

RESEARCH ARTICLE

Structural and Electrical Properties of Al/ZnO_{NRs}/ZnO/p-Si/Al Type MOS Diodes

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ABSTRACT

In this study, Al/ZnO_{NRs}/ZnO/p-Si/Al type MOS diodes with ZnO nanorods, synthesized by hydrothermal method, were fabricated. The fabricated devices were named as MD₁₀₋₂, MD₁₀₋₄, MD₂₀₋₂, MD₂₀₋₃ and MD₂₀₋₄ according to their molar concentration (mM) and the time they were kept in hydrothermal solution (hours). They were produced in different concentrations and times to optimize the electrical properties of the device. The basic electrical parameters of the fabricated structures were investigated by capacitance-voltage (C-V) and conductance-voltage (G/ω-V) measurements at a frequency of 10 kHz at room temperature. The C⁻²-V curves obtained from these measurements were used to calculate parameters such as the breakdown voltage (V_o), zero-supply potential barrier height (Φ_{Bo}), depletion layer width (W_D). Looking at the C-V curves for all structures, it was clearly seen that the aggregation, depletion and reversal regions were formed on the MOS-type diodes. In addition, the effect of interfacial states and series resistance (R_s) were analyzed from the curves. At the same time, the voltage dependent R_s values of MOS type diodes were calculated using the admittance method. According to the calculated data, it was observed that the lower series resistance value was found in MD₁₀₋₂ with low molar concentration and time. For this reason, it was said that the effect of interfacial states decreased in the MD₁₀₋₂ device compared to other structures. Finally, the diameter and arrangement of the nanorods were examined by scanning electron microscopy (SEM) of the MOS type diodes. SEM images showed the formation of well-aligned ZnO nanorods for all the fabricated structures.

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1. Introduction

The metal-oxide-semiconductor (MOS) structure was first proposed in 1959 by Moll, Pfann and Garrett as a voltage-controlled varistor (Sze et al., 2021). In 1960, Ligenza and Spitzer (1960) thermally grown silicon dioxide (SiO₂) on Si semiconductor. This groundbreaking experimental success immediately led to the first report of the Metal-oxide-semiconductor field effect transistor (MOSFET) by Kahng and

Atalla (Sze et al., 2021). The MOS structure, which is used as an energy storage in electronic circuits due to the dielectric properties of the oxide layer in its structure, is the basic structure of modern semiconductor technology (Ohning, 1992; Saghruni et al., 2015).

Zinc oxide (ZnO) is widely used for sensor and optoelectronic device applications due to its wide direct energy band gap (3.37 eV) and high exciton binding energy (60 MeV) at room temperature (30 °C) (Faraz et al., 2020; Demirezen et

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al., 2021). Optoelectronic nanostructured materials have attracted attention due to their superior optical and electrical properties that enable their use in many technological applications (Faisal et al., 2020; Asvini et al., 2023). Recently, vertically oriented ZnO nanostructures in the form of nanorods have attracted increasing attention in applications such as solar cells, field effect transistors, etc. due to their many advantages such as the splitting direction of light absorption, large aspect ratios, low recombination rate (Shi et al., 2010; Yatskiv et al., 2014; Güler et al., 2023).

Yang et al. (2023) grew Co^{2+} doped ZnO nanodispersed ZnO nanodispersions by hydrothermal method and obtained a structure with visible light photocatalysis and oil/water separation, providing a potential treatment strategy for industrial wastewater. Abutalib (2019) stated that the increase in dc and ac conductivities of nanocomposite samples obtained with ZnO nanorods of different diameters prepared by chemical vapor deposition (CVD) makes it a potential candidate for electrochemical device applications. Aspoukeh et al. (2022) discussed methods for the production of ZnO nanorods.

In this study, $\text{Al/ZnO}_{\text{NRs}}/\text{ZnO/p-Si/Al}$ type MOS diodes were fabricated by synthesizing ZnO nanorods on silicon semiconductor by hydrothermal method. In order to optimize the properties of the devices, different molar concentrations and times were used. The structural properties of ZnO NRs were investigated using scanning electron microscopy (SEM). Capacitance-voltage (C-V) and conductance-voltage (G/ ω -V) measurements of the fabricated MOS-type diodes were performed to obtain their electrical properties and the findings were discussed.

