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$POCl_3$ DIFFUSION WITH IN-SITU SiO_2 BARRIER FOR SELECTIVE EMITTER MULTICRYSTALLINE SOLAR GRADE SILICON SOLAR CELLS

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ABSTRACT: We present an innovative process for the formation of a selective emitter by using an advanced phosphorous glass as a barrier layer against subsequent diffusion. The advanced barrier glass was achieved by the formation of a standard phosphorous glass treated with additional thermal oxidation immediately after deposition in the same process tube. The resistant layer is used as a barrier for the second diffusion after selective opening of the finger contact areas by screen printing of a SiO_2 etching paste. The process was applied for multicrystalline Elkem Solar SoG-Si wafers as well as for references from standard EG-Si. The achieved cell parameters were compared with cell results from a homogenous emitter process. While the efficiency was not enhanced so far due to the relatively high shadow loss of the selective emitter solar cells, the open collector voltage could be increased by up to 9 mV and the short wavelength spectral response increased slightly with this selective emitter. The aim of this work was to combine the SiO_2 barrier with the shallow $POCl_3$ diffusion in one process step and the optimization of the screen printing process for selective emitter solar cells.

Keywords: selective emitter, oxide barrier, fiducial alignment

1 INTRODUCTION

Different selective emitter concepts are investigated recently to reduce the front surface recombination velocity, to minimize the contact resistance and to improve the blue spectral response of the solar cell. For example: single deep diffusion, double diffusion process with mask, selectively printing of a doping paste, auto-doping of the surface or selectively application of diffusion barriers [1-3]. For selective emitters highly n+ doped regions are required beneath the Ag fingers at the front side. As the highly phosphorous doped regions deliver a low cell response in the blue region of the spectrum, these areas must be as small as possible and should be located below the Ag metallic contact fingers. Between the fingers a shallow slightly doped emitter is required which can be passivated properly to keep the surface recombination as low as possible and to obtain a high open collector voltage accordingly.

In this work, we present a new process for the formation of a selective emitter by introducing a thermally grown SiO_2 barrier, immediately grown after the shallow $POCl_3$ diffusion in the same process tube. The oxide is used as a barrier for the second diffusion after selective opening of the finger contact areas, by screen printing and drying of a SiO_2 etching paste.

2 EXPERIMENTAL

The experiments were carried out on solar grade silicon feedstock provided by Elkem Solar. Q-Cells organized the crystallization and wafering, and delivered the p-type boron doped multicrystalline wafers, with an area of 156x156mm^2, a thickness of 200µm and a resistivity of about 1Ωcm. For the selective emitter the following sequence process was applied (as shown in the flow diagram sequence represented in figure 1).

First of all, very small holes (Ø80-100µm) were drilled by laser at two different edges of the wafer, to enable the optical alignment of the screen printing cameras based on these two fiducial marks. This method uses artificial vision to find the fiducial points on the wafer, without the need of imprecise alignment on the substrate edges. The laser holes were drilled before the iso-texturisation and industrial cleaning of the wafer, to avoid any laser damage on the wafer surface.

Secondly, iso-texturisation of the multicrystalline wafers was carried out by HF/HNO_3 acid solution (i. e. Rena approach), to minimize the reflection of the incident light on the front side, to enhance light trapping and to remove the laser damage and saw damage on the surface of the as-cut wafers.

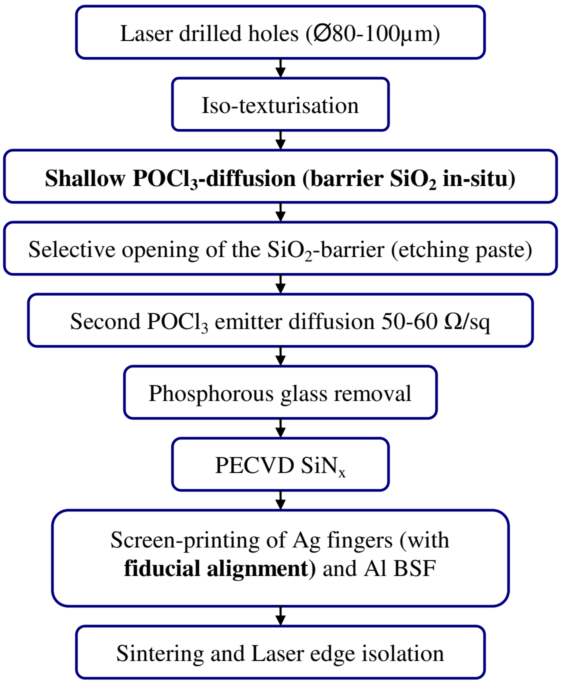

Figure 1: Flow diagram sequence of the selective emitter process, with an in-situ SiO_2 barrier growth after the first shallow $POCl_3$ diffusion.

