First solar cells on electrochemically texturized macroporous silicon

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Abstract:

Electrochemical etching of silicon may prove to be a low cost alternative technique for the efficient texturization of multicrystalline silicon. We report here the first solar cells made on substrates with a macroporous structure, obtained by treatments (i) with HF/acetonitrile (MeCN), with which tubular macropores are produced, and (ii) with HF/Dimethylformamide (DMF), which produce shallower pores separated by cusp-like ridges. Solar cells were made on series of substrates subjected to diferent electrochemical texturization conditions, together with control samples with flat surface, made on the same material and with identical solar cell preparation procedure. No anti-reflection nor passivating layers were used. The spectral response of the MeCn treated samples show an expected increase in external quantum efficiency in the infrared part of the spectrum. Much more interesting, however, is the behaviour of sheet resistance and of spectral response in the visible range, which very dramatically illustrate the need for emitter optimization. The best short circuit currents so far were obtained in the DMF treated cells, which reached 37 mA/cm^2 against 24 mA/cm^2 for the control sample.

Keywords: Multi-Crystalline - 1, Texturization - 2, Porous silicon - 3

1. INTRODUCTION

One of the factors which leads to an increase in solar cell efficiency is the reduction of light losses at the surface of the cell. Although the usual alkaline etching procedures work well on monocrystalline silicon, on multicrystalline wafers they are less efficient due to the random grain orientation.

Electrochemical oxidation of p-type silicon in fluoride containing non aqueous solutions [1-4] permits the formation of macroporous layers which can be very efficient in lowering reflectivity and presumably also in increasing light trapping.

This work reports the first results on solar cell structures fabricated on two types of such macroporous substrates. The present work was aimed mainly at investigating the possible problems for good emitter formation in such unusual texturized surfaces, as part of an evaluation of macroporous surfaces for solar cell fabrication.

2. EXPERIMENTAL

2.1 Macroporous layer formation

Electrochemical oxidation of silicon under constant current conditions (10 mA/cm^2) was performed in a teflon cell using a standard two electrode setup. Two different sets of samples were obtained, the first using HF/acetonitrile (MeCN) as electrolyte, and the second using an HF/Dimethylformamide (DMF) electrolyte, under conditions described elsewhere [3,4].

The electrochemical oxidation using MeCN was performed on monocristaline 10-15 Ω.cm p-silicon. The structures formed are tubular macropores with ~1 μm in diameter, with depth increasing with etch time (in our samples, up to ~10 μm), and thicknesses of walls between pores of the order of tenths of a micron, as illustrated in Figure 1.

For the texturization with DMF, monocristaline p-silicon wafers with resistivity 1-2 Ω.cm were used. The structures obtained by this treatment are shallower macropores, ~1μm in depth and ~1 μm in lateral dimension, separated by very sharp cusp-like ridges, as shown in Figure 2.

The electrochemically treated regions in both types of samples was about 6×6mm^2.

