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Sensors and Actuators B: Chemical

Fabrication of 1D ZnO nanostructures on MEMS cantilever for VOC sensor application

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ABSTRACT

This study reports the fabrication method and sensing performance for novel 1D zinc oxide (ZnO) nanorods and nanotubes grown on nickel MEMS cantilevers. The fabrication of the nanostructures and the cantilevers are simple and low-cost using standard lithography, electrodeposition, and hydrothermal etching processes. 1D ZnO nanostructures increase the total sensitive area for biological and chemical sensor applications. We performed experiments with various VOCs with a real-time sensor system developed in our laboratory. While Ni microcantilevers produced no signal, ZnO nanostructure coated microcantilevers showed good sensitivity and repeatable changes. Furthermore, the nanotube coated microcantilevers showed more than 10 fold increase in sensitivity compared to the nanorod coated microcantilevers which can be explained to the fact that ZnO nanotubes have higher surface area and subsurface oxygen vacancies and these provide a larger effective surface area with higher surface-to-volume ratio as compared to ZnO nanorods. The tests are performed using dynamic mode of operation near resonant frequency using magnetic actuation and optical sensing. The phase stability and the limit of detection of ZnO nanotube coated microcantilevers exposed to diethylamine (DEA) were $0.02°$ and lower than 10 ppm, respectively. ZnO nanostructure coated microcantilevers have good potential for VOC sensor applications especially for amine groups.

1. Introduction

Micro and nano cantilevers have been investigated by many groups for chemical and biological sensors due to their extraordinary sensitivities in mass changes [1–7]. Microcantilevers can be utilized for gas sensor especially volatile organic compounds (VOC) sensing, by thin polymer film coating (poly-etherurethane, poly-epichlorohydrin, poly-isobutylene, poly-methylmethacrylate, ethyl cellulose, poly-dimethylsiloxane ect.) and/or by thin or porous inorganic film coating as sensitive materials [8–18]. Most of the published literature focuses on polymer based mass sensitive gas sensors whereas there is lack of investigation on inorganic based mass sensitive gas sensor.

There are important parameters for mass sensitive micro-nano mechanical sensors: minimum detectable mass (absolute mass sensitivity), low concentration detection, sensor response time, selectivity etc. In order to achieve smaller detectable mass changes lighter cantilevers with higher quality factors is required. The absolute mass sensitivity of nanomechanical cantilevers have been observed down to single molecule level [19–22]. But, single molecule detection requires high concentrations of the analytes, due to the small surface area of the device [21,23]. In order to obtain low concentration gas detection and fast response, microcantilevers were coated with nanostructured materials due to their high total surface area-to-volume ratio [24–27]. Ruan et al. [24] synthesized carbon nanotube (CNT) networks on a microcantilever and investigated explosive vapor sensing of the modified microcantilevers. They obtained that the rising surface to volume ratio with CNTs enables fast adsorption of the gases and improves limit of detection. Similarly, Xu et al. [25] fabricated multi-wall carbon nano-tube (MWCNT) modified microcantilever for trinitrotoluene (TNT) vapor detection. Hence, ZnO nanostructures

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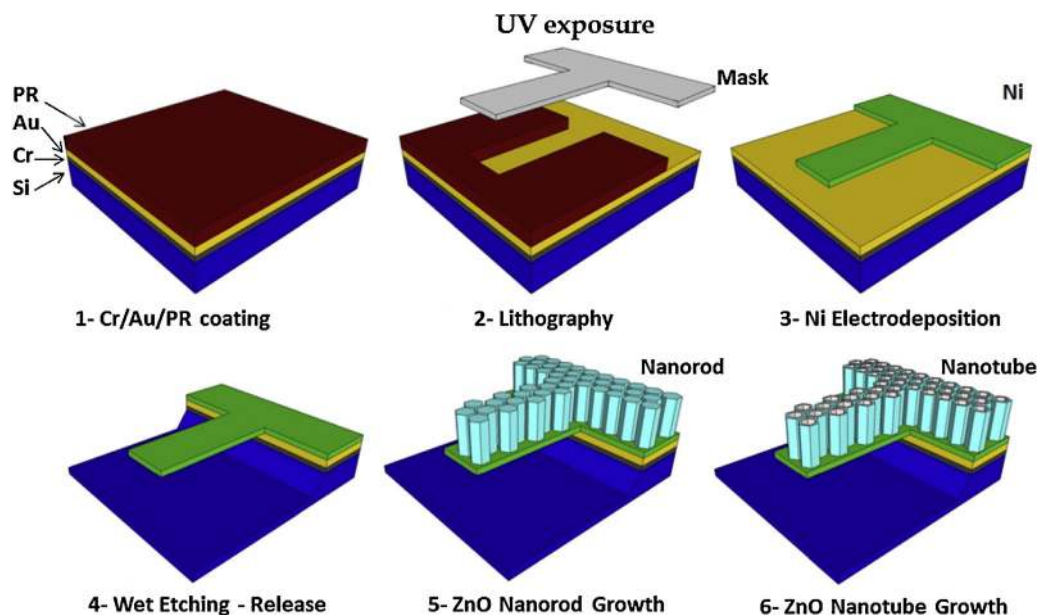E-mail address: nkilinc@gyte.edu.tr (N. Kilinc).

