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ORIGINAL PAPER

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Ionic components dependence of the charge transfer reactions at the silicon/HF solution interface

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Abstract The actual requirements for circuit miniaturization and production economy require obtaining smooth silicon surfaces using diluted chemicals, especially HF treatment. This fundamental research deals with the electrochemical corrosion of n- and p-type silicon substrates in 0.25 M dilute HF solutions, and examines the influence of fluoride ions or protons additives. All experiments were conducted both in the dark and under constant light flux, with solutions thoroughly degassed by high purity argon bubbling. Polarization resistance measurements near the open circuit potential lead to the value of the corrosion current. The kinetics of charge transfer reactions, studied by linear voltammetry, were interpreted as a function of the carrier density in the energy levels of the semiconductor and the concentration of acceptor species in the solution. The influence of these parameters on the surface roughening of the silicon samples was also studied by *ex situ* atomic force microscopy profile measurements.

Key words Silicon · Hydrofluoric acid · Fluoride ions · Passivation

Introduction

Decreasing the dimensions of ultra-large scale integration microcomponents requires obtaining a perfectly clean and stable silicon surface which should be flat at the atomic scale. Roughness is an important factor which may affect [1] the electrical characteristics of the devices. As further miniaturization is required, surface smoothness [2] should be controlled with extreme stringency. Several studies of the surface microroughness and etching rate have been undertaken after wet cleaning in SC1 (NH_4OH, H_2O_2, H_2O) solution which is efficient for the removal of particles [1, 3]. However, HF containing solutions hold an important position as they are the only oxide etchant used in many manufacturing sequences.

Removal of metallic impurities, etching rates, and microroughness of n- and p-type silicon substrates by dipping in HF solutions with various additives were measured by Ohmi et al. [4]. Chabal and co-workers [5, 6] reported that the treatment of silicon with fluoride solutions leads to passivating hydrogen termination bonds, but Fukidome et al. [7] have observed that the electrochemical anodic dark current [8] of n-Si in NH_4F-HF solutions shows a sharp maximum at pH = 6.4. They suggested the formation of a relatively large number of Si-F bonds which play an important role in the kinetics of etching. On the other hand, Allongue et al. [9], using the scanning tunneling microscope technique, indicated that they obtained ideally flat (111) surfaces of silicon in concentrated solutions containing 40% NH_4F. On Si (100) surfaces, high-resolution electron energy loss spectroscopy led to the conclusion that NH_4F addition induced the formation of silicon dihydride with a higher level of microroughness [10]. On the other hand, for low values of pH obtained by HCl addition, multiple internal reflection infrared spectroscopy [11] showed that flat (100) silicon surfaces were passivated by dihydride and monohydride termination bonds. Very recently, the addition of hydrochloric acid in HF cleaning solutions proved to be efficient in the prevention of silicon surface pitting [12].

Electrochemical principles play an important role in the behavior of silicon surfaces during wet treatments [13]. The anodic etching of p-type silicon [14] by HF solutions with various ionic compositions, i.e. containing an excess of protons or fluoride ions, has shown a steep increase of the corrosion rate as a function of the F^- concentration. However, these studies were mainly

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oriented to the formation of porous silicon, the potential scan being up to 6 V and the current density being up to several mA/cm^2 [15, 16].

The present trend in the field of wet treatment is to reach economic requirements for the cost of chemicals and environmental regulations [17]. Equilibria in HF containing solutions have been thoroughly studied for determining the rate and the mechanism of silicon oxide dissolution [18].

In the present study, the electrochemical properties of Si single crystals were investigated within a rather narrow range of potentials near the zero current value. The aim of this study was to reach a quantitative evaluation of the anodic and cathodic components of the charge transfer reactions which are involved in the corrosion current density during simple contact with the electrolyte at the open circuit potential (OCP) of the material. It was important to determine the influence of both the charge carriers in the semiconductor and the donor/acceptor species in the solution. One interesting feature of the studied system is that the potential range between −0.2 and −1.5 V/SCE is always more negative than the equilibrium potential of hydrogen E_H and more positive than the oxidation potential of silicon E_{Si}. This situation promotes the generation of surface minority carriers by charge transfer due to electrochemical reactions.

Experimental

The measurements were carried out using the following procedure developed and tested in a previous study [19]. Silicon wafers, 125 mm diameter and 625 μm thickness, were supplied by MEMC Electronic Materials, Novara, Italy. Two types of silicon substrates were employed:

- n-type wafers, phosphorus-doped, resistivity 20–40 Ω cm ($\approx 2 \times 10^{14}$ atom cm^{-3}).
- p-type wafers, boron-doped, resistivity 11–25 Ω cm ($\approx 10^{15}$ atom cm^{-3}).

These substrates were (100) oriented; one face was mirror polished for semiconductor applications, and the back side was mechanically polished with an "enhanced gettering" treatment to facilitate ohmic contact. These wafers were cleaned with a mixture of pure H_2SO_4 (60%), H_2O_2 (12%), and H_2O (28%) at 100 °C for 10 min to oxidize the surface impurities, then thoroughly rinsed with high-purity 18.2 MΩ, ultramicrofiltered (0.05 μm), deionized water, and finally treated 15 s in a 5% dilute HF solution (DHF) to promote an oxide-free hydrophobic silicon surface.