2. Materials and Methods

To prepare $\text{Al/ZnO}_{\text{NRs}}/\text{ZnO/p-Si/Al}$ type MOS diodes, p-Si substrates with $\langle 100 \rangle$ surface orientation and $1\text{-}10\ \Omega\cdot\text{cm}$

resistivity were immersed in $\text{HF} + 20\ \text{H}_2\text{O}$ solution. They were then rinsed using deionized water with a resistivity of $18\ \text{M}\Omega$. After cleaning, a $100\ \text{nm}$ thick ZnO seed layer was deposited on the p-type Si substrate using RF sputtering technique under $\text{Ar}:\text{O}_2$ (80:20) gas pressure with $10\ \text{mTorr}$. The RF sputtering system was operated at $100\ \text{W}$ and $50^\circ\ \text{C}$ under a pressure of $1 \times 10^{-6}\ \text{Torr}$. The substrates were then immediately annealed at $600^\circ\ \text{C}$ for 30 minutes. A hydrothermal method was used to form ZnO nanorods on the seed layer. For this, two different solutions of 10 and $20\ \text{mM}$ were prepared. They were immersed in $30\ \text{ml}$ of growth solution consisting of deionized water containing zinc acetate dehydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) and hexamethylenetetramine ($\text{C}_6\text{H}_{12}\text{N}_4$) in equimolar concentrations (1:1). They were kept in an autoclave oven at $90^\circ\ \text{C}$ for 2, 3 and 4 hours. The substrates were then dried in an oven at $90^\circ\ \text{C}$. SEM images of ZnO NR's, taken with 120000 magnification, with almost uniform size and $40\text{-}150\ \text{nm}$ diameter are given in Figure 2. After ZnO nanorods were formed, high purity (99.999%) Al ($100\ \text{nm}$ thick) metal was coated on the backside of p-Si substrate using DC sputtering technique for ohmic contact. The $\text{ZnO}_{\text{NRs}}/\text{ZnO/p-Si/Al}$ devices were annealed at $450^\circ\ \text{C}$ for 20 min to ensure low resistivity contact. Finally, $1\ \text{mm}$ radius Al ($100\ \text{nm}$) rectifier contacts were deposited onto the ZnO NR's using a DC sputtering system (Figure 1). The DC sputtering system is Ar gas with pressure $1 \times 10^{-6}\ \text{Torr}$, partial pressure $40\ \text{mTorr}$, substrate rotation speed $10\ \text{rpm}$ and DC power $135\ \text{W}$. The MOS diodes were classified as MD₁₀₋₂, MD₁₀₋₄, MD₂₀₋₂, MD₂₀₋₃ and MD₂₀₋₄ according to molar concentration (mM) and time (h). Wayne Kerr 6500B instrument was used for capacitance-voltage and conductance-voltage measurements of the devices.

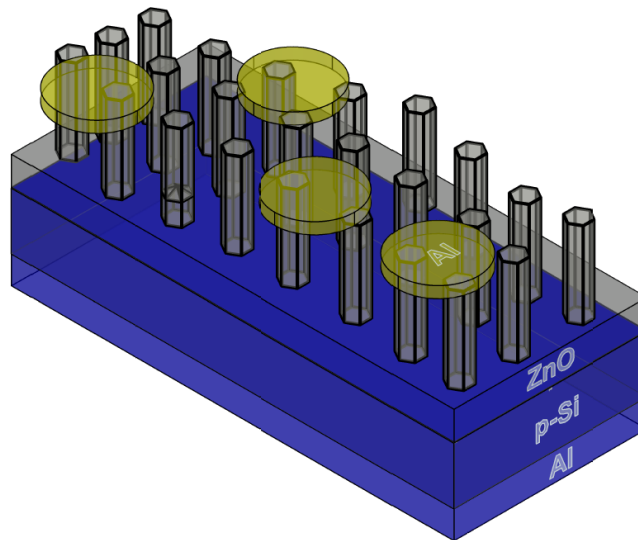


Figure 1. $\text{Al/ZnO}_{\text{NRs}}/\text{ZnO/p-Si/Al}$ MDs.

