Surface texturization in multicrystalline silicon by photoelectrochemical corrosion

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ABSTRACT: We present our first results on a study of photo-etching as a possible alternative for the texturization of multicrystalline silicon. A HF solution, containing Br_2 as an oxidizing agent whose chemical corrosion is readily inhibited by photogenerated electrons, was used. Simple patterns have been etched on p-type silicon, with etch-rate ratios, between dark and illuminated regions, reaching over 10:1. One serious limitation is poor lateral resolution, due to carrier diffusion, which causes very modest etch ratios in patterns with period of the order of the diffusion length.

Keywords: Multicrystalline -1: Texturization -2: Etching -3

1. INTRODUCTION

One limitation to high efficiency in industrial multicrystalline solar cells is the lack of a good low cost surface texturization technique. This is stimulating research into unconventional techniques, such as mechanical texturization [1] [2] and anodic formation of a porous silicon layer [3] [4].

We have started a study on photo-etching as a possible alternative for the texturization of multicrystalline p-type silicon, and present here our first results.

The basic principle is simple: a periodic light pattern is projected on to the semiconductor surface; if etching is strongly dependent on illumination, a surface texture can be produced.

2. EXPERIMENTAL PROCEDURE AND RESULTS

2.1 Photoelectrochemical etching of silicon

A HF solution, containing bromine as an oxidizing agent, was used. The etching of silicon by this solution was previously studied by several authors [5] [6]. Chemical etching of silicon, both n and p types, occurs if the conduction band is depleted at the surface of the semiconductor. If electrons are present, however, they readily reduce surface bromine, efficiently inhibiting chemical corrosion.

A preliminary study on the electron current necessary to reduce all the bromine arriving per unit time at the surface, and therefore to completely inhibit chemical corrosion, is better carried out using n-type silicon. This current, of course, is strongly dependent on bromine concentration and liquid agitation at the semiconductor surface. Figure 1 shows a typical I-V curve obtained for 10mM concentration of Br_2 at low agitation. In the absence of bromine, in the range shown, the current is always small, except at the extreme cathodic region, where hydrogen reduction starts to occur.

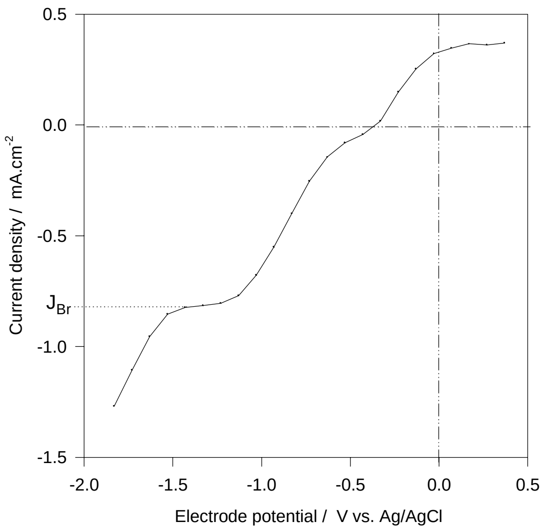

Figure 1. I-V curve for n-type silicon ($n= 4x10^{15}$ cm^{-3}) in 10M HF solution with 10mM concentration of Br_2. Reference: Ag/AgCl. J_{Br} is the cathodic current due to the reduction of bromine. In the J_{Br} plateau region, chemical etching is inhibited.

The curve obtained with the bromine containing solution shows an anodic current, which is attributed to injection of electrons in the conduction band by bromine; but, more interestingly, it shows a clear plateau in the cathodic region attributable to the reduction of bromine by the conduction electrons of the n-type silicon brought to the surface by the cathodic polarization. In this region, the etching rate reduces to a very small value, whereas at the point of zero current, for instance, etch rates of 14 μm/h were obtained.

In p-type silicon, no conduction band electrons exist, and a similar I-V curve obtained in the dark shows a negligibly small current in all the domain shown except where anodic etching of silicon starts, as in Figure 2, curve (A). Etch rates are high (13,7 μm/h) everywhere, due to chemical etching by the bromine, and only increase further in the anodic region. Under sufficient illumination, however, enough electrons are created to produce a cathodic current corresponding to the total reduction of bromine arriving at the surface (J_{Br}, as indicated in the Figure 2, curve (B)), thereby inhibiting corrosion. The illumination intensity used, 0,4 kW/m^2 , was more than enough for this current to be limited by the rate of attachment of bromine molecules to the surface. In fact, with more negative potentials, excess photoelectrons, not used up in bromine reduction, start to reduce hydrogen. The saturation current reached, J_{il} , is now limited by the illumination generation rate. Etch rates are practically nil in all cathodic region; a value of 7 μm/h having been measured even at the J=0 potential.

