Growth of Multidimensional Zinc Oxide Nanorods Array for Enhanced UV Photoresponsivity

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Research Article

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Abstract

Ultraviolet (UV) photosensitive device was fabricated using ZnO nanorod array on substrate with copper electrodes. Facile open aqueous solution deposition technique was used to grow the ZnO nanorods forming an electrical bridge between copper electrodes. Powder X-ray diffraction patterns was used to confirm the polycrystalline wurtzite ZnO phase and scanning electron microscopy (SEM) techniques was employed to characterize the growth morphology of ZnO nanorods. A current-voltage (I-V) characterization in the dark exhibits the back-to-back diode characteristics. In the presence of ultraviolet (UV) radiation, enhanced photo-response was reported wherein photocurrent increases by two orders of magnitude at 2 V bias. This enhancement is mainly due to lateral interfacial contacts between neighboring grain-boundary of the nanorods arrays.

Introduction:

Zinc oxide (ZnO) is II-VI wide band gap semiconducting metal oxide having direct-bandgap of \(~ 3.2\) to \(3.3\) eV. Also, it has a high exciton binding energy of \(60\) meV, thus ZnO is a promising candidate for photonic devices in ultraviolet (UV) spectral range at the room temperature [1]. Recently, quantum size effects and band gap engineering in the ZnO nanostructures have demonstrates novel optoelectronic responses. Therefore, it is used in device systems such as a Schottky diode, photodetector, gas-sensor, photoemission device, field emission device, visible-blind UV photosensor piezo-phototronic devices [2-7]. More detailed survey on nanostructured devices using ZnO material can be found in comprehensive reviews [8,9]. In general, nano-bridging devices are based on lateral growth of suspended nanowires between prefabricated metal electrodes [9]. It has been proved that metal-semiconductor-metal junction leads to either ohmic or Schottky characteristics depending on their work function [10]. Most of the studies have reported a rectifying behaviour in the single or multiple nanorods bridge across trenched or interdigitated electrodes [1,3]. On the other hand, non-linear current-voltage characteristic analogous to back-to-back diode characteristics are often found in bulk and doped ZnO mainly used as high energy surge suppressor and protection devices [11,12]. In pulsed laser depositeed and annealed thin films of ZnO exhibits such non-linear I-V characteristics [13]. The planar nanorod array structures are poorly investigated in this context, despite the fact that planar nanostructured materials could provide large surface area and grain-boundary interconnects enables an added functionality like photoinduced current switching in the related devices [14].

In this paper, we report UV photo-switchable planar ZnO NRs array on copper micro-trenched-electrode fabricated on commercial printed circuit board to follow cost-effective and simplistic design approach. In the recent past ZnO nanorods are grown by various techniques including electrodeposition, thermal evaporation, metal organic chemical vapour deposition (MOCVD), vapour–liquid–solid growth method (VLS), arc discharge method, physical vapor deposition tecniques [15-20]. We used the generic open aqueous solution deposition (OASD) technique reported previously to grow ZnO NRs across microtrenched Cu-electrode [21]. To some extent it provides additional advantages such as control on
growth parameters and uniform deposition on large substrate area, low growth temperature, reproducibility, and cost effectiveness.

