Application of conducting polymer technology in microsystems

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Abstract

Conducting polymers are a new type of organic material that offer enormous potential for application within the field of microsystems. In this paper we review the basic properties of conducting polymers and discuss their application in electronic, mechanical and (bio)chemical microsystems. For instance, we have found that thin films of poly(pyrrole)/decanesulfonate have both a low friction coefficient (ca. 0.1) and wear rate (ca. 1 nm cm^{-1}) that are similar to values observed for PTFE, yet possess relatively high electrical and thermal conductivities. In addition, conducting polymers can be readily electrodeposited onto planar or curved micromechanical structures, such as microslideways, micromotors or microturbines, to provide a bearing material of superior performance to standard micro-engineered materials (e.g. Si, SiO$_2$, Si$_3$N$_4$) and better processability than PTFE. In addition, conducting polymers can be used as gas-sensitive films in microelectronic devices. They have been shown to have a rapid, reversible ppm sensitivity to polar organic compounds (e.g. alcohols, ketones, aldehydes and fatty acids) without interference from common gases such as CO$_2$, CO, CH$_4$ and N$_2$. Conducting polymers are currently being used in commercial electronic noses, and integrated microsystems are being realised with the advent of custom microsensor array devices and application-specific integrated circuit chips.

Keywords: Microsystem; Conducting polymer; Application

1. Introduction to conducting polymers

Conducting polymers were first identified in the 1980s and belong to a class of organic materials which can be electrochemically synthesised from suitable heterocyclic and aromatic heterocyclic monomers (for a review, see Ref. [1]). Electronically conducting polymers have a number of interesting features that make their application in microsystems particularly attractive. First, there is considerable variability in the choice of their chemical structure. Fig. 1 shows the structure of some common monomers and counter-ions (i.e. dopants) that are being used to synthesise conducting polymers. The physical and chemical properties of conducting polymers films are not only determined from their chemical structure but also from the conditions under which they were deposited (e.g. solvents, oxidation potential). This high degree of flexibility provides an enormous range of properties and hence potential applications within the fields of microsensors, microactuators and hence microsystems.

2. Thin film deposition

Conducting polymers can be grown from a wide range of monomers (e.g. pyrrole) in a range of solvents (e.g. water) and in the presence of a number of counter-ions (e.g. an alkane sulfonate). In a three-electrode electrochemical cell, the monomer undergoes several reactions until the polymer becomes insoluble, precipitates out onto the working electrode in the form of a thin film. Polymers can be electrochemically grown in a number of ways: potentiostatically, galvanostatically or by a cycled potential. Fig. 2 shows a typical plot of the deposition process in which a polymer is grown by cycling the applied voltage (ten times relative to a standard calomel electrode) between positive and negative values at 50 mV s^{-1}. The peaks that are visible represent the oxidation and reduction of the polymer as the counter-ion moves into and out of the polymer film as illustrated. Measurement of the total charge passed gives an estimate of the film thickness and the final potential controls the doping level (oxidation state) of the polymer between conducting and insulating.
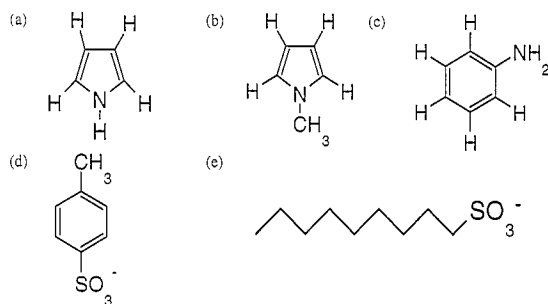
Fig. 1. Several common monomers (a) pyrrole, (b) N-methylpyrrole, (c) aniline and counter-ions (d) toluenesulfonate, (e) nonanesulfonate used to synthesise electronically conducting polymers.

A description of the basic set-up and electrochemical synthesis of poly(pyrrole) can be found elsewhere [2].

The deposition of conducting polymers is well controlled because they can be electrodeposited reliably onto metallisation areas (ranging from 0.01 mm² to 10 cm²) at various thickness (e.g. 0.1–10 μm). The deposition area can be defined by a standard resist provided that it can withstand the various solvents and electrolytes used during deposition. Conducting polymers can thus be readily deposited onto microlithographically defined metallisation areas on silicon wafers or devices. Fig. 3a shows an apparatus that has been designed to deposit conducting polymers onto silicon devices [3]. The electrochemistry takes place in a single drop between the end of a micropipette and on the device surface as illustrated in Fig. 3b. This apparatus permits the sequential growth of a set of different polymers on a single microdevice. The process can be accelerated through the use of an array of pipettes, or through automation. Some conducting polymers can also be dissolved in a solvent and spun down onto a wafer or vapour phase deposited [4] for the mass production of microelectronic devices. Electrodeposition not only
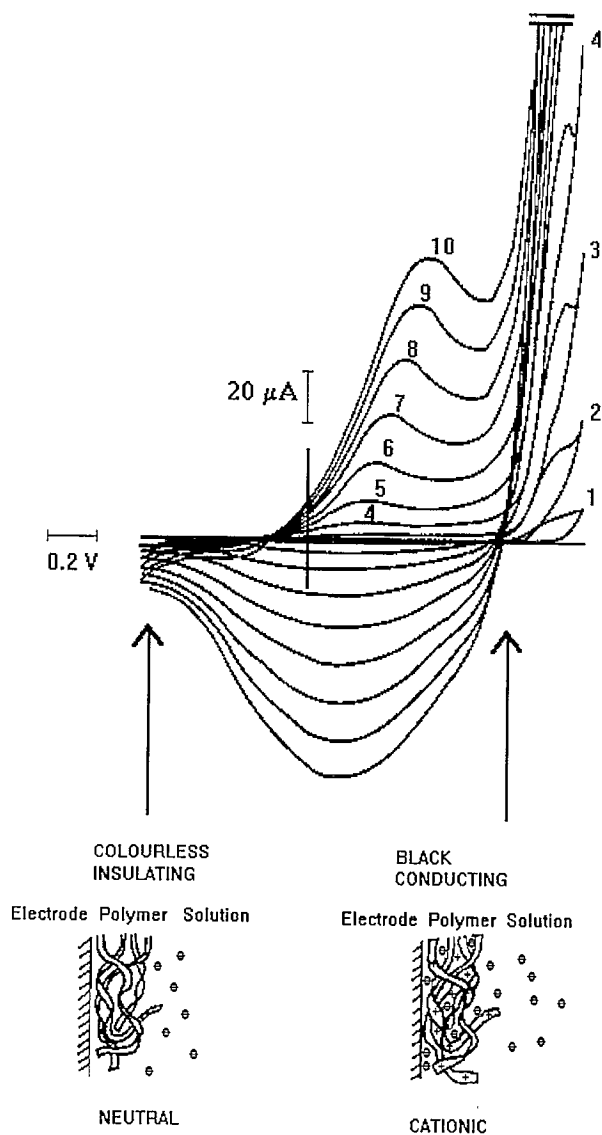