An important feature of the electrochemical experiments was the use of a new cell described in a recent publication [20]. This cell was made of a Teflon vessel pressed upon the silicon active face, and maintained by two black polyvinyl plates. The whole cell was protected against room light by means of a box made of black polyvinyl polymer. A hole on the cover allows the illumination with visible light by an optical fiber device, the intensity of which (1.400 lx) was measured with a luxmeter. Before and during the experiments, the cell was maintained under a controlled atmosphere by a permanent circulation of pure argon gas, N60 grade, containing less than 0.1 ppm residual oxygen, a product of l'Air Liquide company. This technique allowed for very reproducible and reliable results, mainly for the OCP measurements which are very sensitive to many parameters, such as light, dissolved oxygen, and confinement of electrolyte near the O-ring seal. These parameters were found to be responsible for the difficulties encountered by former authors [21, 22] whose results were scattered within a few hundreds of mV, as was pointed out by Föll [23].

The electrolyte solution was generally constituted of 0.25 M (0.5%) HF, prepared from a 40% sub large scale integration grade product, containing less than 1 ppb metallic contaminants, diluted in ultrapure deionized water. The solution was thoroughly degassed by high-purity argon bubbling and then introduced in the cell by argon pressure using the device described in our previous publication [20]. The influence of the ionic components was investigated by addition of either HCl or NH_4F with concentrations up to 1 M, in order to change the ratio H^+/F^- to a considerable extent.

The electrical contact on the back side of the wafer was obtained by depositing a thin Ga-In alloy layer, on which was pressed a gold foil connected to the working electrode plug of the potentiostat. The counter-electrode was a platinum plate; the reference was a saturated calomel electrode (SCE) connected to the electrolyte by means of a bridge made of a Teflon capillary tube filled with a KCl jellied solution. The electrochemical parameters were determined with a Tacussel Radiometer Analytical PGS 201T potentiostat. This device was driven by a Hewlett-Packard PC using the Voltamaster Radiometer Analytical software, which includes several programs for electrochemical techniques such as chronopotentiometry, polarization resistance, linear and cyclic voltammetry, etc. For each run, numerical data were recorded in files which can be used for drawing the corresponding graphs.

These electrochemical studies were complemented by viewing the silicon surface morphology using atomic force microscopy (AFM) working in contact mode. This technique allows the measurement of the surface profile at a subnanometric scale. Our equipment, produced by Molecular Imaging, was driven by a NEC PC. The image processor was the Nanoscope III software, leading to the quantified profile in the z direction of the surface, and to other parameters such as the values of the roughness and the spectral distribution of the microroughness in the (x,y) plane.

Results

The study of the OCP of the n- and p-type silicon substrates in contact with a pure 0.5% DHF solution [24], and the changes induced by the addition of an excess of HCl or NH_4F, showed that the time required to reach a steady value was longer than that observed previously [19] with 5% DHF solutions. For example, in the preceding experiments with 5% DHF the OCP potential was stabilized after ca. 1 min, whereas in the present work the OCP value moves smoothly towards a steady state value during 10–15 min. This variation could be provisionally assigned to the small value of the exchange current leading to a stable configuration of the silicon surface bonds. We observed that the potential of both n- and p-type silicon moves towards more positive values when the solution is enriched with protons, and to more negative values when the solution is enriched with fluoride ions.

Typical results show that the initial value of the p-type silicon rest potential was observed to be near −600 to −650 mV vs. SCE, depending on the electrolyte composition. However, when the sample was in contact with 0.5% HF + 1 M HCl, the potential increased smoothly to a value near −450 mV, whereas with 0.5% HF + 1 M NH_4F, the potential shifted to more negative values and tended to −790 mV after 10 min. Quite similar results were obtained with n-type silicon. It

seems that these well reproducible behaviors could be assigned to the formation of an almost complete layer of Si-H terminal bonds in the presence of an excess of protons, and to the influence of pH in the presence of fluoride ions.

Upon silicon surface lighting by visible light at 1400 lx intensity, a sharp photopotential ΔE was immediately observed (Fig. 1), the response time of our device being 1 s. The characteristics of the ΔE values were similar to those observed with 5% DHF [19], i.e. a large positive ΔE value approximately +400 mV with p-type Si, and a rather small negative shift less than −20 mV with n-type silicon [25]. The ΔE value of the photopotential showed a slight dependence on the initial OCP value. With p-type silicon in HF + HCl electrolyte, the OCP (E_r) being near −450 mV in the dark, the observed photopotential ΔE was +350 mV, but with NH_4F containing solution, E_r was −750 mV in the dark, and ΔE was then +450 mV. With n-type silicon the ΔE values were almost equal to −20 mV when E_r was near −550 mV/SCE, but was hardly visible and almost zero when E_r was close to −700 mV, i.e. in NH_4F containing solutions. It is worth emphasizing this peculiar observation, which shows that the electrochemical responses of n- and p-type silicon semiconductors are not symmetrical although we chose samples with almost equivalent doping levels.

Following a derivation of the Butler-Volmer expression [25], the polarization resistance R_p was measured from the tangent slope at zero current on the voltammogram plotted within a narrow range of potentials of ±50 mV around the OCP. The potential scan rate was 50 mV/min. Even though the signal amplitude was not large, the approximation of the linear response was often not available. The lines obtained on the recorded graphs showed a curvature revealing the rectifying properties of the semiconductor/electrolyte junction. This curvature was more pronounced when the acceptor species in solution matched the semiconductor carriers, for example n-Si in contact with low pH solutions. In this situation, electrons from the semiconductor can react easily with protons, while the anodic reaction involving fluoride ions and holes is inhibited. These experiments were undertaken in order to demonstrate the respective contributions of the charge carriers in the semiconductor and of the acceptor species in the solution, characterized by the voltammograms obtained in the dark. A few examples of these i versus E graphs are shown in Fig. 2. These experiments lead to a very important observation concerning the low value of the polarization resistance in HF + NH_4F solutions and the very high value of this parameter in HF + HCl solutions.

Typical results of the R_p measurements and of the derived corrosion current densities j_{cor} are given in Table 1. All data were obtained with thoroughly deaerated electrolytes by bubbling high purity argon for at least 1 h, prior to the introduction in the cell.

