SYNTHESIS AND CHARACTERIZATION OF DOPED AND UNDOPED ZnO NANOWIRE/NANORODS COATING ON VARIOUS SUBSTRATE (AlN, SiO_2 AND FTO) FOR PHOTOVOLTAIC HYDROGEN SENSOR APPLICATIONS

R. J. RAMALINGAM[a*], J. VIJAYA[b], H. A. AL-LOHEDAN[a], M. A. MUNUSAMY[c]
[a]*Chemistry Department, College of Science, King Saud University, P.O. Box 2455, Riyadh 11451. Kingdom of Saudi Arabia.*
[b]*Catalysis & Nanomaterials Research Laboratory, Department of Chemistry, Loyola College, Chennai 600 034, India.*
[c]*Department of Botany and Microbiology, College of Science, King Saud University, Riyadh 11451, Saudi Arabia.*

Zinc oxide and Ga-doped ZnO nanowires and nanorods are synthesized on various substrate like Fluorine doped tin oxide glass plate, SiO_2 coated Silicon substrate and aluminum nitride coated silicon substrates. The coating process carried out using zinc oxide sol-gel solution. The synthesized material was characterized using XRD (X-ray diffraction), FE-SEM (Field emission scanning electron microscopy), photoluminescence spectroscopy and electrical conductive gas sensor measurements. The fine nanowires formation on FTO plants are clearly seen in FE-SEM results. The ZnO nanorods and Ga-doped ZnO forms nanodisk structures on AlN coated Si substrate. The synthesized doped and undoped ZnO coated various substrate tested for its electrical conductivity measurements under flow of hydrogen gas sensor applications. The electrical property of the as synthesized material was analyzed by I-V characterization.

(Received November 1, 2016; Accepted January 11, 2017)

Keywords: Gallium, Zinc oxide, gas sensor, FTO, Aluminum nitride, nanowires

1. Introduction

Zinc Oxide and doped ZnO with nanorods and nanowire structures have attracted much research interests recently due to their higher electrical and surface properties which have been shown to provide much more potential applications [1] and [2]. ZnO nanowire are typically synthesized by cost consuming techniques like gas phase techniques such as metal organic chemical vapor deposition, chemical vapor transport and pulsed laser deposition (PLD). High-quality single crystalline wires with lengths of several microns can be produced by above methods. Therefore, these methods create many restrictions to substrate choice, and generally have a low final quantity of product generation. In contrast, hydrothermal approaches which can be carried out at temperatures below 200 °C allow potential for scaling up, and provide a straightforward method of producing high-density nanowires and nanorods arrays [1-8]. Greene et al. [8] have grown vertical arranged zinc oxide nanowires on seeded substrates using a solution approach at 90 °C. Qin et al. [4] fabricated a laterally grown ZnO array on a flat substrate with Chromium (Cr) as catalyst. Sun et al. [6] used pulsed laser deposition to compare ZnO seeded and unseeded Si substrates showing that after hydrothermal growth the seeded substrates produced structures comprising of nanowires with nanotubes growing from the wires. Yun et al. [7] doped ZnO NWs with aluminium (Al) using a solution growth method, finding that the size of ZnO nanowires decreased with increasing Al:N concentration. The performance of the thin-film-based SAW devices generally depends on the electromechanical coupling coefficient (K^2) and the acoustic velocity. Interestingly, ZnO films exhibit a relatively better K^2 (3.2%), while AlN film has relatively high acoustic velocity (5600 m/s) [9]. Therein, stack layers of piezoelectric films

* Corresponding author: rjothiram@gmail.com

(ZnO/AlN) have attracted considerable interest for the fabrication of acoustic devices [10, 11]. However, these methods have some drawbacks such as expensive apparatus, difficult procedure, and high temperature process. On the other hand, solution-based technique is an attractive approach for the growth of ZnO nanostructures because of its simple step preparation, low-temperature process, and most importantly suitability for large-scale production on arbitrary substrate [12, 13]. Recently, Jothi Ramalingam et al, (2012) reported the effect of different molar concentration of Ga-ZnO sol-gel solution and reaction condition causes the pure and hybrid nanodisk/nanorods morphology formation on AlN/Si substrate *via* one-pot polymer assisted hydrothermal method [14]. Hydrogen energy is expected to supplant hydrocarbons and becomes the common fuel of the future. Hydrogen is an odorless, invisible and flammable gas. It has a wide range of flammability in air, which is about 4-75% by volume and the lowest limit of hydrogen in air to cause explosion is 5% as mentioned by Schlager and Weisblatt (2006) [15]. This makes it more flammable than other fuels usually adopted. Therefore, it is important to facbricate the sensor device to detecting the low levels of this gas ranging from 0.1-100 ppm as reported by Liu et al (2001) and Xu et al (2008) [16-17]. The traditional hydrogen gas sensors based on semiconductor metal oxide thin film material are identified due to the change of their properties when they interact with the hydrogen. Among the semiconductor metal oxide – based hydrogen sensors are tungsten oxide, tin oxide), and zinc oxide [18-19]. Patrícia et al (2001) reported that the ZnO nanostructure is considered as a promising chemical gas sensitive material. Due to sensitive surface to volume ratio obtained for high – sensitivity gas sensing [20]. The ability of these semiconductor oxides to transfer the gas concentration into electric resistance allows the using of the traditional simple techniques for implantation the final content.

