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Study of ZnO Nanorods Synthesized by Microwave Method

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Abstract: The present studies report, microwave method synthesis of zinc oxide nanorods with controlled morphologies and high-purity. Nanoscale features with good structural integrity were observed through scanning electron microscopy images. The average length and diameter were determined to be 180 nm and 36 nm, respectively. The X-ray diffraction analysis shows the wurtzite hexagonal crystal structure. The sharp and intense peaks indicated high crystallinity of nanorods. The optical bandgap of 3.15 eV was obtained from ultraviolet-visible spectroscopy analysis. Protype of piezoelectric devices were made and the characteristics were investigated. The reliability of the devices were observed till now with 50 cycles.

Keywords: Zinc oxide, Nanorods, Microwave synthesis, Piezoelectric device.

1. INTRODUCTION

ZnO is a semiconductor material, which has attracted a lot of interest because of its unique properties. Nanostructures of ZnO, including nanoparticles, nanorods, nanotubes, and thin films, provide more superior physical and chemical properties compared to their bulk forms. The primary reasons for such improved properties are attributed to increased surface area, quantum confinement effects, and tunable morphology at the nanoscale [1-4].

For realization of these properties, different synthesis methods have been developed for preparation of ZnO nanostructures with high control over size, shape, and crystallinity. Various techniques such as sol-gel [5], chemical precipitation [6, 7], hydrothermal synthesis [8], chemical vapor deposition (CVD) [9], physical vapor deposition (PVD) [10] were widely reported. All the above techniques are either time consuming (hours) and/or expensive. Very limited researchers have used microwave method in which the samples were prepared in seconds to minutes [11].

ZnO nanostructures are utilised in versatile applications. Due to its good light-harvesting properties, it can be used in photovoltaic areas such as in

solar cells applications [12]. High electron mobility characteristics of ZnO can be utilised in transparent electronics [13], spintronics [14]. It's electro-photo response property and chemical properties are used in photocatalytic effect [15] and chemical sensors [16]. Because of its unique mechanical properties, it can be used as piezoelectric devices [17]. Due to its bioactivity, it is used in antibacterial coating [5], antifungal activity [6], antimicrobial agents [18], drug delivery systems [19], and tissue engineering [20].

Here, we emphasize the synthesis of ZnO nanorods in powder form and on the Si(100) substrate in microwave synthesis method. The surface morphologies and structure of the samples were characterized by various techniques. The result were reported for prototype piezoelectric sensors and crude testing.

2. EXPERIMENTAL

ZnO nanorods were synthesized using precursors of zinc acetylacetonate. Polyvinylpyrrolidone (PVP) was used as capping agent. Other ingredients such as ethanol and deionized (DI) water were used as associated materials. A solution was prepared in a beaker with zinc acetylacetonate (1 g) added with ethanol (40 mL). It was then placed on a magnetic stirrer for 15 minutes at room temperature for complete dissolution. Another solution was prepared in another beaker from PVP (0.5 g), dissolved in DI water (40 mL). It was also subjected to magnetic stirring for 15 minutes. The PVP solution was added to the zinc acetylacetonate solution with continuous stirring, so that both solutions could mix up homogeneously. The resulting solution was kept in a round bottomed flask, put inside a commercial microwave oven and subjected to 700 watt for 5 minutes (schematic diagram shown in Fig.1). White coloured solution was observed, which were taken in test tubes and subjected to centrifuge. The white precipitate was collected and washed with DI water and ethanol sequentially for five times. Finally, the white powder was dried in an oven for 70^0 C overnight. The scaffold of ZnO-NR on silicon (Si) were prepared, by putting the Si substrates in round bottom flask along with mixture of both solutions, before putting in microwave oven. After microwave irradiation, the substrates were taken out and rinsed with DI water and ethanol as mentioned above.

