Ammonia sensing characteristics of quartz resonator coated with ZnO nanowires sensitive layer

Hongbin cheng, Lifeng Qin, Fang Li, and Qing-Ming Wang
Department of Mechanical Engineering and Materials Science
University of Pittsburgh
Pittsburgh, PA 15621, USA

Abstract—**In this paper, we present our recent study on the fabrication and characterization of ammonia gas sensors based on quartz thickness shear mode (TSM) resonators employing ZnO nanowires as the sensitive coating layer. c-axis vertically aligned ZnO nanowire arrays were synthesized on the quartz resonator through a simple hydrothermal synthesis route. The ZnO nanowires were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The sensing characteristics, including sensitivity, stability, reproducibility, and response time of the acoustic wave gas sensors have been studied under different concentration levels of ammonia at room temperature. It is demonstrated that the use of the ZnO nanowire arrays on quartz TSM acoustic wave resonator can greatly enhance the sensitivity and sensor response speed due to the fast surface/interface reaction and large surface/volume ratio of the nanowire arrays.**

Keywords- Thickness shear mode, Gas sensor, Quartz resonator, ZnO nanowir arrays

I. INTRODUCTION

It is very important to detect the ammonia at different concentration levels since it is widely used in many areas such as fertilizers, food processing, medical diagnosis, and environmental protection. Acoustic technology has been widely investigated for gas sensor applications in the past years due to high sensitivity and structural simplicity. For example, quartz thickness shear mode (TSM) resonator with active layer has been widely studied for gas detection through the measurement of resonance frequency shift, which are related to mass change of active layer due to gas adsorption and dissociation.

Zinc oxide thin film, a wide bank gap n-type metal oxide semiconductor, is one of the most widely investigated oxide gas-sensing materials due to its high chemical stability, low cost, and good flexibility in fabrication [1]. Piezoelectric ZnO films have also been extensively investigated for surface acoustic wave devices and bulk acoustic wave devices, especially for the detection of inflammable and toxic gases owing to its excellent piezoelectricity, substantial electromechanical coupling coefficient, and good temperature stability [2]. However, the sensing performance such as the response speed is often limited by the grain sizes, surface states, and gas adsorption and dissociation rate and the diffusion rate in the thin films [3]. The emergence of nanoscale science and technology in recent years is making a significant impact on gas sensors. Novel nanoscale sensors show great promise as they have faster response and higher sensitivity than planar sensor configurations due to their smaller diffusion dimension, dramatically increased sensing surface area/volume ratio and more surface dangling bonds. To date, various one-dimensional ZnO nanostructures have been realized in forms of nanowires, nanobelts, micro/nanotubes, and nanocones [4-7]. Those ZnO nanostructures have a high surface to volume ratio, and have been regarded as a promising material to improve the gas sensing performance. Recently, gas sensors based on ZnO nanostructures have been demonstrated for toxic and combustible gas sensing, and these sensor show increased sensitivity and accuracy [8].

However, applying ZnO nanowire arrays for gas sensors based on quartz acoustic devices has scarcely been reported. It is believed that the combination of ZnO nanowire arrays with quartz thickness shear mode (TSM) resonators will provide an ideal gas sensor platform for both higher sensitivity and enhanced response speed. Therefore, in this paper, we present our recent study on the fabrication and characterization of the ZnO nanowires gas sensor using thickness shear mode (TSM) quartz resonators. c-axis vertically aligned ZnO nanowire arrays were synthesized on the quartz resonator by using an utrathin ZnO seed layer through a simple room temperature hydrothermal route. The sensing characteristics, including the sensitivity, stability, reproducibility, and response time of the acoustic wave gas sensors have been tested at different concentration levels of ammonia at room temperature.