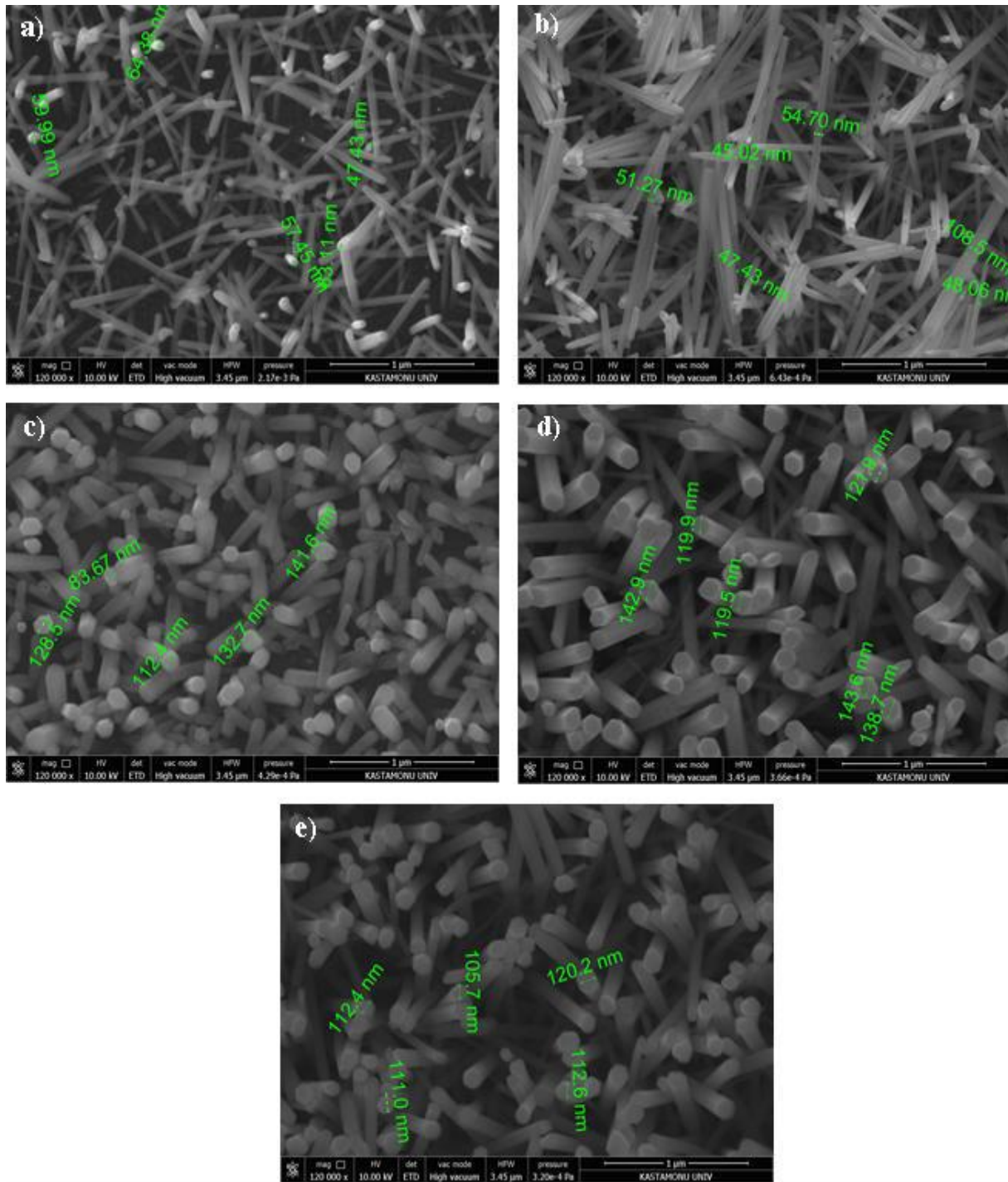


Figure 2. SEM images of ZnO nanorods a) MD10-2 b) MD10-4 c) MD20-2 d) MD20-3 e) MD20-4.

