

Galvanic Cell Formation in Silicon/Metal Contacts: The Effect on Silicon Surface Morphology

X. H. Xia,^{*,†} C. M. A. Ashruf,[‡] P. J. French,[‡] and J. J. Kelly[†]

Debye Institute, Utrecht University, P.O. Box 80000, 3508 TA Utrecht, The Netherlands, and Delft University of Technology, DIMES, Department of Electrical Engineering, Mekelweg 4, 2628 CD Delft, Netherlands

Received January 20, 2000. Revised Manuscript Received March 24, 2000

When p-type silicon is contacted to a noble metal in HF solution containing an oxidizing agent, a galvanic cell can be formed. The oxidizing agent is reduced at the metal and the semiconductor is etched. To achieve a similar effect with n-type silicon, illumination is required. On the other hand, a galvanic cell is formed with both n- and p-type silicon in alkaline solution in the dark. These results are explained on the basis of silicon electrochemistry with the use of energy band diagrams. It is shown that "galvanic etching" can be used to control the silicon surface morphology, e.g., to form microporous or macroporous layers or produce pyramid-free anisotropic structures.

Introduction

The electrochemistry of silicon in alkaline solution differs in a number of important respects from that in acidic solutions.^{1–5} For example, in HF solutions only p-type silicon can be oxidized anodically in the dark. For the oxidation of the n-type semiconductors, illumination is necessary.^{1–3} Clearly, valence band holes are required for the anodic reaction. On the other hand, a significant anodic current is observed with silicon of both types in alkaline solution.^{4,5} These differences have important consequences for the formation of galvanic cells between the semiconductor and a metal in solution. We became interested in galvanic effects for etching device structures in silicon.^{6,7}

In this paper we describe the electrochemical properties of silicon in ohmic contact with a noble metal in a solution containing an oxidizing agent. In particular, we consider differences observed for the two semiconductor types in acidic and alkaline solution. In addition, we describe the effect of galvanic cell formation on the open-circuit etching of silicon and the morphology of the etched surface.

In device technology anodic etching is a widely applied technique. It is used, for example, for the formation of microporous and macroporous silicon.^{8,9} Anodic etch stop techniques are important for micromechanical device fabrication.¹⁰ Anodic polarization of silicon in alkaline solution prevents surface roughening during etching.¹¹

These methods require an Ohmic contact to the semiconductor which is connected to a counter electrode via an external source. Such a contact must be protected from the electrolyte solution by clamping the wafer in a holder; this may introduce stress. In addition, the need for external contacts is a disadvantage in a batch fabrication process. In this paper we show that open-circuit etching with a galvanic cell can be used instead of anodic etching to achieve various surface morphologies such as microporous and macroporous layers in acidic solution and pyramid-free anisotropic structures in alkaline solution. Most of the examples described involve a silicon wafer connected to a separate metal electrode; this allows us to measure the short-circuit current during etching. In device applications, as in one of the examples described below, the metal is directly on the wafer. In this way, the external contacts normally required are avoided.

Before considering the semiconductor/metal system we first review briefly the electrochemistry of silicon in the two types of solution. We then explain the principle of the galvanic cell and present results of experiments illustrating cell formation. Finally, we describe the surface morphologies that can be obtained with this approach.

Experimental Section

The p-type silicon (100) wafers were boron-doped; except where otherwise stated, these had a resistivity in the range 1–15 Ω cm. The n-type samples had the same orientation; these were phosphorus-doped with a resistivity of 10–15 Ω cm. The electrodes were dipped in a solution of 1 M HF + 2 M NH₄F for 1 min followed by washing with Millipore water (16 M Ω) before each measurement to remove native surface oxides. The silicon working electrode was mounted in a Kel-F holder

* Corresponding author. E-mail: x.xia@phys.uu.nl.

[†] Utrecht University.

[‡] Delft University of Technology.

(1) Zhang, X. G.; Collins, S. D.; Smith, R. L. *J. Electrochem. Soc.* **1989**, *136*, 1561.

(2) Smith, R. L.; Collins, S. D. *J. Appl. Phys.* **1992**, *71*, R1.

(3) Eddowes, M. J. *J. Electroanal. Chem.* **1990**, *280*, 297.

(4) Smith, R. L.; B. Kloeck, B.; de Rooij, N.; Collins, S. D. *J. Electroanal. Chem.* **1987**, *238*, 103.

(5) Bressers, P. M. M. C.; Pagno, S. A. S. P.; Kelly, J. J. *J. Electroanal. Chem.* **1995**, *391*, 159.

(6) Ashruf, C. M. A.; French, P. J.; Bressers, P. M. M. C.; Kelly, J. *J. Sensors Actuators* **1999**, *74*, 118.

(7) Ashruf, C. M. A.; French, P. J.; Bressers, P. M. M. C.; Sarro, P. M.; Kelly, J. *J. Sensors Actuators* **1998**, *A66*, 284.

(8) Hirschman, K. D.; Tsybeskov, L.; Dutttagupta, S. P.; Fauchet, P. M. *Nature* **1996**, *384*, 338.

(9) Lehmann, V. *J. Electrochem. Soc.* **1993**, *140*, 2836.

(10) Collins, S. D. *J. Electrochem. Soc.* **1997**, *144*, 2242.

(11) Bressers, P. M. M. C.; Kelly, J. J.; Gardeniens, J. G. E.; Elwenspoek, M. *J. Electrochem. Soc.* **1996**, *143*, 174.

