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SHORT COMMUNICATION

On the capacitive behavior of silicon electrodes modified with ultrathin hydrophobic polymer brushes

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Abstract

The modification of a silicon surface with ultrathin poly(styrene) brushes, obtained by grafting-from, results in a dramatic increase in capacitance as shown by cyclic voltammetry. This difference in the behavior of silicon and poly(styrene) brush-modified silicon electrodes is amplified when the electrochemical measurements are performed under UV light irradiation. The results obtained show that the modification of silicon electrodes with poly(styrene) brushes can improve their capacitive properties even under UV light irradiation.

Keywords Polymer brushes · SI-ATRP · Silicon · Cyclic voltammetry · Oscillations

Introduction

Polymer brushes are defined as dense arrays of macromolecular chains attached to a surface by one end [1]. They are usually prepared via the "grafting-from" method that is by the covalent immobilization of a polymerization initiator onto the substrate surface followed by in situ surface-initiated polymerization (such as surface-initiated atom transfer radical polymerization, SI-ATRP) [2], allowing excellent control over the brush thickness, composition, and surface density. Thanks to their unique physico-chemical properties, polymer brushes provide outstanding opportunities for surface functionalization, generating thin films for integration into various devices [3, 4].

Ultrathin (~ 10 nm) polymer films are of great interest as dielectric layers for organic electronics [5]. The performance of poly(methyl methacrylate) (PMMA) and poly(styrene) (PS) brushes as electrets [6] and as gate dielectrics in all-organic transistors [7–9] has already been described. Applications for ion-gated electrochemical transistors can also be easily envisaged for functional brushes. Our group was the first to report that functional, hydrophilic polymer brushes obtained by grafting-from can make lightly doped silicon wafer electrochemically responsive [10] and that this behavior can be even controlled by means of changes in pH [11]. In the present paper, we would like to describe the electrochemical behavior of both pristine and poly(styrene) brush-modified silicon electrodes.

Experimental

Silicon (100) wafers, single-polished, n-type, phosphorus-doped, and 3–6 Ω cm, with a native oxide layer 1.5 nm thick (ellipsometry), were purchased from Ultrasil Corporation. For the grafting-from of polystyrene brushes, our previously reported protocol was followed (Fig. 1a) [12]. Briefly, the ATRP initiator (3-(2-bromoisobutyramido)propyl)triethoxysilane (BIB-APTES) was self-assembled on acid piranha-cleaned (4:1 *v*/*v* of 98% sulfuric acid and 30% hydrogen peroxide, 1 h at 100 °C, extensively rinsed with water and dried with nitrogen) silicon substrates from its 10-mM solution in anhydrous toluene (4 h at 55 °C, left overnight at 30 °C, washed and gently sonicated with toluene, acetone, and ethanol, and dried with a nitrogen stream). For the growth of polystyrene brushes, in a nitrogen-purged Schlenck flask, 0.1 g (0.7 mmol) of copper(I) bromide was dissolved in a degassed solution of