Fig. 1. A schematic diagram for fabrication steps of ZnO nanostructures coated Ni microcantilevers.

coated cantilever in this study fabricated to enhance total surface area-to-volume ratio and it is expected to obtain improvement in LOD and response time.

Here we present novel chemical sensor material using an inorganic molecule, ZnO, based nanorods and nanotubes grown on top of nickel (Ni) microcantilevers. The electrodeposition method is used for coating the ZnO nanorod on the cantilever. After the electrodeposition of ZnO nanorods, nanotubes are formed by hydrothermal etching of the nanorods. VOC sensing measurements are performed at room temperature in a custom cartridge by using a non-contact based sensor employing magnetic actuation and optical read out.

2. Experimental details

2.1. Microfabrication

The fabrication process of functionalized microcantilevers is shown in Fig. 1. Previously, the fabrication of Ni microcantilevers was reported in details and the usage of these cantilevers for biosensing and viscosity sensor applications was studied [28–32]. After standard cleaning of a 4″-diameter, ⟨1 0 0⟩ single crystalline silicon wafer, a 20 nm/100 nm Cr/Au layer is deposited on the wafer via RF sputtering (steps 1 in Fig. 1). Here Cr layer is used to provide adhesion of gold layer to Si, whereas Au layer serves as the seed layer for subsequent Ni electroplating. On top of Au surface, a positive photoresist (PR), AZ1514H, layer is coated (steps 1 in Fig. 1) and then the cantilever geometry is patterned with UV lithography (steps 2 in Fig. 1). After the electrodeposition of nickel layer the remaining PR is stripped via AZ100 remover (steps 3 in Fig. 1). Cantilevers are released through wet etching of Cr and Au by commercial etchants and finally wet etching of Si in 35% KOH solution at 60 °C (steps 4 in Fig. 1).

2.2. Fabrication of ZnO nanorods

ZnO nanorods are coated on released Ni cantilevers with electrodeposition method without seed layer. The cantilever is set as working electrode in a three electrode system, whereas Ag/AgCl and graphite is utilized as the reference electrode and the counter

electrode, respectively. The detailed ZnO nanorod fabrication on indium tin oxide (ITO) for photovoltaic applications was published before [33]. ZnO Nanorods' production is subject to a serious optimization of critical conditions. The optimized ZnO nanorod production procedure is frankly described in detail as follows; 7 mM KCl and 6 mM ZnCl$_2$ are employed in ultra-pure water. This time, the procedure is carried out in a thermo-stated bath, which is stabilized at 80 ± 1 °C. It should be noted that the temperature control is actually a critical parameter in nanorod growing. Also another optimized parameter is the 0.9 V cathodic voltage, with respect to the reference electrode. With these optimized parameters, we were able to grow ZnO nanorods both on naked cantilevers and on ZnO thin film coated cantilevers under the same circumstances (steps 5 in Fig. 1). Preliminarily results for fabrication of ZnO nanorod coated microcantilevers are published recently in Ref. [34].
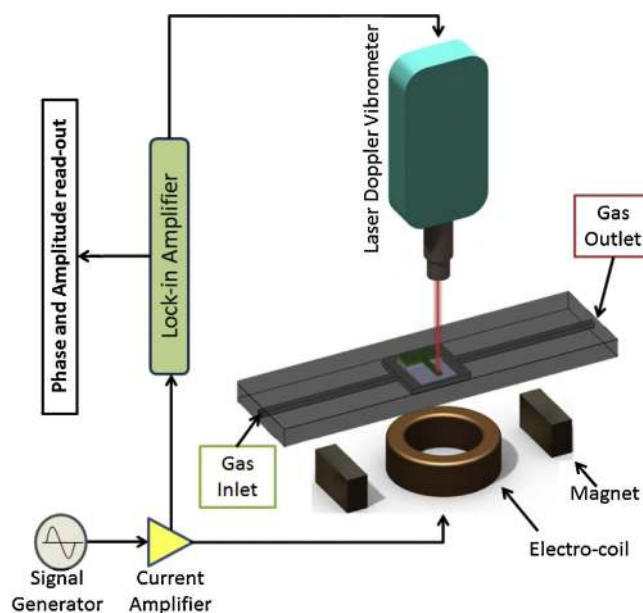

