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The electrical characteristics of a phthalocyanine heterojunction diode

FAHRETTİN YAKUPHANOGLU*, MEHMET KANDAZ, B. FİLİZ SENKAL
[a]*Fırat University, Department of Physics, 23119 Elazığ/Turkey*
[b]*Sakarya University, Department of Chemistry, 54140 Esentepe, Sakarya, Turkey.*
[c]*Istanbul Technical University, Department of Chemistry, 34469, Maslak, Istanbul, Turkey*

The electrical characteristics of nickel(II) phthalocyanine bearing 2'-aminophenylsulfanyl moieties/n-type silicon organic-on-inorganic semiconductor diode have been investigated by current-voltage characteristics. The diode indicates a good rectifying behavior. The ideality factor higher than unity of the diode is due to the interface states and series resistance. The ideality factor of the diode indicates that the NiPc appears to interact strongly with the Si inorganic semiconductor. The ideality factor n, barrier height Φ_b and R_s values of the diode were determined and these electronic parameters vary with temperature. It is evaluated that at lower voltages, the current–voltage characteristics of the diode is controlled thermionic emission, whereas at higher voltages, the current of the diode is controlled by space charge injection limited mechanism.

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1. Introduction

The enormous diversity of phthalocyanines (Pcs) developed over thirty years of research, offers the prospect of readily processed materials and has been the subject of many investigations [1,2]. The molecular design in the phthalocyanine architecture is a determining factor controlling many of the physical properties [3]. To develop molecular semiconducting, and sensing properties altogether we need advanced organic synthesis on the materials in order to develop efficient device [4,5]. The capabilities of semiconducting Pc materials depend on the molecular composition including especially the core centre, position, nature and especially number of the substituents attached to the Pc core [4]. To date, a great variety of symmetrical or asymmetrical phthalocyanines have been comprehensively studied. Despite of low soluble disadvantage of many phthalocyanines, there have nevertheless been a limited number of reports on good soluble functional phthalocyanines [6-8]. These "passive" substituents can however also influence other physical and morphological properties relevant to their application as semiconductor materials, including liquid crystalline behaviour [9].

Phthalocyanines are an important class of organic semiconductors because of their electrical and optical properties and these materials behave semiconductor due to their aromatic chemical structures. These organic materials are stable according to the other organic semiconductors. Phthalocyanines have been used in various electronic applications such as such as OLEDs, sensors, FETs, gas sensing, photovoltaic cells, and organic electroluminescent devices [1-8].

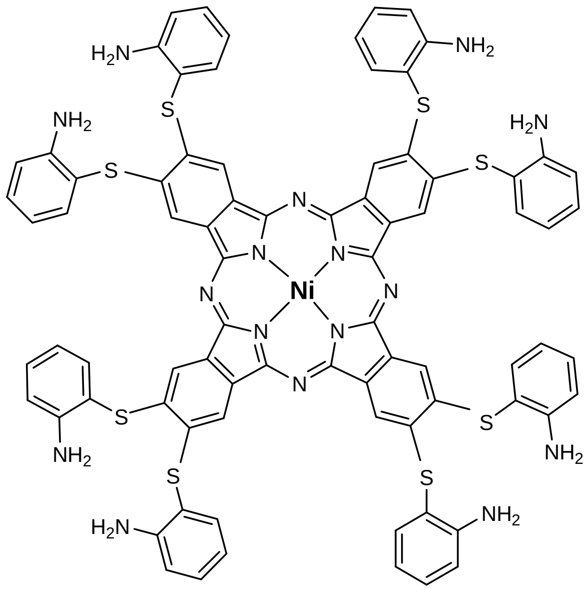
It is evaluated that the new inorganic/organic semiconductor (IO) heterojunction can be prepared using phthalocyanines due their easy thin film process and interesting electrical properties. Furthermore, the organic-on-inorganic diodes haven fabricated easily when compared with inorganic heterojunction diodes. The fabrication of new inorganic-on-organic diodes helps to explain the charge transport mechanism of the IO diodes.

In the present work, we have fabricated an inorganic-on-organic diode using the n-type silicon and 2,3,7,8,12,13,17,18-octakis(2'-aminophenylsulfanyl)-substituted-nickel(II) phthalocyanine. The current-voltage characteristics have been measured and analyzed to gain a deeper explanation about the charge transport mechanism and device performance.

