Gazi Üniversitesi
Fen Bilimleri Dergisi
PART C: TASARIM VE TEKNOLOJİ

Gazi University
Journal of Science
PART C: DESIGN AND TECHNOLOGY

GU J Sci, Part C, 11(2): 398-406 (2023)

A Wide Frequency Range C-V and G-V Characteristics Study in Schottky Contacts with a BODIPY-Pyridine Organic Interface

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Article Info

Research article
Received: 02/02/2023
Revision: 27/04/2023
Accepted: 18/05/2023

Keywords

Capcitance
Conductance
Organic material
Schottky diode

Makale Bilgisi

Araştırma makalesi
Başvuru: 02/02/2023
Düzeltme: 27/04/2023
Kabul: 18/05/2023

Anahtar Kelimeler

Kapasitans
İletkenlik
Organik malzeme
Schottky diyot

Graphical/Tabular Abstract (Grafik Özet)

In this study, we studied capacitance/conductance-voltage (C-V and G-V) characteristics of Au/BODIPY-Pyridine/n-Si/In diode. Au/BODIPY-Pyridine/n-Si/In was produced by spin coating method. Capacitance and conductance measurements of the diode at room temperature are made in dark over the frequency range of 10 kHz to 1 MHz.

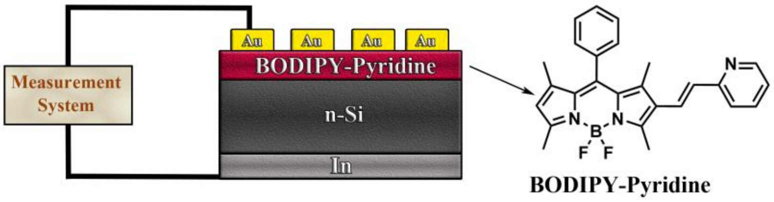

***Figure A**: Measurement system of Schottky diode / **Şekil A:**. Schottky diyotun ölçüm sistemi*

Highlights (Önemli noktalar)

- *Synthesis of BODIPY Pyridine*
- *Production of Au/BODIPY-Pyridine/n-Si/In Schottky diode*
- *XXX Capacitance-voltage (C-V) and conductance-voltage (G-V) measurements*
- *Determination of the series resistance (R_s) and the interface state density (N_{ss}) values*

Aim (Amaç): *In this study, it was aimed to produce an organic interface layered Schottky diode structure and frequency effect on capacitance-conductance-voltage measurements. / Bu çalışmada, organik arayüzey katmanlı Schottky diyot yapısının üretilmesi ve kapasitans-iletkenlik-gerilim ölçümlerine frekans etkisinin incelenmesi amaçlanmıştır.*

Originality (Özgünlük): *In this study, fluorescence active BODIPY based organic material was synthesized and used as an interlayer for MS structures. The forward and reverse bias C–V and G–V characteristics of Au/BODIPY-Pyridine/n-Si/In diode have been investigated at different frequencies and applied bias voltage (± 4 V) ranges at room temperature. / Bu çalışmada, floresan aktif BODIPY bazlı organik malzeme sentezlenmiş ve MS yapıları için bir ara katman olarak kullanılmıştır. Au/BODIPY-Pyridine/n-Si/In diyotun ileri ve geri öngerilim C-V ve G-V karakteristikleri oda sıcaklığında farklı frekanslarda ve uygulanan öngerilim voltajı (± 4 V) aralıklarında incelenmiştir.*

Results (Bulgular): *Capacitance-voltage (C-V) and conductance-voltage (G-V) measurements of Schottky diode was taken in the dark at room temperature in the frequency range of 10 kHz-1 MHz. As a result of the measurements obtained; Interfacial state density (N_{ss}) and series resistance (R_s) parameters were calculated at different frequencies.*

Conclusion (Sonuç): *The series resistance values of the conductance peak as measured by the Nicollian and Brews technique were 3.03 kΩ and 0.27 kΩ in the dark for frequencies of 10 kHz and 1 MHz, respectively. The interface state density values for frequencies of 100 kHz and 1 MHz were calculated using the Hill and Coleman technique to be 1.21 x10^{12} eV^{-1} cm^{-2} and 1.05x10^{11} eV^{-1} cm^{-2} in the dark, respectively. / Nicollian ve Brews tekniği ile ölçülen iletkenlik pikinin seri direnç değerleri, 10 kHz ve 1 MHz frekansları için karanlıkta sırasıyla 3,03 kΩ ve 0,27 kΩ olarak bulundu. Hill ve Coleman tekniği kullanılarak 100 kHz ve 1 MHz frekansları için arayüzey durum yoğunluğu değerleri karanlıkta sırasıyla 1,21 x10^{12} eV^{-1} cm^{-2} ve 1,05x10^{11} eV^{-1} cm^{-2} olarak hesaplandı.*

