Barrier Modification by Methyl Violet Organic Dye Molecules of Ag/P-Inp Structures

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Abstract

This work includes fabrication and electrical characterization of Metal/Interlayer/Semiconductor (MIS) structures with methyl violet organic film on p-InP wafer. Metal(Ag)/ Interlayer (methyl violet =MV)/Semiconductor(p-InP) MIS structure presents a rectifying contact behavior. The values of ideality factor (n) and barrier height (BH) for the Ag/MV/p-InP MIS diode by using the current-voltage (I-V) measurement have been extracted as 1.21 and 0.84 eV, respectively. It was seen that the BH value of 0.84 eV calculated for the Ag/MV/p-InP MIS structure was significantly higher than the value of 0.64 eV of Ag/p-InP control contact. This situation was ascribed to the fact that the MV organic interlayer increased the effective barrier height by influencing the space charge region of inorganic semiconductor. The values of diffusion potential and barrier height for the Ag/MV/p-InP MIS diode by using the capacitance-voltage (C-V) measurement have been extracted as 1.21 V and 0.84 eV, respectively. The interface-state density of the Ag/MV/p-InP structure was seen to change from $2.57 \times 10^{13}$ eV$^{-1}$cm$^{-2}$ to $2.19 \times 10^{12}$ eV$^{-1}$cm$^{-2}$.

Keywords: Organic dye film; MIS diode; Series resistance; Interface states

1. Introduction

Electronic and optoelectronic properties of the organic semiconductor devices have been intensively investigated in recent years [1-6]. Organic semiconductor based device technology is relatively cheap and easy to fabricate compared to inorganic devices. These advantages make these kinds of materials attractive for the previously reported applications [6].

Owing to their stability and barrier height (BH) modification features, organic materials have been employed particularly in metal/semiconductor (MS) diodes [7-14]. Campbell et al. [9] inserted an organic thin film to the metal/semiconductor interface and thus modified the effective Schottky barrier height. They found that the changes in the Schottky barrier height were more than 500 meV and the Schottky diodes with thin organic layers were superior to control Schottky diodes. Tunç et al. [10] reported an Au/polyvinyl alcohol (PVA) (Ni,Zn-doped)/n-Si diode with a barrier height value of 0.78 eV and an ideality factor value of 1.83 at room temperature (300 K). Aydoğan et al. [11] discussed the temperature dependent I–V characteristics of Al/PolyPyrole(PPy)/p-Si Schottky diode. Aydemir et al. [12] fabricated Au/n-Si and Au/PVA:Zn/n-Si Schottky diodes to investigate the effect of organic interfacial layer on the main electrical characteristics. PVA:Zn was successfully deposited on n-Si wafer by using the electrospinning system and surface morphology of PVA:Zn was presented by SEM images. The current–voltage characteristics of these diodes have been investigated at room temperature. The experimental results show that interfacial layer enhances the device performance in terms of ideality factor (n), zero-bias barrier height ($\Phi_{00}$), series resistance ($R_s$), and shunt resistance ($R_w$) with values of 1.38, 0.75 eV, 97.64 $\Omega$, and 203 M$\Omega$ whereas those of Au/n-Si diode are found as 1.65, 0.62 eV, 164.15 $\Omega$ and 0.597 M$\Omega$, respectively[12]. Forrest et al. [13] and Antohe et al. [14] obtained Metal-Interlayer-Semiconductor (MIS) structures by sublimation of organic
thin layers on a semiconductor wafer, subsequently evaporation of various metals and then extracted their ideality factors and BHs.

The electrical properties of MS structures can be modified by organic semiconductors when an organic thin film is placed between the inorganic semiconductor and metal. The studies made in literature have shown that the barrier height could be either increased or decreased by using organic thin layer on inorganic semiconductor [7-14]. The insertion of thin films of organic semiconductors with nanometer thickness in inorganic Schottky diodes introduces a method to control the fundamental device parameters[15]. Methyl violet (MV) with molecular formula C_{25}H_{30}ClN_{3} used in this work is a typical aromatic azo compound. It is an organic dye molecule used extensively as an acid–base indicator due to its radical colour change with varying pH. Its colour originates from absorbance in the visible region of the spectrum due to the delocalization of electrons in the benzene and azo groups forming a conjugated systemThe molecular structure of the methyl violet is given in Fig. 1. The structure of azo dyes has attracted considerable attentions recently due to their wide applicability in the light-induced photo isomerization process, and their potential usage for the reversible optical data storage [16].

