Patterned surfaces in p-type silicon by photodefined etching

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Abstract

We present a simple technique for photodefined etching of p-type silicon. The technique involves wet photoselective corrosion of silicon by an aqueous HF solution containing a strong oxidising agent (bromine). The etching process can be largely inhibited by light, allowing the shaping of photodefined 3-D structures on the surface of p-type silicon samples. These structures are not dependent on crystalline orientation, which is an important advantage in polycrystalline silicon texturing. The fundamentals behind the process, involving electrochemistry of semiconductors, are presented along with a discussion of the process parameters. The process was studied both in open circuit conditions, which have the advantage of requiring no electrical contacts, and with an imposed current, which should allow better etching contrast at any illuminated to dark area ratios. The results clearly demonstrate that it is possible to obtain effective etching inhibition in illuminated regions of the semiconductor, while high etch rates are retained in dark areas. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

We report a study on the formation of surface relief patterns in p-type silicon by photoelectrochemically defined etching. Fundamentals of semiconductor electrochemistry and photoelectrochemistry, together with detailed examples of studies in specific semiconductor/electrolyte systems, can be found in Refs. [1–6]; a few relevant examples of photodefined etching of semiconductors are given in Refs. [7–9]. The basis of photoelectrochemically defined etching of p-type semiconductors can be described as follows.

Incident photons create electron-hole pairs, and since spontaneous band-bending, in p-type semiconductors immersed in electrolyte solutions, is frequently such that it favours the migration of electrons to the semiconductor-electrolyte interface, reactions that require the availability of electrons from the semiconductor will show a rate that is dependent on illumination. Any such reaction that involves etching, or etching inhibition, of the semiconductor, is a candidate for photodefined surface patterning.

In the present study, we chose, for electrolyte, a HF aqueous solution containing a strong oxidising agent (bromine), as in Ref. [9]. Oxidants are known to readily produce semiconductor chemical etching. However, if conduction electrons are available at the interface, electrochemical reduction of the oxidant competes with chemical etching [7–10], and may effectively inhibit it.

A previous study of photodefined pattern formation in p-silicon in a HF solution containing Br_2

showed the possibility of obtaining high etching contrast ratios between illuminated and dark regions, provided the ratio of illuminated to dark areas were very small [11], in accordance with the model proposed in Refs. [7,8] for GaAs. This study was, however, limited to very low etch rates, and to open-circuit conditions. Here it is our aim to extend our understanding of this system, and to extend the study to more interesting conditions for practical purposes, namely to investigate the conditions, in particular the cathodic current density, for effectively inhibiting etching in illuminated regions of the semiconductor, while obtaining higher etch rates in the dark areas.

2. Experimental

Silicon samples were p-type, monocrystalline (20 Ω cm, $L_n \sim 150$ μm) and multicrystalline (0.5 to 2 Ω cm, $L_n \sim 150$ μm).

The electrolyte was an acidic aqueous solution of bromine (15 to 35 mM Br_2, 10 M HF), in a container with a flat transparent window. The sample was held parallel to the window, so that an almost laminar flow could be imposed. Light patterns could be projected onto the sample. The light source was an infrared filtered halogen lamp (filament temperature 3400 K), which provided illumination intensities, at the sample position, corresponding to an effective photogeneration rate in silicon of about 32 mA/cm².

Two different types of experiments were carried out: (i) current potential curve measurements; and (ii) etch rate measurements.

Current was always applied between the sample and a Pt counter electrode, and potential measured against a platinum reference electrode (which was previously calibrated against a standard Ag/AgCl electrode, and found to be a reliable reference in our experimental conditions).

In the etch rate determination experiments, periodic light patterns (usually black and white stripes, obtained simply by passing the light through a projector slide with stripes of opaque material) with spatial periods ranging from 3 mm to 250 μm and different ratios of illuminated to dark areas were used. Shadow borders, defining the 'black' to 'white' light intensity transition region, were less than 10

μm thick, as measured by direct microscopic observation of the projected pattern in the sample position. These experiments were carried out both in electroless conditions and with application of a cathodic current. The etch rates were measured with a Sloan DekTak IIA surface profiler.

3. Results

3.1. Current–potential curves

In Fig. 1, we present three $I–V$ curves obtained in different illumination and agitation conditions. In the dark, the cathodic region shows almost no current, since there are no electrons available in p-type silicon to reduce bromine or hydrogen. In the scale of the graph, the curves obtained with or without agitation of the electrolyte are indistinguishable. As the potential becomes more positive, the current increases rapidly in the anodic region, which corresponds to well known anodic dissolution setting in (possible since in p-type silicon holes are in abundant supply).

