

Synthesis of copper doped Zinc oxide nanowires with enhanced ultraviolet photoresponse behavior

S P Ghosh¹, K C Das¹, N Tripathy¹, A Moharana¹, A Adhikari¹, G Bose², D H Kim³, T I Lee⁴, J M Myoung³, J P Kar^{1*}

¹Department of Physics and Astronomy, National Institute of Technology, Rourkela, India 769008

²FST, IFHE University, Hyderabad, India 501203

³Department of Materials Science and Engineering, Yonsei University, Seoul, Republic of Korea, 120749

⁴Department of Bio-Nanotechnology, Gachon University, Gyeonggi-do, Republic of Korea, 461701

E-mail: karjp@nitrrkl.ac.in

Abstract: This work mainly focused on the synthesis of copper doped zinc oxide nanowires by hydrothermal method, their characterization and their ultraviolet (UV) light sensing response at room temperature. The structural and morphological characterization was carried out using X-ray diffraction and scanning electron microscopy. Enhanced ultraviolet (UV) photodetection property has been achieved for a dopant concentration of 2.5wt% and 5wt% showing UV photosensitivity values (photo-to-dark current ratio) of around 800 and 1800, respectively. This is an order of magnitude higher than the undoped ZnO nanowires. High photocurrent gain is attributed to the trapping of carriers under dark and detrapping them under UV illumination by Cu-related defects. Enhancement in photosensitivity indicates that Cu-doped ZnO nanowires are promising candidates for UV photodetection applications.

Keywords: Copper; Doped; Nanowire; Ultraviolet; Photodetection; Zinc Oxide

1. Introduction

Low dimensional ZnO nanostructures such as nanowires (NW) become an inevitable material for ultraviolet (UV) photodetection due its excellent physical and chemical properties such as large surface area, radiation hardness [1], superior spatial resolution [2] and high electron mobility which provides a platform for versatile applications such as high temperature flame detection, fire alarm, space research, environmental monitoring, and missile warnings, where an installation of UV detector is highly required [3-5]. However, pure ZnO materials typically exhibit a comparatively poor UV sensing performance due to the large n-type carrier concentration and fast recombination rate of photoexcited electron-hole pairs [6]. Therefore, in order to succeed as an efficient photodetector material very high photocurrent gain is necessary. Till date, various types of modifications including

creation of a junction, doping with metals, and fabrication of composites have been associated with nanostructured ZnO in order to enhance the photoconductive gain. Among them doping is an extensively used method to improve the electrical and optical properties of semiconductors. Various group III metals such as Al and Ga, transition metals such as Mn and Fe, and rare earth elements such as Eu and Er have been doped with ZnO nanostructures for different applications [7-16]. Conversely, most of the recent reports comprise either multi-step growth process or require a costly synthesis set-up for doping. Therefore, operationally simple and an efficient method to have enhanced UV detection property in ZnO is needed to be explored. However, the role of Cu as a luminescence activator and as a compensator of n-type materials is of substantial significance. The emission spectra of Cu-doped ZnO extend from the ultraviolet to the infrared region depending on the concentration of copper, defects in ZnO, and excitation conditions [17–19]. In this work, an attempt is being made to enhance the UV photoconductivity behaviour through fabrication of Cu-doped ZnO nanowires by a simple low cost hydrothermal method.

2. Materials and Methods

ZnO nanowires were synthesized by hydrothermal method on glass substrate with a ZnO seed layer deposited on to it by RF magnetron sputtering technique. The details of seed layer deposition are described elsewhere [22]. Here, an equimolar solution of Zinc nitrate and hexamethylenetetramine was taken and for copper (Cu) doping, required amounts copper nitrate have been added to the growth solution to obtain 2.5 and 5wt% of Cu doped samples. The investigations on the crystalline phase and the morphology were carried by X-ray diffraction (XRD; Rigaku/UltimaIV) with a CuK ($\lambda=0.154\text{nm}$) radiation. The morphology of the ZnO NW has been investigated using scanning electron microscopy (SEM; JEOL JSM-6480LV). 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 using a Keithley picoammeter (model 6487). All the measurements were performed at room temperature. 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 for all the samples.

3. Results and discussion

Figure 1 shows the SEM micrographs of the undoped as well as the doped ZnO NW hydrothermally grown at 90°C for 4hrs. It can be seen that the substrate is covered with small ZnO nanowires of about 40–80nm in diameter and $\sim 2\mu\text{m}$ in length. The overall morphology indicates uniformity in the shape and size, with no considerable change in length and diameter with various Cu doping concentration. The X-ray diffraction patterns of all the samples are shown in Figure 2, which show the presence of strong (002) peak, thereby confirms the formation of crystalline ZnO phase. The presence of copper oxide and metal copper has not been identified, which indicates that there is no phase transformation of the grown ZnO NW has been occurred.

