JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 16, No. 9-10, September - October 2014, p. 1137 - 1141

Electrical characterization of n-Si/Copper phthalocyanine based on photodiode

A. A. HENDI*, R.H. Al ORAINY
Physics Department, Sciences Faculty for Girls, King Abdulaziz University, Jeddah, Saudi Arabia

The electrical and photovoltaic properties of n-Si/Copper phthalocyanine hybrid heterojunction device have been investigated by current-voltage and capacitance-voltage measurements. The ideality factor of the diode was found to be 2.08, suggesting that the heterojunction diode indicates a non-ideal diode behaviour. At higher voltages, the space charge limited-conduction mechanism is dominant in the diode. The series R_s and shunt resistance R_{sh} values for the diode were found to be 6.97×10^4 Ω and 1×10^8 Ω, respectively. The photocurrent in the reverse direction of the diode increases with illumination intensity. n-Si/Copper phthalocyanine heterojunction diode gives an open-circuit voltage of 0.092 V and a short-circuit current of 0.08 μA at light intensity of 6 mW/cm^2.

(Received January 16, 2014; accepted September 11, 2014)

Keywords: Photovoltaic device, Heterojunction diode, Organic semiconductors

1. Introduction

Metal/semiconductor junctions have been investigated for electronic device applications [1-2] and in recent years, various organic materials have been extensively used to fabricate electronic devices [3]. An advantage of organic semiconductors is the processability from organic solution, such that simple deposition techniques like doctor blading or screen printing can be applied [4-5]. The organic semiconductors are suitable for use in photoelectric conversion devices due to easy fabrication of devices with low cost [6]. Copper phthalocyanine (CuPc) is one of the well-studied organic photosensitive semiconductors for photovoltaic applications and has been used extensively as an absorber in organic solar cells due to its marked photovoltaic effect and photoconductivity characteristics [7–10]. It has a high absorption coefficient in a wide spectrum and a high photo-electromagnetic sensitivity at low intensities of radiation. It is possible simply to deposit thin CuPc films by vacuum sublimation [11]. Photovoltaic devices based on phthalocyanines can be fabricated by a simple method using a conventional spin coating, dip coating and vacuum deposition techniques. Furthermore, many phthalocyanines show interesting photoconductive and photovoltaic responses and hence have been widely used in Schottky barrier cells and organic photodiodes [12-13]. Also, the devices based on nickel phthalocyanine (NiPc) have been fabricated and photovoltaic and electrical properties of p-NiPc/n-Si and NiPc/p-Si heterojunctions have been investigated. These studies make NiPc a potential candidate for electronic devices. In our previous study, CuPc organic semiconductor was used to convert Al/p–Si Schottky diode to a photodiode [14]. Therefore, in present study, it is evaluated that a heterojunction photovoltaic diode based CuPc phthalocyanine can be fabricated for photovoltaic applications.

In present study, a heterojunction diode including p–n single heterojunction has been fabricated by combining copper-phthalocyanine and n-Si. Electronic and photovoltaic properties of the device have been investigated by current voltage and capacitance-voltage methods under dark and illumination conditions.

2. Experimental details

n-type Si (100) wafer was used as n-type semiconductor. In order to remove the native oxide on surface on n-Si, the wafer was etched 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. Copper phthalocyanine (CuPc) was purchased from Sigma-Aldrich Co. The thin film of CuPc was made by deposition of CuPC on the n-Si wafer having 0.5 mm thickness by adopting dip coating technique [15-18]. The film thickness of deposited film was found to be 50 nm. The contact area of the diode is 7.85×10^{-3} cm^2 and the dimensions of the device are 7x5x0.5 mm^3. The current-voltage (I-V) characteristics of the device under dark and illumination conditions were measured using a KEITHLEY 2400 sourcemeter. The capacitance –voltage measurement of the n-Si/CuPc diode was performed at 100 Hz with a HIOKI 3532-50 LCR meter. The applied voltage was scanned between -2.0 to +2.0 V. The device can be exposed to light coming from a light source to get an intensity of incident power of about 6 mW/cm^2 [19]. Photovoltaic measurements were employed under the light intensity of 6 mW/cm^2 using a 200W halogen lamp.

3. Results and discussion

3.1 Dark current-voltage characteristics of the n-Si/CuPc heterojunction diode

The current voltage characteristic of the n-Si/CuPc diode is shown in Fig.1.

