RAPID THERMAL PROCESSING: A COMPREHENSIVE CLASSIFICATION OF SILICON MATERIALS

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ABSTRACT

Depending on the specific impurities and defect spectrum of a silicon material, the minority carrier lifetime can react diversely to Rapid Thermal Processing (RTP). We have measured the lifetime of silicon materials before and after RTP and have diffused solar cells either by RTP or by conventional quartz tube furnace processing (CFP). Our investigations show that the lifetime of Fz-Si can be preserved during RTP resulting in up to 18.7 % efficient solar cells. For 1.4 Ωcm PV-grade Cz-Si, the stable lifetime after light degradation could be improved by up to 60 % by RTP. In the case of EFG-Si, the same average cell efficiency was obtained with RTP diffusion as with the industrial reference diffusion process. However, in the case of block-cast mc-Si, the lifetime decreases with increasing diffusion temperature indicating that P-diffusion in the second range might provide insufficient gettering.

INTRODUCTION

For the next generation of solar cell manufacturing, RTP for diffusion, oxidation and contact formation is definitely an option. RTP is characterized by extremely short process times down to a few seconds and high heating and cooling rates in the order of 100 K/s. Several authors have reported an acceleration of some thermal processes like phosphorus diffusion and oxidation due to the incident UV part of the utilized incoherent electromagnetic spectrum. In general RTP implies processing at higher temperatures than in conventional quartz tube furnace processing to achieve the same thermal result in several seconds instead of minutes or hours. Depending on the specific impurities and defect spectrum of a material, it is not obvious to know, a priori, how the bulk lifetime will be affected by RTP. The objective of this work is to classify various silicon materials according to their reaction to RTP, i.e. to assess whether the bulk lifetime of the as-grown material is reduced, preserved or even improved. Furthermore, we compare CFP-diffused with RTP-diffused solar cells to assess which thermal process is optimal for a given material and to show the compatibility of RTP with the fabrication process.

EXPERIMENTAL PROCEDURES AND RESULTS

We have investigated four different silicon materials: float zone (FZ) of Wacker, Czochralski (Cz) of Deutsche Solar, edge-defined film-fed growth (EFG) of ASE Americas [1] and directionally solidified block cast multicrystalline Si (ds-mc-Si) of Deutsche Solar [2]. The bulk minority carrier lifetime of these materials was measured before and after different RTP processes. Furthermore, solar cells with a n^{++}-p-p^{+}-structure have been processed either by RTP diffusion or by well established CFP diffusion. Except for the diffusion step, the cells have otherwise been processed identically. Details of sample preparation are given below. All the applied RTP processes featured high heating and cooling rates in the range of 100 K/s.

Float zone silicon

Fz-Si (1.25 Ωcm) with carrier lifetimes exceeding 1 ms was used for the experiments. It is known that the lifetime of FZ-Si can be preserved during conventional high temperature processing if slow cooling rates in the range of a few degrees per minute are applied. The objective of this work was to investigate whether these high lifetimes can be also preserved in the case of RTP using steep cooling ramps close to quenching. At first, Rapid Thermal Diffusion (RTD) of phosphorus was investigated. The plateau temperature during which the actual diffusion takes place was set to 900 °C. The plateau time was varied from 5 to 240 s in order to yield a variety of emitter sheet resistance usable for evaporation or screen printing of front contacts. As a P-source, the highly concentrated Filmtronics P509 dopant was spun-on on the front whereas the back side remained uncoated. After diffusion the phosphorous silicon glass (PSG) and the emitter were etched off. Afterwards, both surfaces were passivated by PECVD-SiN_x yielding surface recombination velocities of about 10 cm/s. Thus, the effective lifetime τ_{eff} measured by microwave-detected photoconductance decay (MW-PCD) is close to the actual bulk lifetime. As can be seen in Fig.1, τ_{eff} is similar to the value of the undiffused reference wafer regardless of the diffusion time. It seems that no degradation occurs during the diffusion at 900 °C. The small differences in τ_{eff} are linked to process induced variations in the surface recombination velocity.

