

Effect of a new methacrylic monomer on diode parameters of Ag/p-Si Schottky contact

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Abstract: 1-[4-(prop-2-yn-1-yloxy)phenyl]ethanone-O-methacryloyloxime (POEMO) is a new methacrylic monomer with side chain alkyne. In this study, Ag/POEMO/p-Si Schottky metal-interlayer-semiconductor (MIS) diode was fabricated and its diode parameters were investigated. Using the forward bias current-voltage (I-V) characteristic, the ideality factor and barrier height of the MIS structure were found as 2.81 and 0.70 eV, respectively. The barrier height value of 0.70 eV obtained for Ag/POEMO/p-Si MIS diode was higher than the value of 0.64 of conventional Ag/p-Si Schottky diode. Cheung-Cheung and Norde methods were also used to extract ideality factor, barrier height and series resistance values, and the obtained results were compared.

Keywords: Schottky diode; electrical characterization; methacrylic monomer.

Vpliv novega metakrilnega monomera na diodne parameter Ag/p-Si Schottky kontakta

Izvleček: 1-[4-(prop-2-yn-1-yloxy)phenyl]ethanone-O-methacryloyloxime (POEMO) je nov metakrilni monomer s stransko alkilno verigo. V tem delu smo izdelali in analizirali lastnosti Ag/POEMO/p-Si Schottky-jeve MIS (kovina-vmesna plast-polprevodnik) diode. Idealni faktor in višina bariere diode pri priključenju prevodni napetosti je 2.81 in 0.70 eV. Dobljena višina bariere v dani strukturi je višja od 0.64 eV pri klasični Schottky-jevi diodi. Za natančno določitev idealnega faktorja, višine bariere in serijske upornosti smo uporabili Cheung-Cheung in Norde metode. Rezultate obeh metod smo medsebojno primerjali.

Ključne besede: Schottky-jeva diode; električna karakterizacija; metakrilni monomer

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1 Introduction

Organic electronic has drawn significant attention due to interesting optical, electrical, photoelectric, and magnetic properties of organic materials in the solid state. The advantages of thin-film formation, light weight, large area and mechanical flexibility provided by organic materials are other reasons of this increasing interest [1]. Furthermore, organic chemistry can tailor the materials properties according to the demand. Electronic devices based on organic materials have found a wide variety of applications including; light emitting diode, organic field effect transistor, Schottky diode, photovoltaic and solar cells [2, 3].

The metal/semiconductor (MS) contacts have crucial importance in electronic devices. However, many of these contacts are not fabricated as barely MS contacts; they are fabricated as metal-interlayer-semiconductor (MIS) contacts [4]. MIS structures are fabricated by covering a semiconductor substrate with an organic/inorganic layer on which a metal electrode is deposited. In an MS contact, the characteristic quantity is the Schottky barrier height which measures the energy distance between the Fermi level and the edge of respective majority carrier band of the semiconductor at the interface. The barrier height of an MS contact can be modified by inserting an interlayer between the metal and

the semiconductor. Therefore, numerous studies have been carried out to implement barrier height modification using organic/inorganic interlayer. In these studies, either increasing or decreasing of the barrier height have been reported [5-9].

The ability of acrylic monomers in copolymerizing to produce variety of structures make it possible to produce the desired properties for a wide range of applications. Therefore, methacrylate polymers are one of the most important commercial polymers [10]. 1-[4-(prop-2-yn-1-yloxy)phenyl]ethanone-O-methacryloyloxime (POEMO) is a new functional methacrylic monomer with side chain alkynes [11]. It is thought that investigation of further application areas for this new methacrylate monomer bearing an important group such as alkynes would be useful. For example, using the monomer as an interlayer at the interfaces in the MS contact may be interesting.

The aim of this study was to investigate diode parameters of a new diode fabricated using a new functional methacrylic monomer, i.e. Ag/POEMO/*p*-Si MIS diode. The current-voltage (*I-V*) measurement was carried out to obtain barrier height, ideality factor and series resistance of the device using *I-V*, *Cheung-Cheung* and *Norde* methods.

