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Selective Emitters for Screen Printed Multicrystalline Silicon Solar Cells

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Abstract – *We present the results of a study aiming at the formation of selective emitter silicon solar cells. Most emphasis has been put on the use of screen printing for junction formation and metallization. In particular our attention has been focused on those processes that seem to be scalable to industry.*
Two main ways of realizing selective emitter are presented in this work :
1- homogeneous diffusion of an heavily doped emitter followed by a chemical etch.
2- doping source deposition (by screen printing) followed by an anneal in a belt furnace.
The doping paste is applied selectively to the front side of a P-type crystalline Si wafer. In only one diffusion step, deeply diffused regions under the printed doping source are formed and in the adjacent regions doping atoms diffuse from the printed source via the gas atmosphere.
The advantages of such structure were demonstrated with spectral response measurements showing an increase in the UV-VIS range of the solar spectrum.
As a result , the selective emitter cell shows a much higher Jsc and Voc than the conventional emitter cell.

Résumé – *Nous présentons les résultats d'une étude dont l'objectif est la réalisation de cellules solaires à émetteur sélectif. Le présent travail est axé sur l'utilisation de la technique de sérigraphie pour la formation des jonctions et la métallisation des contacts. Nous nous sommes, en particulier orientés vers l'application de procédés de fabrication de cellules solaires à émetteur sélectif transposables à l'industrie.*
Deux voies principales de réalisation d'émetteurs sélectifs sont présentés dans ce travail :
1- diffusion homogène d'un émetteur fortement dopé puis gravure sélective par voie chimique
2- dépôt d'une source dopante (par sérigraphie) suivi d'un recuit dans un four à convoyeur
La pâte dopante est déposée suivant les motifs des contacts métalliques sur la face avant des plaquettes en Silicium cristallin de type P. Pendant le recuit thermique, d'une part les régions fortement dopées se forment à partir de la source imprimée et d'autre part, les atomes dopants diffusent dans les régions adjacentes par l'intermédiaire de l'atmosphère gazeuse.
Les avantages d'une telle structure ont pu être observés par mesure du rendement quantique où le gain est visible dans la partie UV-VIS du spectre solaire.
L'étude sous illumination d'une cellule solaire à émetteur sélectif montre une augmentation de J_{sc} et de V_{oc} par rapport à une cellule à émetteur conventionnel.

Mots clés : Cellule solaire – Semicristtalin – **S**érigraphie – Emetteur sélectif

1. INTRODUCTION

Emitter diffusion is one of the crucial steps in the manufacture of multicrystalline silicon solar cells. It has been the subject of a large number of experimental and theoretical studies [1,2]. Emitters can be formed by applying a phosphorus source to the wafer using several commercial techniques such as screen printing, spray-on, spin-on or $POCl_3$ [3]. The use of thick film technology for the fabrication of silicon solar cells offers several advantages. Printing techniques cover a large range of process steps such as the formation of the junction, front and back metallization, back surface field and antireflection coating.

Ideally the highest solar cell conversion efficiency is achieved with shallow junction depth (less than 0.2 µm) [4]. The electrical efficiency of a thick-film metallized solar cell will vary with the temperature-time product used during the firing cycle. On the low side, insufficient metal-to-silicon contact results in a high contact resistance and poor adhesion. On the high side, over firing results in metal migration through the junction which causes shunting. Optimal emitters are a compromise between low dark currents and low contact resistivity [5]. It is therefore desirable to have a relatively low surface doping concentration everywhere on the illuminated surface of a cell except directly beneath the metal electrode. Such an arrangement is referred to as a selective emitter and has been introduced many years ago [6,7].

Two main ways of realizing selective emitter are presented in this paper:

- Homogeneous diffusion of a heavily doped emitter followed by a chemical etch
- Doping paste applied selectively by screen printing followed by an anneal a resistance heated belt furnace.

