



Surface modification of p-Si by a polyethylenimine coating: influence of the surface pre-treatment. Application to a potentiometric transducer as pH sensor

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Abstract

p-Si electrodes coated with linear polyethylenimine (L-PEI) allow the fabrication of a pH sensitive film for potentiometric transducers. The coating is realized in one step through the anodic oxidation of pure ethylenediamine (EDA) charged with 0.1 M LiCF₃SO₃ (Lithium Triflate). Such an electrochemical procedure leads to the thickness control of the coating. The best silicon surface pre-treatment before any coating is obtained with potassium dichromate in sulfuric acid, which leads to OH-terminated p-Si. This pre-treatment allows a uniform thin coating. In this work, the thickness is 2.6 nm. The pH response is high and close to 50 mV per pH unit. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The need of biologic analysis is important and increasing. Many devices based on enzymatic biosensors have to detect variations in pH, since many available enzymes such as hydrolases involve a variation in proton concentration during the catalytic reactions. Among the materials used to prepare biosensors, polyethylenimine (PEI) also called 'senzime' for synthetic enzyme, is one of the most interesting. But its adhesion on surfaces needs chemical treatments [1].

Recently, we showed [2] that the PEI coating of many materials, Pt, Au, Si, glassy carbon, fluorine tin oxide (FTO) was possible in one operation, through the anodic oxidation of primary diamines. The crux of this finding was the use of pure liquid primary diamines,

charged with a salt, for obtaining an electrolyte. Both amino groups must be primary and separated by two –CH₂– groups at least. Ethylenediamine (EDA) or diethylenetriamine (DETA) charged with 0.1 M Li-SO₃CF₃ can give rise to a surface coating by the linear polyethylenimine (L-PEI), through a mechanism already described [3]. Such a coating is interesting because this PEI has high resistivity, about 20 MΩ cm⁻¹, from our measurements.

It has been shown that electro-modified electrodes with conducting polymers could also act as good candidates for substitutes of glass pH electrodes [4]. So far, all pH chemical sensors using polymer coated electrodes were prepared by the electropolymerization of pyrrole [5], aniline [6], thiophene or benzene derivatives [7–10]. With these conductive polymers, measurements are not very reliable due to the random nature of the deposition process. Polymers grown under identical conditions may have different resistances to interferences,

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due to film defects and pinholes [11]. In the case of polypyrrole, it is even necessary to over-oxidize the layer of the conductive polymer in order to prevent it from strong oxidizing agents or from high anodic potentials. But such treatments modify drastically the electrical properties [12,13] of polypyrrole.

With our non-conductive polymer, the films coated at the electrode surface have a uniform thickness and grow thick enough to become insulators with fewer defects and pinholes. Non-conductive polymers usually have a high selective response and high impedance, which is important for eliminating the interferences with other electroactive species [14,15]. It is the case of L-PEI.

Here we focused our researches on the use of p-Si coated with L-PEI. This film plays the role of a pH sensitive film for potentiometric transducers. The influence of different surface treatments of p-Si has been examined.

2. Experimental

2.1. Materials

All the products were from Aldrich (analytical grade). EDA and the salt (LiSO_3CF_3 or LiTrif) were used as received. EDA based electrolyte containing 0.1 M LiTrif was prepared in a glove box under dehydrated Ar atmosphere, in which electrochemical studies were performed as well.

Si (p-type) $\langle 100 \rangle$, $N_A \cong 10^{16} \text{ cm}^{-3}$, was a gift of Rhone-Siltec, France.

2.2. Apparatus and procedure

The potentiometric transducer device, used as pH Sensor, is represented Fig. 1.