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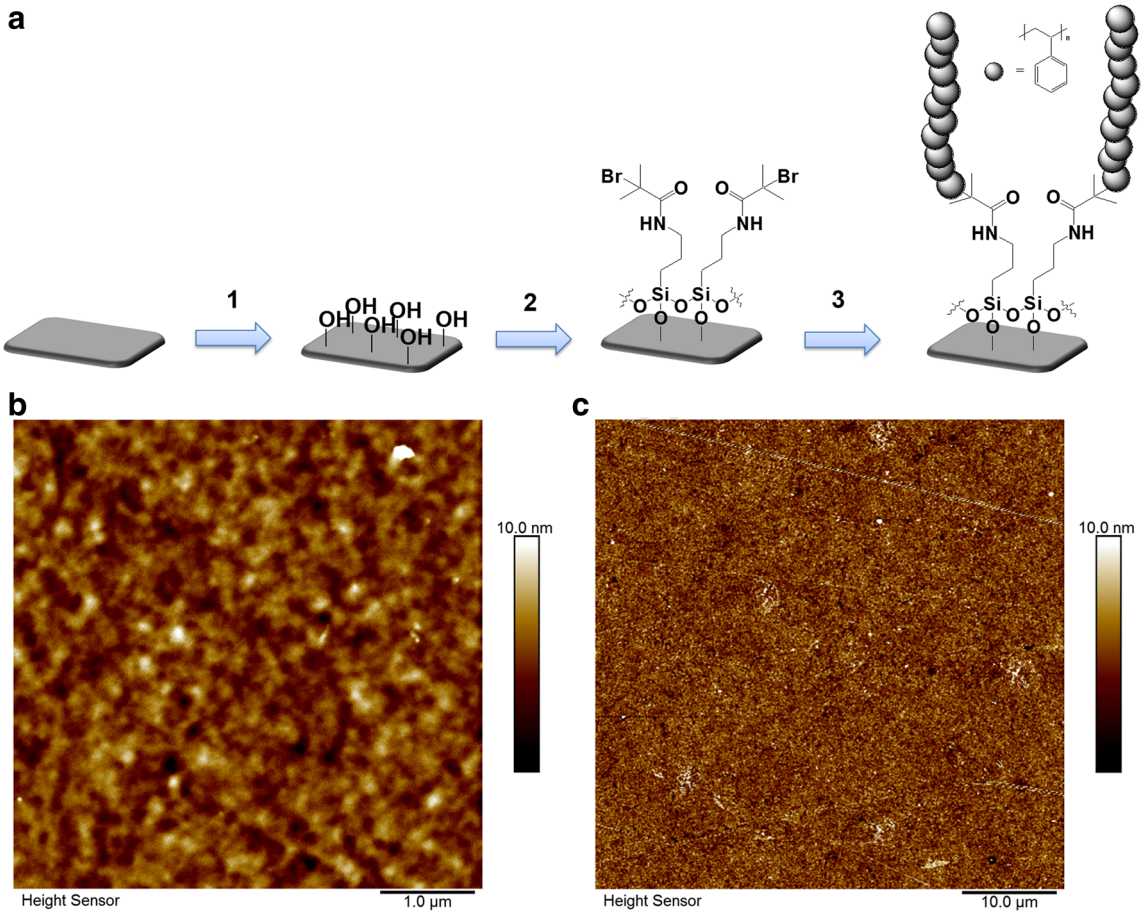

Fig. 1 **a** Formation of PS brushes on silicon wafer by grafting-from: (1) conc. H_2SO_4/conc. H_2O_2 3:1 *v*/*v*, 100 °C, 1 h; (2) anhydrous toluene, BIB-APTES 10 mM, 55 °C, 4 h then 30 °C overnight; (3) styrene, CuBr, PMDETA, dimethylsulfoxide, 90 °C, 1 h. The gray pearls represent the styrene units. **b**, **c** AFM images of the obtained PS brushes

270 μL (1.3 mmol) of pentamethyldiethylenetriamine (PMDETA) in 10 mL of dimethylsulfoxide. Then, 30 mL (~ 260 mmol) of degassed styrene was added and the mixture was stirred under nitrogen. A 5-mL aliquot of this mixture was poured over each initiator-functionalized substrate placed in a nitrogen-purged Schlenck flask. Polymerization proceeded at 90 °C for 1 h in a preheated oil bath. After polymerization, the samples were rinsed extensively with tetrahydrofuran, gently sonicated in the same solvent, and dried under a nitrogen stream.

The thickness of polymer brushes was measured using spectroscopic ellipsometry (M-2000F, LOT Oriel GmbH). The measurements were performed in air, for which a refractive index $n = 1$ was taken. For spectroscopic ellipsometry, determination of Ψ and Δ as a function of wavelength (250–800 nm) was carried out by employing the WVASE32 software package (LOT Oriel GmbH, Darmstadt, Germany), using bulk dielectric functions for silicon, silicon dioxide, and water. The brush-supporting substrates were in all cases considered as consisting of silicon with a 2-nm-thick silicon dioxide film. The analysis of the brush layers was performed using a standard Cauchy model. The morphology of polymer brushes was analyzed by atomic force microscopy (AFM), using the ScanAssistMode™ on a Dimension Icon instrument with ScanAssistAir™ silicon nitride (Si_3N_4) cantilevers with a tip radius of 12 nm, a spring constant of 0.4 N m^{-1}, and a resonance frequency of 70 kHz. Both small area (4 × 4 μm) and large area (50 × 50 μm) scans were taken to demonstrate the homogeneity of the brushes. Water contact angle was measured using a Krüss Easy Drop Standard with DSA1 software. A 3-μL drop of HPLC-grade water was deposited and the contact angle measured after 5 s. For both analyses, at least three measurements were performed on different spots of a same sample and the results were averaged. A Jelosil HG500 halogen lamp (230 V, 500 W, effective power density from 40 cm, 57.5 mW cm^{-2} between 280 and 400 nm, maximum emission at 365 nm) was used as the source of UV light [12]. The electrochemical experiments were performed using a potentiostat/galvanostat Autolab PGSTAT204 (Metrohm, The Netherlands) equipped with a FRA module. A standard three-electrode cell was used, equipped with a saturated calomel electrode, a Pt wire, and a modified silicon substrate as reference, counter, and working electrodes, respectively. Aqueous 0.1 M KCl was used as the supporting electrolyte.

