SELECTIVE EMITTER FORMATION FOR LARGE-SCALE INDUSTRIALLY MC-SI SOLAR CELLS BY HYDROGEN PLASMA AND WET ETCHING

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ABSTRACT: The purpose of this work is the realization of selective emitter multi-crystalline (mc-Si) silicon solar cells using two methods namely hydrogen plasma or chemical solution. The methods consist in etching-back the highly doped emitter region through a screen printed paste by either immersing the wafer in a hydrogen plasma or in a wet chemical solution. We have investigated the etching rate and the surface quality through the sheet resistance of the emitter and optical measurements, respectively.
For mc-Si emitters with initial sheet resistance of R=40Ω/ , the hydrogen plasma etching is found homogeneous and efficient since a very short time just of a few minutes is enough to reach the optimal sheet resistances of about 80-100Ω/ , necessary to ensure the surface passivation purpose. Similarly a wet etching solution has been optimized to assure controllable etching rate of silicon. The fabricated solar cells have shown an improvement in the open circuit voltage and short circuit current for the “dry” and “wet” selective emitter processes versus the homogeneous emitter cells, and an absolute efficiency increase of about 0.25- 0.4% is measured.
Keywords: selective emitter, screen printing, dry etching, multi-crystalline silicon

1 INTRODUCTION

The formation of homogeneous emitter by $POCl_3$ diffusion using the Lydop (Leak Tight Yield Doping) furnace or solid sources leads to a high phosphorus doping level at the silicon surface (> 10^{21} /cm^3). This highly conductive surface (40 Ω/) is needed to reduce the contact resistance, but the drawback is a high surface recombination velocity despite the use of a SiN_x:H passivation layer [1]. The solution is a selective emitter cell process that is composed of highly doped regions beneath the grid contacts and lightly doped regions passivated with a hydrogenated silicon nitride film.

The processes to realize such differential doping should involve the screen printing SP tool. Previously we investigated the method that consists in screen printing the phosphorus doped paste on top of an existing lightly doped homogeneous emitter [2]. Upon a thermal annealing at high temperature, the phosphorus diffuses from the paste and over-dopes the sub-grid areas. This method presents the disadvantages of a three step process (SP+annealing+glass etching) and an additional thermal treatment that can be detrimental to the bulk mc-Si materials lifetime [3]. Another method consists in etching the heavily doped region down to sheet resistance values of about 80-100Ω/ [4-5] thanks to a screen printed paste that serves as a mask for contacts regions. The etching step can be accomplished by using either chemicals solutions (wet etching) or plasma gases (dry etching) using fluorine or hydrogen precursors.

The plasma based technique might be very attractive for the photovoltaic industry because it reduces the chemical wastes and can be easily controllable. Its principle is based on an ionic bombardment at low energies by plasma species, mainly the atomic hydrogen, and the surface atoms which can be pulverized.

In this work, we investigated the fabrication of selective emitter cells either by wet etching using chemical solutions or dry etching using hydrogen atoms. In the case of the dry process, we used a remote plasma reactor and we studied the effect of the processing parameters (plasma etching duration, substrate temperature, biasing voltage, microwave-power and radiofrequency power) on the sheet resistance of the etched emitter. The preliminary photovoltaic results show an improvement in the solar cell performances using a selective emitter compared to conventional mc-Si solar cells.

2 EXPERIMENTS

Figure 1 draws the cross section of the cell structure aimed to in this work.

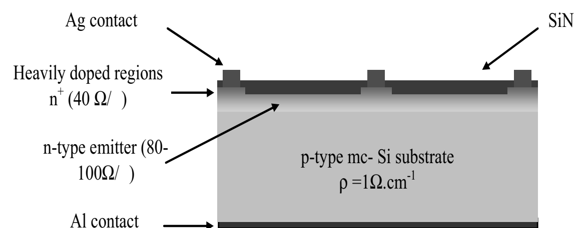

Figure 1: Cross section of the selective emitter mc-Si solar cell.

