Comparative Study of Photoresponse from Vertically Grown ZnO Nanorod and Nanoflake Films

Muni Raj Maurya, Vijaykumar Toutam, and Divi Haranath

ABSTRACT: Zinc oxide (ZnO) based ultraviolet (UV) photodetectors have been fabricated and their photoresponse is studied in Schottky diode configuration. A cost-effective single-step electrochemical deposition method is adopted for the growth of ZnO film with nanorod (NR) and nanoflake morphology. A comparative study of the photodetection parameters based on surface trap states, crystallinity, and strain is done for two different morphology films. Significant photocurrent enhancement is observed for the nanorods under UV light, with appreciable photoresponse in the blue region. A template-assisted growth of ZnO NR film is proposed for better photoresponse and sensitivity of the device, useful for various optoelectronic applications.

INTRODUCTION

Zinc oxide (ZnO) is inherently an n-type semiconductor with a direct band gap of ~3.37 eV and a large exciton binding energy of ~60 meV at room temperature.1 Due to a hexagonal wurtzite crystal structure and a noncentro symmetry of the oxygen atom in a tetrahedral coordination geometry, zinc oxide shows interesting physical and chemical properties. Over the past decade, one-dimensional (1D) nanostructures of ZnO have emerged as a subject of intensive study.3 Due to an increase in the density of trap states at the surface and a large surface-to-volume ratio with a reduction in dimension, ZnO 1D nanostructures have been extensively used for various electronic, optoelectronic, electromechanical, and electrochemical applications.4,5 Devices such as light-emitting diode,6,7 laser diode,8 photovoltaic cell,9 piezoelectric transducers,10−13 gas sensors,14,15 and so on have been realized and can be potentially applied in military, food sector, space technology, pollution control, commercial products, and many more.16

ZnO 1D nanostructures can be grown by several methods such as chemical vapor deposition,17 pulsed laser deposition,18 hydrothermal synthesis,19,20 electrochemical deposition (ECD),21,22 and so on. Compared with other synthesis methods, ECD is more advantageous, as it does not require high vacuum, high pressure and can be operated at lower temperatures. As a result, inexpensive transparent conductive films and plastic can be used as substrates for deposition. Izaki et al23 and Peulon et al24 reported ECD of ZnO on a transparent conducting glass substrate, with its major application in optoelectronics. ZnO 1D nanostructures in various device configurations such as metal insulator semiconductor,25,26 n−p junction,27 Schottky diode,28−30 and so on have been reported depending on its applications. Among these, metal-semiconductor rectifying behavior in a Schottky diode configuration is advantageous for photodetection, as it requires a low bias and has a high sensitivity with a low dark current.31 Photodetectors are basically transducers whose one of the characteristic properties changes when illuminated with light. As a photodetector, ZnO is extensively used for UV detection. A change in conductivity upon illumination is measured for the detection that is mainly due to the depletion region formed by the adsorption and diminished by the desorption of oxygen ions on the surface of nanostructure.32,33 Various 1D nanostructures such as nanowires,34 nanobelts,35 and nanorods (NRs)36 have been exclusively studied in this regard. An efficient photodetector should have a high sensitivity, high speed, high spectral selectivity, high stability, and better signal-to-noise ratio. The photosensitivity and speed of the detector depends on the lifetime of charge carrier and the transit time, respectively. The presence of defects in photodetector material determines the spectral selectivity and stability of the device.37 A higher magnitude of the measured quantity is desirable to improve the signal-to-noise ratio. In ZnO 1D nanostructures, surface defects prolong the carrier lifetime and the reduced dimensionality shortens the transit time. Most of the study for photodetection with ZnO is pertaining to in-plane-fabricated devices. However, devices with vertically grown nanostructures become very important as the surface phenomenon is dominant in the UV detection. The out-of-plane growth offers a large enhancement and an illumination from the back provides a large active area for sensing applications. Also, the study of photodetector character...
istics due to plasmonics from metal nanoparticles decorated on vertically aligned nanorods is still emerging.38,39 Thus, it is very important to have a comparative study of the photodetector characteristics from several vertically grown nanostructures of ZnO.

