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Investigation of electrical properties of organophosphazene layer based photodiode



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ABSTRACT

Keywords: Bandgap Electrical properties Cyclotriphosphazene Coumarin-phosphazene New cyclotriphosphazene compound bearing dioxyphenylcoumarin group (**DCP-1**) was synthesized from the reactions of **7,8-dihydroxy-3-(4-chlorophenyl)coumarin** (3) containing chlorine as a side group at *para* position with cyclotriphosphazene (**DCP**). The structures of the compounds were determined using ¹H, ¹³C APT, ³¹P NMR, FT-IR and elemental analysis spectroscopy methods. The organic layer was deposited onto the p-Si substrate to obtain an Al/p-si/phosphazene (**DCP-1**)/Al diode. The photoresponse and photocapacitance properties of the diode were analyzed under various solar light intensities. The photocurrent and photocapacitance results suggest that the studied device exhibits both photodiode and photocapacitor behavior. The diode indicates a linear photoresponse behavior. The photoswitching behavior of the diode is controlled by solar light intensity. The interface states density of the diode was found to be order of $10^{12} \text{ eV}^{-1}\text{cm}^2$. The value of interface states density indicates that the photocapacitor behavior of the diode is significant for photocapacitor applications.

1. Introduction

Cyclic phosphazenes [hexachlorocyclotriphosphazene (N₃P₃Cl₆;trimer) compounds are functionalized with various substituents. Cyclic phosphazene compounds have many advantages such as ease of functionalization, planar structure and stabilization of functionalized cyclic phosphazene core under heavy chemical conditions [1]. In addition, they are electronically inert so that the side groups accounting for tunability can display their own electronic and optical properties. Electronic and sensor systems can be fabricated using cyclic phosphazene compounds due to their interesting electronic and optical properties. The cyclotriphosphazene compounds can be used in various applications such as capacitors [2,3], flame retardants [4], organic light emitting diodes and fluorescence sensor [5–7] and OFET properties [8], and rechargeable lithium batteries [9]. On the other hand, the coumarin ring is a heterocyclic compound with effective photophysical properties such as large Stokes shifts and high quantum yields and it has two various structures: the merger of the

electron-providing benzene ring and the electron-attracting pyron ring, the benzo- α -pyron and its structural isomer, the benzo γ -pyron. Fluorescence emission of the coumarin compound has been observed due to the interaction of dipole-dipole [10-13]. It is well known that electron attracting/ donating groups are attached to the various positions of the coumarin ring to increase the fluorescence properties. Fluorescence behavioral tendency is increased by attaching electron-attracting groups (heterocyclic aromatic or Cl, CN, CF₃, etc.) to the 3 and 4-position of coumarin compounds [14-17]. Coumarin compounds are an important part of organic heterocyclic dyes and compounds used in sensor technology due to their high optical properties, high light stability, high quantum yield, wide Stokes shift and low toxicity. Due to these features, coumarin compounds are highly used in optical brighteners, light emitting diodes, laser paints, dye sensitive solar cells, biological imaging, nonlinear optical (NLO) chromophores, electrolysis materials, solar collectors and two photon absorption (TPA) materials [18-26]. New type of cyclophosphazene derivatives can be synthesized using the coumarin both as a substituent and the trimeric

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phosphazen as a skeleton in a molecule to obtain lead to new physicochemical properties. There have been studies on physical properties of new phosphazene and polyphosphazene derivatives which are found in this literature [27–33]. Najla et al. [34] have demonstrated that coumarin: GO (graphene oxide) doped Bi_2O_3 exhibits photocapacitor behavior and the photoconductance has been improved due to the coumarin: GO doping under the solar irradiation. This study indicates that the coumarin can be used as a photodopant to improve photoresponse properties of metal oxide.