2. Experimental

The zinc oxide and gallium mixed ZnO coating sol solution was prepared from zinc acetate dihydrate (Sigma-Aldrich), Gallium (III) nitrate hydrate (Alfa Aesar), methoxyethanol, and monoethanolamine (Samchun pure chemical), in a magnetic stirrer for two hours at 70 $^{\circ}$C.

2.1. Preparation of ZnO and doped ZnO sol-gel solution

First to prepare the sol-gel solution, the appropriate amount of Zinc aceetate and mixture of gallium nitrate/zinc acetate poured separately in the solution of methoxyethanol and monethanolamine to get colloidal solution. The above solution is stirred for 2-3 days at slow rate in magnetic stirreter to prepare the colloidal ZnO and Ga-ZnO sol-gel solution. In the present study, 1 weight percentage of gallium was added in total weight of zinc acetate (1% Ga-ZnO). Bulk ZnO prepared with concentration of 0.5 M concentration of ZnO sol-gel solution (based on 0.5 M, zinc acetate weighed).

2.2. Synthesis of ZnO and Gallium nanowires/nanorods on SiO2/Si substrate

The substrate is cleaned with purging with air for 2-3 minutes followed nitrogen gas purging for 5 minutes. The cleaned substrate mounts on spin coating machine. Then, 2-4 drops of ZnO sol or Ga-doped ZnO sol-gel solution is use to drop on SiO_2/Si substrate. The process repeated for 4-5 times to get the film thickness of 300 - 350 nm thickness and the samples were annealed in a furnace at 500 ^{o}C. In the second stage the as prepared thinfilm coated substrate kept vertically and equimolar amount of zinc nitrate (40 mL) and hexamethylene tertramine (40mL) solutions are added in Teflon container followed by heated at 90 ^{o}C for 12 hours.

2.3. Synthesis of ZnO and Gallium doped nanowires on FTO

The same procedure is adopted for prepare the ZnO and Gallium doped ZnO preparation on FTO plates, only different thing we have done is change of the substrate and to observe the final form or nanostructure morphology of ZnO on FTO after hydrothermal process.

2.4. Synthesis of Gallium doped ZnO on AlN/Si substate

For specific application purpose, ZnO and doped ZnO are coated on piezo electric substrate like AlN coated on Si substrate. Reported literature explain the formation of disk shap morphology for ZnO coating on AlN/Si substrate. In the present study, we exploited the role addition of polymer solution to fabricate very find disk shape formation for gallium doped ZnO thin films.

Polyethylenimine (PEI) polymer solution (30 % dissolved in water) is used as polymer additive to fabric the fine nanodisk of ZnO instead of thick nanodisk. The prepared GZO sol (1% Ga-ZnO) solution is coated on AlN/Si by above procedure of spin coating method at 1000-2500 rpm. After each deposition, the films were heated on a heating plate at 300 ^{o}C for 10 min. The final thickness of GZO thin films were deposited to obtain a 300 - 350 nm thickness and the samples were annealed in a furnace at 500 ^{o}C. In the second steop, (hydrothermal process) equimolar amount of 40 mL of zinc nitrate and 40mL solutions of hexamethylene tertramine were mixed with optimized concentration of 3 % polymer solution (10 mL) and the contents were poured into the autoclave. 1% Ga-ZnO film on AlN/Si substrate was fixed vertically by holder inside the Teflon container at 90 ^{o}C for 1 day.

The structure and morphologies were characterized by XRD and FE-SEM connected with energy dispersive X-ray equipment facility (JSM-6500F). The electrical resistivity of the all prepared ZnO and Ga-ZnO thin films on different substrate were determined by Keithley 4200-SCS semiconductor material characterization instrument and silver paste is used to make electrical contact with probes and substrate. Photoluminescence properties of synthesized sample were analyzed by Jobin Yvon HR 800 UV (HORIBA Jobin Yvon, Inc., Edison, NJ) using Ar laser as the excitation source.

