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PHOTOVOLTAIC INVESTIGATION OF Al/p-Si/CuPc/Al PHOTODIODES

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Abstract

Phthalocyanine is used in many scientific and industrial fields such as nonlinear optical devices, electrophotographic applications, photodynamic therapy applications, infrared applications, sensor applications and catalyst applications. The applications of the phthalocyanine molecule in hetero-compound structures have been studied before. The obtained results revealed that phthalocyanine can be used in photodetector and photodiode applications. Organic detectors can be applied to flexible surfaces and their production costs are lower than metal-based photodetectors. Considering these features of organic detectors, phthalocyanine-based organic photodiodes were produced by using copper-phthalocyanine salts in our project. The optoelectronic properties of the produced Al/p-Si/CuPc/Al photodiodes were investigated, and their I–V, I–t, and photoresponsivity behaviours were evaluated. Since I-V measurements show that the current changes with the increase of illumination intensities, our study shows that Al/p-Si/CuPc/Al structures have photodiode properties.

Keywords: Organic Semiconductors, Organic Photodiodes, Organic Photodetectors, Copper(II) phthalocyanine (CuPc), Thermal Evaporation

Al/p-Si/CuPc/Al FOTODİYOTLARIN FOTOVOLTAİK İNCELENMESİ

Öz

Ftalosiyanin, nonlineer optik cihazlar, elektrofotografik uygulamalar, fotodinamik terapi uygulamaları, infrared uygulamaları, sensör uygulamaları ve katalizör uygulamaları gibi birçok bilimsel ve endüstriyel alanlarda kullanılmaktadır. Ftalosiyanin molekülünün heterobileşimli yapılarda uygulamaları daha önceden çalışılmış bulunmaktadır. Elde edilen sonuçlar, ftalosiyanin fotodedektör ve fotodiyot uygulamalarında kullanılabileceğini ortaya çıkarmıştır. Organik dedektörler esnek yüzeylere uygulanabilirler ve üretim maliyetleri metal esaslı fotodedektörlere göre daha düşüktür. Organik dedektörlerin bu özellikleri göz önüne alınarak projemizde bakır-ftalosiyanin tuzları kullanılarak ftalosiyanin temelli organik fotodiyotlar

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üretilmiştir. Üretilen Al/p-Si/CuPc/Al fotodiyotların optoelektronik özellikleri araştırılmış, I–V, I–t ve fototepki davranışları değerlendirilmiştir. I-V ölçümleri aydınlatma yoğunluğunun artmasıyla birlikte akımın değiştiğini gösterdiği için, çalışmamız Al/p-Si/CuPc/Al yapılarının fotodiyot özelliklerine sahip olduğunu göstermektedir.

Anahtar Kelimeler: Organik yarıiletkenler, Organik fotodiyotlar (OLED), Organik fotodedektör, Bakır-ftalosiyanin (CuPc), Termal buharlaştırma tekniği

1. INTRODUCTION

Phthalocyanine is a molecule with advanced optoelectronic properties [1-3] and is used in many applications from textiles to optoelectronic devices, detectors, optical devices, semiconductor technology applications, and infrared absorption applications [4, 5]. Organic diodes obtained from various materials have been reported in the previous studies [6, 7]. However, even though the electrical properties and light sensing properties of phthalocyanine have been demonstrated in previous studies [8, 9], the studies examining the properties of photodetectors produced from phthalocyanine in details have not been available yet.

With the use of organic molecules in electronic technology, the basis of organic electronics technology is formed and developed from organic diodes, organic-based light-emitting diodes (OLEDs) and organic transistors [10]. Before organic electronics technology advanced this far, systems made of semiconductor materials and metallic thin films were used instead. Since these systems are in a solid state, they do not allow to be used on flexible surfaces [11]. Since the metallic thin film technology is not flexible, it is not resistant to external impacts and stresses. The deformations presented on metallic thin films can change the electrical properties of the material as well as cause performance losses due to stress. In addition, since metallic thin film-based technologies require special equipment, the production costs are quite high [12]. The combination of organic and inorganic materials is also used in many studies posing as photodiodes [13-15]. Even though the photodiodes with hybrid heterojunctions promise better alternatives to their metal-based counterparts, they cannot be easily applied to flexible surfaces as their organic-based counterparts. Developments in organic diode technology have eliminated such problems. Organic

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diodes have the advantage that they can be applied to flexible surfaces. The energy ranges of organic diodes can be easily changed by doping [16]. The production costs of organic diodes and transistors are lower compared to metal-based diodes [17, 18]. Therefore, organic diodes have the technology to enable the production of disposable electronic devices. Organic diodes and transistors are more environmentally friendly than metal and semiconductor-based diodes. They do not contain heavy metals and are easier to recycle than metal and semiconductor based electronic devices. Organic-based diodes can be produced by writing and sputtering technologies. Since these materials are great interest to technology companies, great resources are devoted to the development of such materials and their adaptation to technological applications.

