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Deposition of polythiophene films onto *p*-type silicon

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Electrically conductive polythiophene (PT) films were first deposited onto *p*-type silicon by using electrochemical techniques. The deposition of PT were detected by cyclic voltammetry, surface reflection i.r. spectroscopy and scanning electron microscopy (SEM) images. The morphology and conductivity of the PT films deposited on monocrystalline silicon (MS) were much different to those of the films deposited on porous silicon (PS). © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: polythiophene; electrochemical deposition; *p*-type silicon)

Introduction

The electrochemical deposition of PT is a complex process. Many factors such as the solvent (especially the presence or absence of water)[1], temperature[2], and the concentration of the monomer[3] may affect the property of the obtained film. The possibility of the deposition of PT on various substrates depends largely on the width of 'electrochemical window' of these materials exhibited in different electrolyte solutions. Thus, PT has been successfully deposited onto platinum from a concentrated solution of thiophene in acetonitrile[4]. On the other hand, the less noble metallic materials such as iron and aluminium have been considered unsuitable for the electrochemical deposition of PT mainly due to the competing side reactions of the metallic materials or the electrolytes[4,5]. However, for larger-scale applications platinum is too expensive and sometimes its properties (e.g. mismatching thermal expansion coefficients, low ductility) may not be suitable from the point of view of mechanical requirements in construction of heterostructures in which PT would be used.

It is known that polypyrrole (PP) can be deposited under conditions at which PT deposition fails. Thus, PP has been successfully grown on substrates such as Al or Fe[6]. On the other hand, competing metal dissolution has been found to prevent the formation of PT on the same materials[4]. The growth of PT on inorganic semiconductive materials such as *n*-GaAs is highly desirable from a technological point of view[7]. However, it can be accomplished only if an intermediate layer of Pt is deposited on the substrate in order to prevent its degradation during electro-oxidation. The possibility of depositing PP under those conditions is mainly due to a considerably lower oxidation potential for pyrrole (0.6 V vs 0.01 M Ag^+/Ag) as opposed to 1.6 V for thiophene. Accordingly, the key point of deposition on PT on less noble metallic material is search for an electrolyte in which the substrate is stable and the oxidation potential of thiophene monomer is sufficiently low.

Recently, we found the oxidation potential of thiophene monomer in freshly distilled BF_3-ethyl ether solution (BFEE) was only about 1.0 V vs Ag/AgCl. PT could be deposited on a series of metallic materials such as platinum and stainless steel from a thiophene solution (10 nM) of BFEE. This work aims to study the possibility of deposition of PT on *p*-type silicon, a typical inorganic semiconductor, from the same medium.

Experimental

PT depositions and electrochemical examinations were performed in a one-compartment cell with the use of an EG&G potentiostat model 273 under computer control (Princeton Applied Research Co.). The working electrode was MS or PS sheet, and the counter electrode was a platinum sheet with the same size. PS samples were formed by anodic polarization of boron-doped ⟨1 1 1⟩ *p*-silicon wafers (3.44 Ω-cm) according to a published procedure[8]. The average size of the pores is about 10 nm. The anodic potentials were measured vs an Ag/AgCl electrode. A correction of 0.069 V was needed to bring the measured potentials in BFEE originally vs Ag/AgCl to potentials vs the standard hydrogen electrode[9]. The electrolyte used for PT deposition was a freshly distilled BFEE (no supporting salt was added) containing 10 mM thiophene and it was deaerated by dry argon stream and maintained at a light overpressure during the experiments. The applied potential used for electrosynthesis was controlled to be 1.1 V (vs Ag/AgCl). The as-formed samples were finally rinsed in diethyl ether and dried at 50°C under vacuum for 8 h. The deposition of the PT films was detected by cyclic voltammetry, surface reflection i.r. spectroscopy and SEM. The results obtained are briefly summarized below.

Results and discussion

Figure 1A shows the cyclic voltammograms of thiophene at polished MS in BFEE solution; the potential scans shown led to the formation of a film on the surface. As seen from this figure, a couple of waves attributed to the doping and undoping of PT appeared at about +0.6 and −0.35 V, respectively. Their current strengths increased with the continuous potential scan. The oxidation potential of thiophene monomer was about 1.0 V, which was much lower than those in other

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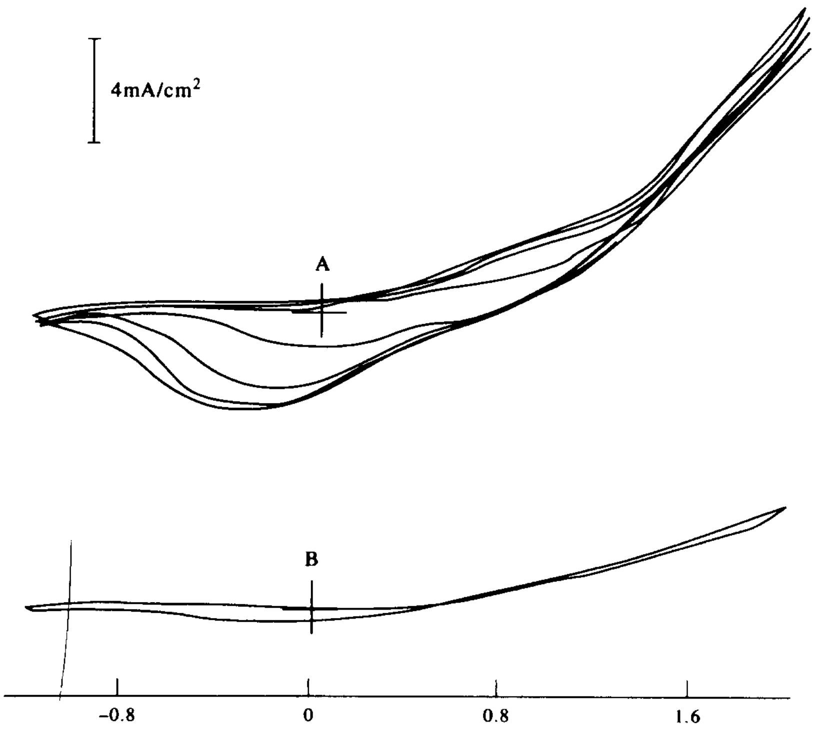