3. Results and discussion

The morphology and fine shapes of synthesized ZnO and doped ZnO with nanorods/nanowires/nanodisk were studied by FE-SEM technique. The recorded results of XRD pattern of ZnO and doped ZnO thinfilms deposited on various substrate are shown in Fig. 1 and Fig. 2. ZnO deposited on SiO_2/Si is shown in Fig.1 and the 2θ values of 31.8°, 34.8°,36.1, 62.6°, 68.9° and 72.6° with corresponding *hkl* values such as (100), (002), (101), (201) and (004) are obtained. In the case of 1% Ga–ZnO/SiO_2 with nanorods sample major diffraction peaks were plotted together with Ga-ZnO/AlN nanodisk samples for comparative study and with corresponding hkl values of (002), (101), (103), and (201). For comparison purpose all XRD pattern of the synthesized samples are shown together in Fig. 8. The respective *hkl* index values of standard data of AlN and ZnO (synthetic) mentioned in bottom part of Fig. 8.

ZnO nuclei is first form the rod shaped with various height and breadth, depends on controlled condition the size of rod can be controlled. Depend on the substrate nature and reactant additive the shape of the ZnO nuclei rods into various morphology. In our present study, SiO_2/Si substrates forms the only ZnO nanorods and it is difficult form the nanowire size. But in the case of ZnO seed on FTO substrate forms the fine nanowires for ZnO and Ga-ZnO.

In general, the major intense diffraction peak observed at (002) plane due to ZnO thin film and in the case nanostructure ZnO with wurtzite crystal structure shows the major intense peak appeared at (101) hkl plane [14]. The crystallite size at major X-ray diffraction peak of (101) is calculated by Scherer equation and it shows 78 nm for 1%Ga-ZnO/AlN (Fig. 8a and 8b) and 69 nm for 1%Ga-ZnO/AlN prepared at different polymer concentration. The less crystallite size of 42 nm was obtained at (002) major peak of (002) of 1%Ga-ZnO/SiO_2 (Fig. 8c).

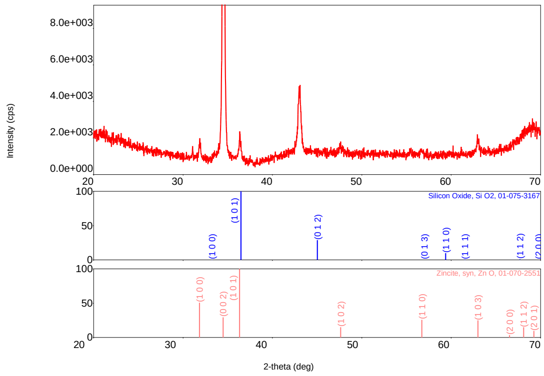

Fig. 1 XRD pattern of ZnO nanorods on SiO_2 / silicon substrate

Table 1 reflects the d-space values and FWHM values, based on the values one can easily calculate the crystallite size. Table 2 shows the Ga-ZnO thinfilm coated on SiO2 substrate and there is little shift in major intense peak of (002) plane value. The gallium incorporation may later the lattice parameters slightly compared to pristine ZnO. The FE-SEM images confirms the formation of ZnO nanorods on SiO_2 substrate and not fine wires are not observed in the case of SiO_2 coated Si substrate.

Table. 1 FWHM and crystallite size of ZnO nanorods on SiO_2 / silicon substrate

No.	2-theta(deg)	D (ang.)	Height(cps)	FWHM(deg)	Int. I(cps deg)	Size(ang.)	Phase name
1	34.5076(15)	2.59699(11)	84822(1189)	0.073(2)	10177(105)	1189(40)	Zincite, syn(0,0,2)
2	36.354(17)	2.4692(11)	1046(132)	0.20(4)	388(18)	445(94)	Silicon oxide (1,0,1) Zincite, syn(1,0,1)
3	42.975(17)	2.1029(8)	2439(202)	0.361(14)	1117(27)	247(10)	Unknown
4	62.933(13)	1.4756(3)	924(124)	0.12(2)	230(16)	832(175)	Zincite, syn(1,0,3)

Table. 2 FWHM and crystallite size of Ga- ZnO nanorods on SiO_2 / silicon substrate