Fig. 2. Typical cyclic voltammogram for the deposition of a thin film of poly(pyrrole) on a gold working electrode, and a schematic representation of the film in its neutral and cationic states the film which defines its oxidation state [2].
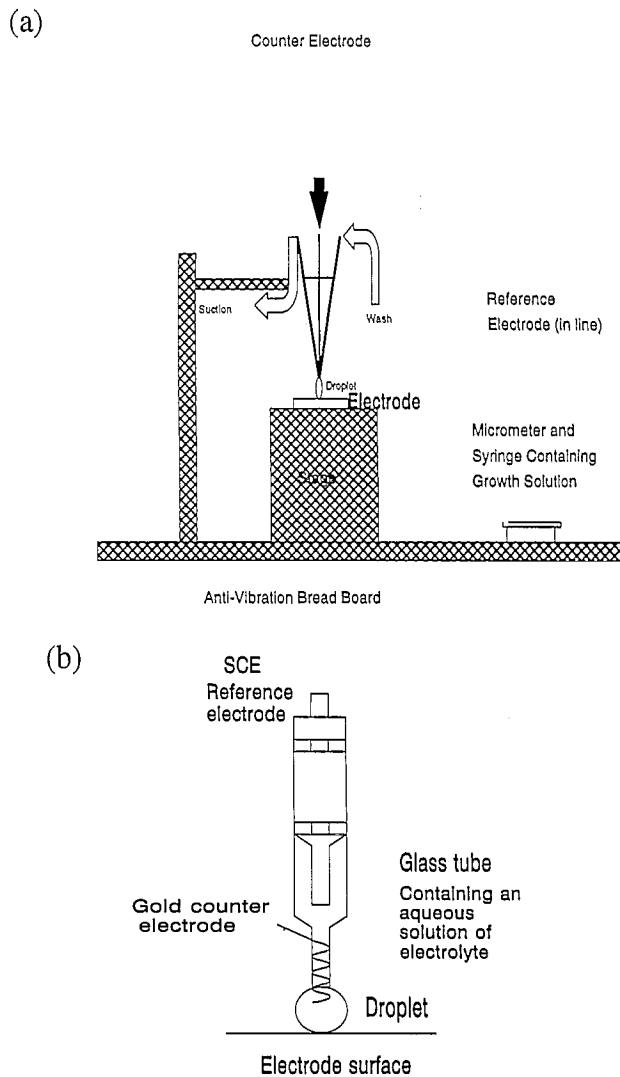

Fig. 3. (a) General apparatus suitable for the on-line microdeposition of conducting polymers onto silicon or other microdevices and (b) micropipette arrangement for electrochemical cell [3].
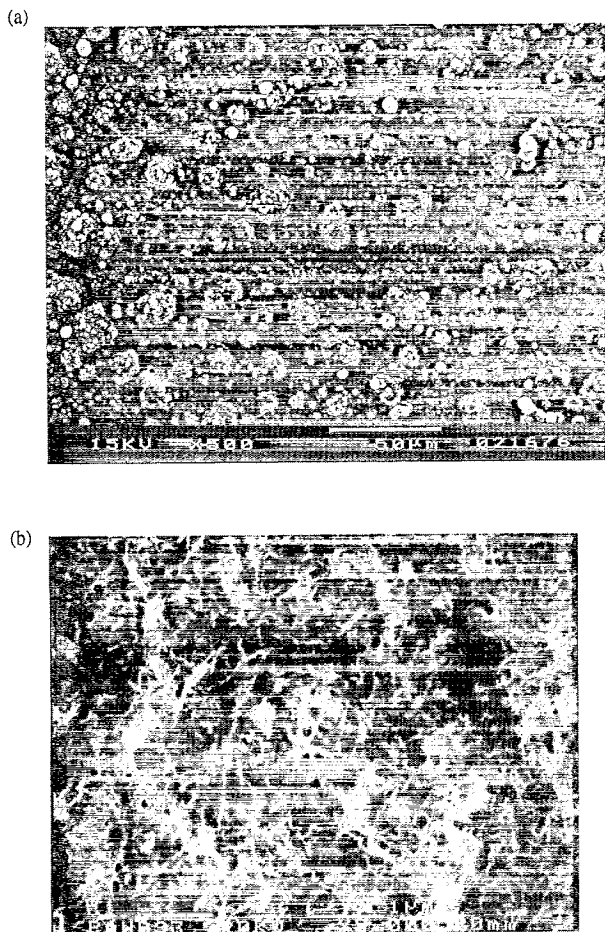
Fig. 4. Scanning electron micrographs of (a) poly(pyrrole)/butanesulfonate, and (b) poly(aniline)/butanesulfonate (n.b. magnifications are different).

permits the selective coating of an area in a single controlled process, but also can deposit films onto convex, concave and even re-entrant surfaces. Polymer deposition takes place at ambient temperatures and so it will not interfere with any integrated electronics or active materials employed within the microsystem.

3. Microstructure and nanostructure

The microstructure of a conducting polymer depends upon the chemical structure, that is the monomer, counter-ion and solvents used, the deposition conditions (e.g. growth current density) and the nature of the substrate [2]. Scanning electron and tunnelling microscopes can be used to show the typical microstructure of conducting polymers [5]. For example, Fig. 4 shows micrographs of poly(pyrrole) and poly(aniline) films grown in an aqueous solution of butane sulfonic acid. Firstly, differences are clearly visible between the two monomers with poly(pyrrole) tending to produce 5–30 μm sized spheroids and poly(aniline) tending to produce a smooth "honeycomb" microstructure. Second, the difference in the size of the counter-ion affects the microstructure of the film. Very smooth conducting polymer films can also be obtained by the suitable choice of the counter-ion. For instance, ultra-smooth poly(pyrrole) films can be obtained by substituting the alkane sulfonate for an alkane phosphonate counter-ion. Fig. 5 shows atomic force micrographs of both poly(pyrrole)/toluenesulfonate and poly-(pyrrole)/methanephosphonate. These show a surface roughness R_q reduced in one case to the nanometric scale (ca. 5 nm), and would appear featureless on a scanning electron micrograph. The samples were grown on a highly polished flat glass substrate and are about 1 μm in thickness; it was found that results obtained from AFM were superior to those from STM.