3. Results and Discussion

The capacitance-voltage (C-V) plots of Al/ZnO_{NRs}/ZnO/p-Si/Al type MOS diodes at a fixed frequency of 10 kHz at room temperature are given in Figure 3. C-V measurements are an important method to investigate the interfacial density of the MOS diode and its response to the applied frequency (Ashery et al., 2020). The C-V plots clearly show the regions of

accumulation, depletion and inversion of MOS structures (Grove & Grove, 1967). Although the behavior of the C-V curves is different for each sample, the accumulation regions are in the region of negative voltages and the reversal regions are in the region of positive voltages. The C-V curves show small and large peaks. These peaks indicate that the load flow in the device occurs in several stages (Al-Qrinawi et al., 2021).

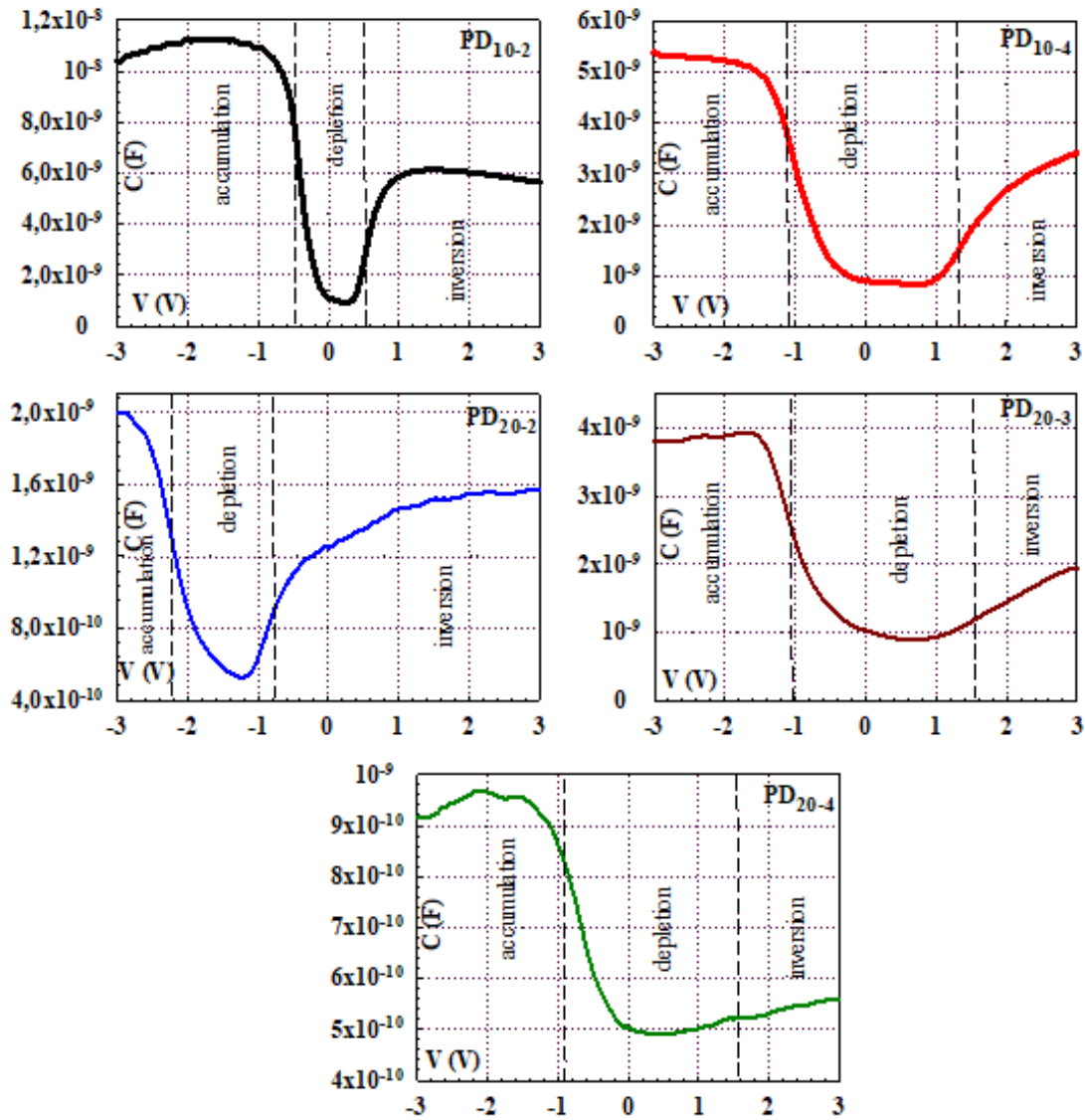


Figure 3. C-V curves of Al/ZnONRs/ZnO/p-Si/Al type MOS diodes.

