

### **Properties of Silicon–Electrolyte Junctions and Their Application to Silicon Characterization\***

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Abstract. A number of interesting and still not fully understood phenomena occur if silicon is used as an electrode in an electrochemical cell. Effects include porous silicon layer (PSL) formation with features on a nanometer scale, surface roughening on a micrometer scale, quantum efficiencies for light generated currents much larger than 1, preferential etching of defects, electropolishing, and voltage or current oscillations. It is shown that despite the complexities of chemical reactions involved, a basic understanding of the electrode behavior is possible from a semiconductor physics point of view and that it can be advantageous to use the silicon – electrolyte junction for analytical purposes. Topics such as defect characterization, measurements of minority carrier diffusion length, or surface recombination velocities can be addressed in unique ways by taking advantage of particular properties of the silicon – hydrofluoric acid system. Based on the general description of the Si – electrolyte junction given in this paper, strengths and limitations of some electrochemical methods are discussed in some detail and illustrated by examples.

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The junction between a silicon crystal and an electrolyte provides not only for fascinating research, including new and unexpected "kristallene Krisen" [1], but offers many properties useful for processing and characterizing silicon. Since a thorough review of all aspects of silicon–electrolyte junctions does not exist, this paper, besides presenting some new insights, attempts to impart at least the flavor of the subject, albeit with a strong bias towards applications in general silicon analytics. A list of topics of interest includes:

(i) Basic physics and electrochemistry. Suffice it to mention the still mysterious porous silicon layer (PSL) obtainable under some conditions [2-6] with its fractal geometry [7] or the equally mysterious current (or voltage) oscillations [8,9] exhibiting all the symptoms of synergy and chaos.

(*ii*) Solar energy conversion. While the main emphasis in this field focuses on semiconductors other than Si [10], there is still a considerable interest in Si as an electrode material [11].

(iii) Understanding wet chemistry in the processing of microelectronic devices. Despite the rapid advance of plasma processing for etching all materials in chip manufacture, even the state-of-the-art technology, e.g., for a 4 Mbit memory, still employs many "wet chemistry" processing steps (mainly cleaning and layer stripping) [12] which are not too well understood and cause considerable trouble in many production lines.

(iv) Controlled dissolution of silicon to obtain special structures. Well known is the use of electrochemical methods for manufacturing thin membranes [13]; other structures may include "black silicon" or super-deep trenches as outlined in [14].

(v) Electrochemical processing steps for microelectronic devices. Many schemes have been proposed that take advantage of the special properties of the PSL [15–17]; others employ anodic oxides or metal deposition.

(vi) Using the silicon-electrolyte junction for characterizing silicon. Preferential defect etching or the measurement and mapping of the minority carrier diffusion length or the surface recombination velocity are some of the possibilities where electrochemical methods offer unique advantages.

<sup>\*</sup> Dedicated to H.-J. Queisser on the occasion of his 60th birthday

This paper concentrates on the last item; the other items are occasionally touched upon when appropriate in the context.

Characterizing silicon can be a formidable task, especially if answers to "simple" questions are solicited: "Why is the yield of functioning devices much higher on wafers from supplier A as compared to supplier B?;" see [12]. Electrochemical methods can naturally cover only some ground in this rather large field; what can be offered is:

(i) Preferential etching of crystal lattice defects. Several modes are possible which are relatively well understood in comparison to purely chemical etches.

(ii) Well-defined dissolution of silicon. Whether done directly or via anodic oxides, it can be used for specimen preparation or for profiling techniques.

(iii) Accurate prediction of the efficiency of a solar cell made from the Si sample under investigation.

(iv) Pin pointing defects in layers by several modes: Anodic or cathodic decoration [18] for shorts in p-n junctions, or H<sub>2</sub> bubble decoration for pinholes in isolating layers [19].

(v) Minority carrier lifetime or diffusion-length measurements in several modes with the option of large-area mapping [9, 20].

(vi) Surface recombination velocity measurement and mapping [21].

(vii) Much more, e.g. capacitance – voltage measurements, leakage current mapping or electro-reflectance studies.

At present, at least two commercially available tools exploit silicon electro-chemistry: the Polaron profile plotter [22], offering measurements of doping profiles by combining (ii) and (vii) of the above list, and the ELYMAT [21], offering diffusion-length and surface recombination velocity mapping.

So far, no restrictions have been made concerning the chemistry of the electrolyte or specific properties of the silicon, for example, doping type or defect density. Unfortunately, a particular method is usually not equally well applicable to both doping types of silicon. Understanding what can be done in given circumstances and selecting the suitable chemical and experimental conditions is therefore not always straightforward. This is probably the main reason why electrochemical methods are viewed with some suspicion by the hard-core silicon community ("it is not only chemistry, but – even worse – electrochemistry").

