# Some Recent Studies on Metal/Polyaniline Schottky Devices

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## SYNOPSIS

An attempt has been made to estimate various electronic parameters such as work function, barrier height, and ideality factor through I-V measurements carried out on metal/polyaniline Schottky junctions. The results of optical studies conducted on chemically synthesized polyaniline used in the fabrication of such Schottky devices have been presented.

## INTRODUCTION

Conducting polymers have recently attracted much attention largely because of many projected applications in light-weight batteries, solar cells, and electrochromic switching and molecular electronic devices.[1-5] Along with various conducting polymers such as polypyrrole, polythiophene, and polyfuran, semiconducting polyaniline has been considered to be an important candidate for such applications. This is primarily because this interesting conducting polymer can be easily prepared both in thin film and in bulk form. Fabrication of solid state heterojunction/Schottky devices using semiconducting polymers is one of the most important applications for such materials. In this context, a Schottky device consisting of metal and polypyrrole was recently reported[6] where it was shown that the electronic parameters controlling the device performance such as rectifying ratio, barrier height, and work function can be conveniently estimated through I-V measurements. As a consequence of these encouraging results, it was thought that similar investigations should be carried out on metal/semiconducting polyaniline Schottky junctions. This paper essentially reports the results of these investigations including the optical absorption studies used in the fabrication of such devices.

## EXPERIMENTAL

The polyaniline used in the fabrication of metal/polyaniline junctions was chemically synthesized by redox polymerization of aniline using ammonium perdisulphate [$(NH_4)_2S_2O_8$] as an oxidant.[7] Distilled aniline $0.2 M$ was dissolved in 300 mL of pre-cooled HCl ($1.0 M$) solution maintained at 0.5°C. Next, $0.05 M$ ammonium perdisulphate (11.5 g) dissolved in 200 mL of HCl ($1 M$) precooled to 0–5°C, was added to the above solution. The dark-green precipitate resulting from this reaction was washed repeatedly with $1 M$ HCl until the green color disappeared. This precipitate was further extracted with tetrahydrofuran and $N$-methyl pyrrolidinone solution using Soxhlet extraction and was dried under dynamic vacuum. The infrared spectroscopic measurements on polyaniline (KBr pellets) were carried out on a Nicolet FTIR model 205 and are shown in Figure 1. The optical spectrum of polyaniline, shown in Figure 2, was recorded in NMP solution in the 300–1400 nm wavelength range using a computerized Hitachi U-3400 spectrophotometer. This spectrophotometer directly gives the product $\alpha \cdot d$, where $\alpha$ is the absorption coefficient and $d$ is thickness of the sample. The energy band gap of polyaniline was estimated using the following relation:

$$\begin{array}{c} \text{Absorption} = (h\nu - Eg)^{1/2} \\ (\alpha \cdot d) \end{array} \qquad (1)$$

Where $\alpha \cdot d$ = absorption, Eg = energy band gap, and $h\nu$ = incident photon energy.
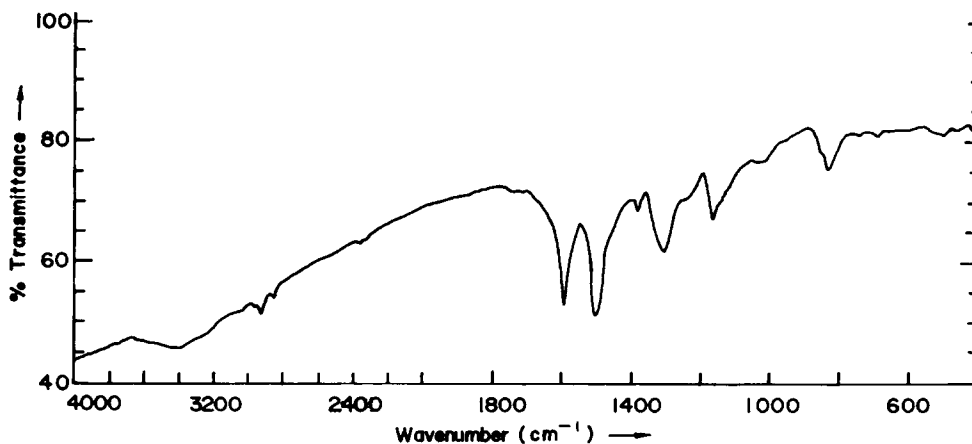
**Figure 1**   FTIR spectra of HCl doped polyaniline.

