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The dual role of Parylene C in chemical sensing: Acting as an encapsulant and as a sensing membrane for pH monitoring applications

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ABSTRACT

In this work, we demonstrate a new property of Parylene C emphasizing on its application in pH sensing technologies. For many decades the material has been extensively used as a biocompatible inert encapsulant of implantable micro-devices. Toward a new understanding of the material's potential, we explore the transformation of Parylene C from a passive encapsulation membrane into an active H^+ sensing membrane using discrete MOSFETs to evaluate its chemical sensing performance. We employ oxygen plasma treatment to functionalize Parylene's H^+ sensing capacity and enhance the chemical sensitivity, drift rates, and reliability of the sensing devices. Moreover, we demonstrate a versatile technique that enables the deployment of the material both as an encapsulant and as a sensing membrane in a single platform, in order to benefit from distinguishable and consistent sensitivities, and low leakage currents during pH measurements. Our investigation reveals that the selective modification of Parylene's surface chemistry yields reliable pH sensing devices, ensuring the best combination of sensitivity (16.3 mV/pH) and leakage currents (6–10 nA) over a reasonably wide pH range (4–10), while drift rates remain in low levels (2.5–20 mV/h). We believe that this study opens up new application horizons for Parylene, which is a new promising material in the emerging field of flexible electronics able to deliver low film thicknesses and high biocompatibility, while facilitating the application of mechanical stimulus.

1. Introduction

Over the past few decades, poly(chloro-para-xylynene) (Parylene C) has been extensively used as a biocompatible encapsulant (barrier medium) of implantable microdevices, such as pacemakers [1] and catheters [2], chemical sensors [3,4], probes [5] and microelectrodes [6]. Parylene's excellent encapsulation properties have been attributed to its pinhole free nature above 100 nm [7], acting as an electrolyte-barrier layer, but also to its hydrophobic surface, resulting in the retraction of electrolytes that come in contact. Besides its numerous encapsulation applications, Parylene has been also employed together with ion-sensitive field effect transistors (ISFETs) to suppress their pH sensitivity and serve as solid state reference electrodes, namely reference field-effect-transistors (REFETs), for differential ISFET/REFET pH measurements. The concept of the Parylene REFET has been introduced by Matsuo et al. [8], who attempted to deposit a thin film of Parylene on a Si_3N_4-gate ISFET in order to render it chemically inert. Nonetheless, the pH response of the Parylene-gate ISFET showed a maximum sensitivity of 28 mV/pH below pH 4, whereas for larger pH values the sensor was ion insensitive. Chemical modification of Parylene's surface with crown ether compounds was also implemented to examine the K^+ sensitivity of the REFET, nevertheless, problems such as decreasing ionic sensitivity response over time and large drift were reported.

The electrostatic coupling between the ions and the gate insulating membrane has been the fundamental functional principle for a variety of well-established H^+ sensing technologies. This principle is mathematically expressed by the equation of electrostatics derived from Coulomb's law stating that the magnitude of the electric field created by a distribution of charges is inversely proportional to the dielectric thickness. This has been also proven by our recent work which demonstrated that thinner passivations result in an increase of the electrostatic coupling of H^+ and, therefore, in an improved sensitivity of the ISFET sensors [9]. This functional property has also been exploited for a different reason; to improve the

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sensors' performance, reliability and lifetime by having the active transducer in a remote location from the chemical sensing site, also known as the extended-gate approach [10,11]. A further deployment of this concept was recently demonstrated by our group, in which discrete metal-oxide-semiconductor FETs (MOSFETs) were employed as the active transducers [12]. A set of devices with passive electrodes coated with an insulating membrane (Si_xN_y or TiO_2) electrostatically couple the electrolyte ions and transduce the availing chemical potentials to the readout circuitry. The rest of the platform is encapsulated with Parylene C to serve as a barrier between the metal interconnects and the electrolyte providing low leakage currents.

The hydrophobic nature of Parylene C certainly has rendered the material extremely popular for encapsulation purposes, nevertheless, its high biocompatibility and mechanical robustness have made the idea of exploiting the material in other applications interestingly appealing. Many research efforts have been realized to alter the hydrophobic properties of Parylene C with particular focus on the biomedical applications. Oxygen plasma treatment has been previously employed to effectively modify the surface properties of such films [13,14], with special emphasis on utilizing the material as a cell culture substrate [15,16]. In other studies, Parylene has been employed for patterning cells and proteins either by enhancing attachment of proteins after UV exposure [17], or as a peel-off stencil [18].

In a recent research work, we extrapolated correlations between oxygen plasma treatment parameters (power intensity, exposure time), hydrophilicity and etching rates, and demonstrated selective hydrophilic patterning for self-alignment applications [19]. We also established that Parylene tends to partially restore its initial hydrophobicity within one week after treatment independently of the treatment conditions, nevertheless, restoration saturates to a certain point at which the material is still considered hydrophilic.

