Electrical characterization of organic-on-inorganic semiconductor Schottky structures

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Abstract

We prepared a methyl red/p-InP organic–inorganic (OI) Schottky device formed by evaporation of an organic compound solution directly to a p-InP semiconductor wafer. The value of the optical band gap energy of the methyl red organic film on a glass substrate was obtained as 2.0 eV. It was seen that the Al/methyl red/p-InP contacts showed a good rectifying behavior. An ideality factor of 2.02 and a barrier height (Φ_b) of 1.11 eV for the Al/methyl red/p-InP contact were determined from the forward bias $I–V$ characteristics. It was seen that the value of 1.11 eV obtained for Φ_b for the Al/methyl red/p-InP contact was significantly larger than the value of 0.83 eV for conventional Al/p-InP Schottky diodes. Modification of the interfacial potential barrier for the Al/p-InP diode was achieved using a thin interlayer of the methyl red organic semiconductor. This ascribed to the fact that the methyl red interlayer increases the effective Φ_b by influencing the space charge region of InP.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Organic materials have been intensively investigated due to their wide range of applications in electronics technology. For example, many devices using polymeric [1–16] and nonpolymeric organic materials [17–29] have been fabricated, including light emitting diodes and devices like an inorganic/organic or a metal/organic heterostructure. During the past 15 years dramatic advances have been achieved in the performances of organic semiconductor devices [30]. Organic light emitting diodes, for example, were first demonstrated in the late 1980s and can already be found in cell phone displays. Attractive features of these materials are the possibility of device processing, compatibility with flexible substrates, and the low materials consumption for ultrathin molecular films, all of which offer the prospect of cheaper photovoltaic energy generation [30]. Large-scale production is easier than with inorganic materials. The greatest feature of organic materials is that they can be tuned chemically to adjust separately the band gap, valence and conduction band energies, charge transport, as well as the solubility or other structural properties [30]. Owing to their stability and barrier height (BH) enhancement properties, nonpolymeric organic compounds have been employed particularly in electronic devices [20, 31–33]. Forrest *et al* [31, 34] and Antohe *et al* [35] obtained metal–insulator–semiconductor (MIS) contacts by sublimation of nonpolymeric organic thin films on a semiconductor substrate, with subsequent evaporation of different metals and then measurement of the ideality factor and the BH. Aydin *et al* [33] obtained MIS contacts by addition of a β-carotene solution on top of the Si substrate; they waited for evaporation of the solution and then measured the ideality factor and the BH. Kilicoglu *et al* [20] obtained MIS contacts by addition of a methyl red solution on top of the Si substrate and waiting for evaporation of the solution; they then measured the ideality factor and the BH. They showed that these contacts for nonpolymeric thin films formed at the metal/semiconductor interface have rectification and enhancement of BH properties [36].

Methyl red, with the molecular formula NC_6H_4COOH (2-[4-(dimethylamino)phenylazo] benzoic acid), is a typical

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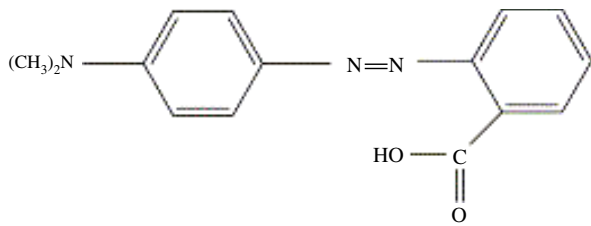[3] Author to whom any correspondence should be addressed.

Figure 1. Molecular structure of the organic compound methyl red.

aromatic azo compound. Its color 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 system. Due to its conjugated structure and richness in 16 π electrons, methyl red has been chosen to form an organic semiconductor layer between Al and a p-InP inorganic semiconductor substrate [20, 25]. The molecular structure of methyl red is given in figure 1. The structure of azo dyes has attracted considerable attention recently due to their wide applicability in the light-induced photoisomerization process, and their potential use in reversible optical data storage [29, 37–39].

In this paper we report the fabrication and electrical properties of rectifying contact barriers using methyl red as an interlayer formed on a p-InP substrate for the modification of Al/p-InP Schottky contacts. The rectifying characteristics of the devices reported here suggest many unique device applications such as MIS, photovoltaic cells and chemical sensors [19, 26–28, 39]. We calculated the barrier height and ideality factor of the organic–inorganic (OI) device by using the thermionic emission (TE) mechanism. Our aim is to study the suitability and possibility of organic-on-inorganic semiconductor contact barrier diodes for use in barrier modification of Si MS diodes. In addition, our purpose is to compare the parameters of the methyl red/semiconductor Schottky diode with those of conventional metal/semiconductor diodes. The characteristic parameters of the device have been obtained from their dark current–voltage and capacitance–voltage characteristics. Also, the optical absorbance spectrum of the methyl red organic film on a glass substrate has been investigated in the UV–visible region.

