

# Controlling of semiconductor/metal junction barrier by 5,10,15,20-tetraphenyl-21H,23H-porphine ruthenium(II) carbonyl

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The electrical characteristics of RuP/p-Si/Al junction barrier have been investigated by current-voltage and capacitance-voltage characteristics. A deviation in I-V characteristic of the diode is observed due to effect of series resistance and interfacial layer. RuP/p-Si/Al diode is a metal-interfacial layer-semiconductor type diode with calculated electronic parameters (ideality factor, series resistance and barrier height;  $n=1.95$ ,  $R_s=6.25\text{ k}\Omega$  and  $\phi_B=1.23\text{ eV}$ ). The obtained barrier height and ideality factor values of RuP/p-Si/Al diode at the room temperature is significantly larger than that for the conventional Al/p-Si Schottky diode. It is evaluated that RuP organic layer modifies electronic properties of metal-semiconductor devices based on p-Si.

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*Keywords:* Metal-semiconductor contact, Organic semiconductor, Series resistance

## 1. Introduction

Metal-semiconductor (MS) contacts play an important role in the performance of semiconductor devices because of their potential application in various electronic and optoelectronic devices. Unless specially fabricated, a Schottky barrier diode (SBD) possesses a thin interfacial native oxide layer between metal and semiconductor. The existence of such an insulating layer converts the device to metal-interfacial layer-semiconductor (MIS) diode and may have a strong influence on the diode characteristics as well as a change of the interface state charge with bias which will give rise to an additional field in the interfacial layer [1-6]. Organic semiconductors can be used as activate components in electronic devices and these materials have potential advantages due to easily processable in low cost and large area device characterization. This has opened a new possibility of replacing conventional inorganic devices by the organic ones [7]. The device performance of a Schottky diode depends on electrical and electronic characteristics of metal/organic semiconductor junction. Therefore, the understanding of electronic properties of interface between metal and organic semiconductor is important for device applications. The organic thin films can be useful and even essential materials for activates electronic devices recently. Schottky diodes have been fabricated and tested by using different semiconducting organic and inorganic compounds. Considerable attention was given in recent years to the preparation and properties of junctions or organic conductive polymers with metals and inorganic semiconductors. It is evaluated that electron transport properties of metal-semiconductor barriers can

be modified by organic semiconductor materials. Furthermore, it has been reported that organic monolayers can control Schottky energy barriers in organic electronic devices [8].

In this study, RuP/p-Si/Al junction barrier has been fabricated to modify electron transport properties of the diode.

## 2. Experimental

The p-Si type substrate was rinsed in deionised water using an ultrasonic bath for 10-15 min and finally was chemically cleaned according to method based on successive baths of methanol and acetone. The substrate was placed in vacuum system for the processes. Al metal with high purity (99.999%) was thermally evaporated on the substrate. 5,10,15,20-Tetraphenyl-21H,23H-porphine ruthenium(II) carbonyl dye content ~80 % (RuP) was purchased from Sigma-Aldrich Chemical Co (Fig. 1). The solution of the RuP was prepared and mixed by ultrasonic effect. The solution of RuP was homogenized for 1.5 hour by mixing with rotation before the deposition. Then, the film of the RuP was prepared by casting the solution on p-Si/Al metal with subsequent drying. The metal contact with RuP layer was formed by Au electrode. The current-voltage (I-V) measurements were performed with 2400 KEITHLEY sourcemeter and GPIB data transfer card for current-voltage measurements. The capacitance-voltage (C-V) measurements were performed by use of HIOKI 3532-50 LCR.

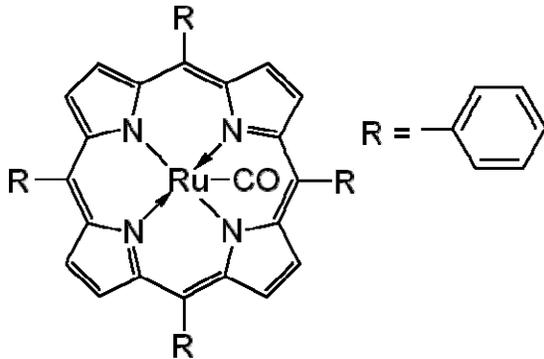


Fig. 1. The chemical structure of the RuP organic compound.

