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Current Voltage Characterization of Zinc Oxide Nanowire Prepared using Chemical Bath Deposition with Different Concentration of HMTA

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Abstract
Zinc oxide (ZnO) is a semiconductor nanostructure metal oxide offers a drastic reduction of energy and electricity consumption which be a potential solution to the energy saving of nano-electronic devices. This research focuses on the deposition and characterization of ZnO nanowire. ZnO nanowires were growth with different concentrations between 0 to 1M of Hexamethylenetetramine (HMTA) on silicon substrate. The morphological and structural were analyzed using field emission scanning electron microscope (FE-SEM) with 0.06M and 0.09M HTMA showed long cylindrical nanowire with uniform diameter around 30-40nm. Conductive atomic force microscopy (C-AFM) was used to analyze the current-voltage (I-V) characteristic of single ZnO nanowire. It is revealed that I-V characteristic similar to Schottky diode curve. The forward and reverse bias voltage of a single ZnO nanowire with 0.03M HTMA showed good rectifying behavior, small turn on voltage at ~1.0V and the junction breakdown observed at the reverse bias of ~-2.7V with good ideality factor at n=1.81. These properties of ZnO nanowires can be guided to provide an opportunity for direct integration of high-performance semiconductor for nanoscale devices.
Keywords: Zinc Oxide; Nanowire; Conductive atomic force microscopy; Hexamethylenetetramine (HMTA)

Introduction

Today's technological advancements have gotten a lot of attention, notably in the field of semiconductor materials. Nanostructured metal oxide has various types such as nanowires, nanorods, nanobelts, nanobridges and nanowalls which have been received more interest of many researchers due to their size, morphology-related properties and emerging applications in novel functional nanodevices [1].

One of the most widely used semiconductor materials nowadays is zinc oxide (ZnO). ZnO received more interest compare to other material due to their unique properties such as direct band gap energy of 3.37 eV, high electrochemical stability, high thermal and mechanical stability at room, non-toxic, excellent optical and electrical properties and easily formed into nanostructured materials [2]. Recently, zinc oxide (ZnO) is chosen as one of the most important nanomaterials for nanotechnology among the one-dimensional nanostructure [3]. Not only that, ZnO also has hexagonal wurtzite crystalline structure and the nanowires has quasi one-dimensional structures exhibiting quantum confinement effects and high surface to volume ratios [4]. There are several methods to synthesis ZnO nanowires such as vapor-liquid-solid, metal organic chemical vapor deposition, pulsed laser deposition, hydrothermal method and chemical bath deposition method. Among these methods, chemical bath deposition (CBD) method is the most preferable method because of the advantage of low evaporation temperature, economical process, low temperature and simple coating process

Therefore, in this work, the effect of changing concentration of HMTA is chosen in order to improve the physical structure of nanowires. This research focus on to grow ZnO nanowires on the optimized seed layer and to show the improvement of ZnO nanowires and study the morphology structural and electrical behaviour of ZnO nanowire.

Materials and Methodology

Growth of nanowire

Sample preparation started with disposition of seed layer by Sol-gel spin coating method. 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. 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.

The process continued with ZnO nanowire growth by using chemical bath disposition technique. Firstly, chemical bath solution is prepared by diluted 0.03 M zinc nitrate ($ZnNO_3$) solution with few drops of DI water and stirred the solution until dissolved. DI water was added until 50mL. After that, continue to dilute 0.03 M HMTA solution with few drops of DI water and stirred the solution HMTA dissolved. The 100 mL of mixed solution is being transferred into beaker. The same technique is being repeated towards the chemical bath solution with 0.07 M HTMA solution. Then, the substrates immerse to the prepared solution and undergoes heating process at 90 ºC for 3 hours. When the heating process finished, the Si substrates were taken out from the oven and being leave for 30 minutes for them to cool at room temperature. Then, the substrates rinsed with DI water to remove residue and continue drying process at room temperature.

Sample 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 ºC. CAFM cantilever having 100 nm diameter with a force constant of 13 N/m and about 1Hz scanning frequency was used for the *I*-*V* measurements. For smooth topography and to measure current imaging, the scanning frequency was kept 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 will be taken at same applied voltage for each sample. The instrument used in this study is the SPA 300HV SPM Unit SPI 3800N. Morphology of ZnO nanowire characterize using Field-emission Scanning Electron Microscope (FESEM, Hitachi SU8020).