The present work is a comparative study of the photoresponse for two different morphology samples that are out-of-plane grown ZnO films under metal–semiconductor Schottky diode configuration. A single-step electrochemical deposition is adopted for the nanostructured growth of ZnO film on a transparent conducting glass substrate. The electrolyte composition and ion concentration are varied for vertical growth of different nanostructures. Influence of the varied structural growth on the spectral photoresponse and sensitivity due to light propagation along the thickness of the film is studied in detail.

**RESULTS AND DISCUSSION**

**Figure 1.** Surface and cross-sectional SEM images of samples A and AE with their corresponding $I$–$V$ characteristics. (a) ZnO thin film of nanoflake morphology in sample A, cross-sectional image in the top-left inset shows the initial growth of ZnO along the $c$-axis beneath the nanoflakes. Bottom-left inset shows a magnified view of the void region between the nanoflakes. (b) SEM image of sample AE prepared by etching sample A. Top-left inset shows the cross-sectional image for the initial growth of NR. Bottom-left inset shows the NRs with a hexagonal facet. (c, d) $I$–$V$ characteristics of samples A and AE under dark and UV (365 nm) illumination, respectively.

Figure 1 shows the scanning electron microscopy (SEM) images of samples A and AE surfaces along with the cross section and their corresponding $I$–$V$ characteristics under dark and UV illumination. A film of densely packed nanoflakes with a thickness of ∼2.5 μm is observed for sample A, as shown in Figure 1a. Cross-sectional image in the top-left inset also shows the formation of a nanorod prior to the growth of nanoflakes. From the bottom-left inset, it is observed that the void region has a nanorod growth. During the initial deposition of ZnO, the growth along the $c$-axis is favored relative to other axes leading to the formation of nanoflakes. This is due to the net dipole moment induced along the $c$-axis from an alternate growth of Zn$^{2+}$ and O$^{2-}$ terminated polar faces on randomly oriented nuclei.40,41 Further deposition leads to the supersaturation of OH$^-$ ion occupancy along the $c$-axis, allowing random occupancy of these ions along other crystallographic axes.42 The competition for growth along the multiple lattice planes suppresses the in-plane growth, leading to the formation of nanoflakes.

Figure 1b shows the SEM image of sample AE surface. Sample AE is prepared by etching sample A, which does a partial removal of nanoflakes. Compared with Figure 1a, the density of nanoflakes in Figure 1b is effectively reduced. The cross-sectional image in the top-left inset shows the initial growth of NRs beneath the nanoflakes. The thickness of sample AE is similar to that of sample A, and ZnO NRs with perfect hexagonal facets are revealed as shown in bottom-left inset. This further strengthens the concept of nanoflake growth under the supersaturated hydroxyl ion occupancy of Zn$^{2+}$ sites. Figure 1c,d shows the $I$–$V$ characteristics under dark and UV illumination of samples A and AE, respectively. Typical Schottky diode characteristics are observed for both samples under dark (black) and UV illumination (red). At 1 V of applied bias, the magnitude of dark current increased approximately by threefold for sample AE compared with that for sample A. This increase in dark current after etching is attributed to a change in the surface morphology. It is observed from Figure 1a,b that the density of nanoflakes on sample A is large compared with that on sample AE. This increases the density of deep-level defects present in nanoflakes,43 acting as trap centers for charge carriers. As a result, lower dark current is observed in sample A compared with sample AE (see Figure 1c,d (black curve)). Significant photoresponse under UV illumination is observed for samples A and AE as shown in Figure 1c,d (red curve). Exposure to UV light with the photon energy higher than the band gap of ZnO generates the electron–hole pairs.32 Photogenerated holes move toward the surface of nanostructure and discharge adsorbed oxygen ions. With the extinction of depletion layer, the conduction region increases and the photogenerated unpaired electrons contribute to a quick rise in current. From Figure 1c,d (red curve), it is observed that on-current under UV illumination at 1 V increased by 9 times for sample AE compared with that for sample A. Hence, it is desirable to have less number of...
nanoflakes for a high magnitude of photocurrent. As the growth of nanoflakes is due to the supersaturation of hydroxyl ion occupancy on Zn\(^{2+}\) terminated polar faces, the suppression of these OH\(^–\) ions leads to the growth of nanorods. Also, doping of metal ions increases the conductivity and wide spectral photoresponse. For this purpose, gold salt is added during ECD. Figure 2 shows the SEM images along with the cross section and corresponding I–V characteristics of samples B and BE prepared by adding gold salt in the electrolyte during ECD. A film of vertically grown high-density NRs along with very few nanoflakes is observed in the SEM image of sample B as shown in Figure 2a with a thickness \(\sim 1.3 \mu m\). The top-left inset shows...
the cross-sectional image of vertically grown NRs. No trace of gold is found in sample B as verified from the EDS data shown in the bottom-left inset in Figure 2a. The near-total reduction in the density of nanoflakes by the addition of HAuCl4 salt is due to the suppression of OH− ion by H+ ions in the electrolyte. This constraint favors the growth only along the c-axis and forms ZnO nanorods.