In conclusion conducting polymers can have radically different morphologies which are mainly determined by their chemical structure rather than other parameters such as the surface roughness of the substrate. This in turn leads to very different physical properties which can be
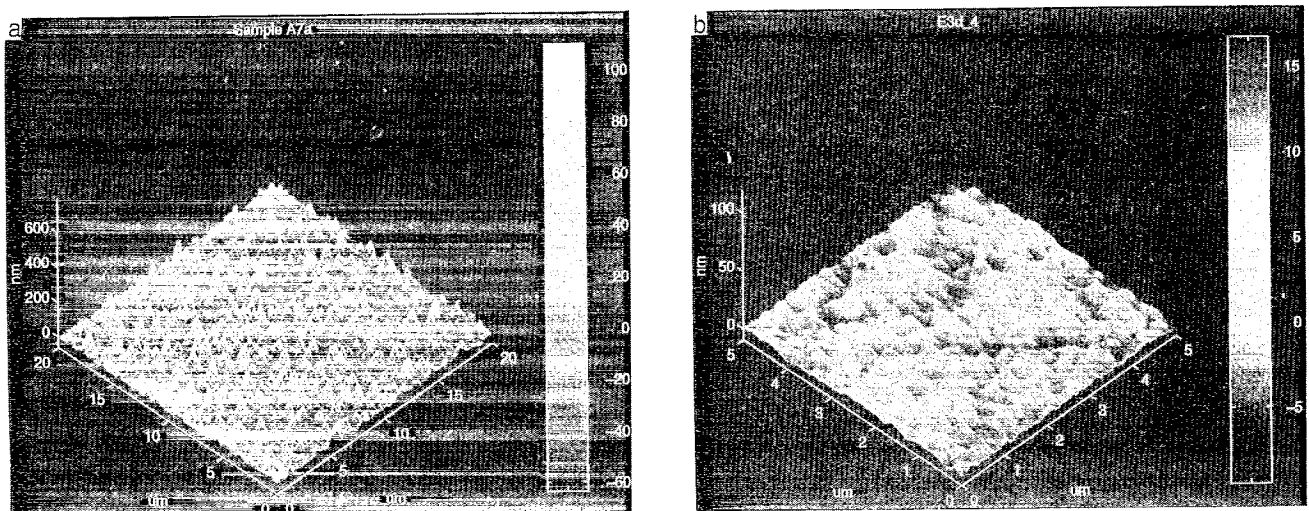

Fig. 5. Atomic force micrographs of (a) poly(pyrrole)/toluenesulfonate, and (b) poly(pyrrole)/methanephosphonate.

Table 1

Electronic properties of poly(pyrrole) and some common materials[a] (values taken at 300°K) [2,6]

Property	Material					
	Poly(pyrrole)	Perspex	Si	GaAs	Al	Au
Electrical conductivity (S cm^{-1})	10^{-5} to 10^{+2}	$<10^{-15}$	4×10^{-4}	1×10^{-8}	$3.8 \times 10^{+5}$	$4.9 \times 10^{+5}$
Temperature coefficient of resistance (10^{-3} K^{-1})	−1 to −10	–	+8	–	+4.3	+3.4
Work function (eV)	4.9	–	5.0	–	4.2	5.1
Thermopower (μV K^{-1}) versus Pt	40 to 5	–	−100	–	5.3	9.2
Band-gap (eV)	2.7	–	1.11	1.35	–	–
Relative permittivity	8	3	11.7	12	–	–

[a]Data taken from Ref. [6].

exploited in a wide range of electronic, mechanical and bio(chemical) microdevices as described below.

4. Electronic properties

The electrical properties of conducting polymers have been widely reported [1]. In the doped state (e.g. the oxidised state for poly(pyrrole)) they are generally good conductors with an electrical conductivity that can approach that of copper but typically lies in the range of 10^{-5} to 10^{+3} Ω^{-1} cm^{-1}. Table 1 lists the electronic properties of some conducting polymers and includes some conventional materials for comparison.

Previous work has shown that the electrical conductivity of poly(pyrrole) is affected by the pK_a of the conjugate acid of carboxylate counter-ion used to dope the films [7]. Here we show that the electrical resistivity of conducting polymers formed of poly(pyrrole) and poly(aniline) depends upon the length of the alkane sulfonate counter-ion (see Fig. 6a). The resistance reaches a minimum at a chain length of eight to nine. The temperature-dependence of the electrical resistance also depends upon the chain length. Its functional form is usually described by a fractional power law that arises from a variable range hopping model [8], but it can be reasonably well approximated over a limited temperature range by the standard equations of

$$R = R_0 \exp\left(\frac{-E_a}{kT}\right) \quad \text{and} \quad R = R_0\left(1 + \alpha_1(T - T_0)\right) \quad (1)$$

where E_a is the activation energy, k is Boltzmann's constant, α_1 is the linear temperature coefficient of resistance, and R_0 and T_0 are constants. Fig. 6b shows the effect of chain length upon the activation energy. Clearly poly(aniline) films exhibit a lower temperature dependence that the poly(pyrrole) with a minimum again observed for a chain length of between 8 and 9. The temperature coefficient α has a typical value of 10^{-4} °C^{-1} that is comparable with a metal (see Table 1). Clearly, the temperature coefficient of the polymer is a function of its chemical structure and so it may be selected to match other device materials.
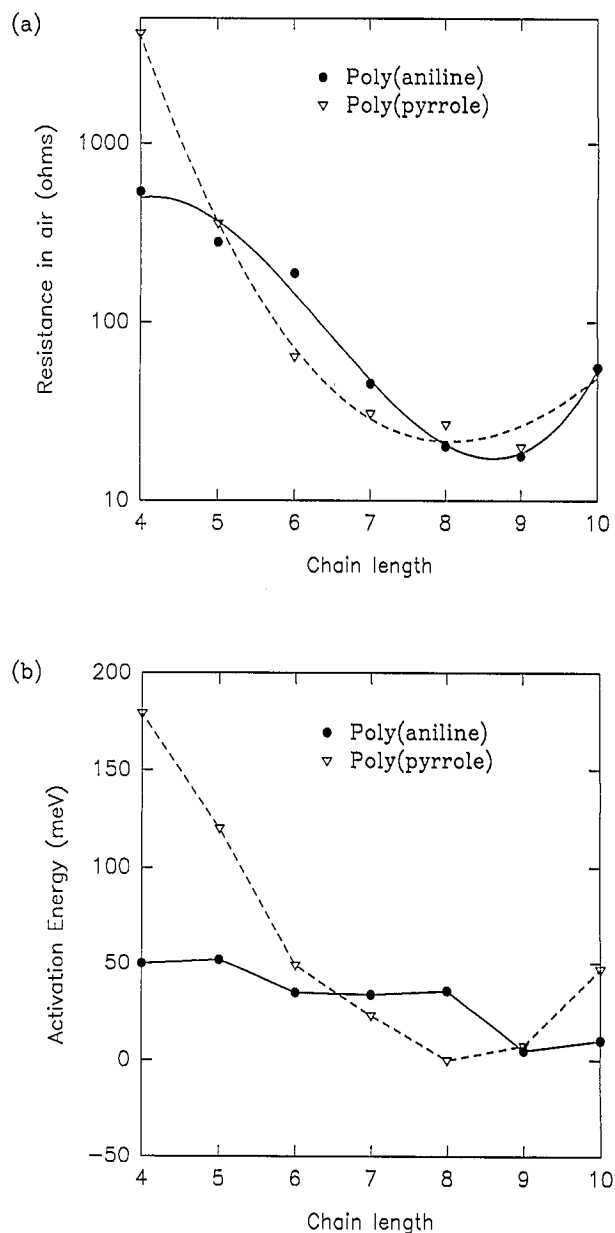