The change in the C values in the depletion region may be due to the reorganization of the interfacial states at the semiconductor-oxide interface, while the change in the C values in the inversion region may be caused by the effect of R_s . The effects of these factors should be minimized to improve the electrical properties of MOS diodes (Nicollan & Brews, 2002; Aldemir et al., 2020).

G/ω -V curves of Al/ZnONRs/ZnO/p-Si/Al type MOS diodes at a fixed frequency of 10 kHz at room temperature are given in Figure 4. It is seen from the graph that G/ω -V curves depend on the applied voltage. The presence of peaks at the bias voltage of the C-V curves and G/ω -V curves is generally attributed to the presence of the interfacial oxide layer in the structure, the ability of the interfacial states to follow the ac signal at low frequency and R_s (Demirezen et al., 2012).

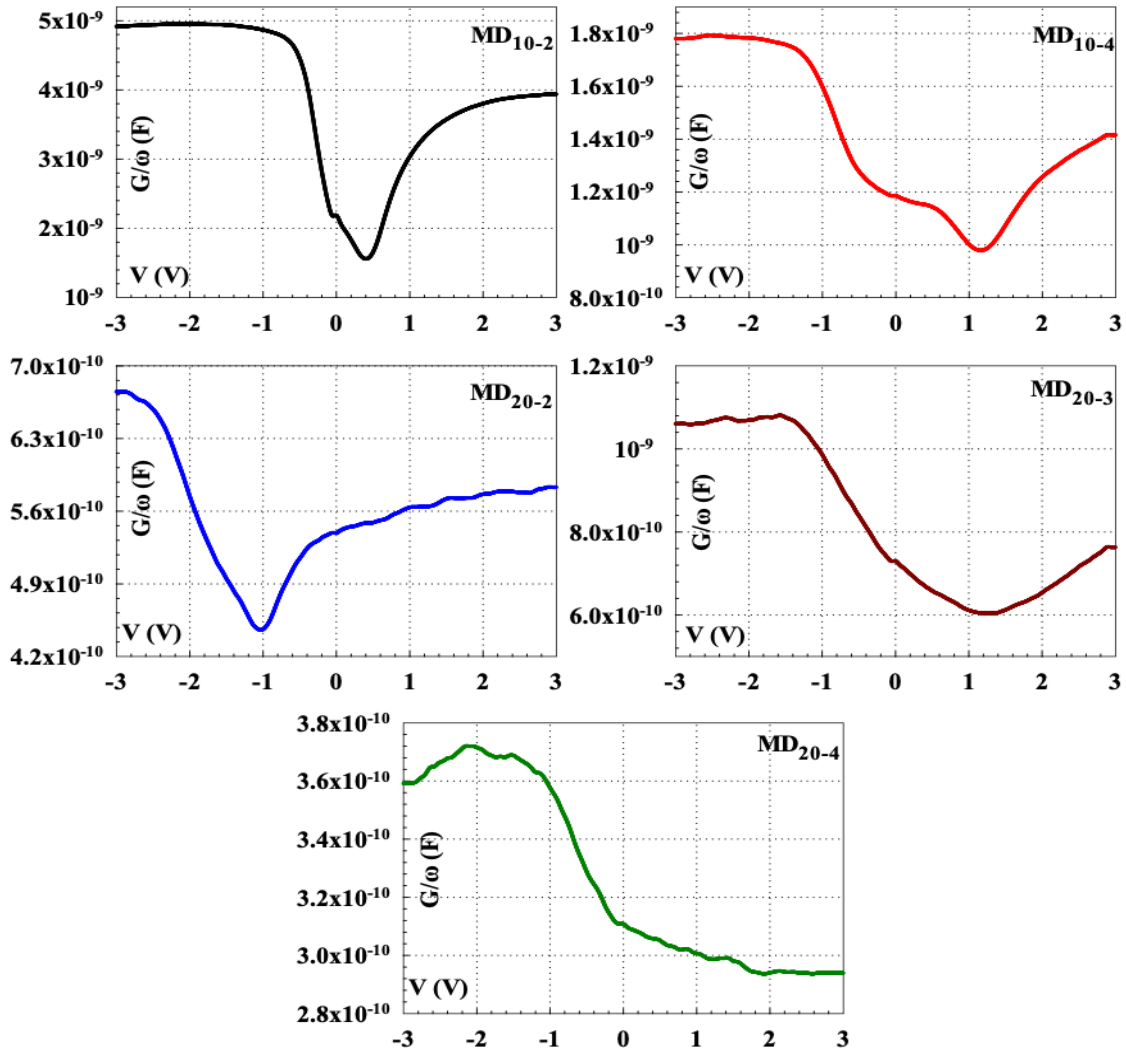


Figure 4. G/ω - V curves of Al/ZnO_{NRS}/ZnO/p-Si/Al type MOS diodes.

C-V and G/ω -V plots of MOS diodes show that they are highly voltage dependent. The voltage dependence is a function