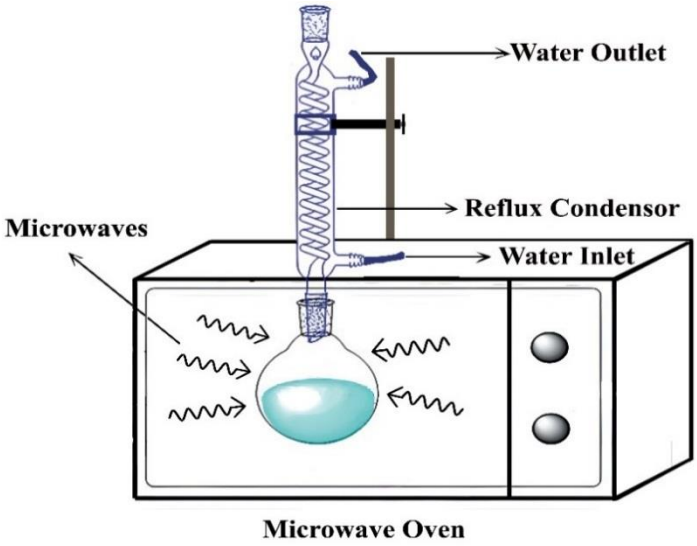

Fig. 1 Schematic diagram of microwave synthesis method setup.

3. RESULT AND DISCUSSION

3.1 Scanning electron microscopy (SEM)

The synthesized samples were characterized using scanning electron microscope (SEM) to reveal their morphology. Fig. 2(A) shows the optical image of as grown powder samples. Fig. 2(B, C, D) show the SEM images of sample at 5K, 50K and 150K magnification respectively. Nanoscale features with good structural integrity were observed. Columnar hexagonal nanorods are clearly viewed. Fig.2 (E, F) show the histogram plot of average diameter (36 nm) and average length (180 nm) of ZnO nanorods. Fig. 3(A-D) show the SEM images of sample at different magnifications. Here also nanoscale features ZnO NRs are uniformly distributed on the Si substrate.

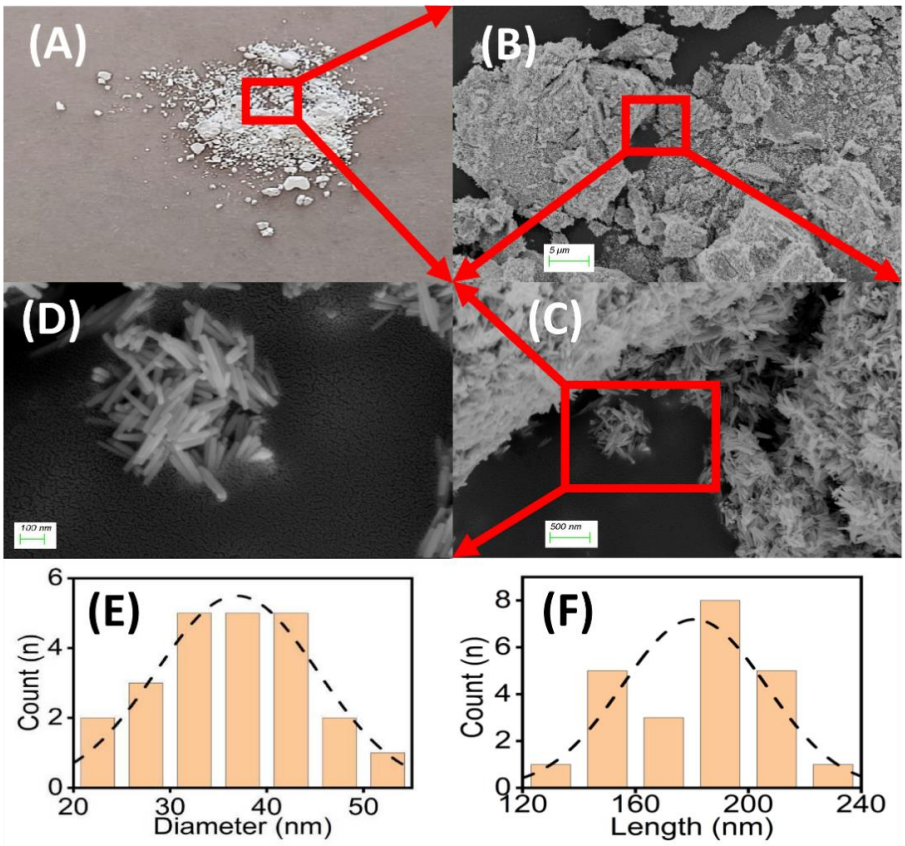

Fig. 2 (A) Optical image of ZnO nano rod powder. (B, C, D) SEM images of ZnO nano rods at 5K, 50K and 150K magnification respectively. (E, F) show the histogram plot of average diameter and length of ZnO nanorods.

