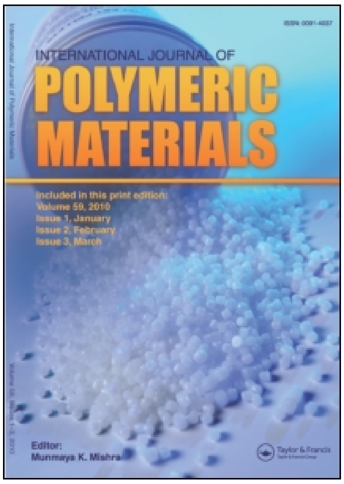

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Determination of the Characteristic Parameters of Polyaniline/*p*-type Si/AI Structures from Current-Voltage Measurements

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A high-quality polyaniline/p-Si structure is produced by electrochemical deposition of soluble polyaniline on p-type silicon substrates. The polyaniline/p-Si contact has clearly demonstrated rectifying behavior by current-voltage curves studied at room temperature. The data have been analyzed and interpreted on the basis of the thermionic emission mechanism. The forward bias I-V characteristics of this device have exhibited an ideality factor of 2.15, a saturation current of 4.48×10^{-9}*A, and a barrier height of 0.78 eV. The diode shows non-ideal I-V behavior with an ideality factor greater than unity that can be ascribed to the interfacial layer, the interface states, and the series resistance.*

Keywords: polyaniline, polyaniline/inorganic semiconductor contact, series resistance, Schottky contact, interface states, interfacial layer

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INTRODUCTION

Conjugated polymers are a new class of materials of great potential for fabrication of solid-state devices [1]. The electrical conductivity of these polymers can be changed from insulating to metallic by chemical or electrochemical doping and they can be used to produce electronic devices such as Schottky diodes, field effect transistors, light-emitting diodes, and photodetectors, among others [1–7]. Owing to the technological importance of metal/semiconductor devices in the electronics industry, the contact properties of polymers, such as the polymer/inorganic semiconductors structures [8–10] and metal/semiconductor ductor polymer contacts [11–12] have been extensively studied experimentally and theoretically [13]. In the field of organic semiconductor materials, polyaniline is one of the most studied polymers and is an attractive and interesting conducting polymer for electrochemical devices because of its simple preparation technique, good chemical stability, and excellent electrochemical properties [9–14]. Its basic properties and application to electrochemical devices have been investigated [15–16]. In the present work the authors have used polyaniline for the preparation of polyaniline/*p*-Si heterocontacts. The current-voltage measurements of the diode have been carried out under laboratory conditions in the dark.

EXPERIMENTAL PROCEDURE

The samples were prepared using mirror cleaned and polished (as received from the manufacturer) *p*-type Si wafers with (100) orientation and 15–20 Ω cm resistivity. The ohmic contact was made by evaporating Al on the back of the substrate, followed by a temperature treatment at 600°C for 3 min in a N_2 atmosphere. The native oxide on the front surface of *p*-Si was removed in a HF:H_2O (1:15) solution and finally the wafer was rinsed in deionized water before polymerization was carried out. The ohmic contact made and the edges of the *p*-Si substrate used as an anode were carefully covered by wax so that the polished and cleaned front side of the sample was exposed to the electrolyte by mounting it in an experimental set-up employed for anodization. A Pt plate was used as the cathode. Anodization process was carried out under constant current conditions of $I = 1\,\text{mA}$ and at room temperature. The electrolyte was composed of 10 mM aniline and 0.1 M tetrabutylammonium tetrafluoroborate. The aniline, obtained from Riedel-deHaen, was used to prepare polyaniline at room temperature. The electrolyte solution was prepared in acetonitrile solvent (Merck trademark). In order to realize polyaniline/*p*-Si

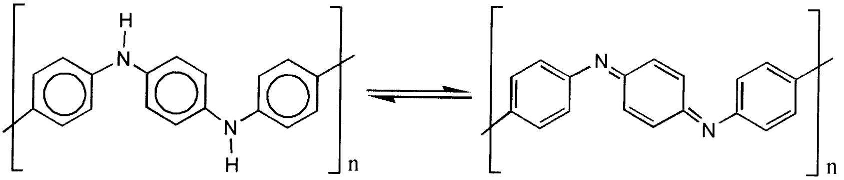

FIGURE 1 Chemical structure of metallic polyaniline polymer.

heterocontacts, the polymer film was electrochemically deposited on the surface of the *p*-Si. The area of the circular polyaniline contacts on the *p*-Si was 0.0314 cm^2. After the polymerization process the polymer-coated Si was cleaned by methanol for 15 min at room temperature. Thus, Polyaniline/*p*-Si/Al structures were obtained.

