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LIGHT-SENSITIVE DIODE CHARACTERISTICS OF COPPER PHTHALOCYANINE FILMS GROWING ON N-TYPE SILICON (100) CRYSTAL

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Abstract. In this work, copper phthalocyanine (CuPc) thin film was deposited by spin coating technique on n-Si substrate. CuPc/n-Si (100) heterojunction diode was fabricated. This heterojunction showed the rectifying behavior such as a good Schottky diode. By using curent–voltage measurement of the Au/CuPc/n-Si/In Schottky diode at dark and day light, a number of diode parameters were evaluated on the basis of the theory of thermionic emission. The ideality factor (n) values were determined as 2.49 and 2.13 for dark and day light, respectively. The barrier height (Φ_B) values were determined as 0.757 eV and 0.776 eV for dark and day light, respectively. The electrical properties of the Au/CuPc/n-Si/In Schottky diode were also characterized in term of capacitance–voltage (*C*–*V*) technique at dark and light. The estimated values of donor concentation (N_d) and barrier height (Φ_B) of the Schottky diode at dark and light were found to be 4.88-2.97 x 10^{13} cm^{-3} and 1.683-1.502 eV, respectively. Further, analysis of the log *I*– log *V* curves, while at low forward bias voltages shows ohmic conduction, at higher forward bias voltages shows that transport through the CuPc thin film is clarified by a space-charge-limited current (SCLC) process.

Keywords: *Schottky diode, Copper phthalocyanine, space-charge-limited current, ideality factor, barrier height*

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1. Introduction

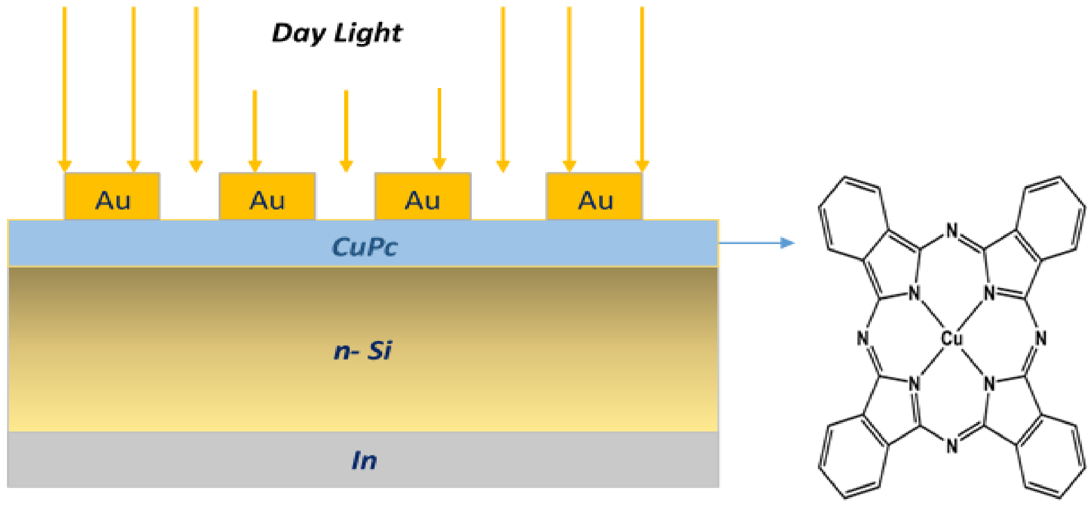
Due to their technological advances in the field of optoelectronics applications, the electrical characteristics of metal-semiconductor (MS) and metal-insulator/organic semiconductor (MIS/MOS) type Schottky barrier diodes (SBDs) have been extensively studied in the last decades. Recently, researchers have reported the effect of organic thin layers on the conduction mechanisms of diodes in the studies of optoelectronic devices and applications (Patil *et al.* 2020; Karimov *et al.*, 2014; Missoum *et al.*, 2016; Oruç *et al.*, 2018; Vijayan *et al.*, 2018; Pfuetzer *et al.*, 2009; Müller *et al.*, 2010). One of them are metal phthalocyanine (MPc) based thin films (MgPc, CuPc, and ZnPc ect.) deposited on a semiconductor substrate by using different techniques. For the future development of molecular devices, a MPc is the most promising materials in very diverse applications such as semiconductor junctions, solar cells, molecular gas sensors, organic light emitting diodes (OLEDs), and organic field-effect transistors (Nozoe & Matsuda 2017; Melville *et al.*, 2018; Grant *et al.*, 2019; Morse *et al.*, 2010; Rodriquez *et al.*, 2013; Melville *et al.*, 2015)

