

## CHAPTER VIII

### APPLICATIONS

#### 8.1 Introduction

Improvement in solid-state device fabrication technology includes three important aspects, viz., materials contacts and encapsulation. At present, the fabrication of solid state devices has been limited to the use of inorganic semiconductors, so the effort to replace them by polymeric semiconductor devices has intensified. Semiconducting polymers have been found potentially suitable for microelectronic device fabrication due to their excellent electrical characteristics. These include polyaniline, polyacetylene, polypyrrole and other conjugated polymers.

The applicability of the concept of doping is the unifying theme which distinguishes a certain class of organic polymers-conducting polymers-from all others. Doping results in dramatic electronic and magnetic changes with a concomitant increase in conductivity to, or approaching, the metallic regime. Doping phenomena and the chief types of dopable organic polymers are described with particular emphasis on polyaniline which is presently being commercialised on a relatively large scale and is the leading conducting polymer for technology, closely followed by polythiophene derivatives. Polyaniline shows considerable promise for

electromagnetic interference (EMI) shielding and is already used in commercial rechargeable batteries. Leading potential technological applications utilize polyaniline film membranes for gas separations, electrochromic windows, redox capacitors and chemical sensors.

Polypyrrole is a conducting polymer with conductivity ranging from 1 to 100  $\text{Scm}^{-1}$ . The conductivity of polypyrrole film suggests applications such as flexible conductive paths in printed circuits, heating films and film keyboards. Polypyrrole films show good electromagnetic shielding effects of about 40 dB over a wide range of frequencies (1-1500 MHz). The electrical conductivity is varied by the level of oxidation or reduction. Many applications of CPs have been tried for electronic devices such as diodes [1] field effect transistors [2] using semiconductive features. Rechargeable batteries [3,4] and color switching cells have also been examined for their electrochemical processes [5].

Polypyrrole is a potentially useful material for the fabrication sensors. It has been used as a sensing material in field effect transistor [6] and ion selective electrodes. It shows interesting gas sensing possibilities which were first demonstrated by Nylander et al [7].

More recently, Miasik et al [8] have reported a device utilizing electrochemically prepared polymer promising convenient and controllable preparation which should lead to a more stable and potentially reproducible sensor material. The mechanism of interactions was attributed to the

p-type semiconducting nature of PPY. Exposure to electrophilic gases, such as  $\text{NO}_x$ , tends to attract electrons out of the polymer matrix, causing an increase in conductivity, whereas nucleophilic gases, such as  $\text{NH}_3$ , will have the opposite effect.

Tomozawa et al [9] have presented the results of strong rectification by metal-polymer (Schottky) diodes made by evaporating metal contacts onto films of a soluble semiconducting polymer casted from solution. They observed that the temperature dependence of current-voltage characteristics differed from that of conventional Schottky diodes and suggested transport processes other than the conventional thermionic emission. i.e., the transport mechanism of polymer diodes differed from that of conventional metal-semiconductor diodes.

In the present study, an attempt has been made to use the polymers of current interest in gas sensing and rectifying applications. The details of the study are presented in the following sections.

## **8.2 Experimental**

Polymer films were prepared by solution casting method onto aluminium/gold electrodes. Just prior to electrode deposition, the substrates were washed in ultrasonic agitation and isopropyl alcohol as described in chapter II. Metal electrodes were deposited on top of the polymer film by vacuum evaporation for sensor and diode configurations

separately. Metal-Polymer-Metal configuration was used for the fabrication of gas sensors. The change in the capacitance values was used as a parameter for sensing the gases. Acetone and methanol were used as the test cases to study the gas sensing abilities of Pani-EB, lightly doped Pani and PPY, and Pani/PPy blend films.

