



# Photodefined etching of n + layers diffused on p-type silicon substrates

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## Abstract

Non uniform n + diffused layers on p-silicon are usually obtained by a uniform doping process followed by etch back in areas defined by a photolithographic mask applied onto the sample. We present a study on an alternative technique to obtain nonuniform n + doped layers using a photoselective etching process, thus avoiding the photolithographic mask. The electrochemical behaviour of n + silicon (as obtained by phosphorus diffusion into p-type samples) in HF solutions was studied, in order to evaluate the sensitivity of anodic current density to illumination, and thus predict the possibility of photocontrolled etching. Current density vs. potential ( $j$ - $V$ ) curves were measured as etching proceeded, and deeper, less doped layers, were exposed to the electrolyte. Two different regimes are suggested by these measurements: at high current densities, the etch rate in the dark regions should be higher than in the illuminated regions, while at low currents the opposite should occur. The high current regime was explored in etching experiments in which several samples were subjected to a dark/illuminated pattern. The prediction of higher etch rates in the dark areas was confirmed; however, total etched depth contrast was experimentally found to be much higher than predicted from the  $j$ - $V$  curves. Contrasts (as measured by sheet resistance) of 59  $\Omega/\square$  in the dark against 34  $\Omega/\square$  in the illuminated regions were obtained. © 1999 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

The aim of this work is to study whether it is possible to produce a nonuniform n-type layer by photocontrolled etching of the n + side of a uniform n + /p junction made on silicon, without the use of any masking film.

Photocontrolled etching is a technique which allows different etch rates on different areas of the surface of a semiconductor immersed in an elec-

trolyte, depending on whether those areas are under illumination or not. The electrochemical behaviour of the semiconductor in the electrolyte is essential to the process and must be illumination dependant [1].

Silicon dissolution in HF is mainly governed by hole supply to its surface [2]; since holes are minority carriers in n-type silicon, it is possible to control this supply by illumination of the sample surface [3]. This means n-type silicon in HF is a system eligible for photocontrolled etching. As an example, in Fig. 1 we show a 5  $\Omega$  cm n-type silicon sample etched at open circuit potential in 10 M HF aqueous electrolyte, by application of a laser spot onto the sample surface. (Here, as in all usual conditions in our

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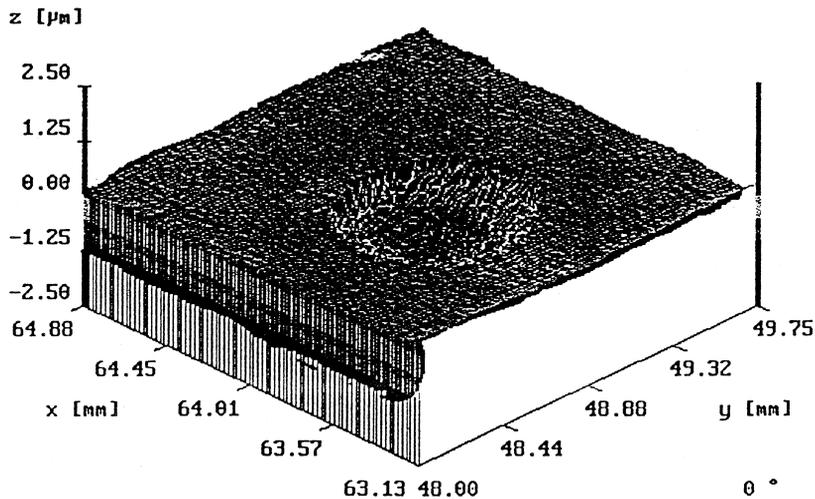


Fig. 1. Profile of the surface of an n-type silicon sample after photocontrolled etching using a 1.5-mW He(Ne) laser spot.

experiments, etching produces porous silicon, which is removed by a quick dip in KOH solution at room temperature.)

In this study, however, we want to concentrate on n+ layers, which differ substantially from lower doping level n layers: n+ silicon has the particularity that even in the dark it can pass high anodic currents [4], and etching occurs even without illumination. No reference was found in the literature on the electrochemical behaviour of n+ silicon under illumination. Since this was necessary to understand the processes leading to photocontrolled etching, we carried out a study of the current density vs. potential ( $j$ - $V$ ) characteristics under different illumination conditions and along the etching process of n+ emitters. Based on this study, we then carried out etching experiments, which clearly demonstrated the feasibility of nonuniform emitters by photocontrolled etching.