In the illuminated condition, photogenerated electrons, whose migration towards the surface is favoured by the energy band bending in the semiconductor, reduce the oxidising agent, bromine, producing the observed cathodic current plateau I_{Br} (between about -1.0 and -1.5 V in Figs. 1 and 2),
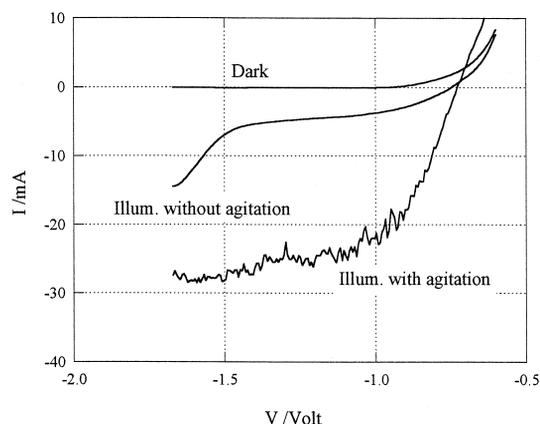

Fig. 1. Current–potential curves for p-silicon in the Br_2–HF electrolyte and (i) in the dark, (ii) illuminated, without agitation, and (iii) illuminated, with agitation.
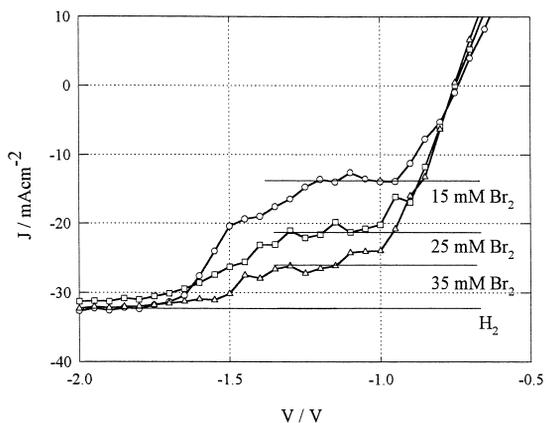
Fig. 2. Current density–potential curves for three different bromine concentrations: 15 mM; 25 mM and 35 mM, showing both bromine and hydrogen reduction current plateaus.

which could correspond to a condition when all bromine ions arriving in the interface would be reduced, and is therefore limited by the bromine supply. That the supply of bromine to the surface plays an important role is illustrated by comparison with the lower curve, obtained for the same concentration of bromine (35 mM) but with agitation of the liquid, where the I_{Br} plateau current is greatly enhanced. At higher cathodic potentials (about -1.5 V), hydrogen reduction sets in, using up the remaining available photoelectrons that were not consumed by bromine reduction. Notice the H_2 hydrogen reduction plateau, very well defined in Fig. 2, which was found to be proportional to illumination intensity: as expected, the maximum cathodic current is limited by the number of photogenerated electrons (and not, of course, by hydrogen supply to the surface, which is very abundant).

Also in Fig. 2, the effect of bromine concentration, under the same illumination and agitation conditions, is evident. As expected, the current plateaus I_{Br}, labeled in the graph by the Br_2 concentration, increase with bromine concentration; however, their variation is less than proportional to concentration, suggesting that simple diffusion to the surface is not the only conditioning factor.

3.2. Etch rates

In the solution studied, silicon is chemically etched at a rate that was found to be practically independent
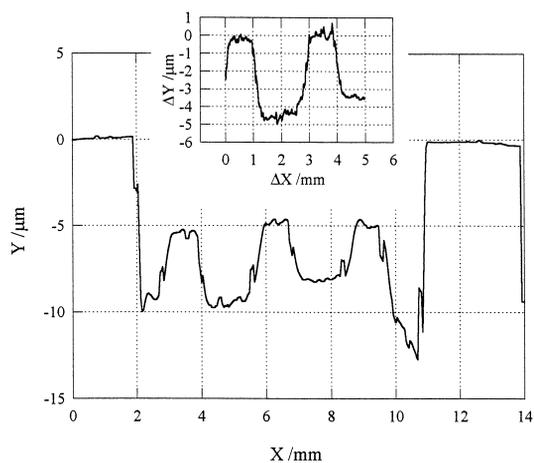

Fig. 3. Profile of an etched sample on which a 3-mm period 'black and white' light pattern was imposed. This sample was etched at open circuit conditions.

of resistivity and crystalline orientation. However, in the presence of light, the photogenerated electrons reduce bromine and, therefore, decrease the chemical corrosion of silicon. This is the basis of our proposed technique for producing surface relief patterns: by applying a light pattern on the surface, we should achieve differential etching rates in the illuminated and dark regions.

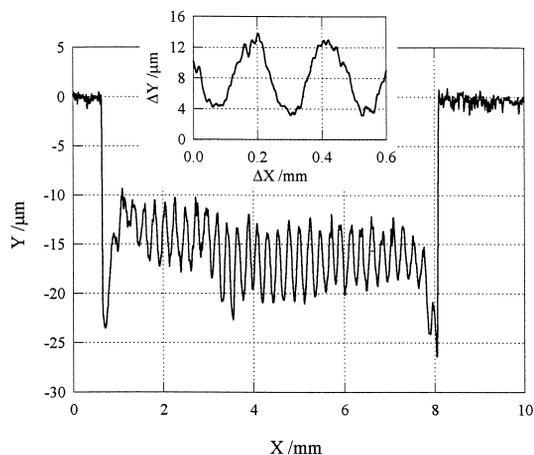All experiments were carried out with 35 mM Br_2, and with constant agitation.

