Local silicon doping as a promoter of patterned electrografting of diazonium for directed surface functionalization†

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We study the influence of locally doped silicon substrates on the electroreduction of diazonium salts. Our results show that the reduction of diazonium salts occurs at moderate potentials compared to the flat band potential of the semiconducting electrode. The underlying doping directs the electrografting, preferentially over doped areas of the substrate. High resolution spatially resolved X-ray photoelectron spectroscopy analysis using a new X-ray photoelectron emission microscope (XPEEM) and soft X-ray synchrotron radiation yields the thickness of the native oxide of the micron scale doped pattern on the substrate. The results as a function of both parameters—reduction potential compared to the flat band potential and thickness of the oxide layer—are discussed. These new results are then compared to data obtained on the localized electrografting of vinylic monomers.

Introduction

Microelectronic devices including transistors, sensors or memories are generally based on interfaces between conducting or semi-conducting and quasi-insulating domains resulting from lithographic steps, ionic implantation, silicon oxide thermal growth and so on. Most of these techniques require many steps and their implementation is often expensive. Moreover, the localized grafting at a micronic or submicronic scale of organic substances on surfaces is often a prerequisite in the design of bioelectronic devices, and can be a valuable component of certain combinatorial screening strategies. Clearly, the microelectronics industry could benefit from a simple process that enables the local functionalization of either highly doped or poorly doped silicon areas, in a single step.

Organic layers can be deposited on surfaces by spin coating, evaporation, spontaneous chemisorption or stamping. The formation of strong chemical bonds between organic molecules and the surface (grafting) is a key point for the properties of the final interfaces. The big advantage of grafted organic layers is that they can be further processed by classical methods of organic chemistry. The present work will focus on surface modification of silicon surfaces. As recently reviewed by Burjak for SiH surfaces, and Reinholdt for silica surfaces, many routes exist for chemical grafting of molecular species on those surfaces.

One promising way to create a robust interface between a silicon and an organic layer is electrochemical deposition. Electrochemistry offers a triggering parameter (the electrochemical potential) to control chemical reactions at semiconductor surfaces in solutions. The electro-initiated polymerization of vinyl monomers on conducting or semi-conducting electrodes relies on the electroreduction of the vinyl group into a radical-anion, which grafts onto the cathode and starts polymerizing. This has proven to be a useful tool for building functionalized surfaces of chemically grafted polymer films on electrodes. Nevertheless, organic electrografting of vinyl monomers requires working under controlled atmosphere, in organic medium and at relatively high cathodic potential.

Other molecules like radicals can also give rise to the formation of graft films. Radicals are often used because they can be easily generated in ambient conditions, both in solution and in gaseous phases. Diazonium compounds, well known thanks to their applications in dye and photo-chemistry, are prone to easily generating radicals. The electrochemical reduction of aryldiazonium salts on various conductive surfaces is a very effective means for generating thin films containing a wide range of chemical functionalities. Both aqueous and nonaqueous solutions of diazonium salts undergo a one-electron irreversible reduction that generates aryl radical species near the electrode surface does not completely impede the further reduction of diazonium ions and a multilayer film grows by coupling between the newly generated radicals and the already grafted phenyl rings. Thus electron transfer through the grafted film to additional reagents in solution leads to multilayer formation, which usually occurs when high reagent concentrations (>1 mM) and long deposition times at excessive negative potentials are used.

† Electronic supplementary information (ESI) available: Complete description of the cleaning process for the locally doped silicon wafers and XPEEM spectra. See DOI: 10.1039/b800572a
To our knowledge, most of the works undertaken on the grafting of diazonium salts on silicon substrates (generally chosen as a reference substrate for its importance in micro-electronic devices) are carried out on Si-H terminated substrates. However, successful grafting of diazonium salts on oxidized surfaces (oxidized metallic surfaces, TiO$_2$) have also already been reported. We have successfully electrografted vinyl polymers on native silicon dioxide. The native oxide layer is thin enough (less than 2 nm thick as measured by XPS) to allow electron tunnelling from the underlying silicon to the electrolytic solution. Since the native silicon dioxide layer does not prevent the electrografting process and the substrates are much more easily produced and manipulated than Si-H ones, we concentrate our study on silicon with its native oxide layer.

The goal of this work is to take advantage of the doping properties of silicon to achieve a “spatially resolved functionalization”, through localized electrografting of organic coating when the substrate is dipped into the electrolytic medium. The originality of our approach is to combine the diazonium electrochemistry and local differences in doping level of a semiconducting electrode. This strategy provides an easy tool for implementing chemical functionalization into common silicon microfabrication technologies. To our knowledge, current studies relate only to the localization of electrolytic metal deposits via the local doping of the semiconductor electrode.

