Araştırma *Uyar vd./Kırklareli University Journal of Engineering and Science 7-2(2021) 221-231*

DOI: 10.34186/klujes.997005 *Geliş Tarihi:17.09.2021* *Kabul Tarihi:22.11.2021*

ELECTRICAL PROPERTIES OF $ZnO:TiO_2$ NANOCOMPOSITE THIN FILMS

Serkan UYAR[1], Burhan COŞKUN[1], Mümin Mehmet KOÇ*[1,2], Mustafa ERKOVAN[3,4]

[1]Department of Physics, Faculty of Literature and Science, Kırklareli University, Kırklareli, TURKEY
[2] School of Medical Service, Kırklareli University, Kırklareli, TURKEY
[3]Department of Computer Engineering, Beykoz University, Istanbul, TURKEY
[4]INESC-Microsystems and Nanotechnologies, Lisboa, PORTUGUAL

Abstract

In this work, $ZnO:TiO_2$ nanocomposites thin films were produced, and electrical properties were evaluated. Nanocomposite nanoparticles were used as thin film source in the preparation which was produced using sol-gel synthesis in different concentrations. Spin coating process was adopted in the preparation of $ZnO:TiO_2$ nanocomposites films. In the thin film preparation pure TiO_2, and nanocomposites in 1:5 $ZnO:TiO_2$ and 1:2 $ZnO:TiO_2$ concentrations were prepared. Electrical properties of the $ZnO:TiO_2$ composites were assessed where capacitance–voltage and conductance–voltage measurements were performed. Adjusted conductance (G_{adj})–voltage (V) and adjusted capacitance (C_{adj})–voltage (V) characteristics were studied. Frequency dependent characteristics were obtained in the electrical measurements. The density of interface states (D_{it}) was assessed; results illustrated that the D_{it} has frequency dependent characteristics.

Keywords: $ZnO:TiO_2$ Nanocomposites; Thin films; Photodiodes; Photodetectors

$ZnO:TiO_2$ NANOKOMPOZİT İNCE FİLMLERİN ELEKTRİKSEL ÖZELLİKLERİ

Öz

Bu çalışmada, $ZnO:TiO_2$ nanokompozit ince filmler üretildi ve bu filmlerin elektriksel özellikleri incelendi. Nano kompozitler üretilirken hidrotermal sentez yöntemi kullanıldı. Üretilen $ZnO:TiO_2$ nano kompozitlerden filmler üretilirken spin kaplama metodu kullanıldı. Film hazırlık süresince katkısız TiO_2 filmler, 1:5 $ZnO:TiO_2$ ve 1:2 $ZnO:TiO_2$ oranında nanokompozit filmler üretilmiştir. $ZnO:TiO_2$ nano kompozitlerin elektriksel özellikleri kapasitans–voltaj ve kondüktans–voltaj grafikleri incelenerek elde edilmiştir. Elde edilen grafiklerden ayarlanmış kondüktans–voltaj ve ayarlanmış kapasitans voltaj grafikleri hesaplanmıştır. $ZnO:TiO_2$ nanokompozit ince filmlerin frekansa bağımlı özellik gösterdiği anlaşılmıştır. Elektriksel karakteristikler kullanılarak ara yüz durum yoğunlukları hesap edilmiştir. Hesaplamalar sonucunda ara yüz durum yoğunluklarının da frekansa bağlı karakteristiğe sahip olduğu anlaşılmıştır.

Anahtar Kelimeler: $ZnO:TiO_2$; Nano kompozitler; İnce filmler; Fotodedektörler; Fotodiyotlar

Sorumlu Yazar: Mümin Mehmet KOÇ, muminmehmetkoc@klu.edu.tr

DOI: 10.34186/klujes.997005 *Geliş Tarihi:17.09.2021* *Kabul Tarihi:22.11.2021*

1. INTRODUCTION

Nanoparticles has mesmerizing structure which was allocated with outstanding optical, electrical, optoelectronic, magnetic properties [1]–[4]. Therefore, nanostructures were deeply researched by researchers from different fields. It was previously reported that intrinsic properties of the nanoparticles can be altered depending on their size [5], [6]. Moreover, producing nanostructures in different chemical compositions and structures often alters their characteristics [7]–[9]. For example, core@shell structures were generally produced for multipurpose applications. Iron oxide based core gives magnetic characteristics to the nanoparticles. Besides, organic shells were often used to reduce cytotoxicity and increase cellular intake. Similarly, producing nanocomposites and nanoalloys can also be used to produce nanostructures with multiple purpose properties. For example, certain metallic nanocomposites addressed as multi modal and multi-purpose nanodrugs [10]–[12]. Producing alloys or composites with iron oxide based materials gives nanostructures a magnetic characteristic.