Cyclic voltammetry (CV) was performed by scanning the potential between − 0.1 and + 0.4 V (SCE) with scan rates variable from 10 to 750 mV s^{-1}. The analyses were performed in the dark, with exclusion of both natural and artificial light, unless otherwise stated.

Results and discussion

Poly(styrene) brushes were obtained on silicon substrates by means of surface-initiated atom transfer radical polymerization (SI-ATRP) (Fig. 1a) and thoroughly characterized to check their quality before performing the electrochemical experiments. A first indication for the successful synthesis of poly(styrene) brushes came from water contact angle (WCA) analysis. The WCA, which for the piranha-cleaned substrates was 0° indicating a completely clean surface, changed to 70° after the functionalization with the BIB-APTES initiator and then to 90°, which is the typical value for poly(styrene) brushes, after polymerization. The thickness of the polymer layer was 15 ± 1 nm as measured by spectroscopic ellipsometry. The morphology of the brushes was investigated by means of atomic force microscopy (AFM). As shown in Fig. 1b, c, the obtained brushes were uniform, compact, and almost free from pinholes. The average roughness R_q values were 1.3 ± 0.1 and 1.6 ± 0.1 nm for the small area and large area scans, respectively. These values are indicative of a smooth surface.

The cyclic voltammetry plots of piranha-cleaned silicon and of PS brush-modified silicon electrodes are shown in Fig. 2a, b. Both are featureless, i.e., no redox peak could be identified, in accordance with our previous findings showing the poor electrochemical properties of silicon wafer [10, 11]. However, this makes the effect of hydrophobic brushes even more evident: first, the total current is reduced by one order of magnitude. Second, the shape of the voltammogram is a rectangle with rounded edges.

To understand these results, the classical treatment of electrochemical capacitors can be applied. Cyclic voltammetry is routinely used to assess the quality of electrochemical capacitors, which are typically built of two similar, high-surface area electrodes. Here, our system can be considered as a capacitor formed by the silicon working electrode and the platinum counter electrode. The CV of an ideal capacitor is depicted in Fig. 2c. A perfectly rectangular voltammetric curve would be indicative of a pure double-layer (non-Faradaic) capacitance. The deviations observed for actual capacitors are due to their electrical resistance and/or to the occurrence of electrode/electrolyte charge transfer phenomena (typically redox reactions) which could arise from reactions occurring at the electrodes, in the electrolyte, or both. For this reason, the shape of CV curves has been widely used as a source of information about these processes. The almost perfect rectangular shape observed for the PS brush-modified silicon electrodes is indicative of an almost ideal capacitive behavior. Because redox processes such as electrolysis of water (which typically occurs at − 1.23 V) and electrochemical modification of the PS brushes (e.g., oxidation) are highly improbable to occur in the explored voltage window, the observed deviation at the edges could be due to resistive phenomena such as the intrinsic electrical resistivity of the brushes and the resistance to ionic transport in the brush-modified electrode. Nevertheless, the use of more sensitive techniques, such as step potential electrochemical spectroscopy, could allow a more precise discrimination between the contributions of electrical double-layer charge storage and diffusional (redox) processes to the overall electrode performance [13].

