Electrical and optical properties of p-type silicon based on polypyrrole-derivative polymer

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The junction characteristics of the conducting polymer NpClPh PPy [N-(p-chloro phenyl) polypyrrole] on a p-type Si substrate have been studied at room temperature. A direct optical band gap energy value of conducting polymer (NpClPh PPy) was obtained as 2.94 eV. The ideality factor and barrier height of Al/NpClPh PPy/p-Si/Al structure were determined from the forward current–voltage characteristics in the dark and were found to be 1.41 and 0.78 eV, respectively. The ideality factor and barrier height values for the Al/NpClPh PPy/p-Si/Al structure are larger than that of conventional Al/p-Si Schottky diode. The contact parameters were calculated from Cheung’s functions and modified Norde’s function. The results found out from different methods were compared with each other. The barrier height value of 0.89 eV was obtained from capacitance–voltage characteristic. The different values of barrier height indicate the existence of barrier inhomogeneities. The conducting polymer (NpClPh PPy) modifies the effective barrier height of conventional Al/p-Si Schottky diode as the organic film forms a physical barrier between Al metal and p-Si.

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1. Introduction

The development of conducting polymers as electronic materials has attracted much attention from both fundamental and technological point of view. Semiconducting organic materials can be used in different condensed matter physics applications, such as organic light-emitting diodes, organic field effect transistors, Schottky diodes, photovoltaic and solar cells and so on [1–4]. Polypyrrole (PPy) has been one of the most studied conducting polymers because of its physical and electrical properties, excellent environment stability, and case of preparation either by chemical or by electrochemical polymerization that have led to several applications in solid state devices and electronics [5–8]. However, its naturally poor solubility in common solvents causes some handicaps to extend the application areas [9]. The modification of the monomer structure could be an effective method to improve the solubility and processibility of polypyrrole [10]. Furthermore, various studies have been carried out on the synthesis and polymerization of derivatives of pyrrole [11]. 3-Substituted and N-substituted pyrroles are the most used derivatives to increase the solubility and fusibility of polymers [12].

Unless specially fabricated, a Schottky barrier diode (SBD) possesses a thin interfacial native oxide layer between the metal and the semiconductor. In this case, the metal-semiconductor diode converts a metal/insulator/semiconductor (MIS) diode because of the existence of such an insulating layer which has a strong influence on the diode characteristics such as ideality factor, barrier height (BH) and series resistance. Many attempts have been made to realize a modification and the continuous control of the BH using an organic semiconducting layer, an insulating layer and/or a chemical passivation procedure at certain metal/inorganic semiconductor interfaces, or to determine characteristic parameters of organic film [13–21].

In this study, we synthesized NpClPh Py [N-(p-chloro phenyl) pyrrole (Fig. 1) and polymerized it chemically using FeCl₃ as an oxidant. The obtained polymer was characterized by Fourier transform infrared spectroscopy (FTIR) and conductivity measurements. The molecule structure of the NpClPh PPy used in this study is given in Fig. 2. Our aim is to fabricate an Al/NpClPh PPy/p-Si/Al and to study the suitability and possibility of organic semiconductor contact for use in barrier modification of the MS diode. For this purpose, we have investigated some important parameters of the
structure by measure techniques such as current–voltage ($I$–$V$) and capacitance–voltage ($C$–$V$).

2. Experimental procedure

2.1. Materials

NMR analysis of NpClPh Py was taken with Bruker Avance DPX-400 MHz FT-NMR spectrometer in CDCl$_3$. FTIR spectrum of NpClPh Ppy was recorded between 4000 and 400 cm$^{-1}$ with a resolution of 4 cm$^{-1}$ on a Perkin-Elmer spectrometer (Beaconsfield, HP91QA). The electrical conductivity of NpClPh Ppy was measured by four-probe system with PCI-DAS6014 connected to computer. Dry powdered sample was made into pellet using a steel die having 13 mm diameter in a hydraulic press under a pressure of 200 MPa.