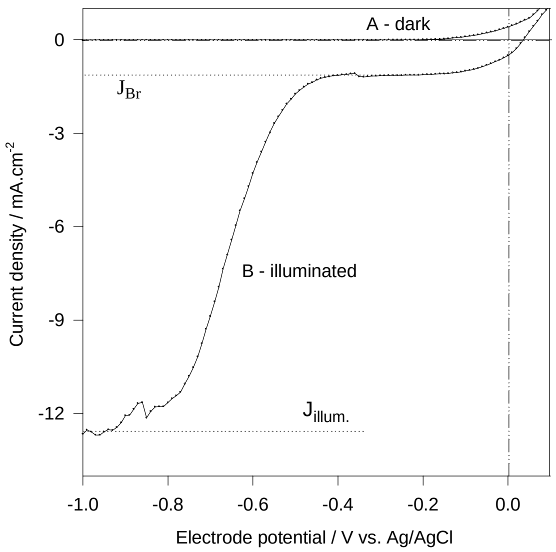

Figure 2. I-V curves for p-type silicon (p= 6.5x10^{14} cm^{-3}) in 10M HF solution containing 10mM of Br_2, obtained in the dark (A) and illuminated with 0.4 kW/m^2 (B). Reference: Ag/AgCl. Etch rates in the dark, where anodic current is negligeable, was 14 μm/h; in the illuminated case, etch rates were ≈ 1 μm/h in the cathodic region, and 7 μm/h in electrodeless condition (J=0).

2.2 Pattern etching in silicon

Pattern etching in p-type silicon was obtained by projection of light patterns on to the semiconductor surface. Br_2 concentrations were 10 and 16mM, in 10M HF solution and illumination intensities of 0.40 and 0.58 kW/m^2 , obtained from infrared filtered halogen lamps, were used.
Etched patterns were measured by profilometry, using both a Dektak mechanical and a Rodenstock optical profilers (this last instrument was proven less reliable, presumably because the microtexturing of the etched silicon surface induces direccional reflexions of the laser spot that produce large spurious steps at grain boundaries, as can be seen, for instance, in the upper right hand corner of Figure 6. Such steps, concerning differences in average etch rates in grains of different orientations, were proven quite small when measured by contact profilometry.)
The present study is restricted to electrodeless conditions. The total current being zero, the polarization of the silicon samples will be such that current due to bromine reduction in the illuminated areas must be compensated by anodic currents everywhere. The ratio of illuminated to total exposed semiconductor area becomes therefore a relevant parameter.
Examples of patterns obtained are shown in figures 3 to 6. In Figure 3, a single light spot was used at 0.4 kW/m^2. As can be seen, the light intensity is sufficient, in the experimental conditions used, to effectively inhibit corrosion in the illuminated area. The etch rate ratio between dark and illuminated area was 11,4 : 1 (see Table 1).

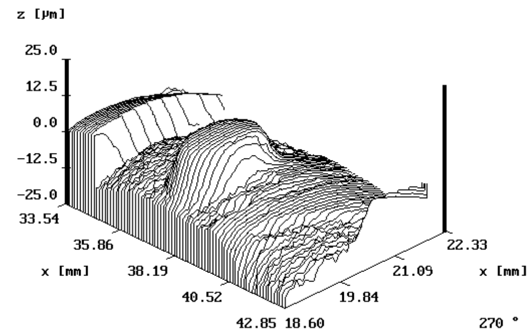

Figure 3. Etched pattern produced in p-type silicon by a single spot, 1 mm diameter and with an intensity of 0.4 kW/m^2. The etch rate at the spot was, within experimental error, 1.2 μm/h.

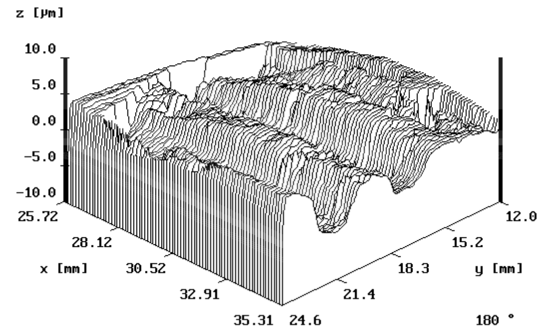

Figure 4. Periodic pattern etched in condition similar to those of Figure 3. Etch rates in illuminated and dark areas were 2 and 8 μm/h respectively.