The electrochemical apparatus was a classical three-electrode set-up using an Ecochemie 'AUTOLAB' (PGSTAT 20) potentiostat-galvanostat. In aqueous solutions, the reference electrode was a saturated calomel electrode (SCE) from Radiometer. The potential response of p-Si electrodes was measured using a high impedance voltmeter (Tacussel millivoltmeter). The buffer solutions were from Prolabo and had an identical ionic strength. The pH measurements were performed

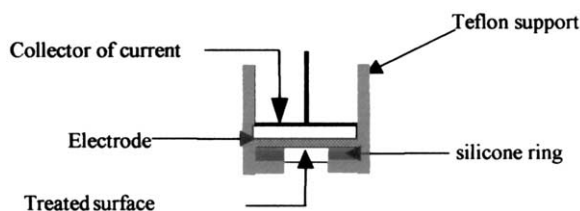


Fig. 1. Scheme of the potentiometric pH electrode device.

using a SCHOTT pH-meter CG840. For capacity measurements a linear sweep of potential was applied to the working electrode, and a modulation of 5 mV amplitude and 10 kHz frequency was superimposed. All voltammetric experiments were carried out at room temperature (293 K). The solutions were purged by ultrahigh purity argon and the experiments were conducted in the dark.

Two kinds of surface pre-treatments were performed for p-Si electrodes after cleaning in hot trichlorethylene, cold acetone, and then ethanol.

We obtained a H-terminated p-Si [16] with aqueous HF treatment. The oxide was stripped in 2% HF during 1 min, then p-Si was etched in 40% NH_4F during 6 min, followed by a careful drying under a nitrogen stream, easy to perform due to the hydrophobic property of the surface.

We obtained an OH-terminated p-Si, (after stripping of the native oxide in 2% HF during 1 min) with potassium dichromate in sulfuric acid (etching during 30 s), then rinsing by pure water and careful drying under a nitrogen stream. This drying is difficult to perform, due to the hydrophilic property of the surface.

Preparation of the L-PEI-coated samples: the silicon wafers (active area: disc of 6mm diameter, 0.283 cm^2) were anodically biased in EDA charged with 0.1 M LiTrif. The reference electrode was a silver wire (noted SRE, for Silver Reference Electrode) placed in a separated compartment without any silver ions that avoids the solution contamination by silver ions [2]. All voltammetric experiments were carried out at room temperature (293 K). The solutions were purged by ultrahigh purity argon. Five scans between 0 and 4 V versus SRE were performed (see Fig. 2) for a scan rate of 20 mV s^{-1} . The modified electrodes were then rinsed with ethanol, and dried at $45 \text{ }^\circ\text{C}$ under an argon stream.

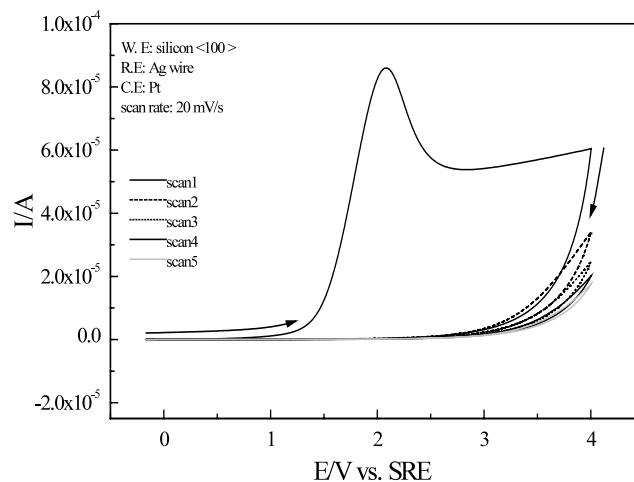


Fig. 2. Voltammogram at a OH-terminated p-Si $\langle 100 \rangle$ electrode in EDA charged with 0.1 M LiSO_3CF_3 . Scan rate: 20 mV s^{-1} . Room temperature. Active area of the silicon wafer: 0.283 cm^2 .

For the Scanning Electronic Microscope (SEM) picture of p-Si pre-treated by HF before the PEI coating, the scan was stopped at +2.0 V versus SRE for a scan rate of 20 mV s^{-1} . For the Atomic Force Microscopy (AFM) characterization, the electrode was biased up to +10 V at a low scan speed, and the thickness was roughly $1 \mu\text{m}$. This thickness was computed from the number of coulombs exchanged during the scan, and the number of electrons needed to oxidize EDA into L-PEI [3].