Transition metals have good electron affinity with outstanding electrical properties. Due to their phenomenal characteristics, transition metal oxides such as AgO, CuO, ZnO, TiO_2 are vastly used in electric, catalytic, optoelectronic applications [2], [8], [13]–[18]. Among those materials, ZnO and TiO_2 nanostructures has an important role in optoelectronic applications ZnO and TiO_2 based materials were commonly researched and successful results were implied in photovoltaics and photodetector applications. ZnO and TiO_2 has good electrical properties with tolerable reflectance and promising absorbance properties. Therefore, ZnO and TiO_2 were found to be two of the most promising photovoltaic device materials.

In our previous study, we investigated the photosensitivity and photoresponsivity properties of our nanocomposite thin films. It was illustrated that our nanocomposite thin films were responsive to light where illumination intensity related photocurrent was observed. In this work electrical and electronical properties of the $ZnO:TiO_2$ nanocomposite thin films were assessed.

DOI: 10.34186/klujes.997005 *Geliş Tarihi:17.09.2021* *Kabul Tarihi:22.11.2021*

2. MATERIALS AND METHOD

In our previous work, production of nanoparticles and sol-gel films were described in detail [19]. Please see the related paper. To sum up, nanoparticles were produced using sol gel method where Titanium(IV)isopropoxide ($Ti[OCH(CH_3)_2]_4$) were dissolved in 10ml 2-methoxyethanol and zinc acetate dihydrate ($(CH_3CO_2)_2Zn$) were stirred in 10ml 2-methoxyethanol where ZnO doped TiO_2 solution were mixed different molar rates. P- type Si was cleaned following cleaning protocols [20]. Cleaned wafers were nitrogen gas dried and nanoparticle solutions were dripped on the wafer. Nanocomposite solutions were spin coated for 30 secs. Nanocomposite coated thin films were baked and Al contacts were applied using thermal evaporation. FYTRONIX FY-7000 solar simulator and electrical characterization device was used in the electrical investigations.

3. RESULT AND DISCUSSION

Capacitance – Voltage (C - V) characteristics of the pure TiO_2 and ZnO doped TiO_2 photodiodes were investigated in Figure 1. C – V behaviours of the nanocomposite thin films were assessed between -5 V and 5 V in varying frequencies between 10 kHz and 1 MHz were used in the assessments. A prominent peak was seen in each graph. The tip of the peak was measured around -2 V, -1 V and 0.8 V for pure TiO_2 photodiodes, 1:5 and 1:2 ZnO doped TiO_2 photodiodes, respectively. The position of the peaks shifts towards positive region with increased ZnO dopant rate. The peaks illustrate the frequency dependence of the diodes where augmented capacitance was observed in low AC signal frequencies. The case confirms that low AC frequencies cannot move the free charges which causes them to stack. Therefore, the increased capacitance was measured for higher frequencies. Higher AC signal frequencies can better trigger the charges and force charges to move within the diode. Hence, the lower capacitance was measured for higher AC signal frequencies. Frequency dependence of the capacitance may be attributed to different artifacts such as hopping mechanism, interface states, series resistance, etc.