2. Experimental details

2.1. Fabrication of the diode and measurements

Tetrahydrofuran, 1.8-diazabicyclo(5,4,0) undec-7-ene (DBU), quinoline, acetone, diethylether, dichloromethane (DCM), chloroform, dimethylformamide (DMF), dimethylsulfoxide (DMSO) and nickel (II) chloride were purchased from Sigma- Aldrich. 2,3,7,8,12,13,17,18-octakis(2'-aminophenylsulfanyl)-substituted-nickel(II) phthalocyanine (NiPc1) was synthesized and was published elsewhere and its chemical structure is given in Scheme 1 [17].



Scheme 1. The chemical structure of 2,3,7,8,12,13,17, 18-octakis(2'-aminophenylsulfanyl)-nickel(II)phthalocyanine

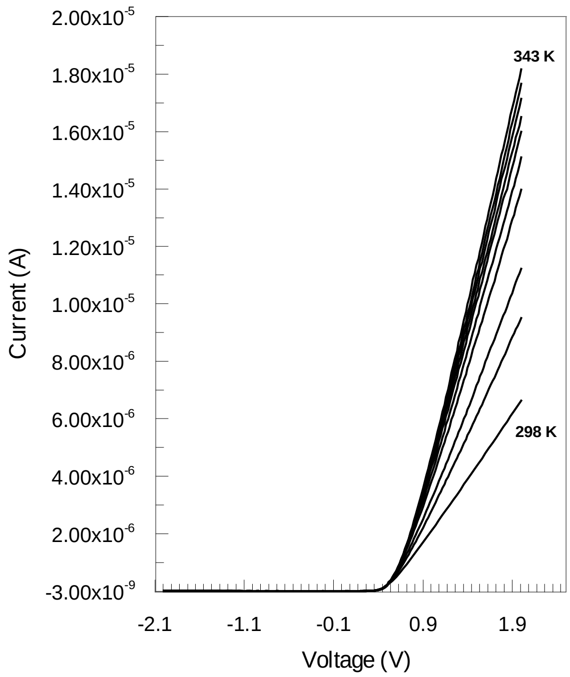
The n-Si/NiPc1 organic/inorganic structure has been prepared using n-type Si and 2,3,7,8,12,13,17,18-octakis(2'-aminophenylsulfanyl)-substituted-nickel(II) phthalocyanine. Firstly, the native oxide on surface on n-Si was removed by HF and then was rinsed in deionised water using an ultrasonic bath for 10-15 min and finally was chemically cleaned according to method based on successive baths of methanol and acetone. Then, the NiPc1 compound was dissolved and the solution was homogenized for 10 minutes by mixing with rotation before the deposition. Then, the film of the NiPc1 was prepared by deposition of solution on the Si wafer by dip coating technique [22]. The current–voltage (I-V) characteristics of the n-Si/NiPc1 diode were performed with 2400 KEITHLEY sourcemeter and GPIB data transfer card for current-voltage (I-V) measurements and the temperature is controlled using LAKESHORE 331S temperature controlled.

3. Results and discussion

3.1. Current-voltage characteristics of n-Si/NiPc1 IO junction

Fig. 1a the current-voltage (I-V) characteristics of the NiPc1/n-Si IO junction at different temperatures with step of 5 ^{o}C. The forward current of the diode increases with increasing temperatures. The IO junction indicates a good rectifying behavior. As seen in Fig. 1b, at lower voltages, the current–voltage characteristics of the diode indicate a non-ideal current-voltage behavior and the current increases exponentially with applied voltage, whereas, at higher voltages shows a power-law dependence of current on voltage, in which the space charge injection limited is valid [18]. In this IO junction, the charge transport is limited by thermionic emission and, in which, the current passes through over the IO barrier. The OI structure behaves like a metal–semiconductor Schottky contact at the low current [19-21]. Thus, we can analyze the current-voltage characteristics of the diode by the following relations [22],

