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The Production of Organic Photodetectors and Determination of Electrical Properties for Optical Sensor Applications

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Keywords

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Photodiode
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Photocurrent

Abstract

In this work, metal-semiconductor photodiodes with organic interlayers were produced, and their electrical properties were investigated under different light intensities. CongoRed was used as interlayer and grown as a thin film using spin coating technique on p-type silicon substrates cleaned by different chemical methods. The changes in electrical parameters of completed Al/CongoRed/p-Si/Al diodes were investigated under dark and different light intensity. From results obtained, it has been seen that the fabricated devices show photodiode properties, and as a result, they can be employed in opto-electronic applications.

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1. INTRODUCTION

Today, with increasing energy demand, the studies on efficient and low cost opto-electronic devices that convert the light into the electrical energy have become important. These devices fabricate using a variety of inorganic, organic, composite and hybrid materials. In recent years, inorganic and organic materials have been often used to develop the electronic characteristics of devices Aoki (2017), and especially organic photodiodes have attracted a lot of attention by researchers due to its electrical and optical characteristics.

Organic photodiodes made of semiconductor/semiconductor or metal/semiconductor structures are devices that convert light into electrical current. Sometimes these structures are also called photo-detectors or photo-sensors. Photodiodes can be used in optical communication and many opto-electronic applications. These structures operate under reverse bias in spite of a normal diode.

Metal/semiconductor structures, also known as Schottky barriers, are formed by coating a thin metal film on a semiconductor. Since high-temperature methods are not used during the production of these structures, no degeneration is observed in carriers (minority) within this structure. However, due to the high thermionic emission dark current, the usage of these structures as solar cells is not effective when compared to the pn junction solar cells. This dark current created by the thermionic emission can be reduced by placing a layer at the metal/semiconductor interface. The structure formed as a result of this process is called "metal/insulator/semiconductor Schottky barrier or briefly MIS type structure. These structures have some advantages than over pn junctions. In such structures, minority carrier lifetimes are preserved. Because low temperature methods are used in their production and thus doping effects are eliminated.

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Studies on devices that combine both organic and inorganic materials are of great interest because of their expansive application areas such as sensors, optics and opto-electronics. In particular, due to their poriferous structures and very large surface areas, the porous silicones have become ideal candidates for hosting certain organic molecules such as sensitive dyes, surfactants and polymers (Chouket et al., 2010).

The addition of organic dyes to a metal/semiconductor interface has enabled the production of many useful devices such as optical wave-guides, light intensifiers, laser materials and sensors. In the past years, organic azo dye has become an attractive material, and has found applications because of its optical properties such as nonlinear optical effects and polarized photo-induced anisotropy (Pham et al., 1995). These materials also have potential application areas as gas sensors, and the absorption bands can be changed as needed.

CongoRed is an organic compound ($C_{32}H_{22}N_6Na_2O_6S_2$) and azo dye that has excellent adhesion to surfaces and broad applicability in light-induced photoisomerization, and has potential uses for reversible optical data storage. Therefore, it is adopted as stable organic semiconductors as an interlayer material for different electronic and opto-electronic applications and used between metal and inorganic semiconductor. Different diode structures and decorated nanoparticles studies related to CongoRed, which is widely studied, can be found in the literature (Kaçuş et.al., 2020; Kocyigit et. al., 2021; 2022).

In this study, the photodiode properties of Schottky structures with organic interlayers have been determined under the dark and different illumination intensities. For this purpose, Al/CongoRed/p-Si/Al photodiodes have been fabricated, and the current-voltage measurements have been executed to analyze the photoconductive behavior of structures at room temperature.

2. MATERIAL AND METHOD

2.1. Substrate Cleaning

In production of organic photodiodes, boron-doped (p-type) silicone semiconductor crystals with a surface (100) orientation grown by Czochralski method were used as a substrate. The diameter, resistivity and thickness of semiconductors were 50.8 mm, 0.8 Ω.cm and 500 µm, respectively. The substrates were subjected to a series of chemical cleaning processes. First, in order to remove the dust and other residues from the surface, an ultrasonic cleaner was used to wash the substrates with trichloroethylene, acetone and isopropyl alcohol, respectively, for 5 min. Then, it was cleaned in a sequence of sulfuric acid + hydrogen peroxide (1:1), and ammonia + hydrogen peroxide (1:1) for 10 minutes. For the etching process, in a sequence of deionized water + hydrofluoric acid (15:1), and nitric acid + hydrofluoric acid + acetic acid (2:1:1) for 2 minutes. After every process the substrates were washed with de-ionized water (18.3 MΩ). Finally, substrates were dried using nitrogen gas.