DOI: 10.34186/klujes.997005 *Geliş Tarihi:17.09.2021* *Kabul Tarihi:22.11.2021*

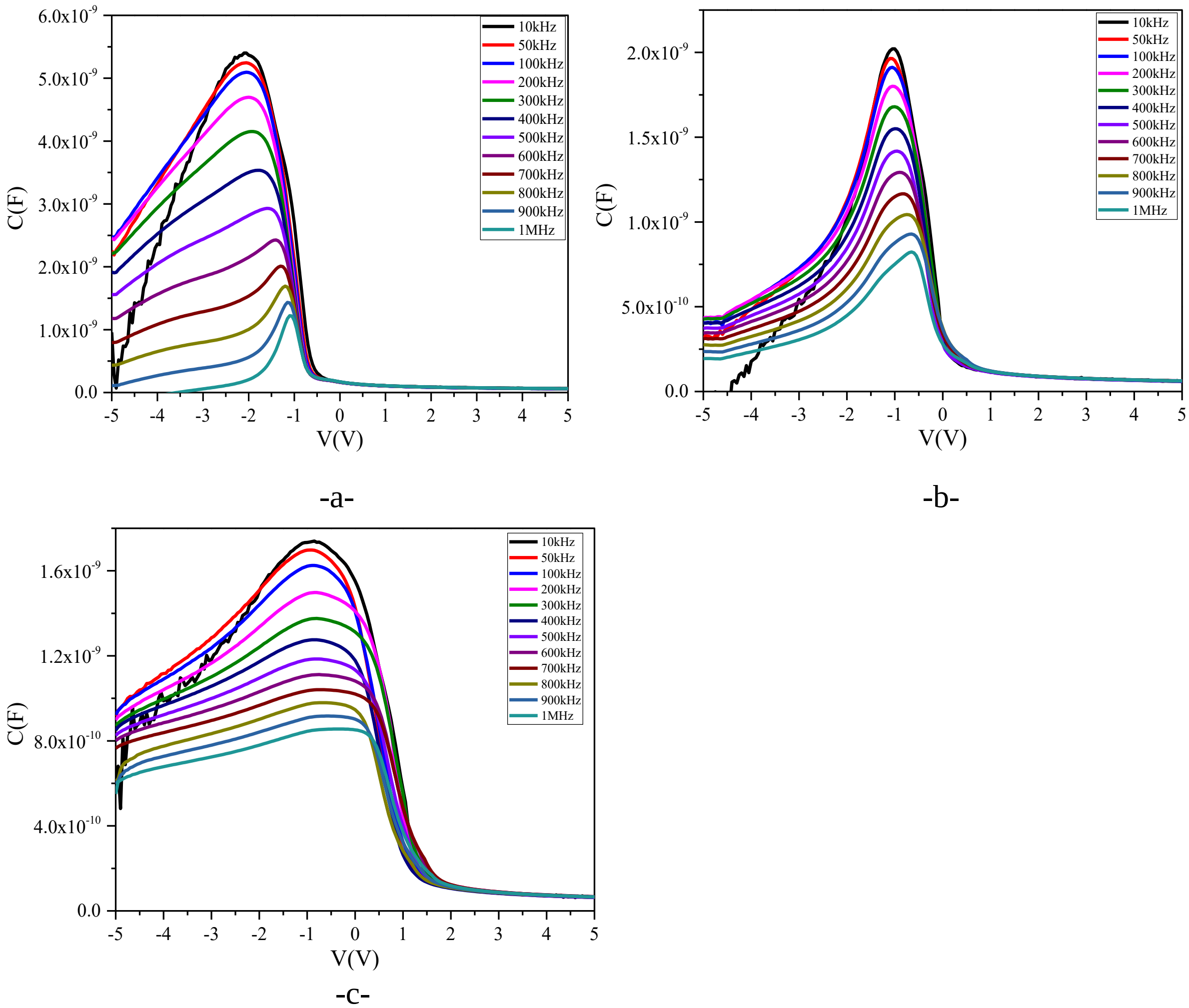

Figure 1: C– V characteristics of pure TiO_2 (a), 0.5 mol ZnO doped 2.5 TiO_2 (1:5 molar rate) (b), and 1 mol ZnO doped 2 mol TiO_2 (1:2 molar rate) (c) photodiodes.

Conductance – voltage (G – V) characteristics of diodes were evaluated between -5 V and +5 V and presented in Figure 2. It was seen that photodiodes illustrate frequency dependent characteristics. Increased signal frequency increases the conductance of the photodiodes. Such characteristics were found to be coherent with the C - V characteristics of the photodiodes. An apparent rise in the conductance was seen in higher frequency where the maximum conductance values were found to be $2x10^{-2}$ S, $8x10^{-3}$ S and $6x10^{-3}$ S for pure TiO_2 photodiodes, 1:5 and 1:2 ZnO doped TiO_2 photodiodes, respectively. It was concluded that ZnO dopant rate slightly decreases the measured conductance of the nanocomposite thin films. Both C – V and G – V behaviours were affected by ZnO dopant and AC signal frequency.

Araştırma *Uyar vd./Kırklareli University Journal of Engineering and Science 7-2(2021) 221-231*