In Figure 4, a periodic pattern is produced for similar conditions, but with a ratio of illuminated to total area of 1:2. The ratio of etch rates (R_D/R_{IL}) in dark and illuminated areas was decreased in average to 3 μm/h, presumably due to the effect of anodic etching even in the illuminated areas (see Table 1).

Table 1

	Etch rate dark, R_D / μmh^{-1}	Etch rate Illum. R_{IL} / μmh^{-1}	Ratio: Illum. area / total area	Ratio: R_D/R_{IL}
1 Spot $\Phi \sim 1$ mm	13.7	1.2	< 1:100	11.4
Lines T~ 4 mm	10.3	3.4	1 : 2	3.0
P. Spots T~ 150 µm	15.6	12.9	1 : 5	1.2

A broadening of any sharp pattern features is, of course, expected, due to lateral minority carrier diffusion.
This is illustrated in Figure 5, where a scan accross the illuminated-to-dark frontier, obtained by contact profilometry, is shown. The broadening of the feature is of the order of the diffusion length measured for that material, L_n= 160 µm.

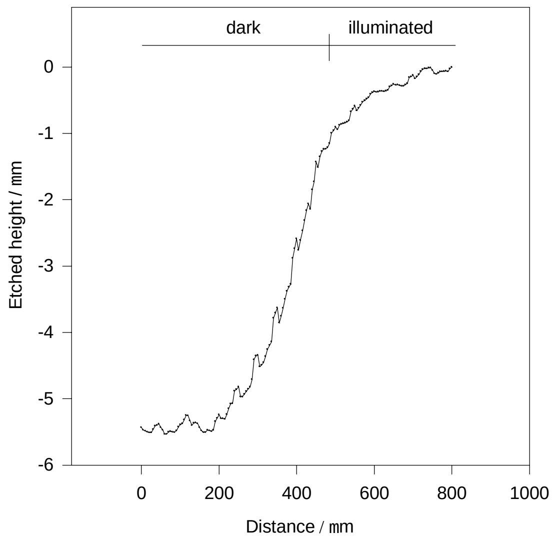

Figure 5. Detailed profile of the transition region produced by a sharp dark to illuminated frontier. Diffusion length was 160 µm.

If one imposes a pattern with a period of the order of the minority carrier diffusion length, which is also the order of that necessary for future solar cell texturing, it is therefore expected that a low contrast between illuminated and dark areas results [7]. This effect is clearly patent in Figure 6, where a pattern with a spatial period of 150 µm was imposed on a sample of L_n= 160 µm. As expected, a very modest contrast in etch rates of 1.2 was obtained.

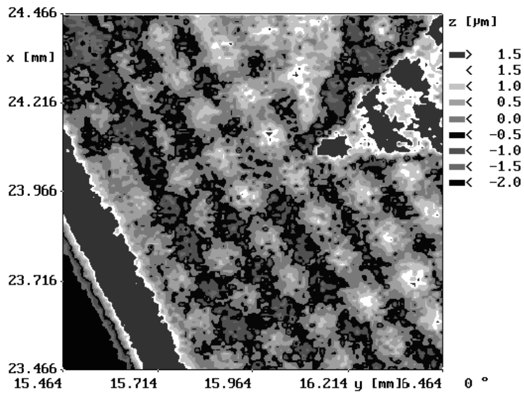

Figure 6. 2-D representation of a periodic pattern etched in condition similar to those of figures 3 and 4. Very low contrast is obtained when spatial periods of the order of L_n are imposed.

3. DISCUSSION AND CONCLUSIONS

We have shown that high contrast relief can easily be obtained, even in electrodeless conditions, with etch rate ratios, between dark and illuminated areas, of the order of 10:1 (depending on the fraction of illuminated area) for patterns with period longer than L_n.
The low etch rates used are a consequence of the voluntary limitation, in the present study, to solutions with low oxidant concentrations, since all processes are easier to control, and low intensities of illumination are sufficient for the inhibition of corrosion. This is justifiable in the present exploratory work; for practical application, higher etch rates will of course be studied. Another limitation in this study, related to the one above, is that only the initial etch rates, which are easier to interpret, were measured; our work did not extend yet to the strong relief needed for solar cells.
The most important limitation in the application of the technique studied is lateral resolution. Since patterns of interest for the texturing of solar cells should have periods in the range of tens of micra, and diffusion lengths for high efficiency should be at least of the same order, photo-etching will not become a practical texturization technique unless ways to overcome this limitation are found.

4. ACKNOWLEDGMENTS

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