The chemical structure of the polyaniline polymer used in this experiment is given in Figure 1. The schematic cross-sectional view of the sample holder together with the polyaniline/*p*-Si/Al structure is shown in Figure 2. The current-voltage measurements of the device were performed at room temperature in the dark, using a HP4140B picoampermeter.

RESULTS AND DISCUSSION

The parameters of the heterocontact were obtained using a simple Schottky model that assumes a well-defined fixed potential barrier at the interface over which the electrons are themionically emitted [9]. The current (I)-voltage (V) equation in respect to the thermoionic emission theory in the presence of interfacial layer is given by [17]

$$I = AA^*T^2 \exp\left(\frac{-q\Phi_b}{kT}\right)\left[\exp\left(\frac{q(V - IR_s)}{nkT}\right) - 1\right] \tag{1}$$

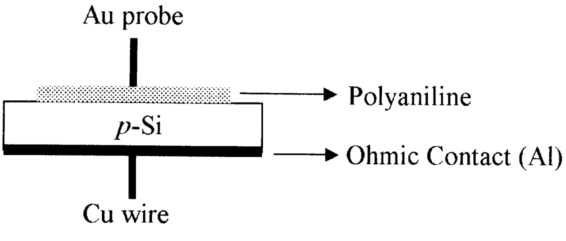

FIGURE 2 A cross-sectional view of fabricated polyaniline/*p*-Si Schottky diode.

where A is the effective area of diode, A^* is the effective Richardson constant; Φ_b is the barrier height; T is the temperature; q is the elementary charge; k is Boltzmann constant; R_s is the series resistance and n is the ideality factor. The saturation current I_o may be denoted by

$$I_o = AA^*T^2 \exp\left(\frac{-q\Phi_b}{kT}\right) \tag{2}$$

and is obtained by extrapolation of the forward or reverse bias current-voltage (I-V) curve to zero applied voltage. The slope of the linear portion of the I-V curve gives the idealty factor, which means that the deviation from the ideal I-V characteristics can be due to the presence of an indefinable interfacial layer that introduces the interface states located at polyaniline/p-Si interface. Such a layer may be formed during the surface preparation.

One often uses Eq. 1 in the literature as given in Reference [17], but the following I-V expression, which has the advantage that the ideality factor n, can be experimentally found is more correct [17].

$$I = I_o \exp\left(\frac{qV}{nkT}\right)\left[1 - \exp\left(\frac{-qV}{kT}\right)\right] \tag{3}$$

The fact that n has a value grater than unity suggests that the voltage applied is not dropped entirely across the depletion region. Rather, it is shared by the interfacial layer, the depletion layer, and substrate resistance. n can be found experimentally by plotting forward and reverse bias $\ln\{I/[1 - \exp(-qV/kT)]\}$ versus V (Figure 3). This graph should be a straight line of slope $q/nkT = d/dV(\ln/[1 - \exp(-qV/kT)])$ if n is constant. The values from this plot are given in Table 1.

The barrier height, as well as the other diode paramerters as the ideality factor n and the series resistance R_s can be calculated using a method developed by the Cheungs using Eq. 1 [18]. Cheung's functions can be written as follows

$$\frac{dV}{d(\ln I)} = IR_s + n\left(\frac{kT}{q}\right) \tag{4}$$

$$H(I) = V - n\left(\frac{kT}{q}\right)\ln\left(\frac{I}{AA^*T^2}\right) \tag{5}$$

and

$$H(I) = IR_s + n\Phi_b \tag{6}$$

where Φ_b is the barrier height obtained from data of downward curvature region in the forward bais I-V characteristics. Eq. 4 should give a