This paper aims to provide a basic understanding of the elementary phenomena at the silicon electrode, discusses the most important parameters that have to be taken into account, and describes the possible exploitation of the observed phenomena for analytical purposes. For simplicity's sake, only diluted hydrofluoric acid (HF) and occasionally acetic acid will be considered as the electrolyte and, for physicists' sake, chemistry and electrochemical language will be omitted as far as possible.

### 1. Basic Properties of the Si-HF Junction

The basic experiment consists of immersing a defined area of a silicon specimen (e.g. the front side of a wafer) into hydrofluoric acid; it is most easily carried out with dilute HF (e.g. 1%-5%). The use of concentrated HF does not change the essential features and is often referred to in the literature but tends to obscure certain details because of violent gassing and other effects tied to rather high current densities in this case. A constant voltage (or current) is applied between the Si and some counterelectrode (typically a chemically inert material such as Pt), and the resultant current (or voltage) is measured.

Since voltage drops across the electrolyte and voltage offsets by the counterelectrode (which forms "one-half" of a battery) are of no importance, a so-called reference electrode is employed close to the Si surface – the experiment is essentially carried out in a four-point probe configuration with separate current and voltage leads. Experimental details such as stirring of the electrolyte, wetting agents added to the electrolyte, back-side contacts, etc., although extremely important for the success of a real experiment, will be neglected here – for details see [23].

If the voltage is varied (not too fast) and the silicon electrode is nonexotic (with respect to doping, defect density, etc.), current-voltage (I-U) characteristics as shown in Fig. 1 are obtained.



Fig. 1. I-U characteristics for p- and n-type Si in agitated 5% HF. Breakthrough occurs at  $\approx 10$  V, corresponding to a specific resistance of  $\approx 0.1 \,\Omega$  cm. Voltage and current scales are representative and not accurate in detail

	р-Туре		п-Туре	
	Dark	Illuminated	Dark	Illuminated
A N O D I C	No influence Forward bia Si dissolution [several ( <i>Special fea</i> – PSL form – Defect et – Electropo – Current/	of illumination used junction ?) different mechanisms] <i>tures</i> nation ching plishing voltage oscillations	Reverse bi Silicon o Specia Etching of defects	<ul> <li>ased junction</li> <li>dissolution</li> <li><i>l features</i> <ul> <li>Photocurrent not</li> <li>proportional</li> <li>to light flux</li> <li>I, U independently</li> <li>adjustable by light</li> <li>Etching of defects</li> <li>in several modes</li> <li>"Black silicon" etch</li> <li>features</li> </ul> </li> </ul>
C A T H O D I C	Reverse biased junction         H2 evolution; Si inert         Special features         - Very low leakage current         - Defect decoration         by H2 bubbles		No influence of illumination Forward biased junction H <sub>2</sub> evolution; Si inert Special features – None of interest here	

Table 1. The six basic electrode configurations and their most important features for diluted HF as the electrolyte

It is evident that p-type and n-type Si behave very differently and that the presence or absence of light or, more specifically, minority carriers is a major factor determining the I-U characteristics of the junction. Since the sign of the current flow (rather than the sign of the voltage) determines the chemical reaction, eight basic situations can be distinguished. Table 1 shows these cases (reduced to six) and identifies their major features.

At a first glance, some similarities to a Schottky contact are apparent, and some applications indeed use the electrolyte instead of a metal layer, but there are also important differences:

(i) Current flow is *always* accompanied by a chemical reaction. With HF as the electrolyte this is *always* dissolution of the Si electrode for anodic currents (positive sign of I; i.e. holes flowing from Si into the electrolyte or electrons flowing from the electrolyte into the Si); and *always* H<sub>2</sub> evolution for cathodic currents.

(ii) The voltage is relatively ill defined because the built-in battery voltage of the Si electrode - its electrochemical potential – is not always a well-behaved quantity but depends on many parameters and may be changing somewhat with time. In addition,  $H_2$  evolution needs a certain minimum voltage ("overvoltage"); otherwise current flow is inhibited. Thus the voltage for zero current flow may not be reproducible within a few 100 mV, and for small cathodic voltages the cathodic current flow is controlled by chemistry rather than by properties of the Si electrode. This may have important consequences for some applications. For example, unlike a Schottky contact, the junction does not change continuously from depletion to accumulation but goes through inversion. As far as most applications are concerned, the voltage is, however, not a parameter of interest (excluding, of course, solar energy applications).

(iii) Photocurrents are proportional to the light flux for p-type Si (for an exception see [24]), but not for n-type Si. For Si wafers differing only with respect to the doping type, photocurrents are considerably larger in n-type Si.