2 Experimental

The synthesis of 1-[4-(prop-2-yn-1-yloxy) phenyl] ethanone-Omethacryloyloxime (POEMO) monomer is shown in Fig. 1. Detailed description of synthesizing method can be found elsewhere [11-12].

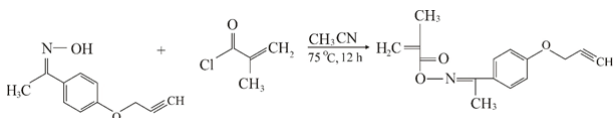


Figure 1: The synthesis of POEMO monomer

Ag/POEMO/*p*-Si MIS diode was prepared using a one side polished *p*-type Si (100) wafer. The wafer was chemically cleaned using the RCA cleaning procedure (i.e., a 10 min boil in $\text{NH}_3+\text{H}_2\text{O}_2+6\text{H}_2\text{O}$ followed by a 10 min boil in $\text{HCl}+\text{H}_2\text{O}_2+6\text{H}_2\text{O}$). Low resistivity ohmic contact to *p*-type Si substrate was made by Al metal, followed by a temperature treatment at 570 °C for 3 min in N_2 atmosphere. The native oxide on the front surface of substrate was removed in $\text{HF}:\text{H}_2\text{O}$ (1:10) solution and finally the wafer was rinsed in de-ionised water for 30 min. Subsequently, POEMO was coated onto front surface of clean silicon substrate directly by dropping POEMO-acetone solution and waited for the evapora-

tion of the solvent at room temperature. The contacting metal dot was formed by silver paste with a diameter of about 1.0 mm (diode area= $7.85 \cdot 10^{-3} \text{ cm}^2$). Ag/POEMO/*p*-Si MIS diode is thus obtained. The current-voltage (*I-V*) measurements of MIS diode were carried out by a Keithley 6487 picoammeter/voltage source at room temperature.

3 Results and discussion

The non-linear *I-V* characteristic of a typical diode behavior is described by the thermionic emission theory as follows [13, 14]:

$$I = I_0 \exp\left(\frac{qV}{nkT}\right) \left[1 - \exp\left(\frac{-qV}{kT}\right)\right] \quad (1)$$

For bias levels larger than $3kT/q$, Eq. (1) can be expressed as:

$$I = I_0 \exp\left(\frac{qV}{nkT}\right) \quad (2)$$

Here V , q , n , k and T and represent the applied voltage, the electron charge, the ideality factor, Boltzmann's constant and the absolute temperature in Kelvin, respectively. I_0 is the reverse saturation current which can be derived from the straight-line intercept of $\ln I$ by extrapolation at zero voltage and is given by:

$$I_0 = AA^*T^2 \exp\left(\frac{-q\phi_b}{kT}\right) \quad (3)$$

where A is the effective diode area and A^* is the effective Richardson constant of $32A \text{ cm}^{-2} \text{ K}^2$ for *p*-Si [14-16]. ϕ_b is the effective barrier height. Once I_0 is obtained, then effective barrier height can be calculated as follows:

$$\phi_b = \frac{kT}{q} \ln\left(\frac{AA^*T^2}{I_0}\right) \quad (4)$$

The ideality factor or the emission coefficient (n) is typically used to measure how the practical diodes deviate from the ideal thermionic emission model or to take into account the contributions of other current transport mechanisms [17]. This parameter can be calculated from the slope of linear region of semi-logarithmic *I-V* plot. Using Eq. (2), ideality factor can be obtained as follows:

$$n = \frac{q}{kT} \left[\frac{\partial V}{\partial (\ln I)} \right] \quad (5)$$

Fig. 2 illustrates the experimental I - V characteristic of Ag/POEMO/ p -Si MIS diode at room temperature. Well-known characteristic features of rectifying contacts are the weak voltage dependence of reverse-bias current and the exponential increase of the forward-bias current [4, 18, 19]. It is obvious that the device exhibits a good rectification behavior. The downward curvature (non-linear region) in the semi-log I - V characteristic at high forward bias values is arisen from the series resistance (R_s) associated with the contact wires or the bulk resistance of the organic interlayer and the inorganic semiconductor.