**Experimental:**

Commercially available printed circuit board (PCB) of copper clad thickness 35 µm was etched by conventional photolithographic technique for obtaining the trenched copper electrode configuration. The channels of these electrodes were 2 cm long and having 150 µm spacing between them. Then substrate was thoroughly washed using detergent, ethanol, and distilled water in an ultrasonic bath for removal of any dirt and oil traces. Finally, it has been dried in nitrogen flow and loaded in the deposition cell. For the facile growth of ZnO nanorods, an equimolar (25 mM) solution of zinc nitrate and hexamethylene tetramine (HMT) was separately prepared using deionised water as solvent. The substrates (Cu-clads) were mounted on Teflon holder and immersed into the solution maintained at equilibrium temperature 95 °C under slow stirring. The deposition was carried out for time duration of 3 hour. The sample substrates were taken out and rinsed several times with distilled water to get rid out of loosely attached ZnO NRs and later dried and checked for the electrical connectivity between electrodes. This process has been repeated 3-4 times till electrical connectivity gets established. Thus, active ZnO nanorods surface area becomes 2×0.0152 cm². At last, the deposited substrates were vacuum dried at 70 °C and were used for further characterization and photoresponse measurement. It is seen that ZnO NRs covers entire surface including copper electrodes and trenched area between electrodes as well. The deposition on copper layer remains practically inactive due to its short circuit contacts with underneath copper layer, therefore electrode masking become unimportant. The electrical connection to copper surface can be made by soldering another copper wire after scraping off ZnO deposits from contact points.

X-ray diffraction (XRD) patterns were recorded at room temperature with Bruker Axis D8-Advance X-ray Diffractometer using Cu-Kα radiation (λ=1.5406 Å). The morphology of device was characterized using Scanning Electron Microscopy (SEM) and elemental analysis was done with the help of energy dispersive X-ray spectroscopy (EDAX) operated at accelerating voltage range from 10 to 20 kV. UV-Vis absorbance spectra were obtained using Scan UV-Vis-NIR V-670 (Jasco) Spectrophotometer. The Photoluminescence (PL) spectra of the device were measured with LS-55 (Perkin Elmer) Spectrophotometer by using Xe lamp as excitation source at room temperature. UV light source peaked at wavelength λ=254 nm (8 Watts) was used for illumination of device. Electrical characterizations in dark and under UV illumination were performed using Keithley 2400-C source meter. Temperature-dependent electrical properties were also measured in dark.

**Result And Discussion:**

The XRD of ZnO nanorods deposited copper electrode is shown in Fig.1 (a). The XRD clearly shows diffraction peaks corresponding to ZnO and Cu only, and absence of copper oxide phases (JCPDS data PDF # 85-1326). The diffraction peaks for different planes of ZnO crystal indicates the polycrystalline growth takes. The peak intensity ratios particularly (002) and (101) planes for the present case are 0.96
and standard powder sample (JCPDS data PDF # 79-0207) is 0.25 indicate preferential orientation along c-axis.

Figure 1 (b) show the growth morphology of ZnO NRs investigated using SEM. The formation of dense nanorods/nanoflowers on the trenched region is seen. Moreover, prominent growth on the edge of copper electrode is seen. The magnified image (inset) from a trenched region clearly illustrates interconnected ZnO NRs growth with flower and tree morphology. Specifically, the NRs growth takes place in the form of interconnected bushes/flowers on the substrate spanning the area between copper-electrodes. Here electrical connections could be established only due to interconnected nanorods. Figure also shows bushes/flowers provide high active surface area necessary for photon harvesting. Figure 2 (a) illustrates the morphologies of ZnO NRs at the edge of the copper electrodes. ZnO Nanorods are densely packed at the edge of the copper electrode suitable for multiple interconnections with neighbouring nano-flower/nano-trees. ZnO NRs morphology at the electrode edges provides excellent contacts between electrodes and ZnO nanorods. The average length of such nanorods was found in the range of 5-7 mm. The SEM images of ZnO NRs bushes between two copper electrodes (see Fig. 2(b)). Dense and interconnected ZnO with flowery morphology can be seen on etched part between the copper electrodes. Particularly growth of ZnO with flowery morphology can be seen where and flowers/bushes are interconnected by overlapping ZnO nano-rods via grain boundary contacts.

Figure 3 (inset) shows the Ultraviolet-Visible (UV-Vis) absorption spectrum of the ZnO. Optical band gap $E_g$ was estimated using the Urbach model by fitting the absorption coefficient $a$ to the equation $a = A(h\nu - E_g)^{1/2}$, where $A$ is a constant related to the material refractive index and the electron/hole masses, $h$ is Plank constant and $\nu$ is frequency of light. Tauc plot of $(a\nu)^2$ versus photon energy (Fig. 3) was used to estimate the optical band gap ($E_g$) of ZnO NRs which is $\sim 3.17$ eV. This corresponds to the absorption maximum at 390 nm and closely matches with the reported literature [1].