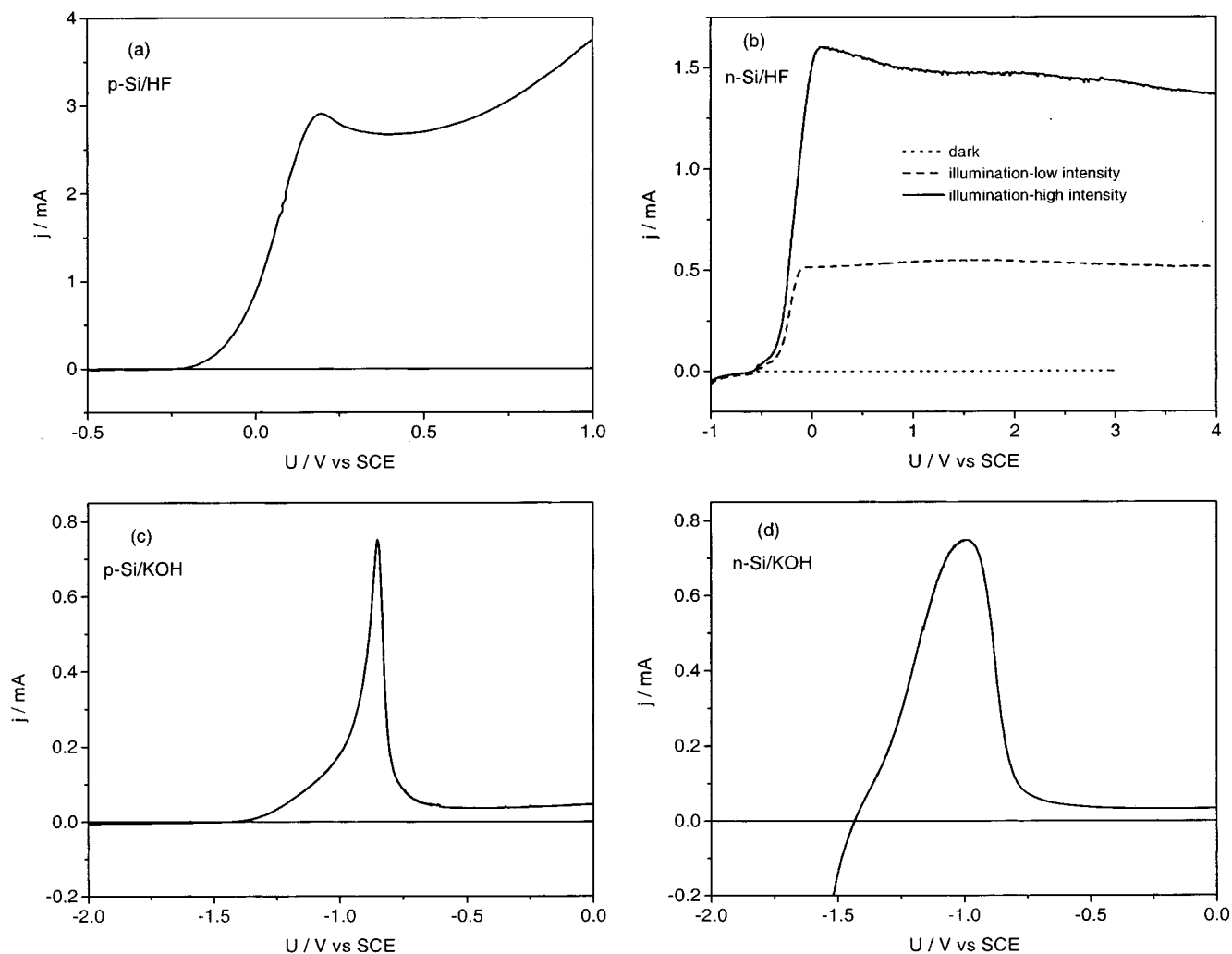


Figure 1. Current–potential curves of (100) silicon in 1% HF solution at room temperature: (a) p-type in the dark, (b) n-type in the dark and under illumination; and in 2.0 M KOH solution (c) p-type and (d) n-type, both in the dark. For the HF measurements the potential was scanned at 20 mV/s from -1.0 V and for the KOH measurements at 5 mV/s from -2.0 V. For part a, 0.008Ω cm Si was used.

with O-ring and electrical contact to a brass disk on the backside of the sample was made using Ga/In eutectic. All chemicals were of p.a. grade (Merck), and used as received.

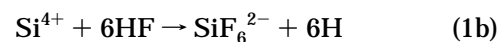
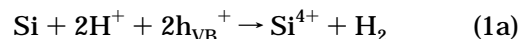
Electrochemical experiments were performed using an EG&G Princeton Applied Research (PAR) 283 potentiostat. A conventional three-electrode electrochemical cell containing a Pt counter electrode and a saturated calomel electrode (SCE) as reference was used. All potentials are referred to SCE. The open-circuit potential and short-circuit current in the galvanic cells were measured with Digital Multimeter (HEWLETT 3478A). For illumination, a white light source (Schott KL 1500) was used. The surfaces of etched silicon samples were examined with a XL30FEG scanning electron microscope (SEM, Philips). Photoluminescence (PL) measurements were performed using a SPEX DM 3000 F fluorolog spectrofluorometer equipped with two double-grating 0.22 m SPEX 1680 monochromators and a 450 W xenon lamp as the excitation source. The excitation spectrum was corrected for the xenon lamp intensity, and the emission spectrum was corrected for the response of the photomultiplier.

