Comparison between SiN x :H and hydrogen passivation of electromagnetically casted multicrystalline silicon material

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COMPARISON BETWEEN SiN_x:H AND HYDROGEN PASSIVATION OF ELECTROMAGNETICALLY CASTED MULTICRYSTALLINE SILICON MATERIAL

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Abstract

This work intends to compare two different passivation methods for electromagnetically continuous pulling silicon (EMCP): remote plasma hydrogenation and remote plasma enhanced CVD of SiN followed by high-temperature sintering. All experiments are carried out on textured and non-textured EMCP samples from the same ingot. To check the effect of high-temperature diffusion on EMCP, a n^+-emitter is formed on one group of the samples using $POCl_3$ diffusion. Passivation capabilities of both techniques are checked using measurements of minority carrier lifetime by means of microwave photoconductance decay mapping. Solar cells are made to compare lifetime measurement with cell parameters.

Keywords: EMCP, SiN, Passivation, PECVD, Hydrogenation

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1. Introduction

Electromagnetically continuous pulling silicon (EMCP) [1] appears to be one of the solutions to meet the increasing production rates in photovoltaic industry. It can show high level of production and usually exhibits lower impurity concentrations than conventional casting material (such as POLIX, BAYSIX,…), especially considering O and Fe impurity levels [2]. However EMCP material exhibits smaller grains and higher dislocation density.

Hydrogen passivation is an essential step in multicrystalline silicon solar cell processing particularly if a low quality material like EMCP is used. It can be introduced by different well-known techniques [3]: deposition by PECVD of a H-buffered silicon nitride layer followed by an annealing step, or microwave induced remote hydrogen plasma passivation (MIRHP). This work intends to compare these two different hydrogen passivation methods applied to EMCP. Passivation capabilities of both techniques are verified using measurements of minority carrier lifetime by means of microwave photoconductance decay mapping. Solar cells are also prepared to study the influence of silicon nitride deposition on the cell parameters.

2. Experimental procedure

2.1 Material

The samples are 10×10 cm² multicrystalline silicon wafers made by electromagnetically continuous pulling (EMCP). They come from the same ingot (M20) produced by EPM-Madylam (Grenoble, France) [4]. This material has already shown a degradation of its electronical properties during $POCl_3$ diffusion: there seems to be no gettering effect [5].

The wafers are 250 µm thick, with a resistivity of around 1 Ωcm. After saw-damage removal half of the samples are KOH-texturised. One part of the samples undergo standard $POCl_3$ diffusion, as described in [7]. Samples are then diced into 5x5 cm², and are submitted to different treatments (see Fig. 1).

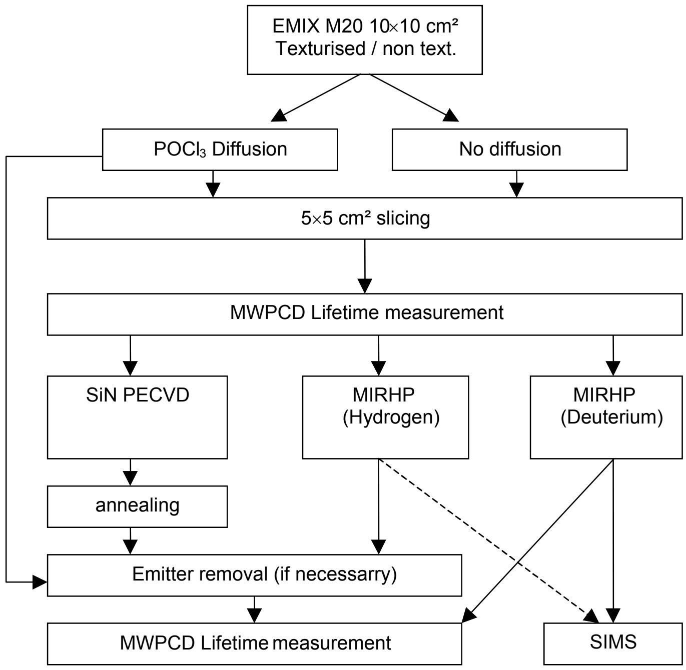

Fig. 1: PECVD experiments diagram.

To check the effect of high-temperature diffusion on EMCP, a n^+ emitter is formed on one group of the samples using $POCl_3$ diffusion. Samples undergo either silicon nitride deposition, or microwave induced remote plasma hydrogenation (MIRHP) in the same PECVD reactor. To study the kinetics of hydrogen diffusion, deuterium is used instead of hydrogen in some samples for SIMS analysis. The total number of processed samples is 24 (4 for each process).