The process chart is the following: The starting silicon materials are p-type mc-Si textured substrates, from PHOTOWATT, with 270µm thick and a nominal resistivity ρ =0.5-1Ω.cm^{-1}. Different emitters were realized by $POCl_3$ gas thermal diffusion using a Lydop furnace. After a conventional cleaning (H_2SO_4(1):H_2O_2(4) for 10 minutes at 80°C temperature, followed by a HF bath (2%) for 5min and a rinsing with deionised water), a anti-etch paste was screen printed out in order to protect the heavily doped zones located beneath the contacts.

After SP of the paste on the wafers, one set of the samples was introduced in the remote plasma reactor for the dry etching. The hydrogen gas flow was fixed at about 30sccm and the substrate temperature at 50°C. The hydrogenation time controls the etched thickness. Another set of samples was immersed in a chemical solution composed of HNO_3:NH_4F:H_2O for wet etching.

The choice of this paste is very important because it must sustain certain criteria such as no pilling, blistering or removal during the dry or wet etching, no chemical reactions with silicon surface and finally it should be easily removed after the etching process without leaving residues especially in the textured areas.

The four point probe and the secondary ion mass spectroscopy (SIMS) were applied on the etched samples to probe the emitter surface properties namely the sheet resistance and the surface concentration respectively. The UV/Vis/NIR spectrometry, optical and atomic force microscopy were used to quantify the surface microstructure and the etched thickness.

For the selective emitter solar cells fabrication, after etching and cleaning, a 85 nm thick hydrogenated silicon nitride layer with refraction index of 2.05 was deposited at 400°C by a remote PECVD using ammonia and silane gases (SiH_4=14sccm, NH_3=21sccm). Then an aluminium paste was screen printed on the whole back surface while a silver paste was auto-aligned screen printed on the (non-etched) heavily doped regions (R = 40Ω/) located in the top surface (figure 1). After the screen printing process, the pastes were dried at 150°C for 10 minutes and a co-firing step is carried out in a rapid thermal annealing furnace using halogen lamps.

3 RESULTS AND DISCUSSIONS

3.1 Low doped homogeneous emitter by Lydop

Figure 2 plots the phosphorus distributions obtained by SIMS after diffusion in the Lydop furnace at different processing conditions.

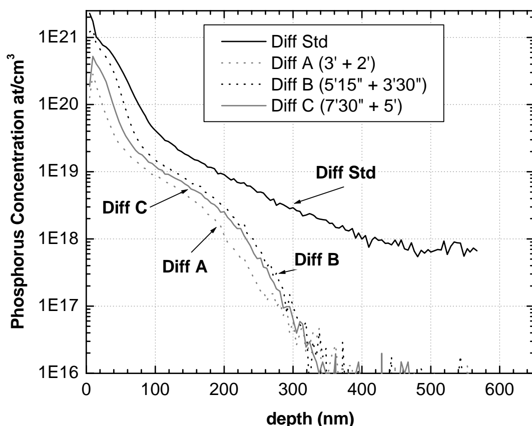

Figure 2: Phosphorous diffusion profiles versus thermal diffusion time in Lydop furnace.

The shape of the phosphorus profiles is representative of the diffusion in silicon from a gas phase. The standard diffusion clearly exhibits a very high phosphorus concentration (> 10^{21} cm^{-3}) and a deep junction while the modified diffusion conditions show lower surface concentration ($5x10^{20}$ - 10^{21} cm^{-3}) and shallower junctions. Additional experiments did not succeed in reducing the surface concentration further. Thus, such homogeneous emitters will not allow reaching low surface recombination velocities, aimed for high efficiency cells. However it is quite clear from figure 2 that etching of a small amount of the emitter has the potential to reach the desired surface concentration, suited for a surface passivation layer. Shallower is the profile, smaller should be the etched thickness, less will be the damage to the surface.

3.2 Silicon etching by hydrogen plasma

The sheet resistance of Lydop emitters is plotted in Figure 3 (t=0). The standard emitter has a sheet resistance of about 40Ω/ . The sheet resistances of samples A, B and C are much higher and they are in accordance with the experimental conditions used for the diffusion. Theses results are also in agreement with the SIMS profiles.

The homogeneous emitters were submitted to hydrogen plasma for silicon etching purpose. The results are plotted in Figure 3.