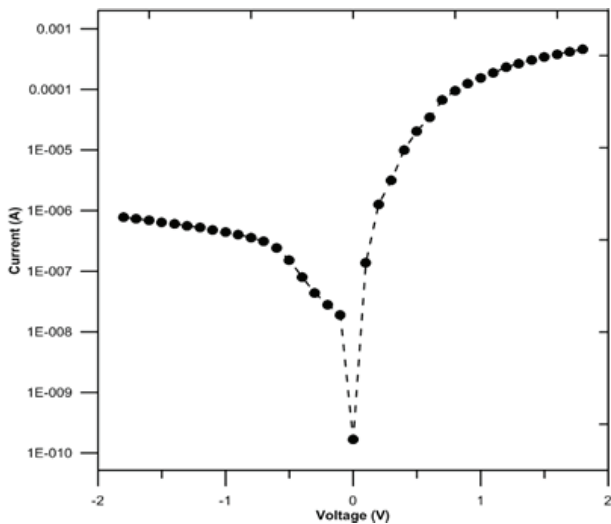


Figure 2: The experimental current-voltage characteristic of the Ag/POEMO/ p -Si MIS diode at room temperature.

On the basis of TE theory, the experimental values of the effective barrier height and the ideality factor were determined from the intercept and the slope of the linear portion of the forward-bias I - V plot, respectively. The obtained values of effective barrier height and ideality factor were 0.70 eV and 2.81, respectively. For an ideal diode, ideality factor should be close to unity; but for real diodes it is usually higher than one as we obtained [20-22]. Ideality factor which is greater than unity shows the deviation from thermionic emission theory. In the literature this case is assigned to the interface states, as well as fabrication-induced defects at the surface [18, 20-24]. In addition; interface state density distribution, quantum-mechanical tunneling, image-force lowering, the lateral distribution of barrier height inhomogeneities, the leakage current, series and shunt resistance are also proposed to explain the deviation [13, 18, 23, 25, 26]. Among these, the series

resistance (R_s) is an important and influential parameter on the electrical characteristics of Schottky barrier diodes. Therefore, determination of series resistance (R_s) value deserves attention for understanding the mechanism of diodes.

The barrier height value of 0.70 eV obtained for the Ag/POEMO/ p -Si device is higher than that achieved with conventional MS contact of Ag/ p -Si whose barrier height value was 0.62 [27]. By means of the POEMO interlayer; a physical barrier is formed between the metal and the inorganic substrate, preventing the metal from directly contacting the Si surface. The POEMO organic interlayer affects the space charge region of the inorganic substrate [18, 28]. Thus, the change in barrier height can be explained by an interface dipole induced by the organic layer [4]. In the literature, many studies have been performed to modify the barrier height of Schottky barrier diodes by forming an interfacial layer between the metal and the semiconductor using the organic thin films [9, 18, 29, 30]. Here, we showed that POEMO could also be used to modify barrier height of Ag/ p -Si diode.

As the series resistance can be negligible at low voltage ranges of a forward bias region, the variation of current with voltage shows linearity. However for higher voltages, the current is deviated considerably from linearity by the series resistance, as can be seen in Fig. 2. Cheung and Cheung proposed a method for the determining the series resistance (R_s) from the high voltage range of an I - V characteristic of a diode [31]. According to Cheung and Cheung, the forward bias current-voltage characteristic of a Schottky barrier diode with a series resistance is given by:

$$I = I_0 \exp \left[\frac{q(V - IR_s)}{nkT} \right] \quad (6)$$

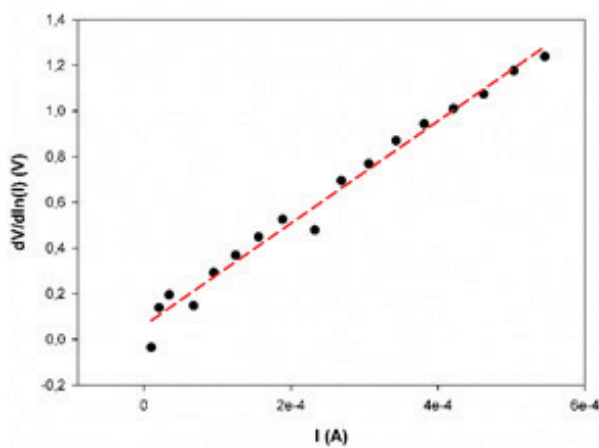
Here IR_s denotes the voltage drop across series resistance of the diode. Using Eq. (6), the electrical parameters viz. series resistance, ideality factor, and barrier height can be determined from the following equations:

$$\frac{dV}{d \ln(I)} = IR_s - n \left(\frac{kT}{q} \right) \quad (7)$$

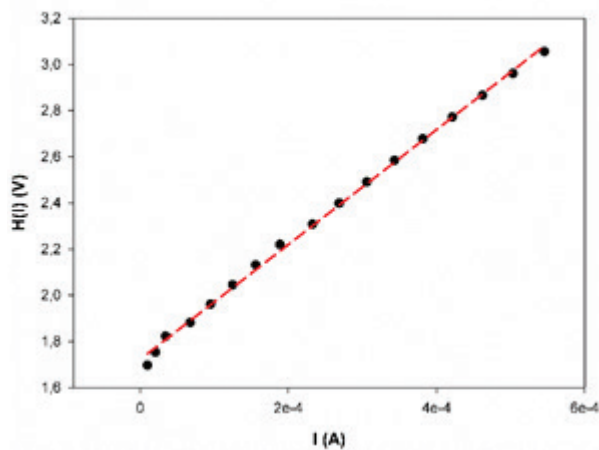
$$H(I) = V - n \left(\frac{kT}{q} \right) \ln \left(\frac{I}{AA^* T^2} \right) \quad (8)$$

$$H(I) = IR_s + n\phi_b \quad (9)$$

The plot of $dV/d(\ln I)$ vs. I gives a straight line for the data of downward curvature region (Fig. 3a). According to Eq. (7), this plot gives R_s as the slope and nkT/q as y -axis intercept. Hereby, n and R_s were calculated as 2.33 and 2.24 k Ω , respectively. The plot of $H(I)$ function is given in Fig. 3b. The slope of $H(I)$ - I plot is equal to series resistance (R_s), whereas the intercept of the y -axis gives $n\phi_b$. Accordingly, using the value of ideality factor obtained from Eq. (7), the barrier height (ϕ_b) and series resistance values were calculated as 0.74 eV and 2.49 k Ω , respectively. The series resistance values determined by two different equations of Cheungs' are close to each other.



a.



b.

Figure 3: Plot of Cheung's fuctions; $dV/d(\ln I)$ vs. I (a), $H(I)$ vs. I (b)

On the other hand, there are differences between the ideality factors and barrier heights obtained from I - V and Cheungs' methods. These differences are attributed to the differences of extraction region in the forward bias of I - V plot. In the I - V method, linear region is used for calculation, while Cheungs' functions are related to the nonlinear region of $\ln I$ - V plot in which the interfacial layer thickness between the metal and the semiconductor, the interface states and bulk series resistance are effective [19, 32, 33].