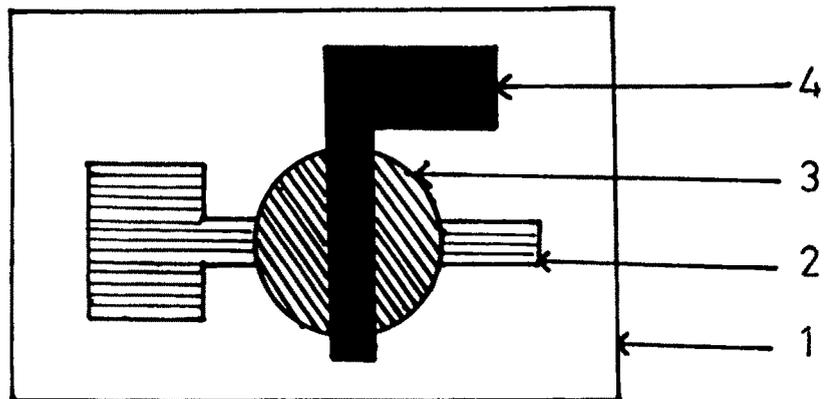
### 8.3 Results and discussion

#### 8.3.1 Chemical Sensor

The Schematic diagram of gas sensor (capacitor configuration) is shown in Fig. 8.1.

Fig.8.2(a) shows the plot between capacitance (C) versus frequency (f) of a Pani-EB film [thickness (d) = 50  $\mu\text{m}$ ]. Curve 'a' represents the variation of the capacitance with frequency when the sample is exposed to acetone atmosphere. The capacitance is found to increase from 1.5 to 300 pF. Curves b & c show the value of capacitance before exposing to gas atmosphere and after removing the gas. It is seen that the capacitor regains its original capacitance values after removing the acetone atmosphere. In the case of methanol gas, the capacitance varies from 5 to 20 pF [Fig.8.2(b)]. The recovery of capacitance value is almost same [curve b & c] for both the cases.

Similarly for acid doped pani film, [Fig.8.3 (a & b)] it is seen that the values of capacitance (two different samples) vary from 10 to 40 nF and



1 Substrate

2 Bottom electrode

3 Polymer film

4 Top electrode

Fig. 8.1 Schematic diagram of gas sensor ( capacitor configuration)

