Journal of Materials Science and Engineering A 6 (3-4) (2016) 51-56
doi: 10.17265/2161-6213/2016.3-4.002

Hydrogen Gas Sensor Based on ZnO Nanoroads Grown on Si by Thermal Evaporation

Hind Ibraheem Abdulgafour[1], Hassan Hadi Darwoysh[1, 2] and Faez Mohamad Hassan[2*]

1. Departement of Physics, Ministry of Science and Technology, Baghdad, AlKerrada 10069, Iraq

2. Department of Physics, College of Education, Al-Mustansiriya University, Baghdad, New Baghdad 10062, Iraq

Abstract: High-quality ZnO (Zinc oxide) nanorods grown on Si substrate have been synthesized for hydrogen gas sensor application through a low-cost catalyst-free process by thermal evaporation at 800 °C. The morphological, structural and optical properties of the ZnO nanorods have been examined. In this study, Pd/ZnO/Pd MSM (Metal-semiconductor-metal) gas sensor has been fabricated based on the ZnO nanorods. The absence of a seed layer and the coalescence of ZnO nanorods were the key factors responsible for the high sensitivity of the gas sensor at room temperature. The sensitivity of ZnO nanorods is measured at different concentrations from 25 ppm to 150 ppm of H_2 gas at room temperature. The highest response of the ZnO/Si sensor was 110% in the presence of 500 ppm of H_2. This high sensitivity can be attributed to the high surface-area- to-volume ratio of the nanorods between the Pd contacts of the MSM configuration.

Key words: ZnO, nanostructures, thermal evaporation, gas sensor.

1. Introduction

Leaked hydrogen fuel could have small negative effects on atmosphere. Using hydrogen as an energy carrier can help reduce air pollution and GHG (Greenhouse gas) emissions associated with fossil fuels. However, if used on a large-scale, it is important that hydrogen does not leak significantly into the atmosphere as it might have some negative environmental effects, such as increasing the lifetime of methane, increasing climate effects and causing some depletion of the ozone layer [1]. In recent years, low-dimensional systems have attracted tremendous interest in nanosensor applications due to their gas sensitivity, UV (Ultraviolet) photoresponse, and optical transparency in the visible region, among other features [2, 3]. In particular, quasi-one dimensional nanowires or nanorods are promising low-cost material for high-speed UV photoconductive nanoscale detectors and gas sensors [4-6]. In the past decade, research on wide band gap semiconductors has focused on ZnO (zinc oxide) due to its excellent properties as a semiconductor. Its high electron mobility, high thermal conductivity, good transparency, wide and direct band gap (3.37 eV), large exciton binding energy and ease of fabrication into micro- and nanostructures make ZnO suitable for a wide range of applications in optoelectronics, transparent electronics, lasing and sensing [7, 8].

Nanorods are some of the most common forms of ZnO that possess several excellent properties, such as high sensitivity to adsorbed oxygen on the surface, excellent electric transport, high photo-sensitivity, optical wave-guiding, and large surface area-to-volume ratio [9]. Compared with the bulk materials used in gas sensors, such as thin films, nanorods have greater gas sensitivity and selectivity and lower operating temperatures [10, 11]. Room-temperature hydrogen gas sensors have received a great deal of interest for use in several applications because of the extremely low power consumption, ability to be used safely in flammable environments, and long lifetime [12-14]. For gas sensing applications, ZnO is one of the promising

[*]**Corresponding author:** Faez Mohamad Hassan, Ph.D., research fileds: solid state physics and nanotechnology.

metal oxide wide band gap semiconductors [16]. In gas sensing, ZnO has been tested for sensing harmful and toxic gases [15]. A common concern about gas sensors based on ZnO thin films is the lack of selectivity and higher operating temperature. In general, its optimum operating temperature range is 400-450 ˚C [16]. Also, Ref. [17] used Pt-coated ZnO nanorods as sensors that were capable of detecting part per million (ppm) concentrations of hydrogen at room temperature. According to the previous reports, the sensitivity of ZnO to gas may be affected by nanostructure surface defects and post-growth annealing in H_2 or O_2 ambient [18]. In this study, an alternative method to synthesize high quality ZnO nanorods on SiO_2/Si by using thermal evaporation method without catalyst is presented. The simplicity, lower cost and suitability of this method in producing high structural and optical quality ZnO nanostructures are very promising for efficient sensing applications; Particularly, the high surface area to volume ratio is the major factor responsible for high performance of the sensors fabricated based on ZnO nanorods.