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DOI: 10.29109/gujsc.1246327

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A Wide Frequency Range C-V and G-V Characteristics Study in Schottky Contacts with a BODIPY-Pyridine Organic Interface

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Abstract

In this study, it was aimed to produce an organic interface layered Schottky diode structure and frequency effect on capacitance-conductance-voltage measurements. In this context, phosphor doped n-type Si single crystal has been used as a semiconductor substrate with a 1-20 Ω.cm resistivity, (100) surface oriention, 2 inches in diameter and 350 μm thickness. The (E)-5,5-difluoro-1,3,7,9-tetramethyl-10-phenyl-2-(2-(pyridin-2-yl)vinyl)-5H-5λ4,6λ4-dipyrrolo [1,2-c:2',1'-f] [1,3,2] diazaborinine (BODIPY-Pyridine) thin film was coated on n-Si using the spin coating technique. Ohmic and rectifier contacts were coated by evaporation of indium (In) and gold (Au) using a thermal evaporation system and Au/ BODIPY-Pyridine/n-Si/In Schottky diode was fabricated. Capacitance-voltage (C-V) and conductance-voltage (G-V) measurements of this structure were gained at different frequencies in the dark. Contingent on the frequency, the series resistance (R_s) and the interface state density (N_{ss}) values were identified by using the conductance and Hill-Coleman method, respectively. The series resistance values decreased from 3.03 kΩ to 0.27 kΩ for the frequency range of 10 kHz and 1 MHz and for 4 V, respectively. The density of the interface state was determined in the range of 10^{11} eV^{-1} cm^{-2}.

BODIPY-Piridin Organik Arayüzlü Schottky Kontaklarda Geniş Frekans Aralığı C-V ve G-V Özelliklerinin İncelenmesi

Makale Bilgisi

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Başvuru: 02/02/2023
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Anahtar Kelimeler

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Kama Yuvası
Schottky diyot

Öz

Bu çalışmada organik arayüzey tabakalı Schottky diyot yapısı üretimi ve kapasite-iletkenlik-voltaj ölçümlerine frekans etkisi amaçlandı. Bu kapsamda, 350 μm kalınlığında, (100) yönelimli, 2 inç çapında, 1-20 Ω.cm özdirençli, fosfor katkılı n tipi bir silisyum yarıiletken kristali kullanıldı. Bu kristalin üzerine "(E)-5,5-difloro-1,3,7,9-tetrametil-10-fenil-2-(2-(piridin-2-yl)vinil)-5H-5λ^4,6λ^4-dipirol [1,2-c:2',1-'f][1,3,2] diazaborinin" (BODIPY-Pyridine) ince filmi spin kaplama tekniği kullanılarak kaplandı. Termal buharlaştırma sistemi kullanılarak indiyum (In) ve altın (Au) buharlaştırılmasıyla omik ve doğrultucu kontaklar kaplandı ve Au/BODIPY-Pyridine/n-Si/In Schottky diyotu üretildi. Bu yapının karanlıkta farklı frekanslarda kapasite-voltaj (C-V) ve iletkenlik-voltaj (G-V) ölçümleri alındı. Frekansa bağlı olarak seri direnç (R_s) ve arayüzey durum yoğunluğu (N_{ss}) değerleri sırasıyla iletkenlik ve Hill-Coleman yöntemi kullanılarak belirlendi. Seri direnç değerleri 10 kHz ve 1 MHz ve 4 V için sırasıyla 3,03 kΩ'dan 0,27 kΩ'a azaldı. Arayüz durumunun yoğunluğu 10^{11} eV^{-1} cm^{-2} aralığında belirlendi.