2.2 PECVD process

All experiments are performed using OXFORD Plasmalab microwave system (f=2.45 GHz) (see Table 1 for detailed deposition parameters). Four samples are processed at the same run. Silicon nitride undergoes rapid thermal annealing after deposition, comparable with contact firing process.

Table 1

PECVD deposition process parameters

Process	Hydrogenation / Deuterisation	Silicon Nitride deposition
Duration	1 H	11’30’’
Substrate Temperature	400°C	400°C

2.3 Lifetime measurements

Lifetime measurement is performed by means of microwave photo conductance decay cartography [6]. It is carried on a Phoenicon Lifetime Mapping System MRM. Each sample is mapped by a lifetime matrix of 101×101 points, which gives a 0.5 mm resolution. Laser excitation wavelength is set to 1047 nm, and measurement is performed under 10% of one sun bias light. To prevent the influence of surface recombination, sample surface is passivated by the following treatment: 10 min cleaning in H_2SO_4/H_2O_2, followed by HF-dip for oxide removal. Iodine and Glycol-based varnish is then applied on the surface.

Each sample is measured before and after the process, except for the $POCl_3$-diffused series. Indeed, no lifetime measurement can be performed with an emitter, which would induce high surface recombination. In this case the emitter is removed by AFN solution.

2.4 Solar cells

Solar cells are made with the same material from the same ingot, according to the standard IMEC process [7]. In this process the silicon nitride deposition step and reactor are different from the one used in § 2.2. Half of the cells have an aluminum back surface field (BSF). Twelve cells are prepared. Reflectance and spectral response measurements are carried out on the same portion of the cell (2×2 cm²) to obtain the internal quantum efficiency (IQE). Results are compared with those of Baysix solar cells made by the same process.

3. Results and discussion

3.1 Wafers results

We must note first that mean lifetime is rather low for the material before treatments ($2.5<\tau<3$ µs). As reported in [5], thermal treatments have strong impact on the mean lifetime: After diffusion, it decreases by 10-15%. Some samples have also been submitted to rapid thermal annealing without silicon nitride, and they show 5 to 10% degradation. Furthermore, the degradation due to thermal treatment can be more important on the highest lifetime values, since they can decrease as much as 50%. We can see a strong asymmetry on lifetime maps, which is due to the geometry of the ingot: it is pulled in a section of 12×12 cm², and then cut into 10×10 cm² wafers, divided in four samples (5×5 cm²). Hence, the lifetime is the worst on the edge of the ingot (bottom left on the maps shown here).

The samples slightly improve after PECVD treatment. For the diffused series, SiN treatment leads to an increase of 20% of lifetime, and hydrogen plasma to a 15% increase. Slightly higher augmentations are reached with non-diffused samples, since SiN increases from 25 to 30% the lifetime. But hydrogen plasma does not lead to real differences between the two series. As shown in Fig. 2, the enhancement is more significant in good areas of the sample. This point is common for both treatments and series.

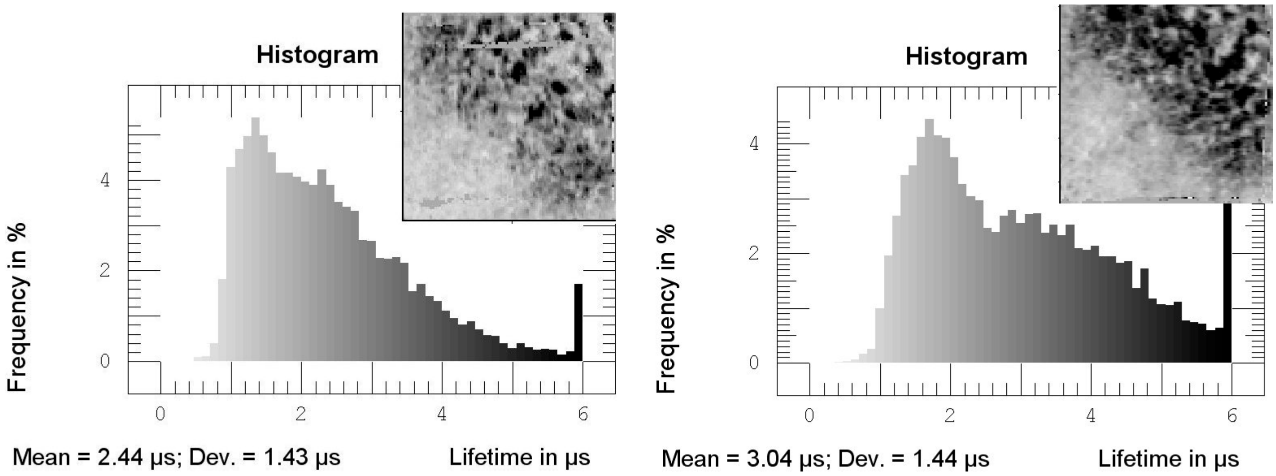

Fig. 2: Lifetime mapping and distribution for a non-diffused sample before (left) and after (right) SiN deposition and annealing. Scale does not vary in lifetime.

