

STUDY ON THE HYDROTHERMAL GROWTH OF ZnO NANORODS FOR PIEZOTRONIC APPLICATIONS

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Abstract: The capability of a certain material to generate an electric charge in response to applied mechanical stress is called as piezoelectric Effect. Metal oxide semiconductors having high piezoelectric coefficient can be cost effectively manufactured by a simple hydrothermal methods at low temperature. These nanostructures are capable of transforming mechanical deformation into electrical power. The nanostructure morphologies and dimensions can be controlled by controlling the growth conditions. When subjected to mechanical deformations, these nanostructures are capable of transforming mechanical deformation into electrical power. Due to the structural noncentralsymmetry, ZnO nanostructures exhibit anisotropic piezoelectric properties. High aspect ratio ZnO nanostructures can be merely designed using hydrothermal methods and these nanowires or nanorods show piezoelectric properties. When subjected to mechanical deformations, these nanostructures undergo a charge separation due to inherent structural asymmetry. Tapping of the separated charges and subsequent accumulation can give a manifestation of mechanical to electrical energy transformation and lead to energy harvesting.

Keywords: ZnO nanorods, piezo-electric, Hydrothermal method

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I. INTRODUCTION

With the decrease in energy consumption of transportable electronic devices, the conception of harvesting renewal energy in human surrounding arouses a renewed interest. From many decades People have studied for ways to store the energy from heat vibrations. The first generator, was invented in 1831 by British scientist Micheal Faraday [1]. After that the batteries became the most power supply for wireless electrical devices. These batteries had vast sizes and weighed enormously too [2]. One propulsion behind new energy harvesting devices is that the need to power sensing element networks and mobile devices while not batteries.

Energy gathering is approaching an interesting technological juncture wherein the power requirements for electronic devices are reduced whereas at an equivalent time, the potency of energy gathering devices have augmented. Out of assorted attainable energy harvesting technologies, piezoelectric vibration energy harvest has emerged as a way of other for powering meso-to-micro scale device [3]. Piezoelectric materials are often used as mechanisms to transfer energy, typically ambient

vibration, into current which will be kept and accustomed to power various devices. A piezoelectric material is one that generates an electrical charge when a mechanical stress is applied. Conversely, a mechanical distortion is formed once an electrical field is applied.

With the evolution of medicine engineering, in vivo observance, detection and treatment of cells and organs appear to be a close-by reality albeit the actual fact that all this still need power supply. With the dimensions, weight and use of hazardous materials of current batteries don't serve the purpose [4]. Realization of self-powered nano systems will result in new avenues during this direction. Piezoelectric nanoparticles can be economically fabricated in metal semiconductor form. Within the last decade about, these nanostructured metal chemical compound semiconductors (ZnO) had drawn worldwide interest for their path breaking properties [5]. Furthermore, ZnO is a broad band-gap (3.37 eV) compound semiconductor which is proper for short wavelength optoelectronic applications [4]. Structurally, it has a number of alternating planes stacked along the central axis. These planes are made of tetrahedrally synchronized O^{2-} and Zn^{2+} ions [6]. The shortage of a

centre of symmetry in wurtzite, combined with massive mechanical device coupling, results in sturdy piezoelectric and pyroelectric properties and conjointly the following use of ZnO in mechanical actuators and electricity sensors. Because of these positive and negative ions, ZnO has distinctive polar surfaces with the basal plane (0001) being the most common polar plane [7]. One end of the polar plane ends with partly positive Zn lattice tip and the other end ends in partly negative oxygen lattice points [7]. These polar surfaces when mechanically disturbed, produces electrical energy.

Electrically charged particles in substances are circulated in space in a way such that the opposed charges cancel each other out [9,10]. Which makes matter electrically equitable or they do not have excess electrical charge and are hence neutral. Certain materials undergo a forced charge unbalance at their surfaces, when a mechanical force is produced in the form of a physical deformation, which in other words is termed as piezoelectricity [11]. Depending on certain attributes of the material, the surface charge separation can occur. These include the crystal structure of the material and the dielectric capacity or in other words how it is aligned with respect to the central axis of the crystal [12].

II. EXPERIMENTAL

A. Hydrothermal growth of ZnO nanorods

One dimensional ZnO nanostructures were synthesized using hydrothermal process. Different conducting substrates were used like FTO and ITO coated glass, cover slip etc. Already synthesized ZnO nanoparticles are used for seeding the substrates. For dense nanorods, nanocrystallites are grown on the substrate itself. The dip coating techniques and dropping techniques were used for making the seed layer on the substrates. The seeded substrates are placed in equimolar solution of hexamine or hexamethylenetetramine ($C_6H_{12}N_4$) and zinc nitrate ($Zn(NO_3)_2 \cdot 6H_2O$) and at $90^\circ C$, such that the seeded side faces down. The chemical bath is changed every 5 hours because the growth rate progressively falls. Annealing is done finally at about $250^\circ C$ for removal of residual hexamine and nitrate from the surface. Hexamine or hexamethylenetetramine ($C_6H_{12}N_4$) discharges OH anions in water when treated thermally and reacts with Zn cations released by zinc $Zn(NO_3)_2 \cdot 6H_2O$ and produces ZnO.