The main focus of this work is the formation of a 90-100Ω/sq shallow emitter by $POCl_3$ diffusion with a successive in-situ thermal oxidation, to achieve a barrier for the following second phosphorous diffusion. This oxide acts as blocker for the second diffusion and has to be locally opened by screen printing with an etching agent, in order to achieve highly doped regions under the Ag contacts. Before the second phosphorous diffusion, the oxide layer was selectively opened with the front grid design by screen printing with a phosphorus containing etching paste (isishape SolarEtch^{TM} BES). For this process, fine lines were screen printed and dried in a belt furnace. As the emitter should only be contacted on the heavily doped area to achieve a good ohmic contact [4], an exact alignment process was necessary between the front side metallization and the opened area. Then, a minimally low passivated and heavily doped illuminated area will be guaranteed. The screen alignment process is the most important step in the achievement of the selective emitter solar cells. To achieve a fit of less than 10-20µm, the screen printer should be precisely calibrated.

The second phosphorous diffusion resulted in an emitter sheet resistivity of 60-65 Ω/sq below the contact fingers, and still 90-100 Ω/sq between the fingers, below the passivated area. This lightly doped passivated emitter ensures good collection properties and low emitter dark saturation currents [5].

Afterwards, the phosphorous glass was removed by HF-dip to enable the passivation of the solar cell. The passivation was carried out by Plasma Enhanced Chemical Vapor Deposition (PECVD) SiN_x on the front side. This coating has also the function of an antireflection layer for the incidence light.

The metallic contacts were made by a screen printing process adjusted with the help of laser drilled holes as fiducial marks on the edges of the wafer. On the front the same grid was used for the etching paste, as for the Ag fingers. On the rear the contact was formed by a full area of screen printed aluminium to form a BSF layer. Before the sintering of the contacts the inks were dried. The contacts were sintered by an infrared furnace.

Later on, the front and the rear side were isolated by laser grooving, obtaining a very high shunt resistance. Afterwards, the solar cells were characterized by IV-curves.

3 SCREEN PRINTING PROCESS

3.1 Fiducial alignment

For the optical alignment it was found that fiducial marks (e.g. as a via made by laser drilling) lead to a more accurate alignment between the screen and the substrate than the alignment as oriented by the edges of the wafer.

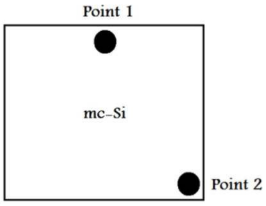

Figure 2: two points were needed to achieve the optical fiducial alignment for the screen printer. The points were 80µm in diameter laser drilled via for the optical alignment.

These fiducial marks enabled an accurate optical detection by the screen printer cameras, because the contrast between the substrate and the back light coming through the via is high. For the fiducial alignment two points were needed at the edges of the wafer. For the Baccini screen printer used in this experiments point 1 was on the upper center part of the wafer with coordinates in mm (x, y) = (0, -78) and point 2 was on the lower right edge of the wafer with coordinates in mm (x, y) = (-78, 78) as illustrated in Figure 2.

3.2 Etching paste opening and alignment

To open the oxide layer a front grid of 150µm fine lines was screen printed by using the BES etching paste of Merck, with a fast etching rate of 1.5 to 4nm/s (see the producers recommendations). This removal process was achieved by drying the phosphorous containing etching paste in a 6 zones infrared conveyor belt furnace for about 2 minutes at 300°C temperatures. Immediately after the drying step the wafers were placed into carriers inside an ultrasound bath for cleaning. The cleaning time was minimized by adding 0.1% KOH to the 40°C heated deionized water. After 1 to 2 min cleaning time some wafers still show problems with the removal of the etching paste because of the surface texture (as shown in figure 4). To verify this effect, a parallel experiment was performed on non textured CZ-Si wafers resulting in an etching time of only few seconds.

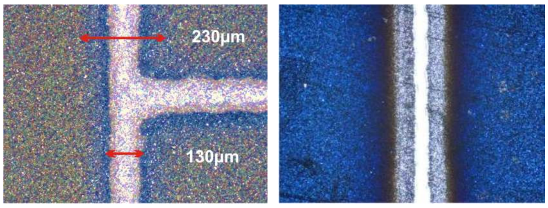

Figure 3: Optical micrograph showing the precise alignment result and opening of the barrier achieved by optical fiducial alignment of the screen printer. The fine etched line (left) became 50µm wider per side than the screen (130µm).

To solve the problems on textured samples mentioned above the cleaning time was increased and the drying temperature was optimized, until the etching paste could be completely removed.

Figure 3 shows two optical microscope pictures of the local removal of the SiO_2 barrier layer achieved on a textured mc-Si surface, and the precise result of the alignment between the etched regions and the Ag grids.