2.2. Formation of Ohmic Contacts

After the chemical cleaning process, the substrates were placed into the evaporation system to achieve ohmic contact, and 1500 Å thick (99.999%) pure aluminum metal was evaporated on the back surfaces of substrates under a pressure of approximately 1.8×10^{-6} Torr. A thickness monitor with a crystal sensor was used to obtain the desired thickness. 10-15 Å/sec was chosen to control the coating speed during the evaporation process. Aluminum coated substrates were heat treated in vacuum environment for ohmic contact formation. For this, the substrates were placed on a special heater made of a 0.1 mm thick tantalum (Ta) plate and heated to create ohmic contact. With this method, the barrier width was reduced by forming an extreme doped layer with same doping type (p^+) as the semiconductor at the Al/p-Si back contact. In this case, the contact resistance gets smaller and made the barrier transparent to the charge carriers.

2.3. Growing of CongoRed Thin Films

CongoRed has been purchased from Sigma-Aldrich. The omic contact formed substrates were placed in a spin coating device to form thin films on their front surfaces. CongoRed solution (0.3% by weight in ethanol) was dropped onto the substrate surfaces with the help of a 25 µl micropipette. The spin coating device was rotated at 2500 rpm for 30 seconds. Then, the CongoRed coated silicon substrates were removed from the coating device and maintained in a nitrogen environment for 45 minutes to remove the solvent.

2.4. Formation of Rectifying Contacts

The crystals coated with CongoRed on their surfaces were placed again into the evaporation system to form rectifying contacts. Aluminum metal rectifying contacts with a diameter of 1.0 mm and 1000 Å thick were formed onto the organic thin film coated surfaces at a pressure of $2x10^{-6}$ Torr. The schematic diagram of an Al/CongoRed/p-Si/Al structure is shown in Figure 1.

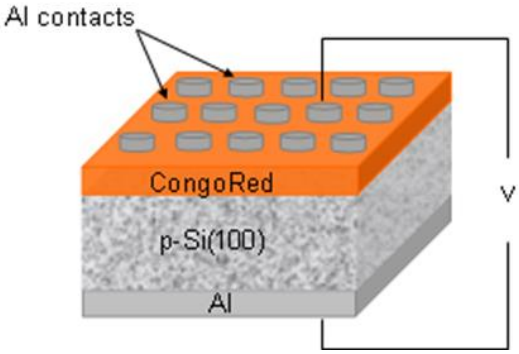

Figure 1. *The schematic diagram of Al/CongoRed/p-Si/Al structure*

2.5. Electrical Measurements

Current-voltage (I-V) measurement of Al/CongoRed/p-Si/Al structures was carried out within the range of -5 to +5 volts, under the dark and different light intensity (20 - 100 mW/cm^2) and at room temperature. For this, Sciencetech brand filter 1.5AM solar simulator was used. The basic device properties such as ideality factor (n), saturation current (I_o), barrier height (Φ_B), and series resistance, R_s of the structures were determined from the measurements at various illumination intensity.

3. RESULTS

Figure 2 depicts the I-V characteristics of Al/CongoRed/p-Si/Al structures obtained under the dark and various light intensity. As seen in Figure 2, the linearity in the LnI-V curves is generally formed in a small bias region. This case strengthens the possibility that the thermionic emission (TE) or minority carrier injection is effective in the current mechanism of the structures. Since the density of states is in equilibrium with the semiconductor and show continuity in the high voltage region, a deviation from linearity has been observed. However, the fabricated organic-based Schottky structures have exhibited a good rectification behavior. Moreover, it is seen from Figure 2, the applied illumination intensities have a systematic effect on the current-voltage curves of device.

It is possible to analyze the diode parameters of the structures by the relationship known as thermionic emission theory. By this theory, $V > 3kT$ is accepted and the following expressions are used for the current-voltage curves.

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

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

Where A, k, T and q are contact area, Boltzmann constant, absolute temperature in Kelvin and electronic load, respectively. A^* is effective Richardson coefficient with the value of 32 $Acm^{-2}K^{-2}$ for p-type silicon. I_0 has found by extrapolating the linear curves to zero bias voltage.