Copper phthalocyanine (CuPc) has become an exciting compound for its use in many applications including organic light-emitting diodes (Ma *et al.,* 2019) and photovoltaic cells (Seoudi & Althagafi 2018) due to its perfect optoelectronic properties, chemical stability and high thermal features. Sekhar Reddy et al. (2017) fabricated Au-CuPc nanocomposite films by concurrent evaporation of CuPc and Au with distinct CuPc and Au concentrations on n-Si wafer. They reported that the barrier height of the n-Si/Al diode with Au-CuPc interlayer increased with decreasing Au concentration. Ullah et al. (2019) fabricated an Al/CuPc/n-Si/Al Schottky diode and investigated its temperature-dependent electronic properties by probing the flow of charge carriers across the barrier. Sekhar Reddy et al. (2018) investigated effects of the thickness of copper phthalocyanine (CuPc) film (2, 5, 10, 15, 20, 30 and 40 nm) on electrical properties of Au/CuPc/n-Si/Al Schottky diode and reported that the Schottky barrier height of the diode decreased with decreasing thickness of the CuPc film up to 15 nm and stayed unaltered for thickness above 20 nm, referred to the incapability of the of the carriers to attain the interface.

In this study, we developed Au / insulator / n-Si Schottky diode to investigate the potential of CuPc film that use as an insulator layer. In recently, there has been many studies of organic materials for their use in Schottky diodes to improve the main Schottky diode parameters such as the ideality factor and the barrier height. A Schottky diode having the requested electronic properties can be achieved in the selection of a convenient interlayer. In this context, phthalocyanines can be considered to be one of the most consistent organic semiconductors for different optoelectronic applications. CuPc films are used to prepare a heterojunction in the form of CuPc/n-Si. The light-sensitive characteristics of the CuPc/n-Si diode are reported by current-voltage and capacitance-voltage measurements. Herein, we demonstrated that carrier conduction of the Au/CuPc/n-Si structure is possessed by space-charge-limited current at higher forward bias region.

2. Experimental details

In the present study, to produce Schottky barrier diode with a CuPc interface, n-type Si (purchased from University wafer) crystal with (100) orientation and wafer thickness of 380 μm was used. To remove the undesirable impurities and surface damaged layer, the crystal was cleaned by the RCA method (Tuğluoğlu *et al*., 2015) and then rinsed ultra pure water (18 MΩ). To form ohmic contact on the back side of Si, indium (In) metal (99.99%, purchased from Kurt J. Lesker) was deposited in a vacuum coating system under 6 x 10^{-5} Torr and then, it was annealed at 400 ^{o}C in flowing N_2 gas in a furnace for 5 min. The CuPc solution was prepared using 10 mg CuPc (purchased from Sigma-Aldrich), 100 ml ammonia and 100 ml ethanol. The CuPc solution was applied on the front face of the n-Si crystal by spin coating method with a Laurell Spin Coater. Lastly, in order to achieve Schottky contact, gold (Au, 99.99%, purchased from Kurt J. Lesker) metal was evaporated under pressure of 6 x 10^{-5} Torr on the CuPc thin film, deposited on the front face of the n-Si crystal. The device was formed in Au/CuPc/n-Si/In structure. Fig. 1(a) displays the diagrammatic demonstration of the Au/CuPc/n-Si/In structure. Fig. 1(b) displays the organic structure of copper phthalocyanine (CuPc). Current-voltage (*I-V*) and capacitance-voltage (*C-V*) measurements were taken in the dark with a Keithley 2400 Sourcemeter and HP 4192A Impedance Analyzer, respectively. The thickness of the organic interlayer was determined approximately 810 nm from capacitance-voltage plot for 1 MHz. The thickness of the organic interlayer was influenced with the fundamental electrical parameters of the device. The current density decreased with the increasing active layer thickness. The electrical characteristic was influenced by the nature and thickness of the electrode that defines the Schottky barrier, which can directly affect the rectification ratio and the leakage current (Khaldi *et al.*, 2018).