Electrochemistry of Silicon

Low pH–HF Solution. A typical current–potential curve for p-type silicon in aqueous HF solution in the dark is shown in Figure 1a. At potentials negative with respect to the open-circuit value ($U_{oc} = -0.285$ V vs SCE) a small cathodic current is observed. Above the

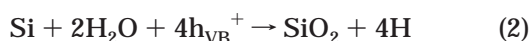
open-circuit potential, oxidation of silicon occurs as indicated by anodic current flow. Two ranges can be distinguished. At potentials below the current peak, direct dissolution occurs and porous silicon is formed. Beyond the peak potential, there is an accumulation of holes at the electrode surface and the HF is depleted at the electrolyte side. The anodic current is limited by the rate of mass transport and the silicon is electropolished.²

In the region of porous silicon formation the dissolution current shows Tafel characteristics with a slope of 60 mV/decade, indicating kinetic control of the charge-transfer reaction at the silicon/electrolyte interface. Anodic dissolution of silicon is initiated by the capture of two valence band holes by a surface bond to form an intermediate.^{1–3} The intermediate reacts with protons to give hydrogen (e.g., $\text{Si}^{2+} + 2\text{H}^+ \rightarrow \text{Si}^{4+} + \text{H}_2$). One hydrogen molecule is formed for each silicon atom etched and the product goes into solution as a hexafluoride complex.³ The reaction can be described by

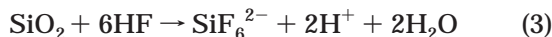


In the electropolishing range the anodic current is only

weakly dependent on potential. Dissolution of silicon involves the formation of a surface oxide.² Four valence band holes are required in this reaction



The oxide is subsequently etched chemically by HF to form the soluble fluoride complex:



The current in both the peak and in the polishing range depends on the HF concentration and the hydrodynamic conditions.

The electrochemistry of n-type silicon in aqueous HF solution in the dark is shown in Figure 1b, dotted curve. At negative potentials, a reduction current due to hydrogen evolution is observed; protons are reduced by conduction band electrons. At potentials positive with respect to the open-circuit potential ($U_{\text{oc}} = -0.59$ V vs SCE) only a very low anodic current is observed (Figure 1b, dotted curve). Anodic dissolution of the n-type silicon requires illumination with light of an energy equal to or larger than the band gap (1.1 eV). On illumination, electron-hole pairs are generated. The holes, forced to the surface by the electric field, cause silicon dissolution. The electrons in the conduction band are measured in the external circuit as an anodic photocurrent, which is dependent on the light intensity. At low light levels the anodic limiting current is independent of the applied potential. In this case microporous silicon is formed across the entire potential range as the current is always determined by the supply of holes (Figure 1b, dashed and solid curves).² At sufficiently high light intensity the cyclic voltammogram in the anodic region (not shown) is essentially the same as that of p-type silicon in the dark, except that it is shifted slightly to negative potentials. Anodic dissolution is mass-transport controlled and electropolishing occurs at sufficiently positive potentials.² Macroporous silicon can be obtained in the transition range between the charge-transfer-limited and mass-transport-limited regimes.⁹

High pH-KOH Solution. Parts c and d of Figure 1 show typical current-potential curves for p-type and n-type (100) silicon in 2.0 M KOH at 45 °C in the dark. At potentials negative with respect to the open-circuit potential ($U_{\text{oc}} = -1.43$ V vs SCE for both type silicon) a cathodic current due to evolution of hydrogen is found with the n-type electrode but not with p-type; this reaction requires conduction band electrons as in acidic solution. In contrast to the low pH case a significant anodic current peak is observed for both electrodes. In the scan to positive potentials a sharp peak indicates passivation of the surface; this is followed by a passive range with a low anodic current. The anodic peak current of n-type silicon is comparable in magnitude to that of the p-type electrode. The magnitude of the peak and passive currents is found to be dependent on the temperature and solution composition. For both electrodes the anodic peak is absent in the return scan due to the presence of the passive oxide layer.

Anodic oxidation of p-type silicon in alkaline solution can be due to a hole reaction (as in acidic medium):



At higher anodic current density oxide is formed and the surface passivates



However, such a hole reaction cannot be responsible for the anodic current of n-type silicon in the dark. Silicon dissolves in alkaline solution as a result of a chemical reaction between Si-Si surface bonds and water;⁵ OH⁻ ions catalyze the reaction and ensure the solubility of the reaction products. The chemical etch rate is considerably as long as there is no oxide present on the surface, i.e., at potentials negative with respect to the peak potential. There is evidence to show that an intermediate of the chemical etching reaction of silicon with water can inject electrons into the conduction band of the n-type semiconductor.^{5,12} In principle, a similar process can occur at the p-type electrode; in this case, holes supplied from the bulk recombine with injected electrons instead of directly oxidizing surface atoms. This possibility is discussed elsewhere.¹³

During open-circuit etching of silicon in alkaline solution the surface often becomes seriously roughened due to the formation of crystallographically oriented pyramids.^{11,14} The exact cause of these hillocks is not clear. However, it has been shown that hillock formation can be suppressed by polarizing the silicon at a potential between current onset and the peak.¹¹

Principle of Galvanic Cell Formation

Galvanic cell formation with a semiconductor/metal contact is most straightforward for the case of a p-type electrode. The principle is illustrated for silicon at low pH in Figure 2. Curve a shows schematically the anodic current-potential characteristics of p-type silicon in HF solution (see case a, Figure 1). For simplicity we consider two oxidizing agents which, for kinetic reasons, are not reduced at the semiconductor. The metal used is noble, i.e., it is not itself oxidized. Curves b-d of Figure 2 are the cathodic current-potential curves measured at the noble metal due to the electrochemical reduction of oxidizing agent. The oxidizing agent of curve b has a redox potential close to or more negative than the anodic peak potential of silicon. When the semiconductor and metal are short-circuited, a mixed potential U_b (Figure 2) is established in the range of active dissolution of the semiconductor. At this potential, the rate of silicon oxidation is equal to the rate of reduction of the oxidizing agent. The system operates as a "battery" with the semiconductor acting as anode and the noble metal as cathode.

In the case of a stronger oxidizing agent (curves c and d, Figure 2) the onset of reduction is at a more positive potential so that mass-transport limitation can be expected in the potential range of active dissolution. Two situations can be distinguished. For a "low" limiting current (curve c), which will be the case for a low concentration of oxidizing agent or an exposed metal area small compared to the silicon area, the mixed

(12) Cattarin, S.; Peter, L. M.; Riley, D. J. *J. Phys. Chem.* **1997**, *101*, 4071.