1. INTRODUCTION (GİRİŞ)

Due to their technological advantages in optoelectronic applications, the electrical properties of metal-semiconductor (MS) and metal-interface layer-semiconductor (MIS) type Schottky barrier diodes (SBDs) have been extensively investigated for a long time [1-3]. The nonideal behavior observed in electrical features of SBDs has been generally attributed to the effect of interface layer properties [4, 5]. The performance of these diodes is particularly influenced by the interfacial layer development at the MS interface, the level of interface states (N_{ss}) at the organic layer/Si interface, and the series resistance (R_s) of the devices. Therefore, it is crucial to identify the interface characteristics of a Schottky diode with an organic base [6]. Also, the frequency dependent C–V and G–V measurements in the wide range of frequency can give us valuable information about the energy distribution of the interface states and of these structures [7]. On the other hand, the series

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resistance R_s of the semiconductor bulk also plays an important role in capacitance–voltage (C-V) and conductance–voltage (G-V) characteristics of SBDs, and it causes that the interface state density N_{ss} obtained from admittance spectroscopy become different from those that would be expected [8].

The use of organic dyes as semiconducting materials in molecular optoelectronic devices has recently gained interest. The key benefits of organic dyes include their easy processing, tunable electrical properties, compatibility with flexible substrates, great optical and thermal stability, low cost, and ease of manufacture for large-area applications. Many optoelectronic devices, including Schottky diodes, photodiodes, organic light-emitting diodes, and solar cells, have been made using organic dyes as semiconductors [9-15].

Due to their unique and desirable properties, such as good photochemical and thermal stability, strong absorption, high fluorescence quantum yield, and good solubility, BODIPY (4,4-difluoro-4-bora-3a,4a-diaza-s-indacene)-based dyes have attracted a lot of attention in recent decades in remarkably diverse applications [13, 16-18]. These factors make the BODIPY a fascinating fluorescent structure that may be used in a variety of devices, including photovoltaics, dye-sensitized solar cells, fluorescent molecular probes, and light-harvesting arrays. Due to its spectroscopic characteristics, the BODIPY has a noteworthy structure in the creation of molecular optoelectronic materials. In order to demonstrate the full potential of π-extended BODIPY compounds in various optoelectronic applications, electrical and optical characterizations of these compounds are also highly required [17, 18].

In this study, BODIPY based dye was synthesized and used as an interlayer for MS structures. The forward and reverse bias C–V and G–V characteristics of Au/BODIPY-Pyridine/n-Si/In diode have been investigated at different frequencies and applied bias voltage (± 4 V) ranges at room temperature. The effects of the insulating layer, series resistance (R_s), and interface state density (N_{ss}) on the conductivity-voltage (G-V) and capacity-voltage (C-V) measurements of Schottky diode structures with metal/Organic material)/semiconductor (MOmS) structure have recently been the subject of studies. In order to assess the electrical characteristics of Au/BODIPY-Pyridine/n-Si/In diode, characteristic measurements of conductivity-voltage (G-V) and capacitance-voltage (C-V) were carried across a wide frequency range (10 kHz–1000 kHz). In order to reduce the impact of the existence of interface states, measurements are also performed at high frequencies. Basic parameters like series resistance (R_s) and interface state density (N_{ss}) were explored dependent on the voltage and frequency as a result of the graphs constructed utilizing the measurements and calculations.

2. MATERIALS AND METHODS (MATERYAL VE METOD)

BODIPY-Pyridine was prepared according to published literature procedures [19] and obtained as a green solid (58% yield). The molecular structure of BODIPY-Pyridine was confirmed by ^{1}H, and ^{13}C NMR spectroscopy [19]. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.57 (d, 1H), 7.64 (dt, 1H), 7.52–7.50 (m, 3H), 7.47 (s, 1H), 7.34– 7.29 (m, 2H), 7.28 (s, 1H), 7.13–7.09 (m, 1H), 6.73 (1H), 6.02 (s, 1H), 2.77 (s, 3H), 2.59 (s, 3H), 1.52 (s, 3H) and 1.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.4, 155.9, 155.0, 149.6, 143.9, 141.8, 139.4, 136.5, 135.1, 132.0, 131.2, 129.5, 129.3, 129.1, 128.2, 127.9, 123.9, 121.9, 121.8, 14.8, 14.5, 14.2 and 13.0.