With this connection, we synthesized the coumarin-bound cyclophosphazenes to fabricate a photodiode. Up to now, there is no any study on photodiode based on the cyclophosphazene derivative containing the dihydroxyphenylcoumarin compound bearing chlorine as side group at *para* position. Chlorine and other species like (-F, -OCH₃, -NH₂, -CH₃, -OH etc) are known as ortho and para directors. These electron rich species donate their electrons to carbon chain causing resonance delocalizing double bond in benzene structure and thus electrophile is directed towards ortho and para positions due to higher electron density in these directions.

Therefore, firstly, 7,8-dihydroxy-3-(4-chlorophenyl)coumarin (3) compound has been synthesized from the interaction of Pyr.HCl with phenylacrylonitrile compound (2) in silica gel filler using a microwave oven. Then the new dioxyphenylcoumarin substituted cyclotriphosphazene compound (**DCP-1**) has been synthesized from the interaction of compound **3** with **DCP**. The structures of **2**, **3** and **DCP-1** compounds were confirmed by using spectroscopy methods. After chemical characterization of DCP-1 sample, we fabricated a Al/p-si/phosphazene (**DCP-1**)/Al device for solar tracking systems. The photoelectric and photocapacitance properties of the diode was analyzed in detail.

2. Experimental details

2.1. Materials and methods

HCP (hexachlorocyclotriphoshphazene) was purchased from TCI Chemicals Company. The 2,2'-dihydroxybiphenyl and sodium carbonate were provided from Merck/Sigma Aldrich, respectively. Pyr.HCl (Pyridine hydrochloride) was purchased from Merck. The solvents required for the reaction and purification steps were purchased from Merck. ³¹P, ¹H, and ¹³C NMR analysis were processed in a Bruker DPX 400 MHz spectrometer. Chloroform- d_1 and Dimethylsulphoxide- d_6 solvents were used as deuterium solvent. The FT-IR analyses were measured on a Perkin Elmer FT-IR spectrometer.

2.2. Synthesis

2.2.1. Synthesis of 3

Compound 2 (1 g, 3.03 mmol), an appropriate silica gel (15 g) and Pyr.HCl (5.2 g, 45 mmol) was mixed in a shilenk tube under the argon atmosphere. The mixture was stirred at 320 W in FYRONIX microwave oven for half an hour. The reaction mixture was acidified by adding of 1 N HCl (150 mL) when it's temperature is cooled to room temperature. The residue was filtered through silica gel after the precipitated part dissolved in acetone (3 \times 30 mL). The liquid part of the product was removed under reduced pressure and obtained the solid part, which was then washed several times with water and thereafter dried under a vacuum. The crude product was subjected to precipitation using ethyl acetate (15 mL) in n-hexane. The final purification step was column chromatography (chloroform:hexane) to obtain target product 3 as a gray solid [35,36]. Yield = 63% (0.56 g). Anal. Calc. for $C_{15}H_9ClO_4$ (MW: 288.68): C, 62.41; H, 3.14; Found C, 62.46; H, 3.19%. FT-IR (KBr, cm⁻¹): 3197, 3398 $\nu_{\text{O-H}}$, 3000, 3090 $\nu_{\text{C-H(Ar)}}$, 2917, 2857 $\nu_{\text{C-H(Al)}}$, 1660 $\nu_{\rm C=0}$, 1563, 1571, 1621 $\nu_{\rm C=C}$. ¹H NMR (400 MHz, DMSO- d_6): δ 6.85–6.87 (1H, d, J = 8.4 Hz, H⁴), 7.11–7.13 (1H, d, J = 8.4 Hz, H⁵), 7.50–7.52 (2H, d, J = 8.8 Hz, H¹³), 7.75–7.77 (2H, d, J = 8.4 Hz, H¹⁴), 8.17 (1H, s, $\mathrm{H}^9\text{)},~9.41$ (1H, s, $\mathrm{H}^7\text{)},~10.19$ (1H, s, $\mathrm{H}^8\text{)}.~^{13}\text{C}$ NMR (DMSO- d_6): δ 143.74 C¹, 134.51 C², 150.32 C³, 113.37 C⁴, 119.84 C⁵, 113.16 C⁶, 142.46 C⁹, 121.08 C¹⁰, 160.36 C¹¹, 132.23 C¹², 130.52 C¹³, 128.63 C¹⁴, and 133.08 C¹⁵.