2. SELECTIVE EMITTER PROCESS WITH SCREEN PRINTED METALLIZATION

Starting material was p-type as cut multicrystalline silicon. The wafers had a 5x5cm^2 area, an average thickness of 400µm and a resistivity of 1Ωcm. The pretreatment of the substrate was carried out in a solution of NaOH to reduce the surface reflective losses as well as to remove the mechanical damage saw and contamination.

After etching the wafers, pn junctions are formed by gaseous diffusion using $POCl_3$, between 850°C and 950°C in an open tube furnace. The parasitic junction at the edges was removed using a dry plasma etching technique.

2.1. Single diffusion and etch-back selective emitter process

First, a heavy P diffusion is carried out to form a deep n^{++} emitter with sheet resistance typically between 10-20 Ω/sq. Next, the front and back contacts are screen printed and fired. After that, the grid contact is protected by means of an acid resistant polymeric paste. This is followed by etching back the emitter in an HF-HNO_3 solution. The aim is to obtain emitters with a sheet resistance of 30, 40, 50 to 80 Ω/sq. Different kinds of emitters were obtained by only changing the etch time as shown in Fig. 1. These cells were cut to four samples of 4 cm^2 area for electrical measurements.

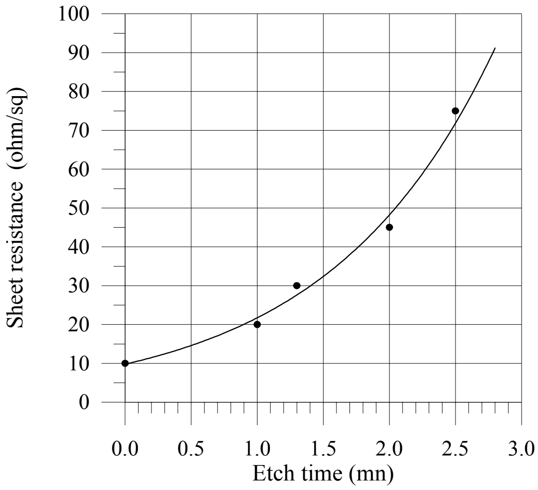

Fig. 1: Emitter sheet resistance vs etching time

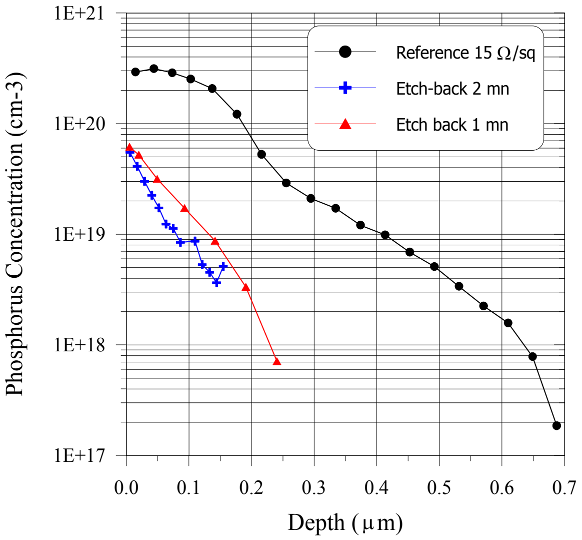

Fig. 2: Stripping Hall profiles of emitters before and after etching

The sheet resistance of the processed emitters on multicrystalline silicon wafers was measured with a four point probe technique. Each wafer was measured at five positions. From Fig. 2, it can be seen that the emitter doping level and its electrical performance are determined by the emitter profile before and after the etch back. Several monocrystalline control samples were selected for emitter profile measurement. The profiles were measured with a HL 5900 Stripping Hall equipment.

Results. In order to investigate the quality of the selective emitter cells, the electrical properties are measured for a 2 x 2 cm^2 test cell. The I-V characteristics of the multicrystalline silicon solar cells are given in Table 1.