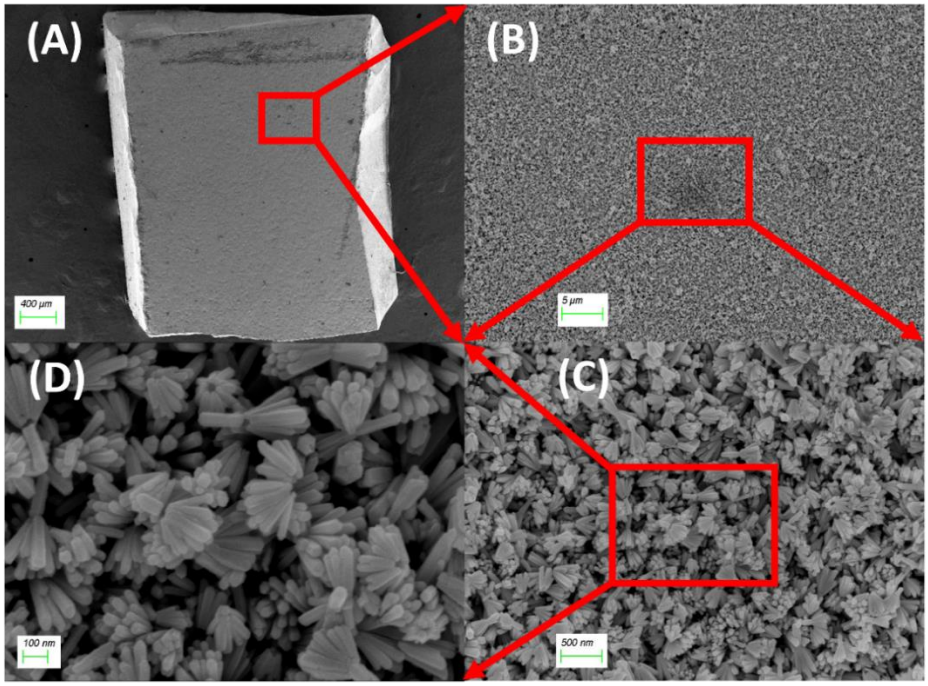

Fig. 3 (A) SEM image of ZnO nanorods growth on silicon (100) substrate viewed at 55X. (B, C, D) SEM images of ZnO nanorods at 5K, 50K and 150K magnification respectively.

3.2 Energy dispersive X-ray analysis (EDAX)

The elemental mapping (attached with EDAX) was done to reveal the uniformity of the presence of Zn and O throughout the powder sample as shown in Fig. 4(A) and fig 4(B) respectively. Fig. 4(C) shows the presence of both Zn and O in the sample with uniformity.

EDAX was carried out to analyze the elemental composition present in the sample qualitatively and quantitatively. Fig 4(D) shows the percentage of Zn and O present in the sample with no significant impurities detected. The atomic and weight percent obtained through the analysis matches the stoichiometric ratio for ZnO, which satisfies the chemical integrity of the sample intended for nanostructures. The EDAX spectrum validated the high purity of ZnO nanorods which is critical for their potential applications.