2.2.2. Synthesis procedure of DCP-1

A mixture of DCP (0.3 g, 0.52 mmol) and Na₂CO₃ (0.22 g, 2.08 mmol) was prepared in a reaction flask (150 mL) using 40 mL of anhydrous xylene (mixture of isomers). 0.52 mmol compound 3 dissolved in 25 mL of xylene and added to the reaction mixture dropwise at 0 °C. After 25 min at 0 °C, the reaction mixture was refluxed for 48 h. When reaction was completed, it was subjected to filtration and then liquid phase evaporation. The obtained solid part was dissolved in xylene (10 mL) and precipitated in *n*-hexane (250 mL). After the filtration process, desired product DCP-1 was obtained by column chromatography separation as a white solid [37]. Yield = 36% (0.14 g). Anal. Calc. for $C_{39}H_{23}ClN_3O_8P_3$ (MW = 790 g/mol): C, 59.30; H, 2.93; N, 5.32. Found: C, 59.51; H, 2.98; N, 5.37%. FT-IR (KBr, cm⁻¹): 3065 ν_{C-H} $_{(Aromatic)},~2928~\nu_{C-H(Aliphatic)},~1741~\nu_{C=O},~1476,~1493,~1578,~and~1633~\nu_{C=C},~1175~and~1190~\nu_{P=N},~974~\nu_{P-O-Ph}.~^{31}P$ NMR (CDCl₃) $\delta/ppm:~36.62$ (2P, t, $P_A(O_2C_{12}H_8)$), 24.56 (1P, d, $P_B(O_4C_{16}H_{10})$). ¹H NMR (CDCl₃) $\delta/$ ppm: 7.18–7.75 (23H, m, H³⁻⁶, H^{12,13}, H^{17,18}). ¹³C NMR (CDCl₃) δ/ppm: 147.80 C¹, 125.54 C², 128.74 C³, 129.90 C⁴, 130.09 C⁵, 121.74 C⁶, 140.25 C⁷, 135.01 C⁸, 132.88 C⁹, 116.14 C¹⁰, 122.37 C¹¹, 108.79 C¹², 140.01 C¹³, 128.51–128.66 C¹⁴, C¹⁶ and C¹⁹, 158.73 C¹⁵, 126.47 C¹⁷, 129.80 C¹⁸.

2.3. Device fabrication

To fabricate the device, the p-Si was cleaned by the RCA method. For this purpose, the native oxide layer was removed at first by using HF etching and then, the substrate was placed in deionized water for 5 min in an ultrasonic bath. Subsequently, the Si substrate was washed for 5 min each in an ultrasonic bath of methanol and acetone and then finally dried by nitrogen gas for device fabrication. The back contact was thermally formed by evaporating the Al metal onto the substrate and annealing at 570 °C for 5 min under the nitrogen environment. The DCP-1 solution was drop cast onto the p-Si substrate to form the organic layer and dried for 15 min at 50°C. The top contact was formed by evaporating Al metal through the mask. The *I-V* (current–voltage) and capacitance–voltage (*C-V*) characteristics of the fabricated diode were determined at room temperature using a FYTRONIX electronic device characterization system (ECS-9000), as shown in Fig. 3.

3. Results and discussion

3.1. Synthesis of the compound

The synthesis of compound **3** was achieved in the presence of silica gel by the reaction of compound **2** with pyridinium hydrochloride in non-solvent conditions under a microwave irradiation [35,36]. To obtain **DCP-1**, 1.1 equiv. of compound **3** and **DCP** were reacted in dry xylene (a mixture of isomers) and Na₂CO₃. The structural characterization of **DCP-1** was provided by ¹H, ¹³C-APT, ³¹P NMR, elemental analysis, and FT-IR spectroscopy. The general synthetic scheme for all the compounds is shown in Scheme 1.

