Chapter 6

APPLICATIONS OF ZnO THIN FILM & NANOSTRUCTURE

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6. Introduction

ZnO Nanomaterials have been extensively studied for application in various kinds of nanoscale functional devices used widely in the chemical industry, medical diagnostics, food technology, ultraviolet testing, national defence and our daily life [1–5]. ZnO nanostructures are good candidates upon which to construct functional devices, because of their low toxicity, good thermal stability, good oxidation resistibility, good biocompatibility, large specific surface area and high electron mobility [6]. With the help of advanced micro-fabrication techniques, ZnO nanostructures have been used widely in field-effect transistors, light emitters, lasers, solar cells and sensing [7–10]. This chapter deals with the probable applications of ZnO film and its nanostructure. Since Zinc oxide has non-Centro symmetric crystal structure, it shows piezoelectricity. We have applied ZnO nanorods array in its simplest form as a vibration sensor, utilizing both its piezoelectric and semiconducting property. The methane gas sensing of ZnO film has also been investigated. The switching behaviour of electrical resistance of ZnO film have been observed, that may find its application in resistive switching.

6.1 Piezoelectric effect in ZnO nanorods array for potential application as vibration sensor

Z.L. Wang et. al. [11] at Georgia Institute of Technology, U.S.A., first proposed the self-powered nanotechnology in 2006, and developed the nanogenerator for the self-powered system. The nanogenerator converts random mechanical energy into electric energy using piezoelectric zinc oxide nanowire arrays. The mechanism of the nanogenerator relies on the piezoelectric potential created in the nanowires by an external strain: a dynamic straining of the nanowire results in a transient flow of the electrons in the external load because of the driving force of the piezopotential. The advantage of using nanowires is that they can be triggered by tiny physical motions and the excitation frequency can be one Hz to thousands of Hz, which is ideal for harvesting random energy in the environment.
6.1.1 Working of a single nanowire ZnO nanogenerator

Figur 6.1 shows the working principle of a ZnO nanogenerator [11]. A Schottky barrier is at the metal tip T- Nanowire (NW) interface. Once being slowly deflected, the asymmetric piezoelectric potential in the NW changes the profile of the conduction band (CB). The local positive piezoelectric potential at the contact area results in a slow-flow of electrons from ground through the load to the tip. The electrons will be accumulated in the tip. When the tip scans across the NW and reach its middle point, a drop in local potential to zero results in a back flow of the accumulated electrons through the load into ground. Once the tip reaches the compressive surface, a local negative piezoelectric potential raises the profile of the conduction band. If the piezoelectric potential is large enough, electrons in the n-type ZnO NW can flow to the tip. This circular motion of the electrons in the circuit is the output current.

![Diagram of ZnO nanogenerator](image)

*Fig. 6.1 Working of a single ZnO nanorod nanogenerator.*
6.1.2 Experimental method

We have prepared ZnO nanorod array on ZnO seed layer coated p-type Si substrate by sol-gel spin coating method and hydrothermal process as described in section 5.1 of chapter 5. The morphology of the nanorods is shown in figure 6.2.

Fig. 6.2 FESEM image of film surface for two different parts (a) & (b).

The piezoelectric properties of the film were measured using 2400 Keithley Source meter and Ultra sonic cleaning unit (TELSonic ULTRASONIC, Model- TPC-15) operating at 33 KHz. The device is made by making two electrical contacts of copper wire on the surface of the nanorods using silver conducting epoxy (TED PELLA), as shown in figure 6.3. The device is fixed to the bottom surface of ultrasonicating chamber using double sided tape, this is shown in figure 6.4. The experimental arrangement is shown in figure 6.5, in which the device is connected to the source meter while being kept fixed in ultrasonic cleaner.
Fig. 6.3 ZnO nanorod array device with electrical contact using silver conducting epoxy.

Fig. 6.4 Top view of ultrasonic cleaner containing the ZnO nanorod array device. The film is fixed inside it using double-sided tape.
6.1.3 Working of ZnO nanorods array as vibration sensor

When the dc voltage is applied to the ZnO nanorods array device using the source meter, while the ultrasonicator containing it was kept OFF, a normal I-V characteristics of the device was recorded, this is shown in figure 6.6. This I-V characteristics is similar to that of ZnO film. When the measurement of I–V characteristics is done while the ultrasonicator was ON, we observe a background spikes in I-V of the device, as shown in figure 6.7. These spikes spans in + ve as well as – ve current directions.
Fig. 6.6 Current–voltage characteristics of the nanorod device when the Ultrasonicator was OFF.

Fig. 6.7 Current–voltage characteristics of the nanorod device when the Ultrasonicator was ON.
The origin of these spikes can be explained by a model proposed by us. When the ultrasonicator is OFF there is no motion in the aligned nanorods in the device and I-V characteristics is similar to the ZnO film. When the ultrasonicator is ON the ultrasonic waves propagate through air in the ultrasonicator and brings the aligned nanorods into vibration, as they have one end fixed and other end free as shown in figure 6.8. Due to this vibration all the nanorods experience bending in random directions. The nanorods surrounding the silver contact, which is used for fixing copper wire in the device while vibrating, bends and touches the silver contact instantaneously, this situation is reverse to that of the single nanorod nanogenerator, in which the metal tip scans across the nanorod diameter but here metal is fixed while nanorod is bending by the influence of external agency to touch the metal. Now this instantaneous bending of nanorod and formation of metal semiconductor contact generates a piezovoltage and the corresponding piezocurrent as described in section 6.1.1. This piezocurrent comes into background of the I-V curve while taking measurement. The spike in – ve current direction corresponds to bending in opposite direction. Thus, this device can be employed to detect mechanical vibration in nanoscale and can be used as vibration sensor, when its output is amplified by means of suitable electronics.

Another interesting observation is found during the recording of I-V of ZnO film. When the ZnO film was pressed hard by the wooden end of a match stick while the recording of I-V was in progress using the computer interfaced Keithley 2400 sourcemeter, similar spike came in the I-V curve, as recorded for the nanorod array device in presence of ultrasonic waves. This confirmed that these spikes are related to the externally applied strain in the material and hence to piezoelectricity.
Fig. 6.8 A Model to explain the observed spikes in I-V curve (Fig. 6.7) after the Ultrasonicator was turned ON.

To confirm that this effect is not due to the noise in the current, two standard carbon resistors of 560 KΩ resistance values are connected in series, which makes the resistance of the combination ~ 1 MΩ. This value is nearly same as of the ZnO nanorod device and the current–voltage characteristics (figure 6.9a & figure 6.9b) of the combination is taken under same conditions as was done for ZnO nanorod device.
Fig. 6.9a Current–voltage characteristics of the carbon resistor when the Ultrasonicator was ON.

Fig. 6.9b Current–voltage characteristics of the carbon resistor when the Ultrasonicator was OFF.
Figures 6.9a and 6.9b shows that there is no noise or spike like variation in I-V curve when the ultrasonication is ON. This implies that the spikes in the current in the nanorod device is due to piezoelectric property of Zinc Oxide and its nanorod morphology which enables to show such effect.

6.2 Conclusions

We have applied hydrothermally prepared ZnO nanorods array as a vibration sensor. Semiconducting nature and piezoelectricity of ZnO are the properties that were utilized for this application. A model is developed for the working of the device based on the single ZnO nanorod nanogenerator.

References