(13) Xia, X. H.; Ashruf, C. M. A.; Kelly, J. J. To be published.

(14) Baum, T.; Satherley, J.; Schiffrin, D. S. *Langmuir* **1998**, *14*, 2925.

Table 1. Results Obtained with Galvanic Elements Consisting of Silicon and a Metal

case	Si type/illum.	metal	oxidizing agent	solution	A_{Si}/A_M	galvanic cell?	$U_{Si/M}$ (V vs SCE)	i_{sc} (mA cm ⁻²)
1	p-type/dark	Pt	O ₂ + H ⁺	1 M HF/H ₂ O	1/4	yes	-0.05	0.40
2	n-type/dark					no	0.35	0
3	n-type/illum.					yes	-0.28	0.46
4	p-type/dark		O ₂ + H ₂ O	2.0 M KOH	5/1	yes	-0.93	0.25
5	n-type/dark						-1.16	0.50

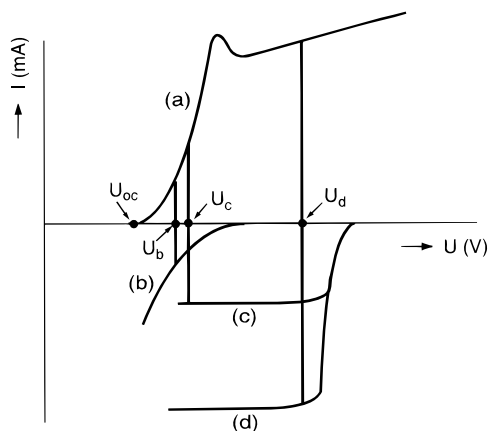


Figure 2. Schematic representation of galvanic cell formation. Curve a shows the current–potential curve for p-Si(100) in an air-saturated HF solution. Curves b–d are the cathodic current–potential curves of oxidizing agents measured at a noble metal electrode in the same solution. The oxidizing agent of curve b has a redox potential close to or more negative than the anodic peak potential of silicon. Curves c and d show the reduction of stronger oxidizing agents with redox potentials at more positive values. Upon connection of silicon to the metal electrode, a mixed potential is established at values of U_b , U_c , and U_d for curves b, c, and d, respectively.

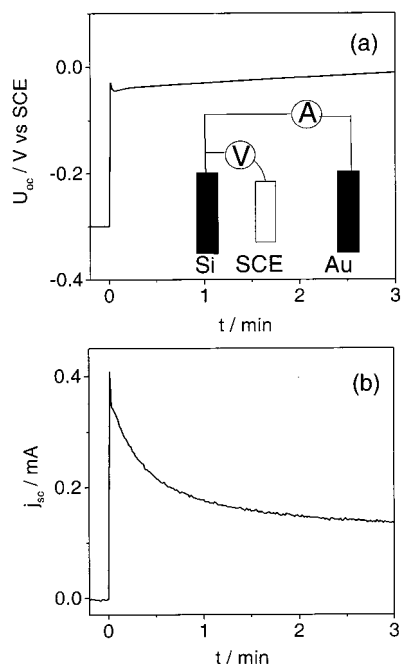


Figure 3. Open-circuit potential (OCP) transient (a) and short-circuit current transient (b) measured after a p-Si(100) electrode was connected to a platinum wire (at $t = 0$) in 1% HF at room temperature in the dark. The experimental setup is shown as inset in part a.

potential of the short-circuited system will again be in the active dissolution range. However, if the limiting cathodic current is increased (curve d), e.g., by raising

the concentration of the oxidizing agent or increasing the metal/silicon area ratio, the mixed potential is at a value U_d positive with respect to the peak potential; i.e., in the polishing range. In the case of an alkaline solution (curves c and d, Figure 1) the semiconductor should passivate in this case.

For device applications, oxygen, naturally present in aqueous solution, is an interesting oxidizing agent. Oxygen can be reduced at gold and platinum. The redox potential is more than a volt positive with respect to the onset potential for anodic oxidation of silicon in both acidic and alkaline solutions.¹⁵ A disadvantage of oxygen is its limited solubility. Therefore, oxygen will generally correspond to case c of Figure 2. In acidic solution H₂O₂ can also be used. This is a very strong oxidizing agent (redox potential = +1.52 V (SCE)), but the kinetics of the reduction reaction are unfavorable at many electrodes. Platinum is an exception; the metal is a catalyst for the decomposition of H₂O₂, and consequently, large reduction currents can be obtained. Depending on the concentration, this system may correspond to case c or case d. The reduction of protons at low pH or of water at high pH to give hydrogen is also a candidate for the cathodic reaction. However, the overpotential for hydrogen evolution is too large at most metals so that reduction only occurs at potentials negative with respect to the onset potential for anodic oxidation.¹⁶ Galvanic cell formation is therefore not expected. Again, platinum may constitute an exception. The overpotential for hydrogen evolution at platinum is low.¹⁶ This corresponds to case b of Figure 2. The mechanism of the reduction of these three oxidizing agents (O₂, H₂O₂, and H⁺ or H₂O) at silicon is complex and the kinetics of the reactions are unfavorable. This has the advantage that reduction should only occur when metal and semiconductor are short-circuited; there is no etching due to the oxidizing agent. It is also possible to use oxidizing agents which inject holes directly into the valence band of silicon. Examples are HNO₃ or IrCl₆⁴⁻ at low pH¹⁷ or Fe(CN)₆³⁻ at high pH.⁵ Such systems do not discriminate between uncontacted silicon and silicon in ohmic contact with a metal.