The -C=N peaks of compound **2** was disappeared in FT-IR spectra of **3**. A clear evidence for the formation of compound **3** is the conversion of $-OCH_3$ groups to -OH that showed OH stretching vibration at 3197 and 3398 cm⁻¹, respectively. The C=O stretching vibrations of the coumarin compound was appeared at 1660 cm⁻¹. Another evidence for the formation of compound **3** is the disappearance of $-OCH_3$ protons at ¹H NMR spectrum of **3**. ¹H, ¹³C-APT and 2D HETCOR NMR spectra of **3**, as shown in Fig. 1. In Scheme 1, number 7 and 8 phenolic –OH protons were resonated at 9.41 and 10.19 ppm.

The disappearance of OH stretching vibrations and -OH peak in ¹H NMR spectra of **DCP-1** indicates the conversion of compound **2**. The



Scheme 1. Synthetic Scheme and Numeration of each P, H and C atom at comp. 3 and DCP-1.

aromatic –CH stretching frequency at 3065 cm⁻¹ was observed for **DCP-1.** The frequency at 1741 cm⁻¹ belongs to the carbonyl group of **DCP-1**. The characteristic P=N stretching frequencies for phosphazene compounds were observed at 1175 and 1190 cm⁻¹. The P–O–Ph stretching vibration was seen at 977 cm⁻¹.

The 31 P, 1 H, and 13 C-APT NMR spectra for **DCP-1** are shown in Fig. 2 (A₂B system). The existence of two distinct 31 P peaks have confirmed the formation of **DCP-1**. Two different phosphorus peaks for **DCP-1** were observed at 24.56 and 36.62 ppm in a doublet-triplet, respectively.

The detailed information of ¹H and ¹³C NMR spectra for **DCP-1** was given in the experimental section. ¹³C peak of **DCP-1** carbonyl was observed at 158.73 ppm. Proposed structures were verified by both proton integral heights in the ¹H NMR and the existence of primary, secondary and tertiary carbon atom peaks in ¹³C-APT NMR.

3.2. Current-voltage (I-V) characteristics of the diode

Fig. 5 shows the forward and reverse *I-V* characteristics of the Al/p-Si/organic layer/Al under various solar light intensities. The *I-V* characteristics of the diode were analysed using the thermionic emission theory. In this theory, the relationship between current and voltage is expressed by the following [38–40],

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

where k is the Boltzmann constant, V is the applied bias voltage, and T is the temperature.

As seen in Fig. 4, the reverse current of the diode increases with solar light intensity, whereas the forward current did not change with solar light. The change in reverse current is due to the separation of electrons and holes at reverse bias, as the separation of charge carries a reverse bias region is significant more than the separation at forward bias region. The forward current of the diode is highly higher than the

reverse current. This means that the diode exhibited a rectifying behaviour. The measure of the rectifying behaviour is defined as ideality factor, which can be extracted from the slope of the linear region of ln (I)–V plot and is expressed as follows [41],

$$n = \frac{q}{kT} \left(\frac{dV}{d(\ln I)} \right)$$
(2)

The ideality factor using the above equation was found to be 6.46. The ideality factor value greater than unity shows the non-ideal behaviour of the diode. This non-ideality behaviour arises from the existence of surface states between silicon and an organic layer, non-homogeneity of the height of Schottky barrier, silicon dioxide layer and series resistance.

Ocaya et al. [42] have fabricated the substituted coumarin doped fullerite organic photodiode. They have reported the ideality factor for the doped samples ranged from 1.65 to 5.86 (20% coumarin doped). Mekki et al. [43] have reported the ideality factor from 3.97 to 9.52 for various graphene oxide doped methylene blue photodiode, Al/p-Si/GO doped MB/Au. These results indicate that organic layer has an important effect on electronic parameters of the diodes. The organic layer creates a series resistance and in turn, the ideality factor increases.