2.2. Synthesis of N-(p-chloro phenyl) pyrrole (NpClPh Py)

N-(p-chloro phenyl) pyrrole, was synthesized according to Clauson–Kaas method [22,23]. 0.059 mol of 4-chloroaniline in 25 ml of acetic acid was mixed in 100 ml flask on the magnetic stirrer. 0.059 mol of 2,5-dimethoxytetrahydrofuran was added to the mixture during 10–15 min. Then, acetic acid was removed from solution using with micro distillation setup. The dark colored precipitate was crystallized and NpClPh Py was observed.

IR ($\nu_{\text{max}} $KBr): 674 cm$^{-1}$ (C–H bending), 723 cm$^{-1}$ (C–Cl), 1017 cm$^{-1}$ (benzene), 1070 cm$^{-1}$ (aromatic C–H bending), 1327 cm$^{-1}$ (C–H bending(alkene)), 1505 cm$^{-1}$ (aromatic ring), 1595 cm$^{-1}$ (C=C stretching), 3040 cm$^{-1}$ (aromatic C=C stretching), 3133 cm$^{-1}$ (C–H stretching alkene).

$^1$H NMR: JHa–Hb: ortho 8.30 Hz, Ha: 7.37 ppm JHb–Ha: ortho 7.82 Hz, Hb: 7.43 ppm; Hα: 7.1 ppm specific triplet peak; Hβ: 6.42 ppm specific triplet peak.

2.3. Synthesis and characterization of N-(p-chloro phenyl) polypyrrole (NpClPh PPy)

NpClPh Py (5.0 × 10$^{-3}$ mol, 0.893 g) was dissolved in 12.5 ml chloroform. On the other hand, the solution includes FeCl$_3$ (5.0 × 10$^{-6}$ mol, 0.081 g) in 10 ml of CHCl$_3$ was prepared and then slowly dropped to monomer solution during 10 min. $n_{\text{max}}/n_{\text{mon}}$ ratio was taken as 2.5. After polymerization time, 24 h, precipitated polymer was filtered and washed with firstly CHCl$_3$ then ethanol until the filtrate was colorless. Finally, the polymer was dried at 50 °C for 24 h under vacuum environment.

2.4. Preparation of Schottky diode

In this study, to fabricate a Schottky diode with polymer interface, p-type silicon wafer with (100) orientation, 400 nm thickness and 1 $\Omega$ cm resistivity was used. The wafer was chemically cleaned by boiling first in NH$_4$OH + H$_2$O$_2$ + 6H$_2$O for 10 min then in HCl + H$_2$O$_2$ + 6H$_2$O at 60 °C for 10 min. The ohmic contact was made by the evaporation of Al with high purity at the back face of the Si wafer. This was followed by a temperature treatment at 580 °C for 3 min in N$_2$ atmosphere. During this process, to remove the native oxide layer formed on the front face, the sample was kept in HF:H$_2$O (1:10) solution for 30 s and finally the wafer was rinsed in de-ionized water for 30 s, then was dried. 30 $\mu$g NpClPh PPy dissolved in 1 $\mu$l N-methyl-2-pyrrolidione (NMP). The solution was directly formed by dropped on the front surface of the p-type silicon substrate, and then waited the solvent to evaporate at room temperature. Finally, in order to realize Schottky contact, Al was evaporated on the polymer layer deposited on the front face of the wafer. The surface area of the Schottky contact formed in Al/NpClPh PPy/p-Si structure is $7.85 \times 10^{-3}$ cm$^2$. All evaporation process was carried out in vacuum coating unit with 10$^{-5}$ Torr operation. Before the fabrication process, all metals were cleaned in acetone and methanol. $I$–$V$ and $C$–$V$ measurements were performed by the use of a Keithley 487 picoammeter/voltage source and a HP4192A LF Impedance analyzer, respectively, at room temperature, in dark.

