Electrical Conductivity Characterization Of Zinc Oxide Seed Layer And Nanowire By Conductive Atomic Force Microscopy

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Abstract. Zinc Oxide (ZnO) is a semiconductor nanostructure metal oxide that offers a drastic reduction of energy and electricity consumption by regulating visible transmission. The rapid advancement of ZnO devices however necessitates increased complexity and compact dimensions. This research focused on the deposition and characterization of ZnO seed layer and ZnO nanowire growth. Spin coating technique was used to deposit ZnO seed layers on the silicon substrate. Chemical bath deposition (CBD) technique was used to grow ZnO nanowire with different concentrations between 0 to 1M of Hexamethylenetetramine (HMTA) on silicon substrate. Electrical characterization of ZnO nanowire was measured by conductive atomic force microscopy (C-AFM). C-AFM is considered as a versatile technique to measure the electronic structures at nanoscale. C-AFM was used to determine the local current-voltage characteristic of ZnO of nanowire. Current-voltage characterization revealed a characteristic similar to Schottky diode curve with forward and reverse bias voltage. Moreover, this ZnO nanowire was identified with good rectifying behaviour, small turn on voltage and good ideality factor. The morphology was confirmed by field emission scanning electron microscope (FE-SEM) which showed ZnO nanowire with different patterns according to concentration of HMTA used during nanowire growth process. ZnO nanowire growth with HMTA below 0.03M showed a flower-like pattern with long hexagonal shape. Whereas, ZnO nanowire grown with 0.06M and 0.09M showed long cylindrical shape with uniform diameter around 30-40nm. These properties of ZnO nanowires can be guided to provide opportunity for direct integration of high-performance semiconductor nanoscale devices.

Keywords: Zinc Oxide, Nanowire, Conductive Atomic Force Microscopy

I. INTRODUCTION

One-dimensional (1D) nanostructures such as nanowire, nanorods and nanotubes have been the key of enhancement in nano technology for their unique properties especially in nanoscale sensors, optoelectronic devices, energy generators, and storage devices [1]. Whereas, ZnO has been recognised as the most favourable research due to their appropriate bandgap, low cost and chemical stability. Not only that, ZnO also has hexagonal wurtzite crystalline structure and the nanowires

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have quasi one-dimensional structures exhibiting quantum confinement effects and high surface to volume ratios[2]. In order to synthesise the nanowire, a lot of approach techniques such as chemical bath deposition (CBD)[2], vapor liquid solid (VLS)[3], pulse laser deposition (PLD) and many more have been used by researcher. CBD method has been widely used as it does not require a high temperature or a vacuum system. Furthermore, it is cost-effective and can provide various morphologies and properties in ZnO nanostructures. Several parameters, including solution and process parameters, influence the properties of ZnO nanowire synthesised using the CBD method [4].In analysing the electrical properties of these nanowires, conductive atomic microscopy is one of versatile devices preferred because the conductivity of any point can be measured by only probing the AFM tip in a few nanometers distance from the surface. With the probe tip diameter of approximately 100 nm, the conductivity of the material was measured more accurately as compared to the conventional I-V measurements [3].