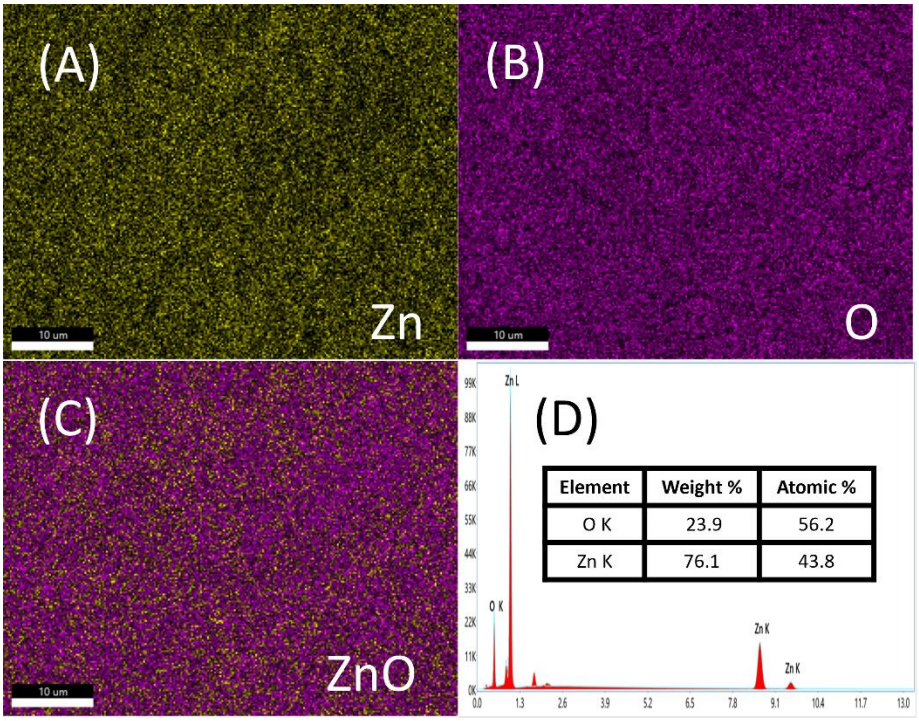

Fig. 4 Elemental mapping of (A) Zn, (B) O and (C) ZnO in ZnO nanorods. (D) EDAX of ZnO nanorods.

3.3 X-ray diffraction (XRD)

The crystalline structure of the synthesized samples was determined by carrying out X-ray diffraction (XRD) analysis. The XRD pattern obtained showed well-defined peaks at 31.72 (100), 34.38 (002), 36.17 (101), 47.46 (102), 56.51 (110), 62.82 (103), 66.37 (200), 67.88 (112), 69.01 (201), 72.48 (004), 76.95 (202). The theoretical calculations also show the peaks at the same positions, corresponding to the wurtzite hexagonal structure of ZnO. These results are consistent with the results of standard JCPDS card No. 36-1451. The sharp and intense peaks indicated the high crystallinity of the nanorods. The results clearly indicate the successful synthesis of ZnO nanorods with desired structural characteristics. The ZnO nanorods grown on Si substrates also shows similar peaks along with some additional peaks at 32.41 and 62.10 2Θ value. We attribute them as some

secondary phases of Si-Zn-O complex or some impurities. (We are in the process of investigate them in future). However, as most of the peaks are well matched with the ZnO powder sample, we assume that ZnO on Si substrate possess good structural integrity.

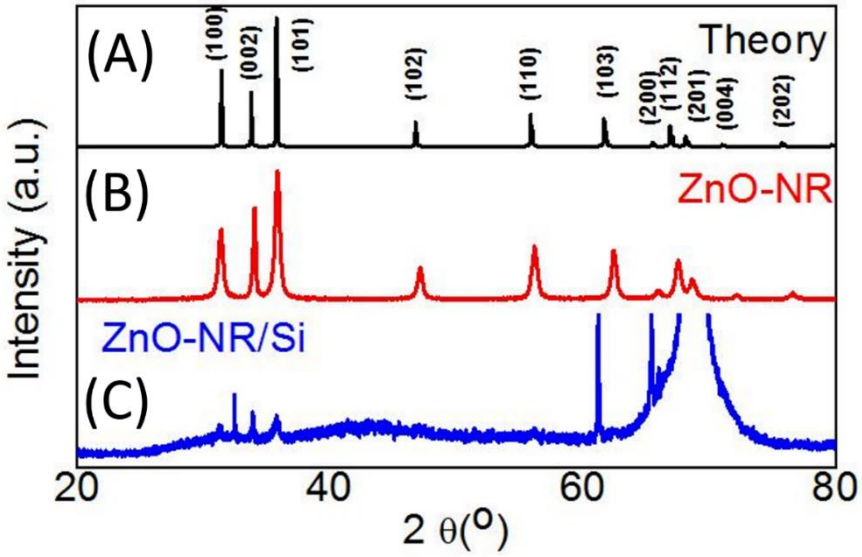

Fig. 5 XRD results of (A) theoretical wurtzite structure ZnO, (B) ZnO nanorods powder (C) ZnO nanorods grown on Si(100) substrate.

3.4 Ultraviolet Visible Spectroscopy (UV-V)

The ultraviolet visible spectroscopy (UV-vis) analysis of the powder sample was done to study its optical properties, specifically the behavior of absorption in the UV-visible region. ZnO nanorods show a characteristic absorption peak at 396 m^{-1} (Fig. 6(A)), which is indicative of their band gap energy of 3.15 eV (Fig. 6(B)) [7]. This analysis provides crucial information on the optical transitions in the visible range. The excellent UV absorption properties of the nanorods may make them useful in optoelectronic and photonic devices [7].