The Au/BODIPY-Pyridine/n-Si/In device was produced utilizing a n-type Si (100) wafer with a thickness of 500 μm and a resistance of 20 Ω-cm. The n-Si wafer was cleaned in an ultrasonic bath using acetone, methanol, and deionized water. Then, using an $HF:H_2O$ (1:10) solution, the contaminants and the natural oxide layer on the surfaces were eliminated. After thermally evaporating indium metal to create an ohmic contact on the back of the n-Si wafer, the wafer was annealed at 350 °C for 30 seconds in an inert gas. Then, 10 mg of the synthesized BODIPY-Pyridine was dissolved in chloroform (1 ml). At ambient temperature, the solution was mixed for an hour. Spin coating was used to form BODIPY-Pyridine thin films at 1200 rpm for 30 seconds. Finally, a metallic front Au contact was created by thermal evaporation on the BODIPY-Pyridine thin film. A quarter of a 2-inch Si crystal was used for the produced Schottky structure. Schottky contact diameter is 2 mm. Purity of both In and Au metal contacts are 99.99%. Thickness of both In and Au metal contacts are 200 nm. Au/BODIPY-Pyridine/n-Si/In (MOmS) device is shown in Figure 1.

A HP 4192A impedance analyzer was used to acquire admittance data from the manufactured device structure. These measurements were examined at room temperature over a wide frequency range (10 kHz–1 MHz).

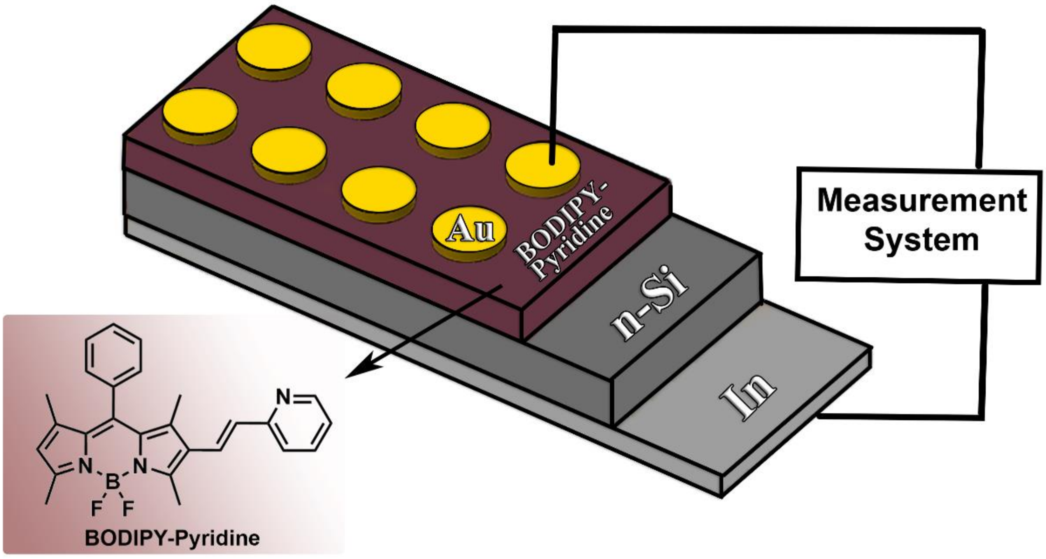

Figure 1. Schematic diagram of the Au/BODIPY-Pyridine/n-Si/In device

3. RESULTS (BULGULAR)

Au/BODIPY-Pyridine/n-Si/In Schottky diode was prepared by thermal evaporation and spin coating method. Capacitance-voltage (C-V) and conductance-voltage (G-V) measurements of Schottky diode was taken in the dark at room temperature in the frequency range of 10 kHz-1 MHz. As a result of the measurements obtained; Interfacial state density (N_{ss}) and series resistance (R_s) parameters were calculated at different frequencies.

Figure 2 and Figure 3 show the C_m-V and G_m-V characteristics measurements of the Au/BODIPY-Pyridine/n-Si/In Schottky diode as function of the applied voltage in the frequency range of 10 kHz–1 MHz at room temperature. The applied voltage range was taken between –4 and +4 V. As shown in Fig. 2, for all frequencies, C_m-V graphs exhibit the inversion-depletion-accumulation zones typical of metal-insulator-semiconductor (MIS) type Schottky diodes. Both frequency and bias voltage affect the C_m values. C_m changes most in the inversion and depletion zones, whereas it virtually never changes in the accumulation region. Due to the interface state charge's inability to contribute the ac signal at higher frequencies, as illustrated in Fig. 2, the value of capacitance decreases with frequency at all voltages [20-23].