The Schottky junctions were fabricated by depositing different metals such as aluminum, silver, tin and indium on various pellets of polyaniline. The I-V measurements on such structures were conducted as reported in our earlier publications.[3,6]

## RESULTS AND DISCUSSION

The result of FTIR spectroscopy carried out on HCl doped polyaniline (Fig. 1) in transmission mode in-dicates that distinct peaks appear at 3400 cm$^{-1}$, 2900 cm$^{-1}$, 1600 cm$^{-1}$, 1300 cm$^{-1}$, and 1175 cm$^{-1}$. The peak at 3400 cm$^{-1}$ has been attributed to stretching vibrations of the secondary amine (N—H). Further, the peaks at 2900 cm$^{-1}$ and 1600 cm$^{-1}$ have been identified as arising from stretching vibrations of the aromatic C—H and C=N groups of polyaniline. Various other peaks such as those observed at 1300 cm$^{-1}$ and 1175 cm$^{-1}$ are due to the presence of several stretching and bending vibrations emanating from C=N bond and to the chloride ion respectively.[8,9]
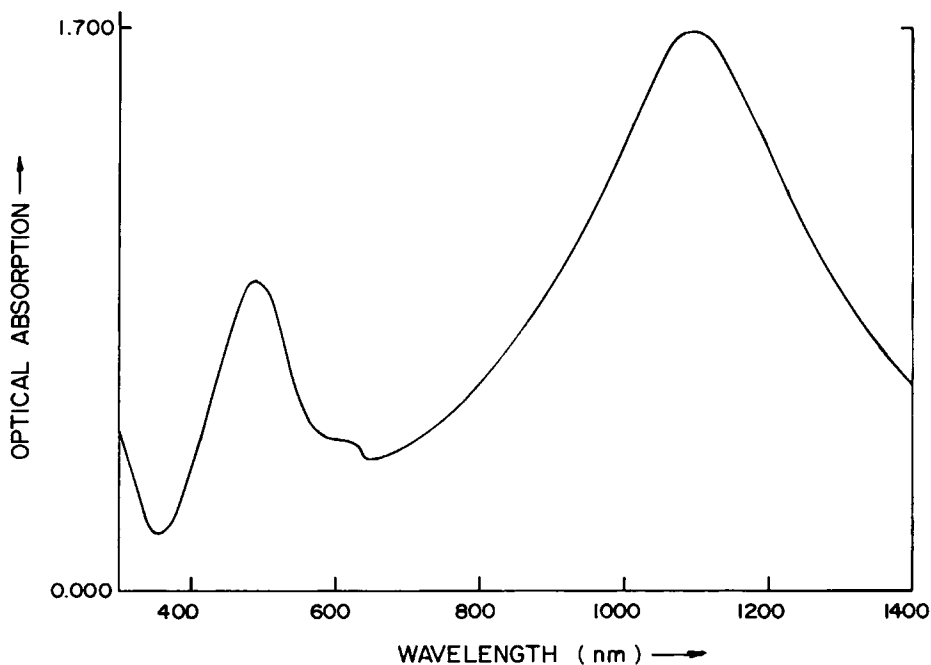


**Figure 2**   Variation of optical absorption of HCl doped polyaniline with wavelength.

tions emanating from C=N bond and to the chloride ion respectively.[8,9]

The optical absorption spectra of polyaniline in the UV-visible range, shown in Figure 2, exhibits distinct absorption peaks at 1100 nm (1.1 eV) and 480 nm (2.6 eV), respectively. In addition, a shoulder can also be seen at about 600 nm. The observed peaks are consistent with those published in literature.[10] The absorption peak at 2.6 eV is due to optical transitions from band c to band a.[11] The results of all these measurements show that the sample utilized for device fabrication is essentially doped polyaniline. The variation of optical absorption with photon energy is shown in Figure 3. The energy band gap of semiconducting polyaniline estimated using eq. (1) comes out to be about 2.0 eV. The optical absorption edge for this conducting polymer has been observed at 0.9 eV, which is consistent with

the value 1.8 eV reported in the literature for fully oxidized polyaniline base.[12] A low value of 0.9 eV observed for optical absorption edge appears to be reasonable in view of the measured electrical conductivity ($\simeq$ 1 Ohm$^{-1}$ cm$^{-1}$) of doped polyaniline. This can be understood in terms of various optical transitions occurring between the localized states within the energy band gap of polyaniline.

