W}$$

This leads to $S \leq$ 20 cm/s (S = 20 cm/s, assuming infinite bulk lifetime).
Consequently, using I/E-solution for surface passivation during lifetime measurements has two important advantages:

- it does not affect the bulk lifetime,
- the obtained S is very low: $S \leq 20$ cm/s.

The disadvantage, compared to SiN_x ,is that the passivation only remains stable for a few hours (Fig 1). If, after this time, the wafer has to be remeasured, the chemical cleaning procedure has to be repeated.

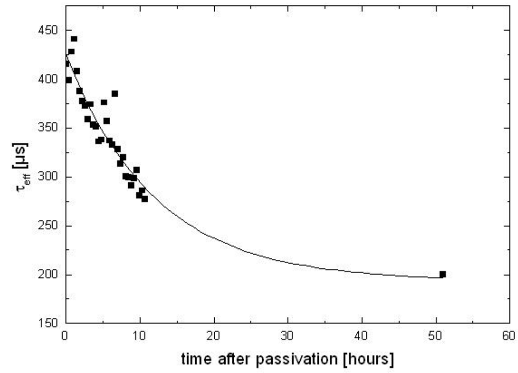

Figure 1: Degradation of I/E surface passivation with time

Figure 1 shows the results of different lifetime measurements on the same n-type Cz-Si wafer, whose surface has been passivated with I/E-solution a t = 0. It can be seen, that the measurements must be carried out within the first 2 hours to avoid an increase of *S* during the measurement.

3 RESULTS AND DISCUSSION

3.1 Gettering and H-passivation

The material casted by Deutsche Solar shows high initial carrier-lifetimes of >100 µs (Fig 3a). One fundamental reason for the requirement of high minority carrier lifetimes in n-type silicon – compared to p-type – is the lower mobility of the holes (for 1 Ωcm Si: $\mu_p \approx 1/3\mu_n$) which is – following Einstein's relation $D = \mu\ (kT/q)$ – equivalent to a lower diffusion coefficient. That means, for the same diffusion length, the lifetime of the holes needs to be three times higher than the lifetime of electrons in p-type Si. Such lifetimes, and even higher lifetimes, exceeding the factor of 3, can however be expected for n-type Si because of the absence of lifetime-reducing boron complexes (B-O), and lower recombination activity of transition metal impurities (e.g. Fe) [4]. This means that it should be possible to produce n-type mc-Si with diffusion lengths of the minority charge carriers exceeding those of the best measured on p-type material.

A summary of the experimental results of gettering and passivation is presented in Fig. 2. The effective lifetime for the untreated wafer – only the saw-damage has been removed – is 102 µs. It can be significantly improved by gettering or H-passivation. Aluminum-gettering proved to be the most effective gettering process (τ_{eff} = 220 µs). Note that the duration of gettering (30 minutes) was much longer than typical spike firing times the effect of P-gettering (same parameters as used for back surface field diffusion) on the lifetime is in the same order of magnitude (τ_{eff} = 204 µs) and was increased to 218 µs by an additional H-passivation step.

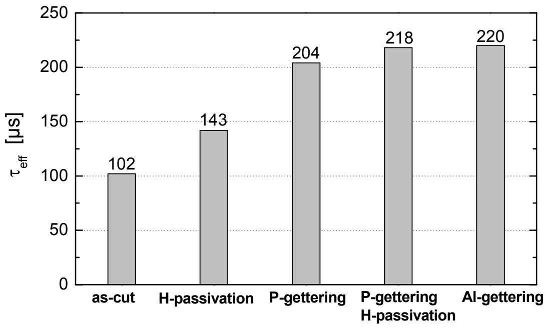

Figure 2: Overview: lifetime after gettering and passivation

As an example, two lifetime-mappings are shown in figure 3a (wafer as received) and figure 3b (wafer after Al-gettering).

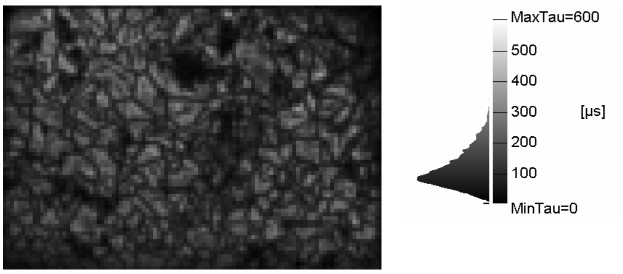

Figure 3a: Initial lifetime mapping (average: 102 µs) (size of the measured wafer-surface: 7×10 cm^2)

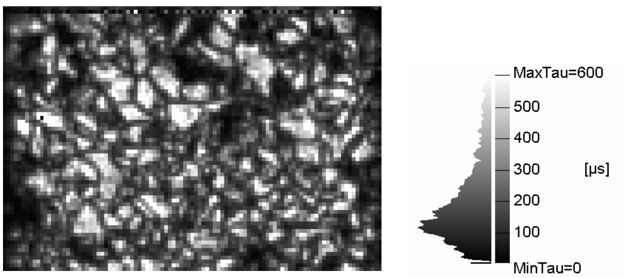

Figure 3b: Lifetime after Al-gettering (average 220 µs) (size of the measured wafer-surface: 7×10 cm^2)

Bright areas represent regions of high L_{eff} (τ_{eff}). A considerable number of grains showed strongly improved lifetimes after Al-gettering and lifetimes up to 600 µs were seen. Initially, the most frequently occuring lifetime was 80 µs, which increased to 115 µs after Al-gettering.