There is a basic asymmetry between n- and p-type silicon: whereas the current flow characteristic essentially changes from forward biased to reverse biased and vice versa if the sign of the majority carriers is changed, the chemical reaction stays the same. Consequently, dissolution of silicon proceeds at the forward biased part of the junction characteristic for p-type Si, implying majority carrier current, and for the reverse biased part of the n-type Si characteristic, implying a minority carrier current. In other words: anodic currents are driven by holes.

## 2. Specific Properties of *p*-Type Silicon and Some Applications

### 2.1 Cathodic Currents

Most easily understood and put to use is the cathodic current regime of *p*-type silicon. For voltages larger than the minimum voltage needed for  $H_2$  evolution (at most a few volts and easily decreased by optimized electrolytes), the junction behaves like a reverse-biased Schottky contact with a very low density of interface states. In the dark, a leakage current flows; current densities as low as  $0.2 \,\mu\text{A/cm}^2$  for areas > 100 cm<sup>2</sup> have been observed [21]. Current breakthrough occurs at a voltage determined by the doping level; in contrast to Schottky contacts, this occurs without irreversible damage to the junction even at high current densities.

If the Si-HF junction is illuminated, a photocurrent is superimposed on the dark current. The collection effici-



Fig. 2. Comparison between I-U characteristics obtained with the silicon–electrolyte junction and with Schottky (MIS) contacts. The current densities in the MIS case are smaller because of light loss in the metal layers. (After [23])

ency of the junction is practically 1; the photocurrent therefore depends only on the conversion efficiency of the Si for the particular light intensity and spectrum employed. This effect can be put to practical use: If a standardized light source is used (e.g. AM 1), the value of the photocurrent relative to that of a "perfect" reference sample allows a very good prediction of the efficiency of a solar cell that could be made with the Si sample under investigation [23]. This is illustrated in Fig. 2.

The method offers several advantages over more conventional techniques:

(i) No preparation for making the collecting contact is necessary. If the leakage is too high because of insufficient surface quality, in situ electro-polishing is possible.

(ii) The method is applicable to very small *and* to very large samples.

(iii) The absorption of the collecting contact is practically zero.

(iv) A mapping of the photocurrent distribution is easily possible if a scanned light beam is used.

The photocurrent is essentially a function of the diffusion length L of the minority carriers and of the collection efficiency of the junction. The latter is dominated by defects, for example, grain boundaries, dislocations or metal precipitates in the space charge region and by the density of interface states.

Given the very low density of interface states at the Si-HF junction [25] and practically defect-free standard Si wafers, the photocurrent depends only on the diffusion length L and the density of minority carriers as a function of depth. Since the latter can be calculated from the spectral intensity of the light source, L can be determined by simply measuring the photocurrent – this is the so-called FPC mode (Front-side Photocurrent) employed in the ELYMAT (Sect. 4).

Standard techniques for diffusion length measurements are also applicable. The basic principles of the surface voltage (SPV) method, for example, are easily adopted to the p-Si–HF junction in the cathodic regime, see [26]. In this case, the dependence of some junction parameter (e.g., photovoltage or photo-current) on the wavelength is the quantity of interest. By adjusting the light intensity at several wavelengths for constant junction response, L can be deduced even if the junction is far from perfect.

Instead of leakage currents or photocurrents, the capacity of the junction can be measured. Information about the space charge region and doping are thus obtainable. In contrast to standard techniques employing Schottky or MOS contacts, depth probing can be achieved not only by varying the applied voltage but also by controlled (in situ) dissolution of the Si by switching to appropriate anodic conditions (see below).

A last class of applications should be briefly mentioned. If current flow is generally inhibited because of isolating layers (e.g.,  $SiO_2$  on the Si, or p-n junctions in the wafer), photocurrent only flows through defects in these layers. The localized H<sub>2</sub> evolution associated with the current pinpoints the defects. Of course, for SiO<sub>2</sub>, an electrolyte other than HF has to be chosen, e.g. acetic acid, which, for cathodic currents, behaves similarly to HF but without dissolving the SiO<sub>2</sub> layer.

The method can be made more quantitative if a scanned light beam is used. Then current flows only if a defect is present and while the defect-containing region is illuminated.

### 2.2 Anodic Currents

For all anodic currents, Si dissolves. The detailed mechanisms and their manifestations are, however, quite different in the three distinct regions separated by  $I_{PSL}$  and  $I_{osc}$ , see Fig. 1, in the I-U characteristics.

The most important properties are listed in Table 2.  $I_{PSL}$  and  $I_{ose}$  increase linearly with the HF concentration. The transition regions they define are rather sharp, particularly if the electrolyte is stirred. Table 2, although greatly simplifying the rather complex electrode behavior, still indicates a number of open questions or puzzles. The most intriguing feature is the formation of porous silicon layers (PSLs), with nanometer-sized pores and walls between pores while still maintaining single crystallinity.