No.	2-theta(deg)	d(ang.)	Height(cps)	FWHM(deg)	Int. I(cps deg)	Size(ang.)	Phase name
1	31.122(11)	2.8713(10)	1818(174)	0.093(13)	201(20)	922(128)	Stishovite, syn(1,1,0)
2	33.064(8)	2.7070(6)	5750(310)	0.03(2)	247(37)	3440(2849)	Unknown
3	34.5227(16)	2.59589(12)	388887(2546)	0.0724(16)	42832(326)	1200(27)	Unknown
4	36.32(3)	2.4713(18)	1172(140)	0.37(6)	847(41)	239(39)	Zinc(0,0,2)
5	42.984(19)	2.1024(9)	3878(254)	0.329(16)	1794(40)	271(13)	Zinc(1,0,1)
6	61.782(11)	1.5003(2)	4106(262)	0.092(13)	538(54)	1046(150)	Stishovite, syn(2,1,1)
7	62.93(17)	1.476(4)	354(77)	1.4(2)	620(90)	72(13)	Unknown
8	69.2240(6)	1.356090(10)	1091536(4265)	0.0482(5)	72048(821)	2091(23)	Unknown
9	69.425(6)	1.35265(10)	53936(948)	0.216(11)	16476(776)	468(23)	Unknown

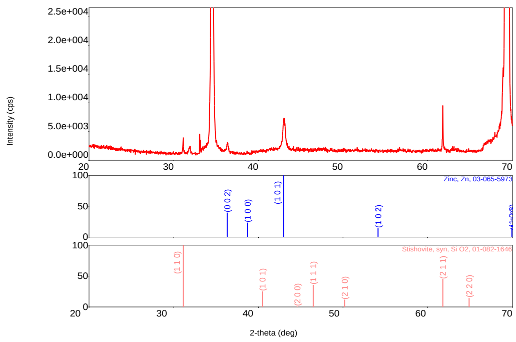

Fig. 2 XRD pattern of Ga-ZnO nanorods on SiO_2 / silicon substrate

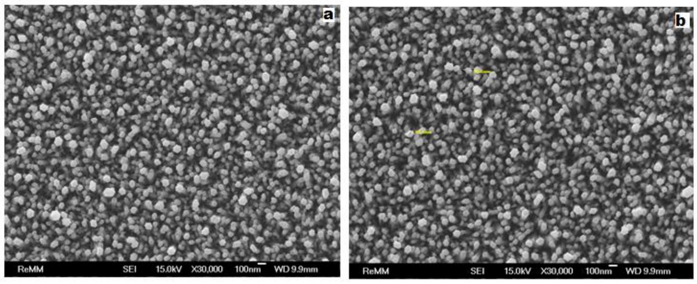

Fig. 3 FE- SEM of Ga-ZnO nanorods/SiO_2/Si

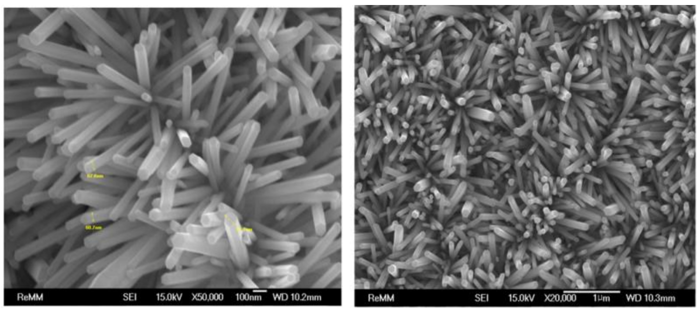

Fig. 4 FESEM images of ZnO on FTO substrate

Fig.4 shows the top view of ZnO nanowires obtained on FTO substrate. The irregular growth of nanowires are growned and the diameter of each nanowire 60-70 nm. The first image is showing closer view at higher magnification like 100 nm scale. The later one recorded at the scale values of 1 um.

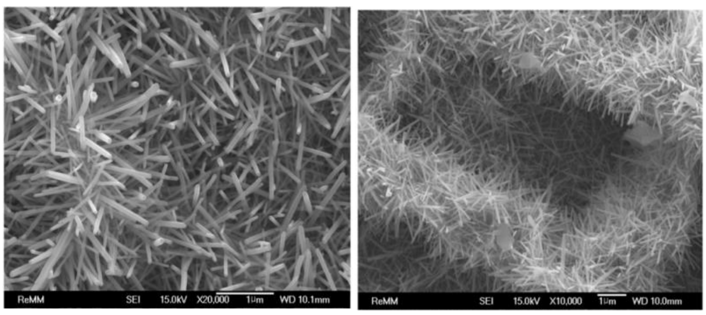

Fig. 5 FESEM images of Gallium doped ZnO on FTO substrate at lower magnification

Fig. 5 shows the ZnO with fine nanowires grown with square shape on the upside of FTO plate. The first image is showing fine individual wires of Ga-ZnO and the next one showing top view of Ga-ZnO nanowires grown on FTO plate.