### 3. Results and discussion

#### 3.1. The current-voltage characteristics of RuP/p-Si/Al junction diode

Fig. 2 shows the current-voltage characteristic of RuP/p-Si/Al diode. We use the thermionic emission theory (TE) to analyze forward *I-V* characteristics of the diode studied. TE theory is described as [9-10],

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

where *n* is the ideality factor and *I<sub>o</sub>* is the saturation current, *k* is the Boltzmann constant, *q* is the electronic charge. The ideality factor for the diode was determined from the slope of forward bias region, as shown in Fig. 2 and was found to be 1.89. Thermionic emission theory is ruled out for this device due to the higher ideality factor value. Thus, *I-V* characteristics of an organic film inserted between metal and semiconductor junction can be analyzed by the following relation [11]

$$I = AA^* T^2 \exp(-\beta t) \exp\left(-\frac{q\phi_b}{kT}\right) \exp\left(\frac{qV}{nkT}\right) \left[1 - \exp\left(-\frac{qV}{nkT}\right)\right] \quad (2)$$

where *A* is the contact area, *A\** is the Richardson constant (32 A/cm<sup>2</sup>K<sup>2</sup> for p-Si) [4], *T* is the temperature and  $\phi_b$  is the barrier height and  $\beta$  is the tunneling constant. When an organic layer with *t* thickness is inserted between metal and semiconductor, the effective barrier height is defined as [12],

$$\phi_{eff} = \phi_b + \frac{kT\beta t}{q} \quad (3)$$

If Eq. 2 is rearranged, one obtains,

$$I = AA^* T^2 \exp\left(-\frac{q\phi_{eff}}{kT}\right) \exp\left(\frac{qV}{nkT}\right) \left[1 - \exp\left(-\frac{qV}{nkT}\right)\right] \quad (4)$$

where *n* is the ideality factor, which generally is larger than unity. The obtained *n* value for the diode studied is higher than unity, suggesting RuP/p-Si/Al diode has a metal-interfacial layer-semiconductor (MIS) configuration. The deviation in *I-V* characteristic is due to effect of series resistance and interfacial layer. In such case, in order to determine the diode parameters, we used the Cheung's method. Cheung's functions can be expressed as [13],

$$\frac{dV}{d \ln(I)} = n \frac{kT}{q} + IR_s \quad (5)$$

$$H(I) = V - n \frac{kT}{q} \ln\left(\frac{I_o}{AA^* T^2}\right) \quad (6)$$

and

$$H(I) = IR_s + n\phi_B \quad (7)$$

where *R<sub>s</sub>* is the series resistance and  $\phi_B$  is the barrier height. Fig. 3a shows that *dV/dlnI-I* plot gives a straight line in series resistance region. The *R<sub>s</sub>* and *n* values were calculated from the slope and intercept of Fig. 3a. The obtained values are *R<sub>s</sub>* = 6.27 kΩ and *n*=1.95. The obtained diode parameters suggests that current-voltage characteristics of the diode is far from thermoionic emission model. The *R<sub>s</sub>* obtained from *H(I)-I* plot is 6.23 kΩ.

The average value of series resistance of the diode was found to be 6. 25 kΩ.

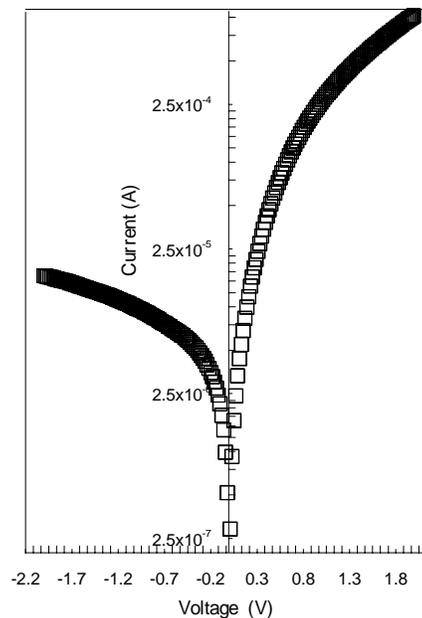


Fig. 2. *I-V* characteristic of the RuP/p-Si/Al diode.