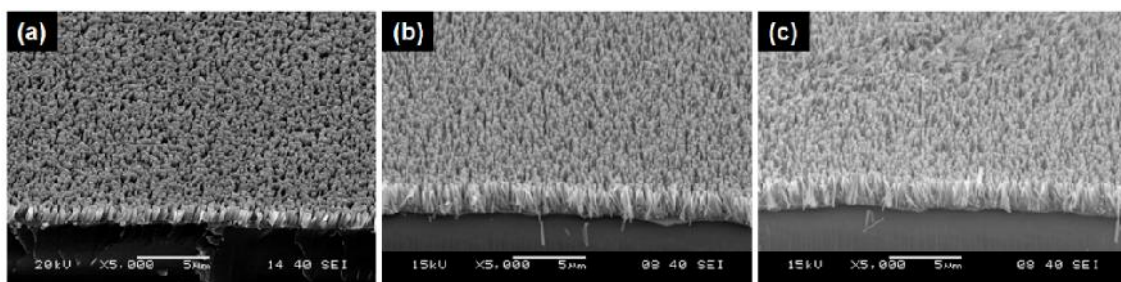


Figure 1. SEM images of ZnO nanowires grown with 0.01M at 90°C for (a) undoped ZnO NW (b) 2.5wt% Cu-doped ZnO NW (c) 5wt% Cu-doped ZnO NW. The scale

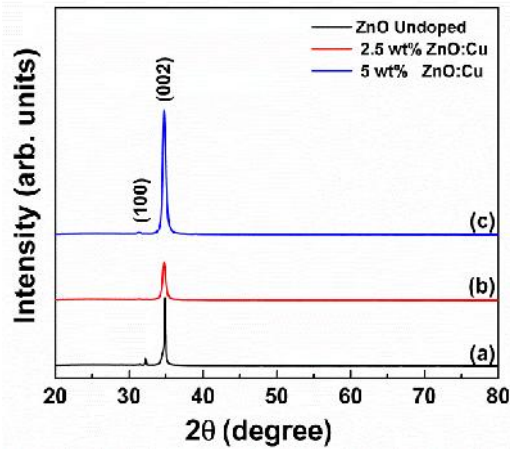
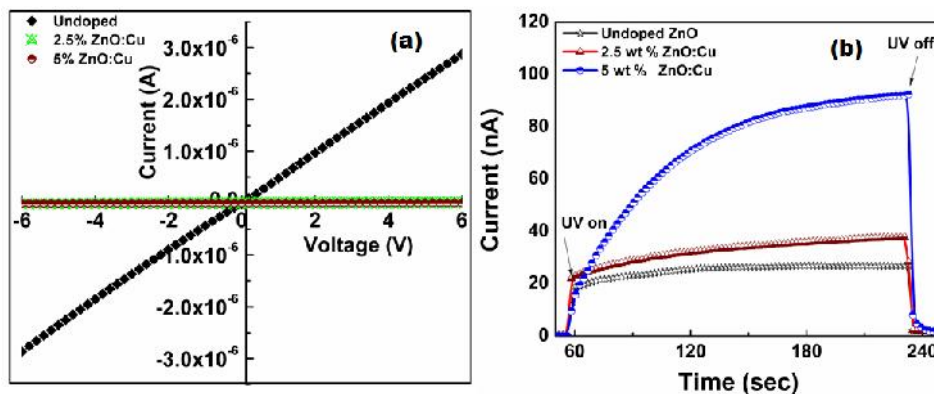


Figure 2. X-ray diffraction patterns of ZnO nanowires grown at 90°C with 0.01M concentration (a) undoped ZnO NW (b) 2.5wt% Cu-doped ZnO NW (c) 5wt% Cu-doped ZnO NW.