## 2. Experimental

Silicon samples, of p-type and 1–2  $\Omega$  cm, cut into 2 cm  $\times$  2 cm squares, were subjected to phosphorous diffusion, so an n+ layer resulted in one face of the sample. The diffusion was carried out at 900°C for 85 min. The phosphorous source was a

planar diffusion source. The emitter thus formed had sheet resistivities in the range of 14–17  $\Omega/\square$ . Ohmic contacts were made by evaporation of a triple layer of Ti (400 Å), Pd (200 Å) and Ag (10000 Å) directly on the emitter. A copper wire was then soldered to the contact, and a polymer mask was applied (i) to define the working area of the electrode in contact with the electrolyte, and (ii) to guarantee the protection of metal contacts from the corrosive HF.

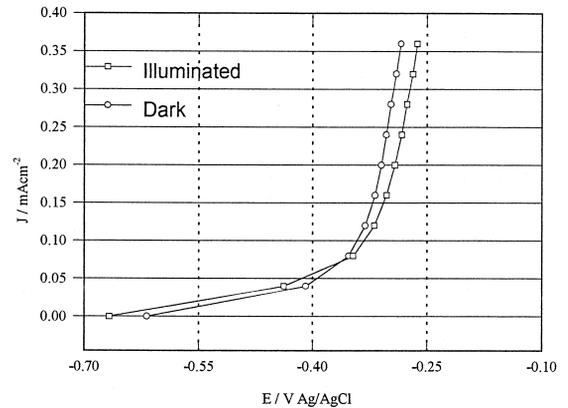


Fig. 2. Current density vs. potential measured with the sample in the dark and illuminated. At low currents the current density is larger if the sample is illuminated; at high currents, the current density is larger in the dark.

The electrolyte was an aqueous solution of 2.5 wt.% HF. For the electrochemical measurements a classical three-electrode arrangement was used, including the sample, an Ag/AgCl reference electrode (in saturated KCl) and a platinum wire as counter-electrode. The reference electrode was connected to the main volume of the cell by a Teflon capillary.

Illumination of the sample was made by an infrared filtered halogen lamp source. Photogeneration was equivalent to about 30 mA/cm<sup>2</sup>. The illumination was uniform during the measurement of the  $j$ - $V$  curves, whereas light/dark patterns were used in the

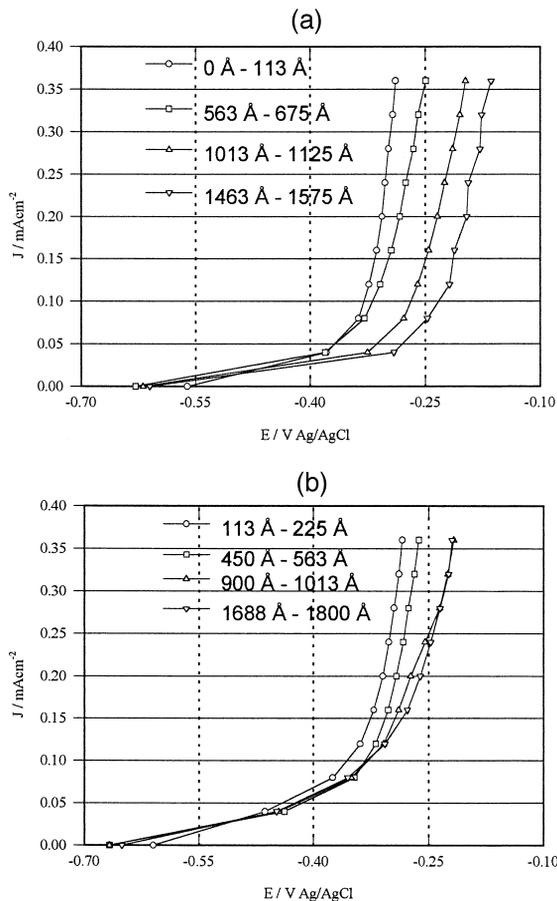


Fig. 3. (a) Evolution of the dark  $j$ - $V$  curves along the etching process. Etched depths before and at the end of each measurement are indicated in the figure. (b) Evolution of the illuminated  $j$ - $V$  curves along the etching process. Etched depths before and at the end of each measurement are indicated in the figure.