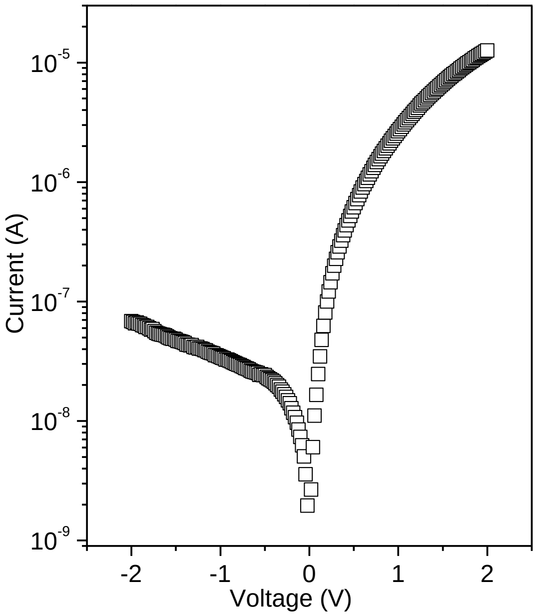

Fig.1 Current-voltage characteristics of the n-Si/CuPc heterojunction diode

The studies in literature demonstrate that dark current-voltage characteristics of the n-Si/CuPc heterojunction diode can be analyzed using the following relation [19-27],

$$I = I_O\left[\exp\left(\frac{q(V-IR_S)}{nkT}-1\right)\right]+\frac{V-IR_S}{R_{sh}} \qquad (1)$$

where n is the ideality factor, I_o is the reverse saturation current, R_s is the series resistance and q is the electronic charge, R_{sh} is the shunt resistance, k is the Boltzmann constant and T is the temperature. The ideality factor and barrier height values are determined by fitting Eq.1 to data and were found to be 2.08 and 0.77 eV, respectively. The obtained n value is higher than unity, suggesting that the diode shows a non-ideal diode behavior. R_s resistance is related to the bulk materials resistance and interfaces between two semiconductors, while R_{sh} resistance is associated with semiconductor-electrode interface properties [20]. Therefore, it is important to determine these parameters. The junction resistance R_j for the device is expressed as [28]

$$R_j = \frac{\partial V}{\partial I} \qquad (2)$$

The R_s and R_{sh} values can be easily determined from the current-voltage plot. At higher voltages, R_j value approaches a constant called series resistance. But, at higher reverse voltages, the R_j value has a constant value called shunt resistance [21-22]. The R_s and R_{sh} values were calculated from the curve of R_j-V plotted and were found to be $6.97\times10^4\ \Omega$ and $1\times10^8\ \Omega$, respectively. The obtained values are higher than that of NiPc/n-Si and NiPc/p-Si heterojunctions [19,22]. At higher voltages, the current of the n-Si/CuPc device varies in the form of $I \propto V^m$. The studies made on organic semiconductors show that this behavior is characteristic for space charge limited currents (SCLC) [29-34] and thus, we can analyze the current-voltage characteristic of the device studied according to Lampert theory. m value was calculated from the slope of plots shown in Fig. 2.

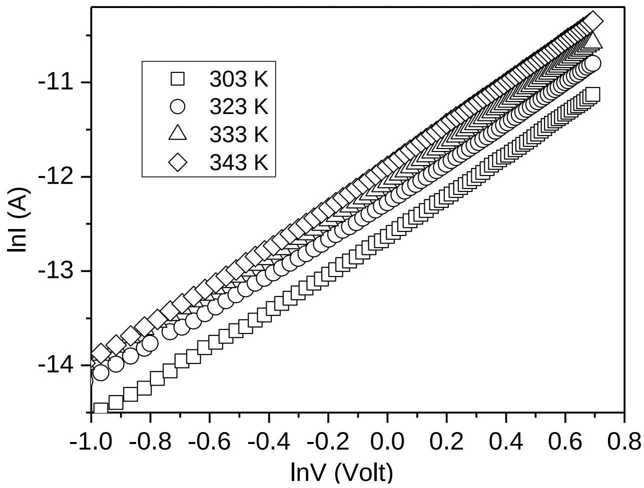

Fig. 2 Plots of lnI-lnV of the n-Si/CuPc heterojunction diode at different temperatures.

At higher voltages, the m value was found to be about 2. This clearly indicates that the hole current in this device is defined SCLC as that of the other organic semiconductors [29-34]. The space charge limited-conduction mechanism (SCLC) is expressed as follows [35]

$$I = \frac{9}{8}\frac{\mu_n \varepsilon A V^2}{d^3} \qquad (3)$$

where μ_n is the mobility of the electrons, ε (ε=3) is the dielectric constant of the CuPc film [36], The mobility of electrons was determined using Eq.3. The obtained μ_n values are 1.91×10^{-8} at 303 K, 2.67×10^{-8} at 313 K, 3.34×10^{-8} at 323 K, 4.21×10^{-8} m^2/V.s at 333 K. These values are in agreement with values in Ref [37]. It is seen that the electron mobility increases with increasing temperature.

