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Controlling of electronic parameters of GaAs Schottky diode by poly(3,4-ethylenedioxithiophene)-block-poly(ethylene glycol) organic interlayer

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ABSTRACT

The electronic properties of metal–organic semiconductor–inorganic semiconductor structure between GaAs and poly(3,4-ethylenedioxithiophene)-block-poly(ethylene glycol) organic film have been investigated via current–voltage and capacitance–voltage methods. The Au/PEDOT/*n*-GaAs contact exhibits a rectification behavior with the barrier height of 0.69 eV and ideality factor value of 3.94. The barrier height of the studied diode (0.67 eV) is lower than that of Ni/*n*-GaAs/In (0.85 eV) and Au/*n*-GaAs/In Schottky diodes. The decrease in barrier height of Au/*n*-GaAs/In Schottky diode is likely to be due to the variation in the space charge region in the GaAs. The obtained results indicate that control of the interfacial potential barrier for metal/*n*-GaAs diode was achieved using thin interlayer of the poly(3,4-ethylenedioxithiophene)-block-poly(ethylene glycol).

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1. Introduction

The most simple of the metal–semiconductor contacts, Schottky barrier diodes, having technological importance requires a complementary understanding of their electrical characteristics [1–7]. As a semiconductor, GaAs with wide band gap property has widely been used as one of the most profitable semiconductor material for its power applications that are excellent transport and thermal properties, a high breakdown voltage, chemical inertness, and mechanical stability. It is well known that the electrical characteristics of a Schottky contact are mainly controlled by its interface properties. Thus, the study of interface states within the forbidden band gap at organic/inorganic semiconductor interface is significant for the comprehending of the electrical properties of Schottky contacts. The turnout of GaAs-based devices, appertaining metal–semiconductor field effect transistors (MESFETs) and hetero-structure bipolar transistors (HBTs), depends on the surface and interface state density. GaAs has a thin native oxide present on its surface inducing a very large surface-state density that results in the pinning of the Fermi level [8–12]. The technological compression bred by the progressive caption of worldwide telecommunication has triggered the improvement of transmitters and receivers based on devices operating at very high frequency. Schottky diodes are often used for complicated applications in telecommunication systems, radio astronomy, radar technology, and plasma diagnostics [13–22]. Electronic features of a Schottky contact can be described by its barrier height [23]. The barrier height is defined as the difference between the edge of the respective majority-carrier band of the semiconductor and the Fermi level at the metal/semiconductor interface [16–26]. As can be understood very easily that research on processes which effect barrier heights at Schottky contacts or metal–semiconductor contacts has a big importance from a basic and a practical angle of view.

The remarkable interest in the electrical and optical properties of organic molecular semiconductors reflects their increasingly widespread use in organic and hybrid inorganic–organic devices [5–7,13–19,27–29]. Much of this activity has been focused on understanding and controlling key parameters such as the interface potential barriers. In these studies, using a range of organic molecules, inorganic Schottky diodes have been modified by monolayer adsorption on the substrate surface. The adsorption of small conjugated molecules of organic layer on the substrate layer strongly modifies the effective barrier heights. Due to interaction of GaAs with metal during metallization having a powerful effect on electrical parameters, the organic interlayer formed at Au/*n*-GaAs interface reducing the effect of interaction has gained a big importance to these kind of diodes in high frequency applications [14–18,26,31–33]. Adsorption of the organic molecules and

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varying potential in the organic semiconductor makes a contribution to the potential drop across the metal/organic interface and a change in metal work function. In this manner, the existence of thin films of organic semiconductors in inorganic Schottky diodes provide an alternative method for the controlling of basic devices [11–18,31–33]. GaAs Schottky diodes modified by organic interlayers are of considerable interest in high frequency applications [34]. The manuscript is on the electrical characteristics of Au/PEDOT/*n*-GaAs/In contact, where the metal/semiconductor interface is modified with a thin layer of poly(3,4-ethylenedioxithiophene)-block-poly(ethylene glycol), 1 wt.% disp. in propylene carbonate (PEDOT) film. Our purpose is to examine whether or not the PEDOT has also been successfully used to continuously vary effective barrier for the metal/GaAs Schottky diode.

