

Electrochemical Fabrication of a P-type Silicon–Polythiophene p–n Junction Diode

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A p–n junction thin film was fabricated by electrochemical deposition of polythiophene on a p-type silicon substrate, followed by controlled-potential electrochemical doping to make the polythiophene layer cation doped.

Electrically conductive polymers such as polyacetylene, polythiophene and polypyrrole have found promising applications in electronic devices.¹ The conductivity of these π -electron conjugated polymers can be controlled by doping from insulating to the metallic region.² Furthermore, polythiophene (PT) is easily formed as a film by electropolymerization of thiophene.³ Therefore, electrosynthesis of PT may provide a route for the fabrication of organic thin film devices.

PT can be electrochemically doped not only by electrolyte anions but also by cations.⁴ Anion-doped PT behaves as a p-type semiconductor, cation-doped PT behaves as an n-type semiconductor. These results suggested the possibility of forming a p–n junction by electrochemical deposition of an n-type PT film on a p-type silicon substrate.

The possibility of deposition of PT on different metallic substrates depends strongly on the width of 'electrochemical window' that these substrates exhibit in different electrolytes.⁵ Thus, PT has been successfully deposited on platinum from concentrated thiophene solution of acetonitrile.⁶ However, the less noble metals such as Au, Ag, Fe, Si, and Al have been considered unsuitable for PT deposition.⁷ This was mainly because the oxidation potential of thiophene monomer in the previously reported systems was very high (ca. 1.6 V vs. 0.01 mol dm⁻³ Ag⁺/Ag), and the dissolution of the substrates during electropolymerization process was unavoidable. Recently, we found that the electro-oxidation potential of thiophene in freshly distilled BF₃–diethyl ether (BFEE) solution was as low as 1.0 V (vs. Ag/AgCl), and that polythiophene could be deposited on a series of metallic substrates include p-type silicon. The deposition of organic semiconductors onto inorganic semiconductors has attracted the increasing attention of many researchers.⁸ Parkhutik *et al.*

have tried to deposit polyaniline films onto p-type silicon, but they succeeded only by using porous silicon layers possessing a pore size of 4 nm as substrate.⁹ On the other hand, we found PT could be successfully deposited on monocrystalline silicon as well as porous silicon from the thiophene solution of BFEE.

A PT film was synthesised on a boron-doped <111> p-type silicon wafer (0.3 Ω cm, 1 \times 1 cm) by electro-oxidative polymerisation of thiophene at a controlled potential of 1.2 V vs. Ag/AgCl in a freshly distilled BFEE solution containing 5 mmol dm⁻³ thiophene. The electrooxidation charge was controlled to be 0.5 C cm⁻². The PT/Si was thoroughly washed with acetonitrile. Then the p-type silicon covered by PT was immersed in acetonitrile containing 0.1 mol dm⁻³ LiClO₄ and electrochemically doped at -1.4 V for 10 min. In all electrochemical measurement, a Pt plate and an Ag/AgCl electrode were used as counter and reference electrodes, respectively.

After drying *in vacuo*, an indium wire was simply pressed onto the surface of PT film to form an ohmic contact. Current–voltage curves of the In/polythiophene/p-type silicon junction were measured.

The deposition of PT onto p-type silicon can be detected by the cyclic voltammograms of thiophene in BFEE solution as shown in Fig. 1(a). The potential scans shown led to the formation of a film on the electrode surface (black blue with thickening deposit). The strong oxidation present at potentials >1.0 V, which promotes polymer generation on the electrode, can be observed on the voltammograms. The polymer is reduced and oxidised between -0.6 V and +1.0 V. The increase of the redox wave currents of the polymer implied that the amount of the polymer on the electrode increased. At the same time an increase in the overpotential of the polymer oxidation maximum was observed. The potential shift of this maximum informs us about the increase of the electrical resistance in the polymer film and the overpotential needed to overcome that resistance.^{10,11} Scanning electron microscopy results showed the polymer films deposited at low applied

