NANORODS ZnO THIN FILM GROWN BY HYDROTHERMAL METHOD BASED PLANAR AND VERTICAL PD/ZnO SCHOTTKY DIODE CONFIGURATIONS

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Abstract: Manufacture and characterization of this paper for nanorods ZnO based planar and vertical Schottky diodes is presented. The ZnO thin film was grown on n-Si- $<100>$ substrates by the hydrothermal process. The performance of the planner Pd/ZnO/Al and Pd/ZnO/Si/Ti/Al vertical diode configurations were analyses and compared. Palladium, titanium, and aluminum have been deposited by thermal evaporation use masks of metal. The crystalline structure and surface morphological details for thin films for ZnO nanorods were described by using (XRD) and (SEM). By applying voltage range from -2 V to 2 V Was measured (I-V) characteristics for two devices. The resulting data for both configurations show a typical exponential relationship between applied voltage and output current for the Schottky barrier diode. According to the measured I-V characteristics electrical parameters are extracted, for example, saturation current, ideality factor, barrier height, and rectification ratio. The simple low-cost nanorods Schottky diodes based on ZnO thin film make them a promising candidate in many electronics and optoelectronic applications.

1. Introduction

Schottky diode is an important device of the metal-semiconductor junctions, which classify as rectifying (Schottky) contact and a non-rectifying (Ohmic) contact [1]. In 1938, the Schottky barrier (SB) model explained by the theory of Schottky-Mott.

This the model assumed that the Schottky barrier formed based on the work function of metal (Φ_m) comparative to the electron affinity of the semiconductor (X) [2, 3]. The Schottky barrier established with n-type semiconductor-metal contact, if the work function of metal (Φ_m) greater than the work function of semiconductor (Φ_s), $\Phi_m > \Phi_s$ [3]. Zinc oxide is an intrinsical bandgap (3.37 eV) n-type wide-band semiconductor. The unique electrical and optoelectrical properties of ZnO make it a promising material in many electronic and optoelectronic applications. ZnO is environmentally friendly, cheap, large exaction binding energy (60 m eV), easy to fabricate, and thermally stable. Besides, it can easily procedure different nanostructures such as nanorods, nanoparticles, nanowires, and nanotubes [4]. Nanostructures ZnO has been fabricated by different physical and chemical deposition techniques [5]. Hydrothermal aqueous solution deposition technique is a very simple and tailorable way to achieve nanostructures ZnO [6, 7]. The ZnO Schottky diodes are an effective device for gas sensors, field-effect transistors,

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light-emitting diodes, and photodetectors [8-10]. To achieve good quality ZnO Schottky diodes ZnO uses metals of low oxygen affinity (for example palladium, gold, and platinum), that prevent oxidation at the interface of metal/ZnO [9, 11]. Many research papers on Pd/ZnO Schottky contacts have been reported grown by various techniques [12]. In the present paper, the investigated of the fabrication Schottky contact configurations and characterization which planner Pd/ZnO/Al and the vertical Pd/ZnO/Si/Ti/Al. A comparative study of two configurations is presented. This paper focuses on nanorods ZnO thin film that deposition by hydrothermal process. Furthermore, the thermal evaporation method is used to metalize Pd, Ti, and Al metal contact through the metal in the shape of rectangular ($2 \times 4 \text{ mm}^2$). For both configurations, electrical parameters were obtained using I-V characteristics. These performance parameters were ideality factor, saturation current, barrier height, and rectification ratio.

2. Experiment Work

In this section, the experimental work is presented. The Si substrate samples with a thickness of $380 \text{ }\mu\text{m}$ with the resistivity of $5 \text{ }\Omega\cdot\text{cm}$. The Schottky diodes manufacture pass through five steps respectively; cleaning substrates, synthesize seed layer, growth ZnO, mask fabrication, and metallization. Three different metals Pd, Al, and Ti are used in the metallization process. The fabrication steps are presented in detail in the following subsection.