The data of Table 1 again lead to the conclusion that, in general, the electrochemical corrosion current of n-Si in the dark was much higher, by a factor of 10, compared to p-Si. Moreover, under irradiation by light, the polarization resistance of p-Si samples undergoes a steep decrease by a factor near 50, while the effect was much less with n-Si. Such results may suggest that the carrier type is not the only factor involved in the charge transfer. Voltammetry on a somewhat wider range of potentials of ±250 mV around the zero current potential was used to obtain information on the kinetics of anodic and cathodic charge transfer reactions without introducing any marked change of the silicon surface state. We always controlled by optical microscopy that, at the end of each experiment, the sample surface appeared perfectly mirror clean and hydrophobic. From our studies, it appeared that a larger potential scan led to an intense corrosion current, which induced a serious variation of the surface properties. In such a situation, the branches of the anodic and cathodic curves could be misleading.

Irradiation of the silicon surface with visible light was useful to change the charge carrier density. Under illumination the generation of minority carriers contributed

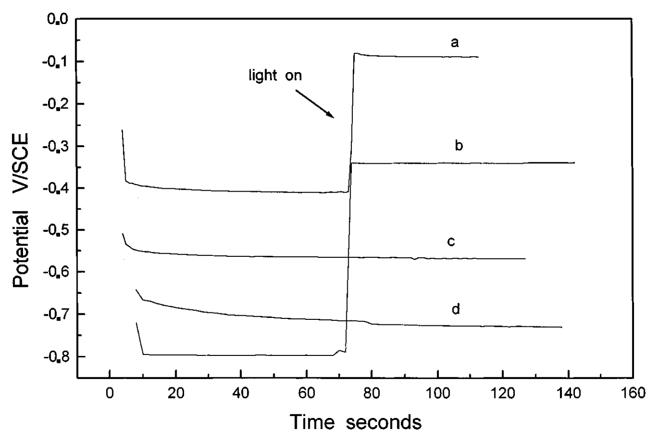


Fig. 1 Electrochemical photopotential of p- and n-Si: *a* p-Si in 0.25 M HF + 1 M HCl, *b* p-Si in 0.25 M HF + 1 M NH_4F, *c* n-Si in 0.25 M HF + 1 M HCl, *d* n-Si in 0.25 M HF + 1 M NH_4F

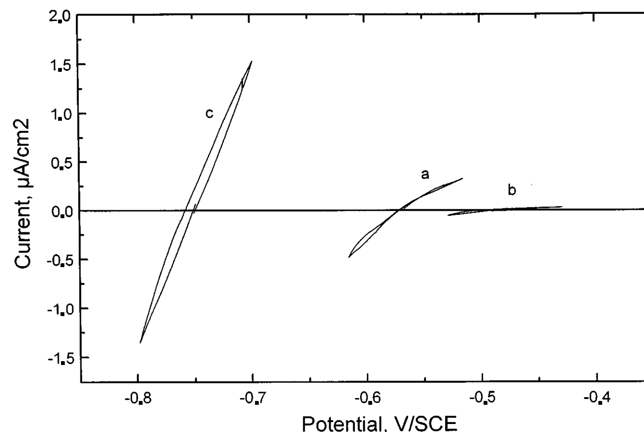


Fig. 2 Voltammogram of n-Si, *i* vs. *E*, in the narrow potential range of ±50 mV around the open circuit potential: *a* in 0.25 M HF, *b* in 0.25 M HF + 1 M HCl, *c* in 0.25 M HF + 1 M NH_4F

Table 1 Effect of electrolyte composition and operating conditions on open circuit potential and corrosion rate of n- and p-Si

	Silicon	Cond.	E_r (mV/SCE)	R_p (kΩ cm^2)	j_{corr} (A/cm)^2	dN/dt (at/cm^2 s)
0.5% HF + 1 M HCl	n-	Dark	−540	1000	2.6×10^{-8}	1.6×10^{11}
		Light	−570	500	5.2×10^{-8}	3.2×10^{11}
	p-	Dark	−480	9000	2.9×10^{-9}	1.8×10^{10}
		Light	−90	200	1.3×10^{-7}	8.1×10^{11}
0.5% HF	n-	Dark	−590	350	7.3×10^{-8}	4.5×10^{11}
		Light	−603	80	3.2×10^{-7}	2.0×10^{12}
	p-	Dark	−550	4000	6.5×10^{-9}	4.0×10^{10}
		Light	−98	100	2.6×10^{-7}	1.6×10^{12}
0.5% HF + 1 M NH_4F	n-	Dark	−700	70	3.7×10^{-7}	2.4×10^{12}
		Light	−710	60	4.3×10^{-7}	2.7×10^{12}
	p-	Dark	−760	6000	4.3×10^{-9}	2.7×10^{10}
		Light	−340	50	5.2×10^{-7}	3.2×10^{12}

to lessen the diode character of the junction. The effect was strongly dependent on the donor/acceptor species in the electrolyte solution. In all cases, the current density was observed to be highly amplified by light at 1400 lx intensity. With p-Si, the specific effect of light was that the cathodic current was amplified by a factor more than 1000 (Fig. 3), while the anodic branch was but a little perturbed, in conformity with the predictions [24]. In the case of n-Si, the generation of holes did not influence the cathodic branch of the voltammogram, but induced a significant change of the anodic current, especially in the presence of fluoride ions as electron donors.