II. METHODOOGY

Seed Layer Deposition

Sample preparation began with the deposition of seed layer by Sol-gel spin coating method. Firstly, silicon substrate was cut into smaller size using the diamond cutter. Then, the substrate was cleaned with ultrasonic bath to remove impurities and rinse away the residues. The process took place at 20°C for 20 minutes. After the ultrasonic bath process, the substrates were rinsed with deionized water (DI water). The process then continued with the drying process using oven at 60°C for 15 minutes to make sure no bubbles were formed on the surface of substrates. Next, the substrates had to be etched using hydrochloric acid (HCL) and acetone to remove thin, highly deformed layer introduced while grinding and polishing the silicon wafer. 0.1M Zinc acetate dehydrate [$Zn(CH_3COO)_2 2H_2O$, ZAD] was used as precursor material, ethanol as solvent and Tri-ethanolamine [$C_6H_{15}NO_3$] as stabilizer agent. 175.6 mg of Zinc acetate dihydrate was prepared and added with 8 mL of ethanol, stirred at 300 rpm. 154 μL of Triethanolamine (TEA) was added drop by drop while the vial was kept heated and rotated in order to form clear and transparent solution under constant stirring. Aqueous continued to be heated by increasing the temperature slowly from 25°C to 60°C. Once the solution turned clear and transparent at stable temperature between 55°C to 58°C, the aqueous solution was kept for 45 minutes while keeping the vial stirred on the hot plate. The aqueous solution was stored for about 12 to 24 hours at room temperature for aging before the deposition process. The process continued with sol-gel solution pipes onto the substrate using pipette with approximation of 30 μL. Then, the substrate was rotated using spin coater machine at 3000 rpm in 30 seconds. Then, the process continued by drying it on a hot plate at 100^{o}C for 10 minutes. Annealing process is needed to remove organic component and solvent from the films.

Growth Of Nanowire

ZnO nanowire growth was done using chemical bath disposition technique. Firstly, chemical bath solution was prepared by diluting 0.03 M zinc nitrate ($ZnNO_3$) solution with a few drops of DI water and the solution was stirred until dissolved. DI water was added up to 50mL. After that, the process continued with diluting 0.03 M HMTA solution with a few drops of DI water and stirring the HMTA solution until dissolved. The 100 mL of mixed solution was transferred into a beaker. The same technique was repeated on the chemical bath solution with 0.07 M HTMA solution. Then, the substrates were immersed to the prepared solution and underwent heating process at 90^0C for 3 hours. When the heating process finished, Si substrates were taken out from the oven and left for 30 minutes for them to cool at room temperature. Then, the substrates were rinsed with DI water to remove the residues and continued with the drying process at room temperature.

Characterization

Conductive atomic force microscopy (C-AFM) was used for electrical characterization. C-AFM experiment was performed in the contact mode between the conductive AFM tip and the top of ZnO nanowire having ambient environment with a relative humidity of about 60% at 18 °C. CAFM cantilever having 100 nm diameter with a force constant of 13 N/m and about 1Hz scanning frequency were used for *I-V* measurements. For smooth topography and the measurement of current imaging, the scanning frequency was kept at about 1Hz [5], the dc bias voltage was kept low between CAFM tip and sample, where the current flow in the amplifier box was kept up to 100 nA. 10 readings were taken at same applied voltage for each sample. The instrument used in this study was the SPA 300HV SPM Unit SPI 3800N. The morphology of ZnO nanowire was characterised using Field-emission Scanning Electron Microscope (FESEM, Hitachi SU8020).

III. RESULT AND DISCUSSION

Morphology Properties of Zinc Oxide Nanowire

The morphology of all synthesis nanowire captured by FESEM showed different patterns of morphology depending on the concentration of HMTA during the growth process as shown in figure 1. Three different types of nanostructures were obtained as tabulated in Table 1. The growth step of ZnO nanowires consisted of reactions that took place between Zn hexahydrate nitrate and HMTA. Zn^{2+} ions reacted with OH^- ions and formed soluble Zn $(OH)_2$ complexes, which decomposed leading to Zn [6]. Once the supersaturation of ZnO concentration was reached, the crystal nucleus of ZnO was formed and the growth process then began [7]. Thus, it can be deduced that the concentration of HMTA during the growth process using CBD technique strongly affects the nanostructure. For nanowire growth at lower concentration of HMTA showed that ZnO nano-flower formed with uniform hexagonal and agglomerate structure. Besides, this flower-like structure consisted of uniformly accumulated nanostructure which can facilitate more numbers of photons through multiple light scattering, which is always desirable for any optoelectronic applications [8]. While at the optimum concentration at 0.06M and 0.09M HMTA, ZnO nanowire showed uniformly long and vertically aligned structure of nanowire. Nanowire growth at 0.07M HMTA formed needle-like structure with non-uniform structure with very thin and long nanowire