The porous structure may be best described in terms of fractal geometry [7], adding even more interest to an already tantalizing subject. A considerable number of papers have been published addressing properties of PSLs, their dependence on experimental parameters and their possible use for microelectronic devices; for references see [15–17]. Until recently, however, practically no explanation was offered as to why PSLs form in the first place. The crude features of a model emerge by following and enlarging somewhat on the ideas given in [5, 6, 14, 27]:

(i) Assuming that for  $I < I_{PSL}$  a space-charge region still exists although the junction is forward biased (junction depleted), a basic tendency for selective growth of randomly nucleated depressions exists because of the current-focusing action of the space-charge region (see Fig. 8 and explanations in Sect. 3.2).

	I < I <sub>PSL</sub>	$I_{\rm PSL} < I < I_{\rm osc}$	$I > I_{osc}$
Dissolution mechanism		· · · · · · · · · · · · · · · · · · ·	
– Valence	$\approx 2$	$\approx 4$	$\approx 4$
<ul> <li>Injected electrons per hole</li> </ul>	3–1	<1	≈0.2
– Basic chemistry	Direct divalent dissolution	Anodic oxide formation? Direct tetravalent dissolution?	Anodic oxide formation Details unclear
Surface appearance	Interference colors/PSL for- mation Thickness dependent on $\langle hkl \rangle$	Shiny/grain structure revealed	Polished/independent of $\langle hkl \rangle$
I-U characteristics	Exponential; following diode equation; independent of stirring	Linear (ohmic); somewhat dependent on stirring	Linear; oscillations for vigorous stirring Current saturation; oscillations without stirring
Applications	Defect etching Specific PSL uses	Defined dissolution Removal of PSL	Defined dissolution Surface conditioning

Table 2. Some important properties of p-Si electrodes anodically biased in diluted HF. "Valence" defines the number of charge carriers needed to bring one Si atom into solution



Fig. 3. I-U characteristics with voltage oscillations starting at  $I_{osc}$  (constant current experiment). The insets show two voltage-time plots for the two current densities defined by the time scale. Numbers are representative for strongly agitated HF with  $\approx 5\%$  concentration and are not accurate in detail

(ii) The pore walls are stabilized against eventual dissolution because below a critical thickness they constitute "quantum walls" with a band gap around 1.5 eV and therefore without any free carriers available for chemical reactions.

These two mechanisms are independent but can act together not only for the formation of PSL on *p*-type Si but also for the generation of a large variety of features on n-Si; see Sect. 3.2.

Porous silicon layers may constitute a new class of semiconductors – fractal semiconductors or multiply connected quantum wall structures – with thrilling new properties. For example, PSLs may not only have a much higher effective band gap than "massive" Si, but may be a *direct* gap semiconductor [5,6], possibly opening the door to a whole new world of optical Si devices! Omitting discussion of the little explored and relatively uninteresting and poorly understood region where  $I_{PSL} < I < I_{osc}$ , we pass to the region  $I > I_{osc}$ , which does merit a few observations. As shown in Fig. 3, very regular current (or voltage) oscillations are observed if the voltage (or the current) is held constant. Electropolishing takes place and dissolution is therefore assumed to proceed via the formation of an anodic oxide, which in turn is dissolved (purely chemically) by the HF. The presence of a dielectric layer is generally held to be responsible for electropolishing; Fig. 4 gives a qualitative explanation. Figure 4a illuminates why the opposite of polishing – surface roughening – takes place for  $I < I_{PSL}$ , or, generally



--- Equipotential lines --- Current paths

Fig. 4. Current distribution across surface irregularities in the case of (a) a space-charge region (SCR) in the Si and (b) a dielectric layer on the Si (oxide). The major voltage drop determining the current flow is either in the oxide or in the SCR; some equipotential planes and the resulting current distribution are shown

speaking, if the current-determining electrical field is the space-charge region within the Si. In both cases, the bending of the equipotential planes around surface irregularities locally focuses or defocuses the electric current, but with reverse effects: surface irregularities are removed if the electric field is outside the silicon, and enhanced if it is inside. The sudden lift-off of a PSL layer (not dissolution!) if the current is raised above  $I_{PSL}$  can then be attributed to the switch-over in mechanism if oxidation already occurs for  $I > I_{PSL}$  or, alternatively, if direct tetravalent dissolution is the dominant mechanism (Table 2), to a switch from depletion to accumulation (destroying the space-charge region) at  $I_{PSL}$ .

Current or voltage oscillations at electrodes (mostly metals) have been observed in many cases. Modern physics has recognized that it is a synergistic phenomenon [28]; recently a connection to chaos theory was also established [29]. What is still lacking, however, is a basic understanding of the underlying, most likely general, mechanism. Existing models (see [29]) have focused on the chemical side but lack either generality for a very general phenomenon or rely on specific assumptions. Here the outline of a model based on the solid-state side will be proposed. With the assumption of a constant current  $I > I_{osc}$ , the following reaction steps are envisioned:

- SiO<sub>2</sub> is anodically grown at a rate faster than its (purely chemically determined) dissolution rate.