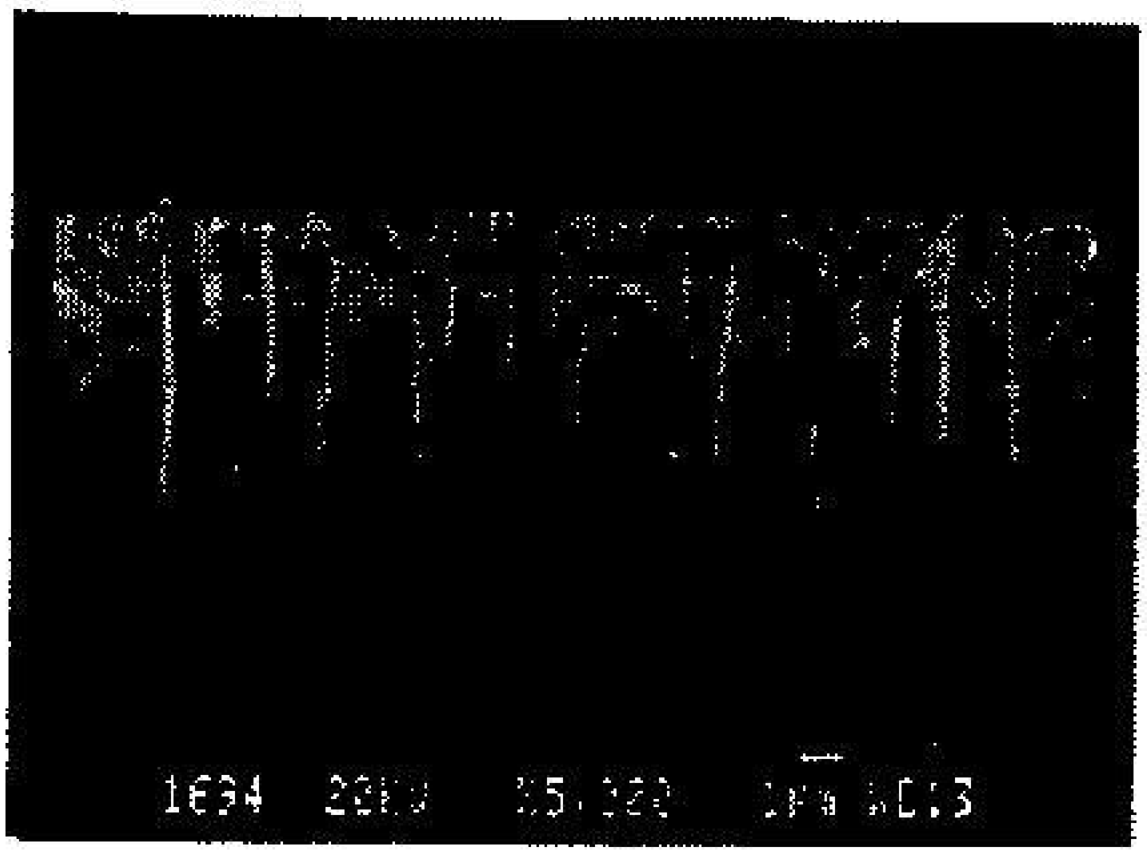

Fig. 1: Tubular macroporous structure of MeCN samples.

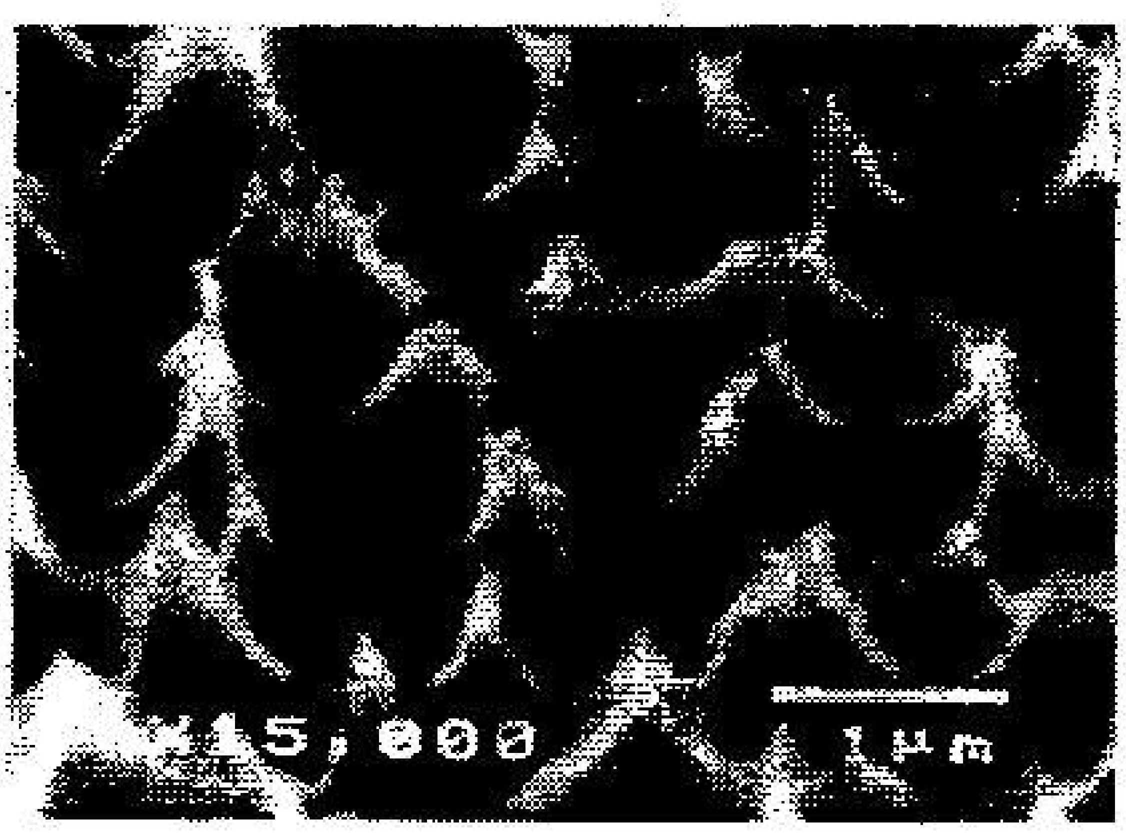

Fig. 2: Shalow macroporous silicon surface structure produced by etching with DMF.