Figure 2b shows the SEM image of sample BE prepared by etching sample B. A compact film of NRs with the total absence of nanoflakes is observed in sample BE with thickness ~1 μm. Etching completely removes the nanoflakes and makes thin-film surface uniform. The cross-sectional image in the top-left inset in Figure 2b shows the compact vertical growth of NRs. The magnified image shown in the bottom-left inset in Figure 2b depicts the hexagonal growth of NRs with small pits on its surface introduced by etching process. The I−V characteristics of samples B and BE under dark and UV illumination are shown in Figure 2c,d, respectively. A low dark current is observed in sample B compared with sample BE due to the presence of nanoflakes. This is analogous to the dark current behavior observed in samples A and AE (see Figure 1c,d). With a decrease in the density of nanoflakes from samples A to BE, the current behavior changes from Schottky to semiconductor characteristics. For samples B and BE, dark current at 1 V is in tens of milliamperes, compared with samples A and AE. Under UV illumination, the photoresponse is observed for both samples B and BE, with tens of milliamperes current difference between excited and dark current. Increased surface trap states in NRs prolongs the photocarrier lifetime; as a result, a higher photocurrent density of the nanostructures-based photodetectors under dark and UV illumination.

Table 1. Time Constant and Optical Band Gap of Samples

| sample | rise time (τr) (s) | decay time (τd) (s) | band gap (Eg) (eV) | lattice strain |
|--------|------------------|-------------------|------------------|---------------|
| A      | 126              | 37                | 3.74             | 1.3 × 10^{-3} |
| AE     | 104              | 118               | 3.76             | 1.1 × 10^{-3} |
| B      | 78               | 227               | 3.76             | 1.02 × 10^{-3}|
| BE     | 55               | 721               | 3.74             | 0.7 × 10^{-3} |

Figure 3c shows the UV−vis absorbance spectra of all of the samples. A wide absorption band, with a prominent peak at ~320 nm, is observed for all of the samples. The optical band gap was calculated from Tauc plot of the absorbance data given by \( aυυ = A(υυ − E_g)^n \), where \( A \) is the absorption coefficient, \( υυ \) is the photon energy, \( A \) is a constant, \( E_g \) is the band gap, and \( n \) is the nature of transition with values 1/2, 2, 3/2, and 3 for direct allowed, indirect allowed, direct forbidden, and indirect forbidden transitions, respectively. As ZnO is a direct band gap, the \( n \) value is taken as 1/2. Figure 3d shows the Tauc plot for the absorption spectrum of sample BE. The band gap as measured from the intercept on the x-axis for \( aυυ = 0 \) is 3.76 eV. The calculated value of the band gap for all of the samples from Tauc plot is given in Table 1. This increase in the band gap is attributed to the polycrystalline nature of ZnO thin films.