DOI: 10.34186/klujes.997005 *Geliş Tarihi:17.09.2021* *Kabul Tarihi:22.11.2021*

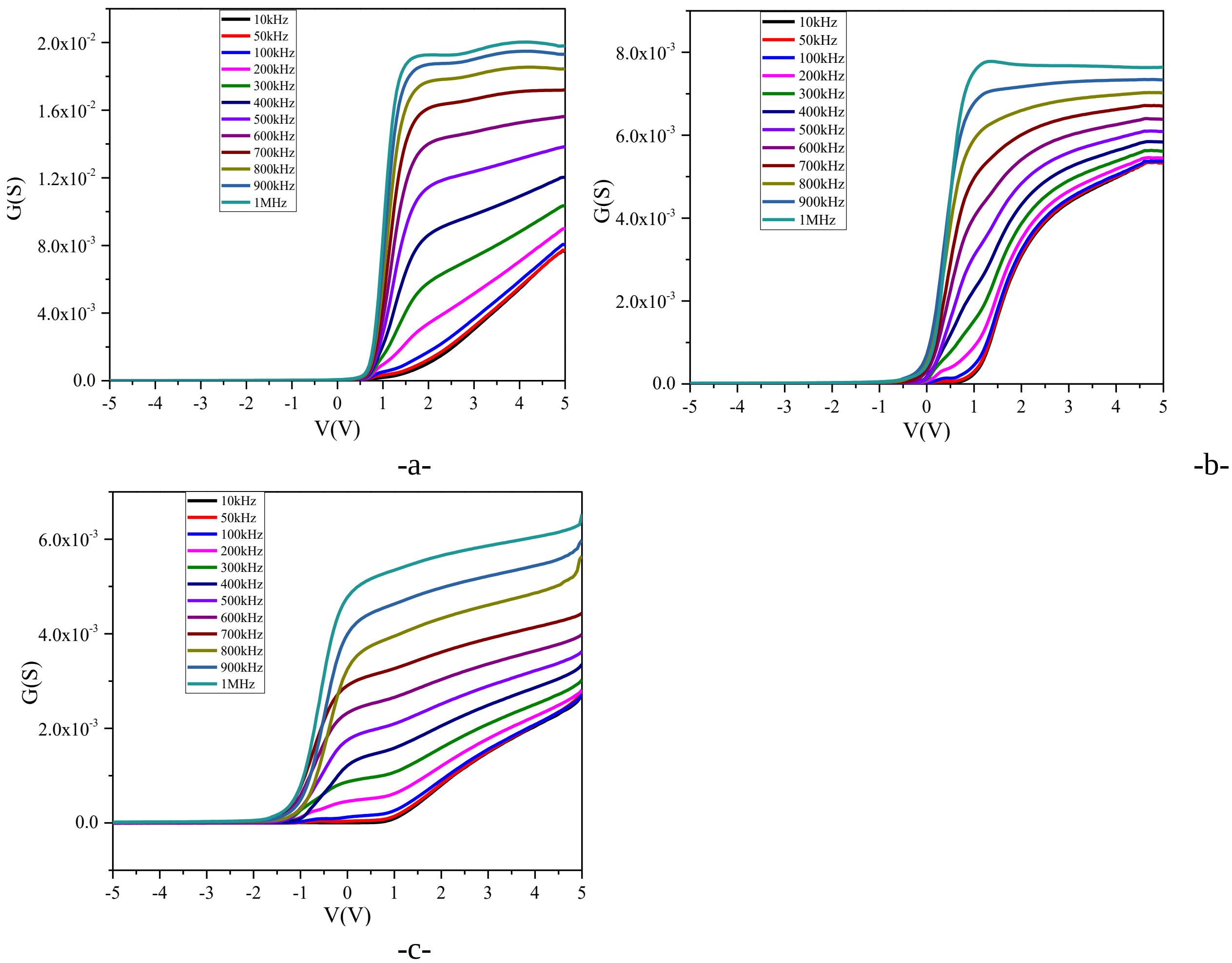

Figure 2: G– V characteristics of pure TiO_2 (a), 0.5 mol ZnO doped 2.5 TiO_2 (1:5 molar rate) (b), and 1 mol ZnO doped 2 mol TiO_2 (1:2 molar rate) (c) photodiodes.

C - V and G - V plots illustrate frequency dependent characteristics, G_{adj} (corrective conductance) and C_{adj} (corrective capacitance) and of the pure TiO_2 photodiodes, 1:5 and 1:2 ZnO:TiO_2 nanocomposite thin films were assessed by the following formula

$$C_{adj}=\frac{[G_m{}^2+(wC_m)^2]C_m}{a^2+(wC_m)^2} \tag{1}$$

and

$$G_{adj}=\frac{[G_m{}^2+(wC_m)^2]a}{a^2+(wC_m)^2} \tag{2}$$

DOI: 10.34186/klujes.997005 *Geliş Tarihi:17.09.2021* *Kabul Tarihi:22.11.2021*

Where "G_m" and "C_m" are measured conductance and measured capacitance and,"ω " is frequency, and "α" is variable parameter [21]

Calculated Corrective capacitance – Voltage (C_{adj} -V) graphs were presented in Figure 3. Peaks were identified for low signal frequencies. The peaks could be seen in positive region. Increased frequency result in a shift in the peaks. In addition, increased ZnO doping also cause a shift in the peaks observed at the C_{adj} -V graphs.