2.2. Solar cell fabrication

Samples with macroporous surface, obtained both with MeCN and DMF electrochemical etching, were used to prepare solar cells. Fabrication steps include phosphorous diffusion at 875 C, from solid source wafers, aluminium back contact and Ti/Pd/Ag contacts on the front. Metallization on the texturized surface was avoided at this stage, so as to isolate this further problem. For this reason, metal fingers were evaporated on to the flat unetched borders of the texturized regions, and were therefore about 6 mm apart.

Exactly the same procedure and geometry was used in the flat surface control cells.

No antireflection, nor passivating layers were used. Also, no back surface field was induced.

3. RESULTS AND DISCUSSION

To characterize the two sets of samples we carried out sheet resistance, spectral response and I(V) curve measurements.

3.1 MeCN samples

Results on emitter sheet resistance, $\rho_\square$, in MeCN tubular macroporous structures are illustrated in the two series of Table I. It is clear that sheet resistance depends not only on diffusion conditions but also on etching time.

Table I : Emitter macroscopic sheet resistences for different etching and phosphorous diffusion times.

Id.	Etch time in MeCn t_{etch} /s	Diff. time at 875 C t_{diff} / s	Emitter sheet res. $\rho_\square$ /Ω
1A	1800	1800	29
1B	1200	"	36
1K	0 (control)	"	55
2A	1500	1200	91
2B	900	"	83
2K	0 (control)	"	75

In fact, increasing electrochemical treatment time t_{etch}, which leads to deeper macropores, may result in variations of $\rho_\square$ in opposite senses: a decrease of $\rho_\square$ is evident in the first series (t_{diff}=1800s) of Table I, whereas an increase is obvious in the second series, with only a little shorter phosphorous diffusion time (t_{diff}=1200s).

Our interpretation is that for sufficiently deep phosphorus diffusion the thin walls between deep pores become mostly n-type, as schematically shown in Figure 3.A, so that the macroscopic effective conductance of the emitter is thus decreased.

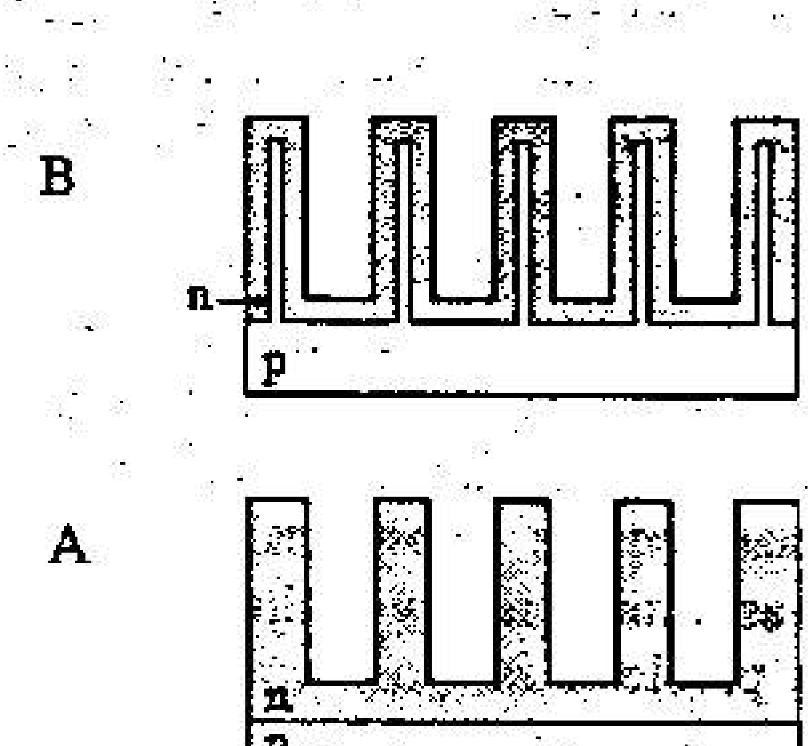

Fig. 3 : Shallow phosphorous diffusion may produce an extensive p-n junction (B), while longer diffusion times may result in totally n-type pore walls (A).