The AFM apparatus was a ‘Nanoscope II’ (from Digital Instrument) used in *ex situ* characterization experiments and in ‘tapping’ mode.

The SEM was a JSM-5800LV type, from JEOL.

The XPS apparatus was a VG-ESCALAB 220i XL.

The FTIR spectrometer was a NICOLET 5PC FTIR.

The profilometer was a Dektak IIA.

The ellipsometer has been built by the LEOM (at École Centrale de Lyon) [17].

3. Results

3.1. Voltammetry at a p-Si electrode in EDA charged with 0.1 M LiTrif

The voltammetric curve at a p-Si electrode is similar to the one obtained for EDA at a smooth Pt electrode [2,6] whatever the pre-treatment. See Fig. 2. The classical voltammetric analysis is not possible because of the broadness of the peak, and because of the irreversibility of the phenomenon. After a scan from 0 up to +4 V versus SRE, the current is almost close to zero, and the further scans between 0 and +4 V show the stability of the coating. See Fig. 2.

Notice that a plateau takes place at potentials higher than 2.5 V versus SRE for the first scan, and the current remains constant for potentials higher than 4 V versus SRE, if the upper potential limit is increased.

3.2. AFM observation

For PEI-coated p-Si $\langle 100 \rangle$ electrodes (after etching by aqueous HF, leading to a H-terminated p-Si surface), *ex situ* AFM (tapping mode) has been performed after one scan up to 10 V in EDA leading to a thick coating ($1 \mu\text{m}$ thickness) of the surface (Fig. 3). After rinsing with ethanol and drying under an Ar stream, AFM picture shows that the coating looks like an egg-box.

For p-Si electrodes pretreated with potassium dichromate in sulfuric acid before PEI coating, leading to an OH-terminated p-Si, very little roughness could be detected, compared with the one observed with H-terminated p-Si wafers coated with PEI.

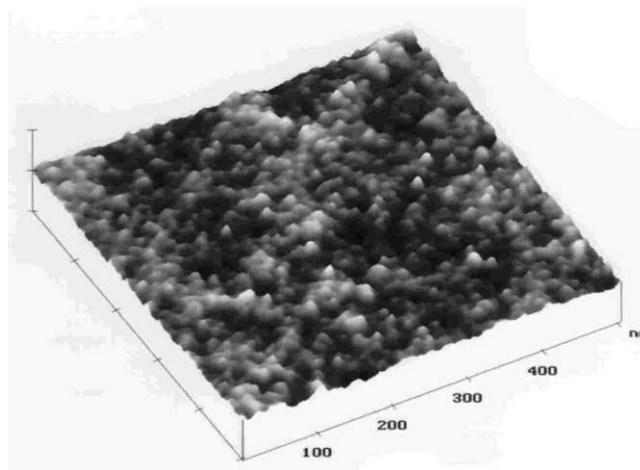


Fig. 3. AFM imaging (tapping mode) of the surface of a H-terminated p-Si electrode coated with L-PEI. Thickness of the coating: $1 \mu\text{m}$. The x scale is the same as y scale.

3.3. SEM observation

For p-Si pre-treated with HF (H-terminated p-Si), the SEM picture (Fig. 4) taken after one scan from 0 up to +3 V versus SRE (scan rate: 20 mV s^{-1}) shows a coating with a ‘clover’-like structure: in some spots, there are clover-like aggregates. After one scan from 0 up to 4 V versus SRE, there is not such a contrast due to complete coating of the surface.

For an OH-terminated p-Si the coating has not the patterns shown in Fig. 4. As soon as the coating takes place, it is regular and all the surface is covered.

From these observations it seems likely that for p-Si treated by HF, the formation of PEI begins only in a few parts of the surface, leading to a clover-like structure, then the coating grows in all ways, leading to the egg box-like structure.