- As long as the oxide is very thin, current flows via a tunneling mechanism, and the voltage required to drive the current is relatively small.

- Above a critical oxide thickness, the voltage has to increase rapidly to maintain current flow.

- The voltage at some point in time exceeds the dielectric strength of the oxide; breakthrough occurs, adding a second mode of current flow.

- The chemical reaction associated with the breakthrough current component is *not*  $SiO_2$  formation but something else (e.g., direct tetravalent Si dissolution at the bottom of discharge channels).

- The formation rate of  $SiO_2$  therefore decreases below the dissolution rate; the thickness of the oxide decreases. - At a critical thickness of the oxide that is smaller than the critical thickness for breakthrough (hysteresis effect), the breakthrough current mode is extinguished; the cycle starts again. While it is not claimed that this model will fully explain electrode oscillations in all systems or even just in Si, it seems likely that it will be a part of any general model that has yet to be found.

Some other properties of the anodic region are discussed for *n*-type Si, where their manifestations are more prominent than in *p*-type Si. Fortunately, one need not understand the electrode reactions in detail in order to put them to practical use. It has been shown, for example, that for  $I \ll I_{PSL}$  lattice defects can be etched preferentially; it is even possible to distinguish between electrically active and inactive defects [30]. No explanation for this phenomenon has been offered so far, but the basic mechanism is relatively clear (in contrast to purely chemical etching!).

Figure 5 illustrates what happens. The current–voltage relationship for  $I \ll I_{PSL}$  is governed by the basic diode equation [31] superimposing two current terms: the generation current and the diffusion current. The switch-over from the generation current to the diffusion current depends on the density of generation centers; in the vicinity of an electrically active defect it occurs at current densities that are larger than in a defect-free region. Consequently, at low current densities, current densities (and therefore etching rates) around electrically active defects are larger than in defect-free regions: preferential etching is observed.

A second mechanism (not shown in Fig. 5a) relies on the dependence of current densities on surface orientation. For different crystal orientations, the voltage scale shifts somewhat. The current densities on the two sides of a grain boundary therefore are somewhat different, regardless of electrical activity. Figure 5b shows the resulting etch features in cross section. Whereas an electrically active grain boundary is delineated by a trench (and a step), electrically inactive ones show only a surface step. Since the relative magnitude of two effects depends on the absolute current density in different ways, one effect can be made to dominate the other, as outlined in Fig. 5b.

This model not only explains the experimental findings but could easily be verified quantitatively. Moreover, it could provide the basis for a deeper understanding of purely chemical etches. Most silicon defect etches are based on the HF–CrO<sub>3</sub> acetic acid system. They can behave quite differently, depending on the mixing ratio. For example, the "Secco etch" [32] delineates defects on all crystal planes, whereas the "Sirtl etch" [33] works only





Fig. 5. (a) Basic current-voltage relationship for a diode with diffusion-current and generationcurrent contributions. At small current densities  $(\leq 1 \ \mu A/cm^2$  in the bulk), defects are etched with optimum selectivity. At current densities  $\geq 1000 \ \mu A/cm^2$  selectivity in etch rates for defects disappears but  $\langle hkl \rangle$  differences may lead to steps across grain boundaries. (b) Representative cross-sections for the two cases

on  $\langle 111 \rangle$  surfaces, in contrast to the "Seiter etch" [34], which works only on  $\langle 100 \rangle$ . For all these etches, the applied voltage as the driving force has been replaced by the chemical potential of CrO<sub>3</sub>. The basic model given above together with a quantitative analysis of the orientation-dependent chemical potential of the Si electrode in the various etches may then lead to a better understanding of the mechanisms of chemical defect etches; see also [27, 35].

# 3. Specific Properties of *n*-Type Silicon and Some Applications

### 3.1 Cathodic Region

In the cathodic region the Si-HF junction is forward biased; the principal chemical mechanism is  $H_2$  evolution. This is not of much interest except, as already mentioned, for pinpointing (via  $H_2$  bubbles) or decorating (via metal deposition if a suitable electrolyte is used) defects in otherwise insulating layers. One more application could be to provide a pseudo-ohmic contact (meaning relatively large currents at small voltages) on the back side of a sample. With this method the (small) currents needed for electrochemical defect etching at the front side can be supplied by an electrochemical "ohmic" contact on the back side.