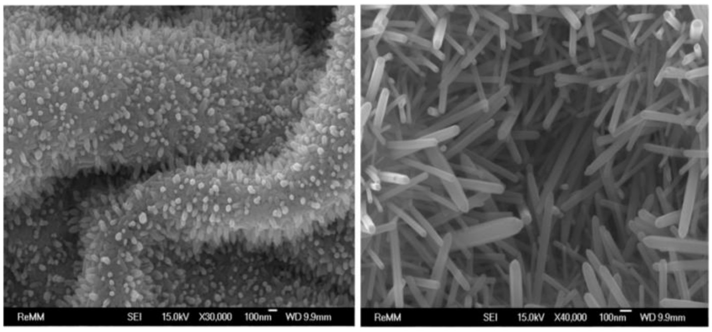

Fig. 6 FESEM images of Gallium doped ZnO on FTO substrate at higher magnification

The first images in Fig. 6 shows the slow rate of growth for Gallium doped ZnO compared to pristine ZnO. The second image shows the closer view of Ga-ZnO nanowire formation on FTO substrate.

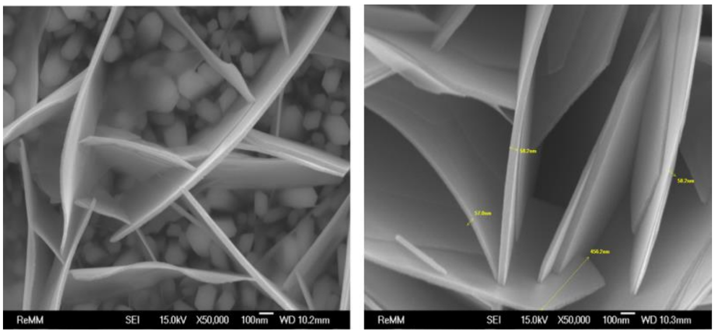

Fig. 7 FESEM images of Gallium doped ZnO on AlN substrate at higher magnification

Figure 7 shows the Ga-ZnO nanodisk morphology at lower and higher magnifications (Fig.1a-b). Gallium doped ZnO on AlN substrate forms the fine nanodisk formation in presence of polyethylimine and at increased concentration of polymer solution forms the thin nanodisk. Ga-ZnO nanodisk prepared by adopting novel methodology using PEI assisted hydrothermal process produces the order arrangement of nanodisk growth at optimized polymer concentration. At polymer concentration of 3% and 4 % produces the fine nanodisk morphology with various thickness of nanodisk. In the case of increased polymer concentration (4%) in hydrothermal process results in the formation of thinner and fine quality of nanodisks formed with the size of 57-58 nm (Fig. 1c and 1d).

The polymer concentration and AlN substrate is playing the important role in the formation of nanodisk morphology and thickness of the Ga-ZnO nanodisk in hydrothermal process. The Ga-ZnO/SiO_2 is shown the fine nanorods morphology formation in polymer assisted hydrothermal method (Fig. 3). Presence of polymer increases the ordered arrangement and higher number of nanorod growth for Ga-ZnO on SiO_2 substrate compared to conventional method prepared ZnO nanorods on SiO_2 substrate [10]. Different size of nanorods is observed with the size ranges of 50 nm to 90 nm (Fig. 3) in the form of hexagonal shaped Ga-ZnO nanorods.

The growth of Ga-ZnO nanostructure formation from aqueous solution involves controlled precipitation on a substrate via hydrolysis & condensation reactions of metal ions and their complexes [12, 13]. However, the nucleation and growth of ZnO nanostructures are greatly affected by chemical species in the interfacial zone. In the previous report in the absence of polymer additive also, ZnO forms the nanodisk shape on AlN/Si substrate. But the shapes of nanodisk is not quite visible and irregular shapes in nanodisk. But in the case of addition of polymer additive with optimized concentration of 3% polymer addition in hydrothermal process provide better nanodisk shapes for Ga-ZnO.

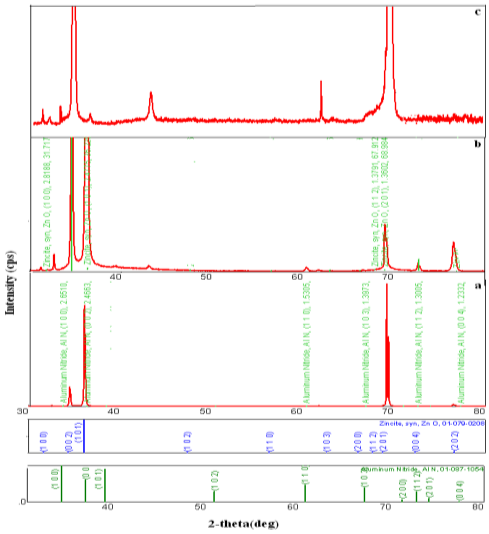

Fig. 8 Comparative XRD patterns of (a) 1% Ga-ZnO Nanodisk/AlN at 3% PEI (b) 1%Ga-ZnO Nanodisk/AlN at 4% PEI (c) 1%Ga- ZnONanorods/SiO_2/Si substrates