Room temperature photoluminescence spectrum of the embedded device using excitation wavelength of 325 nm is shown in Fig. 4. The strong PL emission peaks centered at 396.5 nm and 410.5 nm represent the near band edge emissions and a weak broad band centered at 473.5 nm could be attributed to intrinsic deep level defects in ZnO crystals [8,9].

Photoelectrical characterization in the dark and under incident UV radiation is carried out for different current-voltages bias. A schematic view for the I-V measurements on ZnO NRs-embedded device is presented in Fig. 5 (a). In this case ZnO NRs are in contact with Cu metal electrodes forming Cu-ZnO-Cu (MSM) contacts therefore it is important to discuss the nature of contacts. Figure 5 (b) shows the energy band diagram of ZnO and Copper metal before (a) and (b) after forming heterojunction. Metal-semiconductor junction can lead to Ohmic or Schottky type contacts depending on the work functions of both the metal and the semiconductor. If the work function of the metal ($\Phi_m$) is greater than the work function of the semiconductor ($\Phi_s$), a positive space charge region will be produced in the metal-semiconductor junction. Accordingly, the region will block the transfer of electrons between the metal and semiconductor. This contact type is defined as a Schottky contact. On the other hand, if $\Phi_m$ is lower than
Φᵣ, electrons will flow from the metal to the semiconductor. The contact type is defined as an Ohmic contact. In this case, a negative space charge region will appear at the interface. Then the high electron concentration will create a high conductivity in the metal-semiconductor junction. In our case, the work function of ZnO (5.2 eV) is larger than the work function of copper (4.65 eV) so the Cu-ZnO-Cu contact behave as ohmic contact. This means that electrons flow from the metal (Cu) to the semiconductor (ZnO) to lower their energies, until the positions of these Fermi energy levels get equalized to the same value. Therefore, valence and conduction bands of ZnO move relatively downwards to match Fermi levels [22].

Figure 6 (a) shows current-voltage (I-V) response for ZnO NRs structure in the dark and as a function of UV light intensity peaked at λ=254 nm. UV illumination intensity was effectively varied from 100 to 1885 mW/cm² by varying distance between UV source and the device. Current through the device was increased in discrete step of 5 µA to the maximum value of 100 µA. The plot shows that current rapidly increase for both positive and negative voltage after a threshold voltage bias. This nonlinear I-V characteristic in reversed and forward direction analogous to varistor (back-to-back diode) characteristics.

More importantly, current through the device shows pronounced increase with incident optical power of UV radiation (Fig. 6(c)). Here induced carrier density is proportional to generation of electron-hole pairs due to incident photon flux. These photo-generated electrons are transferred from ZnO NRs to Cu electrodes increases (decreases) the photo-current (photo-resistance) with an order of magnitude compared to values in the dark. Thus, the Cu-ZnO NRs-Cu (MSM) structure acts as a prototype UV photosensitive varistor.

It is well known that the nonlinearity in bulk ZnO varistor is a grain-boundary phenomenon where a barrier to electrons, especially in n-type ZnO, exists in the depletion region of adjacent grains. It has been understood that a double Schottky barrier formed at the additive-rich grain boundary region plays an important role for the appearance of the varistor action. Besides bulk and doped ZnO a non-linear I-V characteristic have been observed in high temperature annealed pulsed laser deposited grown ZnO thin films. In view of past studies on bulk and thin film varistor, the nonlinear characteristic exhibited by the ZnO NRs structure is distinct and important as far as nano-rod based UV photo sensitive varistor. To the best of knowledge such varistor characteristic in an undoped ZnO NRs has not been reported so far. As discussed before in this case ZnO NRs growth takes place in the form of flower and are interconnected each other forming multiple grain boundary contacts which is mainly responsible to this varistor (back-to-back-diodes) characteristics. The devices having a single ZnO contact involves a few grain boundary contacts generally shows diode characteristics instead a varistor characteristic.

