# Properties of Metal-Polyaniline Schottky Barriers

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SYNOPSIS

In the present paper we report studies on metal-polyaniline (PAn) Schottky junctions where PAn is doped with various dopants such as hydrochloric acid (HCl), formic acid (HCOOH), iodine ($I_2$) and methylene blue ($C_{16}H_{18}N_3SCl$). The I-V characteristics for the different Schottky junctions have been reported. Electronic parameters such as Richardson constant, ideality factor, barrier height etc., have been calculated. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

Many of the useful properties of a *p-n* junction can be achieved by simply forming an appropriate metal-semiconductor contact. This approach is obviously attractive because of its simplicity of fabrication; also metal semiconductor junctions are particularly useful when high speed rectification is required.[1,2] Since PAn is found to be acting as semiconductor, it was thought interesting to study metal-PAn Schottky junctions.

A Schottky device consisting of metal and semiconducting polymer like poly-*p*-phenylene has been reported by M. Campos et al.[3] who have also reported I-V and C-V characteristics of the same diode (metal/poly-*p*-phenylene) over a wide temperature range. An attempt has been made by S. S. Pandey et al.[4] to estimate various electronic parameters such as work function, barrier height, ideality factor, and the Richardson constant through I-V measurements carried out on metal/PAn Schottky junctions. They have fabricated junctions by depositing different metals such as aluminium, silver, tin and indium on pellet of PAn.

On account of importance and simplicity of fabrication of Schottky diode, it was decided to study the variation in behaviour of metal/PAn Schottky barrier using variously doped samples viz. HCl, formic acid, iodine, methylene blue doped PAn (as semiconducting material). In the present work we have used gold for ohmic contact and aluminium for forming the rectifying contact. Parameters like Richardson constant, barrier height, ideality factor for these devices have been calculated.

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## EXPERIMENTAL

### Sample Preparation

Polyaniline (PAn) used in the present study was synthesized chemically using aniline as monomer and ammonium peroxodisulfate as an oxidant in equimolar ratio in aqueous media.[5] PAn thus obtained, was in doped form which was converted into base form after treatment with aqueous ammonia. The base form of PAn was redoped with various dopants such as HCl, $I_2$, formic acid and methylene blue. Variously doped PAn powder were pressed into cylindrical pellets of diameter one cm and thickness 0.1 cm.

The thin film of aluminium metal was deposited on one side of the polymer samples by vacuum evaporation technique at pressure of the order of $10^{-5}$ Torr. Aluminium has work function 3.7 eV (i.e., $\phi$Al = 3.7 eV) which is lower than that of PAn, (It has been reported[4] that the work function of PAn lies between 4.1 and 4.28 eV) so it forms rectifying contact (i.e., Schottky junction) with PAn. Similarly on the other side of the polymer samples gold was deposited by vacuum evaporation technique. Since gold has work function 4.8 eV (i.e., $\phi$Au = 4.8 eV) it forms ohmic contact with PAn.

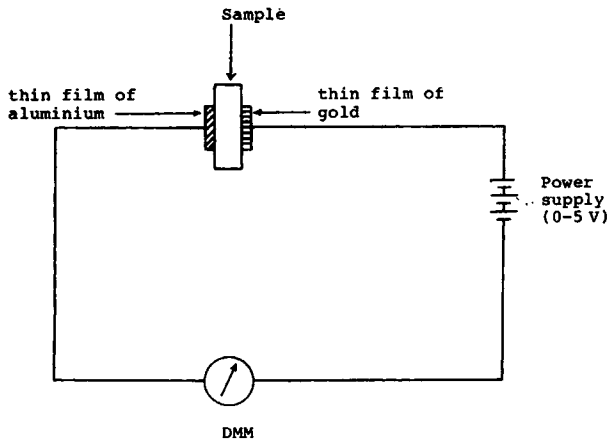


**Figure 1** Circuit diagram for I-$V$ characteristics.

### J-V Characteristic Measurements

A two probe method was used for measurement of J-V characteristics. The specimen was mounted in the sample holder as shown in Figure 1 (sandwich configuration); i.e., one side of PAn-pellet was connected to +ve of the power supply and other side of the pellet was connected to the −ve of the power supply, through a digital multimeter used for measuring current.

Typical dark current density versus applied voltage (J-V) characteristic measurements were made at room temperature in both forward and reverse bias conditions. Typical dark current density versus applied voltage (J-V) measurements were also carried out at various temperatures in the range of 273°K–423°K using power supply, a digital multimeter and a temperature controller.

Schottky barriers containing $p$-type semiconducting materials i.e., variously doped PAn samples are designated as shown in Table I.