3. Results and discussion

3.1. FTIR and conductivity results of NpClPh PPy

Fig. 3 shows the FTIR spectrum of NpClPh PPy. The band at 1595 cm$^{-1}$ is the characteristic vibration of pyrrole ring. The band observed at around 1492 cm$^{-1}$ belongs to in plane $\equiv$CH vibrations for pyrrole and phenyl rings [22]. The bands at around 1000 cm$^{-1}$ belong to out of plane vibrations of $\equiv$CH. The bands in the range of 1300 and 1000 cm$^{-1}$ are characteristic peaks for pyrrole ring [23]. The bands indicated the presence of either pyrrole or benzene ring in the spectrum of NpClPh PPy. The conductivity value of NpClPh PPy was measured as $2.07 \times 10^{-5}$ S/cm.

3.2. Optical properties of the conducting polymer

The optical absorption spectrum of sample was studied at UV–Vis range and it is shown in Fig. 4(a). The spectral variation is expressed by [24]:

$$ahv = B(hv - E_g)^m$$

where $B$ is a constant, $E_g$ is the optical band gap, $a$ is absorption coefficient of the film, $v$ is the frequency, $h$ is a Planck's constant. The exponent $m$ depends on the nature of the transition, $m = 1/2, 2, 3/2, 3$ for allowed direct, allowed non-direct, forbidden direct or forbidden non-direct transitions, respectively. We plotted $(ahv)^2$ versus $hv$ photon energy using the data of absorption spectrum of conducting polymer (NpClPh PPy) shown in Fig. 4(a). The optical energy band gaps of the direct allowed transitions dominates in conducting polymer (NpClPh PPy) were obtained from the intercept of the $(ahv)^2$ versus $hv$ plots with the energy axis at $(ahv)^2 = 0$ as shown in Fig. 4(b). The optical energy gap $E_g$ of the conducting polymer (NpClPh PPy) was determined as 2.94 eV. The optical band gap of the polypyrrole studied was compared with the optical band.
Fig. 3. FTIR spectrum of NpClPPy.

Fig. 4. (a) Optical absorption spectrum of the conducting polymer (NpClPPy) on a glass substrate. (b) $(\alpha h \nu)^2$ versus $h \nu$ plot of conducting polymer (NpClPPy) thin film.

gap of other works. This band gap energy value is in well agreement with the values in previous works. For example, Bakhshi et al. [25] and Bredas et al. [26] reported to be 3.00 eV and 3.16 eV, respectively, for the optical band gap energy of polypyrrole prepared by other methods. Also, we have obtained that the conducting polymer (NpClPPy) has a p-type conductivity using the hot-probe technique.

3.3. Electrical properties of Al/NpClPPy/p-Si

According to the thermionic emission theory, the dark $I–V$ characteristics of Schottky contacts can be expressed as [27–29]

$$I = I_0 \left[ \exp \left( \frac{q(V - IR_s)}{nkT} \right) - 1 \right]$$  \hspace{1cm} (1)

where $V$ is the voltage drop across the Schottky barrier, $R_s$ is the series resistance, $n$ is the ideality factor and $I_0$ is the saturation current determined by

$$I_0 = AA^\ast T^2 \exp \left( -\frac{q\Phi_b}{kT} \right)$$  \hspace{1cm} (2)