Figure 1 Cyclic voltammograms of 10 mM thiophene in freshly distilled BFEE (A) or pure BFEE (B) at MS electrode and at a potential scan rate of 0.2 V s^{-1}

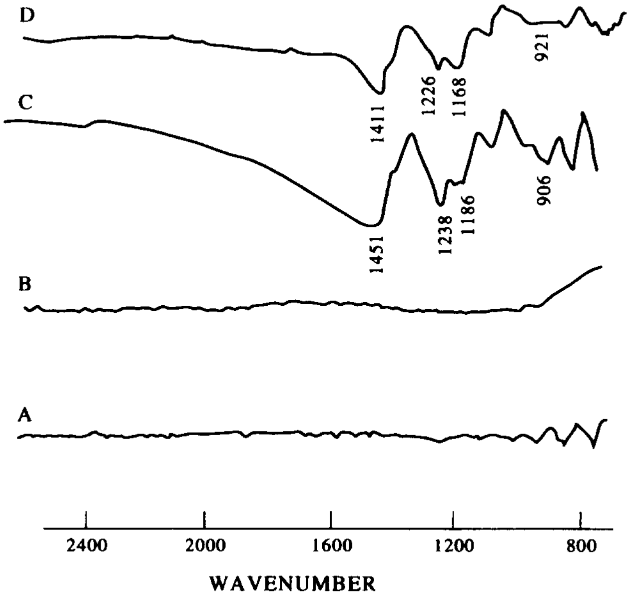

Figure 2 Surface reflection i.r. spectra of MS and PS samples with deposited PT films (1.1 V, 200 s). The curve numbers are explained in the text

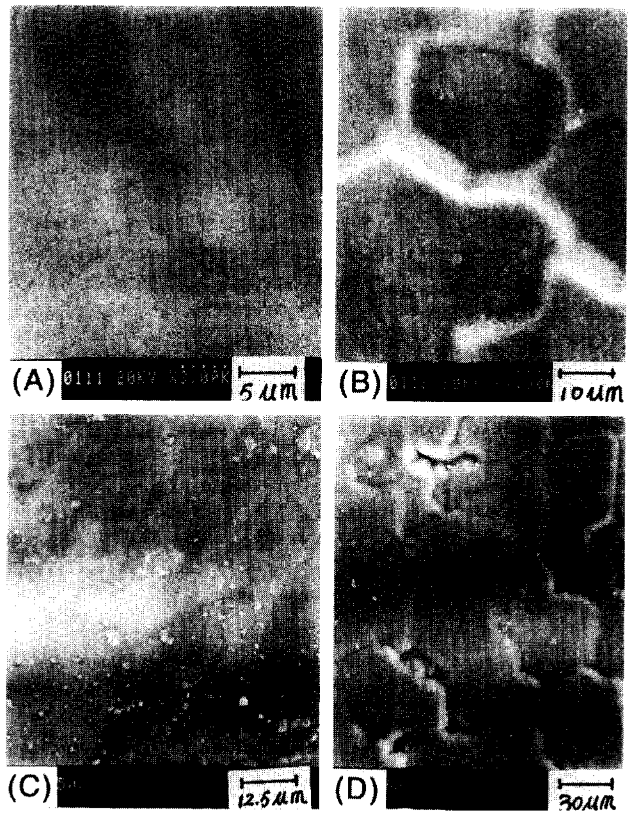

Figure 3 SEM images of bare MS (A), PS (B), or PT film (1.1 V, 2000 s) deposited MS (C), PS (D)

reported systems[4]. It should be noted here that, the CV of pure BFEE showed no redox waves in the same potential scale (*Figure 1B*). Similar CV was found for thiophene at PS.

Figure 2 illustrates the surface reflection i.r. spectra of the PS sample (D), or MS sample (C) electrochemically treated in thiophene solution, in comparison with bare MS (A) and freshly obtained PS (B). It is clear from this figure that curves A and B appeared only in weak i.r. bands near 800 cm^{-1}. However, curves C and D showed additional bands at about 1410–1450 cm^{-1} and 1230–1240 cm^{-1} corresponding to the vibrations in the ring structure of PT molecules, and 1170–1180 cm^{-1} to the stretching vibration of the C–C bond.

Relative thick PT films deposited on the MS and PS substrates may be detected by the use of SEM images. *Figure 3* shows the SEMs of PT films deposited on MS (C) and PS (D), in comparison with clean MS (A) and PS (B). As can be seen from this figure, the surface of PT deposited on polished MS is smooth and compact. However, the surface of PT film deposited on PS was irregular with more defects.

The as-formed PT films were black–blue (doped state) and exhibited good adherence to PS and MS. The surface resistance of the PT layers deposited on MS measured by a four-probe method at room temperature, amount to 10–15 Ω (per square centimetre) and 30–45 Ω for the PT layers deposited on PS. On the other hand, the surface resistance of bare MS was 300–400 Ω and that of bare PS was 1500–2000 Ω.

In conclusion, the results of this work showed the possibility of depositing polythiophene films onto monocrystalline and porous silicon. The morphology and properties of the PT layers deposited on MS were much different to those of the PT films deposited on PS.

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