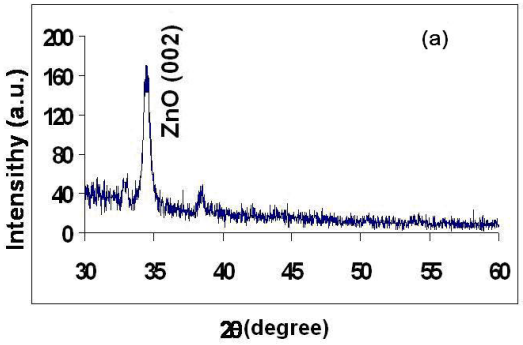
Funding for this project was provided by the National Science Foundation (NSF) under Grant No. CMMI-0510530

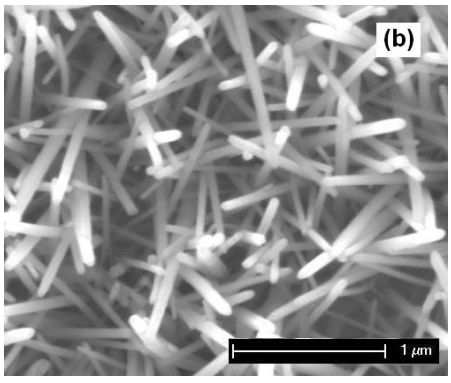
978-1-4244-1795-7/08/$25.00 ©2008 IEEE

II. ZnO NANOWIRE GROWTH AND CHARACTERIZATION

The ZnO nanowire arrays were grown on Au electrodes of quartz resonators according to a two-step hydrothermal method developed by Yang et al [9]. First, the quartz resonator was cleaned thoroughly by acetone/ethanol sonication and then coated with an ultrathin ZnO nanocrystal seed layer on the electrode by thermally decomposing zinc acetate at 350ºC. The hydrothermal reaction solution for the growth of ZnO nanowire array was prepared by mixing 25mM zinc nitrate hydrate, 25mM hexamethylenetetramine and 6mM polyethylenimine solution in a bottle with an autoclavable screw cap. The seeded resonator was immersed vertically in the solution, and the sealed bottle was heated to 90ºC for 6 hours inside a conventional laboratory oven. Subsequently, the sample was rinsed repeatedly with deionized water and annealed in a muffle furnace at 400ºC for 1 hour to remove any residual organics and stabilize nanostructures. The morphology and structure were characterized using scanning electron micscopy (SEM) and x-ray diffraction (XRD).

The XRD pattern in Fig. 1(a) shows that the grown ZnO nanowire arrays can be indexed to the wurtzite phase of ZnO with lattice constants of a=0.325 nm and c=0.520 nm. Only one sharp peak ZnO (002) is found at 34.32 degree position with strong relative intensity. The absence of peaks for other ZnO orientation indicates that ZnO nanowires have a preferred orientation along the c-axis. Figure 1(b) and (c) show typical scanning electron microscopy (SEM) images of ZnO nanowire arrays. The nanowires are found to be uniformly distributed and well aligned normal to the surface of the substrate. The nanowires have a diameter ranging between 50 and 100 nm, and a length of about 1.5 um.





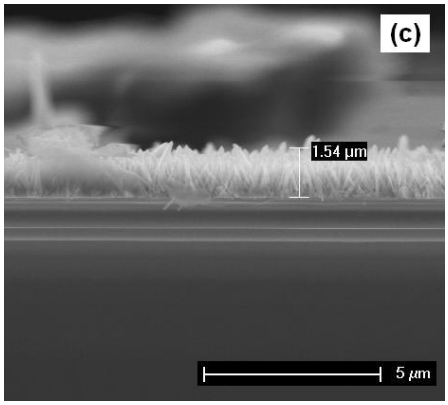


Fig. 1: Characterization of ZnO nanowire arrays (a) XRD, (b) & (c) SEM images: top and cross

III. EXPERIMENTAL SET-UP AND MEASUREMENT

The thickness shear mode (TSM) quartz resonator with ZnO nanowire arrays is schematically shown in Fig. 2. The sensor started from 10 MHz AT-cut polished quartz crystal with gold electrodes. D ZnO nanowires were grown on one side of the resonator using the hydrothermal method as was described in the previous section.