We study the behaviour of locally doped silicon substrates towards the electroreduction of diazonium salts at moderate potential compared to the flat band potential ($V_{FB}$) of the semiconducting electrode. Small area high energy resolution X-ray photoelectron spectroscopy (XPS) analysis is used to analyse the micron scale doped pattern on the substrate and to elucidate the role of the thickness of the oxide layer on preferential grafting.

**Experimental**

Silicon wafers (Si (100) n-type, bulk resistivity 5–15 Ω cm) locally doped by ionic implantation (P$, 50$ keV) were purchased from Ion Beam Services (Peynier, France) and used as cathodes for the electrografting process. The highly doped areas ($10^{19}$ atoms cm$^{-2}$) were micrometer-sized and are the dark regions on the scheme of the pattern in Fig. 1a.

Rectangular samples (5 × 30 mm) were cut from the wafer and used as cathode electrodes. Before electrografting, the wafers were used either as received (thus with the native oxide layer) after usual cleaning (ultrasonic rinsing with water, acetone and ethanol successively to discard organics from the silicon oxide surface), or after etching with hydrofluoric acid to obtain a Si-H terminated surface.

The electrolytic solution was nitrophenyl diazonium tetrafluoroborate (Aldrich, $5 \times 10^{-3}$ mol dm$^{-3}$) in acetonitrile with tetraethylammonium perchlorate (Aldrich, TEAP- $5 \times 10^{-2}$ mol dm$^{-3}$) as the supporting electrolyte. The electrolysis was performed in a one-compartment glass cell, with a standard three-electrode arrangement. Only the front side of the Si sample was in contact with the electrolytic solution and its surface (0.2 cm$^2$) was delimited by an inert gasket. The electrical contact of the working electrode was formed through a continuous gold layer (on a chromium underlayer) evaporated on the backside of the Si wafer. The counter electrode was a 2 cm$^2$ platinum foil, and...
the reference electrode was a silver wire. All potentials given in this work are related to this pseudo-reference electrode.

The electrochemical experiments were performed with an EG&G PAR model 273A potentiostat. The electro-initiated grafting technique consists in applying cyclic linear voltammetry to the solution. For impedance measurement a transfer function analyzer Solartron SI 1255 was added to the potentiostat and was driven by the Zplot®/Zview® software system (Solartron Analytical). Impedance measurements were made at high frequencies (100 kHz) for the determination of the n-type Si wafer's parameters (flat band potential and doping level) using the well-known Mott–Schottky relation.43

The localization of the organic grafts was studied with four techniques:

- Standard X-ray photoelectron spectroscopy was carried out using a Vacuum Generator Escalab 210 spectrometer with an Al Kα monochromatic source. The grafted nitrobenzene molecule has a characteristic spectroscopic feature in the N 1s core level with a binding energy of 406 eV corresponding to the nitrogen group, which can be used as a probe to trace the growth of the grafted layer on the surface.

- Topographic AFM measurements were performed with a Molecular Imaging PicoLe AFM microscope (Scientec, France) in contact mode with a silicon cantilever (NanoAndMore, France). AFM images were analysed with the WSxM software.44

- Scanning spreading resistance microscopy (SSRM). SSRM is an analytical and imaging technique derived from contact AFM that maps 2-D carrier concentration profiles (resistance) in semiconductor materials.45 A conductive probe is scanned in contact mode across the sample, and a DC bias is applied between the tip and sample. The resulting current between the tip and the sample is measured using a logarithmic current amplifier. The main contribution to the calculated resistance comes from the spreading resistance in the vicinity of the tip–sample contact, providing a very local electrical measurement with a high spatial resolution. The measurements were performed on a Digital Instruments Nanoscope IIIa Dimension 3100 AFM equipped with an SSRM module and doped diamond-coated Si tips. The analysis was performed by applying a positive bias of 250 mV to the tip. A high force (> 10 μN) was applied to realize an intimate contact between the probe and the silicon sample such as the spreading resistance dominating the contact resistance.46

- The XPEEM analysis of the silicon substrate with its native oxide layer was done using a NanoESCA (Omicron NanoTechnology GmbH) installed on the ID08 soft X-ray undulator beamline at ESRF.47,48 Built with a fully electrostatic lens system, the instrument uses the imaging double hemispherical electron energy analyser (IDEA) with χ-aberration correction, giving high spatial resolution. In imaging mode, high spatial and energy resolution images can be obtained using secondary electrons and core levels. In spectroscopy mode, using only the first hemispherical analyzer, low noise spectra acquisition with a channeltron detection system is possible with high electron transmittance from a small spot of the sample area. Small spot spectroscopy of the Si 2p core level was performed on doped and undoped areas by closing the iris aperture in the electrostatic lens system. Note that the maximum electron emission angle with respect to the surface, and therefore the microscope’s effective field of view, changes slightly with kinetic energy, but for our purposes—the direct comparison between doped and undoped areas—this may be neglected. Hence, small area XPS spectra could be acquired by closing the iris aperture present in the PEEM electrostatic lens column.

