

HYDROGEN PASSIVATION OF RIBBON SILICON – ELECTRONIC PROPERTIES AND SOLAR CELL RESULTS

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ABSTRACT

Hydrogen bulk passivation of crystal defects plays a major role during solar cell processing of multicrystalline ribbon silicon material. In this study we concentrate on the diffusion and effusion kinetics of hydrogen in different ribbon silicon materials (RGS (Bayer AG), EFG (ASE), String Ribbon (Evergreen Solar)). Electronic properties like majority charge carrier mobility and concentration were investigated by temperature dependent Hall measurements. Deuterium profiles determined with the SIMS method reveal that the diffusion velocity is strongly linked with the interstitial oxygen concentration present in the different materials. Taking into account these results, a confirmed record high efficiency of 12.5% on Bayer RGS silicon (4 cm²) was achieved with an optimized hydrogen passivation step.

INTRODUCTION

During the last years a shift from monocrystalline towards multicrystalline silicon wafers in PV has been observed. This tendency resulted in the fact that the largest fraction of solar cells is now made from multicrystalline silicon wafers (standard cast, Bridgman-type and ribbon) [1]. These materials are becoming increasingly interesting because the gap in efficiency compared to monocrystalline wafers could further be decreased in industrial type processes. This development was possible not least because of material improvements on the wafer manufacturer's side and the incorporation of bulk defect passivation steps during solar cell processing on the cell manufacturer's side. Bulk passivation is normally done by the incorporation of atomic hydrogen into the silicon bulk via a hydrogen rich SiN_x layer which simultaneously serves as an antireflection coating (ARC) and reduces the surface recombination velocity [2]. These bulk passivation steps become even more important in ribbon silicon wafers, which might be the dominating materials of the future.

In this study we focused on three different types of ribbon silicon materials and tried to investigate the diffusion kinetics of hydrogen in the silicon bulk and their impact on electronic properties and solar cell parameters. The method chosen for passivation is the microwave induced remote hydrogen plasma (MIRHP) passivation, which already proved to be very effective in passivating defects in multicrystalline silicon [3,4].

RIBBON SILICON MATERIALS

The boron doped p-type materials under investigation are EFG (Edge-defined Film-fed Growth) from ASE [5], SR (String Ribbon) from Evergreen Solar [6] and RGS (Ribbon Growth on Substrate) from Bayer AG [7]. EFG and SR are already produced commercially, while RGS is still in the R&D phase with a pilot plant under development. All ribbon materials have in common that no silicon losses occur due to sawing of the ingots, which make up to 50% in the case of standard cast or Bridgman-type multicrystalline silicon.

For EFG and SR the directions of pulling and crystallization are anti-parallel to each other. Therefore the pulling velocity v_p is limited by the crystallization velocity and is in the range of several centimeters per minute. Another approach is followed in the case of RGS. In this case the directions of pulling and crystallization are nearly perpendicular to each other and a decoupling of the corresponding velocities is possible, allowing pulling speeds leading to 1 wafer/s. This means a much faster (and therefore more cost effective) wafer production.

The advantage of a more economic material consumption for ribbon silicon has to be faced with a higher crystal defect density in the silicon bulk. Grain boundaries and non-uniform dislocation densities as well as impurities (mainly carbon and/or oxygen) can influence charge carrier lifetimes, diffusion lengths L_{diff} and solar cell parameters. Especially in RGS the high oxygen concentration present has to be handled during wafer crystallization by choosing appropriate temperature ramps (slow or fast) resulting in two 'different' materials which can be distinguished by their interstitial oxygen content [O_i] [8]. Table 1 gives a survey of some material properties.

Table 1: Some properties of the multicrystalline ribbon silicon materials used in this study.

Material	EFG	SR	RGS slow	RGS fast
v_p [cm/min]	1.8	1-2	600	600
Grain size	1-2 cm	1-2 cm	<1 mm	<1 mm
$[O_i]$ [10^{17} cm^{-3}]	<1	<0.5	3-7	20-30
$[C_s]$ [10^{17} cm^{-3}]	10	4	10	10
L_{diff} [μm]	20-100	20-100	<20	<20

ELECTRICAL TRANSPORT PROPERTIES

Electronic transport properties of the majority charge carriers have been determined by temperature dependent Hall measurements. In Fig. 1 Hall mobilities of four samples corresponding to the materials shown in Table 1 are given including a monocrystalline reference (FZ Si). As already observed in earlier studies an anomalous minimum in mobility can be seen at temperatures around 100-200 K. This behaviour is typical for small-grained multicrystalline silicon and can be explained with the assumption of acceptor-like traps at grain boundaries [9].