To complement the electrochemical studies, we determined the surface roughness induced on n- and p-silicon by the HF + HCl, HF, and HF + NH_4F solutions. The measurements were performed by *ex situ* AFM microscopy in contact mode using the Molecular Imaging equipment. The experimental conditions were defined as follows: the 1×2 cm^2 samples were dipped in deoxygenated solutions, in the dark, for 10 or 30 min duration. Two samples of each Si type were prepared, and the scanned surface (2×2 μm^2) was situated in five different places of the crystal surface. The root mean square (rms) values given in Table 2 were obtained from the average of 10–20 separate and rather coherent measurements obtained by the nanoscope software. As the rms data give only the average z values of the profiles, the analysis was complemented by the determination of the spectral density.

The surface obtained with argon degassed 0.25 M HF + 1 M HCl solution, in the dark, was smooth even after 30 min contact, but the difference compared to 0.25 M HF alone was not significant. Roughening by 0.25 M HF + 1 M NH_4F solutions was observed to be much more severe, and confirmed the observation obtained in the electrochemical studies which showed the influence of fluoride ions on the silicon material etching rate.

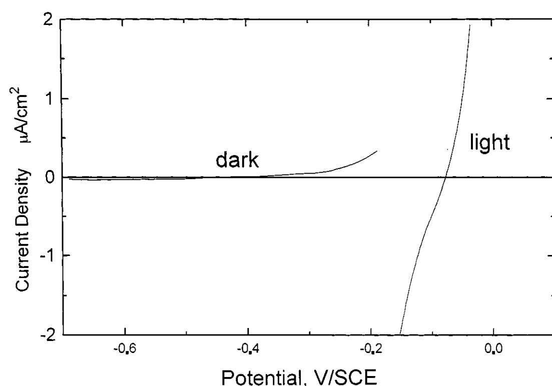


Fig. 3 Voltammograms of p-Si in 0.25 M HF + 1 M HCl, in the dark and under 1400 lx light

Discussion

The treatment of the electrochemical charge transfer taking place at the interface of a semiconductor in contact with a solution containing one redox couple has been developed in several authoritative publications, such as Gerischer's article [26].

The model was based on the exchange of charge between the carriers holes (h^+) or electrons (e^-) in the semiconductor and the redox species in the electrolyte solution, and leads to a formal equation involving the energy levels of charges in both phases. For example, the charge transfer processes implying electrons depend on

Table 2 Roughness evaluation of n- and p-type silicon in HF solutions of various pH values

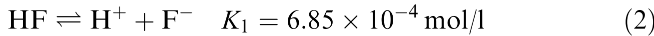
Cleaning solution	Si-type, dipping time	rms (nm)
0.5% HF + 1 M HCl	n-Si, 10 min	0.19 ± 0.01
	n-Si, 30 min	0.28 ± 0.04
	p-Si, 10 min	0.26 ± 0.02
	p-Si, 30 min	0.27 ± 0.01
0.5% HF	n-Si, 10 min	0.38 ± 0.01
	n-Si, 30 min	0.53 ± 0.04
	p-Si, 10 min	0.44 ± 0.03
	p-Si, 30 min	0.29 ± 0.02
0.5% HF + 1 M NH_4F	n-Si, 10 min	1.48 ± 0.15
	n-Si, 30 min	1.15 ± 0.16
	p-Si, 10 min	1.61 ± 0.11
	p-Si, 30 min	1.65 ± 0.06

the density of states in the conduction band and on the number of chemical species involved following the equation:

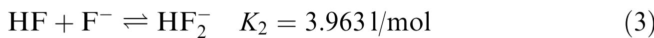
$$I(\varepsilon) = -e\int_{\varepsilon_c}^{+\infty} v^{-}(\varepsilon)N_{\mathrm{o}}(\varepsilon)D_{\mathrm{ox}}(\varepsilon)\mathrm{d}(\varepsilon) + e\int_{\varepsilon_c}^{+\infty} v^{+}(\varepsilon)N_{\mathrm{u}}(\varepsilon)D_{\mathrm{red}}(\varepsilon)\mathrm{d}\varepsilon \qquad (1)$$

where $v^{-}(\varepsilon)$ and $v^{+}(\varepsilon)$ are the frequency factors for energy level ε, $N_{\mathrm{o}}(\varepsilon)$ and $N_{\mathrm{u}}(\varepsilon)$ are the densities of occupied and unoccupied states of the electron in the semiconductor, and $D_{\mathrm{ox}}(\varepsilon)$ and $D_{\mathrm{red}}(\varepsilon)$ are the state densities of electron acceptor and donor chemicals in the solution. It is important to recall that this equation has been established for a semiconductor in contact with only a single redox couple.

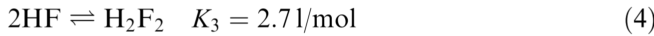
To examine the influence of donor/acceptor species in the electrolyte solution, the concentrations of ionic species in the HF solutions containing HCl or NH_4F additives were determined using the careful calculation technique presented by Verhaverbeke et al. [18], taking into account the ionic equilibria together with the dimerization of neutral HF molecules in solution:



$$HF \rightleftharpoons H^{+} + F^{-} \quad K_1 = 6.85 \times 10^{-4}\,\mathrm{mol/l} \qquad (2)$$



$$HF + F^{-} \rightleftharpoons HF_2^{-} \quad K_2 = 3.963\,\mathrm{l/mol} \qquad (3)$$



$$2HF \rightleftharpoons H_2F_2 \quad K_3 = 2.7\,\mathrm{l/mol} \qquad (4)$$

The influence of other equilibria proved to be negligible in the concentration range of our experiments. Moreover, these authors indicated that the mass action law could be applied with enough precision, without activity coefficient correcting terms. This point was confirmed by several pH and conductance measurements undertaken in our laboratory. The mass law relations, complemented by the matter and charge conservation rules, led to the components of the solutions in Table 3.