(a) (b)

Figure 1. a) The cross-section of the Au/CuPc/n-Si/In Schottky structure
b) the organic structure of CuPc

3. Results and discussion

3.1. Current-voltage analysis of CuPc/n-Si Schottky structure

Based on a thermionic emission theory, the current in CuPc/n-Si Schottky barrier diodes can be described as (Sze, 1981; Tuğluoğlu *et al*., 2015; Rhoderick & Williams 1988; Akın *et al*., 2019)

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

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

where n is the diode ideality factor, Φ_b is the Schottky barrier height, I0 is the saturation current, A is the Schottky area, q is the electronic charge, A* is Richardson constant, and T is the absolute temperature in Kelvin. The values of Φ_b and n are estimated from the forward-bias characteristics of the current-voltage (I-V) through the relations (Tuğluoğlu *et al*., 2015; Yüksel *et al*., 2015; Akın *et al*., 2019).

$$\Phi_b = \frac{kT}{q} ln\left(\frac{AA^*T^2}{I_0}\right) \text{ and } n = \frac{q}{kT}\left(\frac{dV}{dlnI}\right) \quad (3)$$

The current–voltage (*I-V*) curves of the Au/CuPc/n-Si/In Schottky diode under dark and day light are shown in Fig. 2. According to Eq. (3), the values of ideality factor and the barrier height of the diode at dark and day light have estimated to be $n=$ 2.49 and 2.13 and $\Phi_b = 0.757$ eV and 0.776 eV, respectively. The current–voltage characteristics of Al/CuPc/n-Si/Al diode fabricated by thermal vacuum evaporation at 300 K and dark were investigated by Ullah et al. (2019). The values of various junction parameters, such as barrier height and ideality factor were determined from the forward bias *I–V* characteristics. The values of the barrier height and ideality factor were found to be 0.8 eV and 13.4 for junction fabricated at 300 K, respectively. Both the ideality factor and the barrier height values determined by us are lower than the values determined by Ullah et al. (2019). Furthermore, effect of copper phthalocyanine thickness on electrical properties of Au/CuPc/n-Si Schottky diode prepared by thermal vacuum evaporation were investigated by Sekhar Reddy (2018). The ideality factor and barrier height of the Au/CuPc/n-Si Schottky diode with 2 nm-thick CuPc interlayer were obtained as 1.16 and 0.77 eV and those of the diode with 40 nm-thick CuPc film were 1.62 and 0.81 eV, respectively. Pakma et al. have prepared Al/Coronene/n-Si diode and found to be $n=2.81$ and 2.07 and $\Phi_b = 0.697$ eV and 0.755 eV for dark and 100 mW/cm^2, respectively (Pakma *et al.*, 2017). Manthrammela et al. (2019) have fabricated Au/Indigo/n-Si diode and found to be $n=$ 4.39 and $\Phi_b = 0.763$ eV. The high values of ideality factor have related to the presence of CuPc layer at Au/n-Si interface and barier inhomogeneities (Manthrammela *et al.*, 2019). As seen in Fig. 1, the *I–V* characteristics of the Au/CuPc/n-Si/In Schottky diode display that the reverse current of the curves increases with light intensity. After light intensity, the increase in the current value is evaluated as an effect of the generation of hole-electron pairs through the absorption of light incident on the diode and this value is known the net photocurrent (Özerden *et al.,* 2015; Yakuphanoğlu *et al.*, 2007; Akın *et al.*, 2019).