3.2. Capacitance-voltage characteristic of the n-Si/CuPc heterojunction diode

The plot of C^{-2} vs V for the diode is shown in Fig. 3.

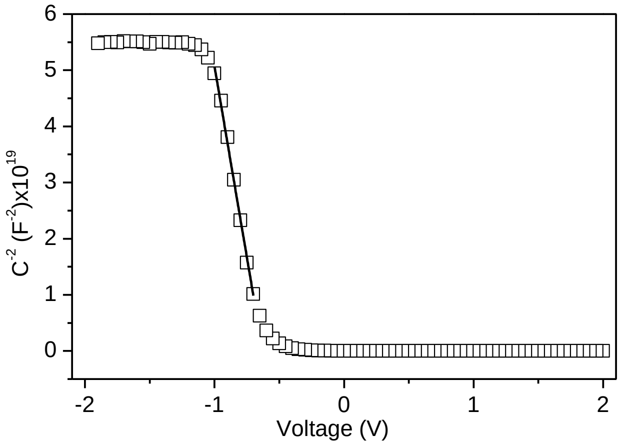

Fig. 3 Plot of C^{-2} vs V of the n-Si/CuPc heterojunction diode.

The relation between capacitance and voltage for p-n junction is expressed by the following relation [19,24-28, 38-39]

$$C^2 = \frac{qN_d N_a \varepsilon_1 \varepsilon_2}{2(\varepsilon_1 N_d + \varepsilon_2 N_a)} \frac{1}{(V_{bi} - V)} \quad (4)$$

where V_{bi} is the built-in potential, ε_1 is the dielectric constant of n-Si, ε_2 is the dielectric constant of CuPc, N_d and N_a are the donor and acceptor concentrations, respectively. For the n-Si/CuPc diode, the depletion layer capacitance can be expressed as

$$N_d = \left(\frac{2}{q\varepsilon_1 A^2} \right) \frac{dV}{dC^{-2}} \quad (5)$$

The values of V_{bi} and N_d can be obtained from the intercept and slope of C^{-2} vs. V plot by means of Eq. 5, respectively. The doping concentration N_d and the built-in potential V_{bi} were found to be $1.44x10^{15}$ cm^{-3} and 0.63 V, respectively. The barrier height for n-Si/CuPc diode can be determined using the following relation [39],

$$\phi_b = V_{bi} + \frac{kT}{q} \ln\left(\frac{N_c}{N_d} \right) \quad (6)$$

where N_c value for Si is $2.8x10^{19}$ cm^{-3} [39] . The ϕ_B value was determined using obtained V_n (0.25 V) value and was found to be 0.88 eV. The barrier heights deduced from I-V measurement is lower than that of C-V technique. The discrepancy between ϕ_b(C-V) and ϕ_b(I-V) can be explained existence of excess capacitance and interface properties. The direct current across the interface is exponentially dependent on barrier height and the current is sensitive to barrier distribution at the interface. Whereas, the capacitance is insensitive to potential fluctuations on a length scale of less than the space charge width that the capacitance-voltage method averages over the whole area. Consequently, the ϕ_b value obtained from C-V measurement is higher than that of ϕ_b value obtained I-V measurements [40].

3.3. Photovoltaic properties of the n-Si/CuPc heterojunction diode

The current-voltage characteristic of the n-Si/CuPc heterojunction diode under light illumination condition is shown in Fig. 4.

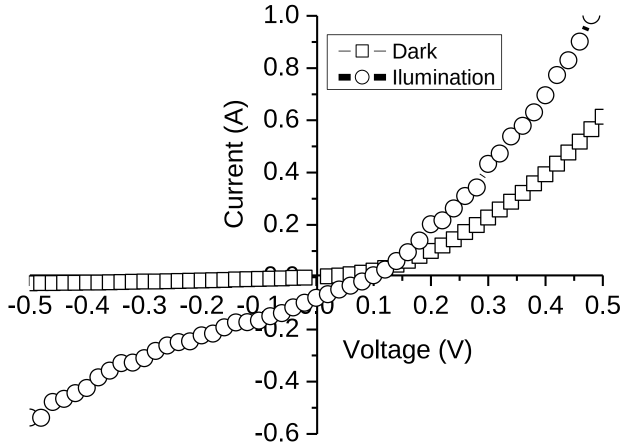

Fig. 4. Plots of current-voltage of the n-Si/CuPc heterojunction diode under dark and illumination conditions.