Result And Discussion

Morphology properties of ZnO nanowire

The morphology of all synthesis nanowire capture by FESEM showing different pattern of morphology depends on the concentration of HMTA during the growth process as show in figure 1. Three different types of nano-structure were obtained as tabulated in table 1. The growth step of ZnO nanowires consist of reactions that take place between Zn hexahydrate nitrate and HMTA. The Zn^{2+} ions react with OH^- ions and form soluble Zn $(OH)_2$ complexes, which decompose leading to Zn [6]. Once the supersaturation of the ZnO concentration is reached, the crystal nucleus of ZnO is formed and then the growth process begins [7]. Thus, it can be deduce that the concentration of the HMTA during the growth process using CBD technique strongly affecting the nanostructure. For nanowire growth at the lower concentration of HMTA showing that ZnO nano-flower form with uniform hexagonal and agglomerate structure. Furthermore, this flowers-like structure is made up of uniformly accumulating nanostructures that can assist the dispersion of numerous photons, which is always desirable in optoelectronic applications [8]. While at the optimum concentration which at 0.06M and 0.09M HMTA, ZnO nanowire shows uniformly long and vertically align structure of nanowire. At 0.07M HMTA, nanowire development forms a needle-like structure with a non-uniform structure and an extremely thin and long nanowire.

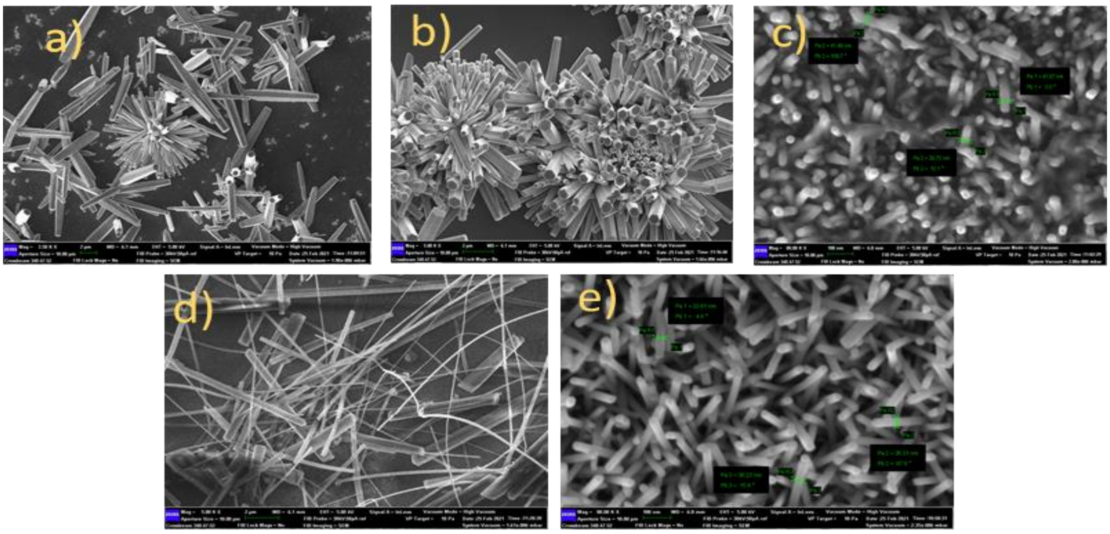

Figure 1 FESEM Image of ZnO nanowire: a) S1, b) S2, c) S3, d) S4, e) S5

Table 1: Nanostructure of ZnO nanowire with different concentration of HMTA during growth process.

Sample	Concentration 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 ZnO nanowire

The I-V characteristic was achieved as the measurement setup in Figure 2 (a). The I-V curve obtained by PtIr-coated silicon cantilever nanotips of CAFM which 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 which is growth at 0.09M HMTA during CBD process with both forward and reverse bias junction to be non-linear and asymmetric. The turn on voltage measure from I-V curve is ~1.0V and the junction breakdown observed at the reverse bias of ~-2.7V. The I-V characteristic obtained from PtIr-coated silicon cantilever and the ZnO nanowire exhibit the rectifying behaviour whereas the bottom contact between ZnO/n-Si is ohmic [9]. The work function of PtIr, ϕ_m ~5.7eV larger than the n-ZnO nanowire, ϕ_s ~ 4.5eV hence PtIr forms a rectifying MS junction with the n-ZnO [10].