It has been observed that Cu- ZnO NRs-Cu junction is highly responsive to 254 nm UV light. I-V characteristic is further analysed by plotting the photocurrent against incident UV intensity at 2 V bias values (Fig. 6 (b). The photocurrent current increases from 25 to 100 mA when the UV light power increases from 180 mW/cm² to 1885 mW/cm², respectively. At low voltage bias the photocurrent increase approximately 4 times while at voltage bias of 10 V, photocurrent increase about 2 orders of
magnitude shows bias dependent photo-response functionality. The solid line fit (Fig. 6 (b) shows a strong linear relationship with a linear coefficient $R^2 = 0.96$, indicating that the present optoelectronic device can potentially be utilized as a quantitative UV sensor. Fig. 6 (c) shows the resistance measured against current increased in steps of 5 µA under dark conditions and UV illuminations of increasing intensity. It clearly indicates that the resistance decreases with increase in the UV light intensity. About two orders of magnitude decrease in resistance is observed as UV illumination intensity increase from 100 to 1885 µW/cm$^2$. We have repeated more than 10 such devices, checking each device at least 5 times. The photo-response of these devices was within ± 2 % error limit.

We have further explored the temperature dependent I-V characteristics at variable temperature conditions. Figure 7 (a) indicates the temperature dependent I-V characteristics of the device in dark (without UV light). In the temperature regime 300 to 370 K, the device does not show much variation in electrical property. But upon increasing the temperature from 370 to 430 K device current increases from 2 to 100 mA at 5V bias (see Fig. 7 (a)). This also seen in the constant resistance value over the temperature ranges from 290-370 K. In the temperature range of 370 K to 430 K the resistance decreases by 1-2 in orders of magnitude, systematically. Due to thermionic effect, desorption of surface species such as oxygen ions ($O^-$,$O^{2-}$) from the surface of ZnO NRs is likely the main component which dominate above temperature of 370 K. Removal of oxygen from the surface results in a large increase in conductivity by freeing up electrons to contribute to conduction. As shown in Fig. 7 (c), in the regime of 290–370 K, log $R$ linearly increases with 1/T. For instance, $R$ decreases from 900 kW to 50 kW as temperature increased from 370 to 430 K. This linear behaviour of log $R$ versus 1/ $T$ suggests that a thermally activated transport mechanism dominantly operates in that temperature regime thus the resistivity of the nanorods decreases which indicates that ZnO exhibits negative temperature coefficient of resistance (NTCR) in high temperature regime.

The time dependent photocurrent response was observed using Keithley source meter 2400 and controls via Lab-View program. Figure 8 shows time dependent photocurrent response under UV illumination ($\lambda$= 254 nm). ZnO NRs are highly sensitive which increases photocurrent faster under UV illumination constant voltage of 5 V. The photoresponsivity of device is defined as ratio of photogenerated current to the incident illumination power however the sensitivity or the contrast ratio of sensors were calculated from the ratio of photocurrent to dark current [23]. Compared with a dark current, the photocurrent under 254 nm UV light illumination increases about 4 times. The photoresponsivity and sensitivity values of the device is calculated to be 0.25 A/W and 4, respectively which also confirms that the responsivity and sensitivity behaves inversely to each other [24].

It has been observed that rise time is only ~ 4 min, but when UV light turned off, the darkcurrent degenerated slowly and it takes ~ 30 minutes recovery time to reach its original state at room temperature (~ 23 °C). This is mainly due to multijunction of interconnected ZnO nanorods array.