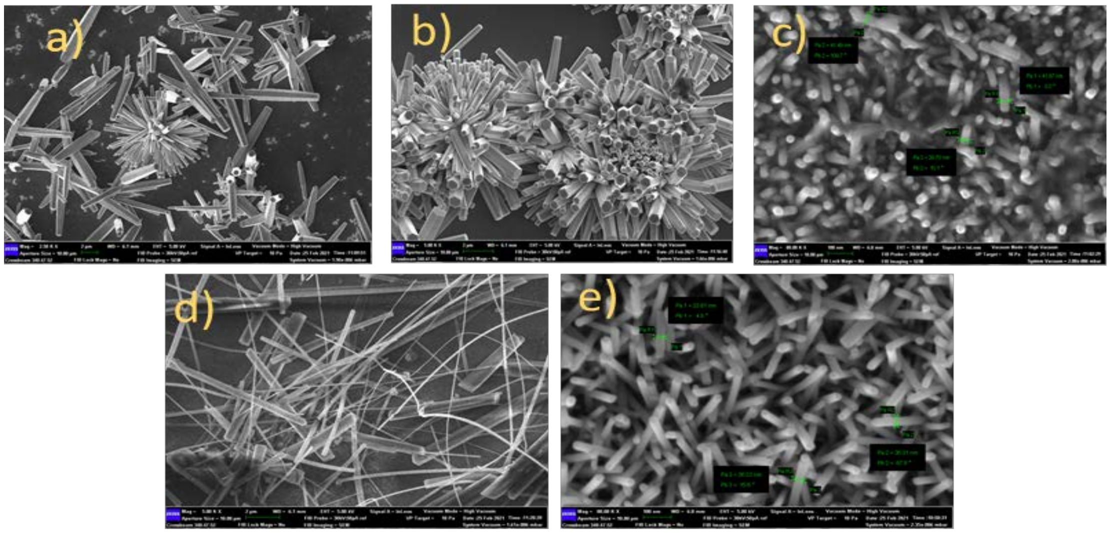

FIGURE 1. shows the Morphology of Zno nanowire by FESEM a)S1, b)S2, c)S3, d)S4, e)S5

TABLE 1. Nanostructure of ZnO nanowire with different concentrations of HMTA during growth process.

Sample	Conc.of HMTA (M)	Morphology	Diameter (nm)
S1	0	Flower-like	>50
S2	0.03	Flower-like	>50
S3	0.06	Nanowire	36.84
S4	0.07	Needle-like	Not uniform
S5	0.09	Nanowire	35.38

Electrical Properties of Zinc Oxide Nanowire

The I-V characteristic was achieved as the measurement setup in Figure 3 a). The I-V curve obtained by PtIr-coated silicon cantilever nanotips of CAFM provided a biased voltage directly on the sample surface on ZnO nanowire in nm-scale. Figure 3 b) and c) show the scanned surface and I-V curve of ZnO nanowire grown at 0.09M HMTA during CBD process with both forward and reverse bias junction as non-linear and asymmetric. The turn-on voltage measure from I-V curve was ~1.0V and the junction breakdown was observed at the reverse bias of ~-2.7V. The I-V characteristic obtained from PtIr-coated silicon cantilever and the ZnO nanowire exhibited rectifying behaviour whereas the bottom contact between ZnO/n-Si was ohmic [9]. The work function of PtIr, ϕ_m ~5.7eV was larger than n-ZnO nanowire, ϕ_s ~ 4.5eV hence PtIr forming a rectifying MS junction with n-ZnO [10].