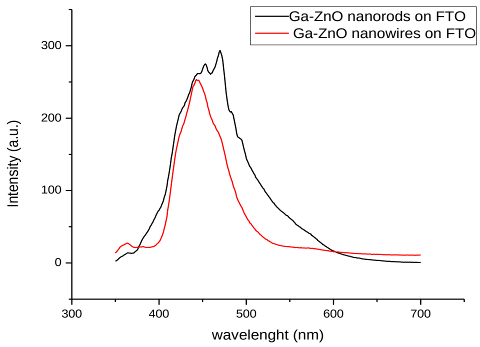

Fig. 9 Photoluminescence spectra of ZnO and Ga-ZnO on FTO substrate

The photoluminescence spectra of ZnO and Ga-ZnO on FTO substrate are shown in Fig. 9. It is very clear in the image after gallium incorporation, there is slight shift in peak at 460 nm and split in the peak observed. The peaks at 460, 476 and 485 nm are visible emission of the respective ZnO samples and its due to intrinsic defects, which is confirmed by reported literature related with PL data of ZnO and Ga-ZnO. [22-23]. Generally a broad visible light emission centered around 620 nm can be found in electrochemically and hydrothermally grown ZnO. This orange-red emission is attributed to radiative transitions present in and it defect-induced energy levels located in the band gap and is assumed to involve interstitial oxygen ions.

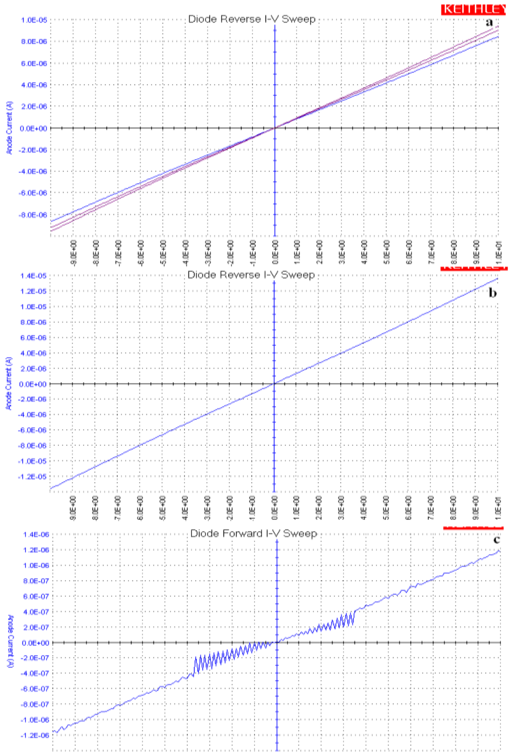

Fig. 10 I-V characteristic curves and electrical conductivity of (a) 1%Ga-ZnO Nanorods/SiO_2/Si (b)Pristine ZnO Nanorods/SiO_2 (c) ZnO Nanodisk/AlN/Si

Fig. 10 shows the electrical resistivity measurement of as synthesized samples and the conductivity of the respective sample measured by I-V characterization. The ohmic behavior and electrical conductivity of 1% Ga-ZnO/SiO_2 is compared with pristine ZnO. Ga-ZnO/SiO_2 shows the stable I-V curve upon multi scanning (Fig.10a) and its shows the electrical conductivity 3 times higher than conventional route prepared pristine ZnO nanorods on SiO_2 substrate. Ga addition in ZnO nanords morphology increases the metallic character of Ga-ZnO due to stable ohomic behavior. 1%Ga-ZnO/AlN shows the vibrated signal for I-V curve due to piezoelectric nature of the AlN substrate and showing the electrical conductivity upon scanning (Fig. 10 c).

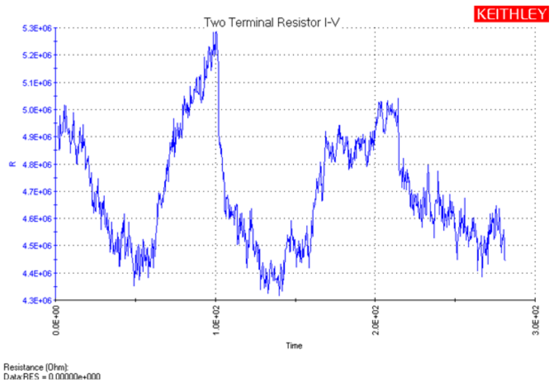

Fig. 11 Hydrogen sensing (1% with concentration of 20 sccm) passing on ZnO nanorods on SiO_2

Fig. 11 shows the hydrogen sensing behavior of ZnO nanorods grown on SiO2 substrate in presence of UV light passing the peak rises and in off time the curve become down. The process is continuing with respect to light sensing and optical property of ZnO species presence in the substrate.