## RESULTS AND DISCUSSION

The electrical properties of the Schottky barriers are studied in the sandwich configuration. Typical dark current density versus applied voltage (J-V) characteristics of the device A are shown in Figure 2. The characteristics are asymmetrical and show a rectifying behaviour.

The carrier transport in metal semiconductor contacts is mainly due to majority carriers, in contrast to the case for $p$-$n$ junctions.[1] The transport of charge from the semiconductor over the potential barrier into the metal could be described by the thermionic emission theory or the diffusion theory

**Table I Abbreviations Used for Different Schottky Junctions**

| Sample | Designation |
|---|---|
| Al/formic acid doped PAn/Au | A |
| Al/HCl doped PAn/Au | B |
| Al/iodine doped PAn/Au | C |
| Al/methylene blue doped PAn/Au | D |

of metal semiconductor rectification. The thermionic emission theory, which is commonly applied for conventional semiconductor and metal contacts, can be applied to describe the carrier transport for high mobility semiconductors. The current density can then be written as

$$J = J_s[\exp(qv/nkT) - 1] \quad (1)$$

where $J_s$ is the saturation current density, V is the applied voltage and $n$ is the diode quality factor. The saturation current density is given by

$$J_s = A^*T^2 \exp(-q\phi_B/kT) \quad (2)$$

where $A^*$ is the Richardson constant, $T$ is the temperature and $\phi_B$ is the barrier height of the metal semiconductor barrier.

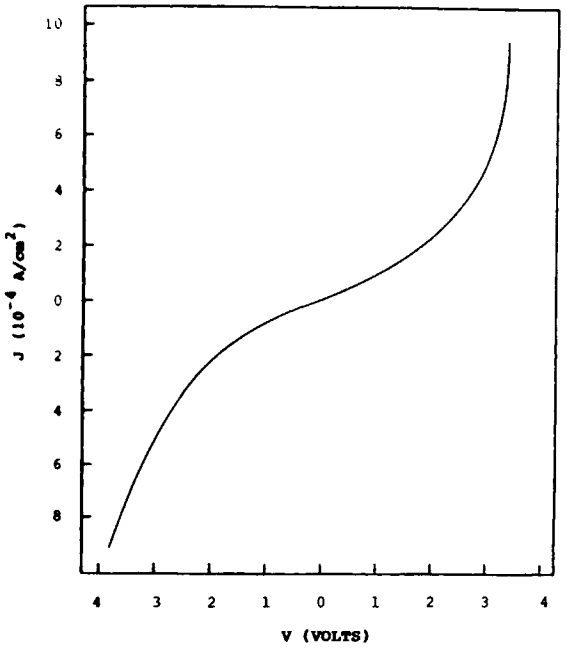


**Figure 2** Room temperature dark current density versus applied voltage rectification characteristics for the sandwich-type device $A$.