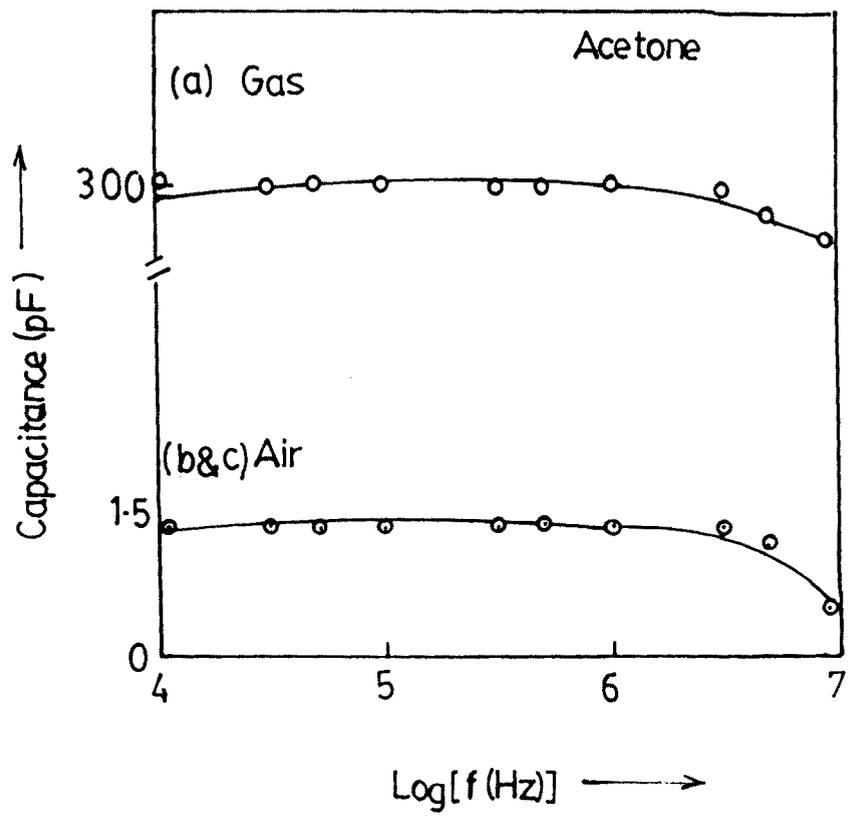


Fig. 8.2(a) Acetone sensing behaviour of Pani-EB film

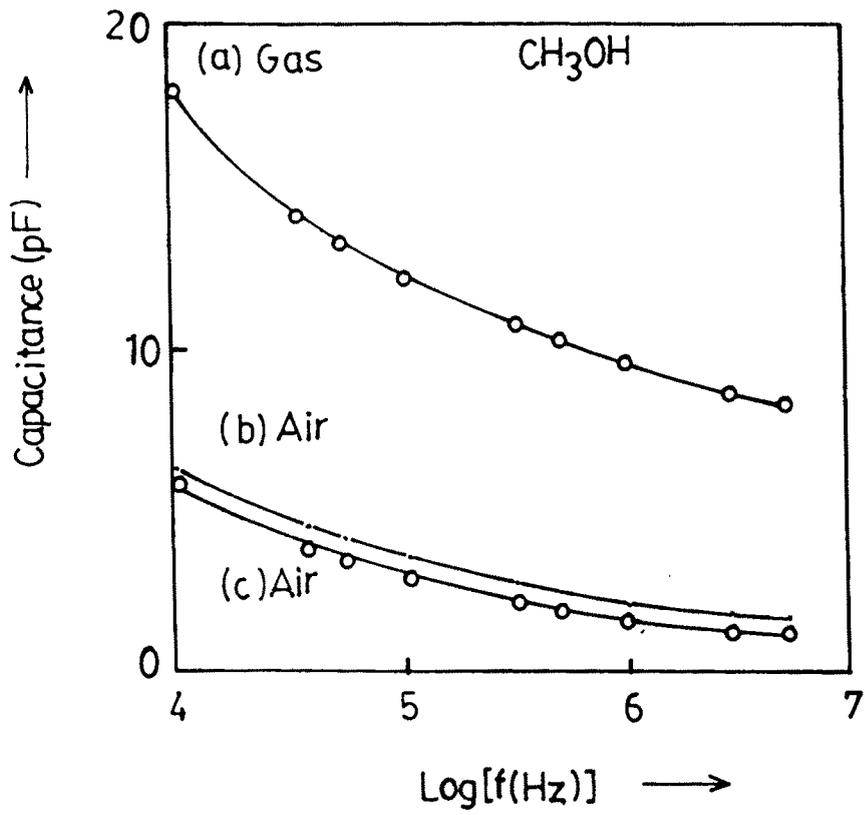


Fig. 8.2(b) Methanol sensing behaviour of Pani-EB film

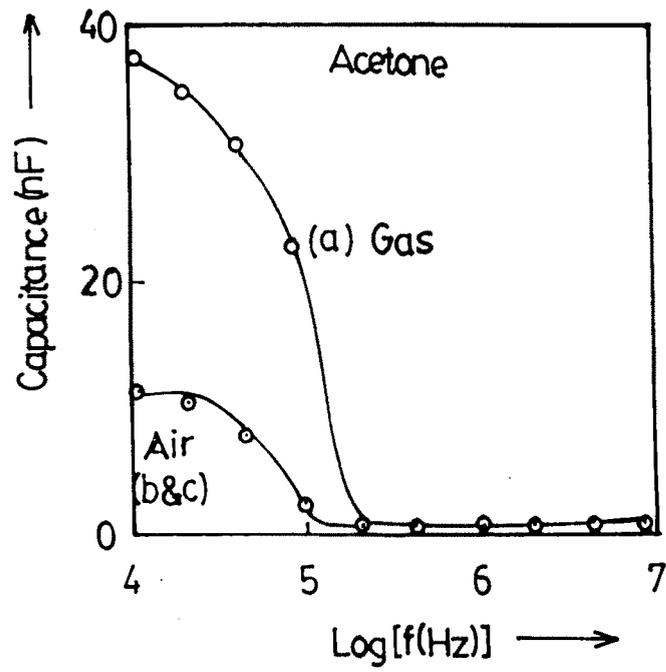


Fig. 8.3(a) Acetone sensing behaviour of acid doped Pani film

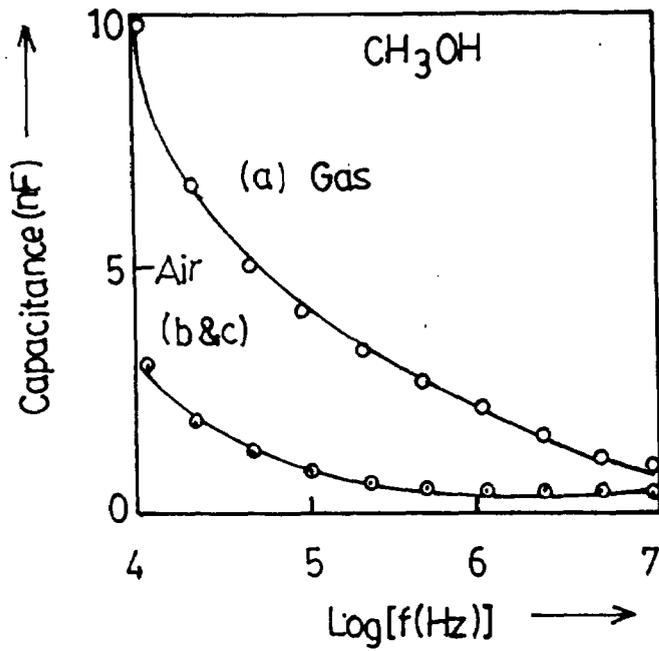


Fig. 8.3(b) Methanol sensing behaviour of acid doped Pani film

3.5 to 10 nF for acetone and methanol gas respectively. The change in capacitance value is high in the low frequency region and almost same in the higher frequency region. Curves b and c represent the value of capacitance before passing and after removing gas.

Fig.8.4(a) shows the variation of  $C$  versus  $f$  for acetone sensing behaviour of PPY film. From the plot it is observed that the value of capacitance changing from 40 to 200 nF in the low frequency range [10 kHz to 100 kHz]. The sensing activity of this film could be observed in the low frequency region with no response in the high frequency region. Same behaviour was observed for methanol on PPY film [Fig.8.4(b)]. Acetone and methanol gas sensing activity of PPY/Pani-EB blend film as shown in [Fig.8.5 (a &b)].

From the above observations it can be seen that Pani-EB and PPY films act as good sensors for acetone and methane gases. The recovery of the capacitance to the original values after removing the gas atmosphere is quick in the case of Pani-EB films which indicates that these gas sensors can be used repeatedly.

### 8.3.2 Schottky barrier diode

The schematic diagram of Schottky barrier diode is shown in Fig.8.6. The device is fabricated on a flat glass substrate, with a thin layer of gold as the ohmic contact, onto which the polymer layer is formed. The top