### 3.2 Anodic Region

Figure 1 shows that the U-I characteristic is essentially identical to that of *p*-type Si (apart from a voltage shift of roughly 500 mV) provided enough minority carriers (holes) are generated by light. All phenomena discussed for *p*-type silicon are therefore also present in illuminated in *n*-type silicon electrodes, in particular PSL formation and current or voltage oscillations. If the light flux is limited, however, the current will abruptly level off to a specific constant value.

This creates a new situation: It is now possible to adjust voltage and current independently via the light flux. In particular, the depth of the space charge region can now be changed without changing the current density.

As already mentioned and shown in Fig. 1, light induces a photocurrent, which is, however, not directly given by the number of holes generated and, moreover, does not increase linearly with the light flux. The reason for this behavior is that for every hole generated by a quantum of light that reaches the junction, up to three electrons may be injected. The total current can therefore be four times the light-generated hole current, and the electron injection current is not constant but depends on the absolute current density, as shown in Fig. 6, see also [36, 37].

It is evident that the electron injection mechanism is connected with the basic chemical reactions taking place above or below the critical current  $I_{PSL}$ . Figure 6 also shows the measured total number v of charge carriers needed to dissolve one Si atom (the valence v of the



Fig. 6. Number n of carriers exchanged across the interface per lightgenerated hole, and number v (valence) of carriers needed to dissolve one atom of silicon

reaction). If this curve is replotted as 4/v, which means the number of "quarter atoms" dissolved by one charge carrier, it is identical to the injection ratio [9]! This is an unexpected insight and can be used to obtain a better understanding of the detailed mechanisms of the electrode reactions.

The differences between p- and n-type silicon for currents  $I > I_{PSL}$  that might be present at large voltages for n-type Si have not been investigated systematically. Some speculations are possible but will not be discussed in the limited space of this paper.

For  $I < I_{PSL}$  a striking new phenomenon occurs in *n*-type Si. The surface may become pitch black in appearance after some time of current flow at voltages larger than  $U_{PSL}$ ; Fig. 7 shows why. The honey-comb like structure of deep trenches accounts for the very low reflection of visible light.

This effect occurs within a fairly large range of parameters such as voltage, currents, and doping levels and was first explained in [14]. In essence, as outlined in



Fig. 7. Microstructure of *n*-type Si after prolonged etching with  $I < I_{PSL}$ 



Fig. 8. Schematic current flow around indentations if (a) the minority carriers are generated close to the front surface (front side illumination) or (b) diffuse to the front side from the bulk (back side illumination). In the latter case practically only the tips of the indentations grow

Fig. 5, the interaction of initial surface irregularities with the space charge region leads to current focussing at the tips of small depressions as illustrated in Fig. 8a. The bottom of a pit therefore grows faster than the sidewalls; the net effect is a roughening of the surface. A neat experimental trick only possible in extremely pure semiconductors such as Si allows this effect to be enhanced to the point of possible applications. If the holes necessary for etching are supplied at the back side of a Si wafer by illuminating the back side instead of the front side (requiring, of course, the diffusion length of the holes to be comparable to the sample thickness), practically all holes are caught at the tips of (intentionally induced) depressions (Fig. 8b). In contrast to front side illumination, where holes are also generated close to the sidewalls of growing trenches thus inducing lateral growth, only the trench tip grows for back side illumination. Using this technique, it is possible to etch trenches with diameters in the micrometer region and depths of several 100 µm in a predetermined geometry. Figure 9 gives an example.

Of course, the possibility of creating surfaces with very large ratios of effective surface area to projected areas and optimized optical properties by controlling trench diameters and depths may have uses beyond microelectronics; suffice it to mention efficient blackbody radiators or nonreflecting solar cells.

It is important to realize that the surface of the trenches or pits created by the current-focusing action of the spacecharge region is *still* covered with a PSL. This means that this mechanism *alone* is *not* sufficient to explain PSL formation. This is not always realized in the PSL literature, where PSL layers and structures specific to *n*-type Si are sometimes confused. As outlined before, the currentfocusing action of a space-charge region may be the first step in the generation of a PSL. Thick PSLs (compared to



Fig. 9. Deep trenches grown by anodic etching of preformed indentations

the width of the space-charge region), however, only form because the walls between the pores are stabilized by the quantum-wire effect, which prohibits movement or generation (for normal light sources) of carriers in the pore walls. Consequently, even if I is raised to values higher than  $I_{PSL}$ , the initially formed PSL does not dissolve but peels off, as outlined in Sect. 2.2.

As far as applications are concerned, the anodic region of *n*-type Si cannot be used as easily for the prediction of solar-cell efficiency or the measurement of diffusion lengths as the corresponding cathodic region of *p*-type Si. In compensation, new modes of defect etching can be employed.