We will see later that the behavior of the coating toward pH depends on the pre-treatment. For p-Si

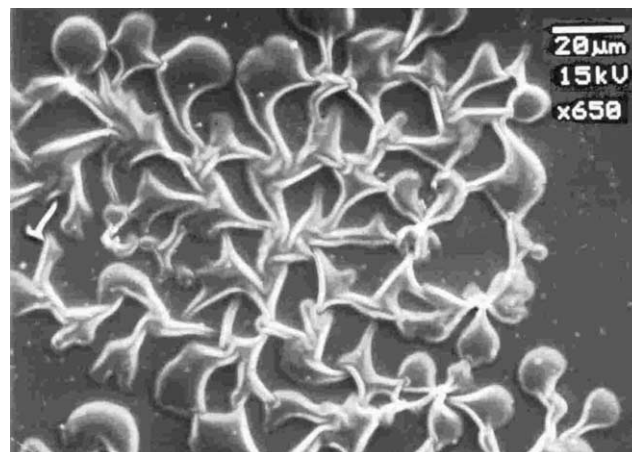


Fig. 4. SEM picture of the surface of a H-terminated p-Si electrode during the L-PEI coating (see text).

pretreated with HF, the pH response is weak. This is likely due to a non homogeneous PEI coating. Since the coating of p-Si treated with an acidic sodium dichromate solution is regular and easy, it is possible that for p-Si treated with HF, some surface silicon atoms can be tied to hydroxyl groups which initiate the growing of L-PEI, leading to defects and holes.

3.4. Nature of the coating

To control the nature of the coating, XPS chemical analysis has been performed. Even after thorough rinsing by pure water, then rinsing by ethyl alcohol, and drying under vacuum, the spectra of any coating showed the presence of the supporting salt, LiTrif. After a weak abrasion, the XPS spectra displayed only one C1s peak at a binding energy (BE) = 285.6 eV and only one N1s peak at BE = 399.1 eV. The same peaks are observed for commercial PEI from Aldrich [18].

3.5. Coating thickness

From Fig. 2, one can see that the voltammogram changes dramatically between the first scan and the following ones. After a few scans no anodic current flows through the coating and consequently, the coating thickness depends on the upper limit of potential of the first scan, since the current does not drop and a plateau takes place for potentials higher than 2.5 V versus SRE. This plateau can extend up to the highest potential value that can be delivered by the potentiostat. For low scan rate, we were able to obtain a maximum thickness of roughly 30 μm for a highest potential of 10 V for the first scan, from profiler measurements. This has been confirmed by IR-near-normal incidence reflectometry, which gives access to the thickness d of the polymer coating. Indeed, from wavelength between two successive interference fringes (λ_m and λ_{m+1}) and the relation:

$$\frac{1}{\lambda_{m+1}} - \frac{1}{\lambda_m} = \frac{1}{2nd} \quad (1)$$

where n is the refractive index of the medium, one can deduce the thickness d of the coating. In our experimental conditions, since n is not known, we can determine the optical path nd of the coating obtained by anodization of EDA charged with 0.1 M LiSO_3CF_3 which is about $nd \cong 45$. Since $n \cong 1.5$ [19], the coating thickness is $\cong 30 \mu\text{m}$, the value measured by profiler measurement.

3.6. Potentiometric measurements versus pH for both kinds of p-Si electrodes passivated by L-PEI

For a polymer-free p-Si electrode, pretreated by HF, the potential response is weak and not linear (about 10 mV per pH).

For H-terminated silicon electrodes, coated with L-PEI, the potential response is linear for a large range of pH including very acidic pH (pH 1–11). Sensitivity is low, and is equal to 21 mV per pH unit (cf. Table 1).

After 3 days, sensitivity toward pH decreased to the level obtained with a bare surface.

For this reason, another way of surface preparation was considered using etching by potassium dichromate in sulfuric acid. A bare OH-terminated p-Si electrode tested for its pH response gives a quasi linear behavior due to the surface nature, with a low sensitivity: 15.5 mV per pH unit (Table 2). This value is low, far from $2.3RT/F$, but it has been observed that the response of silicon electrodes coated with silicon oxide in water is only half of $2.3RT/F$ [20]. We observed the same kind of V_{FB} response toward pH with bare n-Si in liquid ammonia at 213 K, only 23 mV per pH unit, while $2.3RT/F$ is equal to 45 mV per pH unit [21]. The sensitivity should be 29 mV per pH unit at room temperature. One can notice that OH-terminated p-Si is different from native oxide-covered p-Si.