2. Experimental procedure

The cleaned and polished *n*-type GaAs wafer used for the fabrication of the Au/PEDOT/*n*-GaAs diode has (1 0 0) orientation and $7.3 \times 10^{15}\ \mathrm{cm}^{-3}$ carrier concentration according to manufactures' specifications. Before making contacts, the *n*-GaAs wafer was dipped in $5H_2SO_4 + H_2O_2 + H_2O$ solution for 1.0 min to remove surface damage layer and undesirable impurities and then in H_2O + HCl solution and then followed by a rinse in de-ionized water of 18 MΩ. The wafer was dried with high-purity nitrogen and inserted into the deposition chamber immediately after the etching process, Indium (In) for ohmic contacts was evaporated on the back of the wafer in a vacuum-coating unit of 4.5×10^{-5} Torr. Then, low resistance ohmic contact was formed by thermal annealing at 350 °C for 3 min in flowing N_2 in a quartz tube furnace. Then the substrates were inserted into the same vacuum system, and poly(3,4-ethylenedioxithiophene)-block-poly(ethylene glycol), 1 wt.% disp. in propylene carbonate (PEDOT) film was formed on the front surface of the *n*-GaAs/In by spin coating. After film deposition, the Schottky contact was formed by evaporating Au as dots with diameter of 2 mm on PEDOT/GaAs. The current–voltage (*I–V*) and capacitance–voltage (*C–V*) characteristics of the diode were measured by a KEITHLEY 4200 Semiconductor Characterization System under dark conditions.

3. Results and discussion

3.1. Current–voltage characteristics of the Au/PEDOT/n-GaAs diode

Fig. 1 shows the current–voltage characteristics of the Au/PEDOT/*n*-GaAs diode. The Au/PEDOT/*n*-GaAs contact shows a rectifying behavior with non-ideal behavior.

It is well known that according to the thermionic emission theory, the current across a Schottky diode with the series resistance is given by the following relation,

$$I = AA^{*}T^{2}\exp\left(-\frac{q\phi_b}{kT}\right)\exp\left(\frac{q(V-\mathrm{IR}_s)}{nkT}\right) \quad (1)$$

where I_0 is the saturation current, A is the effective diode area, A^* is the effective Richardson constant equal to 8.16 A/cm^2 K^2 for *n*-type GaAs, T is the absolute temperature, ϕ_b is the barrier height, k is the Boltzmann constant, R_s is the series resistance and q is the electric charge. n is the ideality factor, which is a measure of conformity of the diode to pure thermionic emission. The ideality factor, n and barrier height of Au/*n*-GaAs/In Schottky diode were determined to be 3.54 and 0.69 eV, respectively. The barrier height of the studied diode (0.69 eV) without series resistance effect is lower than that of Ni/*n*-GaAs/In (0.85 eV) [35] and Au/*n*-GaAs/In [36] Schottky diodes. The decrease in barrier height of the diode is likely to be due to the variation in the space charge region in the GaAs [30]. The obtained results indicate that control of the interfacial potential barrier for metal/*n*-GaAs diode was achieved using thin interlayer of the poly(3,4-ethylenedioxithiophene)-block-poly(ethylene glycol). The diode gives a higher ideality factor and this can be attributed to the interfacial states and series resistance and the film properties of organic compound PEDOT. If the GaAs surface is prepared by the usual polishing and chemical etching technique, the GaAs surface is inevitably covered with a thin insulating film and thus, interfacial oxide layer will be formed by water or vapour adsorbed onto the surface of the *n*-GaAs before the formation of PEDOT on the front surface of the *n*-GaAs substrate [37,38]. It may form either during surface preparation and metal evaporation or post-deposition thermal annealing [15,37,39–42]. For a sufficiently thick interface layer, the interface states are in equilibrium with the inorganic semiconductor and they cannot interact with the metal. The measurability of interface states of the Au/PEDOT/*n*-GaAs Schottky structure requires an interfacial layer consisting of the native oxide plus the PEDOT layer that separates the interface states from the metal [15]. The Au/PEDOT/*n*-GaAs Schottky diode with the ideality factor value of 3.54 obeys a metal-interfacial layer-semiconductor (MIS) configuration rather than an ideal Schottky diode. At higher currents there is always a deviation of the ideality that has been clearly shown to depend on the interface state density and bulk series resistance, as one would expect and the lower the interface state density and the series resistance, the greater is the range over which ln *I–V* yield a straight line. In order to check effect of series resistance on *I–V* characteristics, we used Norde method given by the following relation,