There are many materials used in organic electronics technology. In recent years, graphene technology has been developing and organic electronics studies have focused on this material [19]. However, since materials such as graphene are difficult and expensive to synthesize, they pose many of disadvantages compared to organic electronics materials. Thus, phthalocyanine can find an important place in organic electronics applications. In many studies, fluorescence behaviour and photocatalytic properties of the phthalocyanine molecule have been observed [20]. Many organic chemists produce derivatives of phthalocyanine molecules and use them in photodynamic therapy applications [1].

Photodiodes find use in many technologies, especially in medicine, imaging and military defence technologies. Organic diodes and organic photodiodes can be made from different materials. Today, graphene and modified graphene are the most popular organic materials [21]. However, since graphene is very expensive, it is important to produce low-cost organic diodes and photodiodes with electrical properties as good as graphene. Various studies have been conducted on the optoelectronic properties of phthalocyanine and it is predicted to be a good candidate for organic electronics applications [8, 22]. In addition, phthalocyanine has been the subject of many studies in terms of its chemical properties [19]. It is estimated that phthalocyanine-based photodetectors can show high performance due to their optoelectronic properties and good absorption of light in the IR wave spectrum [4]. However, when the studies published in the literature are examined, there are limited number of studies that examines the electrical and photodetector properties of photodiodes obtained from phthalocyanine in details. To the best of our

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knowledge, observations on its photodiode characteristics are not investigated even though the studies on the electrical or optical properties of phthalocyanine-based detectors are present [4, 8, 19, 22]. Therefore, within the scope of our study, a photodiode formed from copper-phthalocyanine was produced and optoelectronic behaviours such as I–V, I–t, and photoresponse were investigated.

2. MATERIALS AND METHOD

2.1. The Characterization of Al/p-Si/CuPc/Al Photodiode

Before the production of thin films, cleaning, etching-based purification, and decontamination processes were applied to the p-type Si substrates [21]. In order to clean, Si-based substrates were cleaned by keeping them first in pure water, then in acetone, then in ethyl alcohol and again in pure water for 5 minutes [23]. In the etching process of the substrates, a 1:10 ml concentration of $HF:H_2O$ solution was used. After etching, the substrates were washed, and Al coated on one side using a Nano Vak thermal evaporator at about 100 nm. After this process, Al/p-Si structures were obtained. In order to increase the durability of the Al contacts, they were annealed at 450 °C for 5 minutes and then cooled to room temperature. Then, CuPc was laid on the Al/p-Si structures by thermal evaporation method [24] in vacuum. Al/p-Si/CuPc structures were formed and then the upper contact of the diode was again covered with Al by masking method. Thus, Al/p-Si/CuPc/Al diode was obtained, and its electrical or optical properties were investigated.

3. RESULT AND DISCUSSION

Figure 1 shows the Current (I) – Voltage (V) measurements obtained in the voltage range of -10V to +10V of the Al/p-Si/CuPc/Al photodiode exposed to various light intensities. In order to investigate the optoelectrical and photoresponsivity properties of Al/p-Si/CuPc/Al structures, the illumination intensity was changed between 10 mW/cm^2 and 100 mW/cm^2 in the measurements.

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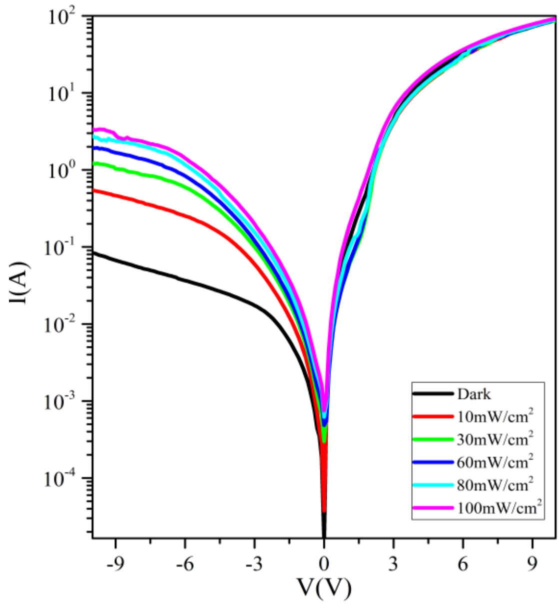

Figure 1. Current (I) – Voltage (V) measurements for Al/p-Si/CuPc/Al photodiode characterized under various illumination.