After anodic passivation by L-PEI and several hours of drying under argon atmosphere, the electrode was tested as a pH sensor. The electrode was allowed to equilibrate for 8 min before the open circuit potential was measured. The electrode exhibits a linear response even for high pH after few days. Results are very interesting: the pH response is high and increases from one test to another from 40 to 50 mV per pH unit, for a few days (see Table 2). The last value 50 mV per pH unit is close to the Nernstian response. Furthermore lifetime of the electrode is increased compared with the Si-H electrode, since after 6 days the electrode is still active.

This difference of behavior between Si-H and Si-OH electrodes modified by L-PEI could be interpreted by a uniform coating for Si-OH electrodes. This uniform coating could be due to hydrogen bonding between OH groups at the Si surface and amino groups from PEI. The type of bonding between Si-OH and L-PEI is currently studied by XPS after abrasion.

Table 1
Potentiometric pH response of a PEI coated p-Si <100> after HF pretreatment, which leads to H-terminated silicon surface

H-terminated p-Si electrode	Bare electrode	PEI coated
Slope of potential-pH curve (mV per pH unit)	-10	-21.5

Table 2

Potentiometric pH response of a PEI coated p-Si <100> after potassium dichromate pre-treatment, which leads to OH-terminated silicon surface

OH-terminated p-Si electrode	Bare electrode	With PEI, first day	PEI coated after few days
Slope of potential–pH curve (mV per pH unit)	–15.5	–42.2	–48.6

3.7. Capacity measurements versus pH for both kinds of p-Si electrodes passivated by L-PEI

Capacity measurements were performed to correlate capacity and H^+ ion equilibrium on the polymer for the Si/PEI/electrolyte structure. Indeed, taking into account the electrically blocking character of these structures, $C(V)$ measurements will exhibit their sensitivity for H^+ ions present in the electrolyte. See Fig. 5 that presents the sensor response for Silicon/PEI/electrolyte structure. This last figure has to be compared with Fig. 6 that presents the (C, V) response of Si/SiO₂ structure. SiO₂ is a thermal silicon oxide and its thickness is the same as in the case of Silicon/PEI/electrolyte. In both cases the passage from depletion to accumulation takes place for the same potential variation, showing thus the same density of interfacial states.

Capacity measurements presented in Fig. 5, reveal a shift of the initial curve (pH 7) and consequently a shift of the flat band potential, ΔV_{FB} , when the proton concentration increases. This shift is the expression of the field effect, which takes place in the depletion layer at silicon surface when amine groups in the polymer are protonated. Fig. 7 presents the experimental ΔV_{FB} versus pH. The mean sensitivity is found to be 45 mV per unit of pH. This intrinsic sensitivity is higher than that of thermal silica which has a sensitivity lower than 16 mV per unit of pH. From the structure capacity in accumulation mode it is possible to deduce the thickness

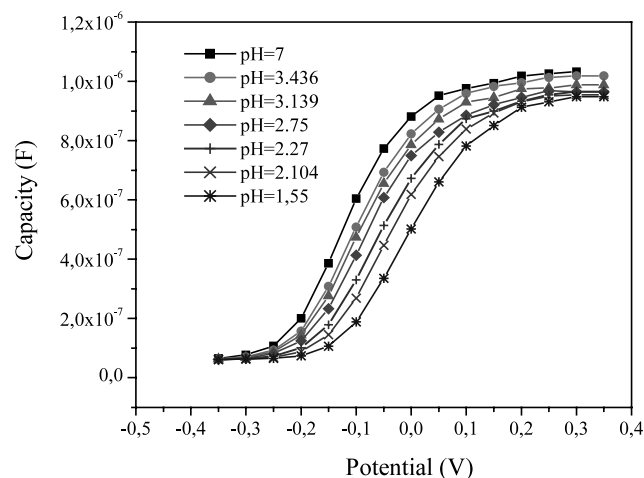


Fig. 5. Capacity measurements performed on an OH-terminated p-Si electrode (<100>) p coated with L-PEI for a modulation frequency equal to 10kHz. Active area of the silicon wafer: 0.283 cm².