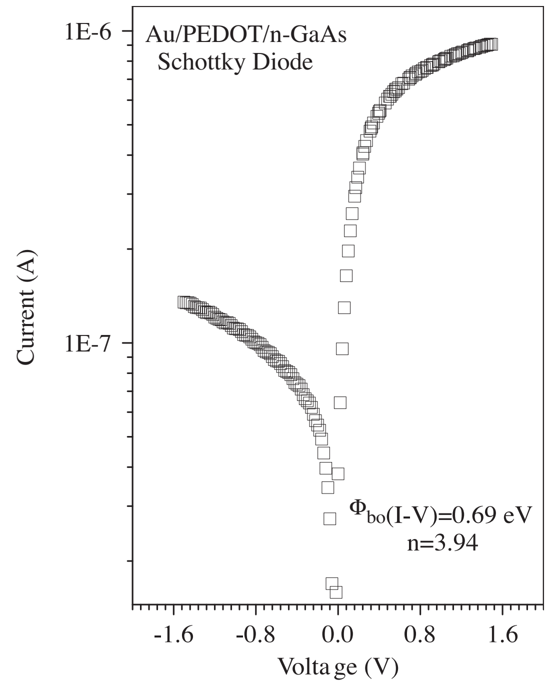

Fig. 1. Current–voltage characteristics of the Au/PEDOT/*n*-GaAs diode.

$$F(V) = \frac{V_0}{\delta} - \frac{kT}{q}\left(\frac{I(V)}{A^{*}AT^{2}}\right) \quad (2)$$

$I(V)$ is the current obtained from the *I–V* characteristics of the diode. The plot of $F(V)$ vs voltage for the diode is shown in Fig. 2.

The $F(V)$ gives a minimum point and thus, the barrier height is calculated by the relation,

$$\Phi_b = F(V_0) + \frac{V_0}{\delta} - \frac{kT}{q} \quad (3)$$

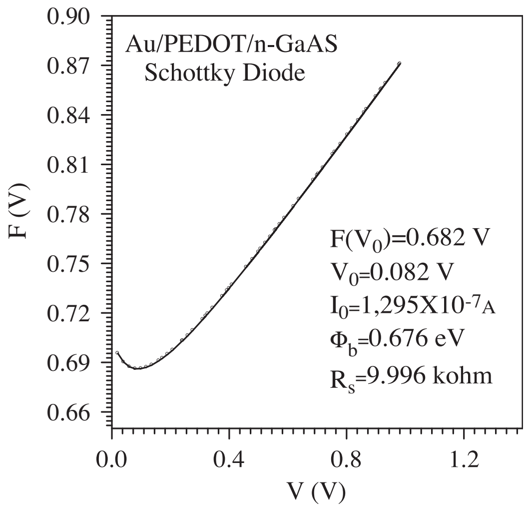

Fig. 2. $F(V)$ vs. V plot of the Au/PEDOT/n-GaAs Schottky diode.

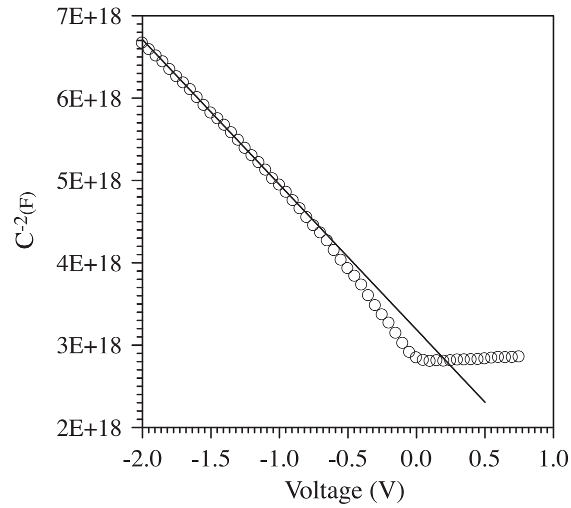

Fig. 3. C^{-2}–V curve of the Au/PEDOT/n-GaAs Schottky diode at 1.0 MHz.

where $F(V_0)$ is the minimum point of $F(V)$. The barrier height was found to be 0.67 eV. Also, the series resistance for the diode is determined by the following relation,

$$R_s = \frac{kT(\delta - n)}{qI_o} \tag{4}$$

where δ is the integer (dimensionless) higher than n and the n value for the diode is 3.94. Thus, δ was taken as 4. The R_s value for the diode was determined using Eq. (4) and was found to be 9.99 kΩ. This is considerable higher due to the interfacial states and series resistance and the film properties of organic compound PEDOT. This causes a non-linear region of forward bias I–V curve of the diode.

