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1989 J. Phys.: Condens. Matter 1 SB133

(http://iopscience.iop.org/0953-8984/1/SB/023)

J. Phys.: Condens. Matter **1** (1989) SB133–SB138. Printed in the UK

Properties of metal/poly(N-methylpyrrole) Schottky barriers

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Received 14 April 1989

Abstract. Barrier properties of a promising conjugated polymer, poly(N-methylpyrrole) (PMPY), with high- and low-work-function metals, gold and indium respectively, have been investigated. The electrical conductivity of PMPY films was varied from insulating to metallic levels by electrochemical oxidation. *I–V* characteristics were used to investigate the junction properties. Heavily doped $PMPY^+$ films were found to form an Ohmic contact with gold (φ_{Au} = 5.1 eV) and a Schottky barrier with indium (φ_{In} = 4.1 eV), this difference corresponding to the difference in work functions. Results indicate a leaky Schottky barrier with high fields producing $\ln J \propto V^{1/2}$ and are interpreted in terms of metal–semiconductor band theory.

1. Background and introduction

The electrical properties of conducting polymers, and especially those derived from heterocyclic monomers, have created enormous interest in the past few years [1–3]. The majority of polymers derived from heterocyclic compounds are p-type, and are attractive to study due to their physical and chemical stability. In particular, polypyrroles are being studied as active materials in novel electronic and optical devices [4, 5], electrochromic displays [6], ion gates [7] and gas-sensitive devices [8]. Previous research at Warwick University has been directed towards metal oxide semiconductors (MOS) gas sensors [9, 10] which suffer from high power consumption, poor specificity and stability. For these reasons we are also actively investigating the electronic properties of conjugated polymers. In this paper we present results for poly(N-methylpyrrole) (PMPY).

2. Experimental details

2.1. Electrochemical sample preparation

Poly(N-methylpyrrole) is readily synthesised using a technique based upon that of Dall'Olio. The cathode consisted of 50 nm of gold vacuum deposited at 0.8 nm s^{-1} upon a 25 mm^2 ceramic tile, and baked for 12 min at 200 °C to improve adhesion. Preliminary tests using cyclic voltammetry demonstrated that the substrate behaved as expected for a pure polycrystalline gold electrode. Polymer films were grown from 0.05 mol dm^{-3} of N-MPY in acetonitrile containing 0.2 mol dm^{-3} of tetrabutylammonium perchlorate as the background electrolyte (at 25 °C). Either cyclic voltammetry or chrono-ammetry was used to grow the blue–black film with an electrode potential, *E*, of 1.4 V against a

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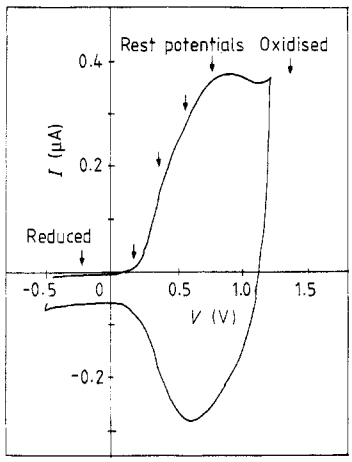

Figure 1. A voltammogram of a poly(N-methylpyrrole) film indicating the rest potentials used to switch between oxidised and reduced states.

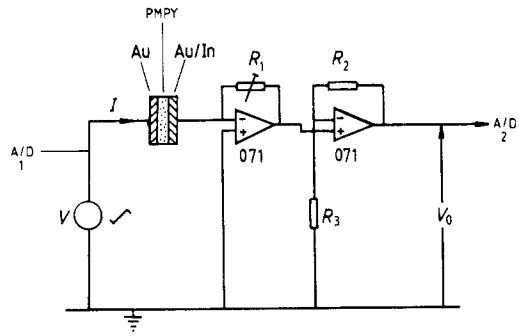

Figure 2. The circuit used to measure the *I–V* junction characteristics of poly(N-methylpyrrole) films with gold or indium.

saturated aqueous calomel electrode. Figure 1 shows the range of rest potentials used after film growth, allowing the film to vary between a fully conducting polymer and a neutral film. Thus, films were prepared with electrical conductivities that spanned the metal–insulator transition and with a range of thicknesses (0.1–1.0 μm). Problems were encountered with the thicker films due to poor adhesion to the gold surface. Finally, after drying the PMPY film, a top electrode was vacuum deposited on to it using either a high- or low-work function metal to form the main junction, i.e. gold or indium.

