Non-uniform emitters in silicon cells by photo-defined etch-back

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Abstract:
We present an exploratory study of an alternative technique for obtaining non-uniform emitters in silicon solar cells, based on photo-defined etch-back of uniform n^+ emitters. Silicon p-type wafers of 0.5 to 1 Ωcm were submitted to heavy phosphorous diffusion, to sheet resistivities in the range of 14 to 20 Ω . They were then immersed in an HF electrolyte, and anodised at a constant current while in the dark, or subjected to uniform illumination or to a light pattern. The existence of two opposite regimes, where the dark or illuminated regions are preferentially etched, was demonstrated. In the second regime, the maximum contrast in etched depth is limited by a cross-over behaviour of the anodic currents. Simple patterns with good lateral resolution and reasonable contrasts, as measured by sheet resistivities, were achieved. The possibility of emitters with continuously graded resistivity was also demonstrated.

Keywords: Etching - 1, c-Si - 2, Porous Silicon - 3

1. INTRODUCTION

The aim of the present work is to study the possibility of using photo-defined etching, a maskless technique, to produce non-uniform emitters in n^+- p silicon solar cells.

Photoelectrochemical anodic etching of high resistivity n-type silicon has been well documented [1-5], and can be understood by the simple idea that silicon dissolution in a HF containing electrolyte is governed by the supply of holes to the semiconductor-electrolyte interface. In the dark, very few holes are present, and very little etching occurs; on the contrary, if illuminated, photogenerated holes allow high etch rates. It is thus easy to conceive selective etching of illuminated areas if a light pattern is projected on to the silicon surface in HF.

However, n^+ silicon, such as that produced by phosphorus diffusion to form emittters in silicon solar cells, behaves very differently in HF, for even in the dark large anodic currents can pass [3]; photoselective etching is thus impaired, and this is probably the reason little work has been done on such a system. Nonetheless, even in n^+ silicon with saturation phosphorus concentration, some light sensitivity is observed in the anodic currents [6]. This led us to explore the possibility of using light patterns to produce non-uniform emitters. The problem involves a continuously changing surface doping concentration, as etching proceeds along the phosphorus depth profile. Understanding the process, in order to find the conditions for non-uniform emitter formation, requires knowledge of the photoelectrochemical behaviour for each exposed layer. In a previous work [6], the possibility of two different regimes, one in which the illuminated regions would be preferentially etched, and another in which the opposite occurred, was suggested. In this last case, a cross-over of etch rates was predicted for deep enough etching. The experimental demonstration of these possibilities, together with the presentation of a few practical results, are the main subject of this work.

2. EXPERIMENTAL

Silicon wafers 20×20mm^2, p-type, 1 to 2Ωcm, were subjected to phosphorus diffusion, from a solid planar source, at 900C, so that n^+ emitters resulted with sheet resistivities from 14 to 20Ω . For the electrochemical experiments, the samples were in general polarised from the n-side; however, in a few experiments, the anodic current was injected through the p-side. Ohmic contacts were evaporated aluminium for the p-side, and Ti-Pd-Ag for front n^+ contacts. Delimitation of the region to be exposed to the electrolyte was achieved with a polymer paste.

The electrolyte was an aqueous solution of 2.5w% HF. Potentials were measured against an Ag/AgCl reference electrode. A platinum counterelectrode was used.

Full illumination of the sample, by IR filtered halogen lamp light, corresponded to a photogeneration rate of ~30mAcm^{-2}. Light patterns were produced by interposition of photographic slides.
Etched depths were evaluated by measurements of sheet resistivity, and also by the thickness of the porous silicon layer (the normal result of etching in our experimental conditions) estimated through its colour. These reasonably agreed with estimates based on total charge passed in etching experiments.

3. RESULTS AND DISCUSSION
Figure 1 illustrates how current-voltage (I-V) curves, obtained with a sample uniformly dark or illuminated, shift as deeper and deeper layers of the emitter are exposed to the electrolyte. If we consider first the two consecutive curves, obtained early in the etching process (etched depths 34 to 45, and 45 to 56nm), two opposite regimes are suggested for a sample subjected to a black and white pattern: (i) at low currents, the etch rate in the illuminated areas should be higher than that in the dark areas, whereas (ii) at high currents the opposite should happen. As etching proceeds to deeper emitter layers, I-V curves shift (as can be seen by comparing curves at etched depths 112 to 124 and 124 to 135nm with the previous ones) in such a way that the illuminated anodic current becomes higher than the dark one at all potentials.