On the contrary, for shallower phosphorous diffusion, a structure such as that in Figure 3.B is probably being obtained, for which an increased depth of the pores can result in an increase of effective sheet resistance. The roles played by pore wall thickness distribution and correlation with etching time, by possible non-uniformity of in-depth phosphorus diffusion and other effects have not yet been modelled and investigated in detail.

This interpretation correlates well with the results on spectral response, such as those shown in Figure 4.

If we first consider curves labeled 1A (deep pores) and 1B (shallower pores), obtained for samples with the same P-diffusion time, a modest gain in spectral response in the infrared by 1A is more than offset by a dramatic decrease in all the visible range. This is expected within our argument: whereas the gain in the near band-gap infrared can be explained simply by a decrease in reflectivity, the huge loss for shorter wavelengths would be the result of an effectively dead layer for hole collection, expected in exclusively n-type pore walls as in Figure 3.B.

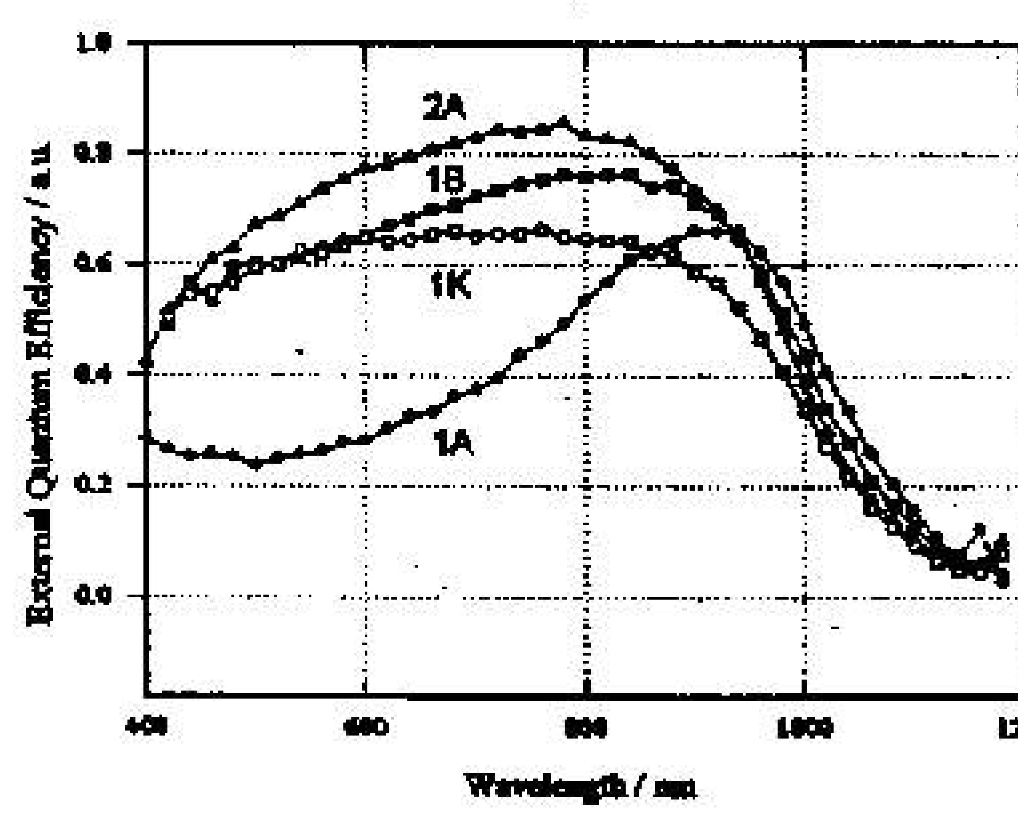

Fig. 4: Spectral response of MeCN samples, identified by labels defined in Table I.

If we now compare these cells with 2A, which has macropores of depth between those of 1A and of 1B but was subjected to lighter doping, a very remarkable increase in response in the visible is observed. This is expected, since the shallower emitter should look more like that in Figure 3B, allowing efficient collection of photogenerated holes. The external quantum efficiency is raised well above that of the control flat cell 1K.

This fact is also confirmed by the I-V curves, which show an increase in the short-circuit current I_{sc} for shallow doping.

V_{oc} was, however, quite low in all macroporous MeCN cells so far (below 400mV), which corresponds to a degradation relative to controls, which showed V_{oc}~500mV. This was not studied in detail for the moment, but three major causes are expected to contribute heavily for this: (i) the large area unpassivated emitter, (ii) the high resistance of the substrates, and (iii) the large distance between front contact fingers coupled with relatively high sheet resistances.