where $A$ is the diode area, $A^\ast$ is the effective Richardson constant, $k$ is the Boltzmann constant, $T$ is the absolute temperature, $q$ is the electron charge and $\Phi_b$ is the barrier height. From Eqs. (1) and (2), ideality factor $n$ and barrier height $\Phi_b$ can be obtained from the slope and the current axis intercept of the linear regions of the forward-bias $I–V$ plots, respectively. The values of the BH and the ideality factor for the NpClPPy/p-Si diode have been calculated as 0.78 eV and 1.41, respectively. The ideality factor ($n = 1.41$) of the Al/p-Si/NpClPPy diode at the room temperature is significantly higher than that of the Al/p-Si conventional Schottky
The obtained $n$ value confirms that the Al/p-Si/NpClPh PPy diode is metal-insulating layer-semiconductor (MIS) configuration rather than an ideal Schottky diode [28,31]. Higher values of ideality factors are attributed to different reasons. These include interface dipoles due to interface doping or specific interface structure as well as fabrication-induced defects at the interface [32–35]. The high values of $n$ can also stem from the presence of a wide distribution of low-SBH patches caused by inhomogeneous lateral barrier [34]. The image-force effect, recombination-generation, and tunneling may be possible mechanisms that could lead to an ideality factor value greater than unity. When the $I_0$ and $\Phi_b$ of Al/p-Si/NpClPh PPy diode are compared with Al/p-Si conventional diode, it is evaluated that the rectifying properties of Al/p-Si diode are modified by NpClPh PPy organic film. The values of $I_0$ and $\Phi_b$ were found to be $2.18 \times 10^{-9}$ A and 0.78 eV, respectively. The barrier height ($\Phi_b = 0.78$ eV) of Al/p-Si/NpClPh PPy diode at the room temperature is higher than that of the conventional Al/p-Si Schottky diode ($\Phi_b = 0.6$ eV) [35]. This suggests that NpClPh PPy organic layer modifies the electronic parameters of the diode.

In the literature, some studies have been made experimentally for the barrier height modification using the organic thin films as interfacial layer. In most of these studies, the authors have been reported that the existence of organic thin films cause an increase in the barrier height value. The barrier height and the ideality factor values at room temperature obtained for p-Si/metal Schottky diodes with organic interfacial layer are listed in Table 1.

$\Phi_b=0.64$ eV

$I-V$ characteristic at forward bias is linear on a semilogarithmic scale, but at higher voltages, a deviation from linearity is observed due to interfacial layer and series resistance which affects the ideality factor of the diode. In such a case, in order to determine the diode parameters, the various models have been developed to determine the barrier height value. The two methods is explained on the basis of two reasons. The first difference between the values of ideality factor obtained from the two methods is explained on the basis of two reasons. The first reason is that the ideality factor value obtained from the forward bias I–V plot and those obtained from the Cheung curves. The other is that the $n$ values are obtained from the different regions of characteristic for the two methods. The $n$ value obtained from I–V characteristic is calculated using the data on the linear region of the curve. In this part of the curve the essential effects on the characteristic are interface layer and interface states [36].

Norde proposed a method to determine value of the series resistance. The following function has been defined in the modified Norde’s method [37]:

$$F(V) = \frac{V}{y} - kT \ln \left( \frac{I}{AA^2T^2} \right)$$

where $y$ is the first integer (dimensionless) greater than $n$. That is, according to our results, the value of $y$ is 2. $I/[V]$ is current obtained from the $I-V$ curve. Once the minimum of the $F$ versus $V$ plot is determined, the value of barrier height can be obtained from Eq. (8).

$$\phi_b = F(V_0) + \frac{V_0}{2} - \frac{kT}{q}$$

Fig. 5. Current (logarithmic) versus voltage characteristic of the Al/NpClPh PPy/p-Si/Al Schottky diode.