The I–V characteristics of the hydrothermally grown ZnO NW and the Cu-doped ZnO NW under dark conditions are shown in Figure 3(a). Linear enhancement of current with sweep in voltage of $\pm 6V$ for both doped and undoped ZnO NW samples depicted good Ohmic nature of the electrical contact. Under dark condition, as-grown ZnO NW shows higher (I–V) current value of $2.0 \times 10^{-6} A$ as compared to the dark current ($1.05 \times 10^{-8} A$) of Cu-doped ZnO NW. This enhancement of dark current in the as-grown ZnO NW is attributed to Copper dopants which are good acceptor to trapped electrons in undoped ZnO NW. Figure 3(b), (c) & (d) show the growth and decay of the photocurrent against time. When UV illumination is ‘on’, an enhancement in current result and when the illumination is ‘off’, the current drops, indicating that the NW are highly UV sensitive. In undoped ZnO NW, the photo-to-dark current ratio is about 60 while the value increases upto 800 when ZnO is doped with 2.5wt% Cu. The value is enhanced further to ~ 1800 when 5wt% Cu is doped in the ZnO NW. From experimental results, the decay time constants for 5wt% Cu-doped ZnO are estimated to be around 4sec by fitting the decay curve using the exponential function. Thus, a considerable photocurrent gain and faster relaxation time is observed in Cu-doped ZnO NW. The UV light treatment generates electron–hole pairs, which are trapped by the surface states and thus the number of electrons in the conduction band of ZnO increases, which causes a sharp increase in the photocurrent. In addition, the photocurrent was not well saturated, which may be due to the presence of surface states in the aqueous grown nanowires. Furthermore, three repeated cycles are displayed in Figure 3(c), steady and reiterated photocurrent behavior indicates no rapid change during the UV exposure with time. Thereby, the hydrothermally grown Cu doped ZnO NW significantly improves the UV sensitivity behavior.



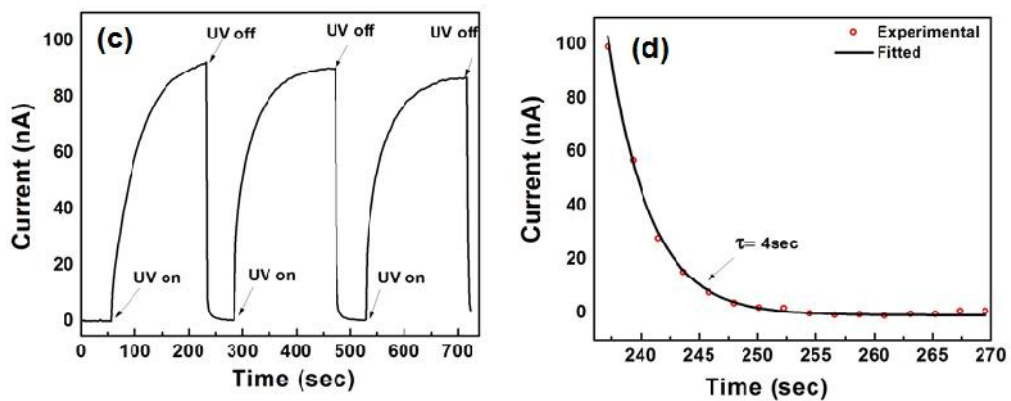


Figure 3.(a) I–V characteristics curves of ZnO NW and Cu-doped ZnO NW array film under dark conditions. (b) The growth and decay of the photocurrent of ZnO NW and Cu-doped ZnO NW under UV illumination.(c) Multi-pulse observation of 5wt% Cu-doped ZnO and (d) Fitted decay curve of the 5wt% Cu-doped ZnO NW under UV illumination.

4. UV detection mechanism of copper doped ZnO nanowires

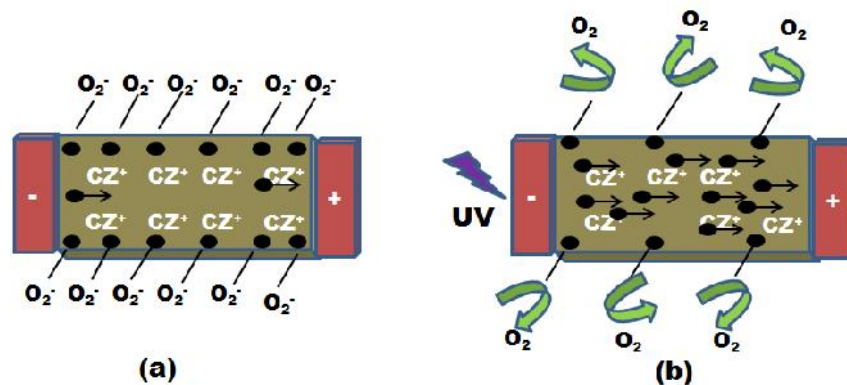


Figure 4. Schematic model to illustrate the mechanism of the hydrothermally grown Cu-doped ZnO NW based UV photodetector (a) During dark condition (b) Under UV illumination