In this paper, we aim toward a new understanding of Parylene C properties beyond encapsulation, and investigate the material's potential in H^+ sensing. We employ O_2 plasma treatment of Parylene in order to improve the chemical sensitivity, drift rates, and reliability of the sensors, and we propose the selective modification of the polymer's water surface affinity to utilize the material both as an encapsulant as well as a pH sensing membrane, by creating hydrophilic areas that are more sensitive to H^+ ions, while maintaining the desired interfaces hydrophobic to ensure low leakage currents during pH measurements. The work presented here demonstrates a new functional approach for Parylene C, which can be employed both for in vitro but also for in vivo chemical monitoring applications.

2. Materials and methods

2.1. Sensors fabrication

PCB-based platforms (Fig. 1a) consisting of passive Au electrodes were thoroughly degreased in acetone, isopropanol (IPA) and deionized (DI) water, and dehydrated for 60 s at 90 °C. Parylene C films were deposited by chemical vapor deposition, using a commercially available coater (PDS2010) by vaporizing (150 °C) and then pyrolizing Parylene C dimer (690 °C), facilitating three distinct thicknesses (540 nm, 1 μm, 3 μm) (Fig. 1b). This set of samples was used for evaluating pH sensitivity of hydrophobic Parylene C. A second group (1 μm, 3 μm) was rendered hydrophilic through oxygen plasma treatment at 400 W using an ultra high purity plasma etcher (Nano UHP) at a working pressure of 0.8 mbar. Two distinct film thicknesses were derived from the 1 μm-thick sensors depending on the exposure time-span: (a) a residual thickness of $\sim$950 nm, resulting from 1 min-treatment, and (b) a thickness of $\sim$200 nm resulting from 10 min-treatment. Film thickness was determined through calibration samples where Parylene C was selectively removed to create a step that was measured by a Veeco Dektak Stylus profiler. A third group of 1 μm-thick Parylene C platforms was rendered hydrophilic on top of the Au sensing sites only. The fabrication process included the patterning of Parylene C as follows: samples were cleaned and dehydrated as described above. Hexamethyldisilazane (HMDS) was spin-coated on the Parylene C coated PCBs, succeeded by a 1.4-μm-thick positive photoresist (AZ5214). The samples were then soft-baked on a hotplate at 90 °C for 60 s, selectively exposed to UV light for 90 s, and developed. Before inserted into the plasma etcher, the samples were prebaked at 110 °C for 60 s for hardening the protective photoresist mask. Oxygen plasma treatment was accomplished at 400 W/10 min, facilitating a film thickness of $\sim$200 nm on top of the electrode sites only, whereas hydrophobic Parylene remained intact (1 μm) at the rest of the platform. For the fabrication of the patterned matrix the same procedure was followed with a different mask layout. For thicker Parylene films (3 μm), photoresist AZ4562 (190 s UV exposure, 2 min development time) was utilized instead, due to its slower etching rate inside the plasma etcher. Plasma treatment was conducted at 400 W/35 min resulting in a $\sim$200 nm Parylene thickness on top of the metal sensing sites. After O_2 plasma exposure, the photoresist was removed by immersing the platforms into ACE, IPA and then DI water.

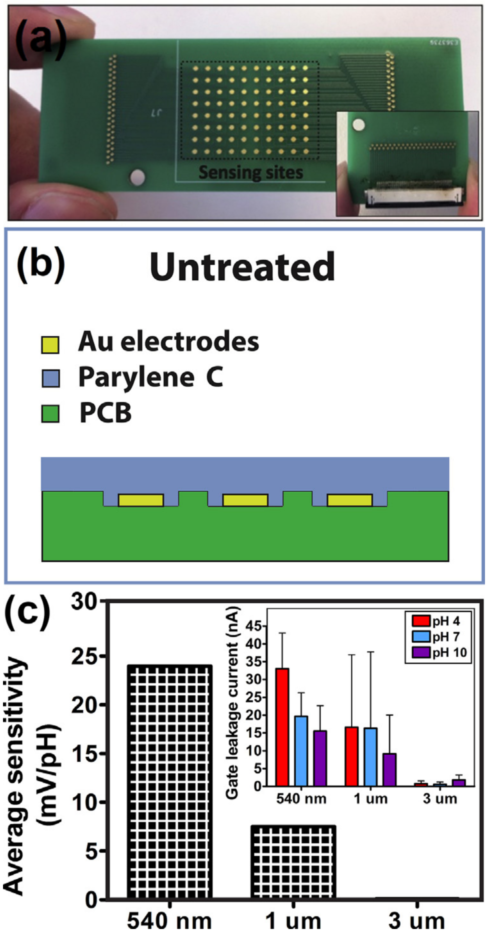

Fig. 1. (a) PCB-based prototype platform with the Au/Parylene sensing sites located in the center. (b) Schematic cross section of the fabrication process of untreated Parylene C sensors. (c) Average sensitivity and corresponding measured leakage currents over 6 channels of untreated 540 nm, 1 μm and 3 μm thick Parylene C films.