The barrier heights and series resistance of the Schottky diodes can also be calculated using modified Norde method [18, 34]. The following function has been defined in the modified Norde method:

$$F(V) = \frac{V}{\gamma} - \frac{kT}{q} \ln \left(\frac{I(V)}{AA^*T^2} \right) \quad (10)$$

Where γ is the first integer (dimensionless) greater than n . $I(V)$ is current obtained from the I - V curve. Fig. 4 shows the change of $F(V)$ versus V for Ag/POEMO/ p -Si diode. After determining the minimum value of $F(V)$ by employing the data in Fig. 4, barrier height and series resistance of the diode can be determined by the following equations:

$$\phi_b = F(V_0) + \frac{V_0}{\gamma} - \frac{kT}{q} \quad (11)$$

$$R_s = \frac{kT}{qI} (\gamma - n) \quad (12)$$

In Eq. (11), $F(V_0)$ is the minimum point of $F(V)$ and V_0 is the corresponding voltage. From the $F(V)$ - V plot and Eqs. (11) and (12), the barrier height and series resistance were found to be 0.72 eV and 3.78 k Ω , respectively. The diode parameters, which were obtained via different methods, were summarized in Table 1. As can be seen in the table, there are differences in values of series resistance obtained from Cheng-Cheung and Norde methods. These differences were originated from the fact that the full-voltage range of forward bias $\ln(I) - V$ data is used in Norde method, whereas only the

Table 1: Diode parameters of Ag/POEMO/ p -Si MIS Schottky diode calculated from I - V , Cheung-Cheung and Norde methods

Diode parameters	I-V Method	Cheung-Cheung Method		Norde Method
	$d(\ln I)$ - V	$Dv/d(\ln I)$ - I	$H(I)$ - I	$F(V)$ - V
Ideality Factor (n)	2.81	2.33	-	-
Barrier Height (ϕ_b eV)	0.70	-	0.74	0.72
Series Resistance (R_s k Ω)	-	2.24	2.50	3.78

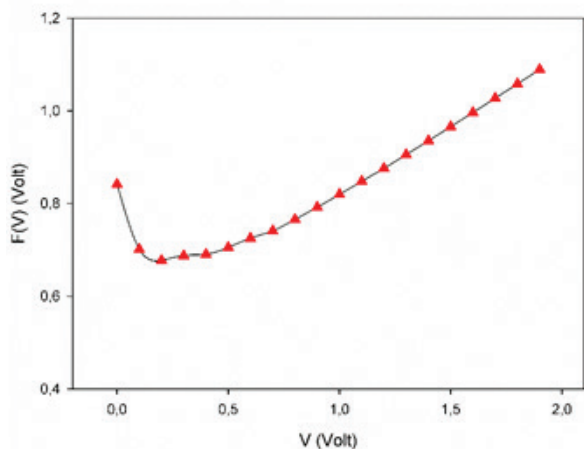


Figure 4: Plot of Norde function; $F(V)$ vs. V

high-voltage region (viz. non-linear part of the plot) of the forward bias $\ln(I) - V$ data is used in *Cheung's* method [35, 36]. High series resistance value is accepted as current-limiting factor for the diodes. Gullu et al. attributed the high series resistance to space-charge injection into POEMO thin layer at higher forward bias voltage. As the tunneling process is especially important for a thin interfacial layer, it is assumed that tunneling starts to control the current flow [18, 37].

4 Conclusions

In this study, we fabricated an Ag/POEMO/*p*-Si Schottky Barrier diode and investigated its diode parameters by *I-V* measurement. The ideality factor, series resistance and barrier height values were calculated by different methods and were compared. Based on the results the following conclusions could be deduced;

- The Ag/POEMO/*p*-Si Schottky Barrier MIS diode showed good rectifying behavior indicating POEMO organic layer could be used as an interlayer.
- The forward current-voltage characteristics indicated a nonlinear behavior because of the series resistance, as verified by the n value was larger than unity.
- We observed that the ϕ_b value of 0.70 eV obtained for the Ag/POEMO/*p*-Si device was different than the BH value of the conventional Ag/*p*-Si contact. This case could be attributed to the POEMO organic interlayer which modifies effective Schottky barrier by affecting the space charge region of the inorganic substrate.
- The differences between barrier heights values obtained from different methods were attributed to presence of series resistance, interface states and the voltage drop across the interfacial layer

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