Fig. 6. Effect of chain length upon (a) the electrical resistance and (b) temperature coefficient of alkanesulfonic acid conducting polymers (device aspect ratio is 125).
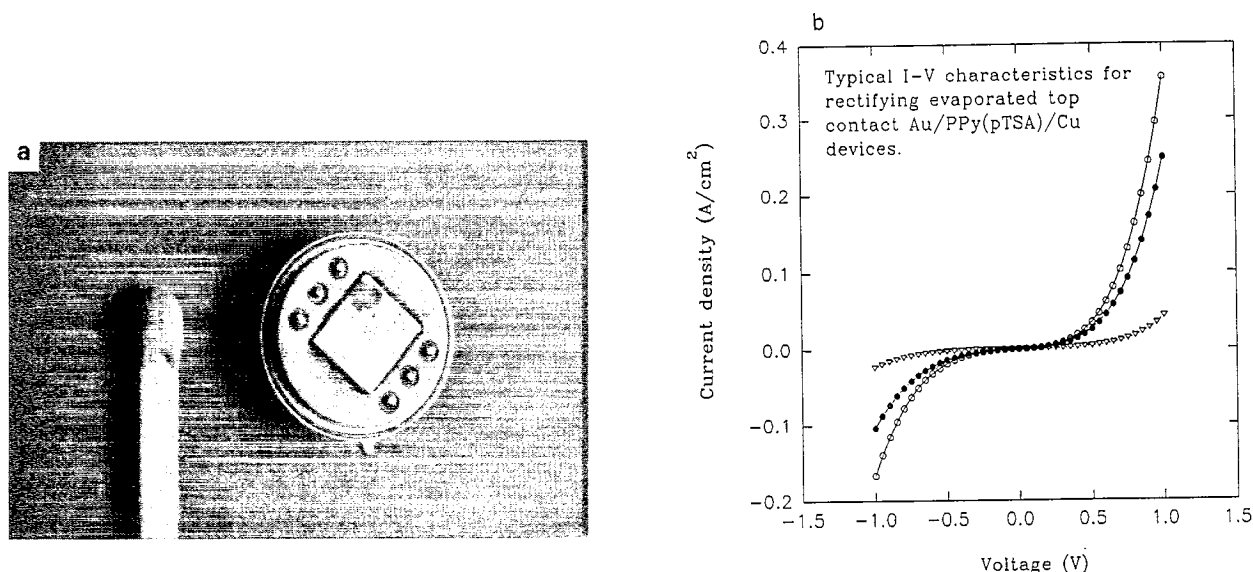
Fig. 7. (a) Photograph of a poly(pyrrole)pTSA/copper Schottky diode and (b) its I–V characteristic [12].

5. Conducting polymers in microelectronic devices

Conducting polymers have also been studied for their application as electrically conductive coatings, for example, anti-static coatings of packaging materials, however care is needed because some polymers are environmentally sensitive and can be oxidised in air or attacked by air-borne gases. In fact, this effect has been successfully utilised in chemical sensors (see Section 7).

Conducting polymers can be described as organic semiconductors in which the type and level of doping is defined by the polymer and its final oxidation state. They have been studied over a number of years for application in microelectronic devices, such as diodes [9], transistors [10] and optoelectronic devices [11]. Much work has been reported on their application within organic diodes with device characteristics varying in quality. For example, Fig. 7 shows a copper-poly(pyrrole)/ toluenesulfonate junction and its I–V characteristic [12]. The low work function metal forms a weak rectifying junction with the polymer while gold forms an ohmic contact. After many years of research, conducting polymers are just starting to be used in organic transistors with a certain degree of commercial success. Although their performance (e.g. switching time) cannot compete with conventional semiconductor materials, they do offer a weight advantage that can be important in special aerospace applications.

6. Conducting polymers in micromechanical actuators

Relatively little has been published on the mechanical properties of conducting polymers. Table 2 illustrates some of the published data on typical conducting polymers, and compares the results with some other materials.

The thermal conductivity compares favourably with conventional (non-conducting) materials which can be of benefit in mechanical components while its strength and density are similar to other materials.

The most promising mechanical application of conducting polymers is perhaps their use as a bearing material in slideways, micromotors, etc. [13]. The tribological properties of conducting polymers have been studied at Warwick University for possible use in low friction bearings. Fig. 8 shows the arrangement of an apparatus that has been built to measure the static and dynamic fric-

Table 2

Mechanical properties of poly(pyrrole) and some common materials (values taken at 300°K) [2,6]