When the diode is forward biased, there is an exponential increase in the current. The light on reverse I-V characteristic of the device is translated downward moved in the –I direction along the current axis, giving an open circuit voltage (V_{oc}) along with a short photocurrent (I_{sc}) [28]. The illumination increases the current in reverse direction, suggesting that the carrier charges are effectively generated due to electron-hole pair generation. The organic semiconductor CuPc absorbs light and gives a charge separation near the interface of the diode and in turn, the reverse current increases the efficient substantially. The current at a given voltage for the n-Si/CuPc junction diode under illumination is higher than that of under dark. The increase in charge production is dependent on the difference in the electron affinities between n-Si and CuPC semiconductors. The fill factor for the device can be obtained from the following equation [41]

$$FF = \frac{V_m I_m}{V_{oc} I_{sc}} \quad (7)$$

where FF is filling factor, V_{oc} is the open circuit voltage, I_{sc} is the short current. I_m and V_m are current and potential values at maximum power point. The device indicates a photovoltaic behavior with a maximum open circuit voltage V_{oc} of 0.092 V and short-circuits current I_{sc} of 0.08 μA. The fill factor FF value for n-Si/CuPc device was found to be 0.09. The obtained FF value is low for solar cell devices. In literature, electrical and solar cell parameters of a Schottky structure fabricated using CuPc and fluorinated tin oxide (FTO) have been investigated and the obtained FF, V_{oc} and I_{sc} values are 0.18, 0.44 V and 2.2 mA/m^2 under 98 mW/cm^2, respectively [42]. In another study, NiPc/p-Si junction has been shown a photovoltaic characteristic with short circuit current (Isc) of 186 μA, open circuit voltage (Voc) of 0.32 V, fill factor (FF) of 0.28 [19]. The obtained electronic parameters of n-Si/CuPc device are lower than that of FTO/CuPc/Al and NiPc/p-Si devices. This suggests that the performance of a CuPc-based thin film cell is strongly impacted by materials purity and the cell responsivity and fill factor increase with hole mobility, which is found in turn to depend on material purity [43].

4. Conclusions

Electrical and photovoltaic properties of the n-Si/CuPc heterojunction diode have been investigated by current-voltage and capacitance-voltage methods. At higher voltages, for the device, the dominant mechanism is space charge limited current mechanism. The photocurrent in the reverse direction increases with illumination intensity. n-Si/CuPc heterojunction device gives an open-circuit voltage of 0.092 V and a short-circuit current of 0.08 μA at light intensity of 6 mW/cm^2.