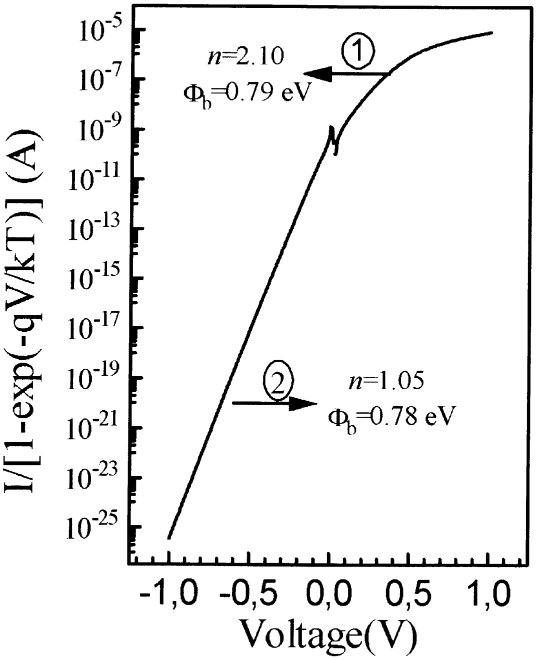

FIGURE 3 ln $\{I/[1-\exp(-qV/kT)]\}-V$ plot of polyaniline/p-Si Schottky diode.

straight line for the data of downward curvature region in the forward bias I-V characteristics. Thus, the slope and y-axis intercept of a plot of $dV/d(\ln I)$ versus I will give R_s and nq/kT, respectively. Using the n value determined from Eq. 4 and the data of downward curvature region in the forward bias I-V characteristics in Eq. 5, a plot of $H(I)$ versus I according to Eq. 5 will also give a straight line with y-axis intercept equal to $n\Phi_b$. The slope of this plot also provides a second

TABLE 1 The Experimental Parameters Calculated by Means of Three Different Techniques

		$\ln\{I/[1-\exp(-qV/kT)]\}-V$			
Parameters	I-V	Forward bias	Reverse bias	$dV/d(\ln I)-I$	$H(I)-I$
n	2.15	2.10	1.05	3.30	—
Φ_b	0.78 eV	0.79 eV	0.78 eV	—	0.73 eV
R_s	—	—	—	3.84 kΩ	4.06 kΩ

determination of R_s that can be used to check the consistency of Cheung's approach.

Figure 4 shows the room temperature forward and reverse bias current-voltage *(I-V)* characteristic of polyaniline/*p*-Si structure. The values of the parameters from these characteristics are $\Phi_b = 0.78\,\mathrm{eV}$, $n = 2.15$ and the forward saturation current $I_0 = 4.48 \times 10^{-9}\mathrm{A}$. These values of the parameters are shown in Table 1. The value of the barrier height of the polyalinine/*p*-Si structure was calculated from the y-axis intercept of the semilog-forward bias *I-V* characteristics according to Eq. 2. The value of the ideality factor *n* was calculated from the slope of the linear region of the forward *I-V* characteristics according to Eq. 1. As can be seen in Figure 4, the forward bias *I-V* curve of the polyaniline/*p*-Si structure deviates from linearity above 0.45 V. The curvature downward in the forward bias *I-V* plot at sufficiently large applied voltage is due to the substrate series resistance and to the continuum of the interface states [13]. From the value of *n* it can be deduced that the device represents polyaniline-interfacial

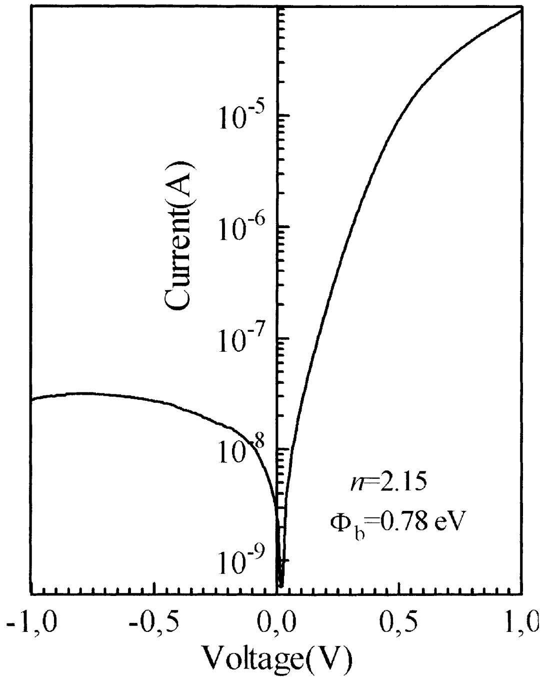

FIGURE 4 The forward and reverse bias current-voltage characteristics of polyaniline/*p*-Si Schottky diode.

layer-semiconductor configuration rather than an ideal diode. Having n values significantly greater than unity is a result of interface states in the polyaniline/p-Si interface [19–21]. In this kind of device, because the front surface of p-Si is exposed to air before forming the polyaniline, there is probably an insulating oxide layer between the polymer and p-Si substrate. In the case of Schottky barrier devices, smaller n values imply a lower density of the interface states [19–23].