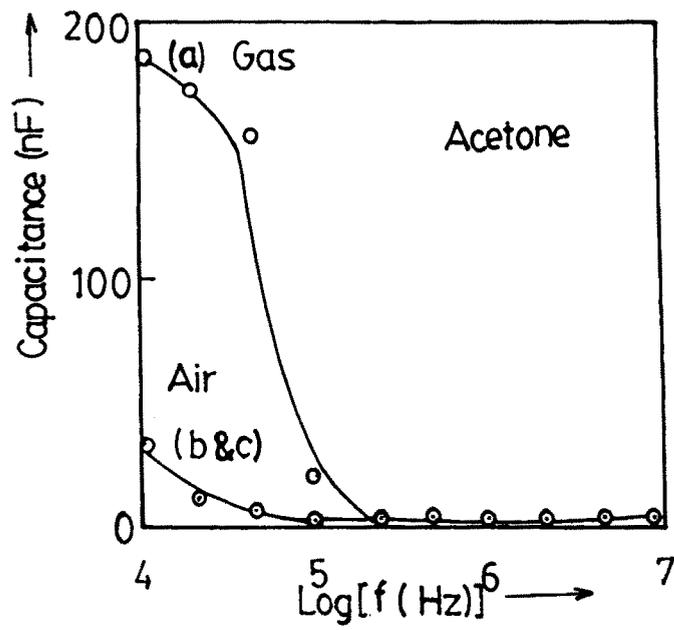


Fig. 8.4(a) Acetone sensing behaviour of PPY film

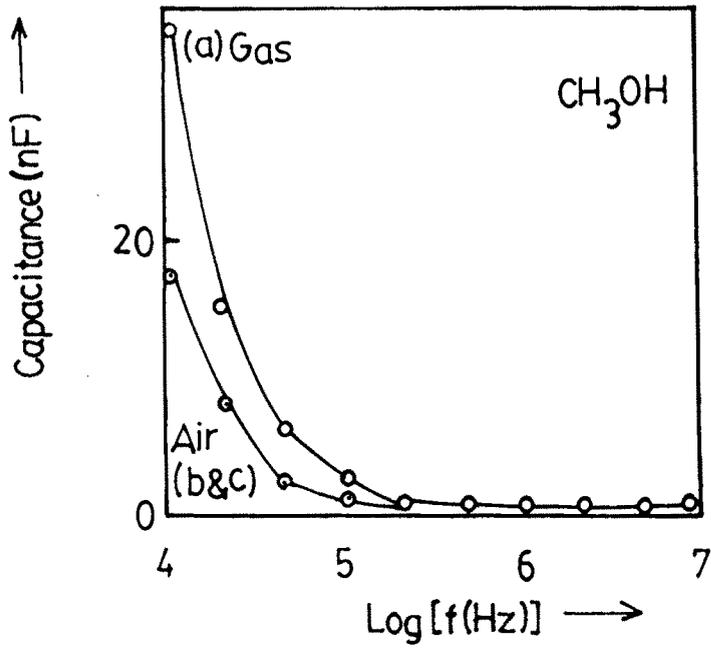


Fig. 8.4(b) Methanol sensing behaviour of PPY film

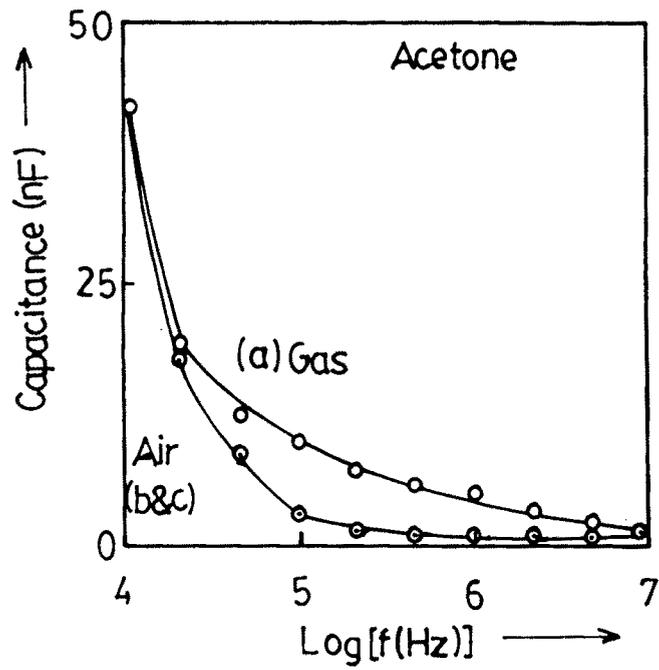


Fig. 8.5(a) Acetone sensing behaviour of PPY/Pani-EB blend film

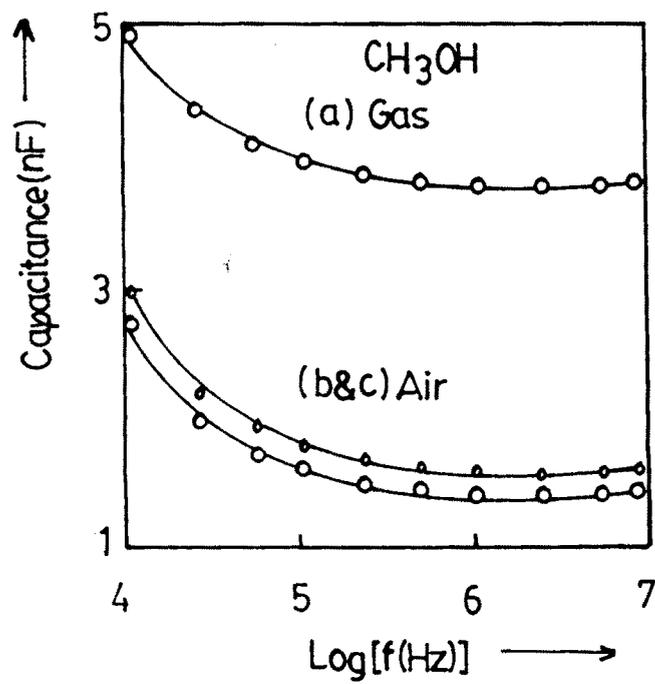


Fig. 8.5(b) Methanol sensing behaviour of PPY/Pani-EB blend film

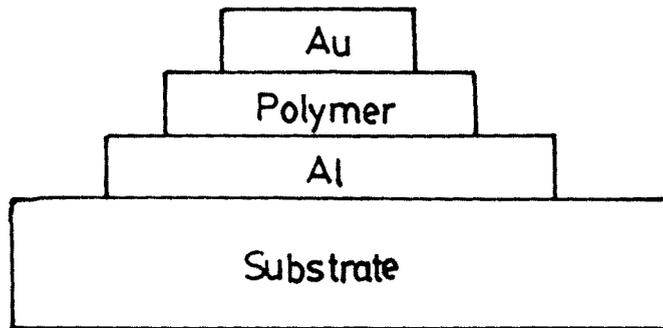


Fig. 8.6 Schematic diagram of Schottky barrier diode

metal contact, i.e., aluminium is formed by thermal evaporation to give the Schottky barrier. The I-V characteristics curve of Pani-EB is shown in Fig. 8.7. From the figure it is seen that the value of current varies from -1 to 2  $\mu\text{A}$  for the voltage range studied [-2 to 2 volts].

While doing the measurements, first the gold electrode is connected to the negative terminal and Al electrode to the positive terminal of a battery. So potential barrier in the semiconductor is reduced, i.e., the electrons are driven across the barrier so that a large net current results as observed in the forward bias of Fig.8.7. If the polarity of the battery is reversed, the potential barrier in the semiconductor is increased. So the diffusion currents in both directions are reduced as observed in the reverse bias. In the case of PPY [Fig.8.9] film, current value increases in the milli ampere range. Also the value of carrier concentration, calculated from the Hall Effect measurement (chapter IV), appears to be the main factor controlling the junction characteristics and hence, the device performance [10]. Similar behaviour was observed for acid doped Pani and Pani-EB/PPY Schottky barrier devices [Fig.8.8 & 8.10].

From the above observations, it is seen that it is possible to prepare Schottky barrier devices using the polymers of the present study with a metal electrode having a work function lower (say for aluminium 4.12 eV) than that of the polymer.