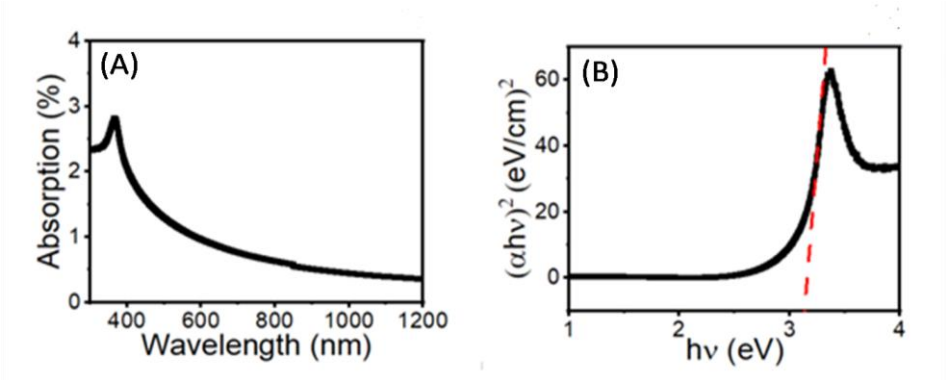

Fig. 6 UV visible spectra ZnO nanorods. (a) Absorption band (b) Tauc plot revealing the bandgap.

3.5 Piezoelectric sensors

A prototype of piezoelectric sensor was fabricated on a flexible substrate. Powder sample of ZnO was mixed with a polymer and sandwiched between two flexible transparent tapes. Copper electrodes were used as terminal (Fig. 7(A)). The strain was applied to the sensor device by bending the substrate and the voltage was measured with the help of a multimeter as shown in Fig. 7(B). The change in voltage in the mV range was observed. Fig. 8. shows the repeatability of the sensor device after 50 successive runs.

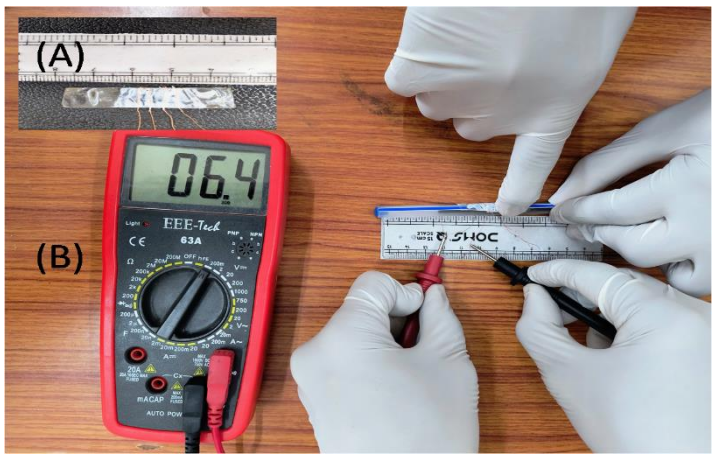

Fig. 7 (A) Prototype of piezoelectric sensor device. (B) Measurement on piezoelectric sensor device.