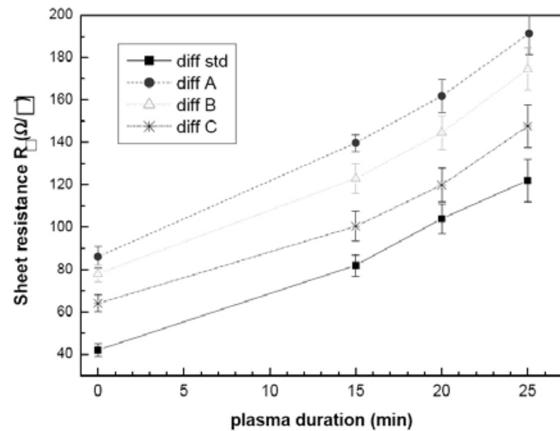

Figure 3: Sheet resistance versus duration plasma etching for different lydop doped emitter emitter. The reactor parameters are: P_{MW} 600W), P_{RF} (250W), V_{bias} (400V), T (100°C).

Whatever is the starting value, we observe that the sheet resistance increases almost linearly with the duration of the plasma etching. For the standard emitter, the sheet resistance increases from 40 up to 70Ω/ after 15 min and reaches about 110Ω/ after 25min of hydrogen treatment. Similarly, the emitter B starts at 80Ω/ and can attain the suited sheet resistance (100Ω/) in about 10min. Thus the lightly doped emitters require a much shorter time of plasma etching to achieve the adequate sheet resistance for passivation purpose.

In order to check the homogeneity of the hydrogen plasma etching process, we applied the plasma etching on three different substrates: textured mc-Si, polished mc-Si and textured sc-Si (single crystalline), all having a standard emitter (40Ω/). The sheet resistance data versus etching time are plotted in figure 4. For these experiments, we have slightly changed some reactor parameters to accelerate the etching process.

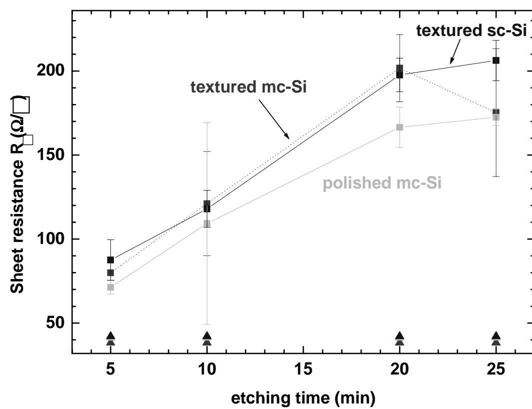

Figure 4: Sheet resistance of the etched emitter versus etching time by hydrogen plasma. The reactor parameters are: P_{MW} (600W), P_{RF} (250W), V_{bias} (600V), T (5°C)

As expected, a similar trend of the sheet resistance versus etching time is observed whatever the nature of the substrate. Saturation is observed for longer etching time probably because almost the whole emitter is etched. We might note that 5-7 minutes are enough to reach a sheet resistance about 80-100 Ω/ . We have applied the atomic force microscopy to evaluate the etched depth. A typical depth profile is shown in figure 5 after 5min of etching. The etched depth is estimated about 40nm, which means an etching rate of about 8nm/min.

Another interesting feature that can be extracted from figure 4 is that the etch rate of the multicrystalline and single crystalline by hydrogen plasma is quite similar. This means that the etching process is not dependent on the crystallographic orientation of the grains. This is of course an important advantage over the chemical etching, which is known to be very sensitive to the crystallographic grains orientations.

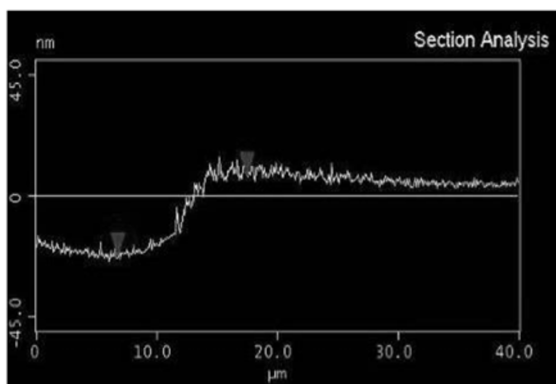

Figure 5: Etching depth profile as measured by the atomic force microscopy method.