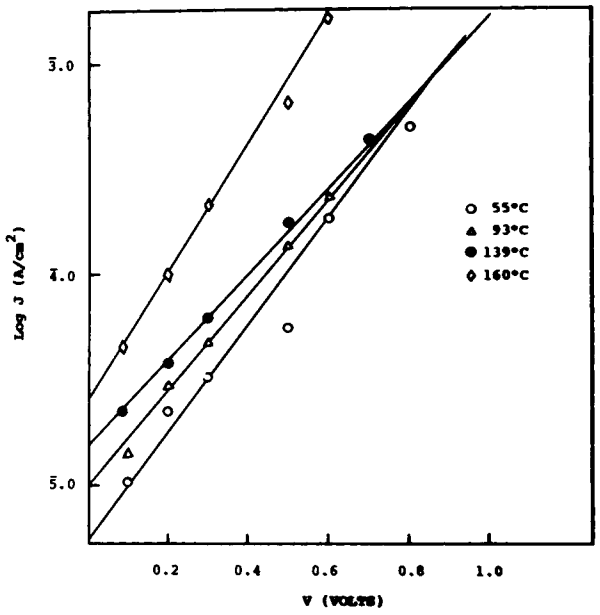


**Figure 3** Temperature dependance of $J$-$V$ characteristics of the device $A$.

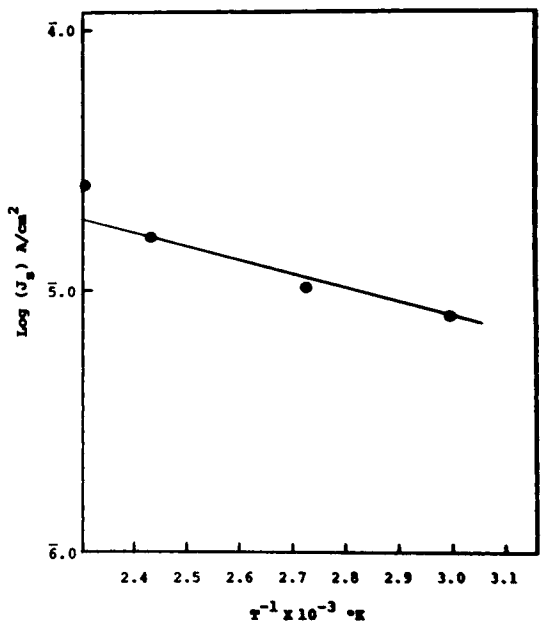


**Figure 4** Temperature-dependence of the extrapolated values of $J_s$ (of device $A$).

In the diffusion theory, which is applied for low mobility and amorphous materials (because of the short carrier mean free path) the saturation current density is given by

$$J_s = q\mu N_c E \exp(-\phi_B/kT) \qquad (3)$$

where $\mu$ is the carrier mobility, $E$ is the surface electric field in the semiconductor, and $N_c$ is the effective density of states in the conduction band. The difference between equations (2) and (3) arises because the electric field is not independent of bias voltage but is proportional to $V^{1/2}$. For large values of reverse bias, the current density does not saturate but increases roughly at $|V|^{1/2}$.

The forward bias J-V characteristic of the '$A$' device at different temperatures are shown in Figure 3. According to equation (2) the $\ln(J_s)$ against $1/T$ plots should yield a straight line with a slope proportional to the barrier height $\phi_B$, where $J_s$ can be obtained from Figure 3 by extrapolating the current density to $V = 0$. This is shown in Figure 4 where $\phi_B = 0.1$ eV.

According to the thermionic emission theory, $J_s$ should follow eq. (2), so that a plot of $\ln(J_s/T^2)$ against $1/T$ should give a straight line. Figure 5 shows a straight line plot of $J_s/T^2$ vs. $1/T$ for device A. The intercept of this line will give $A^*$ (the Richardson constant). In our measurements the calculated $A^*$ ($3.55 \times 10^{-7}$ A cm$^{-2}$K$^{-2}$) for device $A$ is much smaller than the Richardson constant for the free electron (120 A cm$^{-2}$K$^{-2}$), indicating that the diffusion mechanism is dominating, as expected.

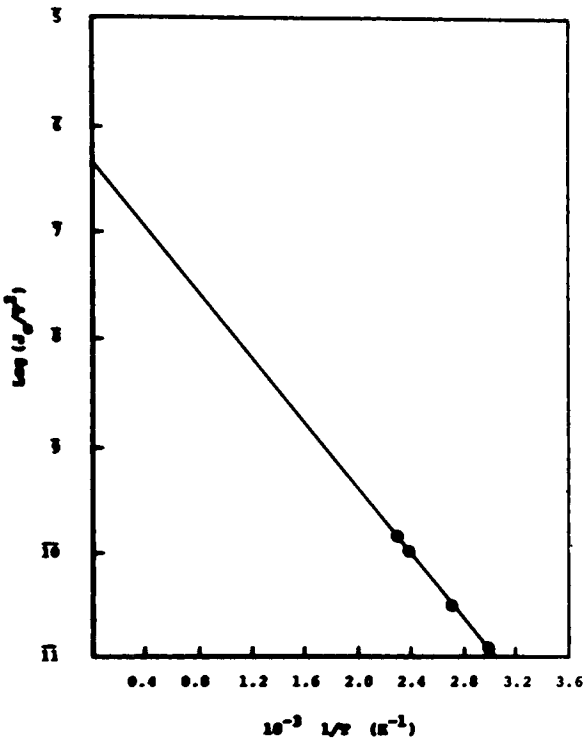


**Figure 5** Plot of $\ln(J_s/T^2)$ vs. $1/T$.

Similar plots and calculations of various parameters are carried out for other devices (B, C, D) and are tabulated in Table II. Typical dark current density versus applied voltage rectification characteristics of the other devices, B, C, D are obtained similar to that of device A and hence are not depicted.

S. S. Pandey et al.[4] have reported the value of $A^*$ calculated for metal/HCl doped PAn junction as $1.2 \times 10^{-6}$ A $m^{-2}$ $deg^{-2}$. For metal/poly(*p*-phenylene) junction *M*. Campos et al.[3] have reported $A^*$ for poly-(*p*-phenylene) $1.3 \times 10^{-4}$ A $cm^{-2}K^{-2}$ where poly-*p*-phenylene was doped with $FeCl_3$. For HCl doped PAn in our experiment $A^*$ was obtained as $2.5 \times 10^{-5}$ A $cm^{-2}K^{-2}$. In our measurements for other devices, A, C, and D, the calculated $A^*$ (shown in Table II) are much smaller than $A^*$ for the free-electrons (120 A $cm^{-2}K^{-2}$). This indicates that the diffusion mechanism is dominating.