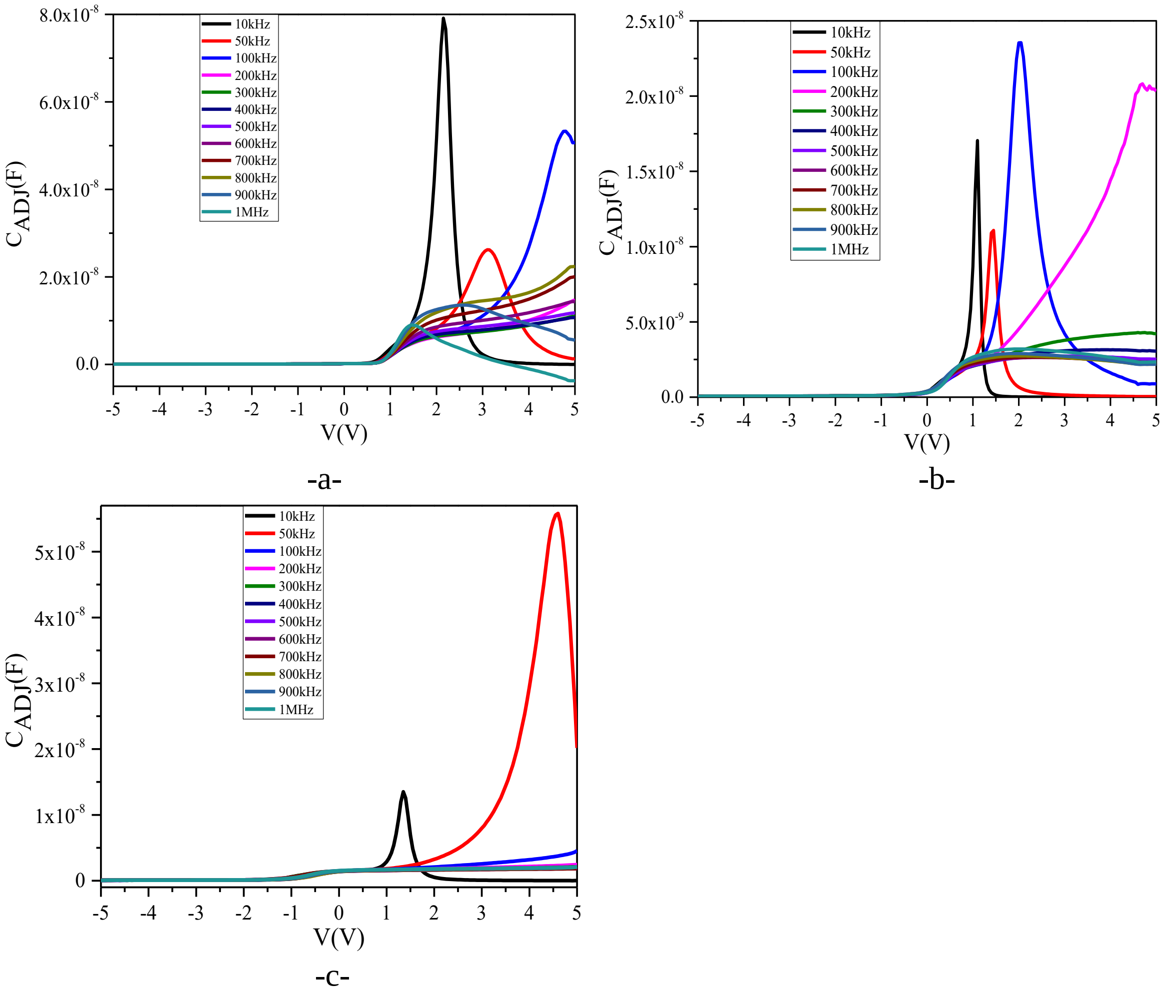

Figure 3: Cadj– V characteristics of pure TiO_2 (a), 0.5 mol ZnO doped 2.5 TiO_2 (1:5 molar rate) (b), and 1 mol ZnO doped 2 mol TiO_2 (1:2 molar rate) (c) photodiodes.

Calculated Corrective conductance – Voltage (G_{adj} - V) plots were given in Figure 4. Apparent peaks were identified in all graphs. The position of the peaks alters depending on the doping rate of ZnO. The position of the peaks observed in G_{adj} -V graphs slightly shift towards the negative

DOI: 10.34186/klujes.997005 *Geliş Tarihi:17.09.2021* *Kabul Tarihi:22.11.2021*

region when the ZnO dopant rate was increased. Peaks show frequency dependent characteristics. Decreased corrective conductance was seen with enhancing frequency values. The case also confirms our previous assumptions that high AC signal frequency helps electrons to move in diodes. The frequency dependent G_{adj} - V characteristics of the diodes also illustrate the existence of interface state; therefore, interface state characteristics of the diodes were also investigated.