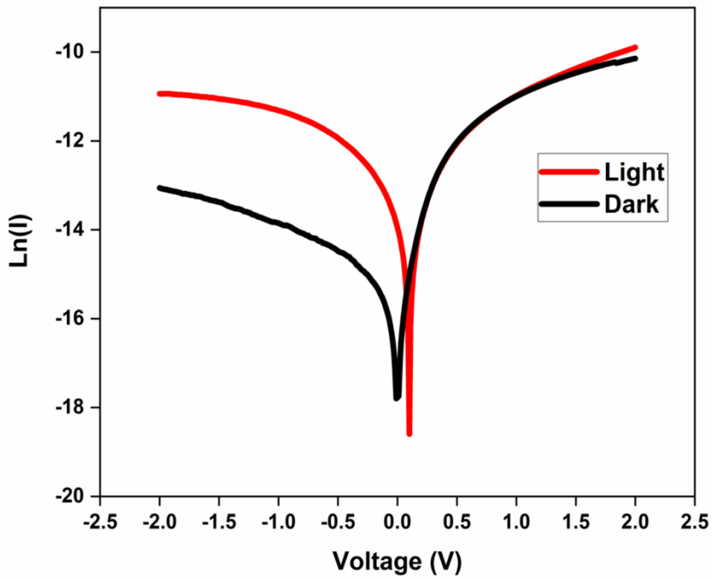


Figure 2. The semilogarithmic plot of the current (*I*) versus bias (*V*) of Au/CuPc/n-Si/In diodes under dark and light

The current-voltage (*I–V*) characteristic of the diode is illustrated in double logarithmic scale as displayed in Fig. 3 to show which mechanisms explain the diode behavior. As seen in Fig. 3, the current displays a power law exponent of the form $I \sim V^m$. There are three different regions in the forward bias, in region I (0.01-0.05 V), the current is proportional to the applied voltage (i.e. $I \sim V$, m=1.08). This shows that the current transport is followed by Ohm's law and is controlled by low voltage tunnelling through the deep-level trap states (Aydoğan *et al.* 2010; Ocak *et al.* 2009). In region II (0.14-0.40 V), the current transport obeys the power law (i.e. $I \sim V^2$, m=2.0) confirming space charge limited current (SCLC) mechanism in which trap-states are filled with charges (Amin *et al.*, 2010) and followed by a linear dependence (i.e. $I \sim V$, m=1.26) in region-III again after 0.85 V.

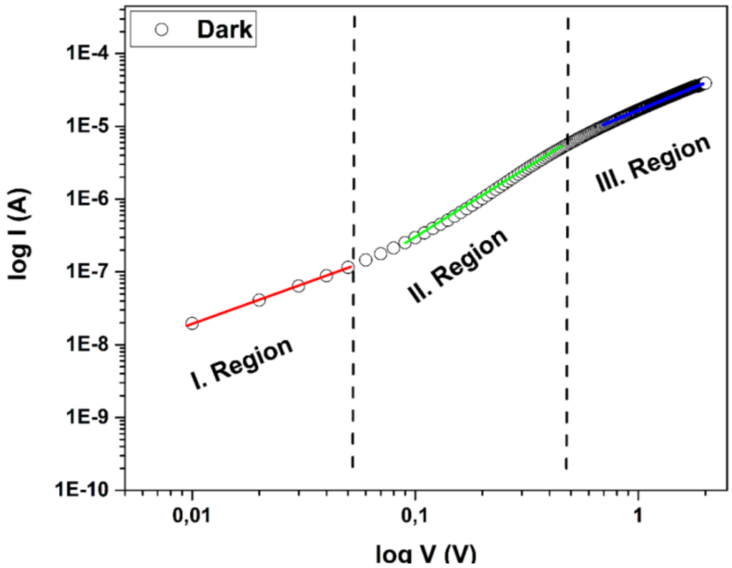


Figure 3. The *log I – log V* characteristics at high forward applied voltages

3.2. Capacitance-voltage analysis of CuPc/n-Si Schottky structure

Fig. 4 displays the measured capacitance-voltage (C-V) measurements under dark and day light at 1MHz frequency for Au/CuPc/n-Si Schottky diode. The *C-V* data of CuPc/n-Si structure can be analyzed by the subsequent equations (Sze 1981; Rhoderick and Williams 1988; Ocak *et al.*, 2009; Aldemir *et al.*, 2011; Tuğluoğlu & Karadeniz 2012):