2.1. Cleaning and Synthesize of Seed layer:

First, the n-Si <100> substrate 2-inch diameter is partition into four. Then clean it in two steps: The first step includes cleaning the substrates via isopropanol alcohol ($\text{C}_3\text{H}_8\text{O}$) to dispose of the organic remains by hand and immersed substrates in trichloroethylene ultrasonic bath for

five minutes, then dip in acetone for one minute. The second step of the process, immersed substrates in a beaker contains 60 mL of hydrogen peroxide (H_2O_2) and 40 ml of sulphuric acid (H_2SO_4) to cast off the organic residues. Later, the substrates cleaning in de-ionized water for five minutes. The substrates will be dried by a dry sterilized paper to take away deionized water [13]. After completing cleaning the samples, the thin seed layer deposited with a sol-gel spin coating technique on silicon substrates. The seed layer solution prepares of ZnO solution. The solution composite of 0.005 M of zinc acetate dehydrates ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) melt in 20 mL of isopropanol ($\text{C}_3\text{H}_8\text{O}$). The solution stirred for three hours at 50°C to produce a homogeneous clear solution. The resultant solution was coated on silicon substrates via spin coater at the rate of spinning speed 3000 rpm for 50 s at room temperature to prepare the ZnO seed layer. After that, the coated substrates were heated for 10 minutes at 100°C to cast off the residual solution, and then the substrates had been cooled to room temperature. Then, substrates were annealed via oven (model: Huppert's Deluxe Furnace) at 300°C for one hour [14].

2.2. ZnO Nanorods Deposition Technique

To grow the ZnO nanorods, the hydrothermal technique is utilized, after the seed layer has been formed. In the process of preparing the nanorods, a solution has contained two solutions mixed, the first solution contained 0.05 M for Zinc nitrate Hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) at room temperature, mixed in 20 ml deionized water which is stirred for 30 minutes. While the second one is containing 0.05 M Hexamethylenetetramine (HMTA) ($\text{C}_6\text{H}_{12}\text{N}_4$) solved in 20 ml deionized water which is stirred for the same conditions. the weight of zinc nitrate and HMATA is; 0.297 g and 0.140 g respectively. The two solvent solutions are mixed and stirred for 20 minutes to be homogenous. The silicon substrates coated by the ZnO seeds layer are immersed in the prepared homogenous solution and kept in an autoclave. The autoclave is heated for 5 h at 90°C [14, 15].

2.3. Contacts

After the growth of the ZnO layer by the hydrothermal method, three metals aluminium, palladium, and titanium are utilized to metalized nanorods ZnO/Si samples via masks. The metallization is done via a molybdenum mask with dimensions of 20 mm × 20 mm which has a rectangular hole of 4 mm × 2 mm which uses thermal vacuum evaporation (model: VSAAMA VAC) system. (Al) and (Pd) is deposited at the top of thin ZnO films are Schottky electrodes thickness 200 nm and distance between 100 μm. It stabilized at the top of the ZnO semiconductor. The thickness of (Ti) and (Al) are 100 nm and 200 nm respectively as layers on the bottom of the sample. The scheme for vertical and planar fabricated devices is shown in Figure.1.

Figure.1 representation of schematic diagram for (a) vertical and (b) planar Schottky diode

3. Characterization

The ZnO thin film morphology and the crystal structures are explored by the X-Ray Diffraction (XRD) and Scanning Electron Microscope (SEM) techniques. The structural characteristics for prepared samples are calculated using the XRD technique including crystallinity and lattice parameters also defects [16]. The specifications of the X-ray diffractometer device are (typical: XRD-6000, lab X) with 2θ starting at (20° to 60°)

and Cu Kα radiation ($\lambda = 1.5405 \text{ \AA}$). by utilizing Keithley (SCS-4200) device to calculated characteristics of I-V are produced from fabricated diode Schottky configurations which are a planar (Pd/ZnO/Al) and a vertical (Pd/ZnO/Si/Ti/Al). The range of applied voltages at room temperature varies from -2 V to 2 V, with step 0.1 V.