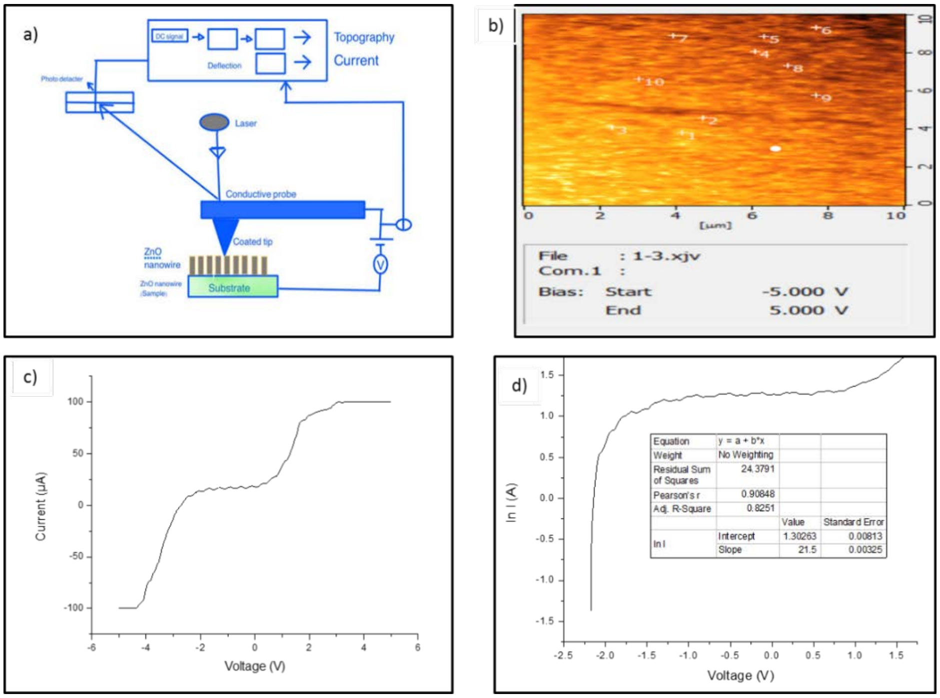

FIGURE 2. a)Schematic of setup C-AFM measurement b) 2-d mapping of ZnO by C-AFM c) I-V plot data of the Schottky contact (Pt/ZnO) for S5 d) Semi-log represents I-V characteristic curve.

I-V characteristic in terms of Schottky diode of ZnO nanowire, ideality factor of the current-voltage can be determined by the following equation:

$$I = I_s \left[\exp\left(\frac{qV}{nkT}\right)\right) - 1 \qquad (1)$$

where,

n= diode ideality factor

q= electronic charge

V= applied voltage

I_s= reverse saturation current

K_B=Boltzmann constant

T= absolute temperature

However, the estimated ideality factor can be determined from the slope of the linear region of a semi-log I-V curve by using the equation:

$$n = \frac{q}{K_B T}\frac{1}{m} \qquad (2)$$

The estimated ideality factor (n) from the slope (m = 21.5) of the linear region of a semi-log *I–V* curve as shown in figure 3 d) using equation Eq. (2) was 1.81, which is slightly greater than the ideal value of 1.02 of diode [11]. The discrepancy from the ideal value is possibly referred to the structural defects, barrier tunneling or generation recombination and to variations in interface composition. The same way for extrinsic impurities may rise the impurity conduction.

I-V curve of ZnO nanowire displayed the typical Schottky contact behaviour. Schottky barrier contact refers to the metal contact between the tips and the ZnO nanowire having large potential barrier height formed once the Fermi energy of metal and semiconductor aligned together. Schottky barrier also refers to metal-semiconductor contact having a large barrier height with low doping concentration that is less than the density of states in conduction band. In this research work, as metal and semiconductor are brought together, the Fermi energies of these two materials must be equal at thermal equilibriums and the resulting band bending at the interface creates potential barrier that is known as Schottky barrier. The electrical properties of nanowire are strongly influenced by atomic structure and gained boundary where this can disrupt the flow of electrons [12].