$$C^{-2} = \frac{2(V_{bi}+V)}{A^2 \varepsilon_s \varepsilon_0 q N_D}, \quad (4)$$

$$\frac{(1/C^2)}{\partial V} = \frac{2}{A^2 \varepsilon_s \varepsilon_0 q N_D}, \quad (5)$$

$$\Phi_b(C-V) = V_{bi} + E_F - \Delta\Phi_b , \quad (6)$$

where V_{bi} is the built-in voltage, N_D is the carrier concentration, A is the device area, ε_0 is vacuum permittivity $\varepsilon_0 = 8.85 \times 10^{-12} F/m$) (Sze 1981), ε_S is the permittivity of the semiconductor, $\Phi_b(C-V)$ is the Schoty barrier height, E_F is the energy difference between conduction band edge and the bulk Fermi level and $\Delta\Phi_b$ is the lowering of image force. As seen in Fig. 4, the capacitance value is smoothly increased with increasing the voltage, showing a sharp rising at higher voltages and then reaches a peak. Figure 5 displays the *1/C²-V* curve extracted the data of Fig. 4 under dark and day light for Au/CuPc/n-Si stucture. As seen in Fig. 5, the *1/C²-V* curve is linear, which displays the formation of Schottky contact. It is calculated that theV_{bi} from the extrapolation of $1/C^2$-V curve to the bias axis. The values of V_{bi}, N_D, E_F and $\Phi_b(C-V)$ from Eqs. (4-6) for dark and light have found to be 1.348-1.165 V, 4.88-2.97 x 10^{13}cm^{-3}, 0.343-0.344 eV and 1.683-1.502 eV, respectively. If Schottky barrier height determined from *C-V* data is compared with determined *I-V* data, one can see that, Schottky barrier height determined from *C-V* is higher than those from *I-V*. This variation can be expressed by a dispersion barrier height due to inhomogenities that form at semiconductor-metal interface. This difference can also be referred to the CuPc layer plus interfacial layer between the n-Si and Au metal. Similar behavior is seen in the literature (Ocak *et al.* 2009; Aldemir *et al.*, 2011; Tugluoglu & Karadeniz 2012). Furthermore, the barrier height values of the Au/CuPc/n-Si Schottky diode fabricated by Sekhar Reddy et al. (2018) varied from 1.05 to 1.12 eV with the variation of CuPc thickness from 0 to 40 nm.

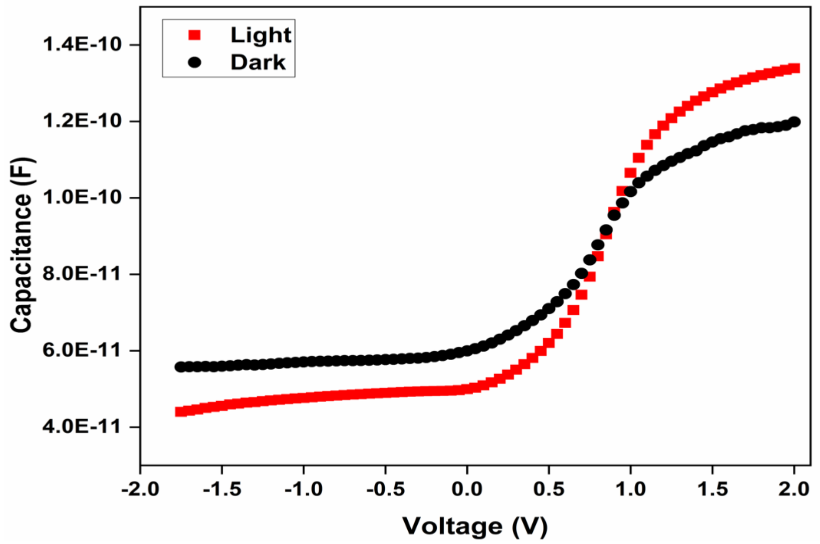


Figure 4. Plots of capacitance (*C*) versus voltage (*V*) of Au/CuPc/n-Si/In Schottky diode in dark and under light