To improve the cell efficiency, front passivation by Rapid Thermal Oxidation (RTO) has been implemented in our cell process. We have taken into account the decrease of R_{sheet} during the RTO step because of the activation of inactive P in the surface region. Prior to RTO, the PSG was removed in HF but no additional surface clean was applied. According to Fig. 1, the lifetime has not been degraded even after the 30 s RTO step at 950 °C.

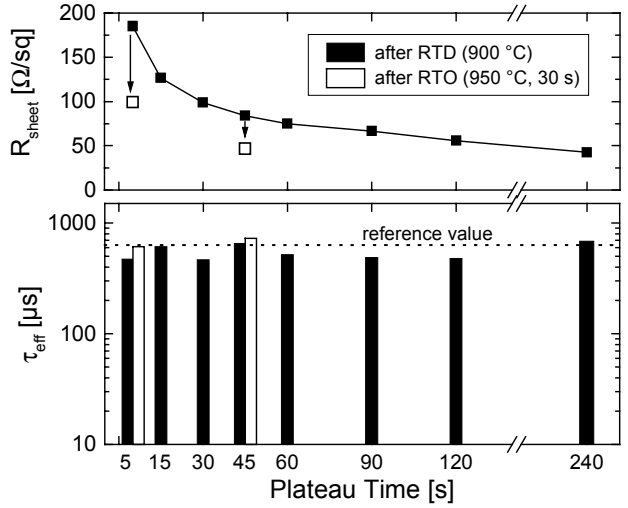

Fig. 1: Evolution of the emitter sheet resistance R_{sheet} and of the effective lifetime τ_{eff} of 1.25 Ωcm Fz-Si samples after RTD and subsequent RTO.

Table I: τ_{eff} of 1.25 Ωcm Fz-Si after RTO at 1050 °C and surface passivation by PECVD-SiN_x.

	Plateau time [s]			
	reference	60	120	180
τ_{eff} [µs]	640	590	620	690

To check if the applied temperatures are too low to detect quenching induced degradation we have carried out RTO at temperatures as high as 1050 °C. As reported in Table I, high lifetimes are preserved even at these high temperatures giving no indication of RTP induced degradation.

We have developed a solar cell process sequence using solely RTP for high temperature steps, i.e. for emitter diffusion, emitter oxide passivation and for rapid thermal alloying of screen-printed Al for formation of a back-surface-field (BSF). The overall high temperature process time is below 2 minutes. The complete sequence was described in [3]. For the 1.25 Ωcm Fz-Si, conversion efficiencies up to 18.7 % have been obtained (cell features evap. front contacts and a double AR-layer).

In summary, the results presented so far demonstrate that the high bulk lifetime of FZ-Si can be preserved during the fabrication of solar cell relevant layers by RTP despite heating and cooling rates of 100 K/s. In this case the maximum achievable efficiency depends rather on the quality of the layers than on the bulk lifetime.

Directionally solidified block cast mc-silicon

The RTD induced changes in the bulk lifetime of mc-Si have been investigated for neighboring wafers from the middle part of an ingot. The objective was to see whether an improvement of the material can be achieved by RTD (e.g. by P-gettering). The wafers were diffused at different temperatures T_{diff} ranging from 860 to 1000 °C. The diffusion time t_{diff} was adjusted to obtain similar emitter sheet resistance (100 Ω/sq). From 860 to 950 °C, we used the Filmtronics spin-on dopant P509 and from 950 to 1000 °C the less concentrated P507 source. The back surface remained uncoated. After RTD the PSG and the emitter were etched off, then both surfaces were passivated by deposition of a PECVD-SiN_x layer. We can not exclude that some hydrogen passivation of the bulk took place during the PECVD surface passivation but we assume this effect to be negligible. The effective lifetime was measured spatially resolved with MW-PCD. The mappings were carried out at 0.5 sun bias illumination with a laser intensity of $1x10^{14}$ photons/cm^2 per pulse.