2.2. I–V measurements

Figure 2 shows a schematic representation of the circuit used to measure the current–voltage characteristics of the devices. The voltage source, V, consisted of a purpose-built voltage ramp using an RS8038 and low-noise buffer amplifier, with a frequency range of 0.005–5 MHz (less than 1% distortion). The current, I, passing through the

junction was converted to a final voltage signal, V_0, via a virtual earth and non-inverting amplifier circuit, where

$$I = [R_2/R_1(R_2 + R_3)]V_0. \tag{1}$$

The analogue current and voltage signals were converted to a 12-bit digital signal by a DT2811 A/D card and recorded with an 8086-based microcomputer. The system was tested and calibrated with a standard resistor before each set of measurements was made enabling a relative accuracy of better than 0.1% to be achieved. Current–voltage derivatives were calculated by a high-order polynomial fit through averaged data blocks and theoretical curve fitting used a Gauss–Newton method with a tolerance of 0.0001. The first derivative at zero bias is the contact resistance R_c and is given by

$$R_c = (\partial I/\partial V)^{-1}_{V=0} \tag{2}$$

and was measured at a low frequency of 0.25 Hz throughout the experimental work. The conductivity, σ, was calculated from the contact resistance, R_c, film thickness (0.1–1.0 μm) and top-electrode area (50.3 mm^2).

3. Experimental results and discussion

3.1. Heavily doped PMPY$^+$ films with high- and low-work-function metals

The *I–V* characteristics of heavily doped PMPY$^+$ films with gold were linear and symmetric as shown in figure 3(*a*). The Ohmic contacts between the high-work-function metal gold ($\varphi_{Au} = 5.1$ eV) and p-type semiconductor indicates a negligible potential barrier, φ_b, where, in the absence of surface states,

$$\varphi_b = (\varphi_{Au} - \psi) - (E_F - E_C) \simeq 0. \tag{3}$$

The Fermi level E_F lies above the top of the conduction band E_C and the electron affinity, ψ, of other conjugated polymers, such as polypyrrole (PPY), has been calculated theoretically by the valence effective Hamiltonian (VEH) method and found to give reasonable agreement with experimental data. Assuming a conjugation length of four for the delocalised PMPY$^+$ (C 2p) π-electron, the band gap E_g is 3.0 eV [12] with the acceptor band typically 0.5 eV above the top of the valence band [13]. From equation (3) we can estimate that the electron affinity of PMPY to be about 2.4 eV which compares with 3.0 eV for PPY junctions [11]. The lower value seems reasonable since the methyl group should hyperconjugate the electron ring and thereby reduce the electron affinity. Figure 4(*a*) shows the band structure of the Ohmic contact for Au/PMPY$^+$ where no depletion layer forms in the junction irrespective of the semiconductor conditions.

Figure 3(*b*) shows the *I–V* behaviour of a heavily doped PMPY$^+$ film with indium ($\varphi_{In} = 4.1$ eV). The formation of a barrier may be explained in terms of the difference in work function ($\Delta\varphi \simeq 1.0$ eV) as illustrated by figure 4(*b*), where the Au/PMPY$^+$ interface forms a Ohmic contact. Interestingly the vacuum-deposited interface appears to be well behaved due to the absence of surface states significantly disrupting the band structure.

3.2. Lightly doped PMPY films with high-work-function metals

Figure 3(*c*) shows the *I–V* characteristics of a lighter doped Au/PMPY junction where a non-Ohmic contact occurs with slight rectification; the asymmetric response may be

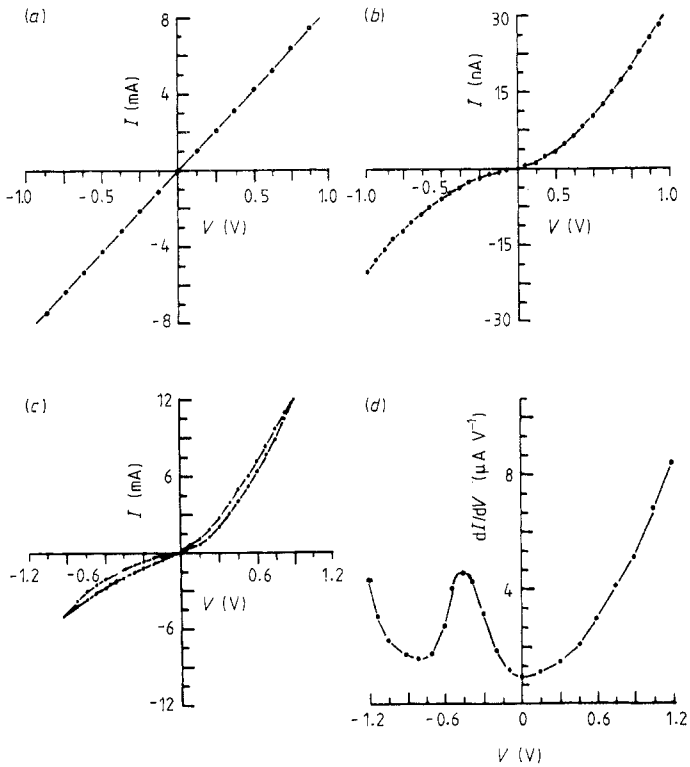

Figure 3. The observed junction behaviour for (*a*) Au/PMPY$^+$ (Ohmic contact), (*b*) In/PMPY$^+$ (Schottky barrier), (*c*) Au/PMPY (rectifier with hysteresis), (*d*) Au/PMPY (inversion layer, modulation).