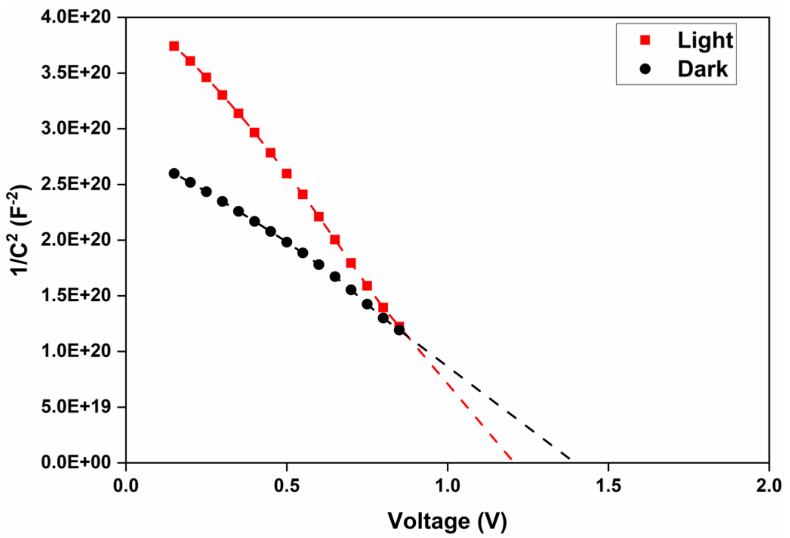


Figure 5. Plots of $1/C^2$ versus *V* of Au/CuPc/n-Si/In Schottky diode under dark and light

4. Conclusions

In this study, we performed the detailed *I-V* and *C-V* analysis of Au/CuPc/n-Si Schottky diodes at dark and day light. For dark and day light measurements, the values of Schottky barrier height (Φ_b) and ideality factor (n) from *I–V* data were determined as 2.49-2.13 and 0.757-0.776 eV, respectively. The Schottky barrier height (Φ_b) values determined from *C–V* data were 1.688-1.502 eV. The calculated diode parameters were improved by the effect of light.

We also observed space-charge-limited current effects in Schottky diodes obtained with CuPc interfacial layer deposited on n-Si wafer using spin coating method. It was seen that the thermionic emission operation forms in the low forward voltage range and the space-charge-limited current (SCLC) was the dominant mechanism in the high forward region.

The diode current value for light was higher than the diode current value for dark at the equal reverse voltage (-2 V). It was shown that the Au/CuPc/n-Si structure exhibited to light-sensitive action. It was evaluated that the Au/CuPc/n-Si structure can be used as a photosensor for optoelectronic.

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References

Akın, Ü., Yüksel, Ö.F., Pakma, O., Koralay, H., Çavdar, Ş., & Tuğluoğlu, N. (2019). Anovel devıce behavıor of al/coronene/n-gaas/ın organıc based schottky barrıer dıode. *New Mat. Compd. Appl., 3*(1), 15-22.

Aldemir, D.A., Esen, M., Kökce, A., Karataş, S., & Özdemir, A.F. (2011). Analysis of current–voltage and capacitance–voltage-frequency characteristics in Al/p-Si Schottky diode with the polythiophene-SiO_2 nanocomposite interfacial layer. *Thin Solid Films, 519,* 6004–6009.

Amin, G., Hussain, I., Zaman, S., Bano, N., Nur, O., & Willander, M. (2010). Current-transport studies and trap extraction of hydrothermally grown ZnO nanotubes using gold Schottky diode. *Physica Status Solidi A., 207(*3), 748-752.