The Φ_B values of Al/CongoRed/p-Si/Al structures is obtained from the point where the linear curve intersects the current axis using the Equation (3). The oxide tunneling probability of the holes is accepted as unity and n has estimated from the slope of the LnI-V curve with the help of Equation (4):

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

$$n = \frac{q}{kT}\frac{dV}{d\ln(I)} \quad (4)$$

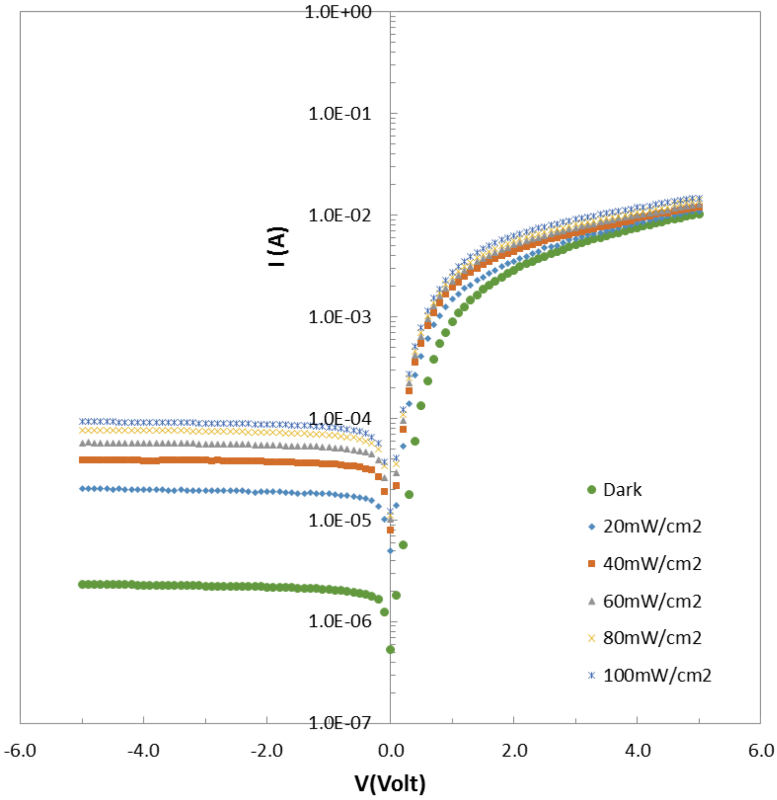

Figure 2. *Current-voltage curves of Al/CongoRed/p-Si/Al structures at dark and different light intensities*

The n and Φ_B values of Al/CongoRed/p-Si/Al structures have calculated for dark and different lighting intensities and are given in Table 1. The obtained n values are in the range of 3.33 to 5.42 and far from the ideal diode characteristics. The high ideality factor has attributed to the interface states or the barrier inhomogeneity (Kyoung et al., 2016). The Φ_B value of Al/CongoRed/p-Si/Al structures has decreased with increasing illumination intensity and obtained in the range of 0.631 - 0.528 eV. The decrease in Φ_B with increase in lighting intensity is attributed to the incremented load carriers as a result of the illumination. Moreover, the increasing in light intensity has increased the current in the reverse bias region from 2.31×10^{-6} to 9.25×10^{-5} A at 100 mW/cm^2. These results are in agreement with literature, and they showed that Al/CongoRed/p-Si/Al structures work as a photosensitive device. Table 1 shows the saturation current values of Al/CongoRed/p-Si/Al structures obtained depending on illumination intensity at room temperature.

Table 1. *The diode parameters of Al/CongoRed/p-Si/Al structures depending on the illumination intensity*

	n	I_o (A)	Φ_B (eV)
Dark	3.33	5.66×10^{-7}	0.631
20 mW/cm^2	4.80	1.12×10^{-5}	0.554
40 mW/cm^2	5.12	1.80×10^{-5}	0.542
60 mW/cm^2	5.26	2.28×10^{-5}	0.536
80 mW/cm^2	5.41	2.72×10^{-5}	0.531
100 mW/cm^2	5.42	3.02×10^{-5}	0.528