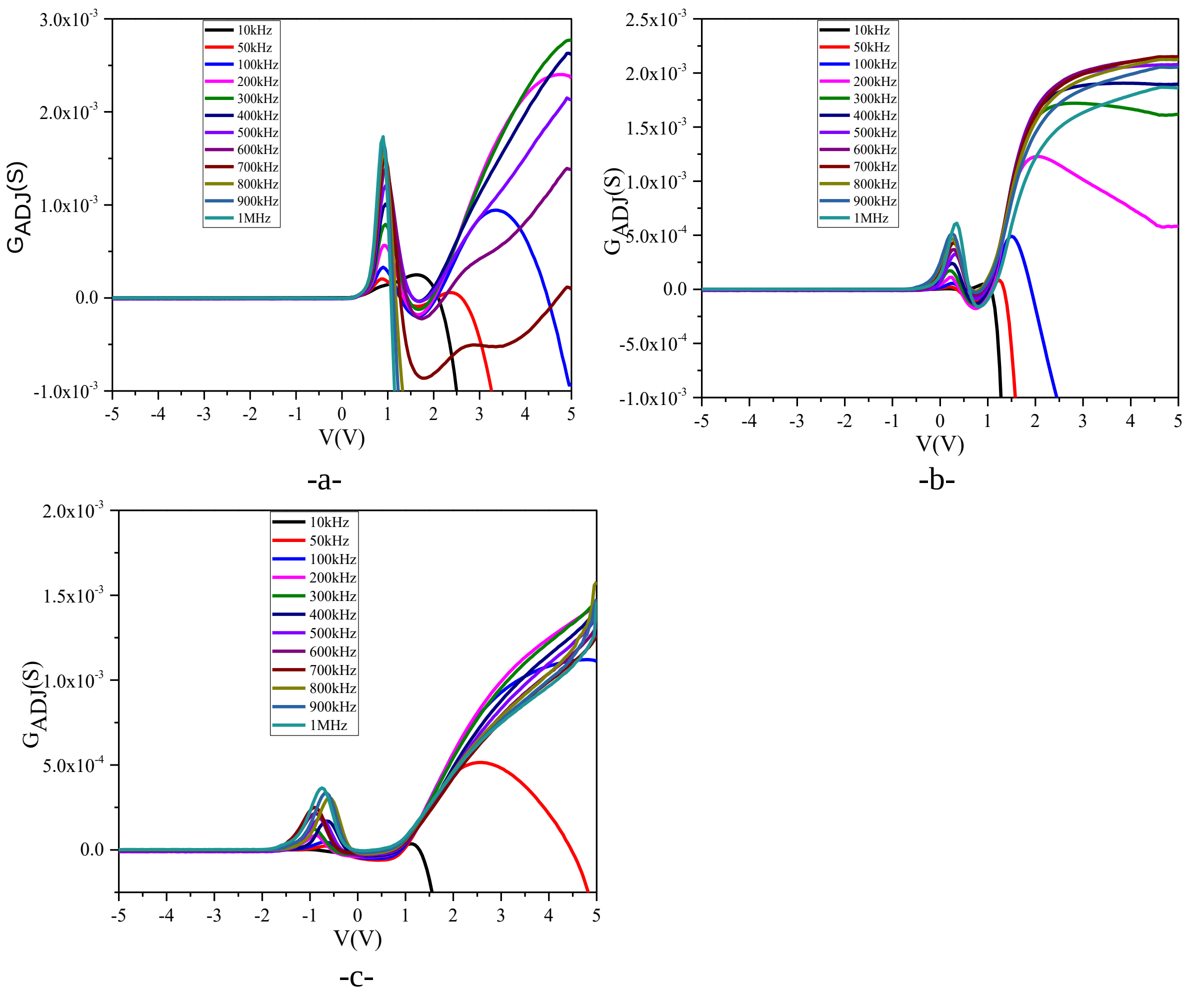

Figure 4: G_{adj}– V characteristics of TiO_2 (a), 0.5 mol ZnO doped 2.5 TiO_2 (1:5 molar rate) (b), and 1 mol ZnO doped 2 mol TiO_2 (1:2 molar rate) (c) photodiodes.

To evaluate the D_{it} (density of interface states) following formula was used.

$$D_{it}=\left(\frac{2}{qA}\right)\left[\frac{(G_{max}/w)}{[(G_{max}/wC_{ox})^2+(1-C_m/C_{ox})^2]}\right]$$

where, the measured capacitance is "C_m", A is the thin film surface area, the measured

DOI: 10.34186/klujes.997005 *Geliş Tarihi:17.09.2021* *Kabul Tarihi:22.11.2021*

conductance is "G_m", capacitance of the insulator layeris "C_{ox}", ω is frequency which is taken as 2πf [22].

D_{it} – f characteristics of the diodes were presented in Figure 5. Figure 5 shows that the D_{it} affected by signal frequency where the lower D_{it} was calculated for augmented frequency. ZnO dopant also affects the D_{it} characteristics of the photodiodes. The highest D_{it} was measured for pure TiO_2 photodiodes that ZnO doping decrease the measured density of states. The highest density of states was found to be $8x10^{12}$ $eV^{-1}cm^{-2}$, $4x10^{11}$ $eV^{-1}cm^{-2}$ and $2.4x10^{11}$ $eV^{-1}cm^{-2}$ for pure TiO_2 photodiodes, 1:5 and 1:2 ZnO doped TiO_2 photodiodes, respectively. Results illustrate that ZnO doping decreases the number of the measured density of state.

