The Schottky device based on doped poly(p-phenylene)

L. M. Goldenberg, V. I. Krinichnyi and I. B. Nazarova

Institute of Chemical Physics of U.S.S.R. Academy of Sciences, Chernogolovka, Moscow Region 142 432 (U.S.S.R.)

(Received March 18, 1991; accepted April 10, 1991)

Abstract

A sandwich-type Schottky element based on doped poly(p-phenylene) has been investigated. The doped poly(p-phenylene) was shown to give rectifying contact for indium. The Schottky device parameters have been evaluated from the voltage—current characteristics.

Introduction

Strong interest in conductive polymers has been generated by the possibility of their application as basic materials in the molecular microelectronic devices, such as field effect transistors, diodes, heterojunctions, etc. [1, 2]. In particular, the conductive polymers are likely to be perspective semiconductive materials and junctions to various metals concerning their application to solar cells [1—3]. The junctions produced with *n*- and *p*-type semiconductive contacts (n-p junction) and semiconductors joined to various metals having an appropriate work function (Schottky barrier) are the most common photovoltaic cells. The latter device is usually constructed with thin *trans*-polyacetylene, polythiophene or polypyrrole films and information on the Schottky barrier composed of poly(*p*-phenylene) (PPP) and metals is unknown so far.

This paper reports on the preparation of a sandwich-type device with Schottky barrier between PPP doped by BF_4^- counterions and indium, as well as on junction characteristics.

Experimental

PPP films were obtained by electrochemical polymerization in the CH_2Cl_2 —Bu₄NBF₄—oleum-benzene system on a Ti electrode under constant current conditions (7 mA/cm²) as described in ref. 4. The film thickness, after washing off by CH_2Cl_2 and drying, was approximately 8 μ m and the d.c. conductivity was 5×10^{-4} S/cm at room temperature.

Platinum and indium foils with PPP film between them were used for the sandwich-type element preparation. A pressure-type element of $7x10^{-2}$ cm² area was used for the measurements of current-voltage characteristics at room temperature and ambient pressure.

Results and discussion

The dark current—voltage characteristic of the sandwich-type device mentioned above is shown in Fig. 1. As seen from the Figure, for the indium electrode, the sandwich-type device possesses an unsymmetrical, strongly non-ohmic rectifying characteristic typical of a Schottky barrier between a metal and *p*-type polymeric semiconductor. A rectification ratio between forward bias current and reverse current at 1 V was obtained as approximately $J_F/J_R = 20$. Note that the platinum electrode gives an ohmic characteristic. The above current—voltage dependence is observed to have an exponential dependence up to $U_F = 1$ V, indicating that the device resistance is not higher than the combination of a polymer bulk resistance, a barrier indium electrode sheet resistance and the resistance due to the back ohmic contact.

According to the thermoionic emission model, the relationship between the forward current density and the voltage for the Schottky device may be written as

$$J_{\rm F} = J_0 \exp(q U_{\rm F}/nkT) \tag{1}$$



Fig. 1. Room temperature dark current density vs. applied voltage rectification characteristic for the In/PPP/Pt sandwich-type device.

where J_F is the current density, J_o is the reverse leakage (saturation) current density of the junction, q is the electron charge, U_F is the forward bias voltage, n is the ideality factor, k is the Boltzmann constant and T is the absolute temperature.

The J_o value may be estimated from

$$J_0 = A^{**}T^2 \exp(-qF_{\rm B}/kT) \tag{2}$$

where $A^{**} = 4\pi qrm^*kh^{-3}$ is the modified Richardson constant, Φ^{B} is the effective barrier seen by the holes in the semiconductor, m^* is the carrier effective mass and *h* is the Planck constant.

To estimate the saturation current density, J_o , the semilogarithmic plot of forward current density versus forward voltage (Fig. 2(a)) was used. From the extrapolation of the linear plot to zero bias voltage the saturation current density



Fig. 2. Semilogarithmic plots of current density vs. $U_{\rm F}(a)$ and $(U_{\rm c}-U{\rm R})d^{0.25}(b)$ for the In/PPP/Pt sandwich-type device at room temperature.

value of $J_0 = 4.7 \times 10^{-7} \text{ A/cm}^2$. So, assuming $m^* = m_e$ and subsequently $A^{**} = 120 \text{ A/(K}^2 \text{cm}^2)$, the barrier height $F_B = 0.78 \text{ eV}$ was determined from eqn. (2).