Despite the advantages of the dry etching by reactive gas plasma such as short time process and no chemical wastes, the drawback might be a surface degradation which results from the ionic bombardments by the energetic plasma species on the atoms of the substrate surface. Some basic optical observations were carried out to probe the surface damage.

Figure 6 plots the reflectance spectra of standard emitter sample before and after plasma etching for 15min. The spectra were measured using a Lambda19 Perkin Elmer UV/Vis/NIR spectrophotometer with an integrating sphere. The spectrum of a polished single silicon crystal is also plotted to serve as a reference. The two peaks E1 and E2, observed at 275 nm and 365 nm respectively are characteristics of the Γ and Δ transitions and indicate the perfect crystalline quality of the silicon reference. The reflectivity spectrum of the mc-Si before plasma processing is lower than that of polished sc-Si because of texturization, However the two peaks are still very well distinguished. After etching, both peaks E1 and E2 vanished strongly. This can be attributed to a damage of the surface induced by the hydrogen bombardment. However this concerns few nanometres from the surface and should not be detrimental to the cell performance since annealing steps (SiN deposition and contacts sintering) will allow to annihilate the surface damage.

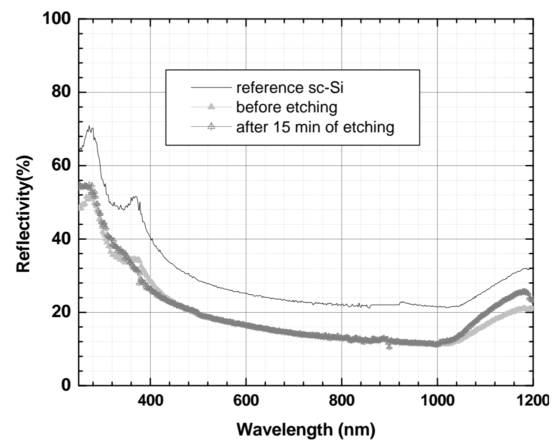

Figure 6: Reflectance spectra of standard emitter sample before and after plasma etching for 15min.

3.3 Selective emitters by wet etching

We have also investigated the etching of the heavily doped regions using chemical solutions. The important criterion to choose the solution was the homogeneity of the sheet resistance on mc-Si substrate after etching. The solution used here is a mixture of HNO_3:NH_4F:H_2O where HNO_3 is employed to oxidize the silicon surface and NH_4F serves to remove the formed oxide. The water is used to speed down the kinetics of the chemical reaction and to homogenize the etching.

The optimization of the chemical etching parameters conducted to the following concentrations: HNO_3(126ml):NH_4F(3ml):H_2O(120ml) at a temperature lower than room temperature. Figure 7 plots the measured sheet resistance versus etching time.

The sheet resistance increase with the time of etching and we might note that 70-80 seconds are enough to reach a sheet resistance about 80-100 Ω/ with a good homogeneity.

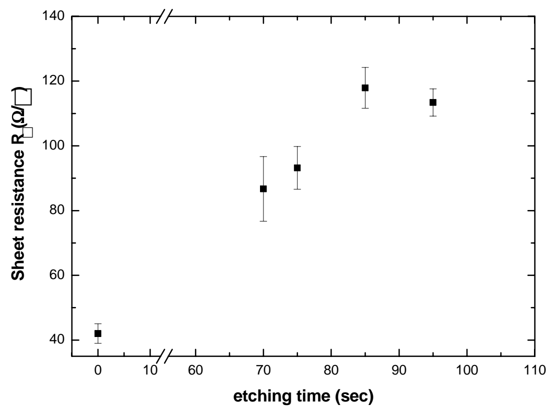

Figure 07: Emitter sheet resistance versus wet etching time.

3.4 Selective emitter solar cells

The process chart for the fabrication of the selective emitter cells by dry or wet etching methods is summarized in figure 8. After contacts firing in a halogen lamps furnace, the solar cells edges are isolated by using a YAG laser to open the junction.