Apparent current difference could be seen in the I-V graph, between forward bias and reverse bias zone. Such cases indicate that Al/p-Si/CuPc/Al structures illustrate diode like behaviours. I-V plots exhibit illumination intensity related characteristics where illumination alters measured current. It was concluded that Al/p-Si/CuPc/Al structures have photodiode characteristics.

Using the results presented in Figure 1, the basic photodiode parameters such as barrier height (ϕ_b), reverse voltage saturation current (I_o), ideality factor (n) and photosensitivity (R) are calculated using Thermionic Emission Theory [25] to determine the optoelectronic characteristics of the diode. Barrier height and ideality factor are calculated by using the characteristic current formula, Equation 1. The photosensitivity (R) of the Al/p-Si/CuPc/Al structure is calculated by using Equation 3.

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

In this equation, I_o is reverse voltage saturation current, q is electron charge, n is ideality factor; R_s is the series resistance, k is the Boltzmann constant, V is the externally applied voltage to the diode, and T is the absolute temperature. The I_o in the formula is calculated using the formula below.

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

In this formula, A* is Richardson's constant (32 A/cm^2K^2 for p-type Si), while A denotes the area of the photodiode.

$$R = \frac{(I_p - I_d)}{PA} \quad (3)$$

In this equation, P is the power, I_d is the current obtained in the dark, I_p is the photocurrent, and A is the contact area of the photodiode.

$$I_{ph} = KP^m \quad (4)$$

Here P is the intensity of the illumination, and m and K are constants.

The calculated ideality factor (n), barrier height (ϕ_b), saturation current (I_o) and photosensitivity (R) of the Al/p-Si/CuPc/Al photodiode are presented in Table 1. Calculations were performed for 100 mW/cm^2 illumination intensity.

Table 1. Ideality factor, barrier height, saturation current and photosensitivity values calculated for Al/p-Si/CuPc/Al photodiode for 100 mW/cm^2 illumination intensity.

n	ϕ_b(eV)	I_o(A)	R(A/W)
8.18	0.350	0.02815	5.56

Although the expected ideality factor value for a perfect diode is 1, the calculated ideality factor value for the Al/p-Si/CuPc/Al photodiode is 8.18. These high values indicate the defective working mechanism of diodes, which is a very common situation in recent studies [21, 26-28]. Organic and organometallic structure-based diodes tend to have high ideality factors. For example, Aslan et al. produced Ti doped amorphous carbon photodiodes and found the ideality factor of the photodiode between 1.84 and 3.17 [26]; Demirol et al., synthesized the chalcone substituted metallo-phthalocyanine photodiodes and ideality factor factor of the diodes was found to be 5.2 [29]; Yakuphanoglu et al. reported the ideality factor of boric acid:nickel (II) phthalocyanine

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photodiodes between 5.93 and 7.07 [30]; Soylu et al. found the ideality factor of zinc phthalocyanine photodiodes between 1 and 9 [31]; Koc assessed the ideality factor of the CuO doped amorphous carbon photodiode between 2.87 and 4.95 [32]. Tataroglu et al. find the ideality factor of graphene–cobalt phthalocyanine structures between 3.5 and 5.2 [33]. This can be caused by anomalies in the diode due to external factors such as defective working mechanism, series resistance, interface conditions, and barrier height inhomogeneity [26, 34, 35]. Barrier height of the diodes were determined as 0.35 eV. Barrier height was found to be coherent with the previous studies. For example, Aslan et al. found the barrier height of Ti doped amorphous carbon photodiodes between 0.46 eV and 0.50 eV [26]. Koc found the barrier height of CuO doped amorphous carbon photodiodes between 0.47 eV and 0.5 eV [32]. Tataroglu et al. reported barrier height for graphene-cobalt phthalocyanine between 0.77 eV and 0.82 eV [33]. Soylu et al. found the barrier height of zinc-phthalocyanine structures 0.1 eV and 1.2 eV [31].

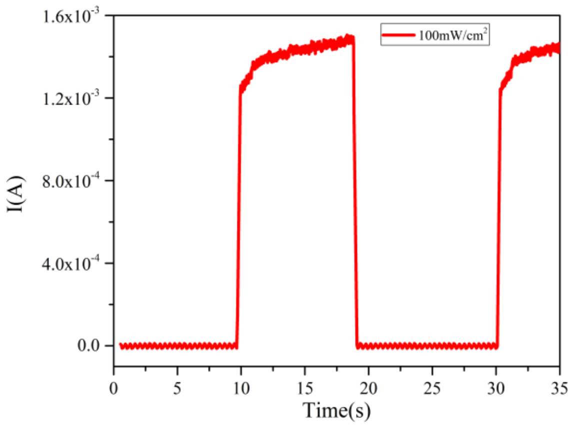

Figure 2. Current(I)-Time (t) measurement for Al/p-Si/CuPc/Al photodiode at 100 mW/cm^2

Current-Time (I-t) measurements of Al/p-Si/CuPc/Al photodiode under 100 mW/cm^2 light intensity were performed and the results are shown in Figure 2. The current was measured by turning on the light at 10 second intervals. When the light was applied to the surface of the Al/p-Si/CuPc/Al photodiode, it was seen that diodes are responsive to lights as measured current dramatically increases. Measured current stays almost stable as long as external light was on. A rapid decrease in the measured current was observed when the light was turned off. This confirmed that the Al/p-Si/CuPc/Al photodiode is light sensitive.