On the other hand, the latter value can be calculated from the formula [5] $E_{\rm T} = E_{\rm T} - E_{\rm T} + M_{\rm T}$ (3)

$$F_{\rm B} = E_{\rm G} - F_{\rm M} + \chi_{\rm S} \tag{3}$$

where $E_{\rm G}$ is the bandgap energy, $\Phi_{\rm M}$ is the work function of the indium and $\chi_{\rm S}$ is the electron affinity of the semiconductor. Using theoretical values of $F_{\rm M} = 4.12$ eV for indium [5], $E_{\rm G} = 3.5$ eV and $\chi_{\rm S} = 2.8$ eV for PPP with aromatic rings tilted with respect to each other by 22° [6], $\Phi_{\rm B} = 2.18$ eV was determined from eqn. (3).

The reason for the difference between the theoretically calculated and experimentally obtained $\Phi_{\rm B}$ values possibly lies in the supposition that the saturation current density $J_{\rm o}$ might be composed of various current densities via thermoionic emission, diffusion, tunnelling and other parallel processes, which occur simultaneously in real systems. On the other hand, the influence of the oxygen in air, current crowding, high series resistance of the quasineutral regions of the sample or the profound surface states effect influence the device characteristics, e.g., its quality. In fact, the quality factor, n = 6.45, was calculated using $\Phi_{\rm B} = 0.78$ eV from eqn. (1) for the device, whereas this value for an ideal diode must be equal to unity.

The reverse bias current density J_R of the Schottky device is well fitted by the following relationship [7]

$$\ln J_{\rm R} = k_{\rm s} (U_{\rm c} - U_{\rm R})^{0.25} \tag{4}$$

typical for Schottky barriers. Here, k_s is the semiconductor constant, U_c and U_R are the contact and reverse potentials, respectively. The linearity of the reverse bias current density versus $(U_c - U_R)$ dependence shown in Fig. 2(b) (the theoretical value of $U_c=1.48$ eV for PPP [6] was used) demonstrates once again the Schottky characteristic of the constructed device. The constant, $k_s=-14.3$ A/(cm²V⁰²⁵), and the current density at zero bias, $J_R^0 = 1.4 \times 10^{-7}$ A/cm² for PPP, were determined from the data of Fig. 2(b). The latter value is close to J_o calculated above. This fact demonstrates that the approach to interpret the obtained current—voltage characteristics of the constructed sandwich-type polymeric device as distinctive for Schottky barriers is correct.

Conclusions

It has been observed that the In/PPP/Pt diode has unsymmetrical, strongly non-ohmic rectifying characteristics. The contact between PPP film with an intermediate dopant level and indium was observed to form a Schottky barrier. To improve the parameters of this device further studies (i.e., analysis of capacitance-voltage, temperature and other dependences) are necessary. This is a consideration for further investigations.

Acknowledgements

This work is supported in part by a Grant-in-Aid for Youth Scientific Research from the U.S.S.R. Academy of Sciences.

References

- 1 H. Kuzmany, M. Mehring and S. Roth (eds.)i *Electronic Properties of Polymers and Related Compounds, Springer Series in Solid State Sciences*, Vols. 1-3, Springer, Berlin, 1985-1989.
- 2 T. A. Skotheim (ed.), *Handbook of Conducting Polymers*, Vols. 1 and 2, Marcel Dekker, New York, 1986.
- 3 H. Koezuka, K. Hyodo and A. G. MacDiarmid, J. Appl. Phys., 53 (1985) 1279.
- 4 L. M. Goldenberg, I. B. Nazarova, O. N. Efimov, R. N. Lyubovskaya, O. S. Roschupkina and A. N. Titkov, *Synth. Met.*, in press.
- 5 J. Kanicki, in T. A. Skotheim (ed.), *Handbook of Conducting Polymers*, Vol. 1, Marcel Dekker, New York, 1986, p. 543.
- 6 J. L. Bredas, in T. A. Skotheim (ed.), *Handbook of Conducting Polymers*, Vol. 2, Marcel Dekker, New York, 1986, p. 859.
- 7 E. H. Rhoderick, Metal-Semiconductor Contacts, Clarendon Press, Oxford, 1980.