



Electrochemical formation of a novel porous silicon/polypyrrole hybrid structure with enhanced electrical and optical characteristics



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ABSTRACT

The electrochemical formation of a hybrid structure composed of a redox-active polypyrrole (PPy) and porous silicon (PSi) layer is demonstrated. PSi layers with pore sizes (~200 nm) are prepared by the electrochemical anodization of *n*-type Si wafer in HF-based solution, whereas the PPy as a *p*-type conducting polymer was prepared by electro-oxidative polymerization of parent monomers in acetonitrile solution using PSi as a working electrode. Uniform and vertically-oriented PPy nanorod arrays were successfully fabricated inside the porous matrix. After pore filling, the electrical conductivity and photoluminescence of as-fabricated hybrid structure were remarkably enhanced. The PSi/PPy heterojunction was fully characterized by a variety of techniques including field emission-scanning electron microscopy (FE-SEM), energy dispersive X-ray spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS), electrochemical impedance spectroscopy (EIS) and cyclic voltammetry. Thermal properties were also evaluated using thermo-gravimetric analysis (TGA) measurements. Formation mechanism and surface properties of such hybrid structure along with its electrical and optical characteristics are addressed and thoroughly discussed.

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1. Introduction

Electrochemical etching of single crystalline silicon in hydrofluoric acid (HF)-based solutions leads to the formation of various nano/macro-pore arrays, known as porous silicon (PSi) [1–5]. The formation of such various pore arrays are essentially dependent on the characteristics of starting silicon substrates, the anodizing solution chemistry and the applied electrochemical parameters [6–9]. The electrochemical etching could be performed either under constant current or potential, however the galvanostatic anodization is preferable as it gives a better control of the layer porosity [10,11]. The extremely large specific surface area, high tendency for oxidation and capability for surface functionalization open the door for a wide range of technological interests in PSi. These include, for examples, chemical and gas sensors [12–17], biosensors [18], optoelectronic and biomedical applications [19,20], a sacrificial layer in micromachining [21,22], templates for micro- and nanofabrication [23–25] and photovoltaic device applications [26–29]. However, the PSi itself is not an ideal

material for devices due to poor electrical and mechanical properties [30]. Incorporation of other conducting materials into the porous matrix may improve the deficient properties of PSi and forms a hybrid structure that offers a unique combination of electrical and optical properties [31,32].

Conducting polymers are potential candidates that could offer the promise of achieving a new generation of materials, exhibiting electrical and optical properties of semiconductors and retaining the attractive processing advantages of polymers. Polypyrrole (PPy) is one of the most extensively studied polymers due to its possible uses in sensors and actuators [33–35], material for corrosion protections [36] and photovoltaic devices [37,38]. The high charge carrier mobility is a substantial condition for several applications of conducting polymers. It is a common observation that the electron mobility in most conducting polymers is quite low compared to the hole mobility in either *p*-type conducting polymers or the electron mobility in inorganic materials based-systems. Hence, there is an increasing attention towards the formation of hybrid structures of conducting polymers and inorganic materials, that expecting to represent a synergic approach to overcome the limitations of conducting polymers based-devices, keeping at the same time their beneficial processability. The combination of conducting polymers and inorganic materials is recently studied for various electronic applications [39,40].

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Particularly, in photovoltaic devices [41–43] such a combination is indispensable to enhance the electron transport properties and would eventually lead to a yet newer class of hybrid photovoltaic devices with competitive efficiencies.

The aim of the present work is to provide a solid base of knowledge for the electrochemical synthesis of PSi/PPy hybrid structures that would have future potential application as a photovoltaic device. Here, we demonstrate the successful fabrication of vertically oriented PPy nanorods inside 200 nm pore arrays of PSi matrix, with emphasis on its electrical and optical performance. The hybrid structure was fabricated via a double-step electrochemical approach; electrochemical etching for PSi formation followed by electrochemical polymerization to deposit the conducting polymer. The surface properties, the electrochemical characteristics, along with thermal and photoluminescence performance are evaluated and thoroughly described.

2. Experimental

2.1. Formation of PSi

Porous silicon (PSi) layers were fabricated, according to our previous procedures [24,44], by a galvanostatic anodization of heavily doped *n*-type Si (100) wafer with a resistivity of 0.01–0.018 Ω cm in 6 wt.% aqueous HF + 8 mM KMnO₄ as an oxidizing agent + 3000 ppm NCW-1001 surfactant (Wako Pure Chemical Ind.). The wafer was initially washed by deionized water and sonicated in acetone for 15 min, followed by dipping in 5 wt.% aq. HF to remove the native oxides. The electrochemical etching was conducted in a two-electrode set up with 0.78 cm² Si working electrode and a Pt rod served as a counter electrode. The anodization process was performed with applied current density of 27 mA/cm² for 180 s, producing pore arrays with sizes in the range of 150–200 nm and layer thickness of 4.5 μ m.