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



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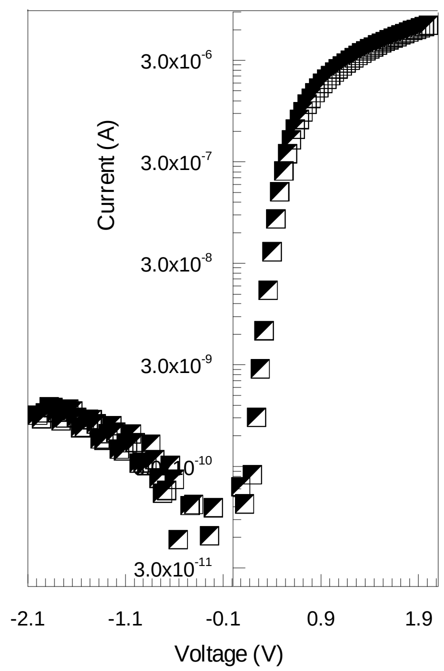


-b-

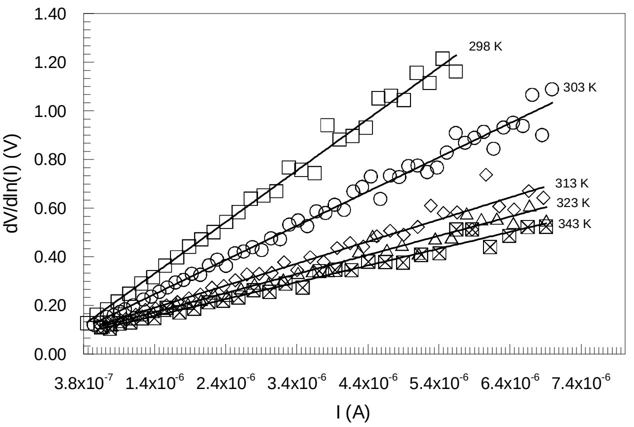
Fig. 1. Current-voltage characteristics of the n-Si/NiPc1 diode a) at various temperatures b) at room temperature in semilogarithmic scale

where n is the ideality factor, V is the applied voltage, k is the Boltzmann constant, T is the temperature and I_o is the reverse saturation current. As seen in Fig. 1b, the n-Si/NiPc1 IO contact indicates a non-ideal behaviour due to the existence of interfacial layer, series resistance effect and the resistance of the organic semiconductor. In the n-Si/NiPc1 IO contact, the carrier transport is injected into organic layer from the inorganic bulk and thus, the non-ideal behavior of the IO contact can be analyzed using Cheung's method and Cheung's functions are expressed as follows [23],

$$\frac{dV}{d\,ln(I)} = n\frac{kT}{q} + IR_s \qquad (2)$$

and

$$H(I) = V - n\frac{kT}{q}ln\left(\frac{I_o}{AA^*T^2}\right) = IR_s + n\phi_b \qquad (3)$$



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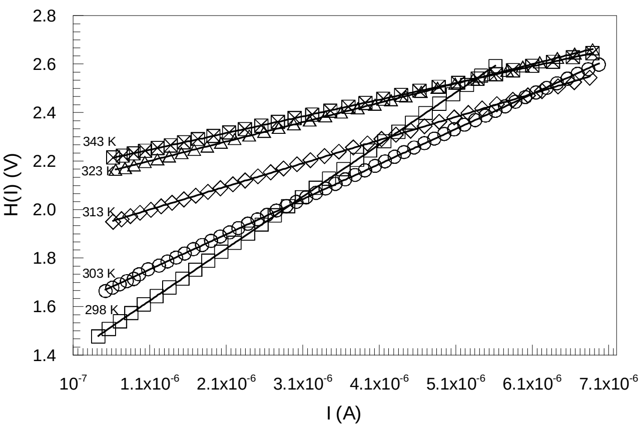
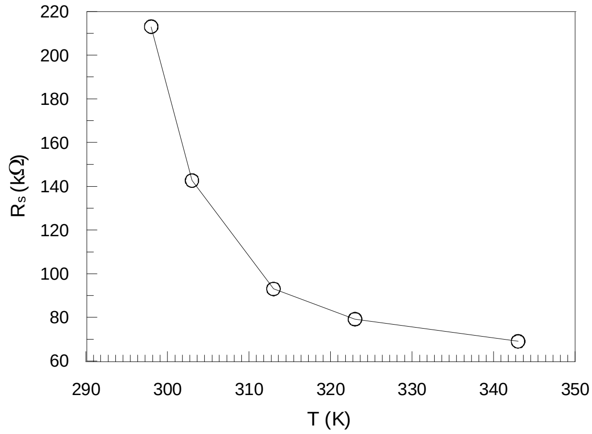


b

Fig. 2. Plots of dV/dlnI vs. I and H(I) vs. I of the n-Si/NiPc1 diode at various temperatures