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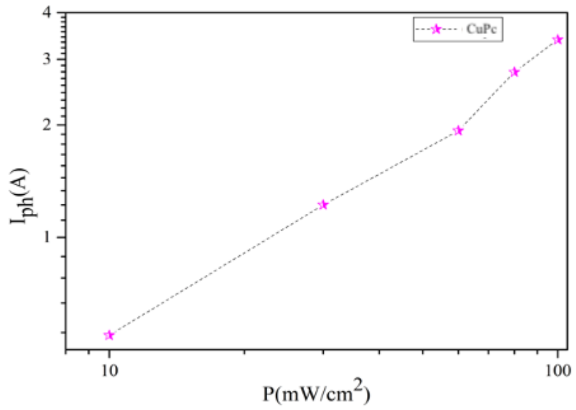

Figure 3. Photocurrent (I_{ph}(A))-Illumination Intensity (P(mW/cm^2)) plot for Al/p-Si/CuPc/Al photodiode.

The photocurrent-light intensity (I_{ph}-P) properties of Al/p-Si/CuPc/Al structures are calculated using Equation 4 [36] and the result is shown in Figure 3. The photocurrents are measured in the range of 10 mW/cm^2 and 100 mW/cm^2 light intensities at -10V voltage, and the highest photocurrent is measured for 100 mW/cm^2 is ~3.7A. Figure 3 also illustrates that photocurrent was highly dependent on the external light illumination. This behaviour shows that Al/p-Si/CuPc/Al photodiodes have potential for solar tracking device applications.

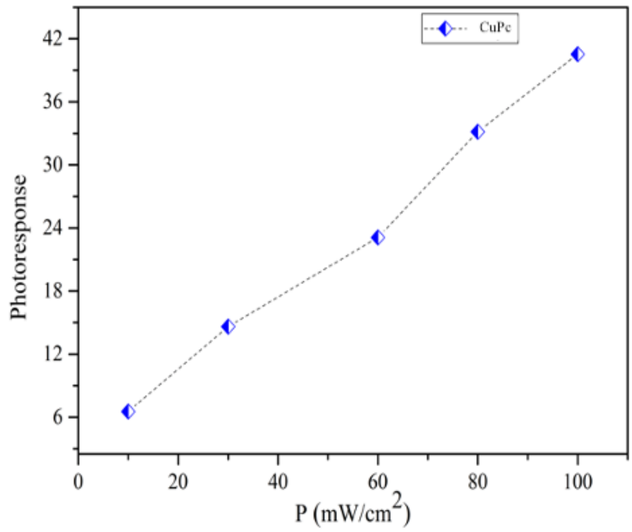

Figure 4. Photoresponse- Illumination Intensity (P(mW/cm^2)) for Al/p-Si/CuPc/Al photodiode.

To evaluate the photosensitivity of the Al/p-Si/CuPc/Al photodiode, the photoresponse-light intensity (Photoresponse-P(mW/cm^2)) measurements are obtained for various light intensities and the results are shown in Figure 4. As the light intensity increases, the photoresponse increases as well. A photoresponse of ~39.5 is measured at 100 mW/cm^2 of light intensity. Photoresponsivity characteristics also illustrates light intensity related behaviours. Such behaviour also supports the case that Al/p-Si/CuPc/Al photodiodes have potential to be used in solar tracking applications.

4. CONCLUSION

In this study, CuPc organic semiconductor solutions are obtained, and then thin films are prepared by coating on p-Si type substrates by Vacuum Thermal Evaporation method. The diodes are produced from these films with Al contacts by metal evaporation method. The electrical properties of these produced photodiodes are investigated under illumination with various light intensities. Based on these results, various properties such as ideality factor, barrier height, saturation current and photosensitivity were analysed. Our assessments revealed that Al/p-Si/CuPc/Al structures exhibit photodiode characteristics. Photoresponsive and photocurrent of Al/p-Si/CuPc/Al structures increases with enhancing illumination. These results show that Al/p-Si/CuPc/Al photodiodes can be used in photodetector applications as solar tracking or harvesting devices.

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