An important parameter to consider when determining the electrical characteristics of metal/semiconductor structures is the series resistance (R_S). Series resistance can occur for many reasons, such as inhomogeneous impurity distribution in the semiconductor, the depletion layer on the semiconductor surface edge under the rectifier contact, the bulk resistance or a dirty film layer formed between the bulk and the ohmic contact. The R_s value of a structure can be calculated by different methods (Norde, 1979; McLean, 1986; Manifacier et al., 1988). In the calculation of R_s of fabricated devices, the modified Norde function ($F(V,\gamma)$) has been used for ideality factor greater than unity (Bohlin, 1986).

$$F(V,\gamma)=\frac{V}{\gamma}-\frac{kT}{q}Ln\left(\frac{I(V)}{AA^{*}T^{2}}\right) \tag{5}$$

Where γ is an optional coefficient ($1<n<\gamma$) greater than n. I(V) expression is the current estimated from current-voltage curves. The Φ_B value of the device is given through the relation

$$\Phi_B = F(V_o,\gamma)-\left(\frac{1}{\gamma}-\frac{1}{n}\right)V_o-\frac{kT}{q}\frac{(\gamma-n)}{(n)} \tag{6}$$

where, $F(V_o,\gamma)$ and V_o are the modified Norde function and the corresponding voltage value, respectively, at the minimum of the F(V) curves. Accordingly, R_s can be estimated with the help of the following relationship.

$$R_s=\frac{kT}{q}\left(\frac{\gamma-n}{I_o}\right) \tag{7}$$

Figure 3 depicts the F(V)-V curves obtained at dark and different illumination intensities by using forward bias I-V measurements. As seen in figure, all Norde functions give a minimum of about 0.4V. The obtained R_s and Φ_B(I-V) values of Al/CongoRed/p-Si/Al structures depending on the illumination intensity are given in Table 2. The barrier height values estimated by using Norde technique are compatible with the values obtained from I-V characteristics. As seen in Table 2, the series resistance decreased with increasing light intensity.

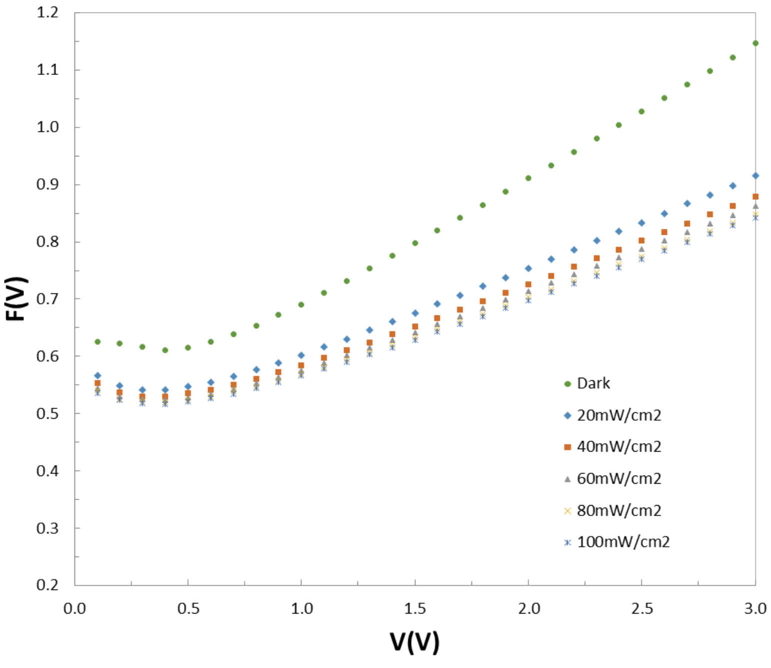

Figure 3. *F(V)-V curves of Al/CongoRed/p-Si/Al structures depending on illumination intensity*

Table 2. *R_s and Φ_B values of Al/CongoRed/p-Si/Al structures depending on illumination intensity at room temperature*

	Dark	20mW/cm^2	40mW/cm^2	60mW/cm^2	80mW/cm^2	100mW/cm^2
Φ_B (eV)	0.626	0.547	0.538	0.532	0.527	0.524
R_s (Ω)	290.5	175.5	73.6	64.6	59.7	55.0

