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Electronic and photovoltaic properties of Au/pyronine G(Y)/p-GaAs/Au:Zn heterojunction

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ABSTRACT

The electrical and photovoltaic properties of thermally vacuum deposited pyronine G(Y), PYR(G), thin films on GaAs single crystal were investigated. The current–voltage (I–V) characteristic of Au/PYR(G)/GaAs/Au:Zn heterojunction diode under dark condition was measured at different temperatures in the range 298–373 K. The device exhibits a rectifying property. The current in the prepared heterojunction was found to obey the thermionic emission model assisted by tunneling in the voltage range ($0 < V \le 0.35$ volts) while in the voltage range ($0.4 < V \le 1.5$ volts), the current is space charge limited dominated by single trap distribution. The current–voltage characteristics allow us to evaluate some characteristic parameters such as the series resistance, R_s , shunt resistance, R_{sh} , ideality factor, n, and the barrier height, Φ_b . The variation of $1/C^2$ with voltage shows a straight line at high frequency that indicates the formation of barrier between PYR(G) and GaAs and the potential barrier height is found to be 0.82 eV at room temperature (298 K). The photovoltaic properties of Au/PYR(G)/GaAs/Au:Zn heterojunction were investigated under illumination by using light intensity of 20 mW/cm² through the finger mesh gold electrode. The short circuit current (I_{sc}), open circuit voltages (V_{oc}), fill factor (FF) and the power conversion efficiency (η) of the device were evaluated from the *I–V* characteristics under illumination.

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1. Introduction

Semiconducting organic materials provide emerging class of electronic materials which have processing and performance advantages for large area utilization [\[1\].](#page--1-0) These materials are of particular interest, since they possess advantageous electrical, optoelectronic and processing properties for design and fabrication of novel class of the semiconductor-based devices, such as diodes, photovoltaic devices [\[2,3\].](#page--1-0)

The rapid development in the field of electronics and optoelectronics greatly increased the demand for newer materials. In this regard, organic materials are of particular interest because they offer a possibility of low-cost large area devices [\[4\].](#page--1-0) They have been used in various applications as photovoltaic cells, rectifying devices, liquid crystal displays and gas sensors, organic light emitting diodes, organic thin-film transistors (OTFT), and organic photovoltaic cells [\[1–5\]](#page--1-0) due to their advantages of low cost, tunability of electronic properties via chemical synthesis and ease of device fabrication. The remarkable interest in the electrical and optical properties of organic molecular semiconductors reflects their increasingly widespread use in organic and hybrid

Corresponding author. E-mail address: hssoliman08@gmail.com (H.S. Soliman). inorganic-organic devices [\[6,7\]. T](#page--1-0)he modified GaAs Schottky diodes by reducing the interaction between metals and GaAs by organic interfacial layers are of considerable interest in high frequency applications [\[6,7\].](#page--1-0)

There is considerable interest in the characterization of the electronic structure of pyronine, because it indicates good optical absorption in both UV and UV–vis regions.

Pyronine is a member of the organic semiconductor materials [synonyms: pyronine Y, pyronine J, pyronine G]. Molecular formula of pyronine, PYR(G): $C_{17}H_{19}CIN_2O$, molecular weight: 302.80 and melting point: 250–260 °C [\[8\].](#page--1-0)

The molecular structure of PYR(G) is shown in [Fig. 1.](#page-1-0) In this structure, two electronic structures are possible [\[9\]](#page--1-0) in which the conjugation is totally different, one where the oxygen is assumed as a positive charge and in the other possible structure the nitrogen assumed as a positive charge. However, because the nitrogen is less electronegative than oxygen, the former can support a positive charge more easily than the latter, and therefore the structure with positive nitrogen is the more likely one.

The crystalline structure of PYR(G) was studied by Soliman et al. [\[10\]. T](#page--1-0)he results revealed a tetragonal system with lattice parameters: $a = b = 4.661 \text{ Å}$, $c = 13.216 \text{ Å}$ and the space group is P4MM.

The molecular system of the PYR(G) has extended conjugation [\[11\]](#page--1-0) which is in fact responsible for its absorption in the longer wavelength; it absorbs the light in the visible region [\[11\]](#page--1-0) from

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Fig. 1. The molecular structure of PYR(G).

440 nm to 660 nm with a maximum at 540 nm. It is also a wellknown material as an electron acceptor in photochemistry and the electronic transition in the molecular system is $\pi-\pi^*$.

The optical band gap analysis of PYR(G) studied by Sharma et al. [\[11\]](#page--1-0) showed both direct energy band gap (2.5 eV) and indirect one (1.5 eV). Recently, Soliman et al. [\[10\]](#page--1-0) reported two indirect energy band gaps in two different energy ranges and explained these energies as the onset and the fundamental energy gaps of PYR(G) thin films and taken the values of 1.88 eV and 2.25 eV, respectively.