2. Matreials and Methods

2.1. Synthesis of ZnO Nanorods

The synthesis process was carried out in a controllable tube furnace with a quartz tube (inner diameter, 25 mm). N-type silicon (Si) wafers cut into 1 × 1 cm^2 pieces with a single polished side were used as substrates. The substrates were ultrasonically cleaned with acetone and IPA (Isopropyl alcohol), and then rinsed with DI water. A pure metallic Zn powder (99.9%) as source material was placed into a ceramic boat. The Si substrates (with the polished side facing the source material) were inserted into a quartz tube. The furnace was slowly heated from 400 ˚C to 800 ˚C. After reaching 800 ˚C, argon (Ar) was introduced with flow rates of 350 scrums, respectively, for 1 hour. After the evaporation, the alumina boat was slowly drawn out from the furnace and cooled to room temperature. A white layer of ZnO was observed on the Si substrate surface. The thickness of ZnO thin film was around 200 nm was measured by reflectometer (F20). The surface morphology and structure of the ZnO nanostructures were examined by SEM (Scanning electron microscopy) JEOL, attached with an energy dispersive X-ray spectroscopy (EDS). The HR-XRD (High resolution X-ray diffractometer) was used for phase identifications.

2.2. Fabrication of Gas Sensor

The (I-V) measurements of the sample were carried out using the Keithley model 2400. Fig. 1 shows the schematic diagram of the gas sensing system. To fabricate a diode gas sensor, MSM with interdigitated contacts (electrodes) forming Schottky barriers was used.

The four fingers of each of the Pd contact electrodes were 0.23 mm wide and 4 mm long, with 0.4 mm spacing, as shown in Fig. 2. The gas sensing experiments were carried out by using a homemade gas sensing chamber. For characterization of the gas sensing device, the test fixture was placed in the chamber with wires connected from the probes to Keithley device to measure the current voltage (I-V) characteristics of the sample. The voltage was biased from 5 V to − 5 V and different concentrations of 2% H_2 in N_2 gas were used in this experiment.

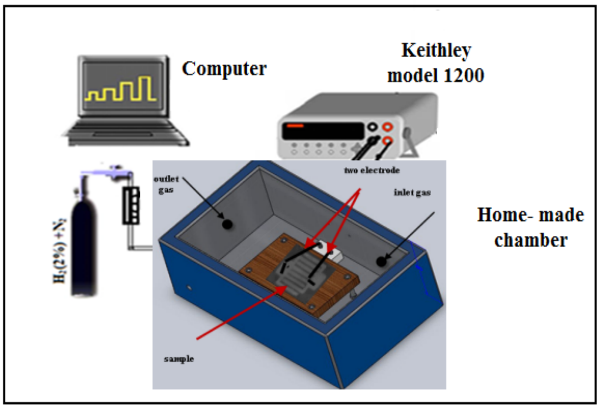

Fig. 1 Schematic diagram of the home-made gas sensor system.

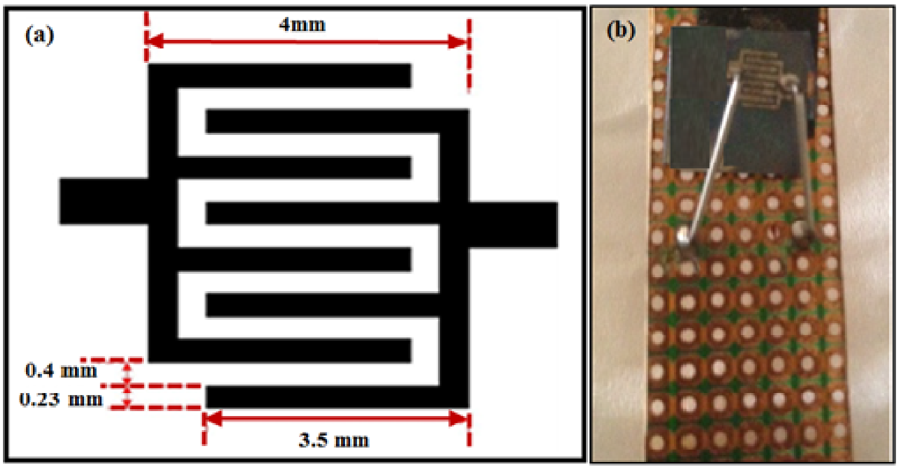

Fig. 2 (a) The structure used in the fabrication of MSM; (b) The photo image MSM gas sensor fabricated on ZnO nanorods.