Table 1: I-V characteristics for a 4 cm^2 cell before and after etch back

Emitter	Jsc (mA/cm²)	Voc (mV)	FF (%)	η (%)
Homogeneous	22.4	524	69.9	8.2
Selective	23.9	535	68.1	8.7

This particular selective emitter has a short circuit current increased by 1.5 mA/cm^2. In addition we observed an enhancement in Voc for the selective emitter in comparaison to the homogeneous emitter. The fill factor of these multicrystalline cells was not optimised.

To investigate further the difference between the selective and conventional emitters, spectral response measurements were performed. Fig. 3 reveals that in the short wavelength range, the selective emitters show a higher external quantum efficiency EQE.

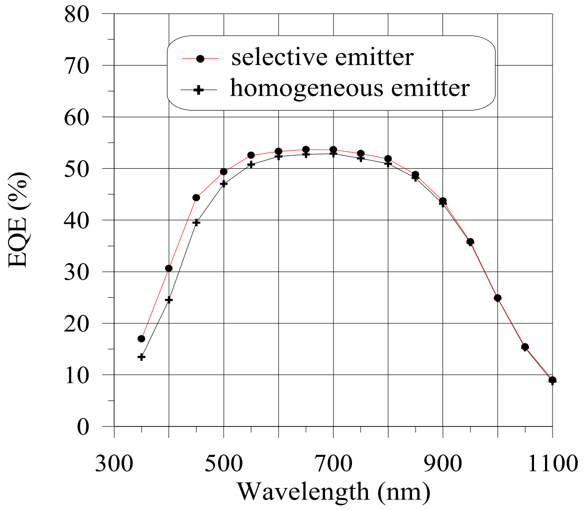

Fig. 3: External quantum efficiency plots for homogeneous and selective emitter cells

2.2. Selective emitter in one diffusion step

This method does not need etching or masking steps. The principle of the process is shown in Fig. 4.

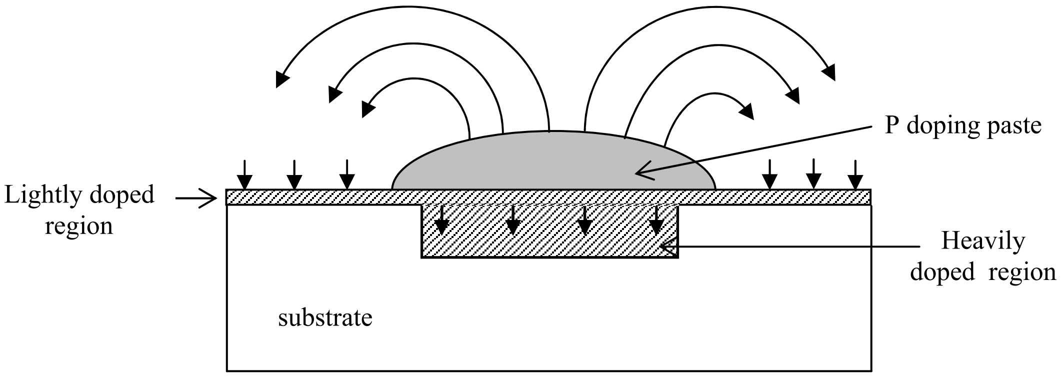

Fig. 4: Principle diffusion illustration

A phosphorus dopant paste is applied by screen printing in the same pattern as the contact grid. During the high-temperature step which occurs in a belt furnace, the silicon beneath the phosphorus source becomes heavily doped while the silicon between the phosphorus screen-printed lines is only lightly doped. This lightly-doped region, created indirectly via gas phase transport of phosphorus, becomes the emitter of the cell. After etching the diffusion glass, metal lines are screen printed over the heavily doped areas, which requires an alignment.