B. Piezoelectric power generating device using ZnO nanorods

The Au sputtered electrode was placed on top of the substrate with ZnO nanorods and firmly affixed using glue at the edges. Leads were taken out from the conducting sides of both the gold coated electrode and the substrate with the piezoelectric nanorod array on it using silver pastes. The gold sputtered electrode is then placed on top

of the nanorods array. We used a Keithley meter for measurement of piezo voltage generated. The arrangement for extracting energy from the ZnO nanorods is shown schematically in Figure 1.

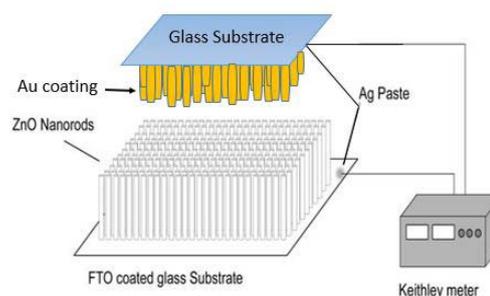


Figure 1: Schematic illustration of the process to produce and extract a piezopotential from an array of ZnO nanorods

III. RESULTS AND DISCUSSION

A. Effect of growth conditions of ZnO nanorods

The growth of the Zinc Oxide nanorods was observed for four different concentrations: 5mM, 10mM, 20mM, and 40mM for growth times of 15h, 20h and 25h.

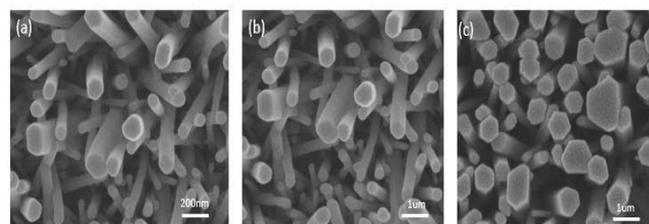


Figure 2: SEM images of ZnO nanorods when grown at a concentration of 5mM for (a) 15h (b) 20h (c) 25h

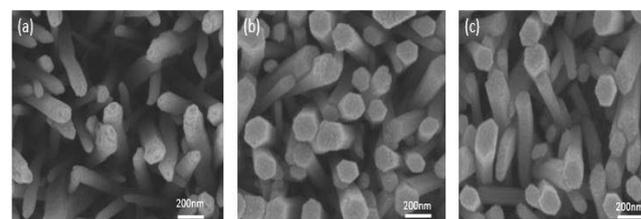


Figure 3: SEM images of ZnO nanorods when grown at a concentration of 10mM for (a) 15h (b) 20h (c) 25h

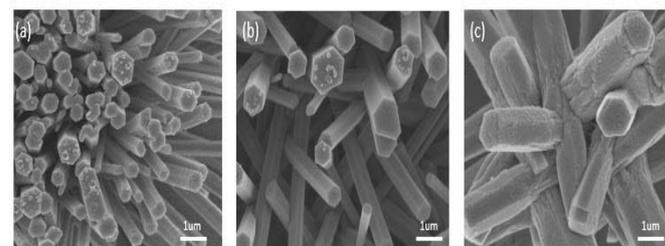


Figure 4: SEM images of ZnO nanorods when grown at a concentration of 20mM for (a) 15h (b) 20h (c) 25h

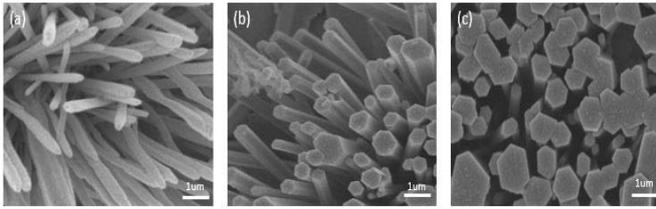


Figure 5: SEM images of ZnO nanorods when grown at a concentration of 40mM for (a) 15h (b) 20h (c) 25h

The rod dimensions grown on substrates can be controlled considerably by controlling certain growth conditions. A measure of the dimensions of the ZnO nanorod is shown in the figure 6. Nanorods grown using different concentration solution showed that the molarity affects the thickness of the rods significantly. Rods grown under decreasing molarity gave thinner rods. Based on the measurement carried out on the SEM images, 10mM concentration was selected for remaining part of the work as a width of the nanorods of 10mM sample was in the range of (100-200) nm and was appropriate for vibration without breakage.