The electrical characteristics of spin coated thin films of poly(3 phenyl azo methine thiophene) (PPAT), sensitized with pyronine (Y) dye sandwiched between indium tin oxide (ITO) and aluminum (Al) have been investigated by Sharma et al. [\[12\].](#page--1-0) The obtained device parameters such as the ideality factor, built-in potential, conductivity were found to be 1.6, 0.75 eV, 5.4×10^{-7} S m⁻¹, respectively. They also found that the illumination of the device from the ITO side with a white light, the values of the short circuit current density (I_{sc}), open circuit voltage (V_{oc}), voltage, fill factor and power conversion efficiency for the device were found to be 2.06×10^{-5} A/cm², 0.75 V, 0.48 and 0.74%, respectively. It was also found that the power conversion efficiency is increased by sensitizing with pyronine (Y) in comparison to purely PPAT based device.

The present communication deals with the designing and characterization of the new type of heterojunction having configuration Au/PYR(G)/p-GaAs/Au:Zn. The electronic parameters controlling the device performance, such as barrier height, ideality factor, series resistance and interface parameters, were evaluated by current–voltage and capacitance–voltage measurements. The photovoltaic properties of the device were also investigated.

2. Experimental procedures

The p-type, Zn-doped, GaAs single crystals with a thickness of 0.45 mm and (100) orientation were used as substrates. Chemical etching of p-GaAs was performed with 2 ml H₂O, 8 mg AgNO₃, 1 g CrO₃ and 1 ml HF solution for 10 min at 65 ◦C. After etching the GaAs wafer was washed several times with distilled water and dried under vacuum. Au:Zn alloy was deposited on one side of the p-GaAs specimen as an ohmic contact, while the other side was coated by PYR(G) film (the powder purity, 99.7%, purchased from Kodak, UK). The deposition rate was kept constant at 4 nm s−¹ and the thickness of PYR(G) film was about 100 nm. The upper ohmic contact electrode was made by evaporation of gold onto the PYR(G) film through a special mask. A schematic diagram of the heterojunction device is given in Fig. 2.

High-vacuum evaporation unit (Edwards 306 A) was used to deposit all films. During evaporation, the vacuum was kept at 10−⁴ Pa. The film thickness was monitored during the evaporation by using the quartz crystal thickness monitor (Edward, type FTM6).

The heterojunctions of Au/PYR(G)/GaAs/Au:Zn were annealed at 373 K for 2 h. It was found that the annealing of the fabricated heterojunction was needed to enhance the performance of the junction. This annealing might remove any channels, which could be raised during the fabrication.

The I–V characteristics at different temperatures were recorded under dark condition by using a stabilized power supply and a high-impedance Keithley 617 electrometer. The temperature was measured directly by means of chromel–alumel thermocouple connected to hand-held digital thermometer. The photovoltaic properties of Au/PYR(G)/p-GaAs/Au:Zn heterojunction was determined by plotting the

Fig. 2. Schematic diagram of Au/PYR(G)/GaAs/Au:Zn heterojunction.

Fig. 3. I–V characteristic of Au/PYR(G)/GaAs/Au:Zn heterojunction at different temperatures.

I–V characteristics using a load resistance under illumination of light from a tungsten lamp. The incident power flux was recorded by a calibrated Lux-meter and calibrated as 8 mW/cm2.

3. Results and discussion

3.1. Dark DC electrical properties of Au/PYR(G)/p-GaAs/Au:Zn device

Fig. 3 shows the current–voltage (I–V) characteristics of Au/PYR(G)/p-GaAs/Au:Zn heterojunction under dark condition at different temperatures in the range 298–373 K. Under forward bias, the current is found to be small until reaching a certain value, and then increased rapidly. On the other hand, under the reverse bias, the current is very small. This behavior can be understood in terms of the change of the width of depletion region by considering a diode behavior [\[13\].](#page--1-0)

The rectification ratio, RR, was calculated from the ratio of forward and reverse current at certain bias as shown in [Fig. 4\(a](#page--1-0)) at room temperature (298 K). The voltage dependence of the calculated RR at room temperature is shown in [Fig. 4\(b](#page--1-0)). Other important parameters namely, the series resistance, R_s , and shunt resistance, $R_{\rm sh}$, can be considered as factors affecting the heterojunction performance. The junction resistance at room temperature as a function of the applied voltages is shown in [Fig. 5. B](#page--1-0)y increasing the forward bias voltages the junction resistance decreases and tends to be constant at certain value, this value gives R_s [\[13,14\]. O](#page--1-0)n the other hand, by increasing the reverse applied voltages, the junction resistance increases and reaches a constant value which is the value of $R_{\rm sh}$. The values of $R_{\rm s}$ and $R_{\rm sh}$ were estimated as 0.510 and $18.78 \text{ k}\Omega$, respectively, at room temperature.

The semi-logarithmic plot characteristics of forward current versus voltage for Au/PYR(G)/p-GaAs/Au:Zn heterojunction measured in the temperature range 298–373 K (Fig. 3) indicate that the current shows an exponential increase with applied voltage in the voltage range $0 < V \le 0.35$ volts. Under higher voltage in the range $0.4 < V \leq 1.5$ volts, the I–V characteristics deviate from the exponential behavior due to the effect of a series resistance on the system. This behavior indicates the presence of two conduction mechanisms depending on the applied voltage bias.

According to the modified Shockley equation, the current across the diode under the application of low bias voltage is given by the following relation [\[15\]:](#page--1-0)

$$
I = AA^*I_s \left[\exp \frac{q(V - IR_s)}{nkT} - 1 \right] + \frac{V - IR_s}{R_{sh}} \tag{1}
$$

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