2. Experimental details

2.1. Chemical cleaning and ohmic contact formation

The organic/inorganic semiconductor diode was prepared using a one side polished (as received from the manufacturer) p-type InP wafer with a doping density of 3.5×10^{17} cm^{-3} from C–V measurements in this study. The wafer was chemically cleaned with $3H_2SO_4 + H_2O_2 + H_2O$ (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 a N_2 atmosphere.

2.2. Deposition of organic film and top contact metallization

After the cleaning procedures and ohmic metallization were carried out, the methyl red solution was directly formed by adding 6 μl of methyl red organic compound solution (0.2 wt% in methanol) on the front surface of the p-InP wafer, and evaporated by itself for drying of the solvent in a N_2 atmosphere for 1 h. Here, we selected an amount of 6 μl of the methyl red solution by considering and testing various factors that could affect the thickness and homogeneity of a given organic film depending on the solution concentration and substrate area. The quality of organic thin films should be also related to other factors, such as the film-forming ability, the molecular symmetry and structure [40]. The thickness of the organic film on the semiconductor was calculated as 66.0 nm from a high frequency C–V technique ($C = \varepsilon_s A/d$). The contacting top metal dots with a diameter of 1.0 mm were formed by evaporation of Al. We also fabricated Al/p-InP without the organic layer for comparison with the electrical parameters of the Al/methyl red/p-InP device. All evaporation processes were carried out in a vacuum coating unit at about 10^{-5} mbar. Crystallization or decohesion of the organic material during device fabrication and/or operation are important [41]. Yan *et al* [42] measured some electrical parameters of a fresh device based on copper phthalocyanin (CuPc) and then stored it in a vacuum (<1 Pa) for 1 week and measured the parameters again. They found that storage in a vacuum has no effect on CuPc, which was agreed with the presupposition of their air stability experiments [42].

2.3. Electrical and optical measurements

The I–V and C–V measurements were made using a Keithley 487 picoammeter/voltage source and a HP 4192A LF impedance analyzer, respectively, at room temperature and in dark conditions (see figure 2). The optical absorbance spectrum of the methyl red thin film a on glass substrate was taken with a spectrophotometer (LKB Biochrom Ultraspec II).

3. Results and discussion

3.1. Optical properties of methyl red organic thin film

The optical absorbance (A) spectrum of the methyl red film on a glass substrate was analyzed by the following relationship [43]:

$$A(h\nu) = B(h\nu - E_g)^m, \tag{1}$$

where B is a constant and E_g is the optical band gap. The exponent m depends on the nature of the transition, $m = 1/2$, 2, 3/2 or 3 for allowed direct, allowed indirect, forbidden direct or forbidden indirect transitions, respectively. Figure 3 indicates the optical absorbance spectra of the methyl red organic film on a glass substrate. Figure 4 shows the plot of $(Ah\nu)^2$ versus $h\nu$ according to equation (1). The optical energy gap E_g of the organic semiconductor was determined as 2.0 eV by extrapolating the linear portion of this plot at $(Ah\nu)^2 = 0$ for $m = 1/2$, which indicates that the direct transition dominates in the films.
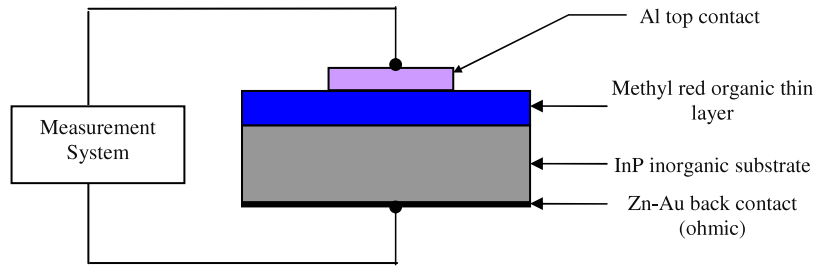
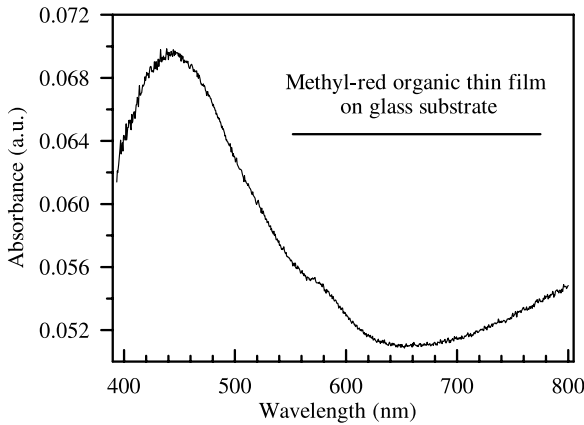**Figure 2.** The components of the methyl red/p-InP OI semiconductor device for the electrical characterization.