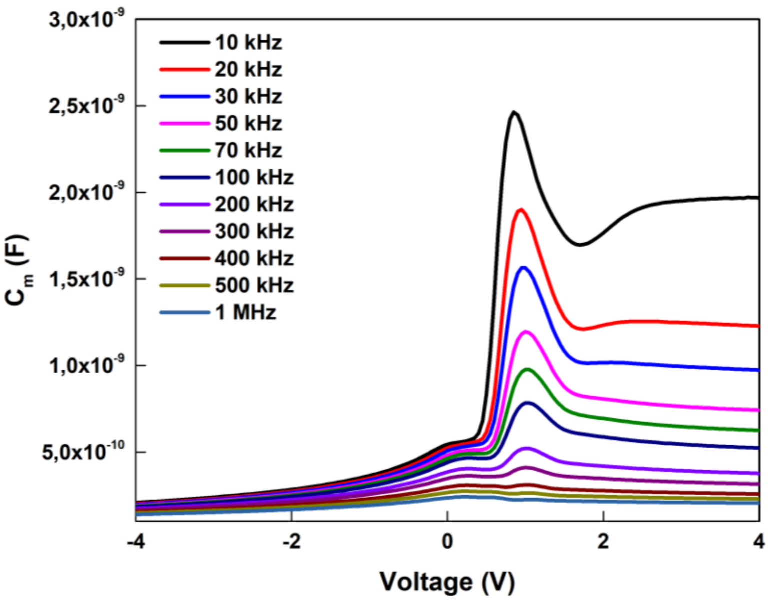

Figure 2. The Experimental capacitance-voltage (C_m-V) characteristics of Au/BODIPY-Pyridine/n-Si/In at different frequencies

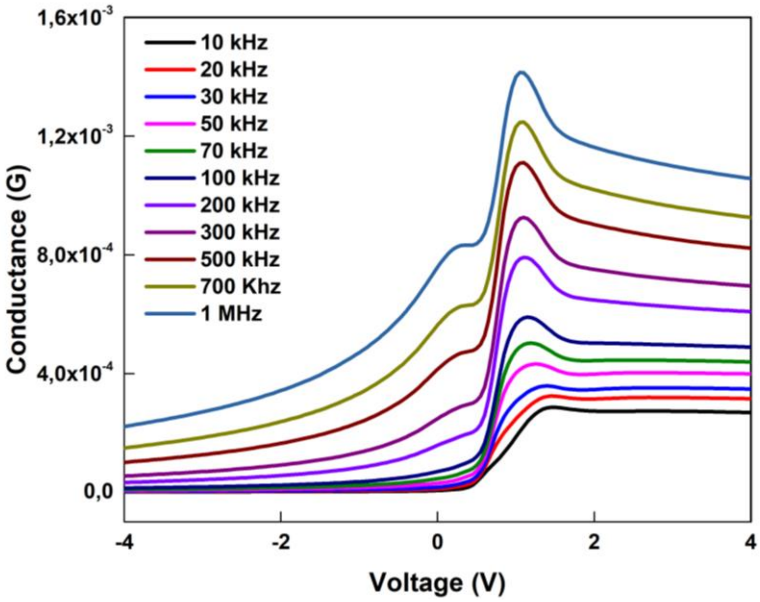

Figure 3. The Experimental conductance-voltage (G_m-V) characteristics of Au/BODIPY-Pyridine/n-Si/In at different frequencies

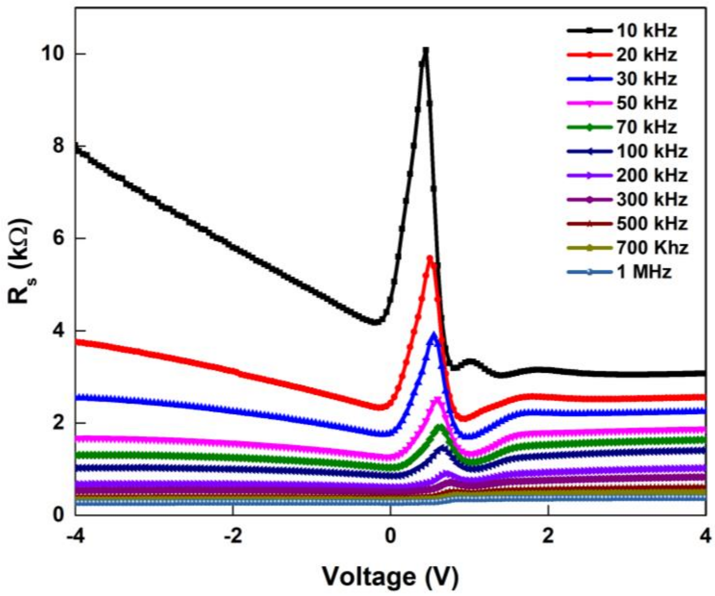

Figure 4. The experimental R_s–V characteristics of Au/BODIPY-Pyridine/n-Si/In diode