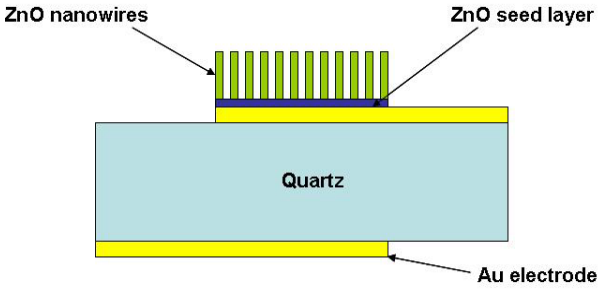


Fig. 2 Schematic of quartz TSM gas sensor coated with ZnO nanowire arrays

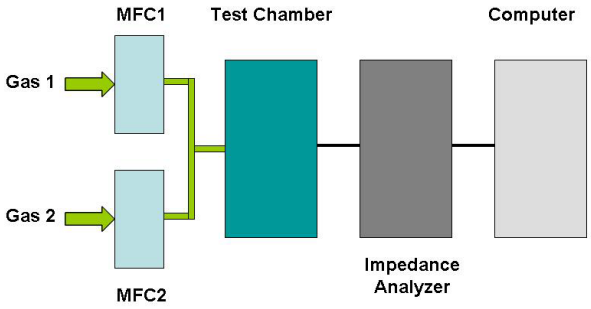


Fig. 3 Schematic of gas sensor test set-up

Fig. 3 shows the schematic diagram of test set-up. It consists of two mass flow meters, a test chamber with quartz TSM acoustic wave gas sensors, an impedance analyzer and a computer for data acquisition and analysis. First, nitrogen gas

with 300 sccm flow rate was delivered through the chamber until the quartz resonator's frequency change becomes less than 1 Hz/10mins. In this state, the quartz TSM resonator sensor reaches the equilibrium condition. Usually, this process takes up to about 6 hours. Then, NH_3/N_2 gas mixture is delivered to the test system for 10mins with the same flow rate as the previous step. Thereafter, 300 sccm N_2 was used again to reset the device. All the processes were undertaken at room temperature and under controlled humidity environment. The impedance spectrum of resonators is achieved through an impedance analyzer (4294A, Agilent), which is used to extract the fundamental resonance frequency through data fitting method. A computer with Hi-Speed GPIB Controller (GPIB-USB-HS, NI) and program (Labview7.0, NI) are used for automatic measurement and data saving.

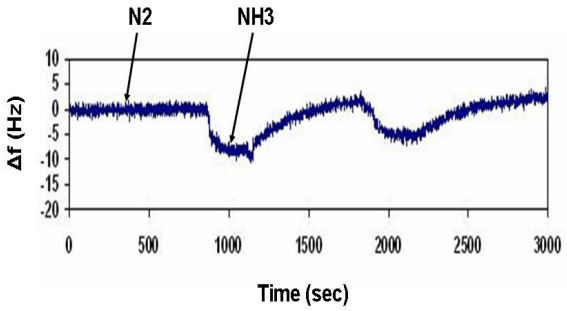


Fig. 4 Time-cycling response (ammonia from 0 to 330ppm)

Fig. 4 shows the time-cycling response of the quartz TSM acoustic wave gas sensor for NH_3 gas concentration change from 0 to 330 ppm). The result clearly indicates that the sensor can produce reproducible sensing response. The frequency decreased due to the adsorption of NH_3 to the surface of ZnO nanowires on the electrode. The response also show that the sensor device was sensitive to NH_3. It is also found that the desorption process of ammonia is much slower than adsorption process. The detection mechanism may be an adsorption-diffusion process. Firstly, the ammonia molecules are adsorbed on the sensitive layer at a short time due to the large surface area of ZnO nanowires. Then the ammonia molecules condense in the capillary-like pores between the nanowires and diffuse download. After a few minutes, the procedure will reach a steady state.