Results and Discussion

i. Electrochemistry. Table 1 gives an overview of results obtained with the various solutions described in the section on galvanic cell formation. We first discuss results for acidic medium, then results for alkaline

(15) *Standard Potentials in Aqueous Solution*; Bard, A. J., Parsons, R., Jordan, J., Eds.; Marcel Dekker Inc.: New York, 1985.

(16) Erdey-Graz, T. *Kinetics of Electrode Processes*; Adam Hilger Ltd.: London, 1972.

(17) Gerischer, H.; Luebke, M. *J. Electrochem. Soc.* **1988**, *135*, 2782.

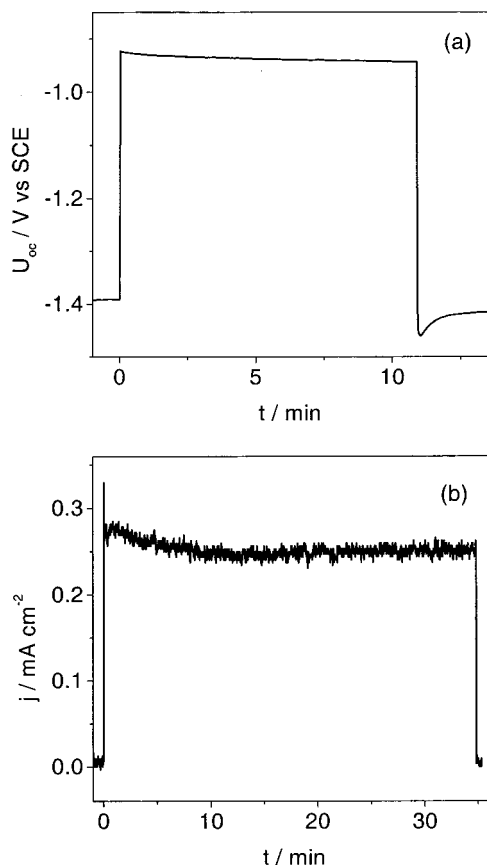


Figure 4. Open-circuit potential–time curve (a) and short-circuit current–time curve (b) of a p-Si(100) electrode in 2.0 M KOH at 45 °C in the dark. The abrupt positive shift of the OCP and abrupt increase in current indicate the connection of the sample to a platinum wire, while the abrupt negative shift of OCP and decrease in current indicate the disconnection of the sample.

medium, and finally, the differences between the systems on the basis of energy level diagrams.

A p-type silicon wafer connected to platinum in an aerated solution containing 1 M HF gives a galvanic cell (case 1, Table 1). The cell produces a steady-state current density of 0.4 mA/cm² (defined with respect to the silicon area). Figure 3 shows potential and current transients measured after the semiconductor and metal are short-circuited (at $t = 0$). While the potential rapidly reaches a positive value and continues to rise slowly, the short-circuit current first rises sharply and then decreases significantly over a period of minutes. The potential is in the range for porous silicon formation. That etching occurs is obvious from gas evolution at the silicon (see eq 1a). Very likely the decrease in current is due to hydrogen bubbles sticking in the pores. This leads to a poor quality porous layer. In the section on morphology, we show how this problem can be alleviated.

When an n-type silicon sample is connected to platinum in aerated HF solution (case 2, Table 1) no short-circuit current is observed in the dark. The potential of the system is close to that of an unconnected platinum electrode in the same solution. The silicon does not dissolve. Clearly, a galvanic cell is not formed in this case. The situation changes under illumination (case 3, Table 1). The potential shifts to a value in the rising part of the photocurrent–potential curve (Figure 2b)

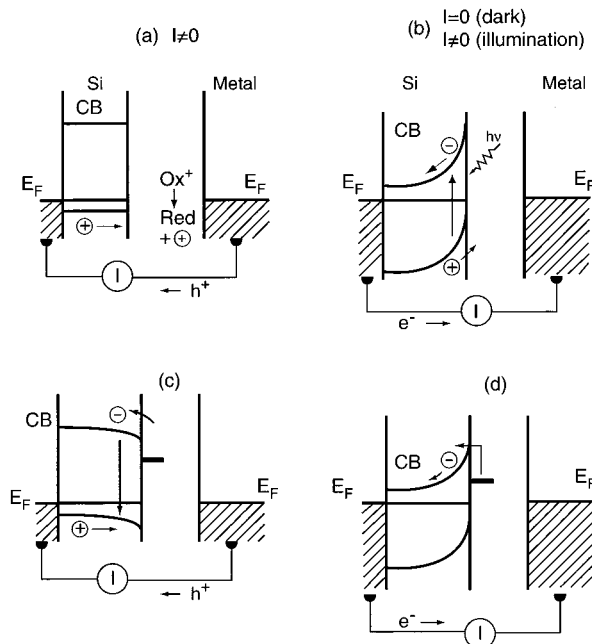


Figure 5. Schematic representation of the energy band diagrams for galvanic cell formation in acidic and alkaline solutions containing an oxidizing agent: in acidic solution (a) p-Si in the dark and (b) n-Si in the dark and under illumination; and in alkaline solution, (c) p-Si in the dark and (d) n-Si both in the dark. For simplicity we assume that the potential drop at the semiconductor–solution interface falls exclusively within the space charge layer of the solid.

and a considerable short-circuit photocurrent is measured. Now, the silicon is etched.