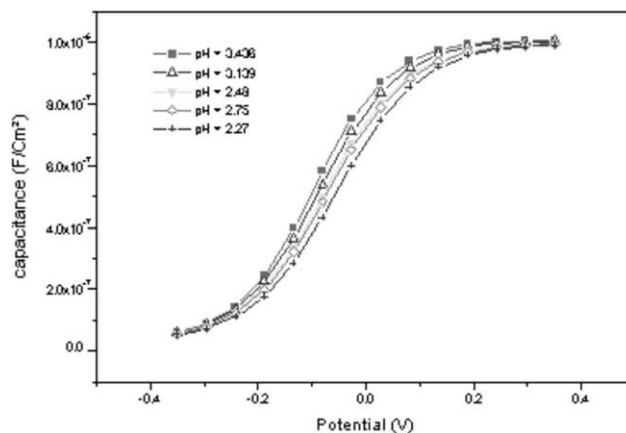


Fig. 6. Capacity measurements performed on a thermal SiO₂/Si interface (Si <100>) p without any L-PEI coating for a modulation frequency equal to 10 kHz. See text. Active area of the silicon wafer: 0.283 cm².

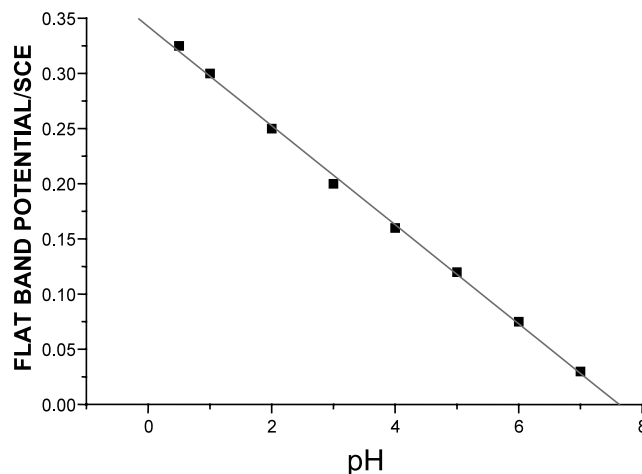


Fig. 7. Shift of the flat band potential ΔV_{FB} vs. pH of a L-PEI coated OH-terminated p-Si (<100>) electrode. Active surface of the silicon wafer: 0.283 cm².

of the PEI layer, at pH 7, with a dielectric constant of 3.8 [19]. The thickness was found equal to 2.6 nm, which is in good agreement with the value obtained by ellipsometric measurements. When pH becomes more acidic the capacity in accumulation mode decreases, which means that a change in dielectric constant and in thickness of PEI film occurs. The modelization of the pH response has been already given [22].

From our observations, very acidic media (pH < 1) are able to etch the PEI coating.

4. Conclusion

The L-PEI coating of p-Si electrode is very adherent, insoluble, and easy to prepare in only one step from anodic biases in pure EDA charged with 0.1 M LiTrif. This procedure simplifies the fabrication of modified electrodes, a process, which often involves an extended series of pre-treatment, activation, and functionalization steps. It also provides a comparatively higher coverage of the immobilized species, and a controlled thickness. Application of this method for the fabrication of silicon-based potentiometric transducers is shown here.

Silicon wafers must be treated by potassium dichromate in sulfuric acid to obtain a surface covered by hydroxyl groups, which allow a uniform coating by L-PEI during the anodization step. A PEI thickness of some nanometers is sufficient to obtain a good response toward pH. A slope as high as 50 mV per pH unit is obtained, a value impossible to obtain with bare silicon wafers.

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