Photoresponse (R) and photosensitivity (S) parameters of structures; have determined using following expressions;

$$R = \frac{J_{ph} - J_d}{P_{in}} \tag{8}$$

$$S = \frac{I_{ph}}{I_d} \tag{9}$$

where, J_{ph}, J_d, I_d and I_{ph} are the photo-current density, dark current density, dark current and photocurrent, respectively. P_{in} is the intensity of incident light coming onto the surface. The R and S values of Al/CongoRed/p-Si/Al structures have found to be 0.11 A/W and 39, respectively, for 2.94×10^{-4} A/cm^2 dark current at 100 mW/cm^2 illumination intensity, and these values are in agreement with the literature. In addition, the obtained photoresponse value of fabricated device is 1.32 times greater than that of the Al/Ru(II)complex/p-Si photodiode Imer et al. (2019) and 12.2 times higher than that of the Al/Quaterphenyl/p-Si photodiode Attia et al. (2016) and 40.7 times higher than that of the Al/Cu(II)complex/p-Si photodiode (Dayan et al., 2020). It has been seen from the results that the produced device has a good photodiode properties.

The photoconductivity behavior of diodes has been analyzed with the following relationship.

$$I_{ph} = BP^m \tag{10}$$

Where B is a coefficient and P is lighting intensity. The m term is the lighting constant and estimated from the slope of graph ln(I_{ph}) - ln(P). This parameter defines the type of photoconductivity mechanism of structures. If the value of the m is between 0.5 and 1, it indicates that photoconductivity is pertaining to the trap levels, and values greater than 1 indicate that photoconductivity is because of the empty trap levels (Yıldırım, 2019). Figure 4 depicts the ln(I_{ph}) - ln(P) graph of Al/CongoRed/p-Si/Al structures and exhibits a linear photoconductive mechanism manner of Al/CongoRed/p-Si/Al structure. The illumination coefficient has found to be 0.95 for this structure. This value is in the range of $0<m<1$ and indicates that the distribution of localized states is continuous existed at the interface (Cavas et al., 2013).

To better understand the mechanism of photoconductivity, the reaction time measurements should be performed in addition to the evaluation of photocurrent changes. Figure 5 gives the transient photo-current curves of Al/CongoRed/p-Si/Al structures depending on different lighting intensities. The transient photo-current measurements help to demonstrate the photoresponse characteristics for various power densities during the on and off position of the device. When illumination begins, the free charge carriers increase and contribute to the flow of current, and consequently the photo-current values rapidly attain saturation. When the illumination ends, the charge carriers decrease and the photo-current drops quickly to its initial level. This represents a reversible switching behavior of device. It is seen from Figure 5, the device responds quickly under different illumination intensities and reaches its maximum photocurrent value in less than a second. This shows that the produced Al/CongoRed/p-Si/Al structures exhibit photoconductive behaviors. Certain photocurrent values observed in each curve under single illumination has attributed to the distribution of charge carriers. They can be captured by traps created by crystal defects or re-excited towards the conduction band by other energy levels (Dahlan et al., 2015).

When the light has turned on, the current of device increased rapidly from 1.27×10^{-6} to 8.95×10^{-5} A and remained almost constant until the light has turned off (Figure 5, at 100 mW/cm^2). Meanwhile, the amount of charge in the trap centers of the device increased depending on the illumination intensity.