Zhang et al.¹⁸ have reported results on the formation of a photoluminescent layer on n-type silicon without an externally applied potential. Illumination was essential for the reaction, which was performed in either aqueous or anhydrous HF. While porous etching was observed in aqueous HF with a gold-backed wafer, etching did not occur once oxygen was removed from the solution. Clearly, as in the present work, a galvanic cell is formed; oxygen reduction occurs at the gold to compensate for the photoanodic oxidation of the semiconductor. The hydrogen overpotential for gold excludes hydrogen evolution as the cathodic reaction in this case. The rate of porous etching of a wafer floated on a mercury pool was lower than that of the gold-backed wafer. The authors attributed this result to the inferior electrical contact with mercury. When a platinum wire was introduced into the mercury, however, the oxidation rate was enhanced because hydrogen could be evolved at the platinum (compare with curve b, Figure 2). This is similar to what we observed in the present work with a platinum cathode at high pH (see below). Platinum, unlike mercury, has a low overpotential for the hydrogen reaction. The observation of porous etching with a gold-backed wafer in oxygen-free anhydrous HF suggests that, in this case, hydrogen evolution occurs in the potential range of photoanodic oxidation.

In contrast to the results at low pH, a galvanic cell is formed with both p-type and n-type silicon in contact with gold or platinum in aerated alkaline solution in

(18) Zhang, Z.; Lerner, M. M.; Alekel, T., III; Keszler, D. A. *J. Electrochem. Soc.* **1993**, *140*, L97.

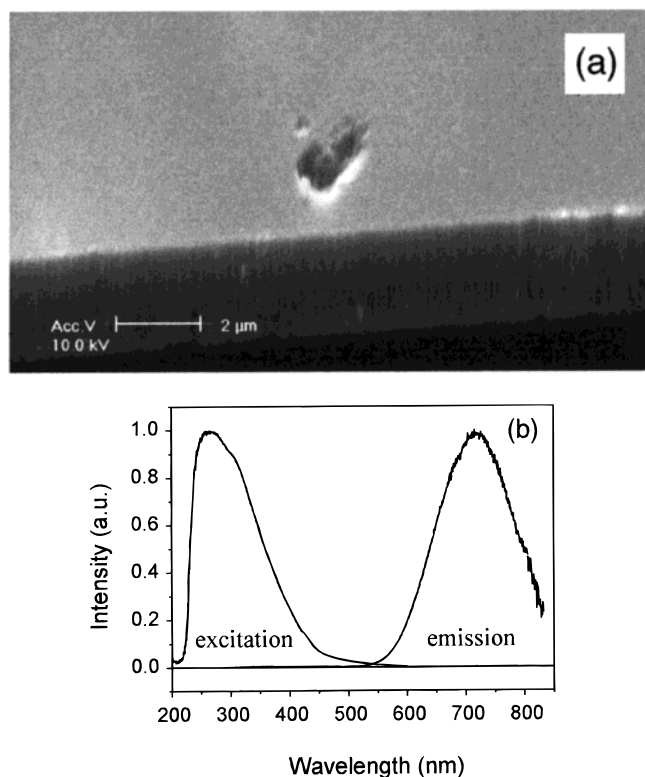


Figure 6. SEM micrograph (a) and photoluminescence excitation and emission spectra (b) of a microporous silicon layer formed on a p-type (100) wafer in contact with platinum after 15 min of etching in an aerated 40% HF/ethanol (1:1) solution in the dark. The thickness of the porous layer was 2.4 μm.

the dark. Results are shown in Table 1 (cases 4 and 5) for a 2.0 M KOH solution at 45 °C. Similar results were observed at room temperature and 70 °C. Figure 4 shows an example of current and potential transients for p-type (100) silicon in contact with platinum. Unlike the HF case, a steady-state potential and current are established as soon as the metal and semiconductor are short-circuited. The potential corresponds to the range for “active” dissolution of the semiconductor. When the solution was purged with nitrogen, the current dropped (from 0.25 to 0.13 mA cm⁻²). Obviously, as in the case of HF solution, two cathodic reactions are sustaining the galvanic cell: reduction of O₂ and of H₂O.

If the rate of the cathodic reaction is increased, for example by using Fe(CN)₆³⁻ as oxidizing agent then it is possible to push the potential beyond the peak value (see Figure 1, parts c and d) and thus passivate the silicon. The same effect can be achieved with oxygen reduction by increasing the area ratio of platinum or gold to silicon.

The essential difference between the systems operating at low and high pH can be understood on the basis of the band diagrams shown in Figure 5. At short-circuit, the Fermi levels in the silicon and metal will be the same. (We assume that ohmic drop can be disregarded.) For the p-type Si at low pH electron exchange between metal and redox system occurs at an energy close to that of the VB of the semiconductor (see Figure 5a). Reduction of the oxidizing agent gives rise to a hole current from metal to semiconductor; the semiconductor dissolves. On the other hand, electron exchange in the case of the n-type semiconductor/metal system will occur at the level of the CB (see Figure 5b). The metal cannot

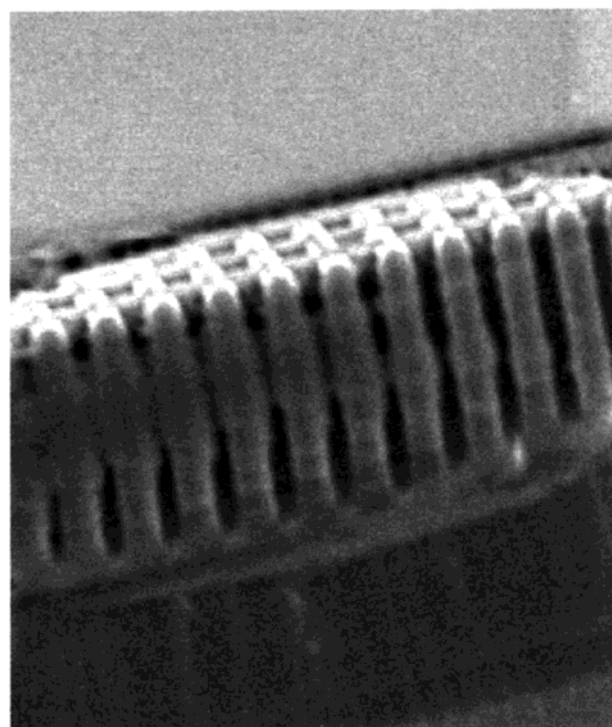
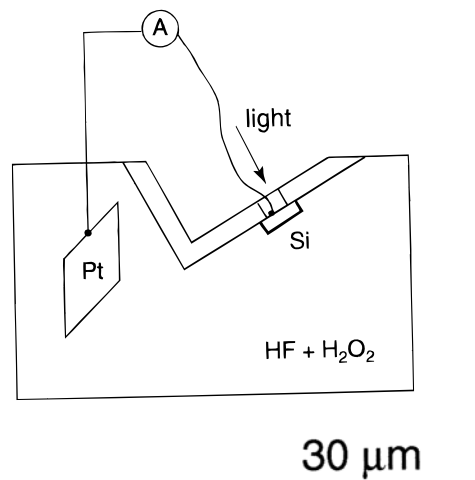


