Quest Journals
Journal of Electronics and Communication Engineering Research
Volume 8 ~ Issue 2 (2022) pp: 08-14
ISSN(Online) : 2321-5941
www.questjournals.org

Research Paper

Fabrication of Zinc Oxide Nanowiresbased Efficient Ammonia Sensors

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Abstract
Fast and accurate detection of ammonia (NH_3) in ambient air is extremely important to avoid gas leakage induced tragedies and save human/livestock lives. Conventional gas sensors with bulky structures, complicated operation procedures and high cost have plagued their application in household monitoring of toxic gases. Here, we report the fabrication of ZnO nanowires based efficient room temperature operating NH_3 gas sensor. Vertically aligned ZnO nanowires were grown on silicon substrate via cost-effective hydrothermal method using commercial microwave oven. Prior to sensor fabrication, the synthesized ZnO nanowires were characterized by scanning electron microscopy and x-ray diffraction measurements to ascertain the nanowire dimensions identify the chemical phase, and analyze the crystallographic orientation. The analysis revealed the formation of 2 (± 0.3) µm long and 100 (± 50) nm wide pure phase ZnO nanowires with hexagonal crystal structure. Further, the ZnO nanowires-based sensing device was fabricated using100 nm thick gold electrode and subjected to NH_3 sensing at an exposure level of 25, 50 and 100 ppm which is far below the advised threshold limit. We explored the underlying science behind NH_3 sensing at ZnO surfaces and calculated a peak sensitivity of 67% at 100 ppm exposure level with a fast detection time of 50 seconds. The obtained results have opened new avenues for the development of affordable, reliable and portable gas sensing technology for households NH_3 exposure monitoring to save future gas leakage tragedies.

***R**eceived 09 Feb, 2022; **R**evised 20 Feb, 2022; **A**ccepted 23 Feb, 2022 © The author(s) 2022.*
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I. Introduction

The globalization of economies and development of countries has given rise to numerous environmental concerns and serious health hazards. Recent gas leak tragedies at Vizag, Andhra Pradesh and Tinsukia, Assam have resulted in an unfortunate great loss of human lives [1,2]. Similarly, Ammonia (NH_3) is also a highly toxic, colorless, flammable, hazardous and life- threatening gas used in various chemical, food processing, agricultural, petrochemical, manufacturing, automobile and medical industries [3]. Ammonia emission in the atmosphere takesplace from multiple sources including cold storage facilities, chemical plants, fertilizer industries and beverage/medicine manufacturers, where it not only pollutes the environment but also led to adverse health effects [4,5]. In all the given scenarios, there are finite chances for ammonia leakagefrom the active plants/industries which can result in significant loss of human lives and livestock. As per American National Institute for Occupational Safety and Health, Ammonia's exposure above 300 ppm is an immediate danger for human life leading to permanent damage of respiratorysystem and loss of vision in humans [6-8]. While in animals, Ammonia exposure causes immunological, growth and reproductivity related problems [6-8]. Besides that, the aerosols of ammonia (depending on their concentration level) create heavy fog and blocks the incident solar irradiation over cities [4]. Therefore, it becomes essential to develop low-cost and room temperature operating NH_3 gas sensors for industrial regulation and constant monitoring at ammonia generation/storage facilities (and nearby households) to avoid ammonia leakage inducedfatalities in future.

In recent years, semiconductor metal oxide (SMO) based chemi-resistive gas sensors has shown significant potential in the field of gas sensing technology [9-16]. The chemi-resistive sensors function on the principle of variation in electrical conductivity (i.e., change in resistance) upon chemical reaction when subjected to a particular targeted gas molecule. These devices offernumerous advantages such as compact size, cost effectiveness, reliable results and simple operation over conventional bulky systems which enhances practicality in outdoor applications. It has been observed that Zinc Oxide (ZnO) based sensors are largely

employed in gas sensing applications due to their non-toxic nature, high selectivity, excellent response, easy fabrication, low cost and good thermal/chemical stability among all the available SMO based material system [17]. ZnO is a multifunctional n-type semiconducting material pursuing wide bandgap (3.4 eV) and large exciton binding energy (60 meV), biocompatibility and high electron mobility which is ideal for gas sensing applications [18-20]. In recent year, the published research has showcased potential of ZnO in the fabrication of NH_3 gas sensors [21,22]. Though, challenges related to poordevice performance due to lower surface area, poor gas interaction and high temperature operation etc. was observed to be a critical issue plaguing the technology advancement [21-23].