References

[1] A. A. AL-Ghamdi, O. A. AL-Hartomy, M. Cavas, F. EL-Tantawy, F. Yakuphanoglu,, Optoelectron. Adva. Mater. – Rapid Comm. **6,** 292 (2012).
[2] A. A. Al-Ghamdi, Omar A. Al-Hartomy, M. Cavas, Farid El-Tantawy, F. Yakuphanoglu, Optoelectron. Adv. Mater. – Rapid Comm. **6**, 320 (2012).
[3] M. Cavas, M. E. Aydın, A. A. Al-Ghamdı, O. A. Al-Hartomy, F. El-Tantawy, F. Yakuphanoglu, J. Optoelectron. Adv. Mater. **14**, 798 (2012).
[4] S. E. Shaheen, R. Radspinner, N. Peyghambarian, H. Jabbour, Appl. Phys. Lett. **79**(18), 2996 (2001).
[5] C. Brabec, Sol. Energy Mater. Sol. Cells **83**(2-3), 273 (2004).
[6] Hooi-Sung Kim, Mi-Ra Kim, Chang-Sik Ha And Jin-Kook Lee, Mol. Cryst. Liq. Cryst. **377,** 49 (2002).
[7] P. Peumans, A. Yakimov, S.R. Forrest, J. Appl. Phys. **93,** 3693 (2003).
[8] C. W. Tang, Appl. Phys. Lett. **48,** 183 (1986).
[9] P. Peumans, V. Bulovic, S.R. Forrest, Appl. Phys. Lett. **76,** 2650 (2000).
[10] A. Yakimov, S. R. Forrest, Appl. Phys. Lett. **80,** 1667 (2001).
[11] Kh. S. Karimov, M. M. Ahmed, S. A. Moiz, M. I. Fedorov, Solar Energy Materials & Solar Cells **87,** 61 (2005).
[12] O. Hofmann, Paul Miller, Paul Sullivan, Timothy S. Jones, John C. deMello, Donal D. C. Bradley, Andrew J. deMello, Sensors and Actuators B **106**, 878 (2005).
[13] R. Takeuchi, M. Takeuchi, Jpn. J. Appl. Phys, **36,** L127 (1997).
[14] F. Yakuphanoglu,Solar Energy Materials & Solar Cells **91,** 1182 (2007).
[15] F. Yakuphanoglu, Burm-Jong Lee, Physica B: Condensed Matter, **390,** 151 (2007).
[16] F. Yakuphanoglu, Physica B: Condensed Matter, **389,** 306 (2007).
[17] M. E. Aydin, Fahrettin Yakuphanoglu, Jae-Hoon Eom and Do-Hoon Hwang, Physica B: Condensed Matter, **387**, 239 (2007).
[18] F. Yakuphanoglu, Phys. Chem. C **111**(3), 1505 (2007).
[19] M. M. El-Nahass, K. F. Abd-El-Rahman, A. A. M. Farag, A. A. A. Darwish, Organic Electronics **6,** 129 (2005).
[20] J. Nelson, The physics of Solar cells, Imperial College Press, UK, 2003.
[21] A. S. Darwish, A. S. Riad, H. S. Soliman, Semicond. Sci. Technol. **10,** 1 (1995).
[22] M. M. El-Nahass, K. F. Abd-El-Rahman, A. A. A. Darwish, Microelectronics Journal **38,** 91 (2007).
[23] M. M. El-Nahass, K. F. Abd-El-Rahman, A. A. M. Farag, A. A. A. Darwish, Organic Electronics **6**, 129 (2005).
[24] M. M. El-Nahass, H. M. Zeyada, M. S. Aziz, M. M. Makhlouf, Thin Solid Films **492,** 290 (2005).
[25] M. M. El-Nahass, H. M. Zeyada, K. F. Abd-El-Rahman, A. A. A. Darwish, Solar Energy Materials & Solar Cells **91,** 1120 (2007).
[26] G. D. Sharma, P. BalaRaju, M. S. Roy, Solar Energy Materials & Solar Cells **92,** 261 (2008).
[27] G. D. Sharmaa, Dhiraj Saxena, M. S. Roy, Thin Solid Films **467,** 220 (2004).
[28] F. Yakuphanoglu, Sensors and Actuators A **141,** (2008) 383 (2008).
[29] G. Adamopoulos, T. Heiser, U. Giovanella, S. Ould-Saad, K. I. van de Wetering, C. Brochon, T. Zorba, K. M. Paraskevopoulos, G. Hadziioannou, Thin Solid Films **511 – 512,** 371 (2006).
[30] S. Senthilarasu, R. Sathyamoorthy, S. Lalitha, A. Subbarayan, Solid-State Electronics **49,** 813 (2005).
[31] S. A. Moiz, M. M. Ahmed, K.h. S. Karimov, M.

Mehmood, Thin Solid Films **516,** 72 (2007).
[32] K. P. Nazeer, S. C. Jain, A. K. Kapoor, M. T. Thamilselvan, D. Mangalaraj, S. K. Narayandass, J. Yi, Polym. Int. **53,** 898 (2004).
[33] M. Kiy, P. Losio, I. Biaggio, M. Koehler, A. Tapponnier, P. Guunter, Appl. Phys. Lett. **80,** 1198 (2002).
[34] A. F. Özdemir, A. Gök, A. Türüt, Thin Solid Films **515,** 7253 (2007).
[35] M. A. Lampert, P. Mark, Current Injection in Solids, Academic, Press, New York, London, 1970.
[36] T. Higuchi, T. Murayama, E. Itoh, K. Miyairi, Thin Sol. Film. **499,** 374 (2006).
[37] R. D. Gould, J. Phys. D. Appl. **9**, 1785 (1986).
[38] R. F. Pierret, Semiconductor Device Fundamentals, Addison-Wesley Publishing Company, New York, 1996.
[39] S. M. Sze, Physics of Semiconductor Devices, second ed., Wiley, New York, 1981.
[40] Ş .Aydoğan, M . Sağlam, A. Türüt, Polymer, **46,** 10982 (2005).
[41] S. Ashok, K. P. Pandf, Sol. Cells **14,** 81 (1985).
[42] K. R. Rajesh, S. Varghese, C. S. Menon, J. Phys. Chem. Sol. **68,** 556 (2007).
[43] R. F. Salzman, J. Xue, B. P. Rand, A. Alexander, M. E. Thompson, S. R. Forrest, Organic Electronics **6**, 242 (2005).

*Corresponding author: dr.asmahendi@hotmail.com