

Silicon-conjugated polymers nanocomposites fabricated by a two-step electrochemical approach

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When a silicon wafer is subjected to electrochemical etching in fluoride-based solution, silicon surface develops pores¹. Such kind of porous structure is often called porous silicon (PS). A variety of pore sizes ranging from a few nanometers up to a few micrometers can be obtained during the electrochemical anodization process, depending on the electrochemical operating parameters as well as the solution chemistry^{2,3}. It is an experimental fact that the degree of porosity of the produced PS layer can be controlled and modulated by adjusting the applied anodic current. PS has attracted increasing interest from basic research and technological applications due to its promising porous structures and high surface area to volume ratio. The scope of applications of as-formed PS may include⁴⁻⁶ microelectromechanical systems (MEMS), photovoltaic conversion, gas and humidity sensors, biotechnology, templates for nanofabrication, and many others.

Electroactive conducting polymers, on the other hand, are new class of materials that can find applications in many recent technological areas. Examples of conducting polymers include: polypyrrole, polyaniline and polythiophene and they are considered suitable and potential candidates to form adherent, efficient electrical contacts with PS compared to the metallic contacts. In several previous reports, polypyrrole and other conducting polymers have been chemically or electrochemically deposited into the PS matrix with a concern to form electrical contacts⁷⁻¹³.

In this work, nanocomposites of silicon and conjugated polymers are prepared by a two consecutive-step electrochemical approach. The main objective is to fill the pores completely with conducting polymers and to clarify the electrochemical growth of the polymer inside the nanopores.

The PS layers were prepared by galvanostatic anodisation of silicon wafer (either *p*- or *n*-type substrates) in HF-based

solutions. Pt wires were used as counter and reference electrodes. The current density was monitored between 1 to 20 mA/cm² for getting the desired pore sizes and morphologies.

We then polymerized the corresponding polymer monomers into the as-formed pores by the electrochemical technique at constant current. Pyrrole is primarily used as an example with a comparative study with both aniline and thiophene.

Figure 1 shows the current transient obtained during the electropolymerization of pyrrole into PS matrix in a solution composed of 0.1M pyrrole monomer in acetonitrile + 0.1 M tetrabutyl ammonium perchlorate at applied potential of 0.8 V measured versus Pt wire.

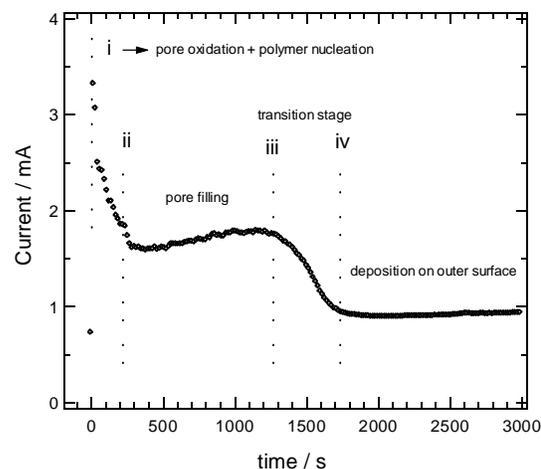


Figure 1 Current transient recorded during the potentiostatic polymerization of pyrrole into porous silicon matrix at 0.8 V.

Characteristic polymerization stages are observed through point (i)-(iv). At point (i), the polymer nucleates with a partial oxidation of porous layer. The pores are being filled with polymer during stage (ii) to (iii), followed by a transition stage of deposition at (iii)-(iv). After point (iv), a preferential polymer deposition takes place at the outer surface. Such behavior of polymer deposition implies that the

polymerization process starts at the pore bottom and propagates to the pore opening.

As-prepared PS/polypyrrole nanocomposite sample was cleaved and inspected for cross-sectional view using SEM. Image (a) of Fig. 2 shows that the porous template is filled with polymer (bright areas=polymer). The porous layer was then dissolved selectively in an alkaline solution to release the polymeric structure. Polypyrrole nanowires in the range of 100 nm diameter are obtained and can be seen in image (b) of Fig.2. The inset shows two separated nanowires, image (c). The formation of nanowires actually is a proof that the deposition of polymer proceeds preferentially at the pore bottom and grows into the outer surface.

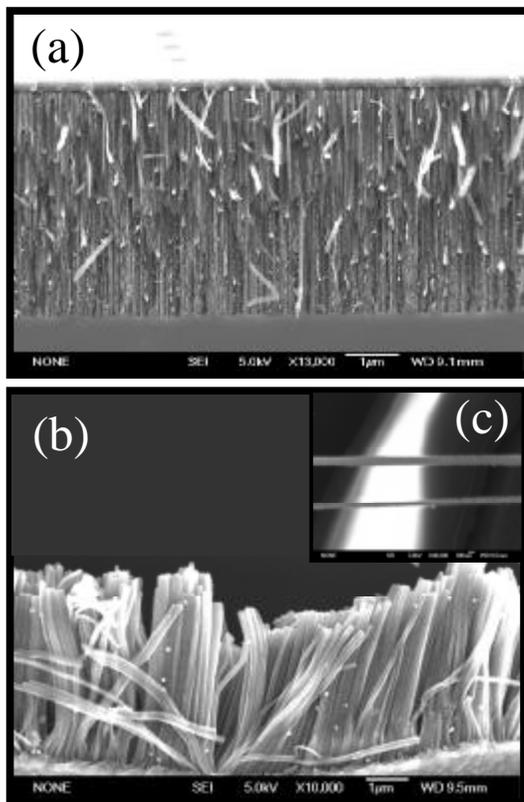


Figure 2 SEM images of cross-sectional view of porous silicon filled with polypyrrole (image a) and polypyrrole nanowires after a selective removal of porous silicon template (image b). Inset shows two single nanowires (image c).

For the sake of comparison, aniline and thiophene were also tested for the electropolymerization into the porous templates. Results revealed that both

polyaniline and polythiophene were successfully deposited inside PS layers using either potentiostatic or galvanostatic modes. The electrochemical polymerization behaviour is similar to the case of polypyrrole. However, much homogenous polypyrrole chains are obtained inside the porous matrix compared to polyaniline or polythiophene. Results of fabrication, chemical and physical analysis, including surface analysis, electrical and optical properties for as-fabricated nanocomposites will be addressed and thoroughly discussed during the conference.

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