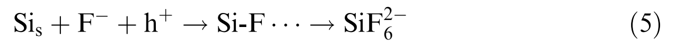
From Table 3, it is clear that adding 1 M HCl to 0.25 M HF reduces the concentration of F^{-} and HF_2^{-} by a factor near 100, while the H^{+} concentration was increased by the same factor, the reverse effect being obtained by the addition of 1 M NH_4F. The effect was well illustrated for p-type Si since the current of the anodic branch was enhanced by a factor roughly proportional to the concentration of F^{-} or HF_2^{-} ions. From our experiments we obseved that increasing the H^{+} concentration in solution contributes to improving the passivating properties of the Si-H surface layer, which weakens the absolute values of both anodic and cathodic current densities.

Table 3 Concentration of constituent species as a function of the composition of the solution

	0.25 M HF	0.25 M HF + 1 M HCl	0.25 M HF + 1 M NH_4F
[HF]	0.1354 M	0.142 M	0.047 M
[H_2F_2]	0.0494	0.054	0.006
[H^{+}]	1.194×10^{-2}	1.0015	4×10^{-5}
[F^{-}]	0.777×10^{-2}	0.973×10^{-4}	0.809
[HF_2^{-}]	0.417×10^{-2}	0.548×10^{-4}	0.191

Such results may suggest that the carrier type is not the only factor involved in the charge transfer. In addition, the energy levels of the valence and conduction bands, and also probably the overall impurity, influence the bonding energy of the silicon lattice and the electrochemical properties of the material. In Gerischer's treatment, the current value is modified by a term g_s, the surface generation rate of the charge carriers. In our previous publication [19], we pointed out that the silicon/HF interface must be considered as a dual redox system because at least two simultaneous electrochemical reactions are involved:

anodic charge transfer



$$Si_s + F^{-} + h^{+} \rightarrow \text{Si-F} \cdots \rightarrow SiF_6^{2-} \qquad (5)$$

cathodic charge transfer

$$Si_s + H^{+} + e^{-} \rightarrow \text{Si-H} \qquad (6)$$

The system is even more complicated if the solution contains dissolved O_2 gas, oxidant species, or metallic contaminants. In this presentation, silicon material is considered as being not only an electron and hole reservoir but also as a redox chemical component, especially when it is in contact with HF containing solutions. Surface charge carrier generation induced by electrochemical transfer may provide factors which disturb the current-potential characteristics.

The effect could be predicted from the following arguments. Firstly, the energy levels of electrons in the Si valence and conduction bands were known from literature data [27], and the Fermi level of n- or p-type samples were calculated from the dopant concentration [27] in the semiconductor. On the other hand, the redox potentials of both hydrogen and silicon in the three solutions, HF, HF + HCl, and HF + NH_4F, were determined by the Nernst relation. In the case of Si, the redox potential was evaluated from Latimer [28] data concerning the thermodynamics of the overall reaction:

$$Si + 6F^{-}_{aq} \rightleftharpoons SiF^{2-}_{6aq} + 4e^{-} \quad E^{\circ} = -1.2\,\mathrm{V/SHE} \qquad (7)$$

Using the ionic concentrations of Table 3, the following data were obtained:

		0.25 M HF + 1 M HCl	0.25 M HF	0.25 M HF + 1 M NH_4F
E_{H}	V/SHE	0.00	−0.11	−0.26
E_{si}	V/SHE	−0.93	−1.10	−1.28

These values were referred to the absolute zero potential of vacuum using the value of −4.31 eV for the standard hydrogen electrode [29]. In our experimental conditions, only these two electrochemical reactions are involved. On Fig. 4 is presented the energy level diagram on a

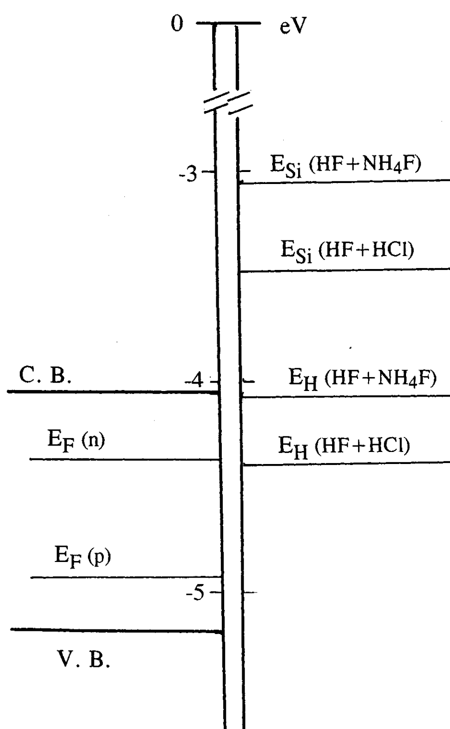


Fig. 4 Electron energy levels referred to zero potential in vacuum of n- and p-silicon matrices, and of redox couples involved in the electrolyte solution

common reference frame separately for the silicon material and the redox species in solution. Also the measured OCP values corresponding to the mixed potential of the dual redox system are indicated in the diagram.