4. Experimental results and discussion

4.1. crystalline surface structure and morphology for ZnO Thin Film

The inset of Fig. 2, shows the XRD pattern with an SEM image for the ZnO layer deposited on n-silicon <100> substrates. The SEM image demonstrates that the hexagonal nanorods are the main form of nanostructure of ZnO patterns. The nanorods arranged perpendicular to the surface of the substrate as clusters in different directions. Nanorods have different lengths and diameters, the average diameters are approximately 116 nm, whereas the length of the nanorods is approximately 2 μm. The SEM examination is compatible with the XRD pattern which has multiple peaks. This is evidence of ZnO nanorods that are settled in more than one direction. XRD absolute intensity (crystallinity) was determined from the strongest diffraction peak. In the Fig. 3, shown, the XRD pattern appears in which four peaks corresponding to the hexagonal planes ZnO crystal (100), (002), (101) and (110), which are shown in 31.8, 34.52, 36.26 and 56.63 respectively [17]. By using Scherrer equation determine crystallite size (D) in (nm)[18] :

$$D = \frac{K_C \lambda}{\beta \cos \theta} \quad (1)$$

Where K_C is a Scherrer constant equal to 0.9, The wavelength (λ) for an x-ray source equal to 1.5406 (nanometer), the FWHM (β) (radians) is the full width of a maximum half and the θ is a maximum position (radians).

Figure.2 XRD pattern with the SEM image for the ZnO layer Precipitated by the hydrothermal process above silicon substrates.

4.2. The Electrical Characteristics and Performance for Pd/ZnO Schottky contact Fabricated.

Fig .3 and Fig .4 show I-V Characteristics I- of vertical Pd/ ZnO/ Si/ Ti /Al and Planar Pd / ZnO/Al Schottky contacts were determined by experimentally testing. The performance I-V characteristics parameters extracted obtained from is calculated according to the thermionic emission theory.

Rectification ratio RR was measurement by (I_F/I_R) at ± 2 V (I_F forward current at $V= 2$ V and I_R reverse current at $V= -2$ V), its obtained 79.13 for vertical and 137.58 for planar Schottky contact. The difference in RR is due to an improvement characteristic of planar than vertical and the lower reverse current of a planar comparison with the vertical Schottky barrier diode. The resulting data can be analyzed in the general by using the Eq. (2) [3, 19]:

Figurer.3 I-V characteristics for the vertical Schottky contact linear, and semi-log curve.

Figure.4 I-V Characteristics of planar Schottky contact linear, and semi-log curve.

$$I = \left[AA^* T^2 \exp \left(\frac{-q\Phi_B}{kT} \right) \right] \left[\exp \left(\frac{qV}{nkT} \right) - 1 \right] \quad (2)$$

A is the contact area of Schottky diode, A^* is the effective constant of Richardson, (theoretically, $A^*=32 \text{ cm}^{-2} \text{ K}^{-2}$ value of ZnO using ($m^* = 0.27m_0$)), k is constant of Boltzmann, T is the absolute temperature, n is the ideality factor, Φ_B is a barrier height, q is an electron charge. The equation can be approximated by applying the condition ($\exp \left(\frac{qV}{nkT} \right) \gg 1$) [20].

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

$$I = I_s \left(\frac{qV}{nkT}\right) \quad (4)$$

The saturation current I_s calculating from intercept $\ln(I)$ vs V with Y-axis under forwarding bias at $V=0$ for a semi-log curve. The saturation current is found to be 5.01×10^{-7} A and 1.42×10^{-6} A for vertical and planar diodes respectively. The Ideality factor(n) equation is obtained by deriving equation (4), where the derivative is equal to slope value for $\ln(I)$ vs V , according to Eq.5, the ideality factor is calculated [21]:

$$\frac{d\ln(I)}{dV} = \frac{q}{nkT} \quad n = \frac{q}{kT} \times \frac{1}{\text{slop}} \quad (5)$$