In order to use studied diode as photodiodes in optoelectronic applications, we need to know the photoconductive or photovoltaic behavior of the diode. For this, the diode should be analyze the photoresponse behavior under various light intensity conditions. The following relation can be used to analyze the photoresponse behavior [44,45].

$$I_{ph} = AP^m$$
(3)

where P is the illumination intensity, A is the constant, and m is the constant whose value can be found by plotting a graph between photocurrent $\log(I_{ph})$ and illumination intensity $\log(P)$ as shown in Fig. 5 and the value of m is found to be 0.26. This value of m suggests the sublinear behavior of the photoresponse.



Fig. 1. (A) ¹H NMR; (B) ¹³C-APT; and (C) 2D HETCOR NMR spectrum of 3 (DMSO-*d*₆).

3.3. Transient characteristics of the diode

Fig. 6 shows the transient photocurrent characteristics of the diode for photoresponse analysis. As soon as the solar light was switched on the diode, the photocurrent of the diode increases immediately to a certain value due to the photo charge pairs generation. When the light was switched off the photocurrent comes back to its initial value because the extra-generated free charge carriers are not available for conduction. The transient photocurrent characteristics of the diodes indicate that the diode can be optically switched by solar light.

In addition, the photocapacitance response of the diode was measured and the transient photocapacitance characteristics are given in Fig. 7. The photocapacitance value increases with the increase in solar light intensity and it drops back to its original level when the light is off. This sudden change in capacitance with change in illumination intensity confirms the photocapacitor behaviour. The diode exhibited the highest photocapacitance at 10 KHz and under the illumination intensity 100 mW/cm². Hence, our device can also be used as a photocapacitor. A similar photo capacitance response has been noted in one of our previous report [46], where cyclotriphosphazene substituted with dioxyphenylcoumarin with methyl group at meta position was used to fabricated the photodiode. The I-V characteristics of Al/HCP-2/ p-Si/Al diode shows higher rectification ratio and a stronger photo capacitance effect was observed.

3.4. Capacitance-voltage and Conductance-voltage characteristics

conductance-voltage characteristics were studied. The dependence of capacitance on frequency and voltage is shown in Fig. 8a. As seen in Fig. 8a, the capacitance doesn't change with frequency at positive voltage. However, capacitance shows a peak at a negative voltage and the height of this peak decreases with an increase in frequency. At low frequencies, the charge carrier can respond to the applied signal and results in high capacitance. The capacitance was adjusted with series resistance and it is seen in Fig. 8b that the adjusted capacitance C_{ADJ} exhibits peak. The peak position shifts from low frequency to high frequency. This change suggests that the charge carriers at interface of the diode follows the frequency of alternating current and in turn, interface states are formed.

This decrease in peak capacitance is attributed to the incapability of the interface charge carriers to follow the high frequency of AC (alternating current) signal. The effect of frequency and voltage on conductance was measured and shown in Fig. 9. The figure shows that the conductance does not indicate any important change at positive voltage, whereas, the conductance value increases with both an increase in frequency and voltage at a negative side. The existence of interface states is the obvious cause of dispersive capacitance. The series resistance, density of interface states and formation of insulator layer cause the nonlinear behaviour in capacitance voltage and conductance voltage characteristics curves. Thus, the corrected capacitance voltage and conductance voltage with a series resistance effect is given by the following relation [47–49],

$$C_{adj} = \frac{(G_m^2 + (\omega C_m)^2)C_m}{a^2 + (\omega C_m)^2}$$
(4)



Fig. 2. (A) 31 P NMR; (B) 1 H NMR; and (C) 13 C-APT NMR spectrum of DCP-1 (in CDCl₃).



Fig. 3. Schematic diagram of the Al/p-si/phosphazene (*DCP-1*)/Al fabricated device.



Fig. 4. Current-voltage characteristics of the Al/p-si/phosphazene **(DCP-1)**/Al diode under various illumination conditions.



Fig. 5. Photoresponse plot between lnP vs. $lnI_{\rm ph}$ of the Al/p-si/phosphazene (DCP-1)/Al diode.