When the semiconductor electrode and the solution are in contact, the Fermi level in silicon and the mixed potential of the dual redox system tend to equalize. For both p- and n-type silicon, the Fermi level is lower than the effective redox potential. Then band bending downward should occur in the semiconductor near the interface for both the conduction and valence bands, as shown in Fig. 5a and b for n- and p-type silicon, respectively. In our opinion, the absolute value of the built-in voltage could not be calculated rigorously because the system is not in thermodynamic equilibrium. Indeed, the electrochemical potential of the electrons corresponds to a steady regime situation involving two irreversible processes, i.e. oxidation of Si atoms and reduction of protons at the semiconductor/electrolyte interface. The bending amplitude is quite different for n-and p-type silicon because of the position of the Fermi level, and also depends on the electrolyte composition which promotes anodic or cathodic processes. In the case of n-Si it seems to be clear that the electrochemical potential of the electrons of the Si/SiF_6^{2-} redox couple is much higher than the conduction band level in the semiconductor material. In the case of p-Si, we note that the potential energy of electrons in the Si/SiF_6^{2-} system is higher than that of the conduction band in the immediate vicinity of the surface. In both cases we suggest that the highly negative standard potential of Si substrate promotes reaction (5) and gives rise to the surface generation of electrons which in turn are available for the reduction of protons following reaction (6). At least we suggest that this mechanism is available in a narrow range of potential near the free potential and corresponding to the corrosion process. In the vicinity of zero current potential, the oxidation of Si substrate may generate enough surface electrons for the change in potential drop in the space charge region to be small,

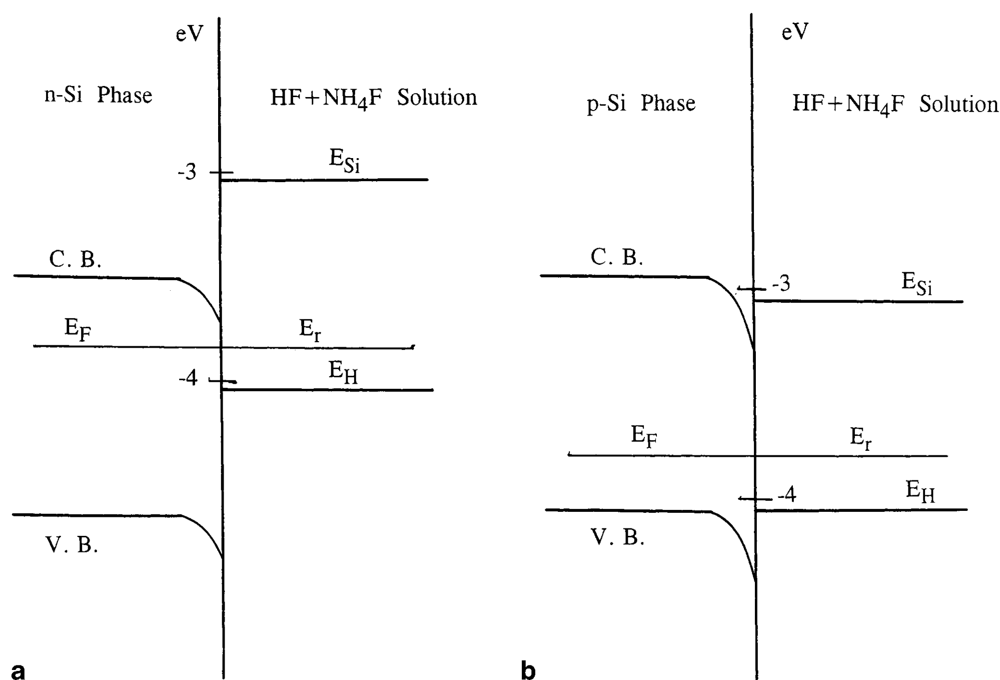


Fig. 5 Adjustment of Fermi level in silicon with open circuit potential in solution: **a** n-Si in 0.25 M HF + 1 M NH_4F, **b** p-Si in 0.25 M HF + 1 M NH_4F

and Eq. (1) to approach a Butler-Volmer relationship [25] which leads to the derivation of the corrosion current density:

$$j_{\mathrm{corr}} = RT/F(\alpha + \beta)R_{\mathrm{p}} \tag{8}$$

where α and β are the transfer coefficients for anodic and cathodic processes, respectively, and where the polarization resistance R_{p} is given by $R_{\mathrm{p}} = (\partial E/\partial j)_{j=0}$.

The proposed model is consistent with two important experimental results obtained in this study:

1. From the position of Fermi level (Fig. 4a and b) the generation of electrons by reaction (5) is much less in p-Si than in n-type semiconductors and could explain the significant difference in the respective corrosion rates.
2. Upon illumination, the generation of excess electrons in p-Si induces a steep increase of the reduction current and results in a sharp positive photopotential, while illumination of n-Si generates h^+ minority carriers which seem to influence the oxidation current of Si material only a little.

The OCP values could be qualitatively interpreted as follows. The values of the OCP reflect the relative variations of the exchange current densities of anodic and cathodic charge transfer reactions which consume h^+ or e^- carriers, respectively. Only the ratio of these values is determining. This interpretation is consistent with the conclusions derived from the voltammograms analysis, which indicated that the current intensity of the anodic branch is dramatically increased by the presence of fluoride ions, thus leading to a shift of potential to more negative values. On the other hand, the addition of H^+ ions contributes to inhibit both the anodic and cathodic charge transfer reactions.

It is now well accepted [6] that, soon after the dissolution of the silicon oxide by HF, the (100) surface is rapidly covered by a passivating layer of terminal Si-H bonds. The Si-H bonds are more stable although their binding energy (3.5 eV) is much less than that of Si-F (5.87 eV) [30]. The passivation is revealed by the extremely high polarization resistance of the interface with the solution. Nevertheless, it is not possible to assume that inhibition is complete, since the measurement of polarization resistance demonstrated that a corrosion current does exist. Even though the rate is small, a number of 10^{11}–10^{12} Si atoms will dissolve per cm^2 per second, while an equivalent number of protons are reduced simultaneously. Starting from the mechanism proposed by Trucks et al. [6] and developed by Gerischer et al. [31], we propose a series of successive steps which could account for this process. Indeed, following Chabal et al. [32], a (100) Si plane shows a well-defined IR spectrum indicating that the Si crystal surface was mainly constituted by silicon monohydride and dihydride, these hydrides being continuously regenerated even though a few Si-F bonds were formed transiently as a first step of the Si dissolution mechanism [33].