Comparing the values of $A^*$ for HCl, $I_2$, formic acid and methylene blue doped samples it is observed that $A^*$ changes as the dopant is changed. $A^*$ depends upon the effective mass of charge carrier, and therefore, upon the mobility of the carrier. It appears from the results that as the dopant is changed the effective mass also changes, giving different values for $A^*$.

The barrier height obtained for HCl doped PAn (device B) is 0.49 V which is almost equal to that reported by S. S. Pandey et al.[4] for HCl doped PAn sample. However the metal used by them for the ohmic contact was silver and in case of our device (B) gold has been used for forming ohmic contact. For other devices, i.e., C and D, the barrier height is comparatively smaller, being 0.27 and 0.25 V, respectively. For device A it is further smaller, being 0.1 V.

$$J = J_s[\exp qV/kT - 1] \tag{4}$$

Equation (4) is the expression for current density due to thermionic-emission-diffusion process.[1]

for $V \gg kT/q$, eq$^n$ (4) becomes

$$J \simeq J_s \exp(qV/kT) \tag{5}$$

From eq$^n$ (1), for $V \gg kT/q$,

$$J \simeq J_s \exp(qV/nkT) \tag{6}$$

where $J_s$ is the saturation current density by extrapolating the current density from the log-linear region to $V = 0$ and $n$ is the ideality factor defined[1] as,

$$n = \frac{q}{kT} \frac{V}{(\ln J)} \tag{7}$$

In eq$^n$ (6), if we put $n = 1$, then we get

$$J \simeq J_s \exp(qV/_{kT}) \tag{8}$$

which is the expression for current density due to thermionic-emission-diffusion process. Since current transport mechanism of Schottky diode is explained[1] on the basis of thermionic emission-diffusion theory, $n = 1$ gives the ideal condition for Schottky barrier.

For Au-Si diode, the ideality factor '$n$' is very close to unity at low dopings and high temperatures.[6] It was reported[6] that for Au-Si diode for higher dopings ($N_D > 10^{17}$ $cm^{-3}$, where $N_D$ is concentration of donar impurities) and lower temperatures the tunneling component dominates the current flow and the ideality factor departs from unity.[6]

From our results it appears that the ideality factor is departing from unity in case of HCl, HCOOH and iodine doped PAn samples. The substantial departure from unity for ideal factor has been attributed to high concentration of dopant. Our results therefore indicate that the concentration of dopant may be high in case of HCl, formic acid and iodine doped PAn-samples.

**Table II Electronic Parameters of Metal/Polyaniline Schottky Junctions (Devices)**

| Device | Barrier Height $\phi_B$ (volts) | Ideality Factor | Richardson Constant A* (A $cm^{-2}$ $K^{-2}$) |
|---|---|---|---|
| A | 0.1 | 1.9 | $3.55 \times 10^{-7}$ |
| B | 0.49 | 2.6 | $2.50 \times 10^{-5}$ |
| C | 0.27 | 2.5 | $1.12 \times 10^{-6}$ |
| D | 0.25 | 1.2 | $1.00 \times 10^{-6}$ |

## CONCLUSION

Thus, chemically synthesised polyaniline can be used for fabricating Schottky barrier. These devices show typical dark current density versus applied voltage characteristics similar to that for inorganic semiconductors.

## REFERENCES

1. S. M. Sze, *Physics of semiconductor devices,* Wiley Eastern Limited, 245 (1993).
2. B. G. Streetman, *Solid State Electronic Devices,* Prentice Hall of India, New Delhi, 183 (1991).
3. M. Campos, B. Bello, Jr., *J. Phys. D: Appl. Phys.,* **26,** 1274 (1993).
4. S. S. Pandey, S. C. K. Misra, B. D. Malhotra, Subbas Chandra, *J. Appl. Polym. Sci.,* **44,** 911, (1992).
5. M. Angelopoulos, G. E. Asturias, S. P. Ermer, A. Ray, E. M. Scherr, A. G. MacDiarmid, M. Akthar, Z. Kiss, and A. J. Epstein, *Mol. Cryst. Liq. Cryst.,* **160,** 151 (1988).
6. C. Y. Chang and S. M. Sze, *Solid State Electron,* **13,** 727 (1970).

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