Ultraviolet photodetection characteristics of Zinc oxide thin films and nanostructures

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Abstract: ZnO thin films were deposited by using RF sputtering technique at 150W and 4x10⁻³ mbar pressure. Post-deposition rapid thermal annealing of ZnO thin films were carried out at 1000°C for 600sec. ZnO nanostructures (nanowires/nanorods) were hydrothermally grown by using equimolar solution of Zinc nitrate and hexamethyltetramine. Morphology of ZnO thin films and nanostructures were investigated using scanning electron microscope. A comparative study on the ultraviolet photodetection behaviour of ZnO thin films and nanostructures were carried out by adopting current-voltage measurement technique at room temperature. ZnO annealed films have shown relatively lower transient photocurrent decay as compared to as-deposited film, which may be due to the faster evacuation of the charge carries. However, in case of ZnO nanorods transient photocurrent decay is relatively slow than that of nanowires, which is attributed to delayed readsoption of oxygen molecules onto the nanorods surface due to its larger width.

Keywords: Thin films; Nanostructures; Photodetection; Ultraviolet; Zinc Oxide

1. Introduction
In recent years, ultraviolet (UV) light is used in many commercial fields such as telecommunications, ozone and pollution monitoring, high temperature flame detection, and missile warning systems [1–3]. The well-established CMOS compatible semiconductor such as silicon (Si) has a limitation for UV detection due to its low bandgap. Since the bandgap energy of Si is 1.1eV, costly high pass optical filters and phosphors are needed to stop low energy photons [4-9]. Therefore, the Si based UV detector performance are significantly reduced due to its efficiency and increase of dark currents [10-11]. However, the bandgap of ZnO (3.37eV) corresponds to the intermediate region between UV and visible light. In addition, outstanding physical and chemical properties of ZnO nanostructures such as large surface area, radiation hardiness [12], superior spatial resolution [13] and high electron mobility provide a platform for versatile applications such as in food processing, sterilization of medical equipment, research laboratories, semiconductor processing industry etc., where an installation of UV...
detector is highly required. In addition, ZnO is also highly desired for thin film transistors, light emitting diodes, solar cells, surface acoustic wave and energy harvesting devices [14-15]. Herein, synthesis of ZnO thin films/nanostructures and study of their UV detection behavior were systematically carried out.

2. UV detection mechanism of ZnO thin films and nanostructures

Intrinsic defects of ZnO that is oxygen vacancies and/or zinc interstitials plays a vital role in UV detection mechanism. The conductivity of ZnO is extremely sensitive to UV light exposure. Basically, the photosensitivity in ZnO is regulated by chemisorption of oxygen [15-19]. In the absence of UV light, oxygen molecules get adsorbed on the surface as negatively charged ions by confining the free electrons, thereby create a depletion layer with low conductivity near the surface:

\[ O_2 (g) + e^- \rightarrow O_2^- \text{ (ads.)} \]  

(1)

When the sample is illuminated with UV light, whose photon energy is more than the bandgap of ZnO, it causes generation of electron-hole pairs. Adsorbed oxygen ions combine with the holes to produce oxygen molecules, which desorbs from the surface. Under bias, the unpaired electrons are collected at the anode; thereby an increase in conductivity takes place with the decrease in the width of depletion layer [20-22].

\[ h^+ (h\theta) + O_2^- \text{ (ads.)} \rightarrow O_2 \]  

(2)

After the UV exposure, oxygen gets readsorbed on the surface until equilibrium is restored. This readsorption is a slow process and significantly lengthens the relaxation time constant for the devices [23-27]. This slow transient can be expressed by an exponential function as [22]

\[ I(t) = I_d + (I_p - I_d)e^{-t/\tau} \]  

(3)

Where I (t) is the transient current, \( I_d \) is the current measured in dark, \( I_p \) is the current measured under UV illumination, t is the time after turning off UV light. Using exponential fit to the experimental data, the decay time constant (\( \tau \)) can be calculated for all the samples. The details of the samples used for UV detection are given in Table 1.

3. Experimental

For UV detection measurement ZnO thin films were deposited by using RF sputtering technique at 150W and 4x10^-3 mbar pressure. Post-deposition rapid thermal annealing (RTA) of ZnO thin films were carried out at 1000°C for 600sec. ZnO nanostructures (nanowires/nanorods) were hydrothermally grown by using equimolar solution of Zinc nitrate and hexamethytetramine. Morphology of ZnO thin films and nanostructures were investigated using scanning electron microscope (SEM).

Top electrodes were deposited by thermal evaporation of aluminum. Ultraviolet photodetection properties were investigated by adopting current-voltage (I-V) and current-time (I-t) measurement. The nature of electrical contact between metal (aluminum) and semiconductor (ZnO) samples has been observed by taking the current-voltage measurement before studying the photodetection behavior. The nature of electrical contact between metal (aluminium) and semiconductor (ZnO) samples has been observed by taking the current-voltage measurement before studying the UV detection behaviour. Linear enhancement of current with sweep in voltage of ±5V for all samples depicted good Ohmic nature of the electrical contact. Fig. 1 represents the current voltage
characteristic of ZnO thin film based UV detector. The details of the samples used for UV detections are given in Table 1.