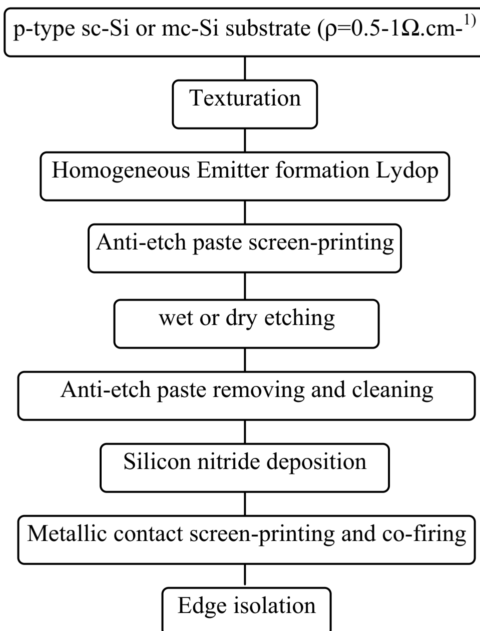

Figure 8: Processing sequences of selective emitter crystalline silicon solar cells.

The current-voltage characteristics were measured under the normal conditions of radiance AM1.5G (100mW/cm²). The table I gives the photovoltaic parameters of the best cells.

For both wet and dry etchings processes, the selective emitter cells show higher open circuit voltage and short circuit current compared to the homogeneous emitter cells. This results from the efficient surface passivation by the SiN_x:H layer made possible thanks to the reduction of the surface doping concentration after etching.

However, the fill factor seems to be very sensitive to the etching process since it is lower for the selective emitter cells. In overall, the solar cell efficiency of the selective emitter cells is 0.25-0.4% absolute higher than for the homogeneous cells. This is in agreement with the simulation results and other experimental works [2,3]. More investigations are needed to optimize such very simple processes.

Table I: Current-Voltage characteristics of selective emitter solar cells. The cell size: 5x5 cm^2.

	I_{sc} (mA/cm²)	V_{oc} (mV)	FF (%)	η (%)
Homogeneous emitter on sc-Si	34.0	587	70.1	14.0
Selective emitter by wet etch. on sc-Si	34.5	592	69.6	14.25
Homogeneous emitter on mc-Si	31.4	581	61	11.1
Selective emitter by dry etch. on mc-Si	32.9	596	59	11.5

For complementary analysis, spectral responses were measured. Figure 9 shows the internal quantum efficiencies of homogeneous and “dry” selective emitter cells made on textured multicrystalline silicon wafers.

As expected, clear improvement in the spectral response is observed in the short and long wavelengths for the selective emitter cell due to the better surface and bulk passivation effect, respectively.

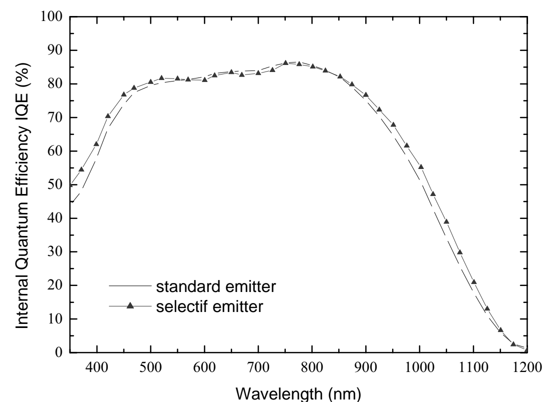

Figure 9: Spectral responses measured on selective and conventional emitter mc-Si solar cells.

4 CONCLUSION

In this study, we have demonstrated the feasibility of selective emitter silicon solar cells by two different etching techniques to thin down the heavily doped regions between the front grid contacts. The chemical and plasma etching parameters were varied in order to get control of the etching process of homogeneous emitters. Application of the etching processes to form selective emitter solar cells shows an improvement of 0,25-0,4% (absolute) in the cell efficiency. The optimization of the etching conditions and large application to multicrystalline silicon wafers is underway.

5 KNOWLEDGMENTS

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6 REFERENCES

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