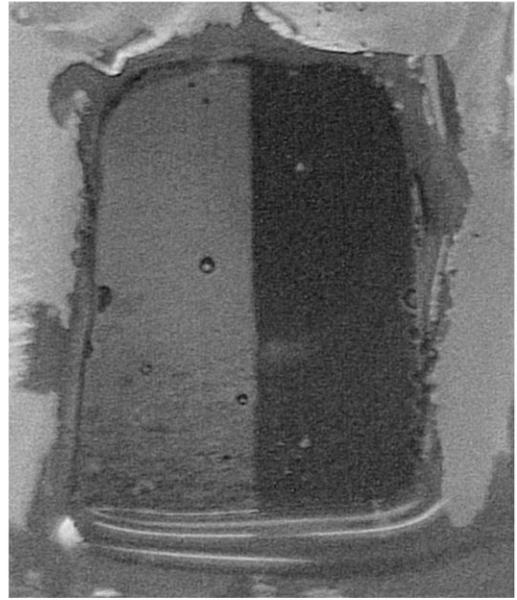


Fig. 4. Photograph of a sample subjected to a photocontrolled etching experiment. Colours indicate different thicknesses of porous silicon.

etching experiments, to create illumination contrast on the sample surface.

Since our aim is to understand the behaviour of the  $n^+$  silicon surface as etching exposes deeper and deeper layers with decreasing dopant concentration, the  $j$ - $V$  curves were taken with stepwise increments of the current, so that an estimation of the corroded depth was possible for each experimental point. Each step lasted for 10 s, during which the potential was measured every 0.5 s, to monitor its settling. Successive  $j$ - $V$  scans, with alternating dark and illuminated conditions, were taken with the same sample, so we could follow its evolution along the corrosion process and evaluate the sample behaviour at each exposed depth of the  $n$  junction layer.

The etching experiments were made with half of the sample area illuminated and the other half in the dark. An anodic current was imposed to the sample for a predetermined time, and the evolution of the potential was checked at regular times.

The etched depths resulting from these experiments were determined qualitatively by the colours of the porous silicon layer, and quantitatively by sheet resistivity measurements. This proved far more

Table 1  
Sheet resistances in the different areas of three of the samples

Time (s)	Charge per total area (C/cm <sup>2</sup> )	$A_{\text{ill}}$ (cm <sup>2</sup> )	$A_{\text{dark}}$ (cm <sup>2</sup> )	Initial sheet resistance ( $\Omega/\square$ )	Sheet res. III ( $\Omega/\square$ )	Estimated etch ( $\text{\AA}$ )	Sheet res. dark ( $\Omega/\square$ )	Estimated etch ( $\text{\AA}$ )
795	0.19	0.42	0.595	14	35.8	850	55.8	1200
794	0.124	0.37	0.545	17	60	1100	84	1300
980	0.127	0.5	0.5	17	33.8	650	59	1100

Estimated etched depths are also shown.

reliable than profilometry for the precise measurement of the fractions of a micron etched away.

### 3. Results

#### 3.1. Current density vs. potential ( $j$ - $V$ ) curves

In Fig. 2 we present two  $j$ - $V$  curves, one taken with the sample illuminated and the other with the same sample in the dark.

Notice that there is a definite dependence on illumination, although of course much less marked than in a less doped n-silicon sample. For low currents, at a given potential, the anodic current is larger when the sample is illuminated than when it is not. For larger currents there is an inversion of this tendency, and the current at a given potential is larger when the sample is in the dark. The direct proportionality between anodic current and etch rate [5,6] leads to the conclusion that two qualitatively different regimes of etching are possible, according to the imposed parameters: one in which the illuminated areas will be preferentially etched, and another, in which it is the dark areas that are most etched. This result is somewhat surprising, since one would expect that the generation of holes by light would always increase the etch rate on the illuminated area.

In Figs. 3a and b, we present the evolution of the  $j$ - $V$  curves of one sample, in the dark and illuminated, with the accumulated corrosion. Notice the tendency for the diminishing of the capacity to pass anodic currents, at a given potential. This effect is not surprising since, as the emitter is being etched, less doped layers are exposed to the electrolyte.

When illuminated, despite an initial decrease, some stabilization follows.

#### 3.2. Etching experiments

In Fig. 4, a photograph is shown of a sample subjected to an etching experiment, with half of the sample area illuminated and the other half in the dark.

The photograph clearly shows different colours on the surface of the sample, which correspond to different depths of the porous silicon film, resulting from different etch rates on the distinct areas of the sample surface.

Table 1 shows sheet resistance measurements along with estimations of the etched depths (based on a complementary error function approximation for the profile of phosphorous concentration).