Figure 4 shows the time-dependent photoresponse of ZnO nanostructure-based photodetectors under dark and UV−vis illumination. In dark, low current is observed for all of the samples and was allowed to saturate for initial 200 s as shown in Figure 4a,b. This is due to the adsorption of oxygen molecules and the redistribution of charge carriers that form a space-charge region along the surface of the nanostructure. On the other hand, when the device is illuminated with UV light, an increase in current is observed for all of the samples (see Figure 4a,b). The increase in current is due to increased conduction with desorption of oxygen ions by photogenerated holes and extra charge carriers in terms of unpaired electrons. A slow rise in the excited current is observed for samples A and AE, compared with sample B and BE, respectively, as shown in Figure 4a,b. This slow response is attributed to the large surface area of the nanoflakes as observed from the SEM data and an increase in the strain as calculated from the XRD data. This increases the depletion region and the density of the deep-level defects. As a result, the gradual accumulation of unpaired electrons by desorption of oxygen under UV light takes place, giving rise to a slow response. On the other hand, a faster response time for samples B and BE is due to the reduced density of the nanoflakes. Among all of the samples, BE has the least rise time of 55 s, as it is completely devoid of nanoflakes (see Figure 2b). The decay time and rise time of photocurrent were calculated by considering 63% raise from the dark current and 37% fall from the maximum excited photocurrent (see Table 1).

Two regimes are observed in the decay response from all of the samples. An initial steep fall in the decay component upon switching off of UV light arises from the fast carrier thermalization, hole-trapping by surface states, and electron−hole recombination. The second regime of decay response is due to the gradual capturing of the electrons by adsorbing \( O_2 \) molecules as shown in Figure 4a,b. Samples A and AE have fast decay response compared with samples B and BE. This is due to the high density of the deep-level defects, present in the nanoflakes, that act as trap centers for the charge carrier. On the
other hand, a large decay time for samples B and BE is attributed to a slow diffusion of O₂ molecule with an increase in the compact nature of the film. Figure 4c shows the enhancement factor and the sensitivity plot of fabricated photodetectors. The enhancement factor of the photodetector is calculated by \((I_{\text{UVmax}} - I_{\text{Dark}})\) and sensitivity by \(((I_{\text{UVmax}} - I_{\text{Dark}}})/I_{\text{Dark}}\). The devices made of sample A have low enhancement compared with those made from sample AE, and similar trend is observed for sample B with respect to sample BE. This is due to an increase in the density of less-conducting nanoflakes compared with high-conducting NRs. In sample BE, wherein a compact and smooth film of NRs is present, the enhancement is maximum. Due to a large dark current, the sensitivity of samples B and BE is less compared with that of samples A and AE. On the other hand, the enhancement of sample BE is significant. Thus, sample BE can be applied where a large signal-to-noise ratio is desirable. A low dark current in sample A offers high sensitivity for easy detection. Sample AE has appreciable sensitivity and enhancement.

As the photoresponse of the device is spread over a wide UV spectral range and near visible region as observed from UV−vis spectrum (see Figure 3c), the response in the blue region using a blue filter is verified. An appreciable enhancement in the photocurrent is observed for samples B and BE using the blue filter as shown in Figure 4d. However, no such response was recorded with other color filters. The response in the blue light is attributed to the desorption of oxygen ions by the direct bombardment with incident light photons through energy transfer.46

As discussed, vertically aligned growth architecture with a high-density nanorod film gives a large enhancement in the photoresponse as a large surface area is available for UV exposure, but at a cost of high dark current. However, nanoflake film shows high sensitivity due to low dark current but low enhancement due to deep-level scattering centers. Also, the prepared films have a high density of nanostructures, which may not allow complete exposure of the surface area for oxygen adsorption. As a result, the sensitivity and response time of the device is affected due to the reduction in the surface coverage and a slow diffusion of oxygen molecule. With a high signal-to-noise ratio as an advantage in fabricated photodetector for sample BE, the sensitivity and response time can be improved by well-separated growth of ZnO NRs. Use of template allows the growth of an array of individual nanostructure, which will provide the maximum surface area exposed for efficient adsorption of oxygen molecules and less trap centers due to reduction in the grain boundaries. Hence, photodetectors with high sensitivity and large enhancement can be obtained by having well-separated vertically aligned growth of nanorods.