3. Results and Discussion

3.1. Characterization of the ZnO Nanorods

The SEM image is shown in Fig. 3. The resulting images of the prepared ZnO depict nanorods structure. The nanorods were linked with neighboring nanorods, which formed a nanorod network. The structures of ZnO nanorod morphology revealed a hexagonal structure with average diameters are about 80-100 nm, and their lengths were more than 500 nm with thickness around 200 nm (Fig. 3).

The XRD pattern shows the hexagonal (wurtzite) structure of the ZnO nanorods. Strong diffraction intensity peaks related to the (002) plane of the ZnO nanorods were observed (Fig. 4). The strongest peak (002) at $2\theta = 34.37^{\circ}$ with FWHM (Full-width half-maximum) of 0.19° showed an excellent quality of the ZnO nanorods that the preferred growth orientation of nanorods is along the c-axis. Furthermore, the strong intensity and narrow width of the ZnO diffraction peaks also indicate that the resulting products had well crystalline.

3.2. Sensing Characterization

These nanorods provide a large surface-area-to-volume ratio to interact with the surrounding gas. The change in the depletion diameter fully occurs in the ZnO nanorods, which result in a significant change in conductivity. In ambient air, the ZnO nanorod surface adsorbs oxygen (O_2) molecules,

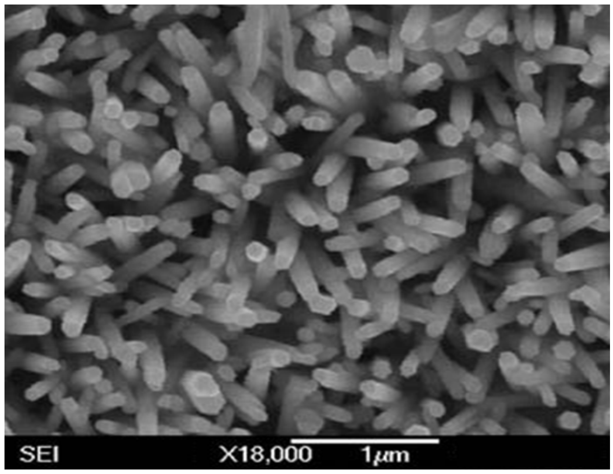

Fig. 3 The SEM images of ZnO nanorods grown at 800 ˚C.

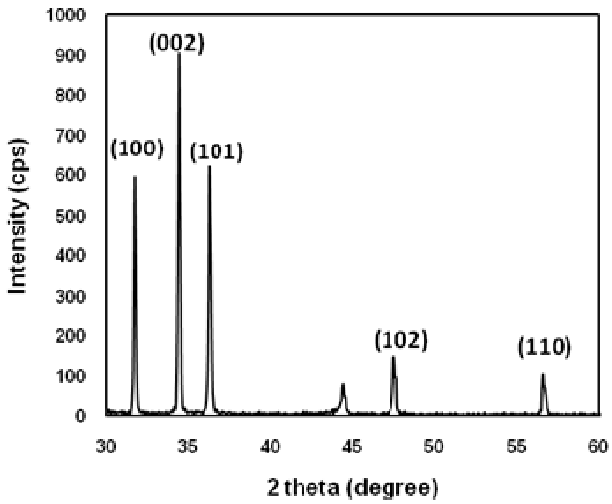

Fig. 4 The XRD spectra of ZnO grown at 850 ˚C.

which results in increased resistivity. In this work, the Pd/ZnO/Pd gas sensor has been successfully fabricated using high-quality ZnO nanorods. Fig. 5 shows the I-V characteristics (linear scale plot) of the Pd/ZnO nanorods hydrogen gas sensors measured for different concentrations (25, 50, 75, 100, 125, and 150 ppm) of H_2 gas at room temperature (300 K). The sensor was found to show good behavior with remarkable increasing of current at different concentrations of H_2 gas with bias voltage from 5 V to – 5 V for ZnO deposited on Si substrate. The increment of the current in the presence of hydrogen may be due to a decrease in the barrier height between the Pd/ZnO interfaces after H_2 adsorption.