Figure 7. SEM micrograph of macroporous n-type silicon galvanically formed in a solution of 5% HF + 1% H₂O₂ for 15 min. The silicon was short-circuited to a platinum electrode in the same solution while the back of the semiconductor was illuminated. Note the resulting deep pores.

supply holes in this case for the oxidation of the semiconductor; an electron extracted from the metal by the oxidizing agent gives an unoccupied level which is about 1 eV above the VB edge of the solid. A galvanic cell is not possible. The situation obviously changes when the semiconductor is illuminated. The strong electric field of the depletion layer separates very efficiently the electrons and holes generated by light. The holes are available for oxidation of the silicon surface; the electrons reduce the oxidizing agent at the metal surface. A “photogalvanic” element is formed. Whether a porous layer results or polishing occurs depends on the photon flux.

As we discussed in the section on silicon electrochemistry, an anodic current is observed with n-type silicon in alkaline solution as a result of electron injection (very likely from a species produced by chemical etching). The

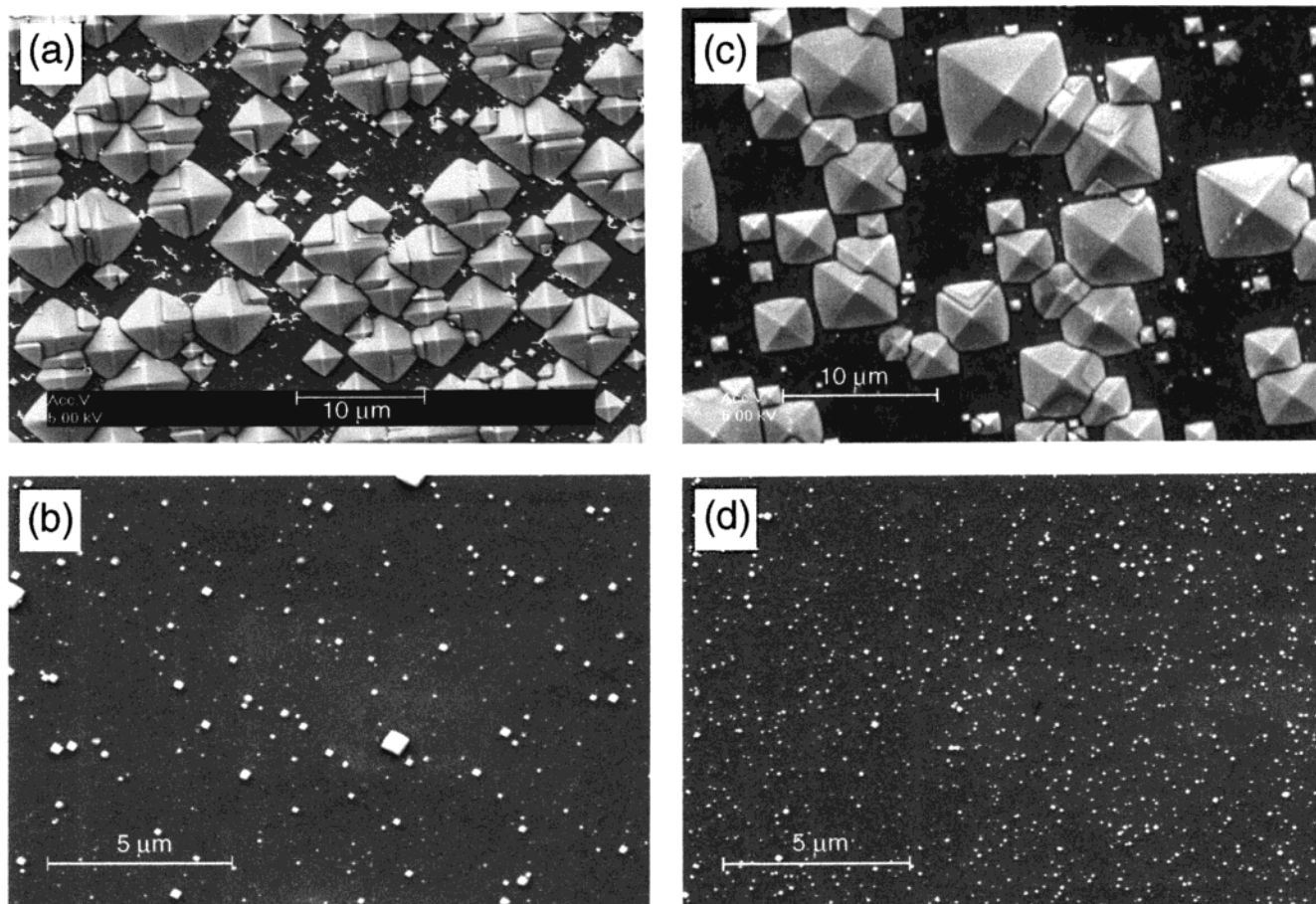


Figure 8. SEM micrographs of a silicon surface etched in 2.0 M KOH in the dark at 70 °C for 30 min. In parts a, p-Si(100), and c, n-Si(100), chemical etching results in the formation of well-defined pyramids; in parts b, p-Si(100), and d, n-Si(100), the galvanic contact suppresses pyramid formation.