Nanostructured ZnO pursing high aspect ratio (surface-to-volume), large number of active sites, enhanced surface reactivity can mitigate the existing challenges and lead to the fabrication highly sensitive NH_3 sensors [23]. It will not only contribute in device performance optimization, but the reduction in device dimensions will enhance their practical application for NH_3 exposure monitoring in households located in the vicinity of active plants/industries. Therefore, the presented report explores the fabrication of ZnO nanowires-based room temperature operating NH_3 gas sensors. The ZnO nanowires were directly grown Silicon (Si) substrates via hydrothermal method and subjected to preliminary material characterization followed by the fabrication of metal semiconductor metal (MSM) based NH_3 sensors (at different NH_3 concentrations). The obtained results were analyzed extensively and the underlying science has been discussed in further sections.

II. Methodology

The growth of ZnO nanowires was performed via wet chemical hydrothermal method as established via Greene et al [24]. A solution of 10 mM Zinc Acetate in Isopropanol was spin coatedon pre-cleaned n-type Si substrate at 2000 rpm. The coated substrates were then dried using pressurized Nitrogen gas and heating at 100^oC for 120 seconds for improve adhesion. The procedure was repeated 3 times to get uniform ZnO seeding layer for nanowires grwoth. Further, the ZnO seeding layers (on Si substates) were immersed (facing downwards) in a mixture of 25 mM Zinc Nitrate hexahydrate and Hexamethylenetetramine (HMTA) solution in deionized (DI) water. The setup was covered with lid and heated in a commercially purchased microwave oven (2.45 GHz) at 700 W for 180 seconds at ambient pressure to synthesize aligned ZnO Nanowires. Finally, samples were then removed from the setup, rinsed with deionized water and blown driedwith Nitrogen gas.

To ascertain the surface morphology and dimension of grown ZnO nanowires, the samples were subjected to scanning electron microscopy (SEM) measurements. X-Ray diffraction (XRD)measurements were performed to characterize the chemical phase of ZnO and analyze its crystallographic structure. In order to fabricate the gas sensor, 100 nm thick gold electrodes (with active areas of 4 x 6 mm) were deposited on the synthesize ZnO nanowire sample. Further, the fabricated device was subjected to room temperature NH_3 sensing measurements at different ppm levels (under 100 ppm) using a custom designed two probe setup equipped with Keithley source meter and mass flow controller for mixing of gases and controlling NH_3 exposure.

III. Results and Discussion

To ascertain the surface morphology and dimension of the grown nanowires, SEM measurementsof the sample was performed. Figure 1a shows the low magnification SEM image of sample confirming the synthesis and uniform coverage of vertically aligned ZnO nanowires over the silicon substrate. The higher magnification images (as shown in Figure 1b) divulged that the diameter and length of the nanowires was observed to be 100 ($\pm$ 50) nm and 2 ($\pm$ 0.3) µm respectively. The SEM analysis also confirmed that the opted methodology resulted in the growthof highly aligned ZnO nanowires pursuing higher surface to volume ratio.