The measured line width after etching is about 230µm for the textured surface. The alignment achieved is precise and reproducible for a screen printing process of selective emitter solar cells.

Figure 4: Partly removed etching paste after several seconds in the ultrasonic bath. The removal had to be optimized due to the isotropic textured surface condition.

4 CELL RESULTS

4.1 IV-Measurements

The measurement of the IV-curve is summarized in the following two tables. The selective emitter is compared with the homogeneous emitter for the Elkem Solar Silicon (ESS) and the reference wafers.

Table I: IV measurement results of the selective and the homogeneous emitter for the (ESS) wafers.

ESS 117		**FF [%]**	**V_{oc} [mV]**	**J_{sc} [mA/cm^2]**	**η [%]**
homog. emitter	avg.	77,6	614,9	32,4	15,4
	best	**78,7**	**616,0**	**32,5**	**15,7**
select. emitter	avg.	77,5	623,5	32,5	15,7
	best	**77,6**	**623,7**	**32,5**	**15,7**

Table II: IV measurement results of the selective and the homogeneous emitter for the reference (ref.) material.

Ref.		**FF [%]**	**V_{oc} [mV]**	**J_{sc} [mA/cm^2]**	**η [%]**
homog. emitter	avg.	77,3	604,6	32,9	15,4
	best	**77,7**	**605,8**	**33,0**	**15,5**
select. emitter	avg.	76,3	609,1	33,0	15,3
	best	**76,3**	**612,2**	**33,1**	**15,5**

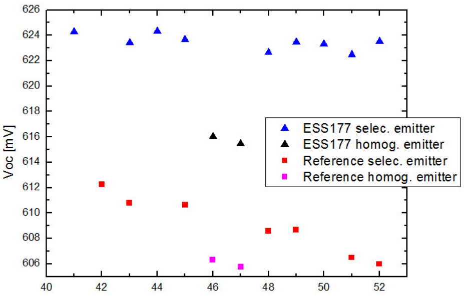

Figure 5: improvement in the open collector voltage for both solar cell groups.

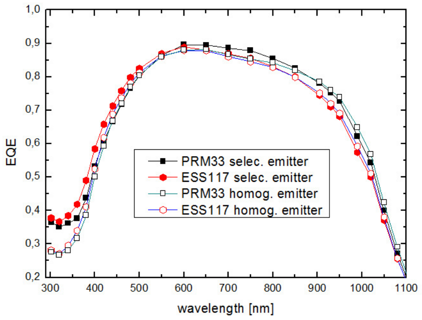

Figure 6: EQE of the selective and the homogeneous emitter solar cells for the ESS and reference materials.

From the results presented on the tables I, II and the figure 5 we can conclude that the ESS wafers showed efficiencies of η=15,7% for both processes, the homogenous and the selective emitter. The reference efficiencies were lower for both emitters. The V_{oc} is clearly enhanced by about 9mV (615→624mV) in case of the ESS and about 5mV (604→609mV) in case of the reference material due to the selective emitter. The J_{sc} should be higher for selective emitters. This is not the case due to higher number of Ag fingers and the respective higher shadow loss. The FF is lower for selective emitters as compared to the standard process. ESS is stable against thermal oxidation, as already demonstrated in previous papers [6]. It is even more stable as compared to references, crystallized and processed in the same manner.

4.2 External quantum efficiency

The external quantum efficiency (EQE) measurements are evaluated for the selective emitter solar cells compared to the homogenous emitter cells, as the figure 6 shows. We see an improvement of the blue response for the selective emitter solar cells, with the best result for the ESS solar cells material.

5 CONCLUSIONS AND DISCUSSION

An innovative selective emitter process was investigated with the use of a modified phosphorous glass, which acts as a barrier against the second phosphorous diffusion. The shallow $POCl_3$ diffusion combined with the in-situ SiO_2 barrier against the subsequent $POCl_3$ diffusion has been demonstrated to work. Hence, although the cell process involves two different phosphorous diffusions, there is no need for an additional process step to create a diffusion barrier layer.

A reliable and reproducible optical alignment process between substrate and screen was achieved, by using two fiducial points. The selective opening of the phosphorous glass by etching paste worked perfectly. Previous investigations have been confirmed, that the Elkem Solar Silicon material is stable against high temperature processes such as thermal oxidation. While the efficiency was not enhanced so far due to the relatively high shadow loss and the not optimum selectivity of the emitter, the open collector voltage could be increased by 9mV in average for the ESS cells and about 5mV for the reference cells. The spectral response is slightly enhanced in the blue wavelength range for the selective emitter cells as compared to the homogenous emitter cells. Further investigation is needed to optimize the selectivity of the solar cell emitter.

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7 ACKNOLEGMENT

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