Fig. 1. The molecular structure of MV molecule.

MV organic material has been considered as one of the most stable organic semiconductors for various electronic and optoelectronic applications. Our aim is to investigate the electrical properties of Ag/MV/p-InP diode by the insertion of MV organic film between InP semiconductor and Ag metal by using current-voltage (I-V) and capacitance-voltage (C-V) measurements and is to compare the electrical parameters of the Ag/MV/p-InP MIS diode with those of conventional MS diodes.

2. Experimental Details

Ag/MV/p-InP MIS diodes were produced by using one side polished (as received from the manufacturer) p-type InP wafer with (100) orientation. The wafer was chemically cleaned with 5H_2SO_4+H_2O_2+H_2O (a 20 s boil). The native oxide on the front surface of p-InP was removed in a HF:H_2O (1:10) solution and finally the wafer was rinsed in deionized (DI) water for 30 s. Before forming the organic layer on the p-InP substrate, the ohmic contact was made by evaporating Au–Zn (90%–10%) alloy on the back of the substrate, followed by a temperature treatment at 450 °C for 3 min in N_2 atmosphere. MV organic layer was directly formed by adding 9 μL of the MV solution (wt 0.2% in methanol) on the front surface of the p-InP wafer, and evaporated by itself for drying of solvent in N_2 atmosphere for an hour. The contacting metal dots were formed by evaporation of Ag metal with diameter of 1.0 mm (diode area=7.85x10^{-3} cm^2). All evaporation processes were carried out in a vacuum coating unit at about 10^{-5} mbar. I-V and C-V measurements for Ag/MV/p-InP MIS contact were measured by using a Keithley 4200 SCS system at room temperature (see Fig. 2). Photoelectric effect on the Ag/MV/p-InP device was measured under 2000 lux light illumination.
3. Results and Discussion