Table 1

<table>
<thead>
<tr>
<th>Structure</th>
<th>$n$</th>
<th>$\Phi_b$ (eV)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu/rhodamine-101/p-Si/Al</td>
<td>1.54</td>
<td>0.78</td>
<td>Temirci and Çakar [13]</td>
</tr>
<tr>
<td>Al/Rh101/p-Si/Al</td>
<td>2.43</td>
<td>0.82</td>
<td>Karatas et al. [14]</td>
</tr>
<tr>
<td>Cu/pyronine-B/p-Si</td>
<td>1.37</td>
<td>0.51</td>
<td>Çakar et al. [15]</td>
</tr>
<tr>
<td>Au/pyronine-B/p-Si</td>
<td>2.01</td>
<td>0.67</td>
<td>Çakar et al. [15]</td>
</tr>
<tr>
<td>Al/pyronine-B/p-Si</td>
<td>2.1</td>
<td>0.75</td>
<td>Çakar et al. [15]</td>
</tr>
<tr>
<td>Sn/pyronine-B/p-Si</td>
<td>1.13</td>
<td>0.79</td>
<td>Çakar et al. [15]</td>
</tr>
<tr>
<td>Polyaniline/p-type Si/Al</td>
<td>2.09</td>
<td>0.79</td>
<td>Çakar et al. [15]</td>
</tr>
<tr>
<td>Polypyrrole/p-type Si/Al</td>
<td>2.00</td>
<td>0.68</td>
<td>Sağlam et al. [16]</td>
</tr>
<tr>
<td>Polyaniline/p-Si/Al</td>
<td>1.38</td>
<td>0.68</td>
<td>Aydın et al. [20]</td>
</tr>
<tr>
<td>Au/polymer/p-Si/Al</td>
<td>1.88</td>
<td>0.78</td>
<td>Aydın et al. [18]</td>
</tr>
<tr>
<td>Al/p-Si/CuPc/Au</td>
<td>2.38</td>
<td>0.71</td>
<td>Yakuphanoglu [19]</td>
</tr>
<tr>
<td>Al/MEH-PPy/p-Si</td>
<td>1.88</td>
<td>0.80</td>
<td>Aydın et al. [20]</td>
</tr>
<tr>
<td>Al/Cr(CongoRed)/p-Si</td>
<td>1.68</td>
<td>0.77</td>
<td>Gülü et al. [21]</td>
</tr>
</tbody>
</table>
where \( F(V_0) \) is the minimum point of \( F(V) \) and \( V_0 \) is the corresponding voltage. Fig. 7 shows the \( F(V) \)-\( V \) plot of the structure. From modified Norde’s functions, \( R_s \) value can be determined as

\[
R_s = \frac{kT(2 - n)}{qE_v}\]

(9)

From the \( F \)-\( V \) plot using \( F(V_0) = 0.74 \) and \( V_0 = 0.18 \) values, the values of \( \Phi_b \) and \( R_s \) of the structure have been determined as 0.77 eV and 47 k\( \Omega \), respectively. There is a good agreement with the values of \( \Phi_b \) obtained from the forward bias \( \ln I-V \) and Norde functions. The value of resistance is dramatically higher than that obtained from Cheung functions. Cheung functions are only applied to the non-linear region in high voltage region of the forward-bias \( \ln I-V \) characteristics. But, Norde’s functions are applied to the full forward-bias region of the \( \ln I-V \) characteristics of the junctions. The value of series resistance may also be very high for the higher ideality factor values. Furthermore, the value of series resistance is very high for this device. This indicates that the series resistance is a current-limiting factor for this structure. The very high series resistance behavior may be ascribed to decrease of the exponentially increasing rate in current due to space charge injection into the NpcIPh Py thin film at higher forward-bias voltage. Thus, Norde’s model may not be a suitable method especially for the high ideality factor of the rectifying junctions, which are non-agree with pure thermionic emission theory. We assume that another mechanism starts to control the current flow. This mechanism is probably tunneling, because the tunneling process is important especially for a thin interfacial layer [29].

The higher ideality factor is believed to be arising due to the voltage drop across an interfacial layer. The density of the interface state proposed by Card and Rhoderick is given by [38]:

\[
N_{ss} = \frac{1}{q} \left[ \frac{E_s}{\delta} (n - 1) - \frac{E_s}{W} \right]
\]

(10)

where \( N_{ss} \) is the density of the interface states, \( E_s \) is the dielectric constant of the interfacial layer, \( W \) is the space charge width and \( \delta \) is the thickness of interfacial layer. In a p-type semiconductor, the energy of the interface states \( E_{ss} \) with respect to the top of the valence band at the surface of the semiconductor is given [39]:

\[
E_{ss} - E_v = \Phi_e - qV
\]

(11)

where \( \Phi_e \) is the effective barrier height. \( N_{ss} \) values are obtained via Eq. (10) and are shown in Fig. 8. The \( N_{ss} \) value decreases with increasing \( E_{ss} - E_v \) value. The values of the density of interface states are of the order of \( 4 \times 10^{11} \) eV\(^{-1}\) cm\(^{-2}\). Similar results have been reported in the literature [40–42]. The density of interface states of Schottky diode with the presence of an interfacial insulator layer is lower than that of Schottky barriers without an interfacial insulator layer [42,43]. These values of interface state density were responsible for the non-ideal behavior of \( I-V \) and \( C-V \) characteristics.