The distribution of the spatial lifetime is plotted in Fig. 2. Compared to the as-grown reference, the diffused samples exhibit much wider distributions. According to the mappings (not shown here), the grain boundaries become more distinct after diffusion. In areas with low initial lifetime, small grains and a high density of grain boundaries prevail. In these areas the lifetime decreases further after RTD, whereas in areas of large grains and higher starting lifetimes the lifetime increases as long as T_{diff} < 920 °C.

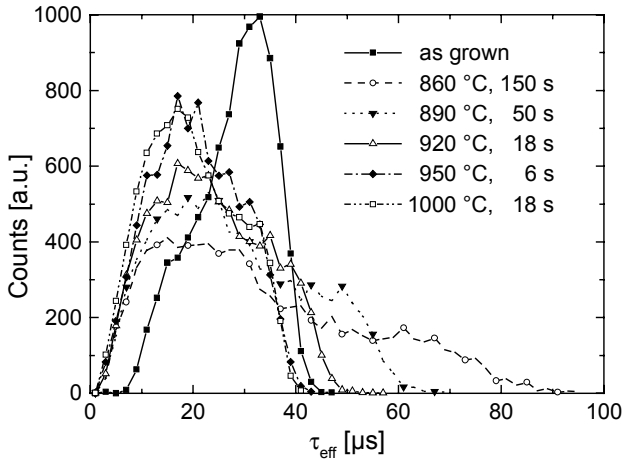

Fig. 2: Distribution of the spatially resolved lifetime of neighboring block cast mc-Si wafers after different RTD.

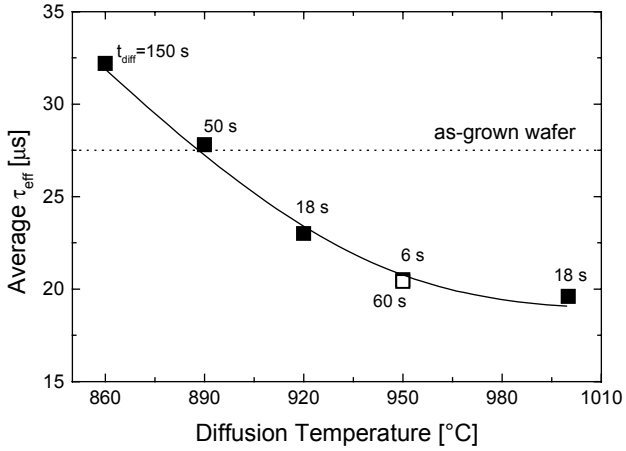

Fig. 3: Average lifetime of the samples from Fig. 4. The two values for 950 °C were obtained by switching from a highly concentrated P-source to a less concentrated one.

The largest improvement of these "good" areas is obtained with the lowest T_{diff} (860 °C) and thus the longest t_{diff} (150 s). As shown in Fig. 3, the average lifetime drops below the mean lifetime of the as-grown wafer already for T_{diff} >900 °C and the respectively short t_{diff}. This means that real RTP with diffusion times in the range of seconds might be too fast to provide the desired lifetime improvement (e.g. by P-gettering of lifetime-limiting impurities).

Boron-doped Czochralski silicon

The lifetime of oxygen-rich p(boron)-type Cz-Si is significantly reduced by illumination or carrier injection until a state of stable lifetime is reached, e.g. after 30 h of illumination under one sun. It is known from recent studies that the underlying defect is correlated with the boron and oxygen content. In the case of CFP it has been shown that the defect concentration can be reduced, resulting in an increased stable lifetime [4]. In a recent paper we have demonstrated that the stable lifetime can be improved by Rapid Thermal Annealing (RTA) as well [5].

The purpose of this work was to study the effect of RTD of P on the stable lifetime of 1.4 Ωcm PV-grade Cz-Si. RTD was performed for 40 s at temperatures ranging from 875 to 1025 °C. Using these RTD parameters and varying the P-concentration of the spin-on dopant, the emitter sheet resistance can be adjusted in a wide range from below 20 up to 200 Ω/sq. After RTD, the PSG and the emitter were etched off and surfaces were passivated by PECVD-SiN_x. Lifetimes were measured by MW-PCD after at least 30 h of illumination induced degradation under 1 sun intensity.