Results

The implanted pattern is easily revealed by atomic force microscopy (AFM) (Fig. 1b,c). Doped areas are lower than undoped ones, with an average height difference of 7 nm (Fig. 1d). This is due to the manufacturing process: successive HF treatments, plasma oxidation and wet oxidative treatments lead to a deeper etching in the doped area than in the intrinsic area as the etching rate is faster on implanted silicon (see ESI for a complete description of the cleaning process).† A schematic view of the surface of the bare sample is represented in Scheme 1.

SSRM measurements made on the bare locally doped samples in presence of the native oxide layer confirm that, as expected, the doped area presents a higher conductivity than the undoped area, (Fig. 2). Indeed, the resistance measured on top of the doped area (1.5 × 10⁵ Ω) is three times lower than that on top of the undoped area (4.5 × 10⁵ Ω). It is important to mention that these values actually reflect the properties of the underlying silicon substrate. Clarysse et al. have established that for high force contact (> 1 μN), the probe punches through the silicon oxide and the underlying silicon undergoes a plastic deformation and phase transformation.49

Electrochemical reduction of the 4-nitrobenzenediazonium tetrafluoroborate salt occurs at moderate cathodic potential (−0.9 V vs Ag wire) on n-type locally doped Si (100) (Fig. 3 left). The average film thickness is a function of the final applied potential and increases with the number of voltammetry cycles. By successive cyclic voltammetry from the rest potential to −1.2 V vs. Ag wire, a multilayer poly(nitrophenyl) film is built on
the surface as shown by the XPS spectrum of the N1s core level. The electrografted coating displays characteristic peaks at 406 and 400 eV which are attributed to the nitrogen of the nitro group and to the grafting of the diazonium, respectively (Fig. 3 right). More specifically, the signal at 400 eV can be attributed to azo groups within the grafted film.

The localization of the electrografted polyphenylene film is clearly evidenced by AFM analyses (Fig. 4) where the level of the doped areas, lower than for the undoped zones on the bare substrate, is now detected in relief after the electrografting process. In other words, when the electrochemical process at moderate polarization potential is applied to the locally doped Si substrate, a localization of the grafting is well observed and follows the underlying doping level of the substrate. Similar results are obtained on Si-H terminated silicon substrates. The grafting is even more efficient on the doped areas of the Si-H terminated substrate (fig. 5). This contrasts with the behaviour of vinyl monomers under cathodic electroreduction. Electrografting vinyl monomers develop preferentially on undoped areas in the presence of the native oxide layer, whereas no localization is observed when the silicon oxide is removed before the electrografting experiment.

Discussion

To explain our new results, we have to consider the conjugation of two factors: (i) the value of the applied potential and (ii) the role of the native silicon oxide layer.

1. The applied potential

At the interface between a semiconductor electrode and an electrolyte in solution, one can observe either an accumulation or depletion regime of majority carriers in the space charge region, depending on the applied potential compared to $V_{fb}$ of the semiconductor substrate. $V_{fb}$ of a semiconductor is the potential at which the Fermi level lies at the same energy as the solution redox potential. There is thus no net transfer of charge and hence no band bending.

$V_{fb}$ of a homogeneous n-doped silicon electrode has been determined from electrochemical impedance spectroscopy experiments recording the capacitance of the electrode as...
The intensity of the signal due to the silicon oxide layer is about 20% higher for the doped area than for the intrinsic zone.

On the basis of the intensity ratio between the signal due to silicon oxide (ISiO2 at 103.0 eV) and the signal coming form the silicon oxide (ISi4+ at 99.0 eV) and as a function of the analyzed zone: (a) doped area, (b) intrinsic area.

The intensity ratios ISiO2/ISi4+ for doped and undoped areas from the relation:

\[ I_{\text{SiO}_2}/I_{\text{Si}^4+} = I_\infty/I_0 \exp \left( -\frac{d}{\lambda_{\text{SiO}_2}} \right) - 1 \]

where

\[ I_\infty = n_{\text{SiO}_2} \sigma_{\text{SiO}_2} \lambda_{\text{SiO}_2} \] and \( I_0 = n_{\text{Si}} \sigma_{\text{Si}} \lambda_{\text{Si}} \)

and \( n \) is the number of atoms per unit volume (2.28 \times 10^{22} \text{ cm}^{-3} for silicon oxide and 5 \times 10^{22} \text{ cm}^{-3} for pure silicon), \( \sigma \) the cross section for excitation of electrons, \( \lambda \) the inelastic mean free path for electrons in the material (\( \lambda_{\text{SiO}_2} = 1.1 \text{ nm}, \lambda_{\text{Si}} = 1.0 \text{ nm} \) for \( h\nu = 400 \text{ eV} \)).