Compared to the anodic etching of defects in p-type Si (which, of course, is also applicable for n-type Si), a new degree of freedom is added. Defect etching can now be done using the leakage-current, the photocurrent or the breakthrough current. This may lead to quite different



Fig. 10. Adjacent areas on a polycrystalline, heavily contaminated n-type Si sample etched in the dark (a) and with light (b). Part (a) shows predominantly the distribution of generation centers and very little grain structure whereas part (b) reveals lattice defects and dopant striations

appearances of the defects, as is shown in Fig. 10. Since the basic reasons for preferential etching are well understood in each mode, defects can be classified, leading to a better understanding of their nature.

Last, but not least, *n*-type Si in the anodic region might be the electrode of choice for studying electrode reactions, especially the current/voltage oscillations, in unprecendented detail. In contrast to metal electrodes studied so far, the added degree of freedom of decoupling current and voltage, together with some other Si-specific possibilities (measuring, for instance, the electron-injection current at the front side as a leakage-current component with a second electrolyte contact at the back side) allow the design of new and powerful experiments not easily realized with other materials.

### 4. The Universal Electrochemical Silicon Analyzer

Based on the principles outlined above and designed for easy, fully automated use in some standard modes as well as for use as a research tool in more exotic modes, a



Fig. 11. Schematic cross section of the electrochemical double cell of the ELYMAT.  $I_{FPC}$ : front side photocurrent;  $I_{BPC}$ : back side photocurrent

"universal" electrochemical analyzer (dubbed ELYMAT) for standard Si wafers has been constructed [21]. Its essential features are shown in Fig. 11.

(i) An electrochemical double cell providing (electrically and chemically) independent electrolyte contacts to the front side *and* back side of a Si wafer.

(ii) Contact needles providing (ohmic) contact at several points at the wafer perimeter.

(iii) Illumination of the front side with a scanned laser beam, ideally at two wavelengths with penetration depths of  $\leq 1 \,\mu m$  and  $\geq 100 \,\mu m$ .

(iv) Fully automatic operation, data collection, evaluation, and display.

(v) Optimal features such as flood-light illumination of front and back side, electrolyte circulation, specialized electronics.

The ELYMAT not only offers most applications already mentioned (with much better performance in some cases), but some new modes, too. It can be used, for example, for the prediction of solar-cell efficiency or for the measurement of diffusion lengths in the cathodic region of *p*-type Si as outlined in Sect. 3.1, but with the added advantage of using the back side electrolytical cell as a large-area ohmic contact that does not need any specimen preparation. This either avoids the tedious task of contact preparation or prevents the uncertainties and current inhomogeneities connected with mechanical point contacts.

Anodic etching of defects is equally possible for *p*- and *n*-type Si. Again, the back side cell may be used as the "ohmic" contact; for *p*-type Si flood-light illumination of the back side is then necessary.

All other possible applications – from electrochemical trench etching to cathodic or anodic defect decoration – can be carried out if the proper adjustments for electrical contacts or, in the case of large currents needed for electropolishing, electrolyte circulation and degassing, are made.

The main strength of the ELYMAT, however, lies in two new modes for mapping the diffusion length L and the surface recombination velocity S of a Si wafer. In the socalled back side photocurrent (BPC) mode, the front side is illuminated with a scanned laser beam with a wavelength of small penetration depth (e.g. 630 nm). All minor-



Fig. 12. Diffusion-length distribution in a 6 in. (15 cm) wafer. "White" areas correspond to small diffusion lengths because of iron contamination. The square grid pattern identifies directly the contamination source as a particular wafer chuck

ity carriers are therefore generated close to the front surface. Some minority carriers will diffuse to the back side of the wafer, where they are collected and measured by an appropriate electrolyte contact as back side photocurrent. The remainder of the minority carriers either recombine in the bulk (described by L) or at the front side surface (described by S). The back side photocurrent is therefore essentially a function of L, S, and, of course, the wafer thickness x; it is given by [21]

$$I_{\rm BPC} = \frac{qp\alpha L}{\alpha^2 L^{2-1}} \times \frac{c + \alpha L}{c\sinh(x/L) + \cosh(x/L)},\tag{1}$$

where q is the elementary charge, p is the number of absorbed photons,  $c = S \times L/D$ , D is the diffusivity of minority carriers, and  $1/\alpha$  is the penetration depth of the light.

Consequently, if S were known, L could be determined and vice versa. Fortunately, the Si-HF junction provides an interface with an exceedingly low value of S [25]. Based on this observation, it has been shown that a properly biased Si-HF junction reduces S to a level where it can be neglected. Then (1) can be simplified to

$$I_{\rm BPC} = \frac{qp\alpha^2 L^2}{\alpha^2 L^2 - 1} \times \frac{1}{\cosh(x/L)}.$$
 (2)

Mapping of the diffusion length is thus possible by solving (2), with a lateral resolution about equal to the wafer thickness, relatively high speed ( $\approx 30 \text{ min for} \ge 10000 \text{ pixels}$ ), and very good accuracy, especially for relatively large diffusion lengths (where conventional methods are difficult to use).