3.2. Capacitance–voltage characteristics of Au/PEDOT/n-GaAs diode

The value of the barrier height can be obtained by the relation,

$$\Phi_b(C - V) = C_2 V_{\mathrm{do}} + V_n \tag{5}$$

where $C_2 = 1/n$, V_n is the potential difference between the Fermi level and the bottom of the conduction band in the neutral region of n-GaAs and can be calculated knowing the carrier concentration N_d and it is obtained from the following relation,

$$V_n = (kT)\ln\left(\frac{N_c}{N_d}\right), \tag{6}$$

where $N_c = 4.3 \times 10^{17}\ \mathrm{cm}^{-3}$ is density of states in the conduction band [17].

In Schottky diodes, the depletion layer capacitance can be expressed as in [8,43,44],

$$C^{-2} = 2(V_{\mathrm{do}} + V)/q\varepsilon_s A^2 N_d \tag{7}$$

where A is the area of the diode, V_{do} is the diffusion potential at zero bias and is determined from the extrapolation of the linear C^{-2}–V plot to the V axis. N_d is the concentration of ionized donors for Si doped GaAs. The N_d is related to the slope of C^{-2} vs V curve and can be obtained from the expression given with $N_d = (2/q\varepsilon_s\varepsilon_0 A^2)[1/(dC^{-2}/dV)]$. Fig. 3 shows the reverse bias C^{-2}–V characteristics of one of the Au/PEDOT/n-GaAs at 1.0 MHz.

The diffusion potential value of 1.81 and doping concentration value of $6.2 \times 10^{15}\ \mathrm{cm}^{-3}$ from the reverse bias C^{-2}–V plot were obtained for the Au/PEDOT/n-GaAs and the barrier height value of 0.72 eV via Eq. (5) using V_p value of about 0.112 V for the diode. The values obtained from the C^{-2}–V (0.72 eV) and I–V characteristics (0.69 eV) are different from each other by 0.03 eV. Generally, the reason for the discrepancy between the I–V and C–V measured barrier heights is clear. The discrepancy is possibly resulted from the existence of interfacial native oxide and the organic PEDOT layers between the semiconductor and Schottky contact metal [43,44]. Moreover, the difference between the measured I–V and C–V barrier height in the metal/semiconductor is because of Schottky BH inhomogeneity. The capacitance C is insensitive to potential fluctuations on a length scale of less than the space charge width and the C–V method averages over the whole area and measures to describe Schottky barrier diode. The direct current I across the interface depends exponentially on ϕ_b and thus sensitively the detailed barrier distribution at the interface, spatial variations of band bending V_p and ϕ_b result in different SBH for the current and capacitance [41,46,47]. The barrier height varies with the applied voltage in the forward bias condition. Because of the potential drop across the interfacial layer, the zero bias barrier height is lower than that of an ideal diode, and similarly the potential across the interfacial layer varies with bias because of the electrical field present in the semiconductor and the change in the interface. Thereby, an additional barrier increase in the forward bias comes from the potential change across the interfacial layer [8,44,45]. The interface state density affects the electronic parameters of the diode. In order to determine interface state density of the diode, we used low and high frequency capacitance–voltage plots. At low frequencies, the interface states respond to the alternating signal, and the low-frequency capacitance is given by [40].

$$C_{\mathrm{LF}} = \frac{\sqrt{\frac{q\varepsilon_s N_a}{2\psi_s}} + qN_{ss}}{\left[1 + \frac{qjR_s}{kT} + \frac{\delta}{\varepsilon_i}\left(\sqrt{\frac{q\varepsilon_s N_a}{2\psi_s}} + qN_{ss}\right)\right]} \tag{8}$$

where δ is the thickness of the interfacial layer, Ψ_s is the surface potential N_{ss} is the interface state density and ε_i and ε_s represent the permittivity of the interfacial oxide layer and that of the semiconductor, respectively.

At high frequency, the interface states cannot follow the AC signal and the capacitance can be expressed as [40],

$$C_{\mathrm{HF}} = \frac{\sqrt{\frac{q\varepsilon_s N_a}{2\psi_s}}}{\left(1 + \frac{qjR_s}{kT} + \frac{\delta}{\varepsilon_i}\sqrt{\frac{q\varepsilon_s N_a}{2\psi_s}}\right)} \tag{9}$$

By using Eqs. (8) and (9), the interface state density N_{ss} can be written as [40],

$$N_{ss} = \frac{1}{q}\frac{C_1}{C_{\mathrm{HF}}}\frac{C_{\mathrm{HF}} - C_{\mathrm{LF}}}{C_{\mathrm{LF}} - C_1}\sqrt{\frac{q\varepsilon_s N_a}{2\psi_s}} \tag{10}$$