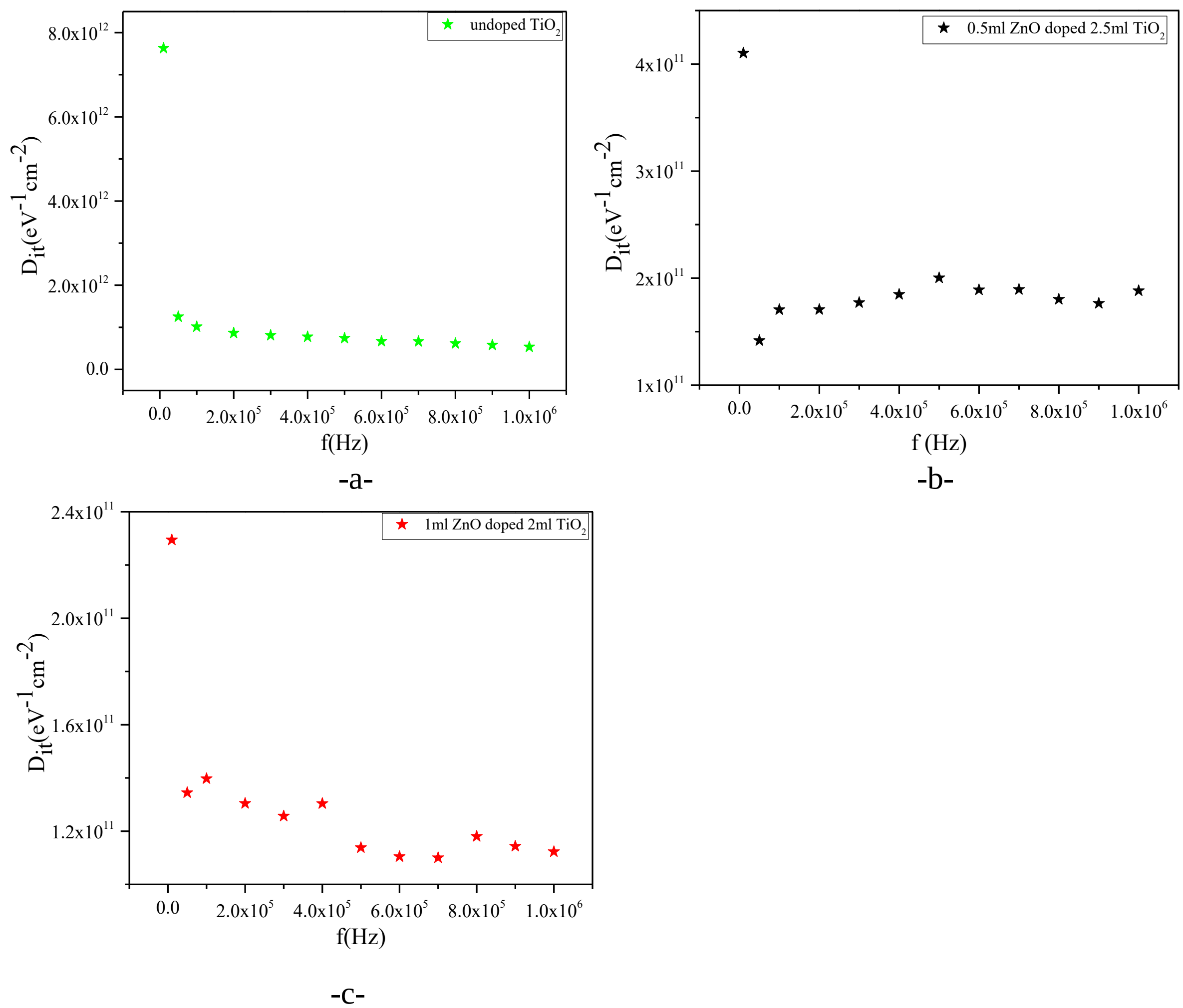

Figure 5: D_{it} – f characteristics of pure TiO_2 (a), 0.5 mol ZnO doped 2.5 TiO_2 (1:5 molar rate) (b), and 1 mol ZnO doped 2 mol TiO_2 (1:2 molar rate) (c) photodiodes.

4. CONCLUSION

Sol gel method was used in the preparation of TiO_2 and ZnO doped TiO_2 nanocomposite thin films. In our previous paper, photovoltaic properties of the photodiodes confirmed where photodiodes response to the visible light. In the paper, enhanced photocurrent and enhanced photocapacitance were observed for augmented illumination intensity. Such a case was confirmed that nanocomposite thin films have the potential to be used in solar tracking applications. In the present work, electrical properties were investigated under various frequencies. Increased AC frequency enhanced the electrical behaviours. Results illustrated that the electrical behaviours of the nanocomposite thin films closely related to the AC frequency properties which were found to be related to the D_{it}. The D_{it} investigations confirmed that increased frequency decreases the D_{it}.

ACKNOWLEDGEMENT

We would like to acknowledge that a part of this work was supported by KLUBAP 202, KLUBAP 207 and KLUBAP 209.

REFERENCES

[1] McNally, M. J., Koç M. M., Torricelli, G. and Von Haeften, K., Nanoscale Stripe Arrays Templated on Moiré Patterns in Graphite, Surf. Sci., vol. 646, no. April 2016, pp. 108–113, 2016.

[2] Kurnaz Yetim, N. et al., Structural, Electrochemical and Optical Properties of Hydrothermally Synthesized Transition Metal Oxide (Co3O4, NiO, CuO) nanoflowers, J. Mater. Sci. Mater. Electron., vol. 31, no. 15, pp. 12238–12248, 2020.

[3] Kurnaz Yetim, N., Aslan, N. and Koç, M. M. Structural and Catalytic Properties of Fe3O4 Doped Bi2S3 Novel Magnetic Nanocomposites: P-Nitrophenol Case, J. Environ. Chem. Eng., vol. 8, no. 5, p. 104258, 2020.

[4] Kurnaz Yetim, N., Kurşun Baysak, F., Koç, M. M. and Nartop, D., Characterization of Magnetic Fe3O4@SiO2 Nanoparticles with Fluorescent Properties for Potential Multipurpose Imaging and Theranostic Applications J. Mater. Sci. Mater. Electron., vol. 31, no. 20, pp. 18278–18288, 2020.