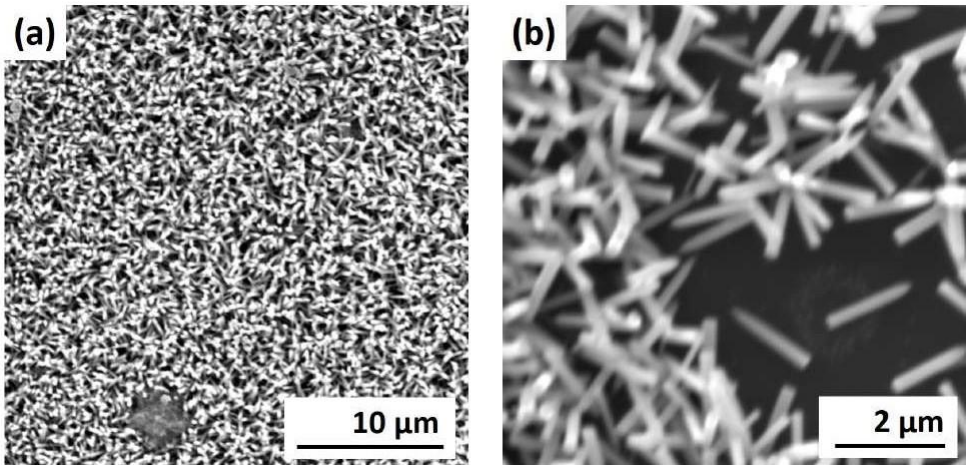

Figure 1: *a) Low magnification and b) High magnification scanning electron microscopicimages of the synthesized ZnO nanowires displaying uniform coverage.*

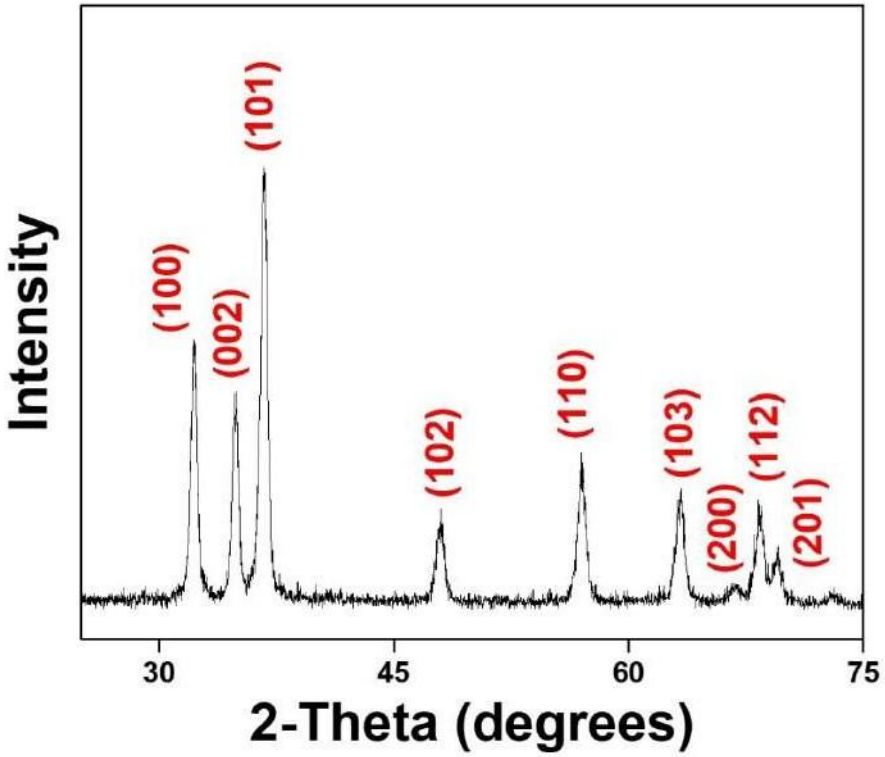

Figure 2: *X-Ray diffraction pattern of the synthesized ZnO nanowires showing differentcrystallographic planes.*

In order to analyze the crystal structure and chemical phase identification, the XRD pattern of the grown ZnO nanowires was recorded over a wide angle range (20 – 80^{o}C). Figure 2 display diffraction peaks located at 31.84°, 34.48°, 36.27°, 47.54°, 56.61°, 62.81°, 66.43°, 67.84° and

69.12° which corresponded to the (100), (002), (101), (102), (110), (103), (200), (112) and (201) planes of ZnO [22]. No extra peak was witnessed in the diffraction pattern which indicated the formation of pure phase of ZnO nanowires with no impurities. The obtained XRD pattern and theidentified diffraction peaks established the growth of ZnO nanowires in hexagonal wurtzite structure (P63mc, a = b = 3.2489 Å, c = 5.2049 Å) [25]. Hence, we observed that both SEM and XRD measurements confirmed the synthesis of pure phase vertically aligned ZnO nanowires in hexagonal crystal structure.