of the Schottky barrier interface density of states and high series resistance (Parlaktürk et al., 2007).

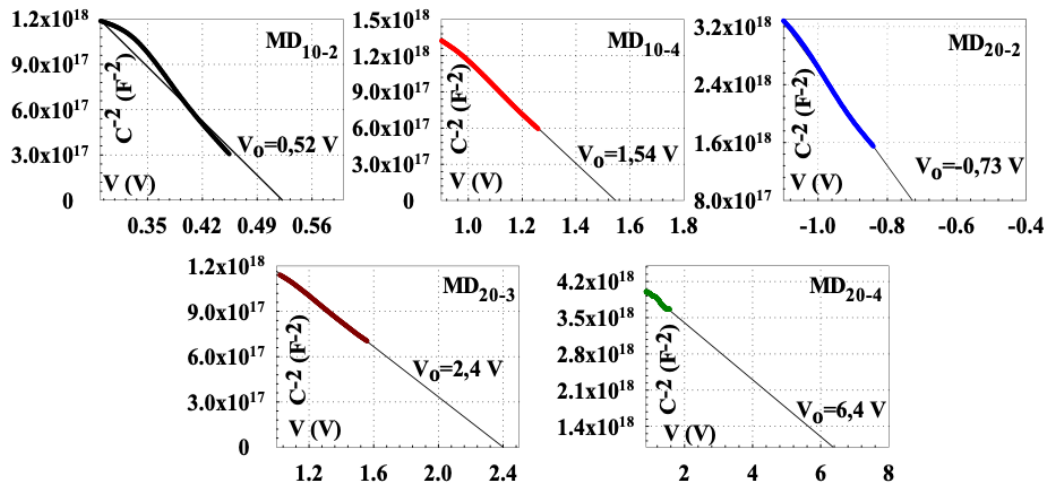


Figure 5. C^2 - V curves of Al/ZnO_{NRS}/ZnO/p-Si/Al type MOS diodes.

C^{-2} -V plots of Al/ZnO_{NRs}/ZnO/p-Si/Al type MOS diodes are given in Figure 5. The graphs show a good linear behavior for each structure. For a Schottky non-ideal diode, the inverse square of the reverse supply capacitance is a linear function of voltage (Sze et al., 2021).

$$C^{-2} = \frac{2(V_R + V_0)}{q\epsilon_s\epsilon_0 N_D A^2} \quad (1)$$

Here, V_R is the applied reverse bias voltage, V_0 is the set-up voltage, q is the Boltmann constant, ϵ_s is the dielectric constant of p-Si semiconductor, ϵ_0 is the dielectric constant of the cavity, N_D is the donor density, A is the area of the diode.

The zero feed potential barrier height Φ_{B0} is calculated from the following equation,

$$\Phi_B(C - V) = V_0 + \frac{kT}{q} + E_F - \Delta\Phi_B = V_D + E_F - \Delta\Phi_B \quad (2)$$

Here, V_D is the zero feed diffusion potential, kT/q is the thermal energy, $\Delta\Phi_B$ is the image force barrier lowering and E_F is the Fermi energy level.