| Property	Material							
	Poly(pyrrole)	Perspex	PTFE	Si	SiO$_2$	Si$_3$N$_4$	Al	Au
Density, ρ_m (kg m^{-3})	1500	1190	2200	2330	1544	3440	2699	19320
Melting point, T_{mp} (°C)	200	350	260	1410	1880	1900	660	1064
Thermal conductivity, κ (W m^{-1} K^{-1})	1–100	0.2	0.24	168	1.4	9–30	140	318
Specific heat capacity, c_p (J K^{-1} kg^{-1})	1000	1500	840	678	730	600–800	904	129
Linear expansivity, α_l (10^{-6} K^{-1})	–ve	85	100	2.6	7–12	0.8	23	14
Young's modulus, E (GPa)	–	3	0.34	190	380	380	70	78
Yield strength, Y (GPa)	–	0.05	0.02	6.9	14	14	0.05	0.20
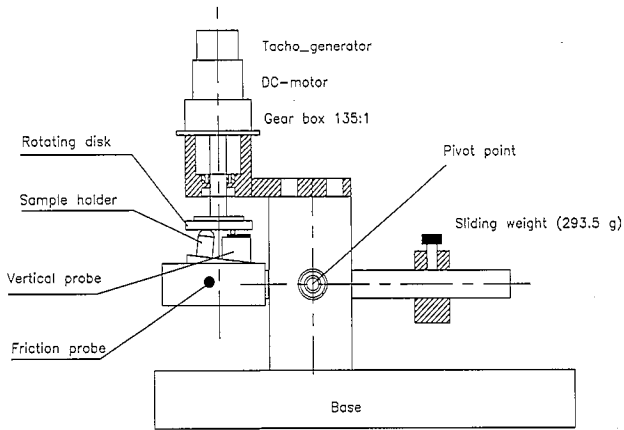
Fig. 8. Apparatus to measure the tribological properties of conducting polymer bearings [14].
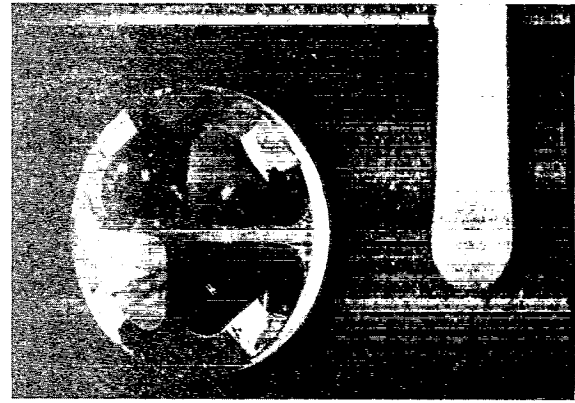

Fig. 9. Test specimen for a low speed conducting polymer bearing. There are four poly(pyrrole) coated areas on the glass planoconvex lens.
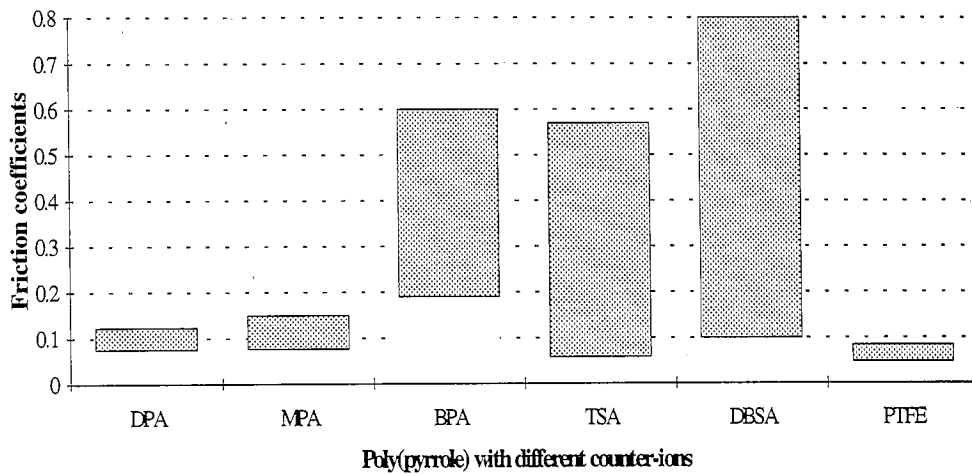

Fig. 10. Friction coefficients observed for various conducting polymer films.

tion coefficient and wear rate of conducting polymers at sliding speeds of 0.1–100 mm s^{-1}. Moderate loads of 0.1–5 N can be applied by the pin-on-disc arrangement with tractional forces measured by an LVDT transducer to a resolution of 5 mN [14]. Conducting polymers (black) were electrodeposited onto thin (250 nm) gold electrodes which had been thermally evaporated onto the surface of commercial convex glass lenses as shown in Fig. 9. A
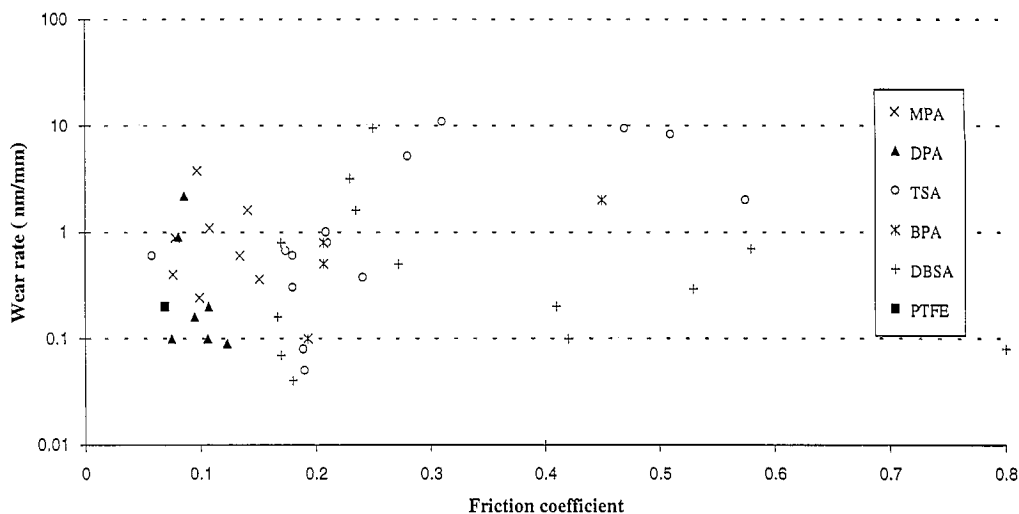

Fig. 11. Plot of wear rate versus friction coefficient for various conducting polymer films.
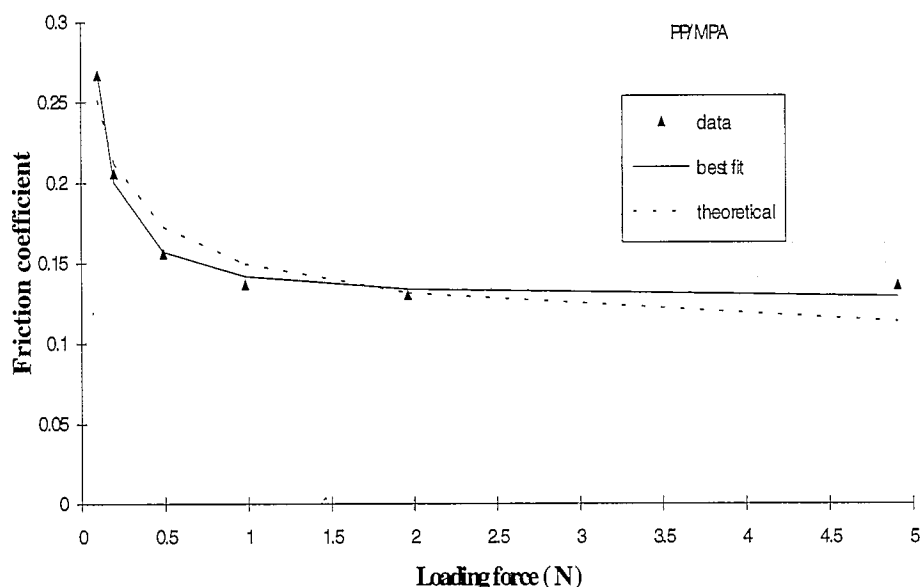
Fig. 12. Characteristic effect of load upon the friction coefficient of a conducting polymer.