Barrier Height (BH) can be determinate by using equation (6) [11]:

$$\Phi_B = \frac{kT}{q} \ln\left(\frac{AA^*T^2}{I_s}\right) \quad (6)$$

The values of the ideality factor are found to be, 3.24 and 4.83 for vertical and planar Schottky diode, respectively. The barriers heights are estimated to be 0.94 eV and 0.93 eV for vertical and planar Schottky diode, respectively. Calculates theoretical barrier height from Schottky- Mott by using Eq $q\Phi_B = q(\Phi_S - \chi)$ is found to be 1.42 eV, where the work function ($q\Phi_S$) for Pd is equal to 5.17 eV, and the electron affinity for ZnO ($q\chi$) is 3.7 eV [6, 22]. The barriers heights which are calculated from the experimental work are less than theoretical. This indicates that the interface states cannot be neglected; the interface states also affect the ideality factor. The ideality factors for fabricated devices are more than unity for an ideal diode that attributed to many reasons. The mechanism in which the current was transferred through the ZnO thin film which forms the basis of the Schottky diode was not only the thermionic emission. The other mechanism such as recombination carrier recombination, inhomogeneity of barrier, uniform distribution of carriers at interfaces, or the mechanism of transport tunnelling and the surface states must

be considered [13]. The presence of interface oxide at the ZnO and palladium layer during technological operations in the manufacturing of semiconductor devices. Where ZnO is readily creating interface layers with one or two monolayers of thickness between 200 to 400 nm (Adsorbed oxygen, hydroxide, heat, etc..), which results in an average surface level of the surface for ZnO. These status lead to high-value of n and non-ideal Schottky diode [23, 24].

5. Conclusion

In this paper, we fabricated and characterized by the vertical and planar Pd/ ZnO NR thin-film Schottky diodes are presented. The performance parameters estimated and analyzed. The ZnO nanorods thin film has grown with the hydrothermal technique above n-Si <100> substrates. XRD and SEM test results confirmed indicated that ZnO nanorods have high surface quality and structural characteristics. Applying the thermionic emission theory, the electrical parameters were calculated and analyzed for both devices. We found the performance parameters divergence from the ideal thermionic emission theory, concluding that the thermionic emission theory cannot govern the current transport mechanism alone. The electrical parameters estimated for two devices found to be in good agreement with those reported by other researchers.

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Conflict of interest

There is no conflict of interest.