A brief discussion on the mechanism of UV photo-response is as follows. The loosely bound oxygen molecules at nanorod-air interface creates depletion region near the NRs surface by capturing free
electrons from the n-type ZnO making negatively charged oxygen ions at the surface. \[ O_2\,(g) + e^- \rightarrow O_2^-\,(ad) \]. In our case upon exposure of UV photons of energy of 4.9 eV (\( \lambda = 254 \text{ nm} \)), electron–hole pairs are generated, \([h\nu \rightarrow e^- + h^+]\), the holes discharge the negatively charged adsorbing oxygen ions to photodesorb oxygen from the ZnO NRs surface and decrease the width of the depletion region. \([h^+ + O_2^-\,(ad) \rightarrow O_2\,(g)]\).

The electrons which are left behind contributes to decreasing resistance of the ZnO NRs. When the illumination turned off, although holes quickly recombine with the electrons, there are still a lot of electrons left in ZnO NRs and oxygen readsorbs on the NRs surface, and captures electrons, as a result current decreases slowly and it takes more time for returning the device to its initial state. This phenomenon of oxygen adsorption or re-adsorption takes place throughout the bulk of the materials. Thus, in device upon exposure of UV light, a lot of unpaired electrons are generated across NRs surface results in a rapid rise in the photocurrent whereas once the UV exposure is turned off it takes more time to drain out all those photogenerated electrons. This is the reason behind the faster current rise time and much slower photocurrent decay [4].

Conclusions:

In summary, we report planer growth of ZnO NRs array across trenched Copper electrodes by open aqueous solution deposition method. ZnO NRs between copper electrodes exhibit UV-Photo-switching property. Temperature dependent electrical properties of this device shows negative temperature coefficient of resistance above 370 K. The ZnO NRs are grown by facile solution procedure, low cast and easy to fabricate yet exhibits multifunction optoelectronic varistor property and perhaps a model prototype nanorod array exhibiting varistor property without any doping.

Declarations

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References


**Figures**

![Figure 1](image_url)

**Figure 1**

(a) XRD pattern of the ZnO NRs embedded between trenched Cu-electrodes; (b) SEM image of the ZnO NRs deposited between Cu-electrodes. The growth is also seen on Cu-electrodes, although the morphology differs. Inset shows magnified image of ZnO NRs deposited on trenched part.
Figure 2

SEM of the ZnO NRs (a) on the edge of copper electrode and (b) between the trench electrodes.

Figure 3

Estimation of band gap energy from Tauc plot of ($\alpha E$)² versus E for the ZnO on Cu electrode. UV-Vis absorption spectrum is shown in inset.
Figure 4

Photoluminescence spectrum of ZnO NRs embedded device.

(a) UV Source

(b) Energy level diagram before and after contact:
- $\Phi_{\text{ev}} = 4.65$ eV
- $\Phi_{\text{ev}} - (\Phi_{\text{ev}} - \Phi_{\text{ZnO}}) = 0.3$ eV
- $E_{\text{g}} = 3.37$ eV
- $E_{\text{v}} = 3.5$ eV
- $\Phi_{\text{ZnO}} = 5.2$ eV

(copper) before contact

(d) After contact

ZnO Nanorods network
Figure 5

(Colour online) (a) Schematic diagram for I-V measurements of the ZnO NRs embedded device; (b) Energy level diagram of Cu - ZnO (i) before MS contact and (ii) after the MS contact in thermal equilibrium.

Figure 6

(Colour online) (a) Current versus voltage curves of the ZnO NRs device in dark and when illuminated with UV (254 nm) photons of variable intensity. Inset shows a characteristic for Vbias for 0 to 10 V.; (b) Photocurrent (the current increase under photon intensity) as a function of incident optical power at 2V bias; (c) Resistance against current measured in dark and under UV illumination of variable intensity.

Figure 7

(Colour online) (a) Current versus voltage curves of ZnO NRs embedded device under ambient temperature variation from 290 K to 430K. Inset shows photoresponse between Vbias = ± 10 V; (b) Resistance against current measured in various temperature from 290 K to 430 K; (c) Resistance vs 1/T plot.
Figure 8

Reversibility of ZnO NRs embedded device copper electrodes at 5V bias voltage.