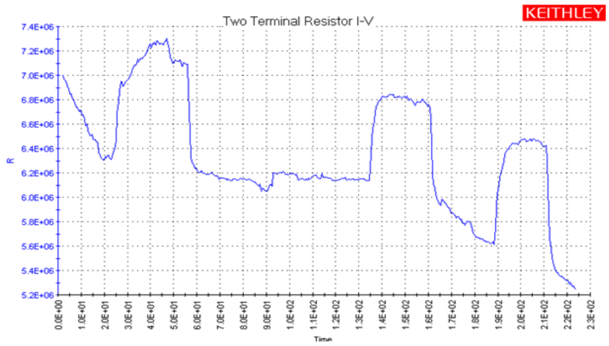

Fig. 12 Hydrogen passing with concentration of 100-20 sccm h2 N2 gas presence and abasence of UV light and in dark condition on Ga-ZnO/SiO_2

Fig. 12 shows the activity hydrogen sensing nature in presence of mixture of gas passing on the substrate in presence of light and dark condition. The smooth and little irregular sensing of hydrogen gas specie on Ga-ZnO coated on SiO2 has been observed.

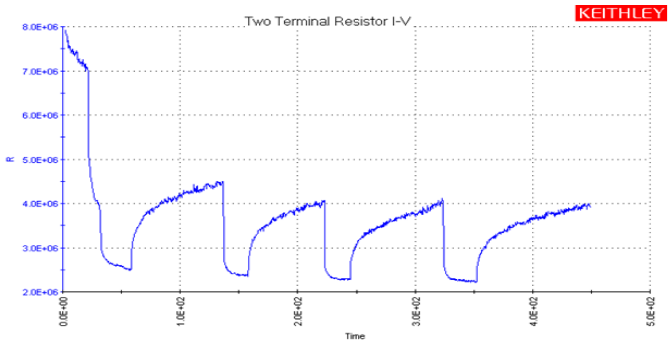

Fig. 13 Hydrogen passing with concentration of 100-20 sccm h2 N2 gas presence and abasence of UV light and in dark condition on ZnO nanowires/FTO. (condition : UV light on tiem 20 sec; off time 126 sec).

Figure 13 shows the ZnO NW activity in presence of mixture of gas and the uniform patter of response obtained compared to ZnO on SiO_2 substrate.

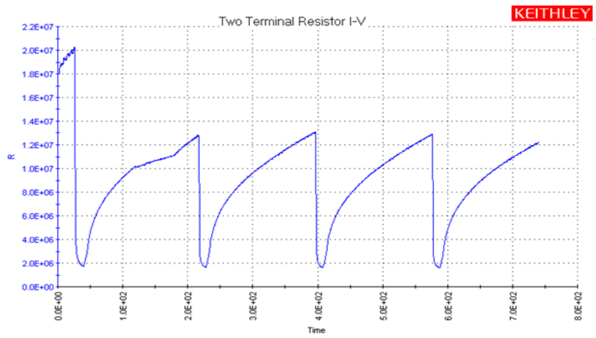

Fig. 14 Hydrogen passing with concentration of 100-20 sccm h2 gas presence and absence of UV light and in dark condition on Ga-ZnO/FTO.

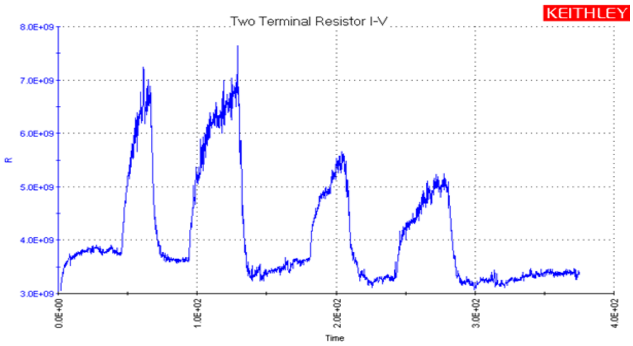

Fig. 15 Hydrogen passing with concentration of 100-20 sccm H2 N2 gas presence and absence of UV light and in dark condition on Ga-ZnO/SiO$_2$. (condition: 1-UV on time 10 sec off 3 min)

Fig. 14 and 15 shows the gallium doped ZnO nanowires on FTO substrate showing good response towards hydrogen gas sensing in presence of pure hydrogen and mixture of inert gas passage on the substrate. The UV light off time and on time are mentioned in the bottom of the figure. Longer time of off time has also showing quick response peak appeared after swich on UV light in presence of gas passage at below 100 ppm of concentration.