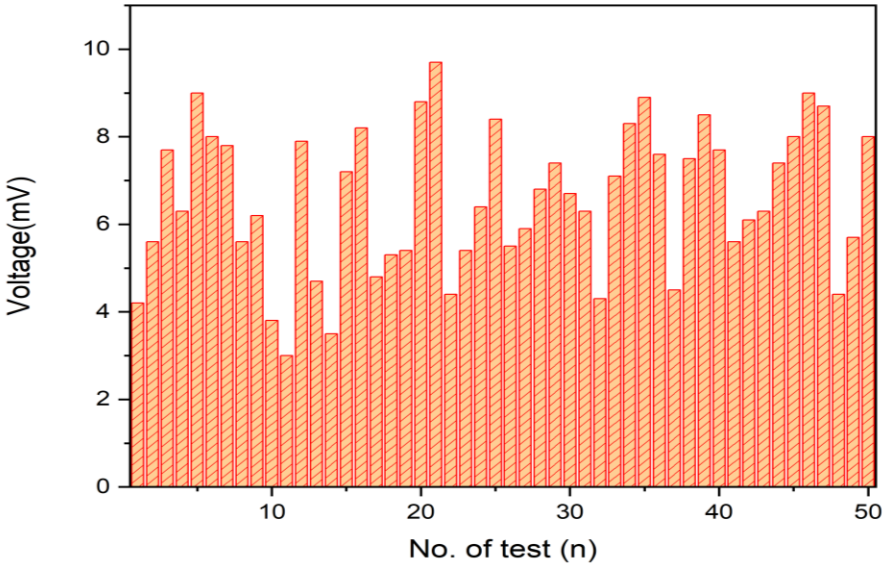

Fig. 8 Piezoelectric sensor device performance.

4. DISCUSSIONS

4.1 Formation of ZnO-NR

Microwaves is a particular region of the electromagnetic waves (1×10^3 to 3×10^5 MHz). When microwave is subjected to a material, it makes the molecules to rotate and vibrate rapidly, generating friction between them, thus heating the sample. This heat spreads uniformly through the solution, causing it to catalysing the reactions needed break the zinc acetylacetonate (Fig. 9) to form Zn and O in atomic/ionic forms.

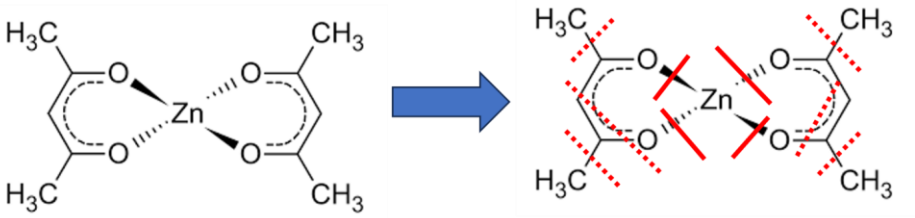

Fig. 9 Schematic diagram of breaking of zinc acetylacetonate.

When Zn makes the bonds with O, it forms ZnO molecule. Accumulation of many ZnO molecules form ZnO small clusters. These small clusters of ZnO can be considered as seeds for further development of ZnO nano structures. The PVP, during the synthesis process, decomposes into

monomers that attached to the surface of ZnO small clusters. These monomers form a protective layer on the surface of ZnO small clusters that prevents them from growing to form large structures. These ZnO/PVP produce curdle which is white in colour and is translucent. When it is centrifuged, white substances settle down at the bottom, leaving the remnant solution at the top. These white substances, when treated with ethanol, PVP gets dissolved. When treated with water, the remnant polymer and ethanol is washed away, keeping only ZnO. Final overnight heat treatment at lower temperature, removes the water, ethanol content if any present in the sample.

4.2 Mechanism of sensor

The piezoelectric voltage generation in ZnO nanorods is due to their non-centro symmetric wurtzite crystal structure. When mechanical stress is applied to the nanorods, (*e.g.* bending, stretching, or compressing) the deformation displaces Zn^{2+} and O^{2-} ions along the nanorod's c-axis, creating a dipole moment and in turn an internal electric field is generated. This leads to charge separation with positive charges being accumulated at the Zn-terminated end and negative charges at the O-terminated end, generating a piezoelectric potential. The high aspect ratio of ZnO nanorods makes them highly sensitive, and performance is size dependent as well as dependent on the degree of crystallinity and alignment. They convert mechanical energy into electrical signals. In our case the obtained signal due to bending of flexible device is in the range of mV. Attempts are in progress to optimise the device model for better performances.

CONCLUSION

ZnO nanorods were successfully synthesized by microwave method in the powder form and on the Si substrate. The SEM analysis confirmed the formation of nanorods that exhibit well-defined average length of 180 nm and diameter of 36 nm. EDAX analysis of ZnO nanostructures confirms the elemental composition of Zn and O with uniformity composition, thereby validating the purity of ZnO nanostructures. The sharp, well-defined peaks in the XRD patterns confirm high crystallinity of ZnO nanorods with wurtzite crystal structure. The UV-visible spectrum of ZnO shows a sharp absorption edge, confirming its direct bandgap. The protype

device confirms the piezoelectric properties of ZnO. Attempts will be made to improvise the device for real applications in day to day life.

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