The Schottky junctions on doped polyaniline were fabricated by depositing metals having work functions lower than that of polyaniline. The metals with work functions higher than that of polyaniline make ohmic contact. The effective junction area was about 0.01 cm$^2$. The resistivity of different polyaniline pellets (thickness 0.1 cm) was within the range 0.1 to 1.0 ohm cm. The results of I-V measurements of the metal/polyaniline configuration using Electrodag, E + 502 as the back ohmic contact are shown
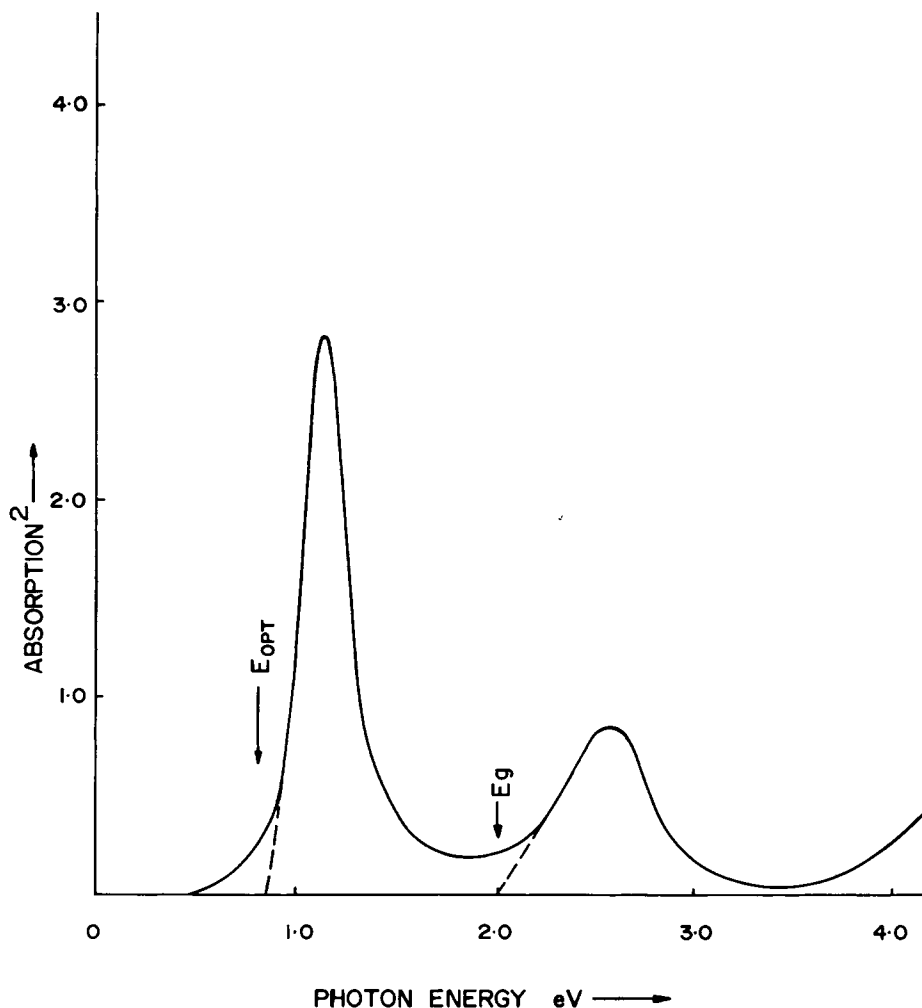


**Figure 3**    Variation of optical absorption of doped polyaniline with photon energy.

in Figure 4. Curve 1 shows the I-V characteristics of the indium/polyaniline structure. This curve indicates, that in the forward bias conditions, the blocking of charge carriers occurs at the interface up to a certain voltage, after which the junction becomes conducting. The I-V characteristics of various other junctions such as those using aluminium, tin, and lead on polyaniline were experimentally determined and are shown by curves 2, 3, and 4 of Figure 4. From these studies it can be concluded that aluminum, tin, indium, and lead make rectifying Schottky barriers with polyaniline. Further, it was discovered that silver with its high work function of about 4.28 eV makes an ohmic contact with polyaniline. Consequently it can be inferred that the work function of polyaniline lies between 4.10 and 4.28 eV.