Conclusions

Zinc oxide and Gallium doped ZnO with various nanostructures are prepared on various substrate. The effect of substrate and reaction condition have been explained for various nanostructures for doped and undoped ZnO. Ga-ZnO on SiO$_2$ substrate is forms the nanorods instead of nanowire.

In the case of FTO substrate, fine nanowires of Ga-ZnO obtained. Ga-ZnO nanodisks are obtained by adopting AlN coated Si substrarte and in presence of polymer additives. Good I-V characteristics are obtained for Ga-ZnO on SiO2 and FTO substrate compared ZnO coated on AlN substrate. The hydrogen gas sensing property of Ga-ZnO on FTO substrate showing good regularity and activity compared to Ga-ZnO coated on SiO2 substrate.

Acknowledgements

The authors would like to extend their sincere appreciation to the Deanship of Scientific Research at King Saud University for funding this Research Group Project No. (RGP-1435-057).

References

[1] PKGS Santra, SZ Ali, P Hiralal, HE Unalan, JA Covington, GAJ Amaratunga, et al. Sens Actuators B;**146**, 559 (2010).
[2] R Gopikrishnan, K Zhang, P Ravichandran, S Baluchamy, V Ramesh, S Biradar, et al. Nano-Micro Lett; **2,** 31 (2010).
[3] B Zhang, N Hu, Y Wang, Z Wang, Y Wang, ES Kong, et al. Nano-Micro Lett; **2**:285–9. 2010
[4] Y Qin, R Yang, ZL. Wang, J Phys Chem C;**112,** 18734 (2008).
[5] B Nikoobakht, A. Herzing, Formation of Planar Arrays of One-Dimensional p−n Heterojunctions Using Surface-Directed Growth of Nanowires and Nanowalls. ACS Nano; **4**, 5877 (2010).
[6] Y Sun, DJ Riley, MNR. Ashfold, J Phys Chem B **110,** 15186 (2006).

[7] S Yun, J Lee, J Yang, S. Lim, Physica B **405,** 413 (2010).
[8] LE Greene, M Law, DH Tan, M Montano, J Goldberger, G Somorja, et al. Nano Lett **5,** 1231 (2005).
[9] Y. J. Yong, Y.S. Kang, P.S. Lee, J.Y. Lee, Vac. Sci. Technol. B **20**, 42 (2002)
[10]T.K. Shing, HH Pan, IC Chen, CI Kuo, J. Tamkang, Sci. and Eng. **7,** 135 (2004).
[11] A.Z. Sadek , W. Wlodarski , Y.X. Li, W. Yu, X. Li, X.Yu, K. Kalantar-zadeh , Thin Solid Films **515**, 8705 (2007).
[12] XD Gao, XM Li, S Zhang, WD Yu, JJ Qiu, J. Mater. Res. **22**, 1815 (2007).
[13] L Vayssieres, Adv. Mater. **15**, 464 (2003).
[14] R. Jothi Ramalingam, G.S. Chung, Mater Lett. **68**: 247 (2012).
[15] Schlager, Neil and Weisblatt, Jayne. Alternative Energy. Volume 1-3, Michigan, USA, Thomson Gale. (2006).
[16] Liu, Wen – Chau, Chen, Huey – Ing, and Pan, Hsi Jen. Hydrogen Sensor. US patent, patent No. US 6, 293, 137. (2001).
[17] Xu, Tao. Ultra-fast and ultra-sensitive hydrogen sensors based on self-assembly monolayer promoted 2- dimensional palladium nanoclusters. US patent No. 7,389,671 B1. (2008).
[18] N. Barsan, U. Weimar, Journal of Electroceramics **7**, 143 (2001)
[19] Chen, Po - Chiang, Shen, Guozhen, Zhou, Chongwu. IEEE Trans. Nanotechnol, **7,** 668 (2008).
[20] Patrícia, Nunes, Fortunato, Elvira, Martins, Rodrigo. Thin film combustible gas sensors based on Zinc Oxide. Mat. Res. Soc. Symp. Proc., Vol. 666. (2001).
[21] M. Liu, H. Kitai, P. Mascher, J. Lumin. **54**, 35(1992).
[22] R. Jothi Ramalingam, Murugan A. Munusamy, Hamad A. Al-Lohedan, Journal of Photochemistry & Photobiology, B: Biology (2016) pp. 202-212.
[23] X.W. Sun, J.X. Wang, A. Wei, Journal of Materials Science and Technology, **24**(4), 649 (2008).