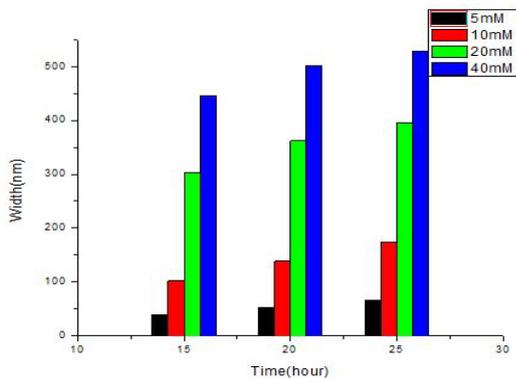


Figure 6: Comparative growth of ZnO nanorods grown at different concentration for different growth time

B. Top electrode fabrication

The SEM image of the metallic gold was sputtered on ZnO nanorods grown on glass substrate is shown in figure 7. ZnO nanorods when subjected to physical deformation produce a charge separation such that the elongated side gets a net positive voltage while the compressed side gets a net negative voltage.

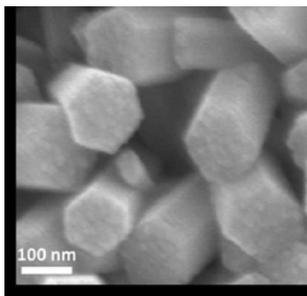


Figure 7: SEM images of Au sputtered ZnO nanorods

In order to ensure proper electrical contact between the nanorods and the FTO coated glass substrate, IV characteristics were studied for applied positive and negative voltages before the integration of the nanorods with the electrode as shown in the figure 8.

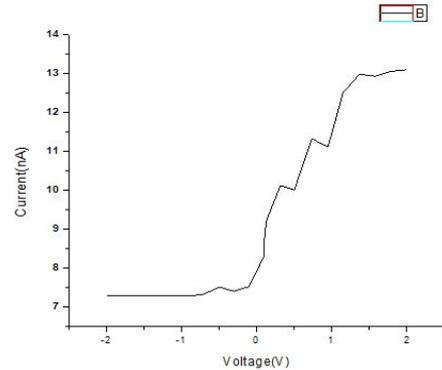


Figure 8: I-V characteristics of the ZnO nanorods grown on the FTO coated glass substrate

We used a Keithley meter for measurement of the current. Application of linear voltages increasing from 0 V to (+/-)2V showed increase in current with increase in voltage establishing the fact that a Schottky contact was formed between ZnO nanorods and FTO conducting glass substrate.

C. Piezo voltage measurement

Whenever a small pressing force is applied on the top electrode of the device, a corresponding voltage is measured by the measuring setup.

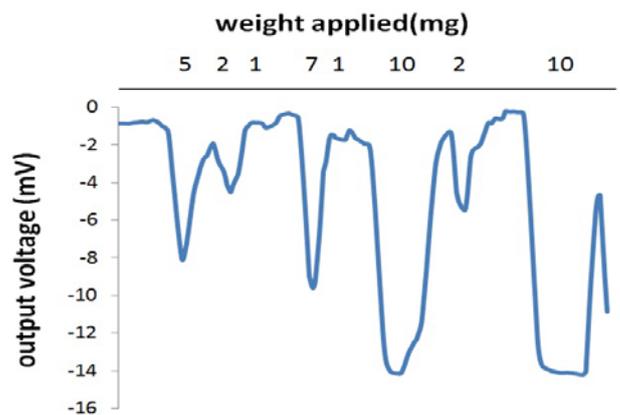


Figure 9: Graphical plot depicting the voltage versus weight plot for piezoelectric potential generated when weight is applied on them

More the applied force more is the generated potential across the nanorods and hence more is the voltage measured in the measuring setup. That is, the piezo voltage generated and detected is dependent on the amount of pressure applied or in other words, the amount of bending of the ZnO nanorods. The pressure force was

created by placing weights on top of the electrode, resulting in bending of the rods. Figure 9 shows the voltage-weight graph for the voltages measured for various weights applied. When the pressure was released, the voltage dropped, signifying that the resilient nanorods return to their original neutral state.

IV. CONCLUSION

ZnO nanorod arrays were built on conducting substrates. Top electrodes were designed and integrated with the piezo-electric nanorods to form piezo-energy harvesting units. When pressure is applied on the top electrode, the ZnO nanorods get bent due to applied force. Charge separation occurs in the ZnO crystals and multiplies to the entire nanorod in such a way, that the elongated side has excess positive charge while the reduced size has excess negative charge. These potentials are picked up by the top electrode, and are detected by the Keithley meter connected across it. When the pressure was released, the voltage dropped, signifying that the resilient nanorods return to their original neutral state.

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