Following ref. 41, we consider \( I_\infty/I_0 \) equal to 0.69 for a photon energy of 400 eV. The intensity ratios ISiO2/ISi4+ measured by XPEEM on the top of the doped area and on the top of the undoped part are 1.40 and 1.12, respectively. The corresponding oxide thicknesses are therefore 1.8 and 1.2 nm, respectively. In other words, a significantly thicker oxide layer is present on top of the doped areas. As the oxide layer can be considered a tunnel barrier for the electronic transfer from the underlying silicon to the solution that initiates the electroreduction process, the 0.6 nm difference in the oxide layer thickness gives rise to a significant difference in the tunneling current between doped and undoped areas.

Localization on locally doped Si-H terminated silicon substrates. For the locally doped Si-H terminated silicon substrates, we just consider the role played by the applied potential as the oxide layer has been removed. In the case of...
the reduction of the diazonium salts, the applied potential (-0.9 V/Ag wire) is close to $V_{fb}$ of the substrate. Band bending is small and the local electron transfer is controlled by the local work function. The higher conductivity of doped areas promotes a faster electron transfer towards the solution than from undoped silicon and thus initiates more efficient electrografting. If the applied potential is far below $V_{fb}$ of the substrate (case of the reduction of the vinlyc monomers), important band bending occurs in the space charge region of the semiconductor, driving the silicon substrate into an accumulation regime and overwhelming the effect of doping. Thus, the substrate behaves in the same way versus the cathodic polarization whatever the local doping. This explains why no localization was observed when we reduced the vinyl monomers on those substrates.\(^5\)

Localisation on locally doped silicon substrates with a native oxide layer. The presence of the oxide layer acts as an additional impediment in the electrical cell modifying the effective cathodic potential on the corresponding area of the substrate. The more negative the potential, the more significant this effect, finally outweighing the local doping, which has the opposite effect on grafting. Moreover a difference in the oxide layer thickness of 0.6 nm is sufficient to significantly change the tunnelling current.

In the case of the reduction of the vinyl monomers, the excess of majority carriers in the conduction band of the doped silicon substrate is no longer the key factor to direct the grafting, because of the high cathodic potential with respect to $V_{fb}$ of the semiconductor electrode. The resulting high accumulation regime levels the doping effect. In these conditions, the thickness of the oxide layer is now the parameter which pilots the preferential grafting. The thicker oxide layer on top of doped areas reduces the current intensity so that implanted silicon areas generate less grafted radical-anions than the un-implanted ones, giving rise to significantly thinner grafted films.\(^5\)

On the contrary, in the case of the reduction of diazonium salts, our results show that the resistive effect of the thicker oxide layer on the doped areas with respect to the undoped zones is compensated by the increase of the conductivity of the underlying doped areas. Thus, the localization of the grafting is still controlled by the doping level of the underlying substrate but, due to the presence of the oxide layer, the yield of the reaction is lower than for deoxidized substrates.

Conclusions

In this work, new results on the electrografting of diazonium salts onto locally doped silicon surfaces have been presented, together with the SSRM and XPEEM analysis of the resulting surfaces. Those new results were then compared with previous ones obtained with vinyl monomers in different conditions, and the whole set of results was fully explained taking into account the respective role of the applied potential and the native oxide layer.

So, this study has shown that electrografting process can be used as a mask-free technique to pattern homogeneous silicon electrodes with local doping. We have shown that polymer grafting could be efficiently directed towards designated areas of the working surface but these designated areas depend in fact on the electro-potential range over which the substrate is polarized. For moderate potentials close to the flat band potential, we benefit from the higher conductivity due to the underlying doping. Even if the native oxide layer is present, the conductivity of the doped zones seems high enough to exceed its inner impedance drop. Thus at moderate potential, the underlying doping directs the grafting. This contrasts with previous results obtained using vinlyc polymers which demonstrated that at high cathodic potentials pushing the substrate into a saturated accumulation regime, the localized grafting is actually directed by the local thickness of the SiO$_2$ layer.

This low cost, one step process, based on electrochemistry, allows localized electrografting of organic matter on designed areas of a composite conducting surface, and may find applications in various fields including microelectronics, biomedical technology and surface technology. More particularly, its selectivity can be used in a beneficial way to protect or functionalize local parts of the same electronic component.

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