The behavior of silicon and PS brush-modified silicon electrodes during cyclic voltammetry was then examined under UV light. The effect of different scan rates (from 10

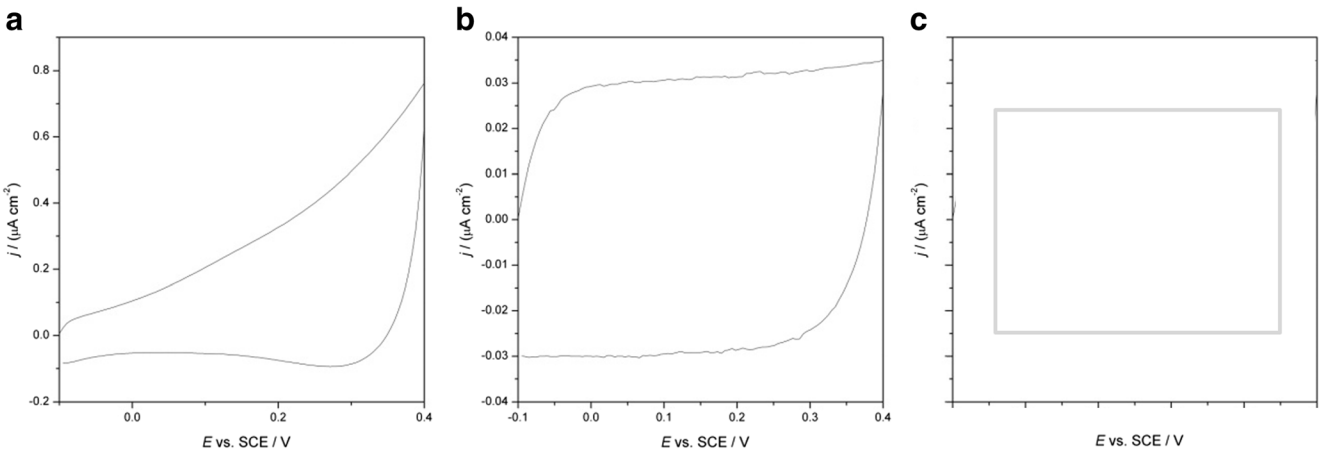

Fig. 2 Cyclic voltammetry plots (scan rate 100 mV s^{-1}) of **a** pristine silicon wafer, **b** PS brush-modified silicon wafer, and **c** an ideal capacitor

to 750 mV s^{-1}) was also tested. As shown in Fig. 3, under UV irradiation, the scan rate becomes more relevant affecting the electrochemical behavior of both types of electrodes. Moreover, a greater difference in the capacitance is observed between the pristine silicon and the PS brush-modified silicon. The conductivity of silicon, and thus the charge transfer toward the electrolyte, increases when it is irradiated by UV light (the band gap energy E_g of silicon being 1.1 eV), thus reducing its capacitance. The capacitance is found to increase again for increasing scan rates. Since poly(styrene) is a hydrophobic and dielectric polymer, the dense brush layer acts as an efficient barrier toward charge transfer, resulting in an almost ideal capacitor. Noteworthy, PS is completely transparent to UV light with $\lambda > 300$ nm [14]. For scan rates below 500 mV s^{-1}, the cyclic voltammetry plots of the PS brush-modified silicon electrodes show an almost perfect rectangular shape, indicating that the PS brush layer stabilizes the capacitive behavior of silicon. Only for higher scan rates, the curves become skewed and the voltammogram edges rounded off.