Further, Ammonia gas sensor was fabricated using metal semiconductor metal (MSM) approach as shown in Figure 3a. Gold electrodes with a thickness of 100 nm and spacing of 4 mmwere deposited on the sample using physical vapor deposition technique. Initially, ambient pressure current-voltage curves (not shown here) were recoded to ensure the proper functioning of the fabricated device. Thereafter, the sample was subjected to NH_3 sensing measurements at different concentration levels. Though, prior to the analysis the obtained results, it is highly important to understand the science behind NH_3 sensing at ZnO surfaces. Figure 3b displays the schematic representation of NH_3 sensing mechanism at ZnO nanowires. The underlying gas sensing principle is based on adsorption–desorption of the targeted gas (i.e., NH_3) on semiconductor metal oxide (i.e., ZnO) surface [26,27]. As shown in Figure 3b, NH_3 gas reacts withsurface adsorbed oxygen ions and further releases electron to conduction band of ZnO nanowires.Due to this reaction, the depletion width and the potential barrier reduces which lead to the increment in the overall conductivity of the fabricated sensor. The charge carrier transfer can be well understood with the help of following equation:

$$2NH_3 + 7O^-_{(adb)} = 3H_2O + 2NO_2 + 7e^- \quad \ldots[1]$$

Thereby, the introduction of NH_3 gas increases the overall conductivity which is supported by our obtained results shown in Figure 4.

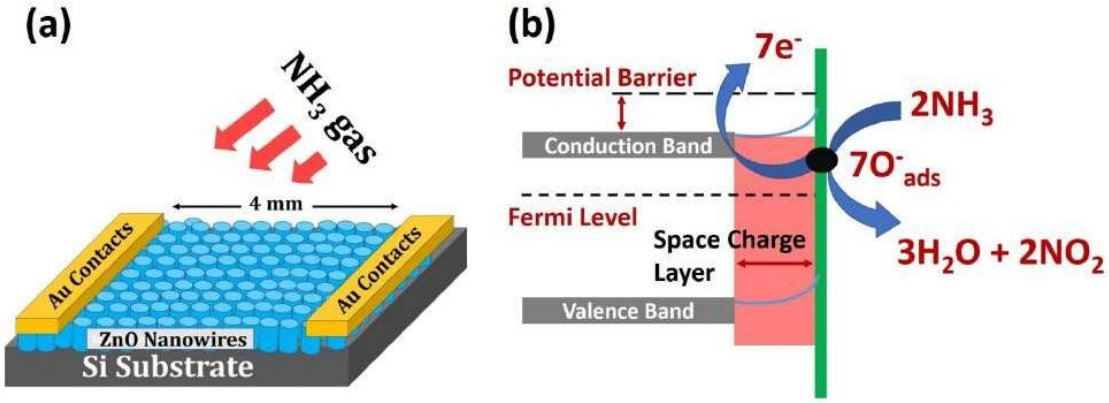

Figure 3: *Schematic representation of a) fabricated gas sensors and b) sensing mechanism andcharge transfer at ZnO nanowire surfaces.*

Figure 4a shows the gas sensing response of the fabricated gas sensor at different NH3 concentration levels. The normalized response-recovery curves were recorded at room temperatureunder constant voltage of 2V at 25, 50 and 100 ppm NH3 exposure levels. The sensitivity (S) of the fabricated device were calculated using the observed changes in device resistance as follows [28]:

$$S = \frac{R_a'' R_g}{R_a} = \frac{\Delta R}{R_a} \qquad \ldots[2]$$

Here, S is the sensitivity of the fabricated sensor, Ra is the resistance of sensors in air, Rg is the resistance of sensor in ammonia and ΔR is the change in resistance. Since the resistance (or sensitivity) of a sensor depends on the concentration of targeted gas, the fabricated device showcased peak sensitivity of 18%, 34% and 67% at NH3 exposure at a concentration level of 25, 50 and 100 ppm, respectively. The higher response at 100 ppm level was ascribed to the higher NH3 concentration leading to enhanced charge transfer.