large number of polymers have been tested with different monomer, counter-ion, film thickness, oxidation state, and load and compared with PTFE. Fig. 10 shows the range of friction coefficients observed for poly(pyrrole) grown under different conditions against the counter-ion used to dope the film. Thin poly(pyrrole)/decanephosphonate films exhibited a low friction coefficient of about 0.1 with a wear rate similar to PFTE of 0.1 nm mm^{-1}. Fig. 11 shows a plot of the observed wear rate against friction coefficient for all the conducting polymer films measured so far. Clearly, this is an encouraging result as a low friction coefficient coupled to a low wear rate makes the polymers suitable for use as a bearing material. The values of the friction coefficient are much better than those observed for conventional micromechanical materials such as SiO_2 and poly-Si. As expected in classical theory, there appears to be a correlation between the surface roughness and tribological properties with ultra-smooth films, as seen from AFM studies (see Fig. 5), giving the best performance.
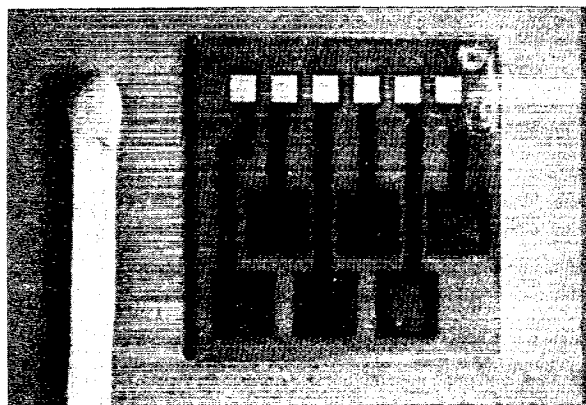
Fig. 12 shows the characteristic effect of the loading force upon the friction coefficient for poly(pyrrole)/methanephosphonate. The theoretical fit is according to Hertzian theory,

$$\mu = S_0 \pi \left(\frac{3R}{4E} \right)^{2/3} L^{-1/3} + \alpha \qquad (2)$$

where S_0 is a pressure-independent shear constant and α is the pressure sensitivity of the shear strength [15], E is the
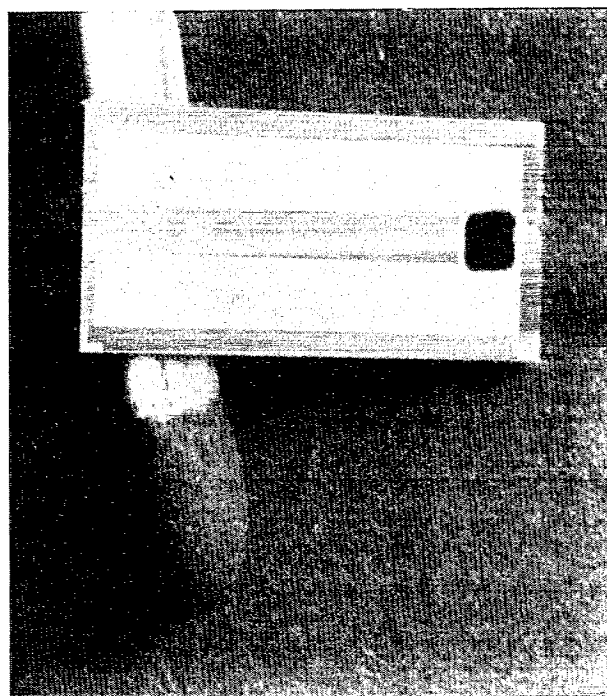

Fig. 14. Conducting polymer resistive microsensor for odour detection. The black polymer is defined by a thin resist which acts as a passivation layer.

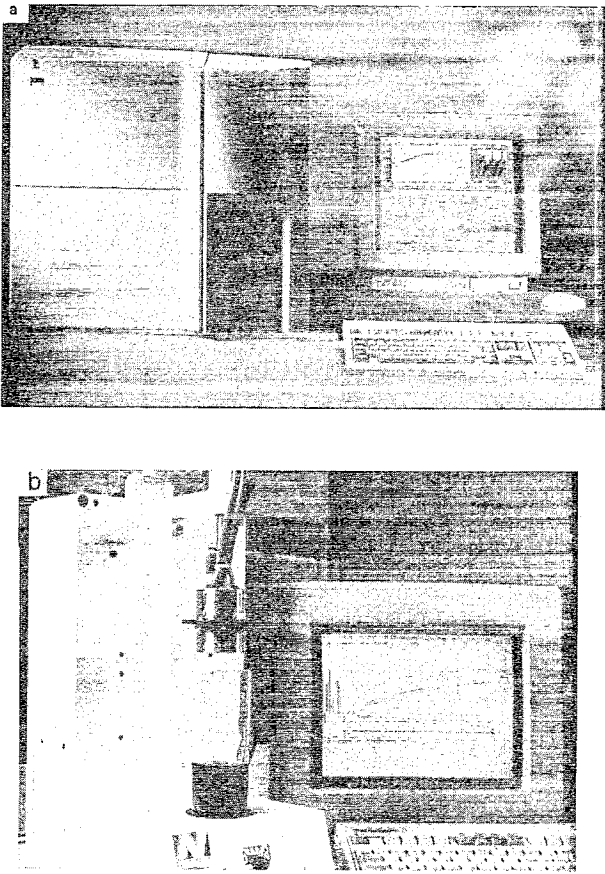Fig. 13. Test specimen for a high speed conducting polymer bearing.