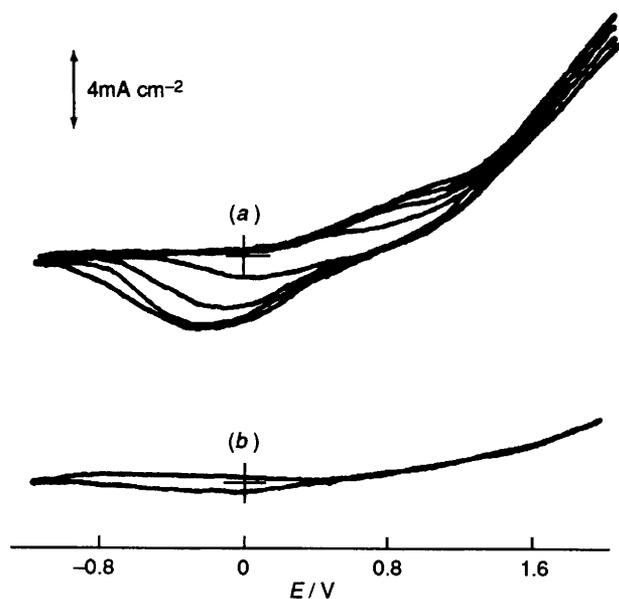


Fig. 1 Cyclic voltammograms of 5 mmol dm⁻³ thiophene in BFEE (a), or pure BFEE (b) at a p–Si electrode and a potential scan rate of 0.2 V s⁻¹

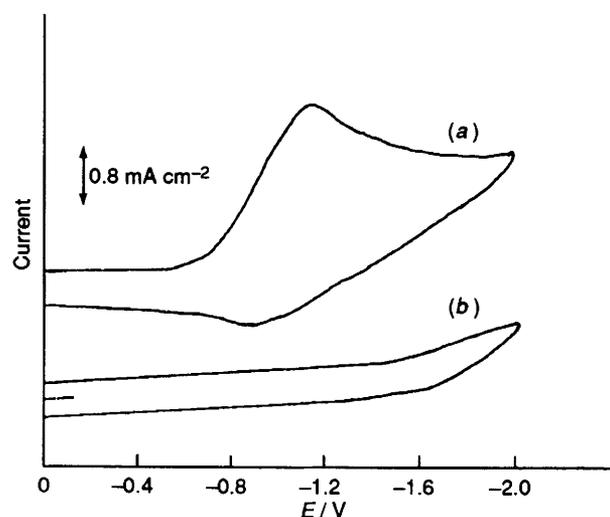


Fig. 2 Cyclic voltammograms of PT film in MeCN containing 0.1 mol dm⁻³ LiClO₄ (a), or the pure electrolyte (b) at a potential scan rate of 0.2 V s⁻¹

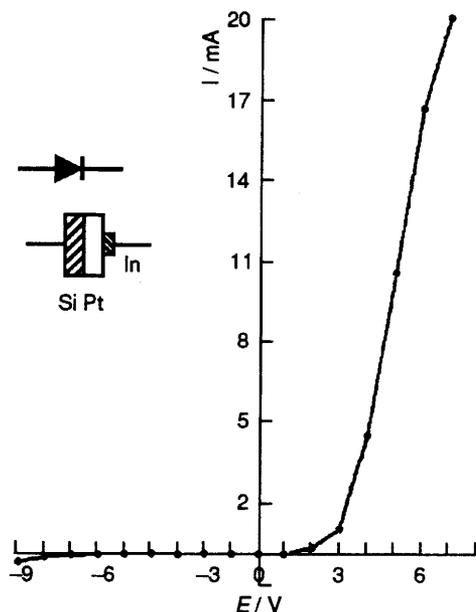


Fig. 3 I - V curve for the In/PT/p-Si junction

potentials (1.0–1.3 V) were very smooth and compact with little defects. The films also have good adhesions to silicon wafers and can be detached only with difficulty. However, the films deposited at high applied potentials were very rough and irregular with many pores. This led to the choice of 1.2 V as controlled potential for the deposition of this polymer.

PT films can be doped by cations such as Li^+ . Fig. 2(a) shows the cyclic voltammogram of PT film deposited onto p-type silicon in acetonitrile containing $0.1 \text{ mol dm}^{-3} \text{ LiClO}_4$. The cation doping wave of the polymer appeared at ca. -1.2

V, and the corresponding undoping wave was found at about -0.8 V. It should be noted here, that both the pure $\text{BF}_3\text{-Et}_2\text{O}$ solution and acetonitrile- LiClO_4 were electrochemically inert in the potential ranges described above [Figs. 1(b) and 2(b)]. Therefore, polythiophene film could be cation doped at -1.4 V for 10 min, when a p-n junction was formed at the interface of silicon substrate and the polymer.

Fig. 3 shows the current-voltage characteristics of the In/polythiophene/p-type silicon junction. A positive current started to flow at about 0.5 V, and a small ohmic current was observed in the negative voltage region. These results indicate that electrochemically deposited n-type polythiophene and a p-type silicon should work as a p-n junction diode.

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