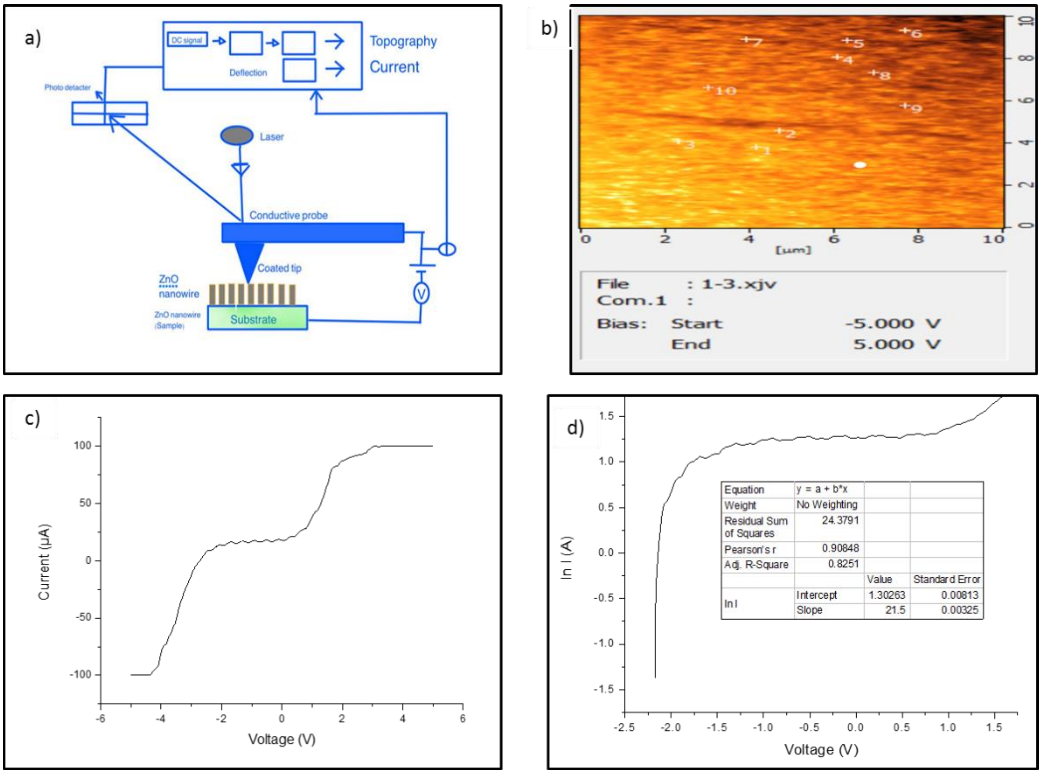

Figure 2 a) Shematic of setup C-AFM measurement b) 2-d mapping of ZnO by C-AFM c) I-V plot data of the Schottky contact (Pt/ZnO) for S5 d) Semi-log represent I-V characteristic curve

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

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

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 equation:

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

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 found to be 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 which may rise the impurity conduction [9].

I-V curve of ZnO nanowire displayed the typical Schottky contact behavior. Schottky barrier contact refers to the metal contact between the tips and the ZnO nanowire having large potential barrier height formed once 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 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 known as Schottky barrier. The electrical properties of nanowire strongly influenced by atomic structure and gained boundary where this can disrupt the flow of electrons [12].

Conclusion

In conclusion, ZnO nanowire successfully growth by chemical bath deposition technique. Beside the concentration of HMTA used for the growth process strongly influence the morphology of the ZnO nanowire. Thus the desire morphology can be controlled with the optimum concentration of HMTA. The electrical property of ZnO seed layer nanowire obtained by Pt-coated silicon conductive tip on the top surface of samples and the best I-V characteristics plotted similar with both forward and reverse bias. The turn on voltage measure from I-V curve is ~1.0V and the junction breakdown 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 found to be 1.81.

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