The forward and reverse bias $\ln\{I/[1-\exp(-qV/kT)]\}-V$ characteristic of the polyaniline/p-Si diode is shown in Figure 3. The value of 1.05 for the ideality factor was obtained from the slope of the linear portion of the reverse bias $\ln\{I/[1-\exp(-qV/kT)]\}-V$ plot. The value of 2.10 for the ideality factor was obtained from the slope of the first linear portion (forward bias) of the same graph. The Φ_b values obtained from this graph (for forward and reverse bias) are almost equal to each other. The values of the calculated parameters are given in Table 1. The deviation from linearity above 0.45 V is due to series resistance and interface layer. The value of n calculated from the first linear region of the forward and reverse bias $\ln\{I/[1-\exp(-qV/kT)]\}-V$ plot was greater than unity. Thus, the non-ideal I-V characteristics indicate that the diode is not in intimate polyaniline-inorganic semiconductor heterocontact; that is, it does not obey the ideal diode theory. This non-ideality can be ascribed to the interfacial layer, interface states, and series resistance. Interfacial layer may be formed during surface preparation.

The plot of the Cheungs' functions [Eqs. (4)–(6)] is given in Figure 5. The values of n and Φ_b were obtained from the vertical axis intercepts of $dV/d(\ln I)-I$ and $H(I)-I$ curves and the values of R_s from their slopes are given in Table 1. Thus, it is clearly seen that the value of 3.30 for n from the downward curvature region, which results from the effect of the series resistance and interface states, is greater than the value of 2.15 obtained from the linear region of the same characteristics reflecting the effect of only the interface states. As seen in Table 1, the values of R_s obtained from $dV/d(\ln I)-I$ and $H(I)-I$ plots are approximately equal to each other. This case shows the consistency of Cheungs' approach.

CONCLUSIONS

This article has demonstrated that the polyaniline/p-Si heterocontacts can be fabricated on cleaved p-Si substrates. It has been shown that the ideality factor from the I-V characteristics of the polyaniline/p-Si/Al structure is much lower than those reported in the literature and its barrier height value is much higher [24–26]. Briefly, electrochemically

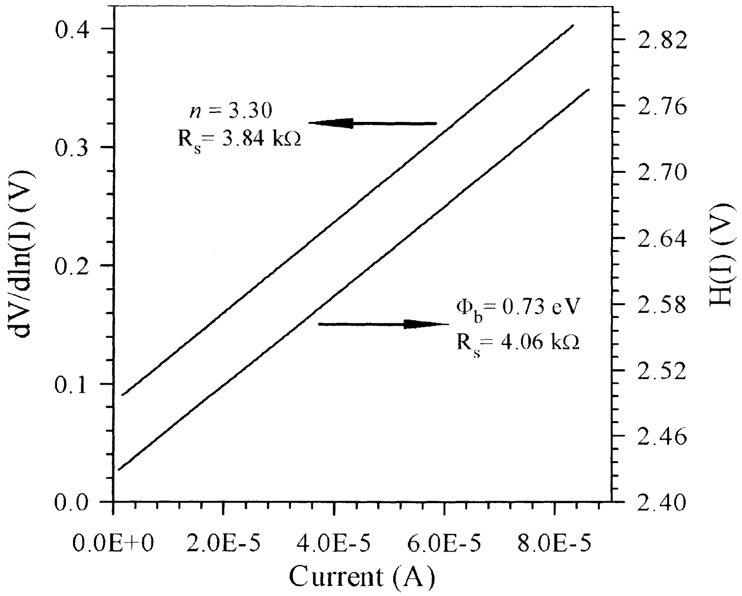

FIGURE 5 Experimental $dV/d(\ln I) - I$ and $H(I) - I$ curves.

deposited polymer films on the p-Si may be used for a rectifying contact formation. In view of that, the authors have polymerized aniline electrochemically on a p-type semiconductor surface and have obtained a polyaniline/p-Si heterocontact. The diode investigated here suffers from barrier lowering due to a high density of interface states and an interfacial layer between the polymer and p-type semiconductor that substantially reduces the performance and reliability of these devices. Despite this, this article has shown that semiconductor polymers are promising for the fabrication of electronic devices.

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