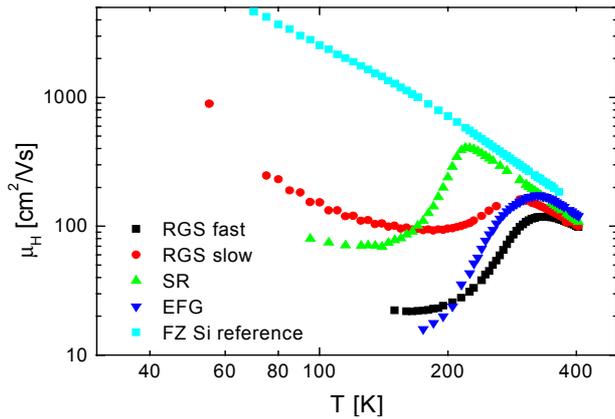


Fig. 1: Hall mobilities of as grown ribbon silicon compared to a monocrystalline reference.

After a MIRHP passivation step samples originating from the same wafers as those shown in Fig. 1 were measured. The results can be seen in Fig. 2.

For all materials the minimum observed in as grown samples has disappeared. This indicates, that the underlying defect level responsible for the observed minimum can be passivated by atomic hydrogen. In the case of RGS the MIRHP passivation was carried out at two different temperatures. While for RGS slow the defect level seems to be fully passivated at a lower temperature (375°C), the minimum in RGS fast vanishes only when a higher temperature (425°C) and a longer passivation time

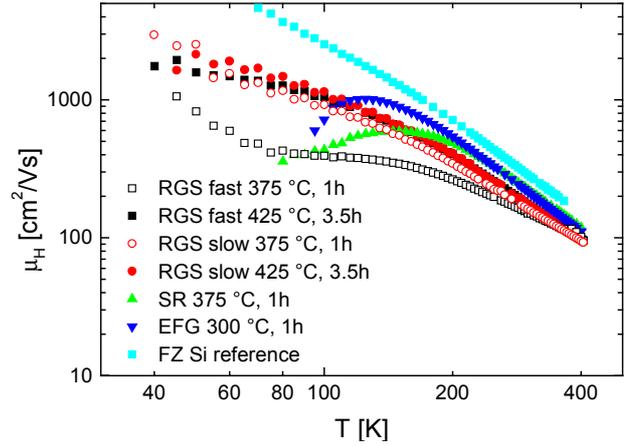


Fig. 2: Hall mobilities of MIRHP passivated ribbon silicon compared to a mono Si reference.

is applied. This indicates, that H-diffusion inside the silicon bulk is influenced by the interstitial oxygen concentration, as this is the only difference between the two RGS materials (Table 1).

After MIRHP passivation the ribbon silicon mobility graphs run parallel to the one of the reference sample, but the absolute values are still significantly lower (up to a factor of three). This can be explained by still present neutral defects (e.g. dislocations) which show no temperature dependence for carrier scattering.

While the temperature dependent majority charge carrier concentration p is not influenced by the H-passivation, the conductivity σ is connected to the mobility μ via

$$\sigma = e \cdot p \cdot \mu_p$$

Therefore σ changes after H-passivation as shown in Fig. 3. The change in σ at room temperature can thoroughly be of a factor of 2 as can be seen for the EFG sample in particular. This influences the electronic

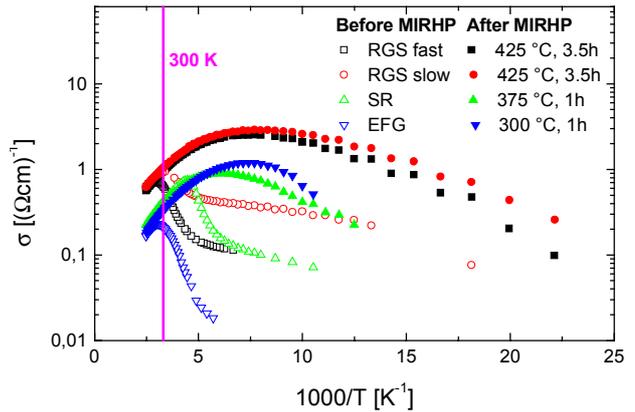


Fig. 3: Conductivity σ before and after MIRHP passivation in ribbon silicon samples originating from the same wafers respectively.

behaviour of the H-passivated solar cell after cell processing. As the experiment was a single shot for each material under investigation, no precise comparison can be carried out because of the poor statistic and the material inhomogeneities (especially for EFG and SR wafers where 'good' and 'bad' areas exist side by side).

DEUTERIUM PROFILES

Diffusion profiles have been determined by SIMS (Secondary Ion Mass Spectroscopy) measurements. As hydrogen cannot be detected in the desired concentration because of residues in the sample chamber, the passivation has been carried out using deuterium (D). D shows no difference in chemical behaviour compared to H, the only difference is the higher mass which leads to a reduced diffusion constant D by a factor of $1/\sqrt{2}$.

For RGS slow and fast the results of different MIRDP passivations are shown in Fig. 4. The samples descend from the same wafers respectively. As the four samples of RGS fast seem to be very homogeneous, RGS slow exhibits more variations on the wafer level. Nevertheless, by comparing the respective passivations for RGS fast and slow a faster diffusion and therefore a higher penetration depth of D is visible for RGS slow with a lower interstitial oxygen concentration.