The sensitivity (S) was determined as the ratio ($\Delta R_{gas}/R_{air}$) of the resistance in hydrogen gas (R_{gas}) to that in air (R_{air}) or also could be measured as a reference to the current ($\Delta I_{gas}/I_{air}$) of the current in hydrogen gas (I_{gas}) to current in air (I_{air}), at fixed applied voltage (1 V). Fig. 6 shows the variation of sensitivity with the H_2 different concentrations at room temperature for Pd/ZnO recorded at 1 V in forward current mode. One may observe that the sensitivity increased gradually with the hydrogen flow rate for this device.

From Fig. 6, it could be seen the sensitivity at high concentration of hydrogen gas (150 ppm) was around 110% for ZnO nanorods at room temperature; this could be due to the improvement of the structural properties of the ZnO nanorods. On the other hand, this might also be due to the increase of the internal surface area, which allows the enhancement of the adsorbate effects; and high activity in surface chemical reactions [19]. Furthermore, this observation coincides with the fact that ZnO/Si sample have a large specific area and therefore provide a large contact area, hence giving it a higher chance to react with gases and increase the sensitivity. The series resistances evaluated from the I-V curves for Pd/ZnO Schottky diode measured at 300 K with different concentrations of H2 gas are shown in Fig. 7. The series resistance decreased exponentially upon the introduction of different concentrations of 2% H_2 in N_2 gas for the ZnO nanorods.

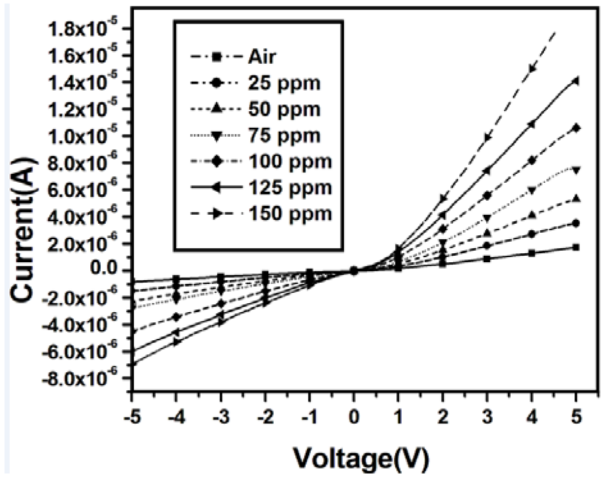

Fig. 5 I-V characteristics (linear scale plot) of Pd/ZnO measured at room temperature for different hydrogen concentrations.

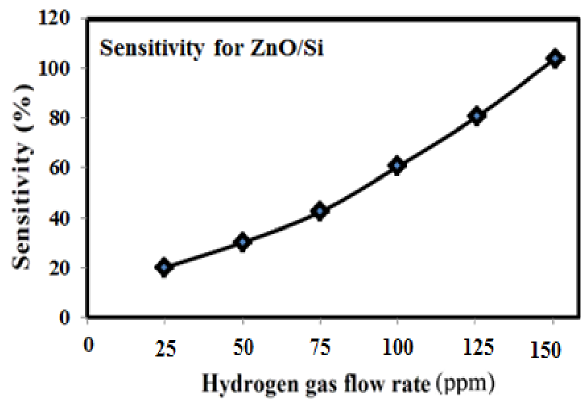

Fig. 6 The sensitivity of Pd/ZnO for nanorods grown on Si substrate.