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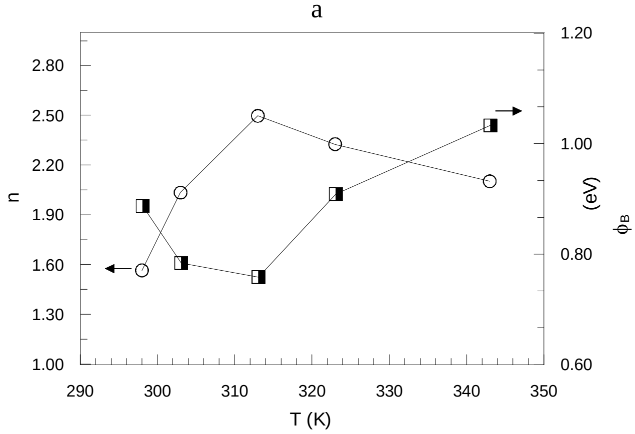

b

Fig. 3 Variation of series resistance, ideality factor and barrier height values of the n-Si/NiPc1 diode with temperature

where R_s is the series resistance and ϕ_b is the barrier height. Figs. 2(a-b) show the plots of dV/dlnI vs. I and H(I) vs. I. The ϕ_b and R_s values were calculated from the plot of H(I) vs. I. The R_s and n values were calculated from the slope and intercept of dV/dlnI vs. I plot. The variation of the n, R_s and ϕ_b values with temperature is shown in Fig. 3(a-b). The series resistance of the diode decreases with increase of temperature. This behaviour is due to the thermal activation of charge carriers at higher temperatures. The n and ϕ_b values vary with the temperature. The n values increase up to 313 K temperature and then decrease. Whereas the ϕ_B values decrease up to 313 K temperature and then, increases. The ideality factor higher than unity is due to interface states and series resistance. The interfacial layer is formed between the organic and inorganic semiconductors and furthermore, the n ideality factor of the device indicates that the NiPc appear to interact strongly with the Si inorganic semiconductor. The obtained series resistance values confirm the consistency of the Cheung's method. The series resistance is higher due to the electrical resistance of the NiPc1. The electrical conductance resulted from series resistance effects can be expressed as,

$$G = G_o\,exp(-\frac{\phi_{bo}}{kT}) \qquad (4)$$

where G_o is a constant, ϕ_{bo} is the zero temperature potential barrier. In order to obtain ϕ_{bo} value, the curve of logG-1000/T was plotted, as shown in Fig. 4. The ϕ_{bo} value was determined from the slope of Fig. 4 and was found to be 0.71 eV. The obtained ϕ_b values indicate a temperature dependent and this dependence is expressed as [24],

$$\phi_b^{RP} = \phi_b^{IV} - T\frac{d\phi_b^{IV}}{dT} \tag{5}$$

where ϕ_b^{RP} is the barrier height obtained from Richardson plot. If $\frac{d\phi_b^{IV}}{dT} \rightarrow 0$, $\phi_b^{RP} \rightarrow \phi_b^{IV}$ would be consistency with Eq.5. The plot of ϕ_b vs. $\frac{d\phi_b}{dT}$ is shown in Fig. 5.

For $\frac{d\phi_b^{IV}}{dT} \rightarrow 0$, ϕ_b value was found to be 0.75 eV. This value is almost in agreement with the value of ϕ_{bo} obtained from conductance-temperature. This suggests that the zero temperature potential barrier for the IO structure can be determined by Eq. 4.

