



# Performance analysis of Schottky diodes based on Bi doped p-ZnO thin films

Brijesh Kumar Singh<sup>a,b</sup>, Shweta Tripathi<sup>a,\*</sup>

<sup>a</sup> Department of Electronics & Communication Engineering, Motilal Nehru National Institute of Technology, Allahabad, 211004, India

<sup>b</sup> Department of Electronics & Communication Engineering, Madanapalle Institute of Technology & Science, Angallu (Village), Madanapalle, 517325, Chittoor District, Andhra Pradesh, India

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## ABSTRACT

In the present paper, Bismuth (Bi) doped ZnO thin film have been deposited using sol gel spin coating technique to produce p-type ZnO films on n-Si substrate. The deposited Bi doped ZnO thin films were characterized using X-ray diffraction (XRD), atomic force microscopy (AFM), hot point probe and hall measurement. The XRD and AFM characterization results shows uniform growth of the film over the entire substrate having polycrystalline nature of the film and Hall measurement and hot point probe method shows p-type nature of the deposited Bi doped ZnO film. Further, Palladium (Pd) and Nickel (Ni) metal contacts have been deposited over separate Bi doped ZnO thin films using vacuum coating method to fabricate Schottky diodes. The current–voltage characteristics have been analyzed by using conventional thermionic emission model, Cheung's method and Norde's technique to calculate the barrier height, ideality factor and series resistance of the fabricated Schottky diodes. From the calculations, it is observed that Cheung's method gives more realistic results for estimating diode parameters.

## 1. Introduction

Semiconductor device technologies depend on metal–semiconductor (M–S) junctions at the nanoscale since it exhibits higher switching speed and lower cut-off voltages compared to conventional p–n junctions [1,2]. The higher switching speed of ZnO predicated Schottky diodes make them captivating for high speed detection purposes. Further, they also possess lower turn-on voltage that is paramount to improve the efficiency of semiconductor devices [3,4]. The magnitude of the barrier height is important to control for the successful development of semiconductor devices so that better functionality can be achieved, this consequently makes it compulsory to understand the M–S junction at the nanoscale. The barrier height (BH) of a M–S interface betokens the difference between the energy position of the semiconductor band edge and the Fermi level of the metal [5,6]. If barrier height is small then saturation current will be large, and forward bias voltage will be smaller. This property makes the Schottky diode preferred choice over other rectifiers for low voltage and high current applications [7]. The rectifying characteristics of M-S nano junctions have been investigated by several researchers indicating improvement in the performance of device in terms of transport process [8]. Further, it has been reported that a Schottky diode possess good rectifying nature regardless the fact that the size of Schottky contact is very small. The rectification characteristics of Schottky diode is correlated to the work function of the metal in somewhat critical manner due to the presence of surface states and interfacial defects [9]. One of the most important characteristics of a Schottky diode is barrier height that depends upon the combination of semiconductor and metal. In respect of n-ZnO based Schottky diodes, several

\* Corresponding author.

E-mail address: [shtri@mnnit.ac.in](mailto:shtri@mnnit.ac.in) (S. Tripathi).

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literature have reported successful fabrication of Schottky diode with different metals [10–14]. However, fewer attempts have been made so far for fabrication of p-ZnO based Schottky contact [15,16]. This is mainly due to unavailability of stable p-ZnO thin film. The literature that have reported n-ZnO based Schottky diode showed lesser barrier height in comparison to p-ZnO based Schottky diodes. Ali et al. [10] reported the Pd/ZnO thin film Schottky contacts based UV photodetector that was grown on p-type Si substrate by sol-gel method. They obtained barrier height of 0.7 eV, and ideality factor of 4 by using conventional thermionic emission model. Somvanshi et al. [11] have reported vertical Pd/n-ZnO thin film Schottky contacts grown on n-Si substrates by thermal evaporation method. They analyzed I-V characteristics of the grown diode by using conventional thermionic emission model, Cheung's method and Norde's technique. Further, they estimated the barrier height as 0.67 eV and 0.67 eV, ideality factor as 2.36 and 5.79 by conventional method and Cheung's method, respectively. However, there is extensive literature for Schottky diodes based on n-ZnO, yet Schottky diodes based on p-ZnO thin films are very limited in numbers. Recently, Agarwal et al. [15] have reported fabrication and characterization of Pd/Cu doped p-ZnO/p-Si and Ni/copper doped p-ZnO/p-Si Schottky devices. They evaluated barrier height of 0.79 eV and 0.802 eV, ideality factor of 2.2 and 1.78 using conventional thermionic emission model and Cheung's method, respectively. Singh et al. [16] reported the electrical characteristics of Au/p-type ZnO Schottky diode synthesized by spin coating sol-gel method. The thermionic emission model gives barrier height  $\sim 0.681$  eV, ideality factor  $\sim 2.3$  and series resistance  $\sim 923\Omega$ . However, Cheung method gives barrier height  $\sim 0.556$  eV, ideality factor  $\sim 2.186$  and series resistance  $\sim 923$ , respectively. As can be observed from the aforementioned literature that barrier height is large for p-ZnO based Schottky diode and ideality factor is smaller for p-ZnO based Schottky diode. In addition to above, p-ZnO based Schottky contact have also reflected better ideality factor and reverse saturation current [15]. Therefore, it can be inferred that p-ZnO based Schottky diodes gives superior performance but somehow limited in reports due to the difficulty in obtaining p-ZnO. In view of the fact that p-ZnO thin films based Schottky diodes are less studied, we have considered the same in our present work. There are some, reports that represents Bi as an effective p-type dopant for ZnO material. In this connection, Huang et al. [17] have reported the deposition of Bi-doped p-type ZnO thin film on n-Si substrate by spray pyrolysis technique. They achieved p-nature in ZnO thin film with Bismuth nitrate concentration larger than 0.3 at.%. They obtained stable hole concentration as  $4 \times 10^{17} \text{cm}^{-3}$  with 5 at.% bismuth nitrate doping. Singh et al. [18] have reported growth of p-type ZnO thin film on p-Si substrate by sol gel spin coating method. Different structural parameters for the Bi doped ZnO thin films such as grain size, lattice parameters, texture and stress have been evaluated as function of Bi concentration. The p-type nature of 10 mol % Bi doped in ZnO film was confirmed by Seeback voltage measurement. The optical band gap of doped films was also observed as a function of Bi concentration and it was found that optical band gap is 3.08 eV for 10 mol % Bi doped ZnO.