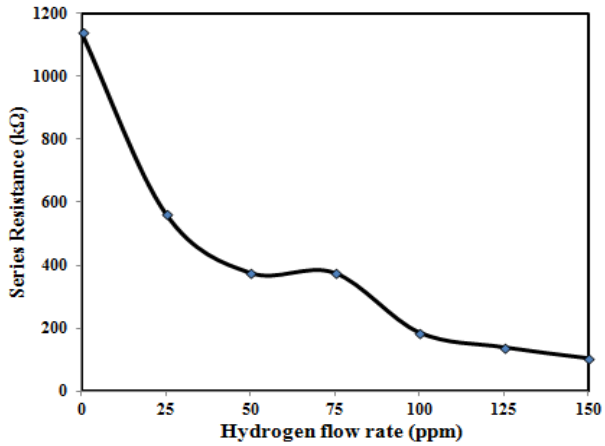

Fig. 7 The series resistance at room temperature of Pd/ZnO nanorods as a function of hydrogen concentrations.

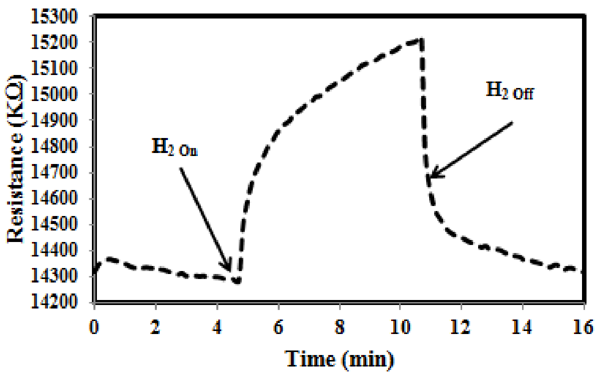

Fig. 8 The response time behavior of Pd/ZnO nanorods Schottky diode sensor at 1 V.

A part from that, the response time is defined as the time taken for the sensor to reach 90% of the saturation current from initial value while the recovery time is defined as the time taken from saturation current to reach 10% of its saturation current value after contact of the test gas with the surface of the sensor. Measured resistance at a bias of 1 V as a function of time is shown in Fig. 8 for Pd/ZnO exposed to 2% H_2 in N_2 in constant concentration 150 ppm at room temperature. As can be clearly seen from Fig. 8, the adsorption and desorption times for H_2 were set at 10 min (H_2 on) and 15 min (H_2 off), respectively. The response and recovery times measured for the sensor were about 5 and 6 min, respectively. Fig. 8 shows the analysis/plot of the rise time and recovery time as a function of H_2 gas concentration (150 ppm). Also, after the injection of hydrogen into the measuring chamber, the resistance of samples changes and becomes stable. After the removal of hydrogen, the resistance of samples reverts to values before hydrogen injection and becomes stable again. It may be seen that the maximum resistance could be attained in less than 10 min. The experimental results indicate the potential of using zinc oxide nanorods face for gas sensing based on Schottky Barriers of Pd/ZnO. Compared with conventional ZnO thin films, the observed enhancement in the gas sensing properties of the ZnO nanorods gas sensor is most likely attributable to the relatively higher degree of surface reaction due to the high specific surface area associated with the nanostructure. Also, a comparison of ZnO rods-like nanostructures with other nanostructures leads us to conclude that the gas sensing properties also depend on other factors, including crystallinity and surface properties, and these need to be studied further.

4. Conclusions

In summary, the growth of ZnO rods-like nanostructure arrays on Si substrates has been demonstrated at 800 °C. The hydrogen gas sensor has been fabricated based on ZnO nanorods synthesized by a catalyst-free thermal evaporation technique by simple and low-cost process worked at room temperature. The good response of the ZnO nanorods gas sensor was 110% when 150 ppm of H_2 gas was injected. The series resistance in the Pd/ZnO nanostructures was decreased exponentially with increasing the flow rate of H_2 gas. The enhanced sensitivity at a lower operating temperature for the ZnO nanorods is attributed to the reduction of grain size and increase in the surface area. As a consequence, the surface activity is enhanced, and the activation energy of the surface-chemisorbed H_2 gases is reduced, enhancing the H_2 gas adsorption.

References

[1] Van Ruijven, B., Lamarque J.-F. and Van Vuuren, D. P. 2011. "Emission Scenarios for a Global Hydrogen Economy and the Consequences for Global Air Pollution." *Global Environmental Change* 21: 983-94.