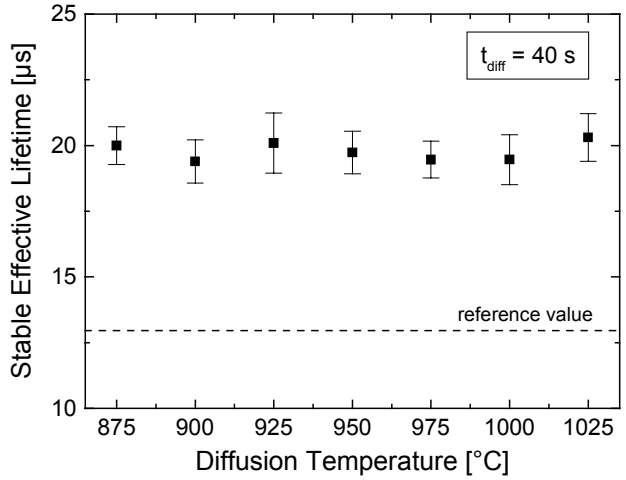

Fig. 4: Stable effective bulk lifetime of RTP P-diffused 1.4 Ωcm Cz-Si after light induced degradation.

Fig. 4 reports the stable effective lifetime as a function of the diffusion temperature. Compared to a non-diffused reference sample the lifetime is improved by 50 to 60 % regardless of the diffusion temperature. We have fabricated solar cells of this Cz-Si according to our standard process sequence described using RTP for P-Al-co-diffusion, RTO for emitter passivation and photolithographically defined front contacts. The best cells exhibit stable efficiencies up to 16.9 %.

Edge-defined film-fed grown silicon

Solar cells were made from EFG-Si (cut into pieces of 5x5 cm^2) according to a laboratory process (see [6] for details) with P-Al-co-diffusion and evaporated front contacts (R_{sheet} ≈100 Ω/sq). The diffusion was carried out either by CFP ($POCl_3$ at 820 °C for 1h) or by RTP (T_{diff} >900 °C, t_{diff} <40 s). Eight cells were prepared per group. It has to be noted that the CFP process has proven to provide excellent gettering in case of block-cast mc-Si yielding cell efficiencies up to 17.4 % [7].

Table II: Average parameters of solar cells made from EFG-Si, P-Al-co-diffused either by RTP or by CFP.

Process		V_{OC} [mV]	J_{SC} [mA/cm^2]	FF [%]	η [%]
CFP		499.4	18.0	73.5	6.6
	+ RPHP	514.6	18.47	74.7	7.1
	+ ARC	533.5	28.22	73.9	11.1
	best cell	*546.0*	*29.8*	*76.3*	*12.4*
RTP		530.7	20.65	76.4	8.4
	+ RPHP	542.3	21.32	76.9	8.9
	+ ARC	554.3	30.66	77.0	13.1
	best cell	*558.3*	*31.8*	*76.4*	*13.6*

In Table II, the average cell parameters after cell completion and after H-passivation (RPHP) and AR deposition are given. All average cell parameters of the RTP cells are significantly higher than those of the CFP cells after each stage of processing. The RTP cells exhibit relatively high performance prior to H-passivation. Since the process of H-passivation was not optimized for EFG, the CFP cells did not improve in the way they usually do (e.g. in production). We know from Fz-Si reference samples that the difference in efficiency can not be attributed to a superiority in cell design, i.e. emitter or Al-BSF. A first hint can be drawn from spectrally resolved light beam induced current measurements (SR-LBIC, see [8]).