3.1. Current-Voltage characteristics of the Ag/MV/p-InP MIS diode

Fig. 3 shows the I-V measurements of the Ag/MV/p-InP MIS diode in dark and under light illumination and Ag/p-InP control MS diode in dark at room temperature. As seen from Fig. 3, MV organic interlayer reduces the current values of the control diode. The Ag/MV/p-InP structure has rectifying property. The voltage dependence of the reverse current and the exponential increase of the forward-bias current are the characteristic properties of diodes. The current curve in forward bias region becomes dominated by series resistance from contact wires or bulk resistance of the organic semiconductor and the inorganic semiconductor giving rise to the curvature at high current in the I-V plot. Also, the reverse bias current of the Ag/MV/p-InP diode is strongly increased by the illumination. This suggests that the carrier charges are effectively generated in the junction by illumination. The device shows a good photovoltaic behavior with a maximum open-circuit voltage (V_{oc}) of 0.17 V and a short-circuit current (I_{sc}) of 0.49 µA under 2000 lux light intensity. By using thermionic emission (TE) theory [17,18], the ideality factor (n) and BH (\Phi_B) can be obtained from the slope and the current axis intercept of the linear region of the forward bias I-V plot, respectively. The values of the BH and the ideality factor for the Ag/MV/p-InP diode have been calculated as 0.84 eV and 1.21, respectively. The ideality factor determined by the image-force effect alone should be close to 1.01 or 1.02 [19-21]. Higher values of ideality factors are attributed to secondary mechanisms which include interface dipoles due to interface doping or specific interface structure as well as fabrication-induced defects at the interface [19-22].
The BH value of 0.84 eV that we have obtained for the Ag/MV/p-InP device due to MG organic layer is remarkably higher than the value of 0.64 eV calculated for reference Ag/p-InP contact in Fig.3. In literature, some experimental studies have been reported for the barrier height modification by using the organic thin films [23]. Recently, Gullu et al. [24] have published a paper about Al/DNA/p-InP diode with barrier height value of 0.98 eV and ideality factor value of 1.26. The obtained barrier height value of the diode was higher than the conventional Al/p-InP [18]. Also, Güllü et al. [16] investigated the electrical characteristics, such as current–voltage (I–V) and capacitance–voltage (C–V) measurements, of identically prepared Al/MV/p-Si Organic/Inorganic (OI) Schottky structures. It has been seen that the methyl violet organic dye layer on the p-Si substrate has exhibited a good rectifying behavior. The barrier heights and ideality factors of all devices have been calculated from the electrical characteristics. Although the diodes were all identically prepared, there was a diode-to-diode variation: the effective barrier heights ranged from 0.6 ± 0.1 to 0.8 ± 0.1 eV, and the ideality factor from 1.6 ± 0.4 to 3.5 ± 0.4. The barrier height versus ideality factor plot has been plotted for the OI devices. Lateral homogeneous BH was calculated as a value of 0.7 eV from the observed linear correlation between BH and ideality factor, which can be explained by laterally inhomogeneities of BHs [16]. In other study, Karataş et al. [25] have fabricated an Al/Rh101/p-Si/Al contact. The barrier height (0.817 eV) of the Al/Rh101/p-Si/Al contact was significantly larger than the barrier height of conventional Al/p-Si Schottky diode. In another study, Çakar et al. [26] have fabricated the Cu/pyronine-B/p-Si, Au/pyronine-B/p-Si, Al/pyronine-B/p-Si and Sn/pyronine-B/p-Si diodes, and the obtained barrier heights for these diodes were larger than the conventional metal/p-Si contact. They [26] have evaluated that the barrier height could be enhanced or modified by using thin interfacial films. It is seen from the above results that the organic layer can be used to vary the effective barrier height of Al/p-Si Schottky diodes. Furthermore, this case may be ascribed to the organic interlayer modifying the effective barrier height by influencing the space charge region of the inorganic substrate [27-30]. The MV organic dye layer forms a physical barrier between the Ag metal and the p-InP wafer. This organic layer can produce substantial shift in the work function of Ag.
the metal and in the electron affinity of the semiconductor and in turn, the organic layer gives an excess barrier of 0.20 eV, i.e., the MV organic layer increases the barrier height of Ag/p-InP. The barrier height of Ag/p-InP contact increases by the insertion of a dipole layer between p-InP semiconductor and MV organic layer. Similarly, Zahn et al. [31] have indicated that the initial increase or decrease in effective barrier height for the organic interlayer was correlated with the energy level alignment of the lowest unoccupied molecular orbital with respect to the conduction band minimum of the inorganic semiconductor at the organic/inorganic semiconductor interface. The obtained results and previous studies have shown that the electrical conductivity, preparation process of organic film, film thickness of the organic semiconductor to be used in device fabrication significantly affect the device performance and electronic parameters of the MS devices. As a result, we have evaluated that Ag/p-InP MS diode could be designed to exhibit the desired properties by means of the choice of the organic molecule [23]. The downward concave curvature of the forward bias I-V plots at sufficiently large voltages is caused by the effect of series resistance \( R_s \), apart from the interface states, which are in equilibrium with the semiconductor [32]. The \( R_s \) value has been calculated by using a method developed by Norde [33-36]. Norde proposed a method to determine value of the series resistance [36]. The following function has been defined in the modified Norde’s method:

\[
F(V) = \frac{V}{\gamma} - \frac{\ln\left(\frac{I(V)}{AA^*T^2}\right)}{\beta}
\]

(1)

where \( \gamma \) is an integer (dimensionless) greater than \( n \). \( I(V) \) is current obtained from the I-V curve and \( \beta \) is a temperature-dependent value calculated with \( \beta = \frac{q}{kT} \). Once the minimum of the \( F \) vs. \( V \) plot is determined, the value of barrier height can be obtained from Eq. (2),

\[
\Phi_b = F(V_0) + \frac{V_0}{\gamma} - \frac{kT}{q}
\]