Fig. 6. Transient response of the Al/p-si/phosphazene (DCP-1)/Al diode.



Fig. 7. Transient photocapacitance response of the diode.

$$G_{adj} = \frac{(G_m^2 + (\omega C_m)^2)a}{a^2 + (\omega C_m)^2}$$
(5)

where, C_m and G_m are determined by impedance analyser and a is determined by

$$a = G_m - (G_m^2 + (\omega C_m)^2)R_s$$
(6)

where C_{adj} is the adjusted capacitance, G_{adj} is the adjusted conductance and R_s is the series resistance. The conductance G and adjusted conductance G_{adj} dependence of applied voltage and frequency are shown in Fig. 9a and b, respectively.

The presence of peak in capacitance and conductance plots is due to series resistance. Thus, the series resistance value for the diode is calculated by using the following relation [47,50].

$$R_S = \frac{G_m}{G_m^2 + (\omega C_m)^2} \tag{7}$$

Fig. 10 shows the frequency dependence of series resistance. The peak series resistance decreases with the increase in applied AC signal frequency. An excess resistance at low frequency is observed due to the interface states following the low frequency signal, which results in a peak formed in the capacitance voltage graph, as shown in Fig. 10. The peak intensity is changed with frequency. The magnitude of the peak is decreased with increasing frequency. This behaviour is due to the numbers of interface charge carriers. The decrease in magnitude of the series resistance peak is related to the charge carriers following frequency. The interface states at the interface of the diode. The interface states affect the diode properties.

Thus, it is important to determine the interface states for the studied diode. The following relation gives the density of interface states for the



Fig. 8. Capacitance plots of the Al/p-si/phosphazene (*DCP-1*)/Al diode a) C-V b) Cadj-V.

diode [51]:

$$D_{it} = \frac{2}{qA} \frac{(G_{adj}/\omega)_{\max}}{[(G_{\max}/\omega C_{ox})^2 + (1 - C_m/C_{ox})^2]}$$
(8)

Where C_{ox} is the capacitance of the interlayer. The value of interface states density (D_{it}) was calculated and is given in D_{it} vs V plot as shown in Fig. 11. It can be seen clearly in Fig. 11 that the D_{it} is decreased with the frequency and then becomes constant at a lower frequency range. This behavior caused due to the low response of the interface state densities at high frequencies. High D_{it} values are the main cause for the non-ideal result for the I–V and C–V characteristics of the diode.

4. Conclusions

Phosphazene (DCP-1) based photodiode was fabricated in this study. The photocapacitance and photoconductance behaviors of the phosphazene (DCP-1) based diode were investigated. The ideality factor value shows a non-ideal I-V behavior of the diode. The transient photoconductance analysis shows that the device can be utilized as a photocapacitor. The interface state charges play an important role and modify the capacitance and conductance values of the diode. Adjusted capacitance and conductance were determined due to the series resistance effect. Finally, the effects of applied AC signal frequency on interface states inside the organic layer were investigated. It was found these states significantly modify the C-V and G-V behavior of the diode.

The obtained results suggest that the phosphazene (DCP-1) based photodiode can be used as photosensor in solar tracking systems.



Fig. 9. Conductance plots of the Al/p-si/phosphazene (*DCP-1*)/Al diode a) G-V b) Gadj-V.



Fig. 10. Rs-V characteristics of the diode at various frequencies.

CRediT authorship contribution statement

Kenan Koran: Visualization, Formal analysis, Writing - review & editing. Bilal Arif: Formal analysis. Dilawar Ali: Data curation. Ayşegül Dere: Formal analysis. Furkan Özen: Formal analysis. Abdullah G. Al-Sehemi: Data curation. A. Al-Ghamdi: Data curation. Ahmet Orhan Görgülü: Supervision, Project administration. Fahrettin Yakuphanoğlu: Data curation, Investigation, Methodology.



Fig. 11. Density interface states dependence on frequency.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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