When the measurements of the diode are analyzed, it can be seen that the capacitance values for the depletion, inversion, and accumulation zones drop with increasing frequency while the capacitance value increases with rising voltage. The reason why the capacitance values decrease as the frequency decreases is due to the fact that the carriers contributing to the capacitance cannot follow the high frequency signal. As can be observed in Fig. 3, the conductance values for the depletion, inversion, and accumulation zones rise with rising frequency and voltage. The C_m and G_m values of diode are affected by interface states density and series resistance parameters [24, 25]. Additionally, it is well known that the conductance peak position of the Schottky diodes changes with R_s and N_{ss}.

Series resistance (R_s) is a crucial parameter at accumulation region and forward voltage for the produced samples. Therefore, when the generated diode is examined in the accumulation zone at all frequency values, the corrected values of series resistance published by Nicollian and Brews [26] are calculated from the measured capacitance and conductance value.

$$R_s = \frac{G_m}{G^2{}_m + (\omega C_m)^2} \quad (1)$$

where, G_m; C_m and are the measured conductance, capacitance, and angular frequency, respectively.

Figure 4 depicts the series resistance–voltage R_s-V graphs of the Au/BODIPY-Pyridine/n-Si/In Schottky diode at different voltages. As shown in Fig. 4, the series resistance value has a peak position for each frequency, and as the frequency value increased, the magnitude of the maxima R_s value dropped. The R_s values (for 4V) were found as 3.03 kΩ and 0.27 kΩ for 10 kHz and 1 MHz, respectively.

The C_m and G_m measurements were corrected to reduce the impact of R_s in the accumulation and depletion zone. In line with this, corrected capacitance, C_c, and corrected conductance, G_c, are expressed by the following equations [21, 27]

$$C_c = \frac{G^2{}_m + (\omega^2 C^2{}_m) C_m}{a^2 + (\omega^2 C^2{}_m)} \tag{2}$$

$$G_c = \frac{G^2{}_m + (\omega^2 C^2{}_m) a}{a^2 + (\omega^2 C^2{}_m)} \tag{3}$$

Where a is a constant and is given as follows,

$$a = G_m - [G^2{}_m + (\omega^2 C^2{}_m)] R_s \tag{4}$$

Figs. 5 and 6 show the corrected experimental forward and reverse bias C–V and G–V characteristics for the Au/BODIPY-Pyridine/n-Si/In diode at different frequencies.

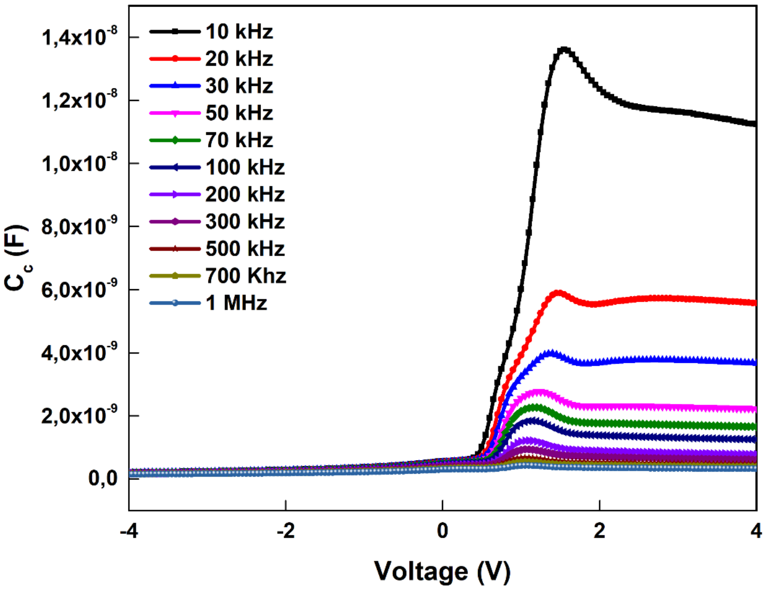

Figure 5. Corrected capacitance–voltage (C_c-V) plots of Au/BODIPY-Pyridine/n-Si/In Schottky diode at different voltages