(2)

where \( F(V_0) \) is the minimum point of \( F(V) \) and \( V_0 \) is the corresponding voltage. Fig. 4 shows the \( F(V) \)–V plot of the junction. From Norde’s functions, \( R_s \) value can be determined as;

\[
R_s = \frac{kT(\gamma - n)}{qI}
\]

(3)

From the \( F-V \) plot by using \( F(V_0) = 0.795 \) V and \( V_i = 0.20 \) V values, the values of \( \Phi_b \) and \( R_s \) of the Ag/MV/p-InP structure have been determined as 0.87 eV and 224.1 kΩ, respectively. There is a difference in the values of \( \Phi_b \) obtained from the forward bias \( \ln I-V \), and Norde functions. Differences in the barrier height values obtained from two methods for the device may be attributed to the extraction from different regions of the forward bias current-voltage plot [37]. The value of series resistance may also be large 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 effect of the series resistance is usually modeled with series combination of a diode and a resistance \( R_s \). The voltage drop across a diode is expressed in terms of the total voltage drop across the diode and the resistance \( R_s \). The high series resistance behavior may be ascribed to decrease of the exponentially increasing rate in current due to space-charge injection into the MV organic thin film at higher forward bias voltage [37].
3.2. Analysis of interfacial features of the Ag/MV/p-InP MIS diode

For a metal/semiconductor diode having interface states in equilibrium with the semiconductor the ideality factor \( n \) becomes greater than unity as proposed by Card and Rhoderick [38] and then interface state density \( N_{SS} \) is given by:

\[
N_{SS} = \frac{1}{q} \left[ \frac{\varepsilon_i}{\delta} \left( n(V) - 1 \right) - \frac{\varepsilon_s}{w} \right]
\]  

(4)

where \( w \) is the space charge width, \( \varepsilon_s \) is the permittivity of the semiconductor, \( \varepsilon_i \) is the permittivity of the interfacial layer, \( \delta \) is the thickness of organic layer, and \( n(V) = \frac{V}{(kT/q) \ln(I/I_0)} \) is voltage-dependent ideality factor. In p-type semiconductors, 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 by:

\[
E_{SS} - E_V = q\Phi_b - qV
\]  

(5)

where \( V \) is the voltage drop across the depletion layer and \( \Phi_b \) is the effective barrier height. The energy distribution or density distribution curves of the interface states can be determined from experimental data of this region of the forward bias \( I-V \) plot. Substituting the voltage dependent values of \( n \) and the other parameters in Eq. (4), the \( N_{SS} \) vs. \( E_{SS}-E_V \) plot was obtained as shown in Fig. 5. It is seen that \( N_{SS} \) value decreases with increasing \( E_{SS}-E_V \) value. The density distribution of the interface states of the diode changes from \( 2.57 \times 10^{13} \) eV\(^{-1}\) cm\(^{-2}\) to \( 2.19 \times 10^{12} \) eV\(^{-1}\) cm\(^{-2}\). Aydogan et al. [32] found that the deposition of polymers on to the inorganic semiconductor could generate large number of interface states at the semiconductor surface, which strongly influence the properties of the PANI/p-Si/Al structure. Çakar et al. [39] have
determined interface properties of Au/PYR-B/p-Si/Al contact. They [38] have found that the interface-state density values varied from $4.21 \times 10^{13}$ to $3.82 \times 10^{13} \text{ cm}^{-2} \text{ eV}^{-1}$. The interface-state density of the Ag/MV/p-InP diode is consistent with those of above mentioned diodes. It is evaluated that interface properties of Ag/p-InP junction are changed by depending on organic layer inserted into metal and semiconductor. The organic interlayer appears to cause to a significant modification of interface states even though the organic-inorganic interface appears abrupt and unreactive [40-42]. The MV organic layer increases the effective barrier height clearly upon the modification of the semiconductor surfaces and the chemical interaction at the interface of the MV organic layer to the $p$-InP and oxide-organic interface states will give rise to new interface states [23].