DOI: 10.34186/klujes.997005 Geliş Tarihi:17.09.2021 Kabul Tarihi:22.11.2021

[5] Aktas, S., Thornton, S. C., Binns, C. and Denby, P., Gas Phase Synthesis of Core-Shell Fe@FeOx Magnetic Nanoparticles into Fluids, J. Nanoparticle Res., vol. 118, p. 365, 2016.

[6] Khan, I., Saeed, K. and Khan, I., Nanoparticles: Properties, Applications and Toxicities, Arabian Journal of Chemistry, vol. 12, no. 7. Elsevier B.V., pp. 908–931, 01-Nov-2019.

[7] Qu, F., Wang, Y., Liu, J., Wen, S., Chen, Y. and Ruan, S., Fe3O4-NiO Core-Shell Composites: Hydrothermal Synthesis and Toluene Sensing Properties, Mater. Lett., vol. 132, pp. 167–170, Oct. 2014.

[8] Kurnaz Yetim, N., Hidrotermal Olarak Sentezlenen Çiçek Benzeri NiO@Fe3O4'ün Katalitik Özellikleri, Düzce Üniversitesi Bilim ve Teknol. Derg., vol. 8, no. 3, pp. 1964–1974, Jul. 2020.

[9] Kurnaz Yetim, N., Kurşun Baysak, F., Koç, M. M. and Nartop, D., Synthesis and Characterization of Au and Bi2O3 Decorated Fe3O4@PAMAM Dendrimer Nanocomposites for Medical Applications, J. Nanostructure Chem., pp. 1–11, Feb. 2021.

[10] Kavousi, F., Goodarzi, M., Ghanbari, D. and Hedayati, K., Synthesis and Characterization of a Magnetic Polymer Nanocomposite for the Release of Metoprolol and Aspirin, J. Mol. Struct., vol. 1183, pp. 324–330, May 2019.

[11] Endo, T., Yoshimura, T. and Esumi, K., Synthesis and Catalytic Activity of Gold-Silver Binary Nanoparticles Stabilized by PAMAM Dendrimer, J. Colloid Interface Sci., vol. 286, no. 2, pp. 602–609, Jun. 2005.

[12] Liu, H. et al., Facile Formation of Folic Acid-Modified Dendrimer-Stabilized Gold–Silver Alloy Nanoparticles for Potential Cellular Computed Tomography Imaging Applications, Analyst, vol. 7, no. 138, pp. 1979–1987, 2013.

[13] Singh, K. et al., In Situ Green Synthesis of Au/Ag Nanostructures on a Metal-Organic Framework Surface for Photocatalytic Reduction of P-Nitrophenol J. Ind. Eng. Chem., vol. 81, pp. 196–205, Jan. 2020.

[14] Lamei, K., Eshghi, H. Bakavoli, M., Rounaghi, S. A. and Esmaeili, E. Carbon Coated Copper Nanostructures as a Green and Ligand Free Nanocatalyst For Suzuki Cross-Coupling Reaction, Catal. Commun., vol. 92, pp. 40–45, Mar. 2017.

[15] Hariharan, C., Photocatalytic Degradation of Organic Contaminants in wWater by ZnO Nanoparticles: Revisited, Appl. Catal. A Gen., vol. 304, no. 1–2, pp. 55–61, May 2006.

[16] Aslan, N. et al., Ti Doped Amorphous Carbon (Al/Ti-a:C/p-Si/Al) Photodiodes for Optoelectronic Applications, J. Mol. Struct., vol. 1155, pp. 813–818, 2018.

DOI: 10.34186/klujes.997005 Geliş Tarihi:17.09.2021 Kabul Tarihi:22.11.2021

[17] Koç, M. M., Photoelectrical Properties of Solar Sensitive CuO Doped Carbon Photodiodes, J. Mol. Struct., vol. 1208, p. 127872, May 2020.

[18] Coşkun, B. et al., Optoelectrical Properties of Al/p-Si/Fe:N Doped ZnO/Al Diodes, Thin Solid Films, vol. 653, pp. 236–248, May 2018.

[19] Uyar, S., Coşkun, B., İlhan, M. and Koç, M. M., Optoelectronic Properties of ZnO:TiO2 Nanocomposite Thin Films, J. Mater. Electron. DEVICES, vol. 5, no. 1, pp. 21–27, Sep. 2021.

[20] Özden, S. and Koç, M. M. Wet-Chemical Etching of GaAs(211)B Wafers for Controlling the Surface Properties, Int. J. Surf. Sci. Eng., vol. 13, p. 79, 2019.

[21] Nicollian E. H. and Goetzberger, A., The Si-SiO2 Interface-Electrical Properties as Determined by the Metal-Insulator-Silicon Conductance Technique, Bell Syst. Tech. J., vol. 46, no. 6, pp. 1055–1133, Jul. 1967.

[22] Yakuphanoglu, F. and Aslam Farooq, W., Photoresponse and Electrical Characterization of Photodiode Based Nanofibers ZnO and Si, Mater. Sci. Semicond. Process., vol. 14, no. 3–4, pp. 207–211, Sep. 2011.