The depletion layer capacitance of Schottky diodes, \( C \), can be expressed as [27]

\[
C^2 = \frac{2(V_0 + V)}{q\varepsilon_0 N_A A^2}
\]

(12)

where \( A \) is the area of the diode, \( V_0 \) is the intercept voltage and \( V \) is determined from the extrapolation of the linear \( C^{-2} \)-\( V \) plot to the \( V \) axis, \( \varepsilon_0 \) is the dielectric constant of the semiconductor, \( N_A \) is the acceptor concentration of the p-type semiconductor substrate. Fig. 9 shows the reverse bias \( C^{-2} \)-\( V \) characteristic of the devices at 1000 kHz and 300 K. The BH and carrier concentration values for diode were extracted from its reverse bias \( C^{-2} \)-\( V \) characteristic. The barrier height value obtained from the reverse bias \( C^{-2} \)-\( V \) characteristic has varied 0.89 eV. A doping density has been determined about \( 1.27 \times 10^{15} \) cm\(^{-3}\) from the reverse bias \( C^{-2} \)-\( V \) characteristic. The barrier height obtained from the \( C-V \) measurements is higher than obtained from the \( I-V \) measurements. The barrier heights deduced from two techniques are always different due to the nature of \( I-V \) and \( C-V \) measurements. The discrepancy between \( \Phi_b (C-V) \) and \( \Phi_b (I-V) \) can be explained by distribution of Schottky barrier height due the inhomogeneities such as non-uniformity of the interfacial layer thickness and distributions of the interfacial charges [44,45]. The inhomogeneities affect apparent Schottky barrier height, as the current across the interface depends exponentially on Schottky barrier height and the current is

![Fig. 7. \( F(V) \) versus \( V \) plot of the Al/NpCIPh PPY/p-Si structure.](image)

![Fig. 8. Variation of \( N_{ss} \) values with \( E_{ss} - E_v \) for Al/NpCIPh PPY/p-Si diode.](image)

![Fig. 9. Capacitance versus voltage characteristic of the Al/NpCIPh PPY/p-Si diode.](image)
sensitive to barrier distribution at the interface [45,46]. The barrier height obtained from the C–V method includes an average value of the Schottky barrier heights of patches available in the contact [45,46].

4. Conclusion

$I$–$V$ and $C$–$V$ characteristics of the Al/NpClPh PPy/p-Si/Al structures have been investigated. The values of the ideality factor, barrier height and series resistance calculated using different methods were compared. It has been seen that NpClPh PPy conducting polymer on the p-Si substrate indicates a good rectifying behavior.

We have compared the parameters of the conducting polymer (NpClPh PPy)/p-Si Schottky diodes with those of conventional MS diodes. Al/NpClPh PPy/p-Si/Al structure has MIS configuration rather than an ideal Schottky diode. The existence of the conducting polymer has caused an increase in the barrier height value in some studies previously reported. By using the capacitance–voltage measurement, the barrier height and free carrier concentration values for the Al/NpClPh PPy/p-Si/Al diode have been calculated as 0.89 eV and $1.27 \times 10^{15}$ cm$^{-3}$, respectively. The $\Phi_B$ (0.89 eV) value obtained from $C$–$V$ measurement is higher than the $\Phi_B$ (0.78 eV) value obtained from $I$–$V$ measurement. The density distribution of the interface states of the diode was determined to vary from $7 \times 10^{11}$ eV$^{-1}$ cm$^{-2}$ to $0.4 \times 10^{11}$ eV$^{-1}$ cm$^{-2}$. It is evaluated that the conducting polymer(NpClPh PPy) can be used in the device modification and some applications of the metal-semiconductor diodes.

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