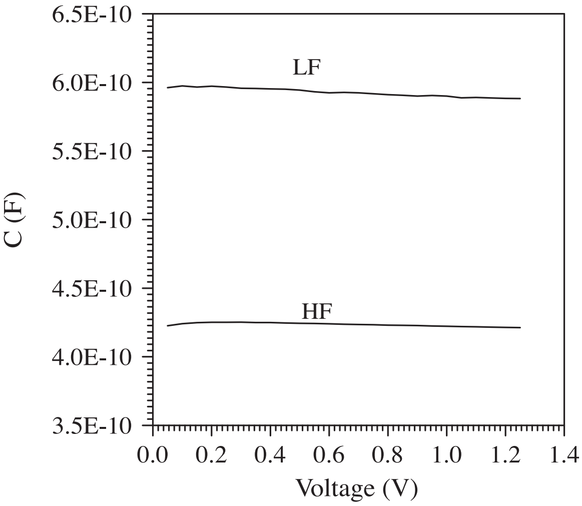

Fig. 4. High frequency and low frequency–voltage plot.

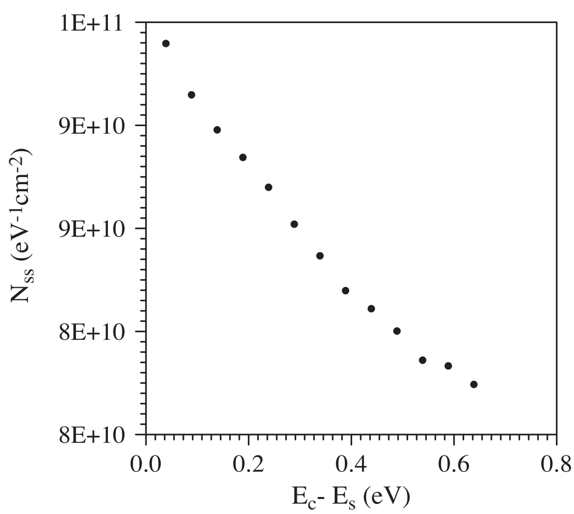

Fig. 5. Interface state energy distribution curve of Au/PEDOT/*n*-GaAs Schottky diode.

where $C_1 = \varepsilon_i/\delta$. However, for a Schottky diode the native oxide at the interface is about 5–10 Å and $C_1 \gg C_{LF}$ and one obtains,

$$N_{ss} \approx \sqrt{\frac{q\varepsilon_s N_a}{2\psi_s}} \frac{(C_{LF} - C_{HF})}{qC_{HF}} \tag{11}$$

Thus, knowing the experimental values of C_{LF}, C_{HF} and ψ_s one obtains the value of interface state density (N_{ss}).

Furthermore, in an *n*-type semiconductor, the energy of the interface states E_{ss} with respect to the bottom of the conduction band at the surface of the semiconductor is given by,

$$E_c - E_{ss} = q\phi_b - qV \tag{12}$$

Fig. 4 shows the plots of measured *C–V* data at 10 kHz and 1 MHz.

It is seen from the plot that the low-frequency capacitance decreases with the applied voltage while the high frequency capacitance remains almost constant. The interface state density, N_{ss}, was calculated from the experimental values of C_{LF} (measured at 10 kHz) and C_{HF} (measured at 1 MHz) by using Eq. (11). The surface potential ψ_s values were obtained from experimental *I–V* data. Thus, the value of N_{ss} was determined as a function of E_c–E_{ss} by means of Eq. (12) and the energy distribution plot of the interface states (N_{ss} vs. E_c–E_{ss}) is shown in Fig. 5.

The N_{ss} values of the diode change from 1.0×10^{11} to 0.8×10^{11} eV^{-1} cm^2, when E_c–E_{ss} is change from 0.0 to 0.8 V. This confirms that the density of interface state varies with applied bias and each of E_c–E_{ss} values corresponds to a position inside the GaAs band gap. The interface states between the organic semiconductor compound and inorganic semiconductor structure play an important role in the determination of the characteristic parameters of the devices. The presence of the interface layer, interface states and fixed surface charge causes the reverse bias and forward bias characteristics of Schottky devices not to obey the ideal Schottky diode characteristics.

4. Conclusions

In this study, an Au/PEDOT/*n*-GaAs structure was fabricated using PEDOT interlayer and *n*-GaAs substrate. This diode showed a rectifying behavior and yielded different barrier height in comparison to conventional GaAs diode. The energy distribution of the interface state density and other electronic parameters of the diode calculated by the help of the current–voltage and capacitance–voltage methods. The control of the electronic properties of *n*-GaAs Schottky diode was achieved using thin interlayer of the poly(3,4-ethylenedioxithiophene)-block-poly(ethylene glycol).

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