Fig. 2. Schematic view of measurement principle and setup. Actuation of Ni cantilevers is achieved with an external coil. LDV is utilized for optical read-out.
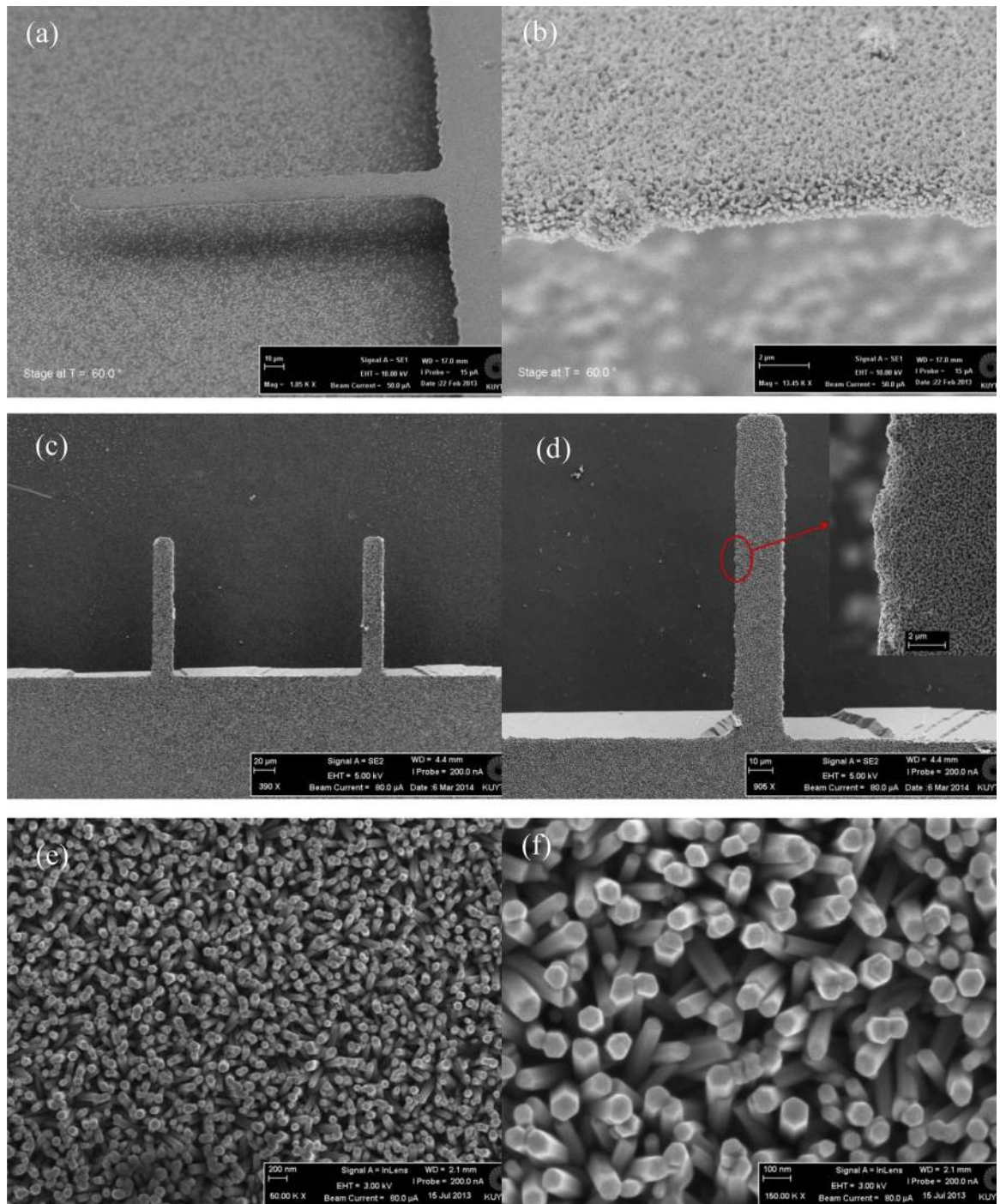
Fig. 3. SEM images of ZnO nanorod coated Ni microcantilever at increasing magnifications. (a and b) shows 60° tilted views and (c–f) shows top views.