Figure 3. Optical absorbance spectrum of methyl red organic film on glass substrate.
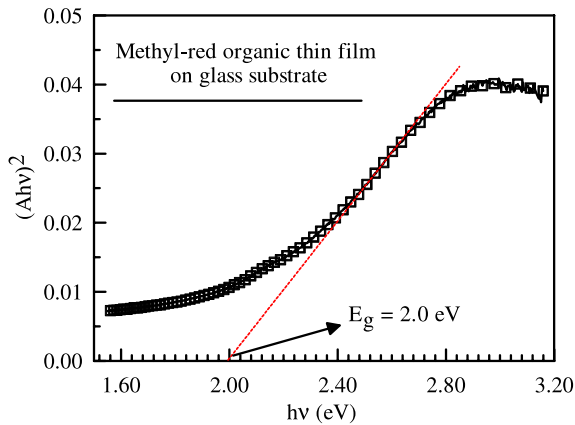

Figure 4. $(Ah\nu)^2$ versus $h\nu$ plot of the methyl red organic thin film.

Figure 5. Current versus voltage characteristics of the methyl red/p-InP OI device and the Al/p-InP reference diode.

3.2. Electrical properties of the methyl red/p-InP structure

Figure 5 shows the experimental semi-log $I–V$ characteristics of the reference (Al/p-InP) and the Al/methyl red/p-InP OI Schottky device at room temperature. As can be clearly seen from figure 5, the methyl red/p-InP OI Schottky device has good rectifying properties. The weak voltage dependence of the reverse bias current and the exponential increase of the forward bias current are characteristic properties of rectifying interfaces. The current curve in forward bias quickly becomes dominated by series resistance from contact wires or bulk resistance of the organic layer and the inorganic semiconductor
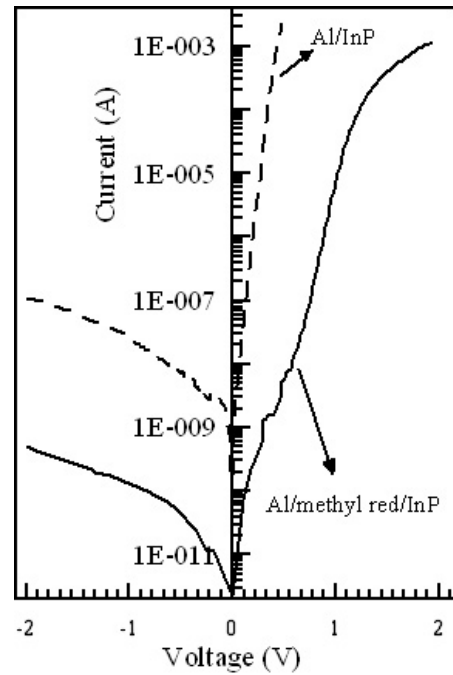
layer, giving rise to the curvature at high current in the semilog $I–V$ plot. The figure indicates that the leakage current of MS Schottky diodes decreases at a significant rate with respect to that of the methyl red/p-InP OI Schottky device. This will be discussed below together with the barrier height because the leakage current is inversely proportional to the barrier height. Discussions about the barrier height are valid for the leakage current too. According to the thermionic emission theory [44, 45], the ideality factor n and BH Φ_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 methyl red/p-InP diode have been calculated as 1.11 eV and 2.02 eV, respectively. The ideality factor determined by the imageforce effect alone should be close to 1.01 or 1.02 [46–48]. Our data clearly indicate that the diode has an ideality factor that is significantly larger than this value. Higher ideality factor values 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 [46–49]. According to Tung *et al* [48], the
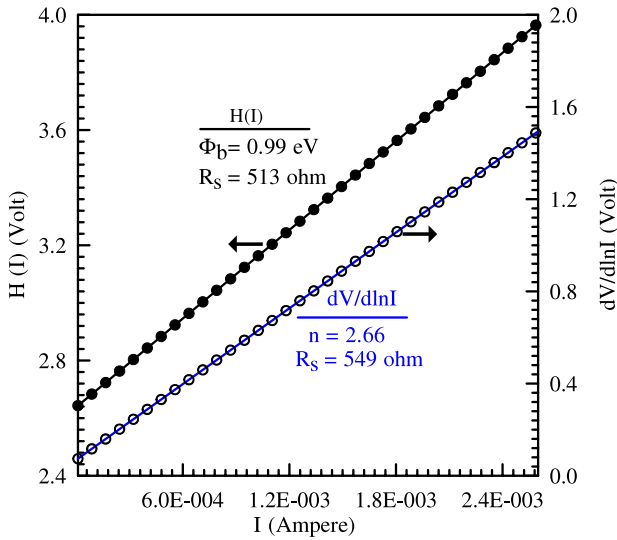
Figure 6. $\mathrm{d}V/\mathrm{d}\ln I$–$I$ and $H(I)$–I plots obtained from the experimental I–V data in figure 5.