E_F is obtained from the following equation,

$$E_F = \frac{kT}{q} \ln\left(\frac{N_C}{N_D}\right) \quad (3)$$

N_C is the effective density of states in the conduction band of the semiconductor and is obtained from,

$$N_C = 4,82 \times 10^{15} T^{3/2} \left(\frac{m_e^*}{m_0}\right)^{3/2} \quad (4)$$

m_e^* is the effective electron mass, m_0 is the free electron mass and $m_e^*/m_0 = 0.98$.

$\Delta\Phi_B$ is expressed by the following equation (Sze et al., 2021),

$$\Delta\Phi_B = \left[\frac{qE_m}{4\pi\epsilon_s\epsilon_0}\right]^{1/2} \quad (5)$$

E_m maximum electric field is expressed by,

$$E_m = \left[\frac{2qN_D V_0}{\epsilon_s\epsilon_0}\right]^{1/2} \quad (6)$$

The electrical parameters obtained using the above equations for MOS diodes are given in Table 1. The increase in molar concentration also increased the barrier height. This is due to the increase in the density of interfacial states. It is clearly seen that MD₂₀₋₂ exhibits a different behavior in terms of build-up voltage and barrier height. The shift of the set-up voltage to the negative region indicates that the oxide charges in the oxide layer are higher (Özben, 2007).

Table 1. Electrical parameters of Al/ZnO_{NRs}/ZnO/p-Si/Al type MOS diodes obtained from C^{-2} -V plot.

Sample	$N_D(\text{cm}^{-3})$	$E_F(\text{eV})$	$V_0(\text{V})$	$\Phi_B(C-V) (\text{eV})$	$\Delta\Phi_B(\text{eV})$	$W_D(\text{cm})$	$E_m(\text{V/cm})$
MD ₁₀₋₂	$8,28 \times 10^{13}$	0,214	0,52	0,75	0,00615	$3,02 \times 10^{-4}$	$3,45 \times 10^3$
MD ₁₀₋₄	$1,55 \times 10^{14}$	0,199	1,54	1,75	0,00944	$3,79 \times 10^{-4}$	$8,11 \times 10^3$
MD ₂₀₋₂	$4,67 \times 10^{13}$	0,228	-0,73	-0,48	0,00580	$4,76 \times 10^{-4}$	$3,07 \times 10^3$
MD ₂₀₋₃	$4,02 \times 10^{14}$	0,175	2,40	2,58	0,01339	$2,91 \times 10^{-4}$	$1,63 \times 10^4$
MD ₂₀₋₄	$8,92 \times 10^{14}$	0,155	6,4	6,56	0,02088	$3,23 \times 10^{-4}$	$3,97 \times 10^4$

There are many methods in the literature to calculate the series resistance values of MOS diodes. In this study, series resistance values are obtained by using the admittance method with the following equation (Norde, 1979; Özben, 2007; Al-Qrinawi et al., 2021).

$$R_s = \frac{G_m}{(G_m^2 + C_m^2 \omega^2)} \quad (7)$$

The capacitance and conductance values in the strong accumulation region are C_m and G_m , respectively. The R_s -V graph of Al/ZnO_{NRs}/ZnO/p-Si/Al type MOS diodes is given in Figure 6. In line with the data obtained, it is seen from the figure that the series resistance values of MD₁₀₋₂ produced at low

molar concentration and time are lower compared to other structures. This indicates that the interfacial states for MD₁₀₋₂ are reduced and the electrical properties of the device are improved. However, a thicker oxide layer can lead to a larger series resistance (Şenarslan et al., 2020).

It is seen that the voltage dependent R_s values give peaks in the ± 1 V range except MD₂₀₋₂. The peak values of MD₂₀₋₂ are in the negative voltage region. This behavior of R_s is attributed to the restructuring and rearrangement of interfacial states localized between the semiconductor-oxide and in the forbidden energy range (Sze et al., 2021).