2.3. Fabrication of ZnO nanotubes

ZnO nanotubes are fabricated by chemical etching of ZnO nanorods in diluted KOH solution (steps 6 in Fig. 1). Aqueous 0.125 M KOH solution is prepared in auto cleavable glass baker. Then vertically aligned ZnO nanorods on Ni cantilever are placed in this solution and aged for 1 h at 80 °C. After etching process, ZnO nanotubes are rinsed in deionized water and isopropyl alcohol, respectively. The surface morphology of ZnO nanorods and nanotubes coated Ni cantilevers is analyzed by scanning electron microscopy (ZEISS EVO LS15).

2.4. VOC sensing measurements

ZnO nanostructure coated Ni cantilevers are actuated magnetically with an external coil. The coil is driven with a high power broadband current amplifier with a fixed current. The actuation signal is a sinusoid generated by a signal generator and applied via coil driver electronics. The actuation frequency is typically within 3 dB of the resonant frequency of the cantilever. A Laser Doppler Vibrometer (LDV) is used for the optical read-out. The phase between the cantilevers mechanical motion and the actuation signal is monitored real-time. The phase between the input
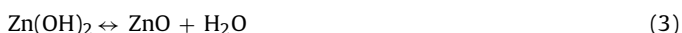
signal and the output signal is monitored with a Lock-in Amplifier (Stanford Research SR830). When there is a gas adsorption by the ZnO nanostructures a shift in the resonant frequency occurs. Due to this shift, the phase corresponding to the excitation frequency varies and the absorbed gas amount can be obtained by monitoring the phase variation. The phase variation ($\Delta\phi$) is defined as $\Delta\phi = \phi_{gas} - \phi_0$ where ϕ_{gas} and ϕ_0 are the phase angles between the actuation signal and the LDV output signal under analyte and carrier gases respectively. Fig. 2 shows a schematic view of the measurement setup. Temperature is a crucial parameter for mass sensitive bio-chemical sensors. In order to stable the temperature of the measurement cell, a controller unit with a 0.1 K precision is used during the experiments.

In order to dilute the VOCs in dry air, a certain amount of VOC was injected into the tedlar gas-sampling bag pre-filled with dry air, through a septum with a gas tight micro syringe. The diluted VOCs were manually exposed to ZnO nanostructure coated cantilever sensors with syringes by using laboratory syringe pump in order to control the flow rate. One syringe was contained dry air for cleaning process and the other was used for diluted VOCs exposure. The volumes of syringes were 50 ml and this limits the exposure and cleaning times during the measurements. The exposure and purging times were manually fixed depending on the nanostructure as about 100–150 s and 150–300 s respectively.

3. Results and discussion

3.1. Fabrication and structural characterization

ZnO nanorods were successfully fabricated on Ni microcantilevers by electrodeposition technique at 80 °C without seed layer coating. Fig. 3 shows the SEM images of ZnO nanorods coated Ni cantilever. It is clearly seen from the tilted-view SEM images in the figure that the ZnO nanorods are coated uniformly and covers the entire cantilever surface. The top-view SEM images of ZnO nanorods with different magnification shows that the ZnO nanorods are well aligned and hexagonal-shaped. The diameter and the length of the ZnO nanorods are approximately 100 nm and 1 micrometer respectively. ZnO nanorods are uniformly coated on whole Ni cantilevers and Ni anchor surfaces as seen in top SEM images (Fig. 3c–f). Electrochemical growth mechanism of the ZnO nanorods has two parts: solution chemistry process and electrochemistry process [35]. First, oxygen reduction occurs on or near the substrate surface, and then the hydroxide ions are formed. Zn^{2+} ions and OH^- ions generated ZnOH and transform ZnO on the surface when the temperature higher than 40 °C. The reactions during the electrodeposition of ZnO nanorods could be summarized as below [36]:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \tag{1}$$