6. References

1. W. Mtangi, "Electrical characterization of ZnO and metal ZnO contacts," University of Pretoria, 2010.

2. W. J. N. Schottky. (1938). "Semi-conductor theory in barrier layers," vol. 26, no. 843, p. 280, 1938.
3. S. M. Sze and K. K. Ng. (2006). Physics of semiconductor devices. John Wiley & sons.
4. M. Willander, O. Nur, N. Bano, and K. J. N. J. o. P. Sultana. (2009). "Zinc oxide nanorod-based heterostructures on solid and soft substrates for white-light-emitting diode applications," vol. 11, no. 12, p. 125020.
5. S. Faraz, H. Noor, M. Asghar, M. Willander, and Q.-u. Wahab. (2009). "Modeling and simulations of Pd/n-ZnO Schottky diode and its comparison with measurements," in Advanced Materials Research, vol. 79, pp. 1317-1320: Trans Tech Publ.
6. Q. Gu et al. (2008). "Au/n-ZnO rectifying contact fabricated with hydrogen peroxide pretreatment," vol. 103, no. 9, p. 093706.
7. B. Coppa et al. (2005). "Structural, microstructural, and electrical properties of gold films and Schottky contacts on remote plasma-cleaned, n-type ZnO {0001} surfaces," vol. 97, no. 10, p. 103517.
8. A. B. Yadav, R. Shankar, R. Kumar, A. Pandey, and S. Jit. (2013). "Analysis of temperature-dependent IV characteristics of Pd/ZnO/n-Si Schottky diode by sol-gel method," in Proc. Int. conf. on Microelectronics, Communications and Renewable Energy, pp. 1-4: IEEE.
9. T. Varma, C. Periasamy, D. J. S. Boolchandani, and Microstructures. (2017). "Performance analyses of Schottky diodes with Au/Pd contacts on n-ZnO thin films as UV detectors," vol. 112, pp. 151-163.
10. D. Somvanshi and S. J. I. E. D. L. Jit. (2014). "Effects of Sn and Zn Seed Layers on the Electrical Characteristics of Pd/ZnO Thin-Film Schottky Diodes Grown on n-Si Substrates," vol. 35, no. 9, pp. 945-947.
11. D. Somvanshi, S. J. J. o. N. Jit, and Optoelectronics. (2014). "Analysis of I-V characteristics of Pd/ZnO thin film/n-Si Schottky diodes with series resistance," vol. 9, no. 1, pp. 21-26.
12. L. Rajan, C. Periasamy, and V. J. P. i. S. Sahula. (2016). "Electrical characterization of Au/ZnO thin film Schottky diode on a silicon substrate," vol. 8, pp. 66-68.
13. G. M. Ali, J. C. Moore, A. K. Kadhim, C. J. S. (2014). Thompson, and A. A. Physical, "Electrical and optical effects of Pd microplates embedded in ZnO thin film based MSM UV photodetectors: A comparative study," vol. 209, pp. 16-23.
14. G. M. J. J. o. A. Ali and Compounds. (2020). "Performance analysis of planar Schottky photodiode based on nanostructured ZnO thin film grown by three different techniques," p. 154859.
15. N. Yu et al. (2014). "Synthesis of ZnO film on P-GaN/Si (111) by one-step hydrothermal method," vol. 550, pp. 206-209.
16. R. Kohli. (2012). "Methods for monitoring and measuring the cleanliness of surfaces," in Developments in Surface Contamination and Cleaning: Elsevier, pp. 107-178.
17. D. Somvanshi and S. Jit. (2014). "Electrical characteristics of Pd/ZnO nanowires (NWs)-based Schottky diodes grown on Zn seed layer coated n-Si substrates," Proc. Int. conf. on Emerging Electronics (ICEE), pp. 1-4: IEEE.
18. N. Shakti and P. J. A. P. R. Gupta. (2010). "Structural and optical properties of sol-gel prepared ZnO thin film," vol. 2, no. 1, p. 19.
19. G. M. Ali, A. Dwivedi, S. Singh, and P. J. p. s. s. c. Chakrabarti. (2010). "Interface properties and junction behaviour of Pd contact on ZnO thin film grown by a vacuum deposition technique," vol. 7, no. 2, pp. 252-255.
20. R. K. Pandey, A. K. Singh, and R. J. A. A. Prakash. (2013). "Enhancement in

- performance of polycarbazole-graphene nanocomposite Schottky diode," vol. 3, no. 12, p. 122120.
21. Y. Kumar, H. Kumr, G. Rawat, C. Kumar, B. N. Pal, and S. Jit. (2016). "Electrical and optical characteristics of Pd/ZnO Quantum dots based Schottky Photodiode on n-Si," in 2016 IEEE International Symposium on Nanoelectronic and Information Systems (iNIS), pp. 214-217: IEEE.
  22. P. N. M. Ngoepe. (2013). "Optoelectronic characterisation of AlGa_N based Schottky barrier diodes," the University of Pretoria.
  23. B. Coppa et al. (2004). "In situ cleaning and characterization of oxygen-and zinc-terminated, n-type, ZnO {0001} surfaces," vol. 95, no. 10, pp. 5856-5864.
  24. N. Zhang, K. Yu, L. Li, and Z. J. A. s. s. Zhu. (2008). "Investigation of electrical and ammonia sensing characteristics of Schottky barrier diode based on a single ultra-long ZnO nanorod," vol. 254, no. 18, pp. 5736-5740.