The barrier height $X_b$ (in volts) of the metal/ polyaniline junction can be calculated using the relations:[13]

$$J = J_0.\exp.(qV/nkT)\qquad(2)$$

**Table I**   Electronic Parameters of Metal/Polyaniline Heterojunctions

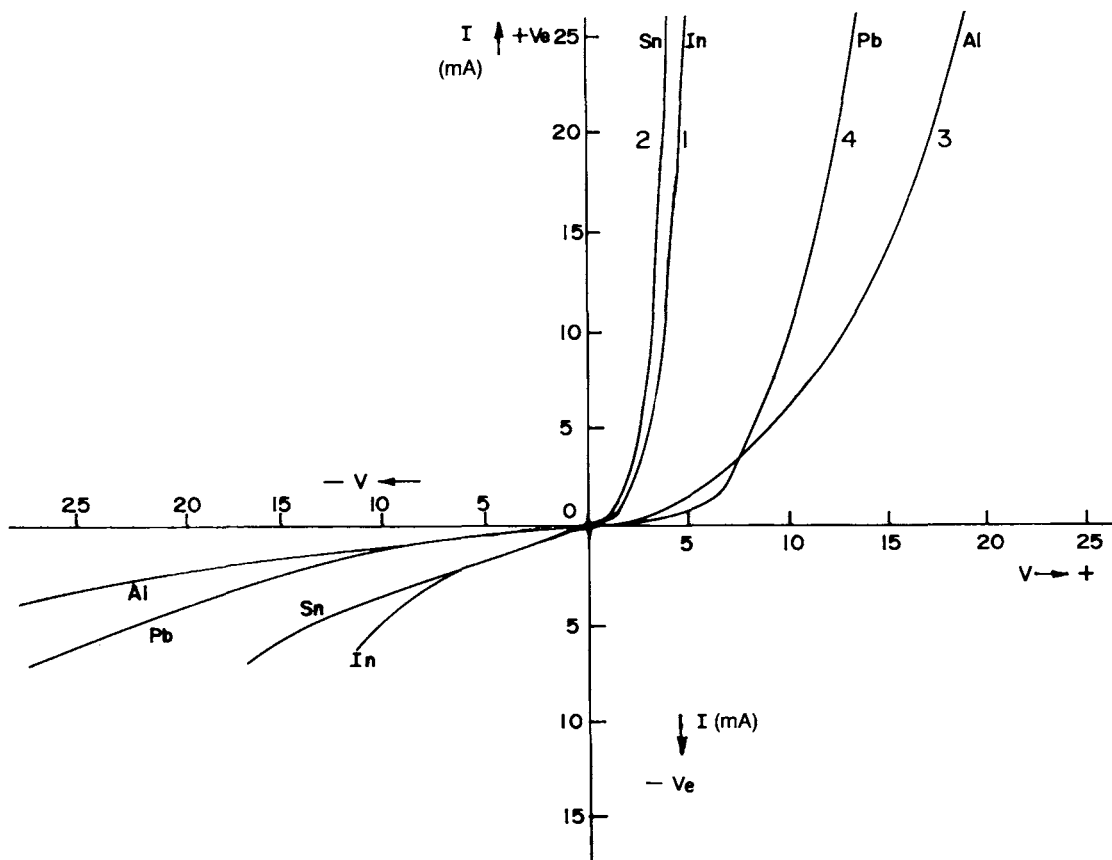| Metal | Work Function[14] (eV) | Barrier Height (Volts) | Ideality Factor |
|---|---|---|---|
| In | 4.12 | 0.4 | 1.9 |
| Sn | 4.11 | 0.4 | 4.9 |
| Pb | 4.02 | 0.5 | 6.9 |
| Al | 3.74 | 0.4 | 2.8 |

where $J_0$ is reverse saturation current density that can be estimated using the relation

$$J_0 = \overset{*}{A}.T^2.\exp.(-qX b/kT)\qquad(3)$$

where $\overset{*}{A}$ = Richardson constant

$$= (1.2 \times 10^{-6}\ A\ m^{-2}\ degree^{-2})$$

$n$ = ideality factor



**Figure 4**   I-V characteristics of metal/polyaniline heterojunctions, with various metals.

$T$ = absolute temperature

$k$ = Boltzman constant

The barrier height, the ideality, factor and the work function[14] for different metal polyaniline Schottky junctions have been calculated and are given in Table I. A lower value of ideality factor (1.9 for indium/polyaniline junction compared to that of 1.02 for metal/inorganic semiconductor junction[15]) indicates that this metal makes a relatively better rectifying barrier with polyaniline. It may be interesting to mention that no I-V characteristics could be obtained for undoped polyaniline.

## CONCLUSIONS

The results of I-V measurements conducted on metal/semiconducting polyaniline Schottky junctions have been systematically analyzed. From these measurements various device parameters such as ideality factor and barrier height of metal/polyaniline junctions have been estimated. The work function of polyaniline has been found to lie between 4.10 eV and 4.28 eV. Excellent rectification has been observed for indium/polyaniline junctions.

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