![Fig.5](image)

Fig.5. The density distribution of the interface states of the Ag/MV/p-InP junction.

### 3.3. Capacitance-Voltage characteristics of Ag/MV/p-InP contacts

The capacitance-voltage measurements provide knowledge about the fixed charge concentration and barrier height for MIS diodes. Any variation of the charge within a p-n diode with an applied voltage variation yields a capacitance which must be added to the circuit model of a p-n diode. The junction capacitance dominates for the reverse-biased diodes, while the diffusion capacitance dominates in strongly forward-biased diodes [43]. Fig.6 shows the C-V characteristics of the Ag/MV/p-InP MIS junction for 10 kHz, 100 kHz and 500 kHz frequencies. Capacitance values decrease with increasing frequency. This occurred at lower frequencies because the interface states could follow the alternative current signal and yield an excess capacitance that depended on the frequency [43].
Fig. 6. The C-V plots at frequencies of 10 kHz, 100 kHz and 500 kHz for the Ag/MV/p-InP MIS diode.

Fig. 7 shows the C²-V characteristics at frequencies of 10 kHz, 100 kHz and 500 kHz for the Ag/MV/p-InP MIS diode. The C²-V plots are linear which indicates the formation of Schottky junction [44]. By using standard Mott-Schottky relationship between capacitance-voltage [17,18], the values of diffusion potential (V_d), barrier height and acceptor carrier concentration (N_A) for the Ag/MV/p-InP MIS diode were calculated from the linear region of its C²-V plot. The values of diode parameters are given in Table 1. As seen from the obtained values, the difference between \( \Phi_b (I-V) \) and \( \Phi_b (C-V) \) for the Ag/MV/p-InP MIS contact originates from the different nature of the I-V and C-V measurements. Due to different nature of the C-V and I-V measurement techniques, barrier heights deduced from them are not always the same. The capacitance \( C \) is insensitive to potential fluctuations on a length scale of less than the space charge region and C-V method averages over the whole area and measures to describe BH. The DC current \( I \) across the interface depends exponentially on barrier height and thus sensitively on the detailed distribution at the interface [17,45]. Additionally, the discrepancy between the barrier height values of the devices may also be explained by the existence of an interfacial layer and trap states in semiconductor [38,46].
Fig. 7. The $C^2$-V plots at frequencies of 10 kHz, 100 kHz and 500 kHz for the Ag/MV/p-InP MIS diode.

Table 1. Some diode parameters calculated from the $C^2$-V plots.

<table>
<thead>
<tr>
<th>Frequency (kHz)</th>
<th>$V_d$ (V)</th>
<th>$\Phi_b$ (eV)</th>
<th>$N_A$ (x10^{17} \text{cm}^{-3})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>1.48</td>
<td>1.32</td>
<td>2.79</td>
</tr>
<tr>
<td>100</td>
<td>2.01</td>
<td>1.77</td>
<td>2.13</td>
</tr>
<tr>
<td>500</td>
<td>1.87</td>
<td>1.66</td>
<td>1.11</td>
</tr>
</tbody>
</table>

4. Conclusion

In conclusion, we have performed the electrical characterization of the Ag/MV/p-InP Schottky diodes. It has been shown that the MV organic film on $p$-InP wafer indicates a good rectifying property. The barrier height and the ideality factor of the diode were calculated from the $I$-$V$ characteristic. We have compared the electrical parameters of the Ag/MV/p-InP contacts with those of reference MS diodes. We have reported that the BH value of 0.84 eV obtained for the Ag/MV/p-InP diode was higher than the value of 0.64 eV of the reference Ag/p-InP MS diode. This has been attributed to the fact that the MV
organic film increased the effective BH by influencing the space charge region of InP. The interface-state density of the Ag/MV/p-InP MIS structure was reported to be in the range of $2.57 \times 10^{13}$ eV$^{-1}$cm$^{-2}$ - $2.19 \times 10^{12}$ eV$^{-1}$cm$^{-2}$.

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References