IV. CONCLUSION

In conclusion, ZnO nanowire was successfully grown using chemical bath deposition technique. Besides, the concentration of HMTA used for the growth process strongly influences the morphology of ZnO nanowire. Thus, the desired morphology can be controlled with the optimum concentration of HMTA. The electrical property of ZnO seed layer nanowire was obtained by Pt-coated silicon conductive tip on the top surface of samples and the best I-V characteristics were plotted similar with both forward and reverse bias. The turn-on voltage measure from I-V curve was ~1.0V and the junction breakdown was observed at the reverse bias of ~-2.7V. The ideality factor (n) from the slope (m = 21.5) of the linear region of a semi-log *I–V* curve was 1.81.

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REFERENCES

1. M. A. Khan, S. Sakrani, S. Suhaima, Y. Wahab, and R. Muhammad, “Synthesis of Cu2O and ZnO nanowires and their heterojunction nanowires by thermal evaporation: A short review,” *J. Teknol.*, vol. 71, no. 5, pp. 83–88, 2014, doi: 10.11113/jt.v71.3861.
2. S. Paiman, T. Hui Ling, M. Husham, and S. Sagadevan, “Significant effect on annealing temperature and enhancement on structural, optical and electrical properties of zinc oxide nanowires,” *Results Phys.*, vol. 17, no. May, p. 103185, 2020, doi: 10.1016/j.rinp.2020.103185.
3. M. A. Khan, S. Sakrani, S. Suhaima, Y. Wahab, and R. Muhammad, “Synthesis of Cu2O and ZnO nanowires and their heterojunction nanowires by thermal evaporation: A short review,” *J. Teknol.*, vol. 71, no. 5, pp. 83–88, 2014, doi: 10.11113/jt.v71.3861.

4. E. Pourshaban, H. Abdizadeh, and M. R. Golobostanfard, "ZnO Nanorods Array Synthesized by Chemical Bath Deposition: Effect of Seed Layer Sol Concentration," *Procedia Mater. Sci.*, vol. 11, pp. 352–358, 2015, doi: 10.1016/j.mspro.2015.11.124.

5. A. Das, P. Mathan Kumar, M. Bhagavathiachari, and R. G. Nair, "Shape selective flower-like ZnO nanostructures prepared via structure-directing reagent free methods for efficient photocatalytic performance," *Mater. Sci. Eng. B*, vol. 269, no. February, p. 115149, 2021, doi: 10.1016/j.mseb.2021.115149.

6. M. Chelu *et al.*, "High-quality PMMA/ZnO NWs piezoelectric coating on rigid and flexible metallic substrates," *Appl. Surf. Sci.*, vol. 529, no. July, p. 147135, 2020, doi: 10.1016/j.apsusc.2020.147135.

7. R. Tao *et al.*, "Performance of ZnO based piezo-generators under controlled compression," *Semicond. Sci. Technol.*, vol. 32, no. 6, 2017, doi: 10.1088/1361-6641/aa691f.

8. Hofstetter, D., & Morkoc, H. (2010). *ZnO Devices and Applications review*. *98*(7), 1255–1268.

9. I. Beinik *et al.*, "Electrical properties of ZnO nanorods studied by conductive atomic force microscopy," *J. Appl. Phys.*, vol. 110, no. 5, 2011, doi: 10.1063/1.3623764.

10. S. K. Panda, S. B. Sant, C. Jacob, and H. Shin, "Schottky nanocontact on single crystalline ZnO nanorod using conductive atomic force microscopy," *J. Nanoparticle Res.*, vol. 15, no. 1, 2013, doi: 10.1007/s11051-012-1361-z.

11. S. Pal, S. Maiti, U.N. Maiti, K.K. Chattopadhyay, Low temperature solution pro- cessed ZnO/CuO heterojunction photocatalyst for visible light induced photo-de- gradation of organic pollutants, CrystEngComm 17 (2015) 1464–1476.

12. Kuphaldr, T.R (2020). *Lessons in Electric Circuits-Vol.3-Semiconductors*. [online]. Available at https://www.technocrazed.com/lessons-in-electric-circuits-vol-3-semiconductors (Accessed: 26 December 2021)