Fig. 4. Profile of an etched sample on which a 0.23-mm period light pattern was imposed. This sample was etched at open circuit conditions.
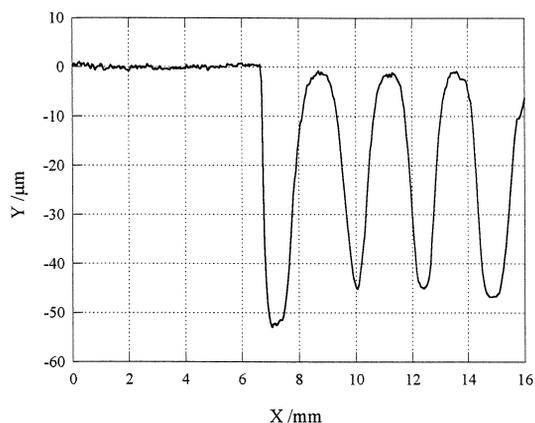
Fig. 5. Profile of a sample on which 2.5 mm period light pattern and a cathodic current (as described in the text) were imposed.

In a first set of experiments, no current was applied to the sample (open circuit conditions). One example of the results obtained under these conditions are shown in Fig. 3 for a long period pattern. The etch rates were about 30 μm/h in the dark regions, and a half that in the illuminated regions.

A second example, for a higher pitch, also 'black and white', pattern, is shown in Fig. 4. It is patent that the contrast between etch rates in dark and illuminated regions has decreased. The detail gives a hint to an explanation: the profile is far from the 'square wave' shape of the imposed illumination intensity.

In a second set of experiments, a cathodic current was imposed, carefully chosen so that the current density in the illuminated area should be 28 mA/cm^2, just in excess of the bromine reduction plateau, with the hope that total inhibition of etching might then occur. An example of the results is shown in Fig. 5. As can be seen, the etch rate in the dark regions was about the same as before. However, in the illuminated regions the etch rate is now close to nil, as expected.

4. Discussion

4.1. Lateral contrast

It is clear that the etched profiles are rather smoother than the 'black and white' light pattern

imposed. The light pattern was sharp to about 10 μm, whereas profiles show transition regions one order of magnitude higher. This is to be expected, since photogenerated electrons will diffuse in the bulk of the semiconductor, and thus blur any sharp pattern by a scale of the order of the electron diffusion length in the semiconductor [3], which was $L_n \approx 150$ μm. This cannot be avoided in the present experimental conditions; however, preliminary simulations of carrier generation and transport suggest that it is possible, in principle, to overcome this limitation. This possibility will be explored in future work.

4.2. Depth contrast

In open circuit conditions, we were not able to inhibit completely the chemical corrosion in the illuminated regions. The reason for this is the following: when a semiconductor is non-uniformly illuminated, in open circuit conditions, the effective potential will be a mixed one, between the dark and the illuminated ones at zero current, and determined by the ratio of illuminated to dark areas, since the cathodic current in illuminated regions must equal the anodic current in dark areas. Except for very low such ratios, the cathodic current in the illuminated area will be much smaller than the necessary current for the total inhibition of chemical corrosion, i.e., the bromine current plateau. This is the main reason why we obtain relatively high etch rates in the illuminated areas: the area ratios used in this set of experiments were only 1:2 and 1:3.

In order to achieve a better inhibition of etching in the illuminated areas, we carried out a series of experiments with an imposed cathodic current, previously selected from I–V curves such as those in Fig. 2. The aim was to achieve a current density in the illuminated areas equal to the bromine reduction plateau, since in these conditions total inhibition could be hoped for. The bromine concentration (35 mM) was chosen to match the intensity of illumination, that is, as high as possible while producing a bromine reduction plateau current (indicated 35 mM in Fig. 2) below the total photocurrent, indicated H$_2$ in Fig. 2. Under these conditions, not only high

chemical etch rates should result for the dark areas, but also few photogenerated electrons would be left for hydrogen reduction when the bromine plateau is exceeded. The advantage, in the present experiments, is that very little hydrogen can ever be evolved, so almost no bubbles were formed that could further blur the etched patterns. (For future experiments, according to simulation, this should also be a condition to help overcome the lateral resolution problem.) The experimental results confirmed that almost total inhibition was indeed reached.

5. Conclusions

A study was carried out in which etching rates were determined for both open circuit and cathodic bias conditions. The results obtained showed that samples etched in open circuit condition presented an in-depth contrast which was less than the one obtained when imposing a cathodic current. An explanation is presented, taking into consideration the current-potential behaviour of p-type silicon in the acidic bromine electrolyte. Based on this behaviour, we were able to choose the adequate current in order to obtain total inhibition of the etch rate on the illuminated area of the samples.

We have shown that by carefully selecting the oxidising agent concentration, the light intensity and the working current (keeping agitation constant), total inhibition in the illuminated areas is achieved, thus enabling photoselective corrosion with a good differential etch rate.

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