Table 2. Influence of Galvanic Element Formation on Silicon Morphology

case	si-type/illum.	metal	oxidizing agent	solution	A_{Si}/A_M	T (°C)	\bar{I}^c (mA cm ⁻²)	structure
1	p-type/dark	Au	O ₂ + H ₂ O	40%HF/H ₂ O (1:7) + 2 drops Triton X-100	1/3.5	20	0.32	uniform microporous layer
2		Pt		40% HF/ethanol (1:1)	1/11		0.95	uniform microporous layer
3	n-type/illum. from back	Pt	1% H ₂ O ₂	5% HF	1/40		2.3	macroporous layer
4	p-type/dark		O ₂ + H ₂ O	2M KOH	1.5/1	70	1.35	pyramid-free surface
5	n-type/dark						1.6	

electrons are used to reduce the oxidizing agent at the metal (Figure 5d as in the case of an n-type sample illuminated in HF solution. If this short-circuit current is lower than the peak current (see Figure 1), then the semiconductor dissolves via a chemical and an anodic reaction; if the short-circuit current exceeds the peak current, silicon will be passivated. In the case of p-type silicon in KOH solution two mechanisms are possible: direct exchange of holes at the semiconductor/solution interface (as in HF solution) or electron injection followed by electron/hole recombination (as is shown in Figure 5c).

ii Morphology. Formation of Porous Layers. Microporous silicon can be formed by galvanic etching in aerated HF solutions using gold or platinum as contacting metal. However, as the transient of Figure 3 shows, the current in aqueous HF solution is not stable and the porous layer was not uniform. We suspected that

this could be due to the blocking of the pores by hydrogen bubbles. This is confirmed by experiments in which either a surfactant (Triton X-100) was added to the solution (case 1, Table 2) or a HF/H₂O/ethanol solution was used (case 2, Table 2). The latter is widely used for anodic etching to obtain photoluminescent silicon. Very likely the surfactant or alcohol ensures the release of hydrogen bubbles from the pores. Figure 6a shows a microporous layer formed on a p-type wafer in contact with platinum after 15 min etching in an aerated 40% HF/ethanol (1:1) solution. The porous structure was uniform, and the thickness of the layer was 2.4 μm. Uniform layers with a thickness greater than 10 μm could be readily grown. Under UV illumination, the porous layers obtained galvanically showed a clear photoluminescence visible to the naked eye in the dark. The excitation and emission spectra (Figure 6b) are similar to those observed with wafers etched anodi-

cally.¹⁸ We have shown that a photoluminescent layer is formed on a gold-backed p-type wafer under similar conditions.⁶

Microporous silicon can also be made by open-circuit etching ("stain etching") of the semiconductor in aqueous HF/HNO₃ solution.¹⁹ The holes required for oxidation of the solid are supplied by reduction of HNO₃. The latter is, however, a complicated reaction.²⁰ An induction period is often observed before stain etching commences.¹⁹

Figure 7 shows a SEM picture of macroporous n-type (100) silicon formed in 5% HF + 1% H₂O₂ solution. The experimental setup is shown on the top. In this case, illumination was performed from the backside of the sample with a white light source. The front side was masked with grid and subsequently etched chemically in KOH solution to form inverted pyramids (by anisotropic etching). The inverted pyramids were used as starting points for the macropore formation. A separate Pt counter electrode was contacted to the backside. The etch time was 15 min and an etch rate of 2 μm/min was achieved. The Pt/exposed silicon area ratio was about 40. However, this ratio may be decreased when the oxidizing agent concentration and light intensity are increased. The pores shown in Figure 7 have a width of 3 μm and a length of 30 μm.

Pyramid Suppression. Anisotropic etching of silicon in alkaline solution under conditions of high etch rate generally gives rise to roughened surfaces.^{11,14} Examples are shown in Figure 8a for p-type and Figure 8c for n-type (100) silicon etched for 30 min in 2 M KOH at 70 °C. A high density of square-based pyramids with

dimensions of a few micrometers are observed. Bressers et al.¹¹ showed that pyramid growth could be prevented by applying a potential to the silicon between the point of current onset and the peak potential. The etch rate is not significantly affected. The improved morphology was attributed to a change in surface chemistry. During chemical etching the surface is hydride-terminated while anodic polarization gives rise to a surface which is oxide or hydroxide terminated.

Parts b and d of Figure 8 show that the same effect can be achieved by replacing the external voltage source by a galvanic cell based on gold or platinum in aerated KOH solution at 70 °C (Table 2, cases 4 and 5). In both cases the large pyramids are not observed after etching in the dark. Ashruf et al.⁷ have shown that when the cathodic current is increased (for example by increasing the area of noble metal exposed to solution) the silicon passivates. Using this effect they developed a galvanic etch-stop technique for producing beams and membranes.

Concluding Remarks

In this paper we have shown that the galvanic approach can be used to achieve microporous and macroporous silicon layers or produce pyramid-free anisotropic structures. In particular, we describe the electrochemical requirements that have to be met in order to ensure a successful application of the method. It is clear that when etching silicon in contact with a metal, one needs to be aware of possible galvanic effects, as described in this paper.

Acknowledgment. The authors would like to thank Dr. A. P. Vink for performing the photoluminescence measurements. This work was carried out as part of a Brite/EuRam project BE97-4371.

CM9912066

(19) Steckl, A. J.; Xu, J.; Mogul, H. C. *Appl. Phys. Lett.* **1993**, *62*, 2111.

(20) Kooij, E. S.; Butter, K.; Kelly, J. J. *Electrochem. Solid. Lett.* **1999**, *2*, 178.