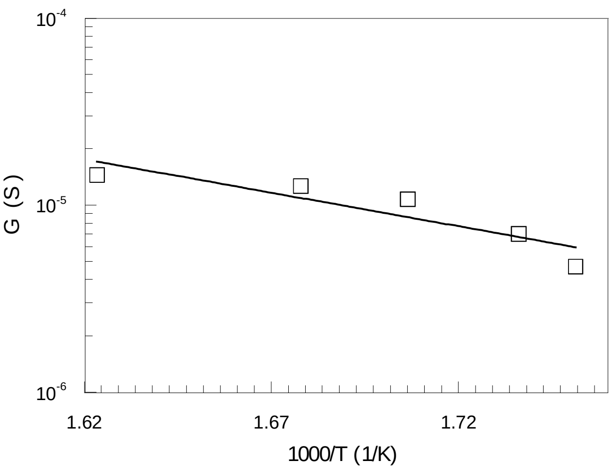

Fig. 4. Plot of logG-1000/T of the n-Si/NiPc1 diode

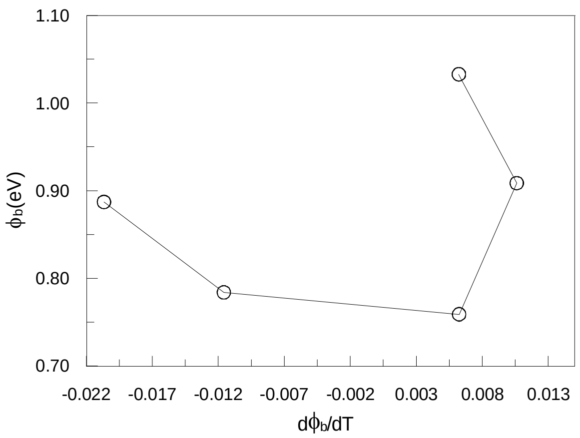

Fig. 5. Plot of ϕ_b vs. $\frac{d\phi_b}{dT}$ of the n-Si/NiPc1 diode

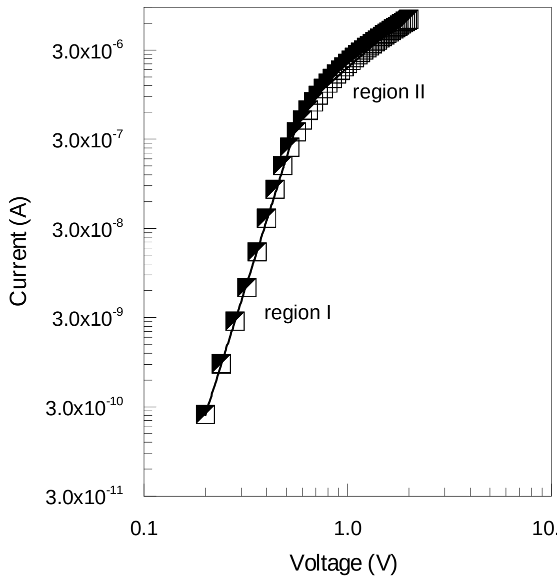

Fig. 6. I-V characteristics of the n-Si/NiPC1 diode

At higher al fields, the space charge limited mechanism is valid for the IO contact. In order to analyze the space charge mechanism, I-V characteristics of the diode were plotted in logarithmic scale and are given in Fig.6. Fig. 6 shows different three current regions by analyzed via $I = AV^m$ relation. Here m is a constant which determines the charge transport mechanism. m values for regions I and II were calculated from the slope of logV-logI plot and were found to be 7.23 and 2.00, respectively. The obtained m value for the first region suggests a superquadratic behavior, which is caused by the low concentration of charge carriers. In region II, the increase rate of current with voltage decreases due to space charge injection into organic layer. Thus, the second region can be expressed by the relation [18, 25],

$$I = \frac{9}{8}\varepsilon A\mu\frac{V^2}{d^3} \tag{6}$$

where ε is the dielectric constant, μ is the mobility of the charge carriers. The mobility of the charge carriers was determined using Eq.6 and was found to be 7.90×10^{-2} $cm^2/V.S$. The obtained mobility value is a typical value for the IO structure [18].

4. Conclusions

The charge transport properties of nickel (II) phthalocyanine bearing 2'-aminophenylsulfanyl moieties/n-type silicon organic-on-inorganic semiconductor diode have been investigated by current-voltage characteristics. The IO diode indicates a good rectifying behavior. The electronic parameters, ideality factor n, barrier height ϕ_b and R_s values of the diode vary with temperature. At lower voltages, the current–voltage characteristics of the IO diode is controlled thermionic emission, whereas at higher voltages, the current of the diode is controlled by space charge injection limited mechanism.

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*Corresponding author: fyhanoglu@firat.edu.tr
fyhan@hotmail.com;