Fig. 15. Two commercial electronic noses which exploit conducting polymer technology: (a) 20 polymers in an electronic nose made by Aromascan Plc (UK) and (b) 12 polymers in an electronic nose made by Neotronics Scientific Ltd (UK).

composite elastic modulus, R the radius of the specimen, and L is the normal load. The curve does not follow pre-
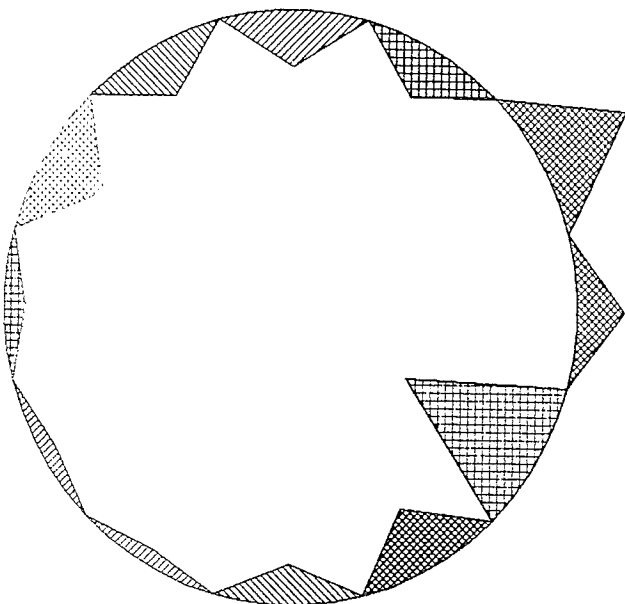
cisely the $L^{-1/3}$ law but is closer to an inverse law (best fit).

Micromotor bearings require good tribological properties at much higher speeds than discussed here. A new apparatus has been designed to measure friction and wear at speeds of up to 10 000 rev. min^{-1}. The test specimen has been redesigned and is prepared by conventional UV lithography upon a flat substrate (see Fig. 13). The high speed test specimen consists of a set of six separately addressable conducting polymers on thin gold electrodes on an alumina tile (or silicon wafer). This work is currently in progress and the results are not available.

Conducting polymers are generally well behaved in clean aqueous or organic solutions. Thus, they could be used in microfluidic systems for low friction parts in microvalves or microturbines. However, conducting polymers can be sensitive to the presence of ions which could change the doping level of the film and hence its physical properties. These types of polymers can be used in other applications which require small mobile counter-ions (e.g. organic batteries).

7. Conducting polymers in bio(chemical) microsensors

It is well known that the electronic properties of certain conducting polymers can be modified by the presence of a gas or vapour. Consequently, conducting polymers have been used to make a number of chemically sensitive microelectronic devices such as resistors [16], diodes [17], transistors [18], and coatings for quartz crystal microbalances [19]. Conducting polymer technology offers several benefits over other gas-sensitive materials. First, the reaction process takes place at room tem-

Fig. 16. Difference plot of fresh and stale crisps using a conducting polymer electronic nose (from Neotronics Scientific Ltd, UK).
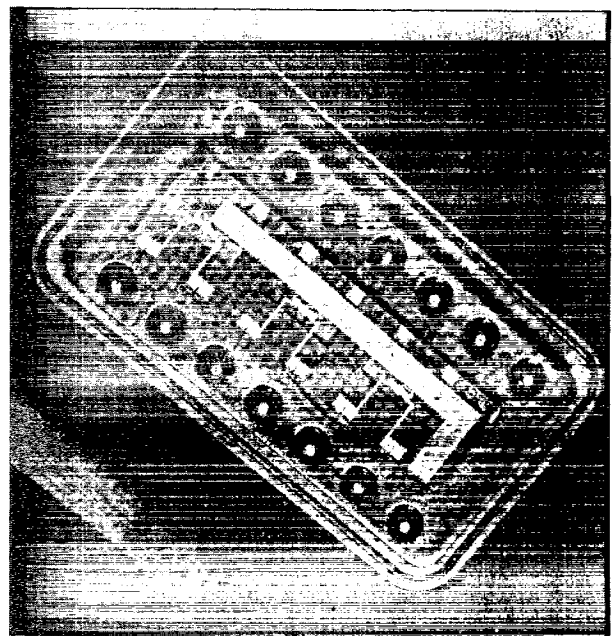

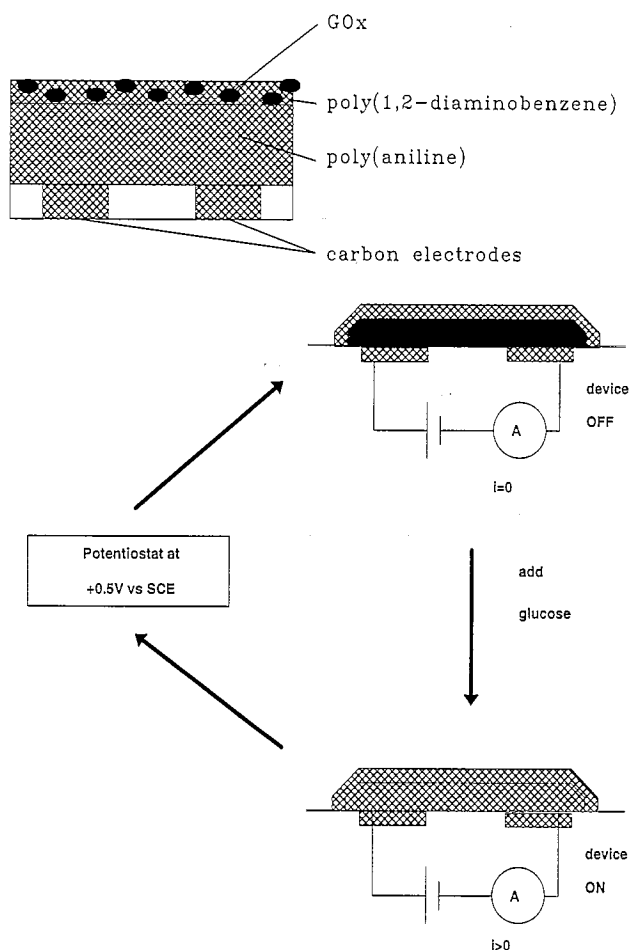Fig. 17. Microsensor array device with conducting polymer resistive elements [23].

Fig. 18. Application of a conducting polymer in a biosensor: (a) device layout and (b) response to glucose concentration [24].

ducting polymers are being used in electronics noses where an array of non-specific sensors is coupled to a pattern recognition system [21]. In this case the non-specificity gives the device a wide range of responses to differing smells such as coffees, beers, wines etc. Conducting polymers are currently exploited in the two commercial electronic noses shown in Fig. 15. The main applications of this technology have been in the food industry (e.g. freshness of food, maturing of cheese, characterisation of oils and taints) for beverages (e.g. roasting of coffees, quality of Scotch whiskeys, wines, orange juice etc.) as well as petrochemicals and pharmaceuticals. For example, the instrument can be used to discriminate between the different smells arising from fresh and stale crisps, as can be seen from the difference plot in Fig. 16.

Fig. 17 shows a microsensor array onto which conducting polymers have been successfully using the apparatus described above (Fig. 3). This micromachined device can be run at 40°C with minimal power consumption and can form part of a miniature instrument (for details see [23]). Such a micronose could be manufactured at low cost and used to measure air-borne pollutants such as benzene or it could used to replace the flame ionisation detector in a miniature gas chromatograph.