The results meet the previous established conclusions [4,5,8]: competition exists between intra and inter-grain defects. It can explain the fact that the enhancement is stronger on the good area, where the size of the grain can reach a few millimetres. On the opposite, the size of grain (<1 mm) on the edge prevents the sample from passivation. However our process parameters do not seem to be well suited with this material, since the improvement is rather low.

SIMS analyses have been made on "deuterised" samples, but the profiles are really difficult to analyse, since they strongly depends on grain orientation on the impact of ion beam.

3.2 Cells results

Despite the poor results concerning lifetime measurement after PECVD treatment, the solar cells results demonstrate the good capabilities of EMCP material. Table 2 indicates that EMCP can lead to 13.4% efficiency solar cells.

Table 2

Average I(V) measurements for solar cells, with or without aluminum backside.

average	Jsc (mA/cm^2)	Voc (mV)	FF (%)	Eff. (%)
Baysix	32.26	600.35	74.03	14.34
Al-Baysix	33.49	608.10	75.80	15.43
EMCP	30.97	594.30	73.30	13.44
Al-EMCP	31.48	596.08	71.63	13.49

An interesting point appears concerning the effect of aluminium backside on the cell. It has been shown that when Al and SiN anneal are simultaneously performed at high temperature, it exists a positive interaction that gives better enhancement than the addition of BSF (Back surface field) and hydrogenation from SiN effects [9]. In fact Al annealing generates vacancies (V) which can participate in the diffusion of hydrogen, which generally occurs by a {H-V} combination [10].

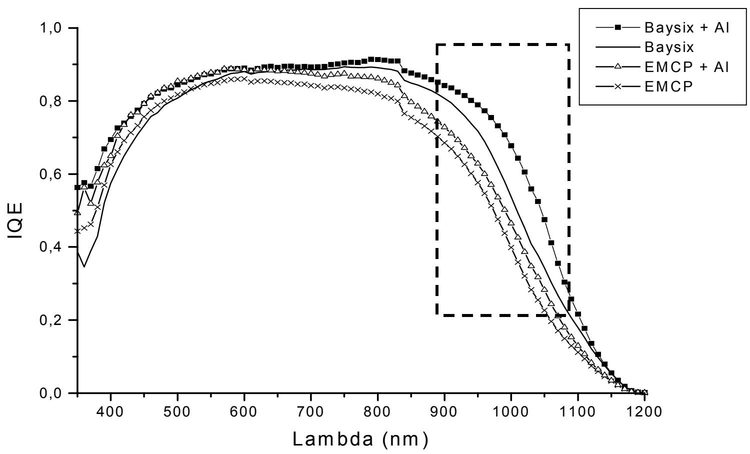

Fig. 3: Comparison on average IQE between Baysix and EMCP, depending on the presence of an aluminum backside. The rectangle area emphasizes on the base region of the cells.

Table 2 shows that Al-backside greatly enhances the efficiency of Baysix cells, particularly in terms of Voc. But the improvement is rather low for EMCP cells. We can verify this statement with internal quantum efficiency measurements (IQE) in Fig. 3. First of all, EMCP IQE is lower than Baysix one's in the base region of the cell. Then the increase with Al-backside is smaller for EMCP. We can estimate that the Al-backside mainly exhibits a BSF effects on EMCP cell. This fits with the lifetime results of § 3.1: the hydrogen treatment does not greatly increase lifetime. Hydrogen diffusion maybe be enhanced with Al-backside, but the efficiency of its passivation is affected by extended defect of the material, principally dislocations and grain boundaries [5].

4. Conclusion

Competition exists between intra and inter-grain defects in EMCP material, due to the small grain morphology of the material. Passivation results are not optimized with our plasma parameters, since only 25% of improvement is achieved. This small enhancement do not allow us to differentiate the impact of the different treatments. Further study would imply deep level transient spectroscopy (DLTS) and high-resolution EBIC, to find out which defects are annihilated by hydrogen treatment. The results obtained on solar cells lead to the same conclusion: the combination of aluminum backside and SiN passivation leads to notable improvement for Baysix cells, but is less important on EMCP cells. This could be due to the lack of hydrogen passivation efficiency in this material.

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