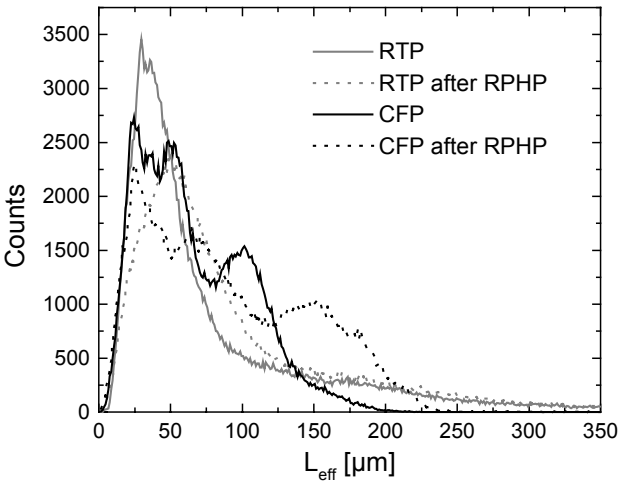

Fig. 5: Distribution of the local effective diffusion length L_{eff} measured by SR-LBIC for the best cells of Table II.

In Fig. 5, the distribution of the effective diffusion length L_{eff} of the best CFP and the best RTP cell from Table II is plotted. It is stretched towards higher values in the case of RTP. This observation holds for the distribution before and after H-passivation. Noticeably, only RTP cells exhibit regions of L_{eff}>250 µm already prior to H-passivation which might explain the surprisingly high efficiencies at that stage.

In a previous publication [6] we had presented the first results of the attempt to implement RTP into the solar cell production sequence of RWE Solar. The P-Al-co-diffusion had been replaced by a one sided P-diffusion. R_{sheet} had been decreased to meet the demands of the industrial contact formation process. At RWE Solar the contacts are formed by co-firing of the Ag front grid through SiN_x:H and the Al back contact to achieve an efficient H-passivation [9]. The first results had indicated that the RTD emitter profile had to be adjusted to the contact formation process or vice versa. For this reason, in a close co-operation with RWE Solar we have designed various RTD emitter profiles by varying the P-source, the diffusion temperature and the diffusion time. For each type of emitter RWE Solar slightly adjusted the contact formation process for optimization.

Table IV: Mean parameters of EFG solar cells diffused either by RTP at the FhG-ISE or by the reference process at RWE Solar. All cells were finished at RWE Solar.

Emitter	V_{OC} [mV]	J_{SC} [mA/cm²]	FF [%]	η [%]
RTD (T>900°C, t =60 s)	585.4 (± 5.1)	31.1 (± 0.6)	75.2 (± 0.7)	13.7 (± 0.4)
RTD (T<900°C,t =300 s)	592.5 (± 4.8)	31.8 (± 0.6)	74.8 (± 1.4)	14.1 (± 0.5)
Reference of RWE Solar	589.3 (± 3.7)	31.7 (± 0.6)	74.9 (± 1.2)	14.0 (± 0.3)

According to Table IV, with 300 s RTD we have achieved the same average cell efficiency as with RWE Solar´s standard diffusion. The 60 s RTD yields high fill factors but slightly lower Voc and Jsc than the reference. At the moment we are not sure if this is caused by a somewhat higher P-doping or by a lower bulk lifetime. So far, the best RTD-EFG-cell has exhibited an efficiency of 14.6 %. The results indicate that RTD might be implemented into the industrial process sequence without sacrificing cell efficiency.

CONCLUSIONS

In this work various silicon materials have been classified according to the change of their bulk lifetime after RTP. We have shown that the high bulk lifetime of Fz-Si can be preserved during RTP. By the application of RTD, RTO and Al-BSF formation by RTP-alloying of screen printed Al we have achieved efficiencies of up to 18.7 %. On the contrary, block cast mc-Si seems to react rather negatively to RTD. With increasing diffusion temperature the average lifetime decreases and above 900 °C it drops below the initial lifetime. Obviously, RTD with diffusion times in the second range is too fast to provide the desired lifetime improvement. However, the stable lifetime after light degradation of 1.4 Ωcm PV-grade Cz-Si is increased by more than 60 % by RTD. So far, our best all-RTP-processed Cz solar cell has exhibited a stable efficiency of 16.9 %. Another material which reacts positively to RTP is EFG-Si. By adjusting the RTP emitter profile and the industrial contact formation process, the same average cell efficiency was obtained as with the industrial reference diffusion process. This indicates that EFG-Si is suited for RTP, what could lead to a significant reduction of the diffusion time in production.

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