Aydogan, S., Incekara, U., Deniz, A.R., & Turut, A. (2010). Extraction of electronic parameters of Schottky diode based on an organic Orcein. *Microelectronic Engineering, 87,* 2525-2530.

Grant, T.M., Rice, N.A., Muccioli, L., Castet, F., & Lessard, B.H. (2019). Solution-Processable n-Type Tin Phthalocyanines in Organic Thin Film Transistors and as Ternary Additives in Organic Photovoltaics. *ACS Appl. Electron. Mater.* 1, 494−504.

Karimov, K.S., Moiz, S.A., Tahir, M.M., Ahmed, N., Tariq, R., Abbas, S.Z., & Zafar, Q. (2014). Nickel phthalocynanine – metal Schottky diode as photodetector. *Journal of Optoelectronıcs and Advanced Materials*, 16, 1430-1435.

Khaldi, W., Boubaker A., Nasri, A., Lmimouni, K., & Kalboussi, A. (2018). Electrical Study of Pentacene-Based Metal–Semiconductor–Metal Structure: Schottky Barrier and Active Layer Thickness Effects. *IEEE Trans. Electron. Devices,* 65, 5009-5013.

Ma, Y.Y., Hua, X.C., Zhai, T.S., Lia, Y.H., Lua, X., Duhma, S., & Funga, M.K. (2019). Doped copper phthalocyanine via an aqueous solution process for high-performance organic light-emitting diodes. *Organic Electronics, 68,* 236-241.

Manthrammela, M.A., Yahia, I.S., Shkira, M., AlFaifya, S., Zahran, H.Y., Ganesh, V., & Yakuphanoglu, F. (2019). Novel design and microelectronic analysis of highly stable Au/Indigo/n-Si photodiode for optoelectronic applications. *Solid State Sciences, 93*, 7-12.

Melville, O.A., Lessard, B.H., & Bender, T.P. (2015). Phthalocyanine-Based Organic Thin-Film Transistors: A Review of Recent Advances. *ACS Applied Materials & Interfaces, 7*, 13105–13118.

Melville, O.A., Grant, T.M., & Lessard, B.H. (2018). Silicon Phthalocyanines as N- Type Semiconductors in Organic Thin Film Transistors. *Journal of Materials Chemistry C*, 6, 5482−5488.

Missouma, I., Ocak, Y.S., Benhaliliba, M., Benouis, C.E., & Chaker, A. (2016). Microelectronic properties of organic Schottky diodes based on MgPc for solarcell applications. *Synthetic Metals*, 214, 76-81.

Morse, G.E., Helander, M.G., Maka, J.F., Zheng, H.L., & Timothy, P.B. (2010). Fluorinated Phenoxy Boron Subphthalocyanines in Organic Light-EmittingDiodes. *ACS Applied Materials & Interfaces, 2*, 1934–1944.

Muller, M., Dinnebier, R.E., Jansen, M., Wiedemann, S., & Plug, C. (2010). Theinfluence of temperature, additives and polymorphic form on thekinetics of the phase transformations of copper phthalocyanine. *Dyes and Pigments, 85*, 152-161.

Nozoe, S. & Matsuda, M. (2017). Enhanced Emission by Accumulated Charges at Organic/Metal Interfaces Generated during the Reverse Bias of Organic Light Emitting Diodes. *Applied Sciences-Basel*, 7, 1045-8.

Ocak, Y.S., Kulakcı, M., Kılıçoğlu, T., Turan, R., & Akkılıç, K. (2009). Current–voltage and capacitance–voltage characteristics of a Sn/Methylene Blue/p-Si Schottky diode *Synthetic Metals, 159*, 1603-1607.

Oruç, Ç., Altındal, A. (2018). Comparative study of *I–V* methods to extract Au/FePc/pY.S., Tombak, A., Kılıçoğlu, T., & Türüt, A. (2015). Electrical and photoelectrical properties of Ag/n-type Si metal/semiconductor contact with organic interlayer. *Thin Solid Films, 597*, 14–18.