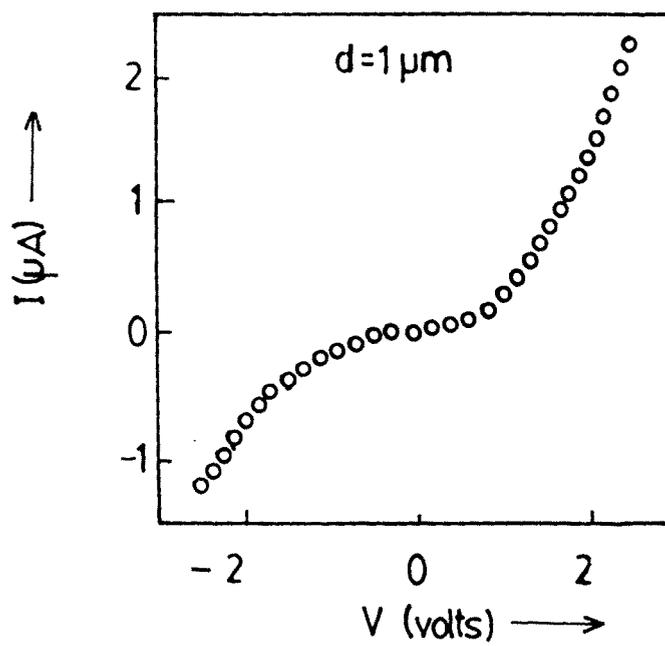


Fig. 8.7 I-V characteristics of Pani-EB film

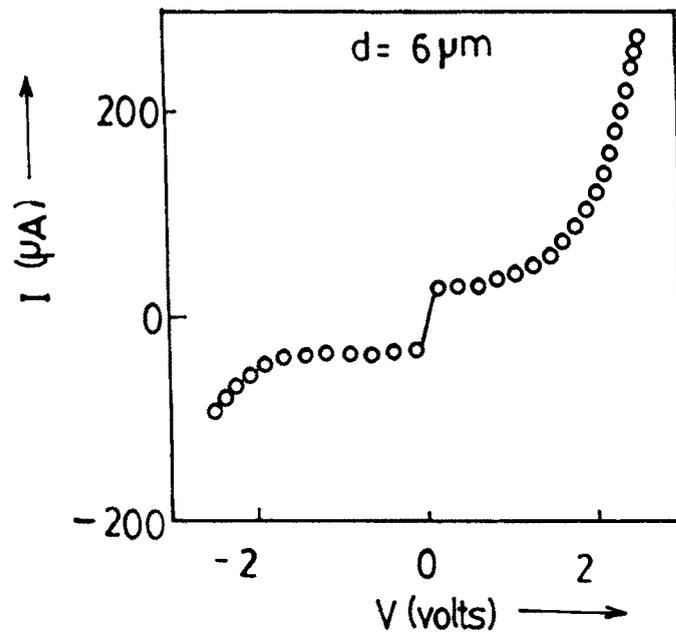


Fig. 8.8 I-V characteristics of acid doped PANI film

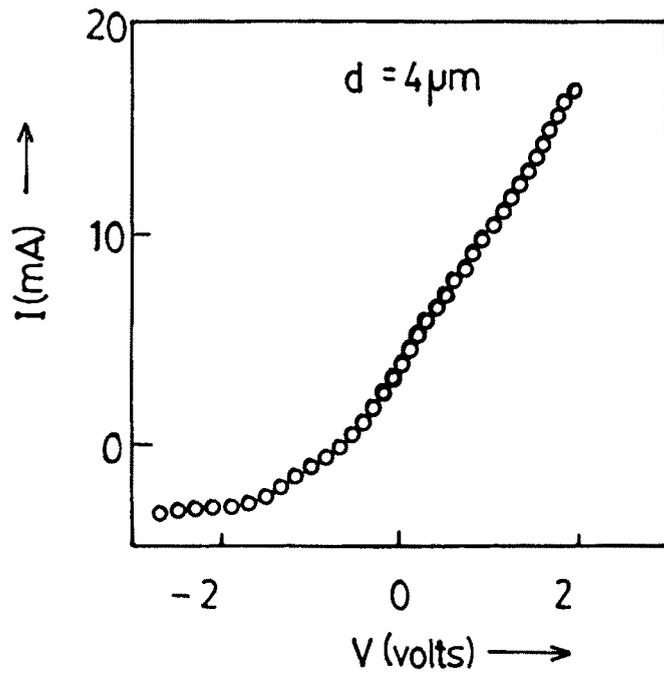


Fig. 8.9 I-V characteristics of PPY film

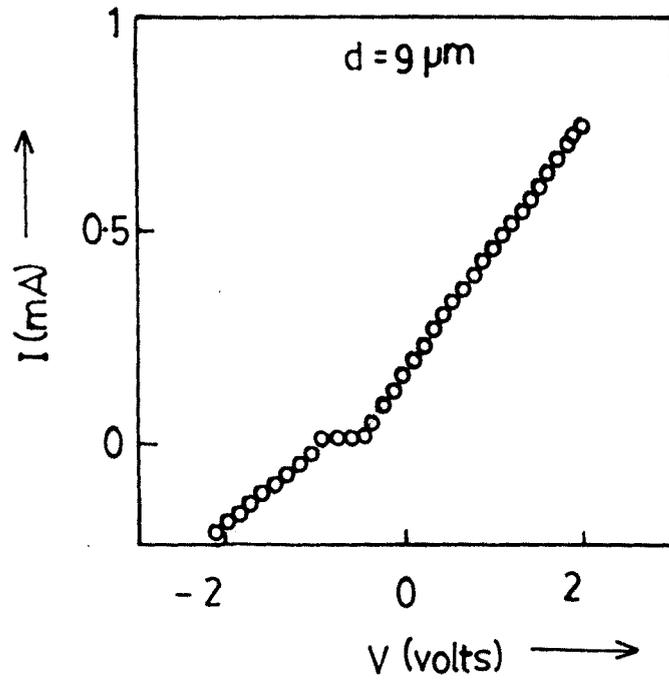


Fig. 8.10 I-V characteristics of PPY/Pani-EB blend film

**Table 8.1** Chemical of sensors

Polymer Films	Gas sensed	Reponse to gas	Recovery	Result
Pani-EB	Acetone	Instantaneous	Recovered	Indisposable
	Methanol	”	Not fully	Disposable
Acid Pani	Acetone	Instantaneous	Recovered	Indisposable
	Methanol	”	”	”
PPY	Acetone	Instantaneously	Recovered	Indisposable
	Methanol	”	”	”
PPY/Pani-EB	Acetone	Instantaneously	Recovered	Indisposable
	Methanol	”	Not fully	Disposable

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