Figure 4 schematic diagram of UV detection mechanism of Cu-doped ZnO nanowires. In the absence of UV light, adsorption of oxygen on ZnO NW surface results in the formation of depletion layer by capturing free conduction electrons. Under UV illumination, photogenerated holes recombine with the adsorbed oxygen molecules near to the surface of ZnO NW. Subsequently, oxygen molecules are desorbed from the surface of ZnO NW leads to the enhancement in photocurrent by generating more number of free carrier concentration. During dark condition Cu^{2+} ions acts as deep acceptor trap centre and interacts with the ZnO native donors to form $[Cu_{Zn} + Zn_i]^0$ complex [20-21]. Thus, the dark current is further reduced in the Cu-doped ZnO NW array, as supported from the I–V curves in Figure 3(a). However, when the ZnO NW are exposed to UV light, ionisation of Cu-Zn complex results in great enhancement in photocurrent by releasing the electrons back to the conduction band. Thus, due to copper doping the trapping and de-trapping rate of electrons increases as compared to the adsorption and desorption of oxygen molecules which results in faster relaxation time of hydrothermally grown copper doped ZnO NW.

5. Conclusions

In this work, Cu-doped ZnO NW was hydrothermally grown in order to improve the UV sensitivity response. UV photodetection behavior has been obtained by adopting current-voltage (I-V) and current-time (I-t) measurement. It has been observed that addition of Cu dopant to the hydrothermally grown ZnO NW, results in higher UV sensitivity and faster relaxation time due to faster trapping and detrapping of electrons by Cu dopants in ZnO NW. From experimental results, faster decay time constants for 5wt% Cu-doped ZnO is estimated by fitting the decay curve using the exponential function and found to be around 4sec. Through the introduction of Cu dopants into ZnO NW, a simple and efficient way is proposed to improve the UV sensing properties of ZnO NW which can be deliver a platform in order to achieve room temperature operated next generation of metal oxide UV detectors and sensors.

Acknowledgement

This work was supported by the Department of Science and Technology (DST), India sponsored Indo-Korea project (INT/Korea/P-16/2013). This research was also supported by the International Research & Development Program of the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT & Future Planning (Grant number: 2012K1A3A1A19038371).

References

- [1] Liu A, (2008) *Biosensors and Bioelectronics* **24** 167-177.
- [2] Chen Y J, Nie L, Xue X Y, Wang Y G and Wang T H (2006) *Appl. Phys. Lett.* **88** 083105.
- [3] Lin W Z, (2004) *J. Phys. Condens. Matter* **16** R829.
- [4] Ramirez A, Subramanian M, Gardel M, Blumberg G, Li D, Vogt T (2000) *Solid State Commun.* **115** 217-220.
- [5] Schreiber P, Dang T, Smith G, Pickenpaugh T, Gehred P and Litton C (1999) *Proc. SPIE* **3629** 230-48.
- [6] Goldberg Y A (1999) *Semicond. Sci. Technol.* **14** R41.
- [7] Schuler T and Aegerter M A (1999) *Thin Solid Films* **125** 351.
- [8] Yamamoto T and Yoshida H K (2001) *Physica B* **155** 302/303.
- [9] Han J, Senos A M R and Mantas P Q (2002) *Mater. Chem. Phys.* **75** 117.
- [10] Han S J, Song J W, Yang C H, Park S H, Park J H, Jeong Y H and Rhie K W (2002) *Appl. Phys. Lett.* **81** 4212.
- [11] Park Y K, Han J I, Kwak M G, Yang H, Ju S H and Cho W S (1998) *J. Lumin.* **78** 87.
- [12] Zhao X, Komuro S, Isshiki H, Aoyagi Y and Sugano T (2000) *J. Lumin.* **1254** 87-89.
- [13] Kryshab T G, Khomchenko V S, Papusha V P, Mazin M O and Tzykunov Y A (2002) *Thin Solid Films* **76** 403/404.
- [14] Kutty T R N and Raghu N (1989) *Appl. Phys. Lett.* **54** 1796.
- [15] Lee J B, Lee H J, Seo S H and Park J S (2001) *Thin Solid Films* **61** 398/399.
- [16] Dingle R (1969) *Phys. Rev. Lett.* **23** 679.
- [17] Robbins D J, Herbert D C and Dean P J (1981) *J. Phys. C: Solid State Phys.* **14** 2859.
- [18] Dahan P and Fleurov V (1998) *Phys. Rev. B* **57** 9690.
- [19] Razeghi M and Rogalski A (1996) *J. Appl. Phys.* **79** 7433.
- [20] Liu J, Smith RW, Mei WN (2007) *Chem. Mater.* **19** 6020-6024.
- [21] Hill W, Coleman C (1980) *Solid-State Electron* **23** 987-993.
- [22] Ghosh S P, Das K C, Tripathy N, Bose G, Kim D H, Lee T I, Myoung J M and Kar J P (2015) *J. Mater. Sci.: Mater. Electron* **26** 7860-7866.