Pakma, O., Cavdar, S., Koralay, H., Tuğluoğlu, N., & Yüksel, O.F. (2017). Improvement of diode parameters in Al/n-Si Schottky diodes with Coronene interlayer using variation of the illumination intensity. *Physica B*, 527, 1-6.

Patil, V.V., Lee, K.H., & Lee, J.Y. (2020). Isomeric Fused Benzocarbazole as a Chromophore for Blue Fluorescent Organic Light-Emitting Diodes. *Journal of Materials Chemistry C*, 8, 8320-8327.

Pfuetzner, S., Meiss, J., Petrich, A., Riede, M., & Leo, K., (2009). Thick C60:ZnPc bulk heterojunction solar cells with improved performance by film deposition on heated substrates. *Applied Physics Letters, 94*, 253303-3.

Rajesh, K.R. & Menon, C.S. (2005). Investigation of electrical properties of organic Schottky diodes using MgPc- the effect of oxygen absorption and post deposition annealing. *Semiconductor Science and Technology, 20*, 464–468.

Rhoderick, E.H. & Williams, R.H. (1988). *Metal–Semiconductor Contacts* 2nd edn. (Oxford: Claredon).

Rodriguez-Morgadea, M.S., Pelleja, L., Torres, T., & Palomares, E. (2013). Ti(IV) Phthalocyanines for Dye Sensitized Solar Cells, *Journal of Porphyrins phthalocyanines, 17*, 814–820.

Sekhar Reddy, P.R., Janardhanam, V., Jyothi, I., Sri Harsha, C., Rajagopal Reddy, V., Lee, S.M., Won, J., & Choi, C-J. (2018). Effect of copper phthalocyaninethickness on surface morphology, optical and electrical properties of Au/CuPc/n-Si heterojunction. *Applied Physics A*, 124, 115-10.

Sekhar Reddy, P.R., Janardhanam, V., Jyothi, I., Chang, H.-S., Lee, S.-N., Lee, M.S., Rajagopal Reddy, V., & Choi, C.-J. (2017). Microstructural and electricalproperties of Al/n-type Si Schottky diodes with Au-CuPc nanocomposite films as interlayer. *Superlattices Microstruct*ure, 111, 506–517.

Seoudi, R. & Althagafi, H.A. (2018). Dependence of Copper Phthalocyanine Photovoltaic Thin Film on the Sizes of Silver Nanoparticles. *Silicon, 10*, 2165-2171.

Sze, S.M. (1981). *Physics of Semiconductor Devices* (New York: Wiley).

Tuğluoğlu, N. & Karadeniz, S. (2012). Analysis of current–voltage and capacitance–voltage characteristics of perylene-monoimide/n-Si Schottky contacts. Current Applied Physics 12, 1529–1535.

Tuğluoğlu, N., Çalışkan, F., & Yüksel, Ö.F. (2015). Analysis of inhomogeneous barrier and capacitance parameters for Al/rubrene/n-GaAs (100) Schottky diodes. *Synthetic Metals, 199,* 270-275.

Ullah, I., Shah, M., Khattak, S.A., & Khan, G. (2019). Temperature Effect on Electronic Parameters of CuPc/n-Si Heterojunction. *Journal of Electronıc Materıals*, 48, 5609-5616.

Yakuphanoğlu, F. (2007). Electronic and photovoltaic properties of p-Si/C70 heterojunction diode. *Physica B, 400*, 208–211.

Vijayan, L., Thomas, A., Kumar, K.S., & Jinesh, K.B. (2018). Low Power Organic Field Effect Transistors with Copper Phthalocyanine as Active Layer, *Journal of Science: Advanced Materials and Devices*, 3, 348–352.

Yüksel, Ö.F., Tuğluoğlu, N., Şafak, H., & Kuş, M. (2015). The modification of Schottky barrier height of Au/p-Si Schottky devices by perylene-diimide, *Journal of Applied Physics 113,* 044507-044511.