[2] Heo, Y. W., Norton, D. P., Tien, L. C., Kwon, Y., Kang, B. S. and Ren, F. et al. 2004. "ZnO Nanowire Growth and Devices." *Materials Science and Engineering: R: Reports* 7: 1-47.

[3] Li, Q. H., Liang, Y. X., Wan, Q. and Wang, T. H. 2004. "Oxygen Sensing Characteristics of Individual ZnO Nanowire Transistors." *Applied Physics Letters* 85: 6389-91.

[4] Chow, L., Lupan, O., Heinrich, H. and Chai, G. 2009. "Self-Assembly of Densely Packed and Aligned Bilayer ZnO Nanorod Arrays." *Applied Physics Letter* 94: 163105-8.

[5] Lupan, O., Chai, G. and Chow, L. 2007. "Fabrication of ZnO Nanorod-Based Hydrogen Gas Nanosensor."

Microelectronics Journal 38: 1211-6.

[6] Chai, G., Lupan, O., Chow, L. and Heinrich, H. 2009. "Crossed Zinc Oxide Nanorods for Ultraviolet Radiation Detection." *Sensors Actuators A Physics* 150: 184-7.

[7] Bai, X. D., Gao, P. X., Wang, Z. L. and Wang, E. G. 2003. "Measuring the Work Function at a Nanobelt Tip and at a Nanoparticle Surface." *Applied Physics Letters* 82: 4806-8.

[8] Janotti, A. and Van de Walle, C. G. 2009. "Fundamentals of Zinc Oxide as a Semiconductor." *Reports on Progress in Physics* 72: 126501-9.

[9] Akhavan, O., Mehrabian, M., Mirabbaszadeh, K. and Azimirad, R. 2009. "Hydrothermal Synthesis of ZnO Nanorod Arrays for Photocatalytic Inactivation of Bacteria." *Journal of Physics D: Applied Physics* 42: 225305-14.

[10] Schmidt-Mende, L. and MacManus-Driscoll, J. L. 2007. "ZnO-Nanostructures, Defects and Devices." *Materials Today*10: 40-84.

[11] Tonezzer, M. and Lacerda, R. G. 2012. "Zinc Oxide Nanowires on Carbon Microfiber as Flexible Gas Sensor." *Physica E: Low-Dimensional Systems and Nanostructures* 44: 1098-102.

[12] Wright, J. S., Lim, W., Norton, D. P., Pearton, S. J., Ren, F. and Johnson, J. L. et al. 2010. "Nitride and Oxide Semiconductor Nanostructured Hydrogen Gas Sensors." *Semiconductor Science and Technology* 25: 024002.

[13] Sun, J., Xu, J., Yu, Y. S., Sun, P. and Lu, F. G. 2012. "UV-Activated Room Temperature Metal Oxide Based Gas Sensor Attached with Reflector." *Sensors and Actuators B: Chemical* 169: 291-6.

[14] Choi, K. J. and Jang, H. W. 2010. "One-Dimensional Oxide Nanostructures as Gas-Sensing Materials: Review and Issues." *Sensors* 10 (4): 4083-99.

[15] Morkoc, H. and Ozgur, U. 2008. Zinc Oxide: Fundamentals, Materials and Device Technology. John Wiley & Sons, Germany.

[16] Lee, J. H. 2009. "Gas Sensors Using Hierarchical and Hollow Oxide Nanostructures: Overview." *Sensors and Actuators B: Chemical* 140: 319-36.

[17] Tien, L. C., Sadik, P. W., Norton, D. P., Voss, L. F., Pearton, S. J. and Wang, H. T. et al. 2005. "Hydrogen Sensing at Room Temperature with Pt-Coated ZnO Thin Films and Nanorods". *Applied Physics Letters* 87 (22): 222106.

[18] Ahn, M. W., Park, K. S., Heo, J. H., Park, J. G., Kim, D. W. and Choi, K. J. et al. 2008. "Gas Sensing Properties of Defect-Controlled ZnO-Nanowire Gas Sensor." *Applied physics letters* 93 (26): 263103.

[19] Korotcenkov G. and Cho, B. K. 2010. "Silicon Personification: State of the Art." *Critical Reviews in Solid State and Materials Sciences* 35: 153-260.