Finally, electronically conducting polymers combine a number of properties which make them attractive materials for application in an enzyme-based biosensor. First, biosensors do not require as high an electrical conductivity as other polymer sensors which extends the flexibility of chemical design. Secondly, many conducting polymers can be used in neutral aqueous solutions which is the condition required for enzyme activity and finally the polymers can be reversibly doped giving a large change in resistivity [24]. Fig. 18 shows the structure of a microelectrochemical switch in which glucose oxidase is immobilised in an electropolymerised layer of 1,2-diaminobenzene on top of a poly(aniline) film. On addition of glucose, the polymer is reduced and so switches from its insulating form to its conducting form in about 10 s, the polymer can then be returned to its oxidised state by applying a voltage of +0.5 V versus SCE. The response saturates at high glucose concentrations as can be

perature rather than elevated temperatures such as 300–400°C for metal oxides, or 150–200°C for phthalocyanines and catalytic gate MOSFETs. This means that an array of conducting polymers does not have a high power consumption and can be readily used in a handheld portable instrument. Perhaps the most successful application has been the use of a conducting polymer as a variable resistor in which the gas entering the film modifies the bulk resistance of the device. Fig. 14 shows the basic arrangement of a conducting polymer chemoresistor. The polymer has been grown across the $10\,\mu m$ gap between two gold electrodes on a SiO_2/Si substrate [20]. The active area of $1.25\ mm^2$ has been defined by a standard photoresist with special conditioning to make it stable in organic and aqueous solutions. Conducting polymers have been shown to respond reversibly in seconds and to be sensitive at the ppb to ppm level to volatile organic compounds such as alcohols, ketones, aldehydes, and fatty acids [21]. They have also been shown to respond to low levels of reactive gases such as ammonia and NO_2. [22]. However, the poor specificity of conducting polymers and a sensitivity to humidity have limited their commercialisation as a gas sensor to date. Instead, con-
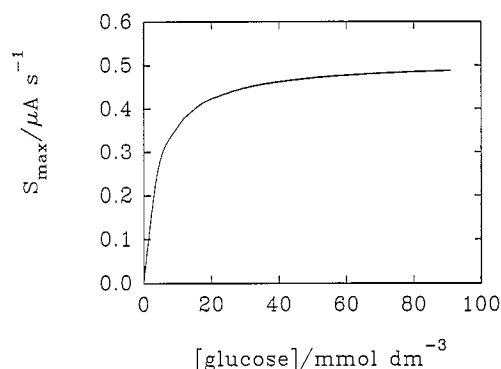

Fig. 19. Response of a conducting polymer based glucose switch [24].

seen from Fig. 19 where the change in drain current reaches a peak value of about 0.5 μA s^{-1}.

8. Conclusions

During the past 10 years conducting polymers have been studied extensively in laboratories all over the world. Their basic attraction lies in their designer friendliness which permits a wide range of applications since their properties can be modified readily. Their desirability is enhanced for many engineering applications because they have both a low friction coefficient and wear rate and can be developed at low cost. In this paper we have considered a number of possible applications and shown that their high potential to enter the microsystem marketplace as chemical and biosensors, microelectronic devices, bearing materials, and micromechanical actuators. We have shown that when combined in an array that they are already available as electronic noses and we believe that over the next few years many new products will become available.

Acknowledgements

References

[1] T.A. Skotheim (ed.), *Handbook of Conducting Polymers*, Dekker, New York, 1986.

[2] J.W. Gardner and P.N. Bartlett, *Nanotechnology*, 2 (1991) 19.

[3] P.N. Bartlett and J.W. Gardner, Patent Application No. 9400855.4, Jan. 1994.

[4] A. Nannani and G. Serra, *J. Mol. Electron.*, 6 (1990) 124.

[5] L. Madsen, B.N. Zaba, M. Van der Sluijs, A.E. Underhill and K. Carneiro. *J. Mater. Chem.*, 1 (1991) 503.

[6] A.M. James and M.P. Lord, *Macmillan's Chemical and Physical Data*, Macmillan Press, 1992.

[7] S. Kuwabata, J. Nakamura and H. Yonelyama, *J. Electrochem. Soc.*, 137 (1990) 1788.

[8] D.S. Maddison, R.B. Roberts and J. Unsworth, *Synth. Met.*, 33 (1989) 281.

[9] S. Chandra, *Appl. Phys. Lett.*, 58 (1991) 51.

[10] Y. Ohmori, H. Takahashi, K. Muro, M. Uchido, T. Kawai and K. Yoshino, *Jpn. J. Appl. Phys.*, 30 (1991) L610.

[11] J. Barker, *Hybrid Circuits*, 14 (1987) 19.

[12] T.T. Tan, J.W. Gardner, J. Farrington and P. N. Bartlett, *Int. J. Electron.*, 77 (1994) 173.

[13] P.N. Bartlett, D.G. Chetwynd, J.W. Gardner and S.T. Smith, UK Patent No. 941644., September, 1994.

[14] S.T. Smith, S. Harb, V. Eastwick-Field, Z.Q. Zao, P.N. Bartlett, D.G. Chetwynd and J.W. Gardner, *Wear*, 69 (1993) 43.

[15] I.L. Singer, R.N. Bolster, J. Wegand, S. Fayeulle and B.C. Stupp, *Appl. Phys. Lett.*, 57 (1990) 995.

[16] P.N. Bartlett and S.K. Ling-Chung, *Sensors and Actuators*, 19 (1989) 141.

[17] H. Koezuka and S. Etoh, *J. Appl. Phys.*, 54 (1983) 2511.

[18] K. Yoshino, H. Takahashi, K. Muro, Y. Ohmori and R. Sugimoto, *J. Appl. Phys.*, 70 (1991) 5035.

[19] Y. Kunugi, K. Nigorikawa, Y. Harima and K. Yamashita, *J. Chem. Soc., Chem. Commun.*, (1994) 873.

[20] J.W. Gardner and P.N. Bartlett, UK Patent No. W093/03355, Feb. 1993.

[21] J.W. Gardner and P.N. Bartlett (eds.), *Sensors and Sensory Systems for an Electronic Nose*, Kluwer, Dordrecht, 1992.

[22] T. Hanawa, S. Kuwabata and H. Yoneyama, *J. Chem. Soc., Faraday Trans.*, 184 (1988) 1587.

[23] J.W. Gardner, A. Pike, N.F. De Rooij, M. Koudelka-Hep, P.A. Clerc, A. Hierlemann and W. Goepel, *Sensors and Actuators B*, 26 (1995) 135.

[24] P.N. Bartlett and P.R. Birkin, *Synth. Met.*, 61 (1993) 15.