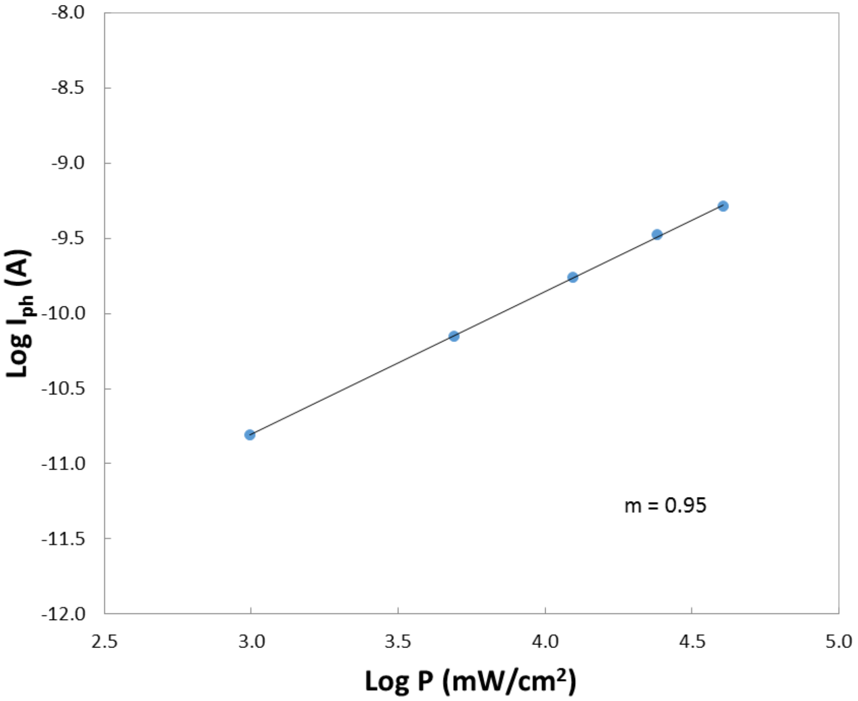

Figure 4. *The variation of photocurrent of Al/CongoRed/p-Si/Al structures depending on illumination intensity*

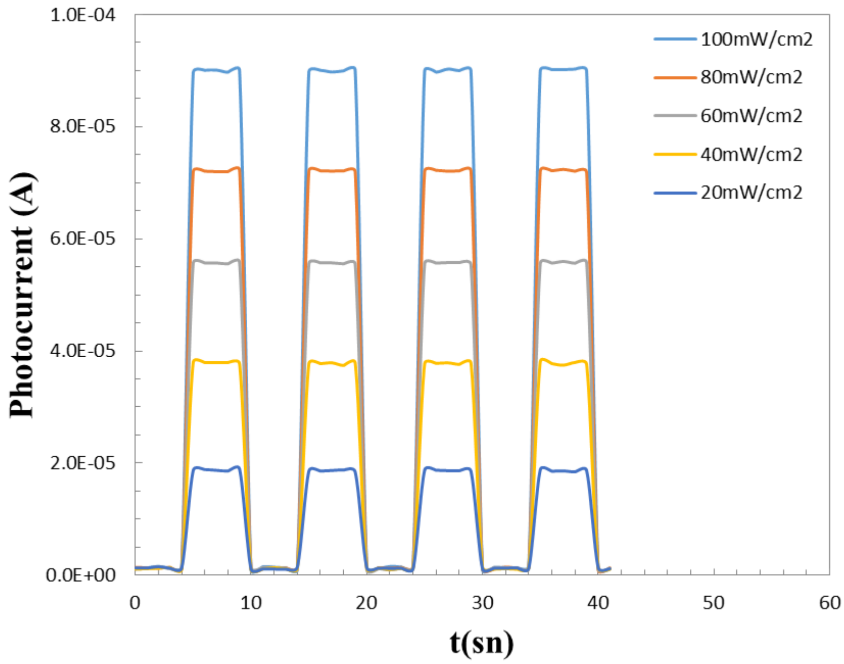

Figure 5. *Transient photocurrent curves of Al/CongoRed/p-Si/Al structures*

4. CONCLUSIONS

This study is aimed at the usability of Al/CongoRed/p-Si/Al structures with organic interlayer as a photodiode device. Therefore, an organic compound CongoRed has grown as an interlayer in a metal/semiconductor Schottky structure using spin coating technique. The sensitivity to the light of fabricated structures has been investigated at dark and under different light intensities.

When forward bias I-V curves of Al/CongoRed/p-Si/Al structures are examined, it is seen that different illumination intensities have a systematic effect on the I-V curves of the structure and this effect causes an increase in device current depending on the light intensity. The n value of the structures is greater than unity and the linear region in the semilogarithmic current-voltage curves is small. This strengthens the possibility that TE or minority carrier injection is effective in the current mechanism of the structures. Since the density of states is in equilibrium with the semiconductor and show continuity in the high voltage region, a deviation from linearity has been observed. However, the fabricated organic-based Schottky structures have shown a well rectification behavior.

Since n value is greater than unity, the modified Norde function is used to calculate R_s values of devices. From experimental results, it is seen that the R_s decreased with increasing of illumination intensity.

The photosensitivity and photoresponse parameters of the structures have been determined and found to be in agreement with previously published similar studies. From the obtained illumination coefficient using photoconductivity curves, it is concluded that the photo-conductivity mechanism is realized by empty trap levels. In this study, the experimental results show that the produced organic-based Al/CongoRed/p-Si/Al structures exhibit photodiode properties and could be used in opto-electronic applications.

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CONFLICT OF INTEREST

There is no conflict of interest between the authors.

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