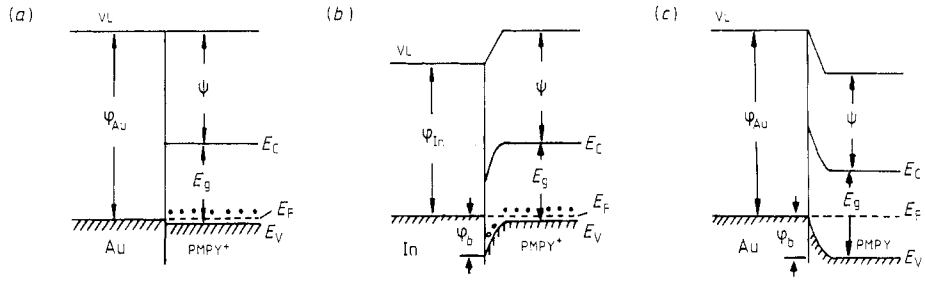

Figure 4. The band structure across junctions for (*a*) Au/PMPY$^+$ (Ohmic contact), (*b*) In/PMPY$^+$ and (*c*) Au/PMPY (undoped polymer). (VL ≡ vacuum level.)

caused by oxidation of the exposed polymer surface (prior to electrode deposition) creating a single Schottky barrier. Some hysteresis was observed at low-voltage ramp rates, probably caused by polarisation of perchlorate ions. More interestingly, the derivative of the *I–V* curve is shown in figure 3(*d*) for another lightly doped Au/PMPY junction. The modulation in conductivity may be caused by the Fermi level crossing the intrinsic level of the majority carriers producing inversion at a particular reverse bias voltage. Undoped Au/PMPY junctions show an *I–V* characteristic similar to that observed

for In/PMPY$^+$, a behaviour consistent with the Fermi level lying half-way between the valence and conduction band with $\varphi_b \simeq 1.2$ eV—see figure 4(*c*).

4. Analysis of the results

The observed barrier height of In/PMPY$^+$, $\simeq$0.9 eV, is close to that expected from the difference in work functions ($\Delta\varphi = 1.0$ eV), and indicates a negligible density of surface states on the *conducting* polymer.

These electrode-dependent results initialy suggest that the current is emission-limited and may be described by a Richardson–Schottky rather than a Poole–Frenkel mechanism, in which the current density J is related to the bias voltage V by $\ln J \propto \beta V^{1/2}$ [14], where β is a constant that is often related to the dielectric constant and film thickness. The experimental data give a tolerable fit to $\ln J \propto V^{1/2}$ at high fields ($>10^3$ V cm^{-1}) for lightly doped Au/PMPY and heavily doped In/PMPY$^+$ junctions. β was found to be $\simeq$4.1 for Au/PMPY and $\simeq$3.3 for In/PMPY$^+$ junctions. However, the observed values of β are larger than the expected theoretical values from a simple theory that suggests an accumulation of space charge, enhancing the field near the electrodes, while the leaky Schottky barrier obtained for In/PMPY$^+$ shows the inadequacy of a simple model.

The conductivity of conducting PMPY$^+$ was calculated from the Ohmic contact resistance and was typically 1×10^{-5} S cm^{-1}. The loss of conductivity compared with that of PPY (40 S cm^{-1}) is caused by the N-methyl group causing the tetramer to become non-planar and is similar to that observed elsewhere [3]. The activation energy of conducting PMPY$^+$, as defined from $kT^2\,\partial(\ln\sigma)/\partial T$, was found to be $\simeq$1 meV indicating a pseudo-metallic state.

To summarise, we have investigated the junction properties of poly(N-methylpyrrole) films with a high- and low-work-function metal across the intrinsic–extrinsic semiconductor transition. Electrochemically and vacuum-deposited metal/conducting polymer interfaces seem to behave similarly and the *I–V* characteristics may be broadly explained by Schottky barrier theory. Junction stability, consistency and ease of fabrication are potential advantages in their application as varistors where the barrier height is sensitive to chemical absorption [15].

Acknowledgments

The authors wish to thank Dr P Bartlett for many stimulating and useful discussions and Dr R Whitaker for help with the electrochemical preparation of samples.

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