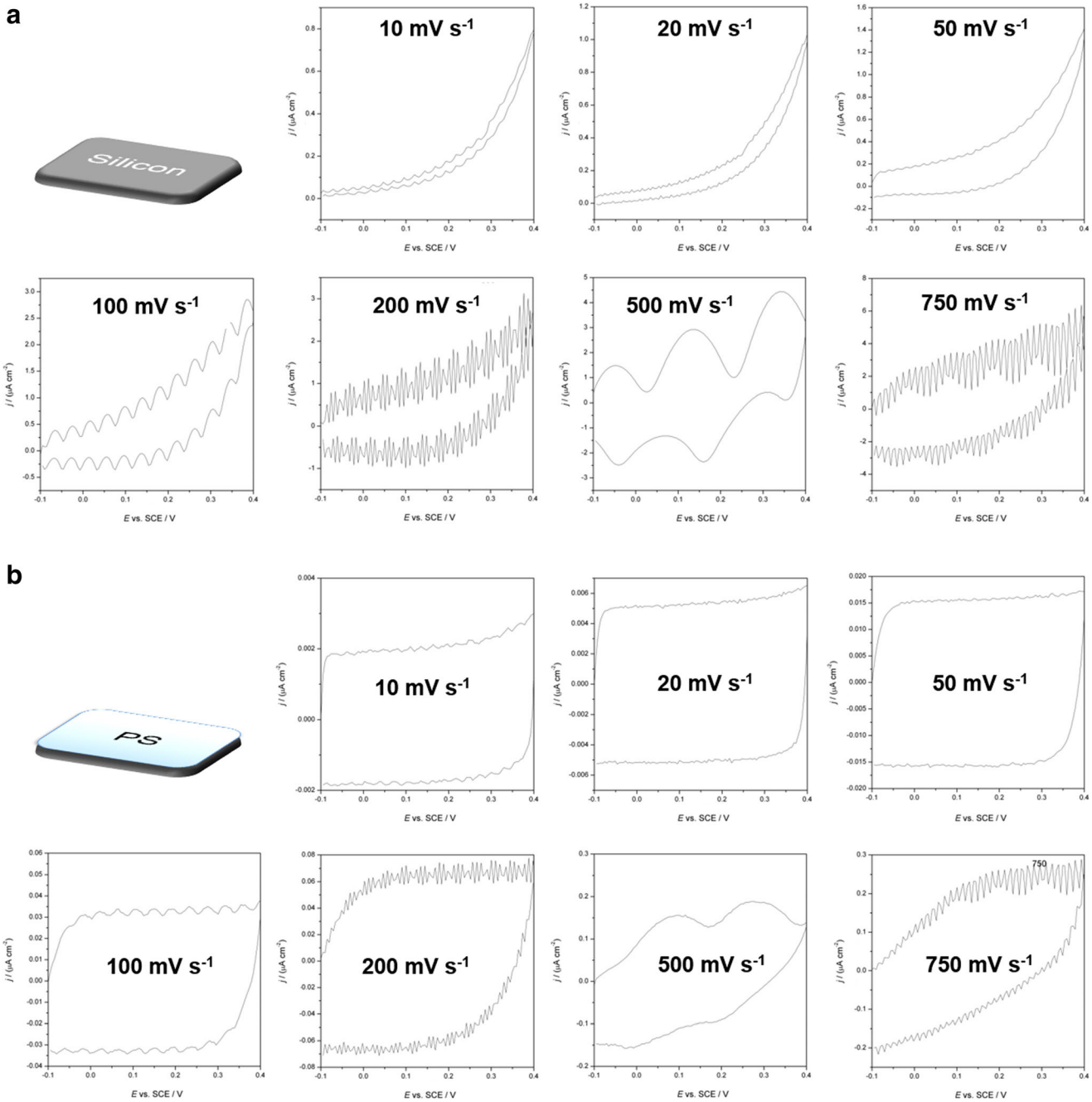

Fig. 3 Cyclic voltammograms for the pristine silicon (**a**) and PS brush-modified silicon (**b**) electrodes under UV irradiation. The corresponding scan rates are indicated in each plot

Notably, the CV plots for both kind of electrodes under UV irradiation displayed current oscillations. These oscillations were dependent from the scan rate, with the same shape and period for the pristine silicon and PS-modified electrodes. However, their amplitude was lower for the latter electrode. Many electrochemical systems are known to exhibit complex non-linear behavior such as spontaneous oscillations of current or potential and even spatial pattern formation when maintained far from thermodynamic equilibrium [15]. This is true for silicon as well, but the reported oscillations are due to profound surface physico-chemical changes, such as oxidation (anodization) and restructurization, manifesting under harsh conditions (e.g., use of hydrofluoric acid or fluorides) [16], which is not the present case.

It is not trivial to explain the observed oscillations and they could even be an artifact generated by the experimental conditions. We hypothesize that the electrical potential variable in time would alter the movement of the photogenerated charge carriers inside the silicon, resulting in oscillations which could be amplified by the experimental setup. As M. T. M. Koper already argued for more conventional electrochemical oscillating systems, it is still not known what would happen if the electrode potential would be held strictly constant, by ruling out any residual uncompensated resistance or by using automatic internal resistance compensation. In other words, is not known if oscillations would be possible under truly potentiostatic conditions, where the electrode potential is a parameter rather than a variable [15].

Regardless of the nature of these oscillations, however, we demonstrated that an ultrathin layer of a hydrophobic polymer, obtained by grafting-from, can dramatically modify the capacitive behavior of silicon wafer and even stabilize it in the presence of UV light.

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