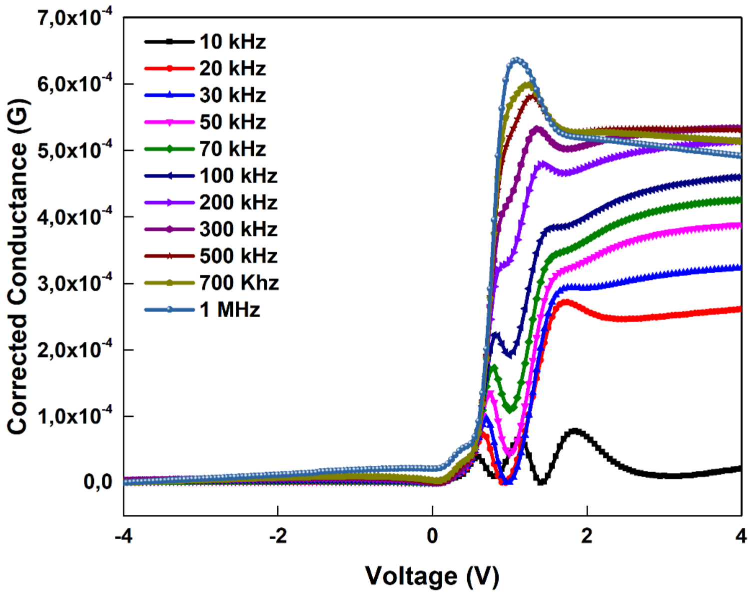

Figure 6. Corrected conductance –voltage (G_c-V) plots of Au/BODIPY-Pyridine/n-Si/In Schottky diode at different voltages

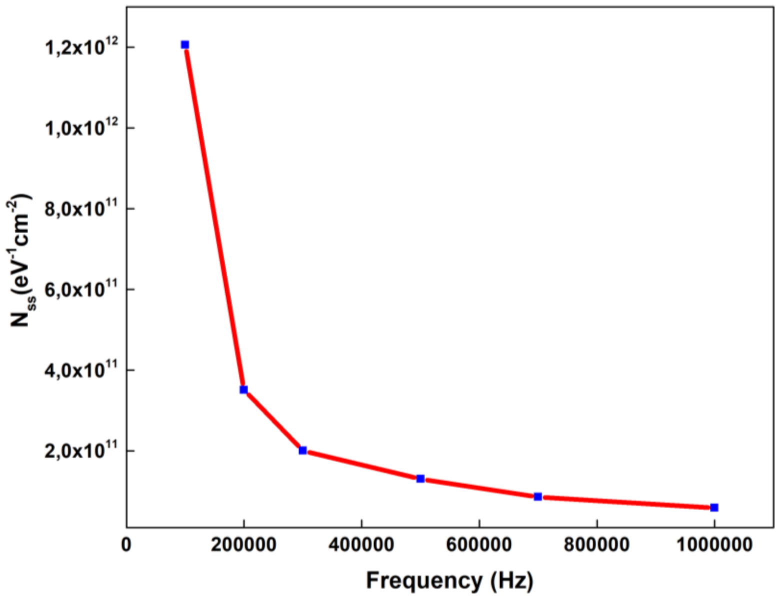

Figure 7. Variation of interface state density (N_{ss}) with frequency

As mentioned above, the series resistance effect on the device characteristics is clearly apparent when the corrected C–V and G–V characteristics are compared to the uncorrected ones at each frequency. When Figure 5 is considered, it has been determined that there is an increase in the capacitance values after the series resistance correction and the real capacitance values remain constant depending on the increasing voltage in the accumulation region. In Figure 6, it has been found that a smooth peak is observed at every frequency in the depletion region and the corrected conductivity values, especially from the depletion region to the accumulation region, decrease depending on the increasing voltage. The peaks that occur in the depletion region in the conductance curves are due to the concentration of the interface states in the forbidden energy range in a special region [26, 28]. This situation in the C_c-*V* and G_c-V graphs shows that the effect of R_s values is significant and that the effect of these Rs values should be subtracted from the measured C_m-V and G_m-V graphs. If the R_s effect is not removed from the relevant measurements, the accuracy and reliability of the obtained parameters will be reduced.