The tabulated results clearly show that etching of the n+ layer is deeper in the nonilluminated area of the surface, which is consistent with the  $j$ - $V$  curves above.

### 4. Discussion

The  $j$ - $V$  curves do show illumination dependence sufficient for differential photoetching to be considered in n+ emitters. However, since the differences between the dark and illuminated behaviour are relatively small, and our interpretation of photocontrolled corrosion depends crucially on these differences, a discussion of the precision and reproducibility of the measurements is important.

The largest contribution to the uncertainty in current density is due to the measurement of the sample

area; however, this is irrelevant for comparison of the curves obtained with the same sample, and relative errors are in fact negligible.

The uncertainty in the potential is more relevant. But while differences of up to 0.05 V could be observed among the results obtained with the three different samples studied, the relative shifts between pairs of curves in any given sample were quite reproducible. The relevant uncertainty in potential is estimated as less than 0.01 V.

We therefore felt confident enough to carry out a simulation study of an etching experiment using the  $j$ - $V$  curves and their evolution along the etching process. It was assumed that half of the sample was illuminated and that a constant anodic current was applied. The sum of the partial currents must be equal to the applied current and the potential was

assumed to be the same for both areas. Assumption of divalent dissolution for this regime suggests that 1 Å is etched for each 0.16 mC/cm<sup>2</sup>. Fig. 5 shows the evolution of the current densities and of the accumulated etched depth.

Comparison of the difference of etched depths obtained in this figure and that estimated from the experimental results (Table 1) shows qualitative agreement, but quantitatively the experimental contrast is larger than expected from the simulation. This discrepancy indicates that we are not yet in a position to be able to predict quantitatively the results of a photocontrolled etching experiment based solely on the present  $j$ - $V$  curves. However, there is no doubt that the  $j$ - $V$  curves point out the correct qualitative trends, since all seven samples subjected to photocontrolled etching at the high current regime showed very reproducible results. The low current regime was not yet so well explored; only one sample was studied, and it did show the expected trend, that is, higher etched depth on the illuminated side, but this result should be confirmed in other samples.

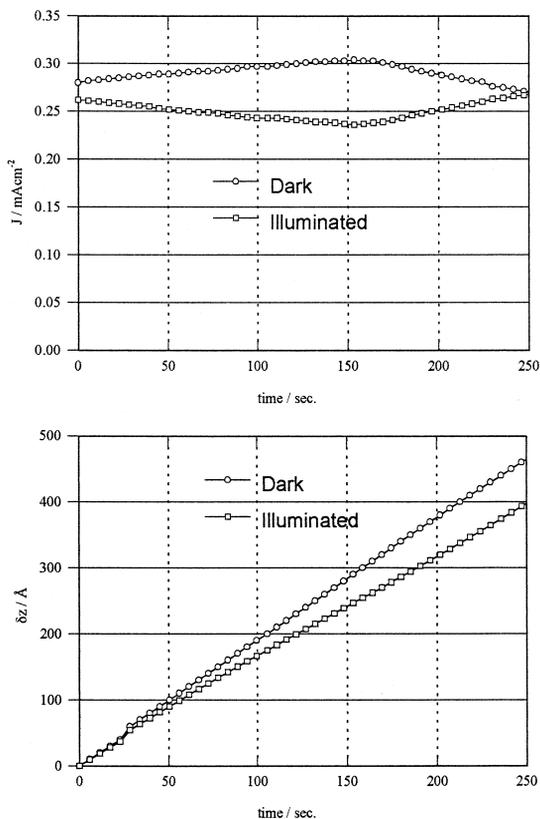


Fig. 5. Evolution of (top) current densities and (bottom) etched depths predicted from the  $j$ - $V$  curves, up to the point of maximum contrast between the two regions. The maximum contrast is 70 Å, while experimental contrasts were about 400 Å.

## 5. Conclusions

We have shown that it is possible to achieve photoselective etching in  $n+$  layers diffused on  $p$ -type silicon. Samples onto which a light pattern was imposed were differently etched according to the local illumination conditions, indicating the possibility of using photoselective etching to create nonuniform  $n+$  layers on  $p$ -type substrates, without the use of a protective mask.

A study of the electrochemical behaviour in HF of the  $n+$  diffused layer on  $p$ -type silicon was presented. Although results were qualitatively in accordance with the etching experiments, further investigation is necessary to allow us to predict quantitatively the etched depths.

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