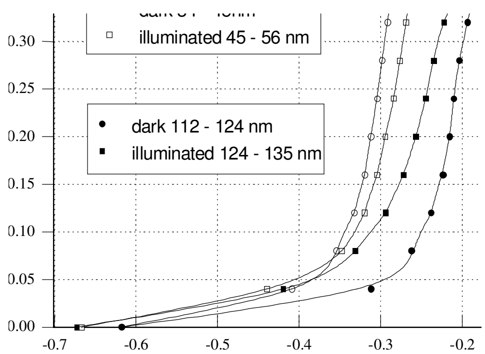

Fig. 1: I-V curves obtained for n^+ phosphorus diffused silicon in successive dark and illuminated sweeps, at etched depths as indicated.

In patterned etching, photoinduced differential etching will expose simultaneously to the electrolyte areas with different etched depths. The anodic current division between illuminated and dark regions, at the same (shifting) potential, can be estimated from I-V curves such as those shown in Figure 1; however, large errors may result in the iteration process.
A direct check of anodic current division was achieved using the modified experimental set-up illustrated in Figure 2. This was used, in particular, to check the cross-over behaviour of the anodic currents in the high current regime, as shown in Figure 3. The two samples, cleaved from the same P-diffused substrate, had the same exposed area. Total current was kept constant at 0.2mA for a total exposed area of ~1cm^2.

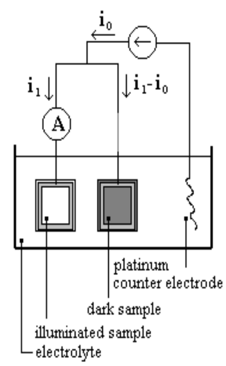

Fig. 2: Modified experimental set-up to allow separate measurement of currents in dark and illuminated areas.

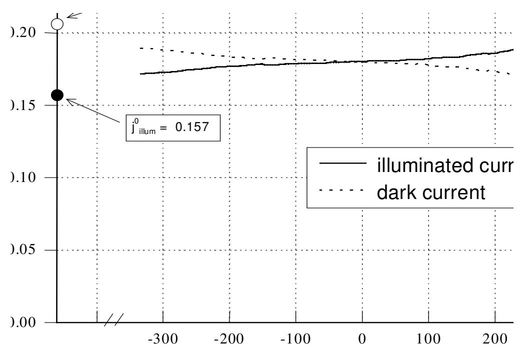

Fig. 3: Cross-over behaviour of anodic currents in dark and illuminated areas.

This clearly shows that for initial high currents (above initial cross-over) a limit to contrast in etched depth between dark and illuminated regions exists. Beyond the cross-over time, etch rate in the illuminated area becomes greater than that in dark areas, progressively reducing the previously achieved difference in etched depth.
Final results of differential etching experiments in this regime are illustrated in rows 2 and 3 of Table I.

On the other hand, if we impose a total anodic current below the initial cross-over point (low current regime), it should be possible to obtain deeper etching in illuminated than in dark areas. This possibility is demonstrated in row 1 of Table I: with the same total charge passed, but at the low current regime, an opposite variation of sheet resistance of dark and illuminated areas was demonstrated (although with low contrast).
Photo-defined etching also raises the interesting possibility of emitters with a continuous variation of sheet resistivities, such as that illustrated in Figure 4.

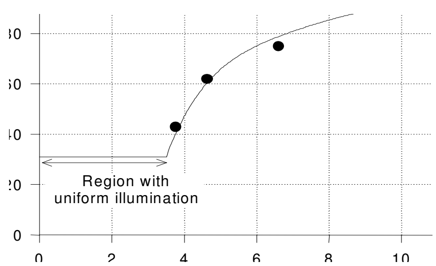

Fig. 4: Emitter with graded sheet resistivity obtained by photodefined etching.

depths of the porous silicon produced in the etching process.

4. CONCLUSIONS

We have initiated a study of the conditions to obtain differential etching in order to explore the possibility of maskless formation of non-uniform emitters in silicon solar cells. The existence of two opposite regimes, where the dark or the illuminated regions are preferentially etched, was demonstrated. In the second regime, the maximum contrast in etched depth is limited by a cross-over behaviour of the anodic currents.
Simple patterns with good lateral resolution and reasonable contrasts, as measured by sheet resistivities, were achieved. The possibility of emitters with continuously graded resistivity was also demonstrated.

5. ACKNOWLEDGEMENTS

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