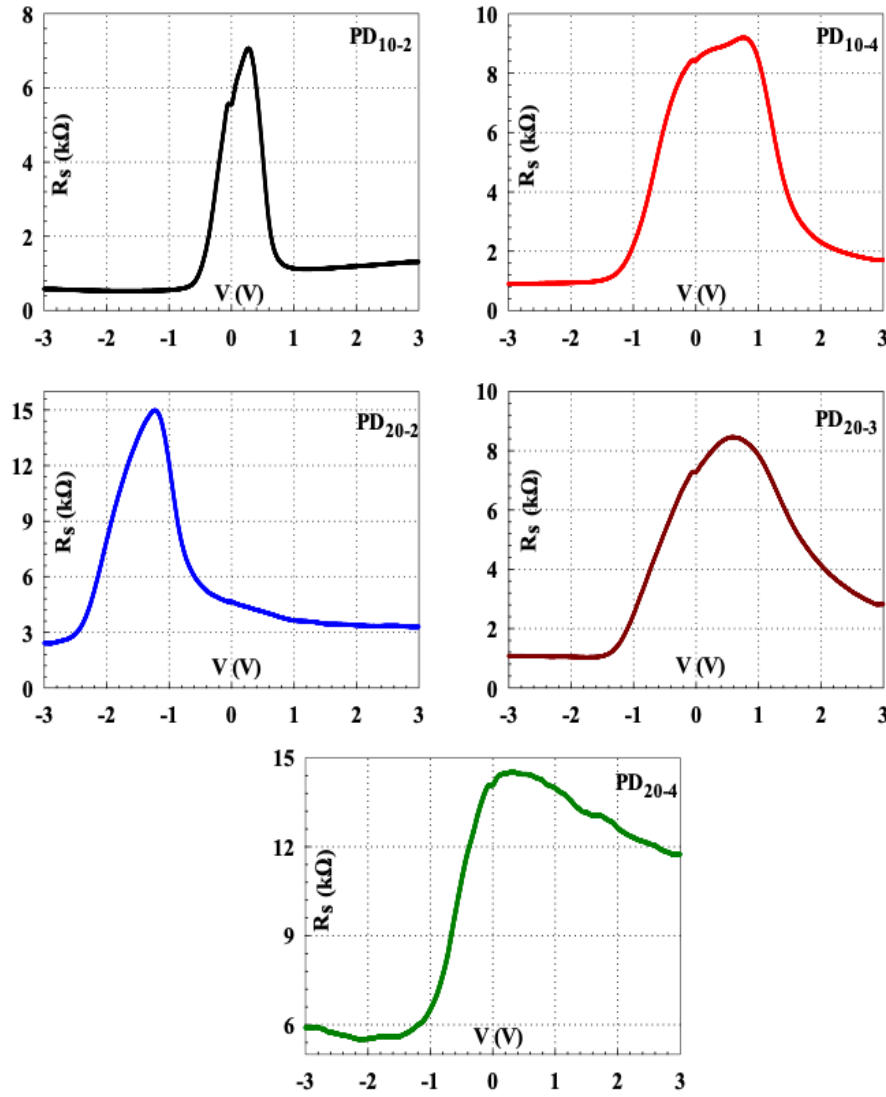


Figure 6. R_s -V curves of Al/ZnO_{NRS}/ZnO/p-Si/Al type MOS diodes.

4. Conclusion

The capacitance and conductivity values of Al/ZnO_{NRS}/ZnO/p-Si/Al MOS type diodes consisting of hydrothermally grown ZnO nanorod arrays were measured at ± 3 V and 10 kHz frequency. C-V and G/ω -V graphs were obtained from the measurement results. Some basic electrical parameters of MOS type diodes were calculated from C^{-2} -V graphs. From the results, it was observed that the values of breakdown voltage V_o and barrier height Φ_B increased with increasing molar concentration. The MD₂₀₋₂ sample, on the other hand, exhibited a different behavior and the drying voltage shifted to the negative voltage region. This was attributed to the higher oxide charges in the oxide layer. The R_s -V characteristics of the MOS type diodes were also obtained using the admittance method. The results show that ZnO nanorods are significantly grown and well aligned by the hydrothermal method. It is also observed that the increase in molar concentrations for nanorod fabrication and the residence

time in the hydrothermal solution significantly affect the performance of MOS-type diodes.

Conflict of Interest

The authors declare that they have no conflict of interest.

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