In the case of EFG material, which is shown as a reference in Fig. 4 the D concentration is in the range of the detection limit (10^{15} cm^{-3}).

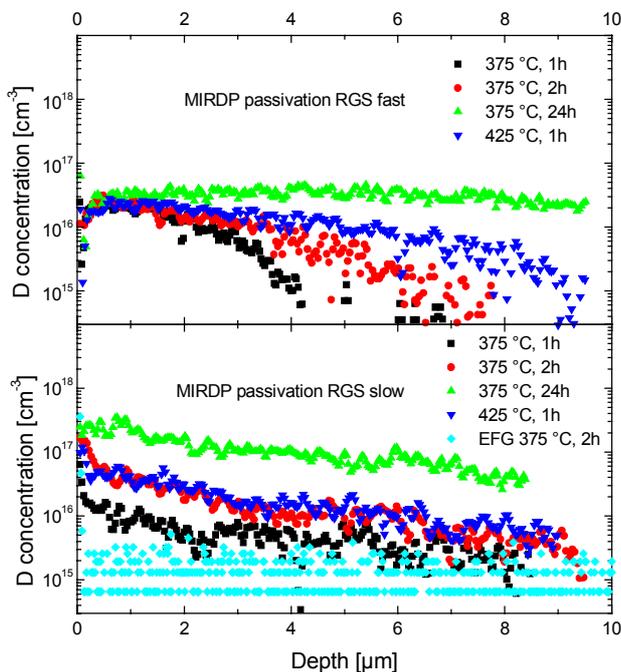


Fig. 4: D concentration profiles determined by SIMS measurements for RGS fast (high $[O_i]$, top) and RGS slow (less $[O_i]$, bottom) with EFG as a reference (carried out in collaboration with Bayer AG, Uerdingen, Germany).

HYDROGEN DIFFUSION AND EFFUSION

A comparison between EFG and RGS material concerning diffusion kinetics on a solar cell level has been shown previously [10,11]. In this former studies the behaviour of J_{sc} has been investigated for different MIRHP passivation temperatures and times. It was clearly visible that EFG can be fully passivated at lower temperatures and comparably short passivation times. We believe that this is mainly due to the very low oxygen content in EFG material.

Results of hydrogen effusion out of EFG cells without antireflection coating acting as a barrier are also given in [10]. There it could be shown that effusion starts at relatively low temperatures $>325 \text{ }^\circ\text{C}$. First results within the present study for RGS indicate that effusion from the bulk can be neglected for temperatures below $400 \text{ }^\circ\text{C}$ and significantly begins to occur at temperatures above $450 \text{ }^\circ\text{C}$. This indicates once more that hydrogen diffusion is slowed down in RGS. We believe that this is due to the higher content of (decorated) lattice defects (dislocations, grain boundaries) especially because of the high oxygen concentration either in the form of New Donors (RGS fast) originating from the high initial interstitial oxygen concentration and formed after cell processing between $600 - 900 \text{ }^\circ\text{C}$ or in the form of large precipitates (RGS slow) formed during the slow cooling down after crystallization.

SOLAR CELLS

With the obtained results our standard solar cell process used for ribbon silicon solar cells could be adapted to the properties of the different ribbon silicon materials. For RGS this process includes a mechanical texturing of the wafer surface [12], and an optimised MIRHP passivation step carried out before photolithographical metallization. The confirmed efficiencies of 12.5% for several cells represent by far the highest values obtained on RGS material. In the case of EFG and SR we expect to present higher efficiencies soon, as the values listed in Table 2 have been obtained by using not state-of-the-art material and a not yet fully optimized cell process.

Table 2: Highest efficiencies obtained on ribbon silicon solar cells (4 cm^2) including a MIRHP passivation step (* confirmed measurement at JRC calibration lab).

Material	Surface	Efficiency
RGS slow	Mechanically textured	12.5%
EFG	Flat	14.5%
SR	Flat	14.5%

CONCLUSION

Hydrogen passivation of crystal defects plays an important role during solar cell processing of ribbon silicon. Normally bulk passivation in industrial type multicrystalline cell processes is done via a hydrogen rich SiN_x ARC. In this paper we presented a study investigating the kinetics of hydrogen diffusion in ribbon silicon and their influence on transport properties and solar cell parameters using MIRHP passivation.

We observed a strong dependence between passivation velocity and interstitial oxygen concentration [O_i]. RGS material with a high [O_i] needs higher passivation temperatures and/or longer passivation times as compared to RGS material with a lower [O_i]. EFG and SR can be passivated at even lower temperatures which could be explained by their very low [O_i].

The conductivity σ can be significantly increased after H-passivation even at room temperature because of the enhanced mobility. This effect nearly doubles σ at room temperature for the EFG sample.

An optimization of the MIRHP passivation step within the solar cell process leads to confirmed record high efficiencies for RGS solar cells of 12.5%.

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