The continuous electrochemical corrosion of Si surfaces is assumed to involve the following steps. Starting with hydride bonds, a first oxidative step leads to a $Si^{\cdot}$ radical having a free electron which could either link with another H atom and heal this corrosion initiation, or transiently capture a F^- ion. The Si-F bond contributes to weaken the neighboring Si-Si bonds, and leads to the formation of a soluble silicon fluoride compound. This step, in turn, leaves unbonded Si atoms at the surface. Again, these atoms can either continue to react with F^- ions leading to soluble species, or to link with H atoms and heal this corrosion initiation. Moreover, we assume that the continuous Si oxidation necessarily results in the evolution of H_2 molecules on cathodic sites. In the classical hydrogen evolution reaction model [29], the formation of hydrides is considered as a step preceding the evolution of H_2 molecules which leave transient $Si^{\cdot}$ free radicals. Again, these Si atoms can react either with F^- ions or with protons, the reaction rate being related to the corresponding ionic species.

Finally, an interesting correlation was established between the electrochemical corrosion current and the surface roughness. It must be recalled that only the anodic charge transfer reaction leads to a material loss, but the effect should be negligible if the dissolution process was uniform. However, the mechanism of anodic processes on the Si-H lined surface gives evidence for a localized corrosion. Moreover, anodic reactions continuously concentrated on the same sites would result in very deep pits. This was never observed in our experiments. In a first approximation, roughness was quantified by the determination of the rms values, which show that the roughness amplitude is much higher when Si is treated with 0.5% HF + 1 M NH_4F. Figure 6a–c gives a 3D representation of the surface structure obtained by AFM observation in contact mode, after 10 min dipping of Si samples with the three different hydrofluoric solutions, under the well-defined conditions, i.e. degassed electrolyte and in the dark.

However, the definition of rms shows that it does not account for the dimensions of the pseudoperiodical profile on the x,y plane. In fact, starting from the definition of rms:

$$R_{\mathrm{q}} = \left(\frac{1}{L}\int y^2(x)\mathrm{d}x\right)^{1/2} \tag{9}$$

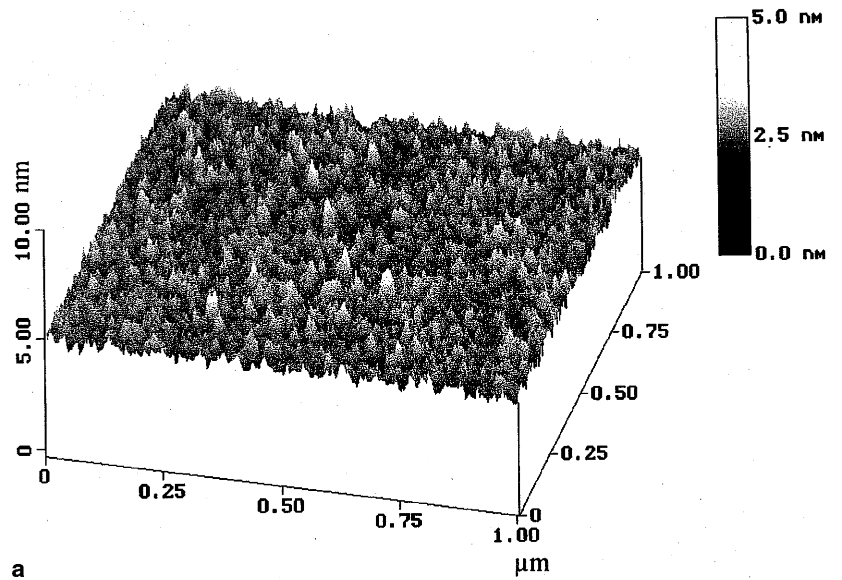
and in a first assumption the linear profile could be represented by a pseudoperiodical profile which could be represented by a Fourier series such as:

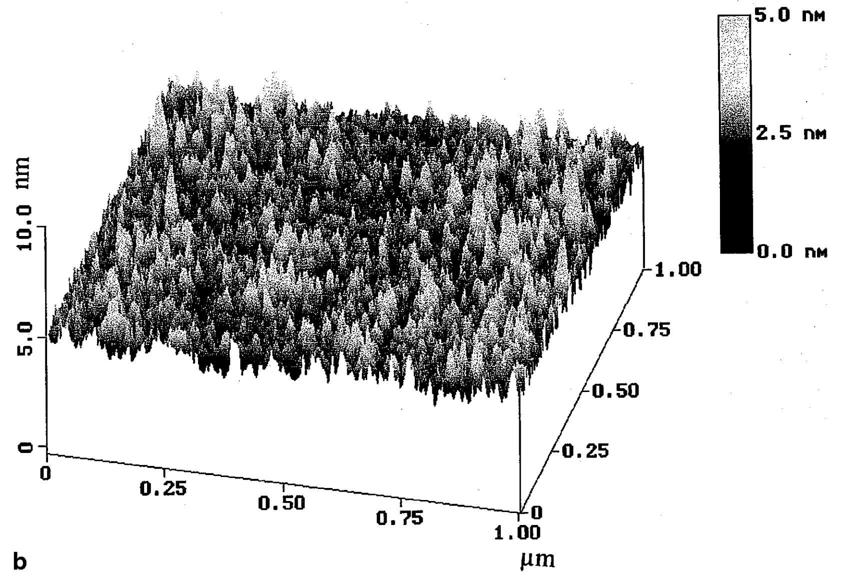
$$y(x) = \sum a_i \sin\frac{2\pi x}{\lambda_i} \tag{10}$$

Then:

$$y^2(x) = \sum a_i^2 \sin^2\frac{2\pi x}{\lambda_i} + 2\sum a_i a_j \sin\frac{2\pi x}{\lambda_i}\sin\frac{2\pi x}{\lambda_j} \tag{11}$$