2.2. Electrochemical polymerization of pyrrole into PSi layer

The electrochemical polymerization was performed on the wet porous layer after rinsing in ethanol. Pyrrole (C₄H₅N) monomers with a concentration of 0.1 M were polymerized at a constant current of 150 μ A in acetonitrile (CH₃CN) solution in the presence of 0.1 M tetrabutylammonium perchlorate (Bu₄NClO₄) as a supporting electrolyte. A three-electrode cell was connected to a computerized potentiostat–galvanostat. A Pt wire was used as a quasi reference electrode calibrated with Ag/AgCl (potential of Pt wire = 0.21 \pm 0.02 V vs. Ag/AgCl). In order to verify that the entire volume of porous matrix was uniformly infiltrated with polymer, the corresponding potential transient of the galvanostatic process was recorded.

2.3. Characterization of PSi/PPy hybrid structure

Morphological investigation for as-formed hybrid structure was done using field emission-scanning electron microscopy, FE-SEM (JSM-7600F-JEOL) on the cleaved samples, coupled with energy dispersive X-ray spectroscopy (EDS) for chemical analysis. Surface analysis was performed using X-ray photoelectron spectroscopy (XPS); a thermo scientific K-ALPHA, XPS, England. The recorded binding energies have been calibrated by taking the C1s peak at 285.0 eV as a reference. The electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV) and current–voltage (*I*–*V*) curves were measured using the electrochemical workstation, ZahnerZennium, Germany. The measurements parameters and the data acquisition and storage were controlled with Thales software. Thermo-gravimetric analysis (TGA) and differential scanning

calorimetry (DSC) were applied to assess the thermal stability of the polymer using SETARAM instrumentation TG-DSC16, at a heating rate of 10 K/min from 100 to 800 °C. Photoluminescence (PL) was measured at room temperature by means of Spectrofluorophotometer, SHIMADZU RF-5301PC using a 150 W xenon lamp as an excitation source.

3. Results and discussion

3.1. Electropolymerization of pyrrole

The polymerization process was conducted under a galvanostatic condition using 150 μ A. A typical potential transient (*E*–*t* characteristic) is shown in Fig. 1. Different characteristic stages of galvanostatic polymerization could be recognized. At the early stage of polymerization, polymer nucleation takes place at the pore tips, simultaneously with a partial oxidation of PSi. This stage is accompanied by a rapid potential rise. An intermediate period of a nearly steady state of potential is related to the polymer growth inside the pores. A stage transition from polymerization inside the pores to polymerization at outer porous surface is accompanied with an appreciable potential rise of 0.14 V; this step is indicated by “transition stage”. A potential rise means an increase of overpotential, which is likely observed when actual electrode area is decreased. The transition stage is not sharp and it takes 5 min polymerization time to reach onto the top surface. The charge consumed during this stage was \sim 14% from the total polymerization charge. Such a behavior can be either related to the different pore lengths or to the inhomogeneous PPy growth inside the porous matrix. Generally, the amount of polymer deposited in the interior of the pores can be controlled by the value of polymer-formation charge passing before transition stage. Similar deposition transients have been observed previously for the electrodeposition of poly(bithiophene) [45], poly(3-dodecylthiophene) [46] and PPy [5,32,47] into *p*-type PSi. It is likely that after the transition stage the pores are completely filled with polymer. A thin film of dark brown PPy was visually detected after the transition stage. A constant potential is consequently observed during the polymerization at the outer surface, the process here seems to be superficial. Compared to our previous works using smaller mesopore sizes, one could conclude that as the pore size increases in the current work to 200 nm, the amount of charge needed to deposit the polymer and completely fill the pores increases, and consequently the polymerization time is extremely prolonged. Additionally, it is worthy

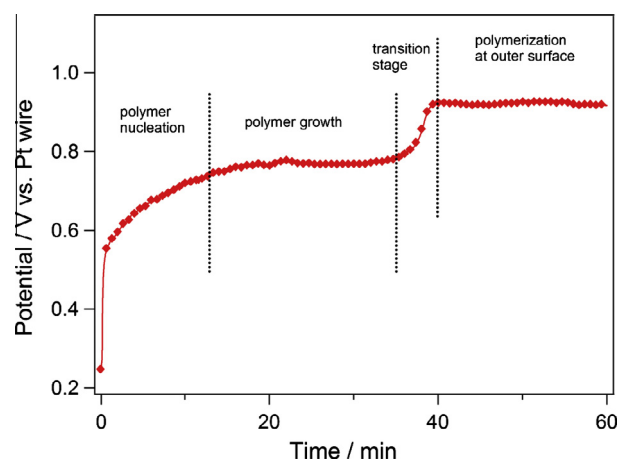


Fig. 1. Potential vs. time (*E*–*t*) characteristics recorded during the electrodeposition of PPy into PSi layer in a solution composed of 0.1 M pyrrole monomers + 0.1 M Bu₄NClO₄/CH₃CN, at an applied current of 150 μ A.

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