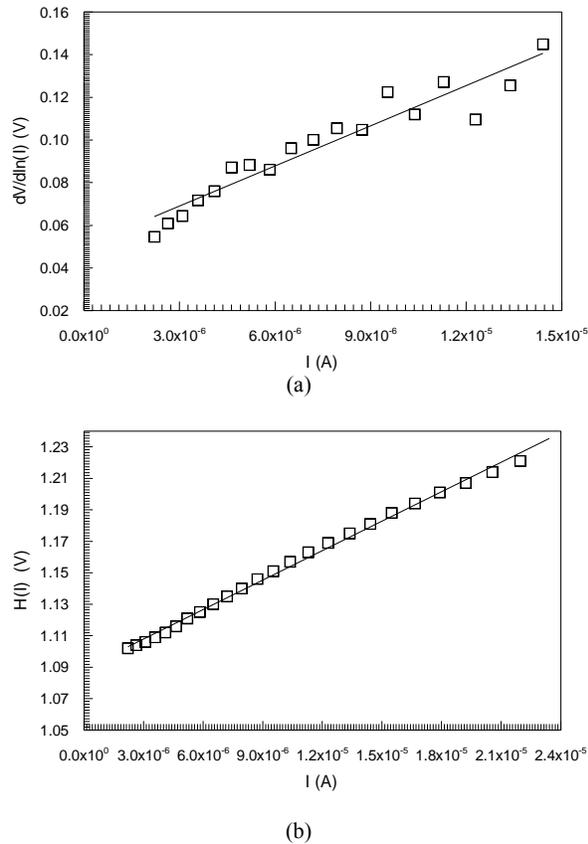


Fig. 3. Plots of  $dV/d\ln(I)$ - $I$  and  $H(I)$ - $I$  of RuP/p-Si/Al diode.

### 3.2. Capacitance-voltage characteristics of RuP/p-Si/Al junction diode

The capacitance-voltage (C-V) curve of RuP/p-Si/Al diode at 500 kHz is shown in Fig. 4. When an organic layer is inserted between metal and semiconductor, the capacitance dependence of applied voltage can be expressed as [14]

$$\frac{1}{C^2} = \frac{2(V_{bi} + V)}{A^2 \epsilon_s q N_a} \left[ 1 - 4 \left( \frac{\epsilon_s d}{\epsilon_m W} \right)^2 + \dots \right] \quad (8)$$

where  $V_{bi}$  is the built-in potential,  $\epsilon_s$  is the dielectric constant of semiconductor,  $N_a$  is the doping concentration,  $d$  is the thickness of organic layer,  $\epsilon_m$  is the dielectric constant of organic layer and  $W$  is the depletion width.  $N_a$  value was calculated from the slope of Fig. 4 and was found to be  $7.40 \times 10^{15} \text{ cm}^{-3}$ . For non ideal structures, the barrier height can be obtained from the following relation,

$$\phi_B = C_2 V_d + V_p \quad (9)$$

where  $V_p$  is the potential difference between the Fermi level and the top of the valence band in the of p-Si given by

$$V_p = kT \ln \left( \frac{N_v}{N_a} \right) \quad (10)$$

where  $N_v = 1.82 \times 10^{19} \text{ cm}^{-3}$  is density of states in the valence band [4]. The  $V_d$  value was determined from  $C^{-2}$ - $V$  plot and was found to be 2.02 V. The barrier height was calculated from C-V curve using obtained  $V_d$  and  $V_p$  (0.20 V) values. The obtained barrier height is 1.23 eV. In previous studies, various p-Si/Al with organic semiconductor diodes have been prepared and investigated their electrical properties [15-16]. In agreement with earlier results of ours, we find that organic semiconductor materials can completely change electronic properties of metal-semiconductor devices. The ideality factor ( $n=1.95$ ) of the diode used in this study is lower than that of Zn(Phen)q/p-type Si/Al ( $n=2.05$ ), pyronine-B/p-type Si/Al ( $n=2.02$ ) and polypyrrole/p-type Si/Al ( $n=2.00$ ) Schottky diode, whereas it is higher than that of Al/MEH-PPV/p-Si ( $n=1.88$ ) and PPy/p-Si/Al ( $n=1.78$ ) diodes [15-19]. It is evaluated that the organic layer modifies electronic properties of metal-semiconductor devices.

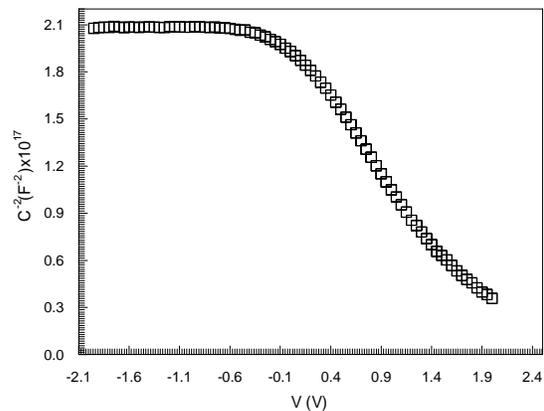


Fig. 4. Plot of  $C^{-2}$ - $V$  of RuP/p-Si/Al diode.

### 4. Conclusions

The electrical characteristics of the RuP/p-Si/Al Schottky diode were investigated by current-voltage and capacitance-voltage characteristics. The RuP/p-Si/Al Schottky diode is a metal-insulator-semiconductor (MIS) type diode with calculated electronic parameters (ideality factor, series resistance and barrier height;  $n=1.95$ ,  $R_s=6.27$  (6.23)  $\text{k}\Omega$  and 1.23 eV). It is evaluated that RuP organic layer modifies the electronic properties of metal-semiconductor devices based on p-Si.

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