The second term of Eq. (11) is cancelled by the integration and the rms value is:





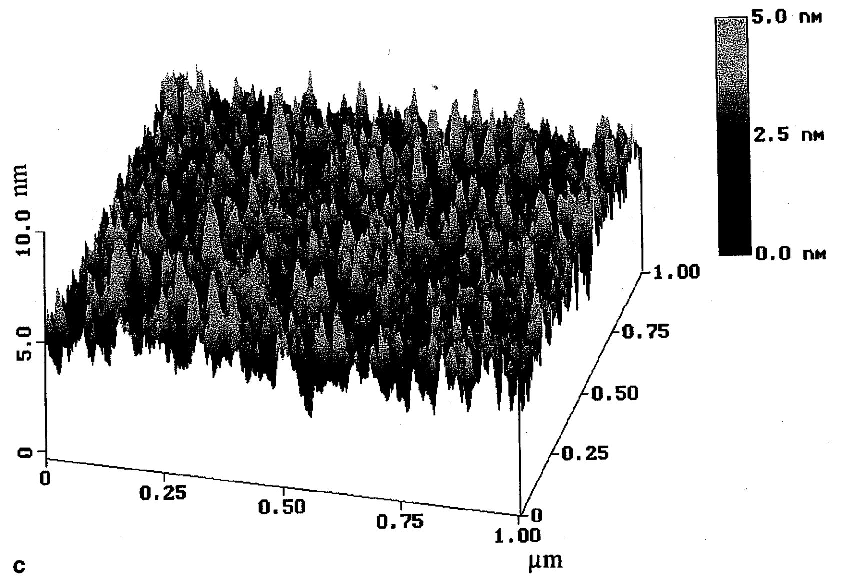


Fig. 6 3D surface profile of p-Si after 30 min dipping in the dark in deaerated HF solutions: **a** 0.25 M HF (*z* range 5 nm), **b** 0.25 M HF + 1 M HCl (*z* range 5 nm), and **c** 0.25 M HF + 1 M NH_4F (*z* range 10 nm)

$$R_q = \left(\frac{\sum a_i^2}{2}\right)^{1/2} \quad (12)$$

It appears that R_q does not account for the microscopic spectral distribution of the roughness. For this reason it was preferable to examine the power spectral density (PSD) which is equivalent to $a_i^2(\lambda_i)$. Using the Molecular Imaging software, the PSD values of the samples are presented in Fig. 7 and show that the wavelength distribution associated with the roughness profile is almost independent of the electrolyte composition, even though this figure again exhibits the deleterious influence of NH_4F in dilute HF solutions. This last result suggests that during the electrochemical corrosion process, when a $Si^{\cdot}$ radical with a free valence bond is formed, the probability for this radical to combine with an H atom and to restore the passivated state is high, and then the dissolution mechanism should be randomly distributed.

Conclusion

This fundamental study of the respective influence of protons and fluoride ions in 0.25 M HF solutions leads to useful information concerning the possible use of highly diluted reactants for the silicon surface wet processing. The electrochemical techniques permitted determination of the corrosion rate of Si wafers in these solutions. In general, the corrosion rate was extremely slow under definite conditions such as with thoroughly degassed reactants and in a light sheltered cell. The corrosion proceeds continuously in the steady regime, as a consequence of the free potential value which is much more positive than the equilibrium potential E_{Si}, and much more negative than E_H. The addition of fluoride ions has a harmful effect on the corrosion current and the resulting roughness, but this conclusion should not be extended to the extremely concentrated [9, 34, 35] solutions of buffered etchants usually employed in industrial processes. On the other hand, an excess of protons introduced by diluted HCl contributed to largely improve the passivating properties of the surface and to inhibit the dissociation of HF molecules which play an important role in the dissolution of silicon oxide [18].

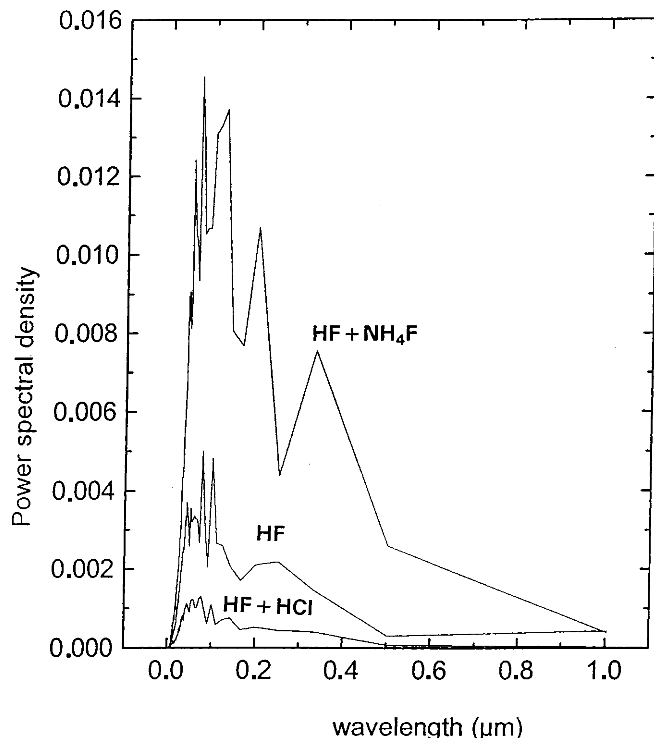


Fig. 7 Power spectral density for the surface profile of p-Si after 10 min dipping in the dark in deaerated solution: in 0.25 M HF + 1 M HCl, in 0.25 M HF, and in 0.25 M HF + 1 M NH_4F

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