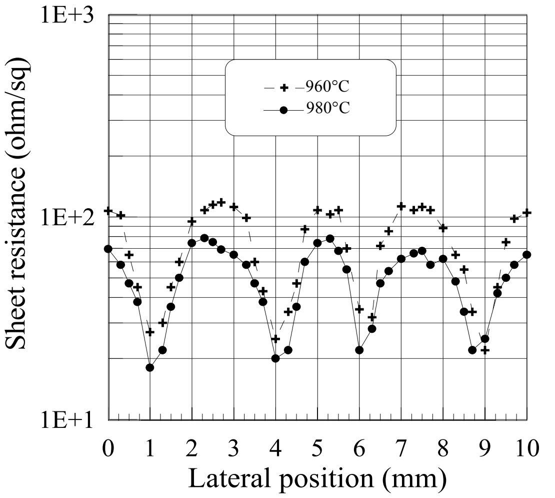

Fig. 5: Sheet resistance line scan for two diffusion temperatures

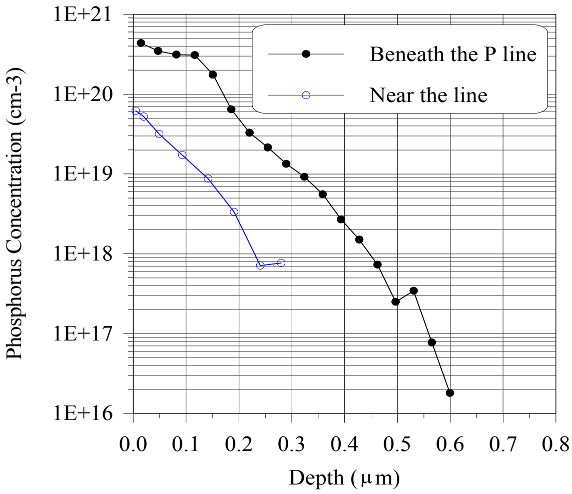

Fig. 6: Stripping Hall profiles for a selectively doped emitter

Results. To verify that this simple method is able to produce a selective emitter in only one diffusion step, monocrystalline samples were selected for emitter profile and sheet resistance measurements. Fig. 5 shows a four point line scan measurement perpendicular to the printed dopant grid for two diffusion temperatures.

For a preliminary advance, one phosphorus line is screen printed, dried as usual and heat treated in a belt furnace at high temperature, typically 980°C. Then, the emitter profiles were taken at the regions of highest and lowest sheet resistance, (see Fig. 6).

These measurement results prove that a selective emitter is realized. Both deeply diffused regions with a high surface concentration and shallow emitter regions with a low surface concentration are formed. The next step is the back and front screen printed metallization which is the most critical process.

Table 2 shows the short circuit current obtained for multicrystalline cells fabricated using these two methods in comparaison to homogeneous emitter.

Table 2: Short circuit current comparaison between the two process

Emitter type	Jsc (mA/cm^2)	Enhancement on 4 cm^2 mc solar cell
Homogeneous	22.5	-
Selective 1	24.0	1.5 mA/cm^2
Selective 2	23.8	1.3 mA/cm^2

3. CONCLUSIONS

This paper described selective emitter processes in combination with screen printed contacts. Selective emitters have been made in two different ways. Each one of them has specific advantages and disadvantages.

The first method, the etch back process, is carried out in a diluted CP_4 type solution, wafer by wafer in order to have reproducible results. A second important drawback of this process is that the front surface passivation can not be performed.

On the other side, the second process requires a perfect alignment between the front contact grid and the invisible highly doped areas, which could be performed with a printer equipped with digital cameras. The second obstacle is the screen deformation after several printing cycles which causes a reproducibility problem of the electrical characteristics.

But the main advantage of this selective emitter process is that the processing sequence does not require any additional processing step such as etching or masking with reference to a homogeneous emitter process.

NOMENCLATURE

EQE : External quantum efficiency [%]
J_{sc} : Short circuit current density [A/cm²]
η : Conversion efficiency [%]
FF : Fill factor [%]
V_{oc} : Open circuit voltage [V]

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