Figure 7. Capacitance versus voltage characteristic of the methyl red/p-InP OI device.

high values of n can also be attributed to the presence of a wide distribution of low-SBH (Schottky barrier height) patches caused by the laterally inhomogeneous barrier. Also, the image-force effect, recombination–generation, and tunneling may be possible mechanisms that could lead to an ideality factor value greater than unity [16, 44, 48].

As mentioned above, the value of 1.11 eV for Φ_{b} for the methyl red/p-InP contact is higher than the 0.83 eV obtained from the I–V characteristic of the Al/p-InP MS reference diode (the conventional diode) shown in figure 5. These findings indicate that for the methyl red organic thin film formed on an inorganic substrate the barrier height of MS Schottky diodes is enhanced at a significant rate. The case may be ascribed to an organic interlayer modifying the effective barrier height by influencing the space charge region of the inorganic substrate [23, 50]. It is known that the organic film forms a physical barrier between the metal and the InP substrate, preventing the metal from directly contacting the InP surface [17, 18, 21–26, 50]. The methyl red organic layer appears to cause a significant modification of interface states even though the organic/inorganic interface becomes abrupt and unreactive [17, 18, 21–26, 50].

Thus, the change in barrier height can qualitatively be explained by an interface dipole induced by passivation of the organic layer [21, 23–25]. Kampen *et al* [21] have observed by photoemission spectroscopy investigations that S passivation reduces the surface band bending on n-type doped GaAs; on the other hand, the band bending on the surfaces of p-type doped GaAs increases. Similarly, Zahn *et al* [22] have indicated that the initial increase or decrease in effective barrier height for the organic interlayer is correlated with the energy level alignment of the lowest unoccupied molecular orbital (LUMO) with respect to the conduction band minimum (CBM) of the inorganic semiconductor at the OI semiconductor interface.

The diode indicated a non-ideal current–voltage behavior due to the ideality factor being higher than unity. This behavior
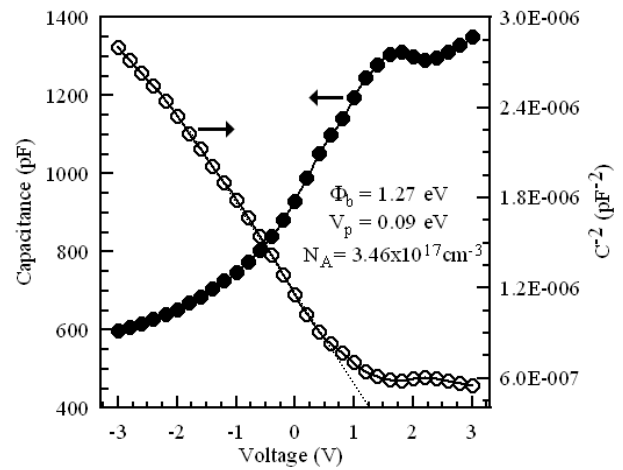
results from the effect of series resistance and the presence of an interfacial layer [51]. We used Cheung's functions [51] to obtain a precise series resistance R_{S}, n, and Φ_{b} for the device. Figure 6 shows the plots of $\mathrm{d}V/\mathrm{d}\ln I$–$I$ and $H(I)$–I obtained by using the Cheung functions. The values of series resistance R_{S} and ideality factor n were found to be 549 Ω and 2.66, respectively, from the $\mathrm{d}V/\mathrm{d}\ln I$–$I$ plot. Also, the values of series resistance R_{S} and barrier height Φ_{b} were found to be 51 Ω and 0.99 eV, respectively, from $H(I)$–I plot. The R_{S} values obtained from the two methods are in agreement with each other due to the consistency of the Cheung functions [51].