Table 1. Comparative study of UV detection behaviour of various samples.

| Sample No. | Sample Type   | Growth Condition             | UV on/off ratio | Decay Constant (τ in sec.) |
|------------|---------------|-----------------------------|----------------|---------------------------|
| S1         | ZnO thin film | 150W, 4×10⁻³mbar, Ar/O₂-2:3 | 1.5            | 47                        |
| S2         | Annealed film | 1000 °C, 600sec             | 1.7            | 21                        |
| S3         | Nanowires     | 95 C, 0.01M                 | 6.1            | 39                        |
| S4         | Nanorods      | 75 C, 0.05M                 | 2.9            | 57                        |

Fig. 1: Current-voltage plot of ZnO thin film based UV detector in air ambient.

Fig. 2: SEM images of ZnO thin films (a) As-deposited (S1), and (b) annealed at 1000 °C in air ambient for 600sec (S2). The scale bar represents 100nm.

4. Results and discussions

4.1. Morphological properties of ZnO thin films and nanostructures

Fig. 2 (a) shows the SEM images of rf sputtered ZnO thin films deposited at (150W, 4×10⁻³mbar, Ar/O₂-2:3). Smaller granular structure with uniform and continuous morphology of ZnO film has been observed. Fig. 2 (b) shows the SEM images of ZnO thin film annealed at 1000 °C in air ambient for 600sec. Longer annealing period provides sufficient time and thermal energy to the ZnO microstructures for subsequent growth and as a result rough and porous surface is obtained [28].
Fig. 3: FESEM images of ZnO nanostructures (a) ZnO Nanowire (S3), and (b) ZnO nanorods (S4). The scale bar represents 5µm.

Fig. 3 (a) depicts the tilted cross-sectional SEM images of ZnO nanowires. The nanowires were grown at lower concentration (0.01M at 95°C) and results thin and long nanowires with a diameter < 30nm, and the length around 5-6µm. Fig. 3 (b) depicts a nanorod-like morphology with a concentration of 0.05M at 75°C. Although low temperature favours the formation of nucleation sites, it does not have enough energy for the subsequent growth of nanostructures. It indicates that the growth temperature is not sufficient for faster growth along c-axis. Therefore, the length of nanostructures was restricted and as a result short nanorods are obtained.

4.2. UV detection of ZnO thin films

Fig. 4: Current-time and decay curve of (a) as-deposited (S1), and (b) RTA processed ZnO thin film (S2) under UV exposure.

Fig. 4 (a) and (b) shows current-time and decay curve of (a) as-deposited (S1), (b) RTA processed (S2) ZnO thin film. The on/off ratio for the sample S1 is 1.5, whereas it is found to be 1.7 for S2. Fig. 2 (a)
(b) also shows the transient photocurrent decay of samples S1 and S2 with decay time constant ($\tau$) value of 47 sec and 21 sec, respectively. Annealed films have relatively lower decay constant ($\tau$), which may be due to the faster evacuation of the charge carries. The relatively better response of sample S2 may be due to the annihilation of surface trap states during RTA process. In addition, the sample S2 has shown the quasi saturation of photo current.

4.3. UV detection of ZnO nanostructures

Fig. 5 (a) and (b) shows current time and decay curve of ZnO nanowires (S3) and ZnO nanorods (S4) under UV excitation. The on/off ratio of ZnO nanowires (S3) photodetector is about 6.1, whereas it is found to be 2.9 for sample S4. From experimental results, the decay time constants $\tau_1$ and $\tau_2$ are estimated to be around 39 sec and 57 sec, respectively by fitting the decay curve using the exponential function. However, the photocurrent was not well saturated for both sample S3 and S4, which may be due to the presence of surface states in the aqueous grown nanowires/nanorods. Secondly, in case of nanorods (S4) the decay time constant is relatively slow, which is attributed to delayed evacuation of charge carriers.

![Fig. 5](image)

**Fig. 5:** Current-time and decay curve of (a) ZnO nanowires (S3), and (b) ZnO nanorods (S4) under UV exposure.

5. Conclusion

Ultraviolet photodetection properties of ZnO thin films and nanostructures were obtained by adopting current-voltage (I-V) and current-time (I-t) measurement. Annealed films have shown relatively lower decay constant ($\tau$) than that of as-deposited ZnO films, which may be due to the faster evacuation of the charge carries. Among different nanostructures, ZnO nanowires have shown higher on/off ratio as compared to ZnO nanorods which is attributed to their higher aspect ratio. From experimental results, the decay time constants $\tau_1$ and $\tau_2$ are estimated to be around 39 sec and 57 sec, for nanowires and nanorods, respectively by fitting the decay curve using the exponential function. The above experimental results can provide a platform in order to achieve room temperature operated next generation of metal oxide UV detector.
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