**CONCLUSIONS**

In conclusion, a comparative study of the photodetector characteristics based on the surface trap states, crystallinity, and strain is done for vertically grown ZnO films of nanoflakes and nanorods prepared by electrochemical deposition. The influence of hydroxyl ion concentration on the growth mode and its effect on the photodiode characteristics is discussed. It was found that ZnO nanorod films are suitable for a large enhancement in the signal for the UV detection and ZnO

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**Figure 4.** Time-dependent photoresponse of electrodeposited ZnO nanostructures at a constant bias of 1 V. (a, b) Switching behavior of samples A, AE and B, BE under UV (365 nm) illumination, respectively. (c) Enhancement and sensitivity parameter plot of fabricated photodetector with device schematic. (d) Blue filter photoresponse of samples B and BE.
nanoflakes for a high sensitivity. Well-separated growth of ZnO nanorods is proposed to increase the surface area and reduce the charge carrier loss for a fast response and a high sensitivity.

**EXPERIMENTAL SECTION**

For the electrochemical deposition of ZnO film, a glass substrate coated with ~125 nm of indium tin oxide (ITO) and resistivity ~15–20 Ω cm is used as a cathode and platinum (Pt) as an anode. Sample A is prepared by ECD in the aqueous ± of 10 mM zinc nitrate hexahydrate [Zn(NO₃)₂·6H₂O] and 0.1 M potassium chloride [KCl] for 1 h at constant voltage of 1 V and temperature of 80 °C. Sample AE is prepared by etching sample A with Pt as the counterelectrode in a solution of 5 mM zinc chloride [ZnCl₂] and 0.1 M KCl under a constant reverse bias of 1.1 V at 85 °C for 3 h. Sample B was prepared by same method as sample A, except for the addition of 0.1 M gold salt [HAuCl₄·3H₂O] in deionized water to the electrolyte in 1:10 (v/v) ratio. Sample BE was prepared by etching sample B, similar to the conditions used for the preparation of sample AE. All of the samples were annealed at 300 °C in an inert atmosphere for 3 h.

Field-emission scanning electron microscope (Zeiss, Auriga) is used for the morphological observations of the grown samples. The crystalline nature of the grown film is characterized by a high-resolution X-ray diffraction (HRXRD) (PANalytical X'Pert PRO MRD System) using Cu Kα radiations (λ = 1.5406 Å). Optical properties of all of the ZnO films (samples A, AE and B, BE) were measured using Perkin-Elmer Lambda 950 UV/vis/NIR spectrophotometer. Photodetectors in diode configuration were fabricated using ITO of the sample substrate as an electrode for through exposure of light and silver film of thickness ~500 nm with area 4 × 4 mm² on the sample as the counterelectrode. Current–voltage (I–V) measurements were performed by the source-measuring instrument (Keithley model-2612A) using the labview program. Fabricated photodetectors were put in a dark box and voltage is swept from −1 to 1 V with an increment of 50 mV. For a particular voltage, the current value is averaged over five data points. Time-dependent photoresponse was measured for all of the samples at a constant bias of 1 V in UV (365 nm) illumination with a power density of 97 ± 3 μW cm⁻² and the visible region using appropriate color filters.

**AUTHOR INFORMATION**

**Corresponding Author**

*E-mail: toutamvk@nplindia.org. Tel: +91-11-45608359.

**ORCID**

Vijaykumar Toutam: 0000-0002-9462-0643

**Notes**

The authors declare no competing financial interest.

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