A typical result is shown in Fig. 12. The variation in diffusion length for this wafer was caused by iron contamination of  $\approx 100$  ppt. The usefulness of pictures like this one to the microelectronic community is obvious because the source of the contamination identifies itself by its "fingerprint".

Of course, if L happens to be much smaller than the wafer thickness, the back side photocurrent is too small to be accurately measured (although a lock-in technique may remedy the situation somewhat). In this case the photocurrent at the front side would be measured (FPC mode) employing a second light source with a larger penetration depth.

A particularly outstanding feature of the ELYMAT is its capability of mapping the surface recombination velocity S; a feature not provided by any other method. In this case two independent measurements are performed. In a first run, the back side photocurrent is measured (as in the BPC mode) but with the front side surface not



Fig. 13. Maps of the surface recombination velocity of a wafer partially dipped in HF as a function of time. The S(t) diagram resulting from several runs is also shown



Fig. 14.  $I_{BPC}$  as a function of band bending at the front surface (expressed in volts; flat band not at 0 V) as measured (a) and as a result of calculations (b)

immersed in HF. Then  $I_{BPC}$  is a function of S and L as given in (1). Before the second run, the front cell is filled with HF, reducing S to essentially zero. Again  $I_{BPC}$  is measured, yielding L. Substituting the L values obtained for every pixel in (1), together with the  $I_{BPC}$  values of the first run, finally yields S. The whole procedure can be performed automatically; Fig. 13 shows a typical result.

This DPC mode (delta photocurrent), however, is only a first step in surface characterization with the ELYMAT. Equation (3) essentially assumes flat-band conditions at the surface; in reality the measured value of S is a function of band bending. If an inert electrolyte such as acetic acid is chosen, band bending can be adjusted by the voltage applied between the electrolyte and the silicon wafer. Since acetic acid is not really inert (anodic oxidation, for example, may occur under certain conditions), experiments have to be designed with some care. Nevertheless,  $I_{\rm BPC}$  can be measured as a function of band bending; Fig. 14a gives an example. Maximum current flows for large cathodic potentials, since all electrons generated by light are repelled by the surface. A minimum current flows for small voltages, presumably around flat-band conditions. The value of S can be deduced from the difference in maximum and minimum current with the help of (3):

$$S = \frac{D\alpha(1-A)}{A - \alpha L \tanh(x/L)}$$
(3)

with  $A = I_{\min}/I_{\max}$ .

The recovery of  $I_{BPC}$  for anodic voltages is somewhat unexpected since electrons are now attracted by the surface. However, if the light-induced generation current is larger than the recombination current at the surface, inversion will occur, reducing the density of holes to a value where recombination at surface states is negligible. A quantitative analysis of the model outlined above indeed yields the observed dependence of  $I_{BPC}$  on voltage (Fig. 14b). Moreover, it predicts in a quantitative manner the shape of the  $I_{BPC}$ -V curve as well as its dependence on light intensity, wavelength and so on [38]. This opens new possibilities for surface analysis with the ELYMAT: Probing the slopes of the  $I_{BPC}$  vs voltage curve locally, for example by measuring the response to superimposed small alternating voltages or to modulated light flux, will yield more information about surface conditions than the simple (3) while still maintaining the possibility of largearea mapping.

#### 5. Conclusions

Silicon, although probably the most thoroughly investigated material, still exhibits unexpected and puzzling properties if used as an electrode in an electrochemical cell. Most prominent are the formation of porous silicon layers (PSLs), pronounced current or voltage oscillations, and peculiar etching structures.

This paper attempted to provide a basic understanding of the Si-HF electrolyte system with the aim of elucidating the manifold uses of Si-electrolyte junctions for analytical purposes. Simple models and explanations were offered, in part for the first time, for effects such as PSL formation, current or voltage oscillations, anodic defect etching, and deep trench etching. The guiding principle in most cases was the interaction of the spacecharge region with defects or surface irregularities. It was shown that details about the chemical reactions are important neither for a basic understanding of most phenomena nor for many applications as long as proper experimental conditions are chosen. Chemical mechanisms, e.g. electron injection for anodic currents, however, do impose restrictions on the generality of some methods, e.g., quantitative photocurrent measurements.

Taking advantage of several unique properties of the Si-HF system allowed a universal electrochemical analyzer to be designed. By means of an electrochemical double cell and a scanned light source several characterization modes such as diffusion length mapping or surface recombination velocity mapping are possible. More modes of operation could be envisioned, e.g., "quantitative" defect etching, provided more research is undertaken to establish a still missing detailed understanding of the physics and chemistry of the Si-electrolyte junction.

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