There are different methods for calculating the interfacial state density in MIS type Schottky diodes [29]. The distribution profile of the interface states for the produced sample was determined using the Hill-Coleman method at different frequencies [30]. If the corrected conductivity values of the Schottky diode produced according to this method go to a maximum in the consumption region, these maximum values are proof that there are interfacial states occurring at the organic/inorganic interface. After subtracting the series resistance effect from the conductivity values measured for Au/ BODIPY-Pyridine/n-Si/In Schottky diode, peaks were observed at all frequencies in the depletion region in the corrected conductivity values. According to the Hill-Coleman method, the N_{ss} values of the MIS/MOmS structure can be determined from the following equation [30],

$$N_{ss} = \frac{2}{qA} \frac{(G_{c,max}/\omega)}{(G_{c,max}/\omega C_{ox})^2 + (1 - C_c/C_{ox})^2} \quad (5)$$

Where $G_{c,max}$ is the value of peak of the G_c-V plots, C_c is the capacitance of the diode related to $G_{c,max}$, A is the diode area, q is the elementary electrical charge, $\omega(=2\pi f)$ is the angular frequency and C_{ox} is the capacity of the organic layer, which is obtained from the values in the accumulation region of the corrected capacitance and conductivity measurements at 1 MHz.

Fig. 7 demonstrates the variation of N_{ss} with different frequency. It is clearly seen that the N_{ss} value is decreased with an increase in frequency. N_{ss} values were calculated as 1.21 x10^{12} eV^{-1} cm^{-2} and 1.05x10^{11} eV^{-1} cm^{-2} at 100 kHz and 1 MHz frequencies, respectively. This decrease results from the behavior of interface charge carriers [29]. Çavdar et. al. [31] produced the Al/Gelatin/n-Si Schottky structure and reported the values of series resistance and interface state density were determined as 810 Ω and 1.52 x 10^{12} eV^{-1} cm^{-2} for 30 kHz and 38 Ω and 3.38 x 10^{11} eV^{-1} cm^{-2} for 1 MHz. Zeyrek et. al. [32] produced the Al/Perylene/p-Si Schottky structure and reported the values of series resistance and interface state density were determined as 438 Ω and 3.40 x 10^{12} eV^{-1} cm^{-2} for 30 kHz and 148 Ω and 1.47 x 10^{12} eV^{-1} cm^{-2} for 1 MHz.

4.CONCLUSIONS (SONUÇLAR)

In this study, we investigated capacitance/ conductance-voltage (C-V and G-V) properties of Au/BODIPY-Pyridine/n-Si/In diode. Au/BODIPY-Pyridine/n-Si/In was produced by spin coating and thermal vaporization method. Capacitance and conductance measurements of the Au/BODIPY-Pyridine/n-Si/In Schottky diode at room temperature are made in dark over the frequency range of 10 kHz to 1 MHz. Both voltage and frequency have an impact on the values of conductance and capacitance. A MIS-type diode behavior was evident in the diode's capacitance characteristics, which included inversion, depletion, and accumulation zones. For frequencies of 10 kHz and 1 MHz, the series resistance values of the conductance peak determined by the Nicollian and Brews approach were 3.03 kΩ and 0.27 kΩ in dark. The interfacial state density was shown by the peaks in the depletion zones of the corrected conductance curves. For frequencies of 100 kHz and 1 MHz, 1.21 x10^{12} eV^{-1} cm^{-2} and 1.05x10^{11} eV^{-1} cm^{-2} in the dark were computed as the interface state density values using the Hill and Coleman method. According to measurements, the density of the interface state is within the range of 10^{11} eV^{-1} cm^{-2}, which is suitable for electronic device technology. When the manufactured diode is compared to the existing research, The created diode can also be used in electronic applications, according to the testing results.

ACKNOWLEDGMENTS (TEŞEKKÜR)

This study was supported by Giresun University Scientific Research Project. (Project Number: FEN-BAP-A-250620-62)

DECLARATION OF ETHICAL STANDARDS (ETİK STANDARTLARIN BEYANI)

The author of this article declares that the materials and methods they use in their work do not require ethical committee approval and/or legal-specific permission.

Bu makalenin yazarı çalışmalarında kullandığı materyal ve yöntemlerin etik kurul izni ve/veya yasal-özel bir izin gerektirmediğini beyan eder.

AUTHORS' CONTRIBUTIONS (YAZARLARIN KATKILARI)

***Enis TAŞCI*:** He conducted the experiments, analyzed the results and performed the writing process.

Deneyleri yapmış, sonuçlarını analiz etmiş ve makalenin yazım işlemini gerçekleştirmiştir.

CONFLICT OF INTEREST (ÇIKAR ÇATIŞMASI)

There is no conflict of interest in this study.

Bu çalışmada herhangi bir çıkar çatışması yoktur.

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