In this article, we have analyzed the rectifying characteristics of Schottky contacts (obtained by Pd and Ni metals) composed by growing highly c-axis oriented Bi doped p-ZnO (10 mol% Bi doped ZnO) thin films onto n-Si substrates by sol gel spin coating technique. To the best of our knowledge no work has been reported for fabrication and characterization of Pd/Bi doped p-ZnO/n-Si and Ni/Bi doped p-ZnO/n-Si Schottky diodes. We have investigated the electrical properties of the M-S diode by considering conventional thermionic model. Further, to predict the performance more realistically, we have incorporated the effect of series resistance and the analyzed the I-V characteristics by Cheung's and Norde's methods. Further, an endeavor has been made to compare the properties of the fabricated diodes with the already published results to establish the performance of the same.

## 2. Experiment

Earlier to the deposition of Bismuth doped ZnO thin films, n-Si substrates were cleaned by a mixture of DI water,  $\text{NH}_4\text{OH}$  and  $\text{H}_2\text{O}_2$  taken in the ratio of 5:1:1. Further, to remove natural and ionic impurities from the surface of the substrates a mixture of DI water, HCL and  $\text{H}_2\text{O}_2$  in the ratio of 6:1:1 was used. Finally, buffered HF solution was used to remove the deposited oxides from the surface of the substrate. The 10 mol % bismuth doped ZnO sol was prepared by integration of zinc acetate dihydrate ( $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ ) as a precursor, isopropanol as a solvent, diethanolamine (DEA) as a stabilizing agent and bismuth nitrate pentahydrate ( $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ ) as a dopant source. Here 10 mol % Bi doped ZnO thin films have been deposited since it shows stable and repeated p-type conductivity with hole concentration of  $1.1 \times 10^{18} \text{cm}^{-3}$  and mobility  $6.9 \text{cm}^2/\text{V}\cdot\text{s}$  in comparison to other doping concentration as reported in our earlier literature [18,20]. Finally, the prepared sol was stirred at  $80^\circ\text{C}$  for 1 h and reserve for ageing at room temperature for 24 h. Subsequent to that 10 mol % Bi doped ZnO thin films were deposited by spin coating route on the cleaned n-Si substrate at 2000 rpm for 20 s. The as deposited samples were then preheated at  $100^\circ\text{C}$  for 10 min to evaporate the organic residuals like DEA and isopropanol. To increase the film thickness the deposition process was repeated for five times. At last, to improve the crystalline quality of the deposited film samples were annealed in a furnace at  $500^\circ\text{C}$  for 1 h. After that a set of the annealed Bi doped ZnO film samples were used for characterization and another set of the samples were used for fabricating the schottky diodes. The Pd and Ni metal dots of area ( $A \sim 0.502 \times 10^{-2} \text{cm}^2$ ) were deposited on the half portion of separate bismuth doped ZnO thin film samples using shadow mask technique. Further, ohmic contacts of Aluminum metal were also deposited following the same analogy on remaining half portion of the previously deposited samples. The prepared devices were annealed at  $500^\circ\text{C}$  after contact deposition to enhance surface passivation. The schematic of fabricated device structures can be seen in Fig. 1. To determine the type of conductivity in the deposited Bi doped ZnO thin films hot point probe method [19,20] were used. The Hall measurement and hot point probe measurement clearly shows the p-type nature of the deposited films, the measurement was repeated several times to authenticate the consistency of p-type nature of Bi doped ZnO films. The detailed results of p-type conductivity of 10 mol % Bi doped ZnO have already been published in separate literature [16,21].

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