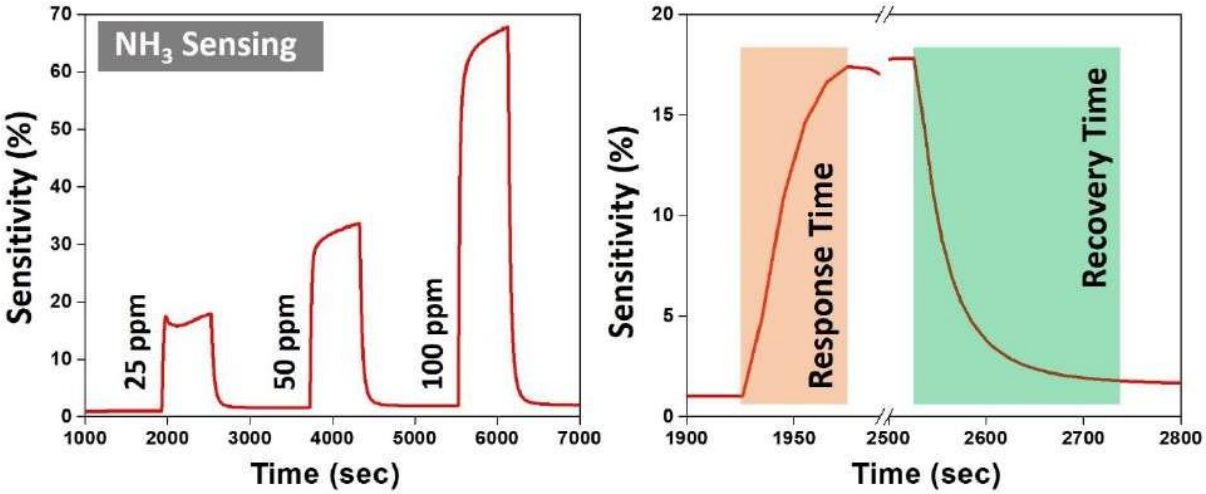

Figure 4: *a) Sensing response curves of the fabricated sensors at different gas concentrationsand b) response and recovery time calculations.*

Finally, another important figure of merit parameter of the fabricated sensor, i.e., response & recovery time were also calculated by fitting of sensing response curves. It is important to understand that response time is the time required to reach the 90% of its maximum value while recovery time is time required to fall to the 10% of its maximum after removal of the target gas asshown in Figure 4b. The calculated response & recovery time of the fabricated sensor was nearlysimilar at all NH3 concentration levels and remained in the vicinity of 50 sec and 180 sec, respectively. It refers that the fabricated sensor would be able to detect NH3 exposure in less than1 minute and would normalize to the original state within 3 minutes of blocking the gas exposure.These

obtained results are in close agreement with other published reports, where comparable values of sensitivity, response and recovery time have also been reported [16,21,22, 26-28]. Though, the obtained value of response time was slightly higher, though it indeed sufficient to avoid ammonia leakage related fatalities. Further improvement in response time can be achievement by increasing the device operation temperature (above 100^{o}C), but it will than hamperthe cost effectiveness and will also limit the household application.

IV. Conclusion

In conclusion, we have displayed the fabrication of room temperature operating NH_3 gas sensors using vertically aligned ZnO nanowires. High quality ZnO nanowires were grown on n-type silicon substrate via wet hydrothermal method using a commercial microwave oven. Surface morphology and dimensions of the synthesized nanowires were ascertained by SEM measurements while XRD pattern analysis was employed to confirm the formation of pure phase ZnO indicating hexagonal crystal structure. Further, the ZnO nanowire-based gas sensor was fabricated using metal semiconductor metal approach, and gold electrode decorated device was subjected to NH_3 exposure at a concentration level of 25, 50 and 100 ppm. It was observed that room temperature NH_3 exposure led to significant changes in device conductivity and a peak sensitivity of 18, 34 and 67% were obtained at a concentration level of 25, 50 and 100 ppm. The fabricated gas sensor also divulged high switching rate with a response & recovery rate of 50 sec and 170 sec.

Acknowledgment

I am highly thankful to my teachers and parents for their kind support, motivation and constant encouragement. I sincerely thank Dr. Monu Mishra for his mentorship, guidance and assistance inperforming the experiments.

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