3.2 DMF samples

DMF treated samples don't show the type of dependence on etching time that was found in MeCN samples; on the contrary, one finds experimentally that sheet resistance values are about the same as for the flat control samples. This can be explained by the much shallower surface texturization.

The results on spectral response show simply a general overall increase of the response in the whole spectrum when compared to the control samples. This increase, which is also confirmed by the short circuit current, can be explained by the lower reflectivity (~10%) of the electrochemically texturized cells.

In Fig.5 we present the I-V curves for the best DMF cell compared to the flat control cell. (Current densities are calculated for active area.)

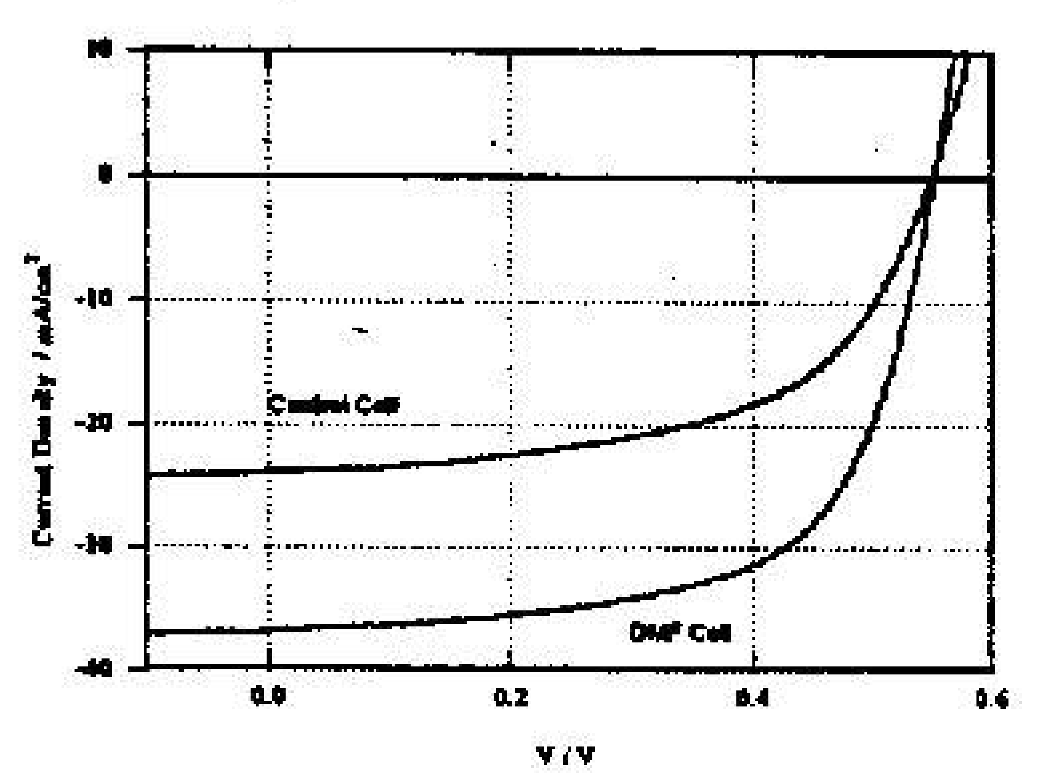

Fig. 5: Current density versus voltage in control cell and in a DMF texturized cell.

Two main conclusions can be extracted from these results: (i) there is a large short circuit current gain, which is compatible, within experimental error, with the decrease in reflectivity; and (ii) V_{oc} remains much the same in texturized samples as compared to the flat control, demonstrating that texturization does not introduce noticeable degradation in this respect, neither from sheet resistante nor

from other effects, such as an increase in total unpassivated area. The conversion efficiency was 12.6%, which is quite good for such a simple procedure.

4. CONCLUSIONS

We have demonstrated that in MeCN texturized samples it is possible to form cells with a large gain in spectral response as compared to flat cell controls, compatible with the decrease in light reflectivity. However, great care has to be taken to optimize emitter formation, since drastic losses in short circuit current can occur for deep phosphorus diffusion. This was interpreted as being due to the thin pore walls becoming mostly n-type, thus preventing effective hole collection. This interpretation is corroborated by our sheet resistance study.

Open circuit voltage was quite low (≤400mV); no study of this effect was made yet.

DMF texturized cells show a less interestingly elaborate surface structure, but, on the other hand, good cells are rather more straightforward to obtain, and results easier to interpret. Open circuit voltage was the same as for the control cell, and short circuit current and efficiency conversion about what one could expect from the gain in decreased reflectivity.

5. ACKNOWLEDGMENTS

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