3.2 Effect of B-diffusion on material quality

The temperatures used for boron-diffusion in the electronic industry are usually above 1000°C, due to the smaller diffusivity of boron compared to phosphorous. In addition, the boron diffusion was thought not to have a gettering effect, unlike phosphorous which has been shown to partly compensate some degradation effects. Therefore, boron diffusion may be expected to degrade mc-Si.

We measured the bulk lifetime of a mc-Si wafer before (figure 4a) and after BBr_3-diffusion in an open-tube furnace (935°C for 1h - sufficient to obtain R_{sheet} = 50 Ohm/sq) and removal of the doped region (figure 4b). The average lifetime remained nearly unchanged, some areas showed even higher lifetimes after the diffusion. Since such high temperatures without any gettering will certainly cause some degradation of multicrystalline material (due to dissolution of impurity precipitates), this is a strong indication of gettering by the boron-silicide (boron-rich-layer) which was present in our diffusion conditions and which is supposed to have a gettering effect on electrical defects/metallic impurities.

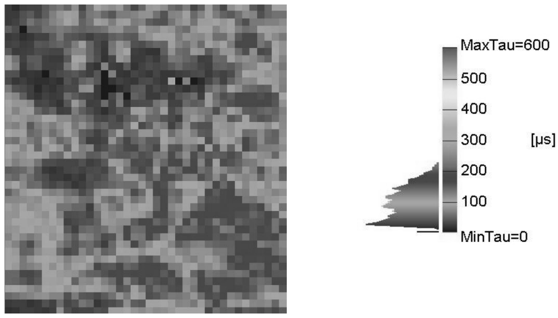

Figure 4a: Initial lifetime mapping: averaged τ_{eff} = 95 µs (size of the measured wafer-surface: 4×4.2 cm^2)

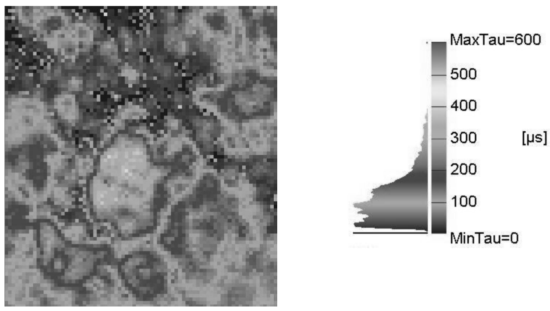

Figure 4b: Lifetime mapping after boron-diffusion: averaged τ_{eff} = 108 µs (size of the measured wafer-surface: 4×4.2 cm^2)

Application of boron spin-on dopant and diffusion in a belt furnace leads to degradation of the material and to diminished carrier lifetimes. In our experiments so far, this degradation is only slightly reversible; the bulk-lifetime can be recovered somewhat by phosphorous-gettering. A detailed study of the different responses of p-type and n-type mc-Si to gettering and also to hydrogenation is underway.

4 CONCLUSION AND OUTLOOK

We showed that n-type mc-Si has high minority charge carrier lifetimes and diffusion lengths. Starting from an initial value of 100 µs, the carrier lifetime was improved to values up to 220 µs by applying gettering techniques that are used in standard solar cell processes (Al- and P-gettering). This corresponds to a diffusion length of 470 µm. With this diffusion length, the quality of the material is even sufficient to make efficient rear junction cells on thin substrates. It is remarkable that the increase of the lifetime concerns the largest part of the wafer area.

In addition, it has been shown that PECVD- SiN_x can change the bulk properties of n-type mc-Si even when not fired. This has to be taken into account for all investigations aiming to determine the influence of solar cell processing steps on bulk lifetime.

The influence of the starting material (quality and dopant type) and the PECVD parameters on the bulk passivating effect of PECVD SiN_x will be investigated in detail.

Fabrication of BBr_3 diffused n-type mc-Si cells using a high-efficiency processe is in progress. Lifetime-measurements after different processing-steps will be performed to monitor the improvement or degradation through these processes. Particularly the effect of BBr_3-diffusion with creation of a boron-silicide (or boron-rich) layer, which our results presented above showed to have a gettering effect, will be tested.

Solar cells based on the tested material have been processed using two different solar cell approaches (front junction and rear junction cells). Details on solar cell processing and solar cell characterisation can be found in two additional contributions to this conference [5],[6]. This work confirms the potential for new solar cell concepts based on high bulk lifetime using n-type mc-Si. Recently produced ingots showed initial lifetimes of 120 µs averaged over 12.5 × 12.5 cm^2, which corresponds to L_{eff} = 360 µm.

ACKNOWLEDGEMENTS

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