Figure 7 shows the reverse bias capacitance–voltage (C–V) and C^{-2}–V characteristics of the methyl red/p-InP devices at 500 kHz and room temperature. By using the capacitance–voltage relationship [41, 42], the values of barrier height and acceptor carrier concentration for the methyl red/p-InP OI devices were extracted as 1.27 eV and 3.5×10^{17} cm^{-3}, respectively, from the linear region of its C^{-2}–V characteristics. As seen from the mean values, the difference between $\Phi_{\mathrm{b}}(I$–$V)$ and $\Phi_{\mathrm{b}}(C$–$V)$ for methyl red/p-InP OI devices originates from the different nature of the I–V and C–V measurements. Due to the difference in 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 the C–V method averages over the whole area and all measurements to describe Φ_{b}. The DC current I across the interface depends exponentially on barrier height and thus sensitively on the detailed distribution at the interface [44, 52]. 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 the semiconductor [53].

3.3. Stability of the methyl red/p-InP structure

At nanoscale thickness regimes (1–100 nm), the instability of thin organic films at their interfaces (organic/inorganic or
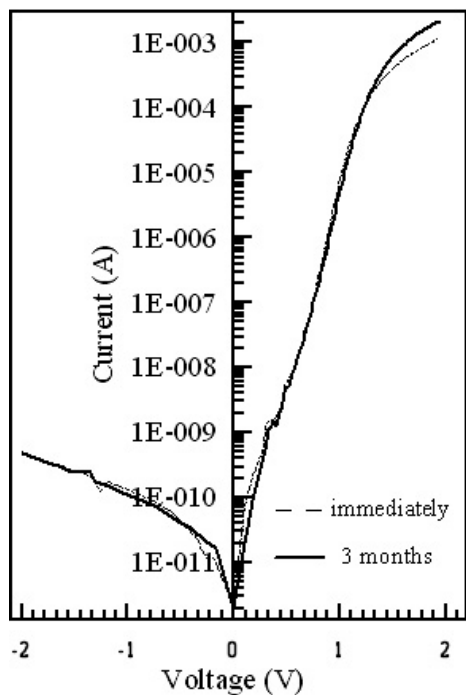
Figure 8. Current versus voltage characteristics of the methyl red/p-InP OI device immediately after fabrication and after three months.

organic/organic) is a major problem facing the fabrication of electronic devices with organic semiconductors and conductors. The instability is caused by a mismatch between semiconductor, conductor and insulator long-range van der Waals (VDW) interactions. For highly polar and conjugated (semiconducting and conducting) organics, where the molecular orientation becomes a sensitive function of thickness, other short-range intermolecular forces and retardation effects may also play an important role in determining the presence or absence of instability. Localized heterogeneities such as particulates, secondary oxide layers on the substrate/wafer or chemical contamination essentially increase the breadth of parameter space and the complexity of the interactions [54].

It has turned out that the thermal stability of thin organic films is not only related to technical details of the fabrication procedures, but also constitutes rather fundamental challenges [55]. It is thus a prerequisite to understand and to control:

- interdiffusion at organic/metal interfaces during and after growth,
- thermally induced de-wetting effects at organic/inorganic interfaces,
- structural phase transformations of the organic material at temperatures often not far from the temperatures of operation,
- the vapor pressure of low-weight organics at elevated temperatures [55].

Figure 8 shows the time stability of electrical measurement of an Al/methyl red/p-InP device. As clearly seen from

figure 8, the current–voltage characteristic of this device remains nearly unchanged after 3 months. On the other hand, this structure clearly has a stable situation in view of the aging time. This case may be attributed to the stability of the organic material [56].

4. Conclusion

In conclusion, we have studied the electrical characteristics of the prepared methyl red/p-InP OI Schottky contacts formed by evaporation of organic material solution directly to a p-InP substrate. It has been seen that the methyl red organic dye thin film on the p-InP substrate shows a good rectifying behavior. The barrier height and ideality factor of the device has been calculated from the $I–V$ characteristic. We have studied the suitability and possibility of organic-on-inorganic semiconductor contact barrier diodes for use in barrier modification of InP MS diodes. In addition, we have compared the parameters of the methyl red/semiconductor Schottky diodes with those of conventional MS diodes. We have observed that the Φ_b value of 1.11 eV obtained for the Al/methyl red/p-InP device is significantly larger than BH values for conventional Al/p-InP MS contacts. Thus, modification of the interfacial potential barrier for metal/InP diodes has been achieved using a thin organic interlayer of methyl red. This has been attributed to the fact that the methyl red interlayer increases the effective Φ_b by influencing the space charge region of InP.

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