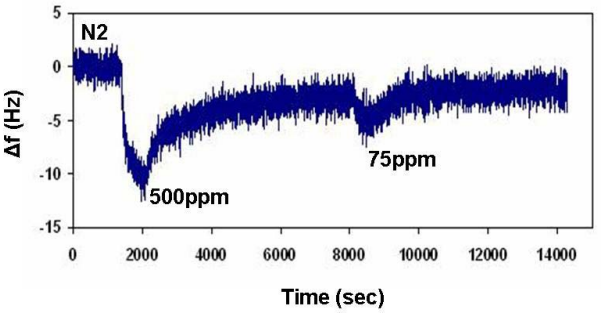


Fig. 5 Response to different ammonia concentration levels

The sensor response to NH_3 in nitrogen at different concentration levels was shown in Fig. 5. It can be seen that the frequency shifts were increased with higher concentration of NH_3 due to more ammonia molecules were adsorbed on the sensitive layer.

IV. CONCLUSIONS

In summary, ZnO nanowire arrays were grown on the quartz TSM acoustic wave resonator by a two-step hydrothermal method at temperature of 90°C. The device coated with ZnO nanowire arrays exhibited good gas sensing properties to NH_3. A good reproducibility has been achieved for this gas sensor, which could be attributed to the stabilized ZnO nanostructures under the test conditions. The response time of the sensor is fast due to the large surface area/volume ratio of ZnO nanowires. In addition, this work demonstrates that the combination of ZnO nanowire arrays with quartz TSM< acoustic wave resonators will provide a promising gas sensor platform for both higher sensitivity and enhanced response speed.

ACKNOWLEDGMENT

The authors would like to acknowledge the financial support from National Science Foundation (NSF) under Grant No.CMMI-0510530.

REFERENCES

[1] N. Koshizaki, T. Oyama, "Sensing characteristics of ZnO-based NO_x sensor", Sens. Actuators B 66, pp. 119-121, 2000.

[2] S.J. Ippolito, S. Kandasamy, K. Kalantar-zadeh, W. Wlodarski, K. Galatsis, G. Kiriakidis, N. Katsarakis and M. Suchea, "Highly sensitive layered ZnO/$LiNbO_3$ SAW device with InOx selective layer for NO_2 and H_2 gas sensing", Sens. Actuators B 111, pp. 207-212, 2005.

[3] G. S. T. Rao, and D. T. Rao, "Gas sensitivity of ZnO based thick film sensor to NH3 at room temperature", Sens. Actuators B 55, pp. 166-169, 1999.

[4] M. Huang, S. Mao, H. Feick, H. Yan, Y. Wu, H. Kind, E. Weber, R. Russo, and P. Yang, "Room-Temperature Ultraviolet Nanowire Nanolasers", Science 2001.292: p. 1897.

[5] Z.L. Wang, "Nanobelts, Nanowires, and Nanodiskettes of Semiconducting Oxides - From Materials to Nanodevices", Adv. Mater, 2003: p.432-436.

[6] H. Cheng, J. Cheng, Y. Zhang, and Q.-M.Wang, "Large-scale fabrication of ZnO micro-and nano-structures by microwave thermal evaporation deposition" J. of Crystal Growth, 2007.299: p.34-40.

[7] L. Greene, M. Law, D. Tan, M. Montano, J. Goldberger, G. Somorjai, and P. Yang, "General route to vertical ZnO nanowire arrays using textured ZnO seeds", NANO letters,

[8] Z.P. Sun, L. Liu, L. Zhang, and D. Z. Jia, "Rapid sythesis of ZnO nano-rods by one-step, room temperature, solid-state reaction and their gas-sensing properties", Nanotechnology , 2006.17: p. 2266-2270.

[9] Lori E. Greene, Matt Law, Dawud H. Tan, Max Montano, Josh Goldberger, Gabor Somorjai, and Peidong Yang, "General route to vertical ZnO nanowire arrays using textured ZnO seeds", NANO letters 5, pp. 1231-1236, 2005.