$$Zn^{2+} + 2OH^- \leftrightarrow Zn(OH)_2 \tag{2}$$

$$Zn(OH)_2 \leftrightarrow ZnO + H_2O \tag{3}$$

Electrochemical deposition of ZnO nanorods on ITO substrate have been achieved for solar cell applications in a previous work [33]. In this study, electrochemical growth of ZnO nanorods on Ni microcantilevers substrate is achieved for the first time and VOC gas sensing properties of the functionalized Ni microcantilevers are investigated. Fig. 4 shows the current variation during the electrodeposition of ZnO nanorods. A sharp decrease is observed during the first minute due to the resistance increase during the nucleation of ZnO on Ni microcantilevers substrate. Afterwards, the current tarts to increases till minute 3 while the ZnO grains were formed as previously investigated by Guo et al. [35]. After 3 min, the current remained constant for a short time and started to decrease with
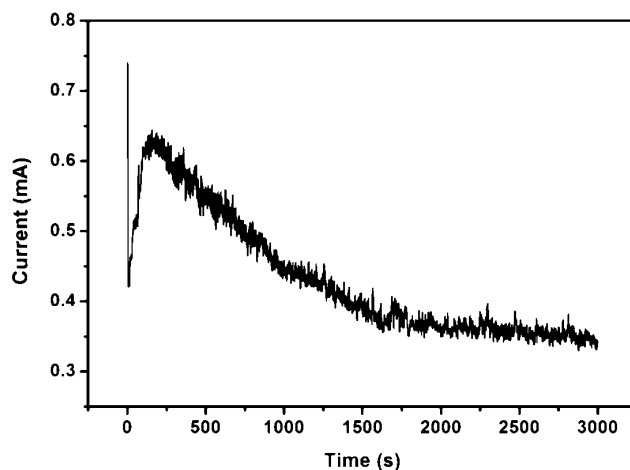

Fig. 4. The current versus time plot during the electrodeposition of ZnO nanorods on the Ni microcantilever sample.

time. The decrease in the current could be related to a loss of oxygen in the reaction medium. Formation of ZnO requires the OH^- ions and reduction of O_2 in the reaction medium causes reduction of OH^-.

ZnO nanotubes were synthesized on Ni microcantilevers by hydrothermally etching the ZnO nanorods at 80 °C for 1 h. Fig. 5 shows the top SEM images of a ZnO nanotubes coated Ni cantilever with various magnifications. ZnO nanotubes with the outer diameters of about 100 nm were observed and ZnO nanotubes were vertically aligned on the microcantilevers. When the ZnO nanorods were etched to obtain ZnO nanotubes, the top edge of the hexagonally shape were disturbed as seen in Fig. 5. If desired, the shape could be maintained better by adjusting the process parameters such as concentration, etching time, solution type, and temperature. The formation of ZnO nanotubes in aqueous KOH solution could be clarified with selective dissolution of the top and the side surfaces of ZnO rods [37–39]. The etching of ZnO nanorod is based on chemical reaction between ZnO and OH ions. After this chemical reaction, soluble complex product occurs and the chemical reaction is given below [40];

$$ZnO + 2OH^- + H_2O \rightarrow Zn(OH)_4^{2-} \tag{4}$$
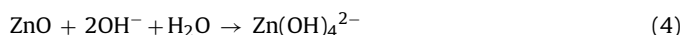
Generally, the thermodynamically stable crystal structure of ZnO was hexagonal wurtzite crystal system and also the crystal structures of fabricated ZnO nanorods were hexagonal wurtzite. In the form of hexagonal wurtzite crystal structures, ZnO has chemically active polar faces ($[0\,0\,1]$, $[0\,0\,\bar{1}]$) and chemically stable non-polar faces ($[0\,\bar{1}\,0]$, $[\bar{1}\,0\,0]$, $[1\,\bar{1}\,0]$) which are very important for growing nanorods or selective dissolution of nanorods. The polarity of faces is based on chemical bonding of Zn atoms. While growing rate of polar faces was faster than non-polar faces, the etching rate of polar faces was slower than other [39–41].

3.2. VOC sensing

The VOC sensing properties of ZnO nanostructures coated Ni microcantilevers are investigated by measuring the phase angle between the actuation signal and the optical readout signal when the functionalized microcantilevers are exposed to various VOC vapors at room temperature. Details of the magnetic actuation and sensing system developed in our laboratory can be found in Refs. [28,31].

Fig. 6 shows the change in the phase while the devices are exposed to varied concentration of diethylamine (DEA) in dry air. The exposure and purging times of ZnO nanorods coated
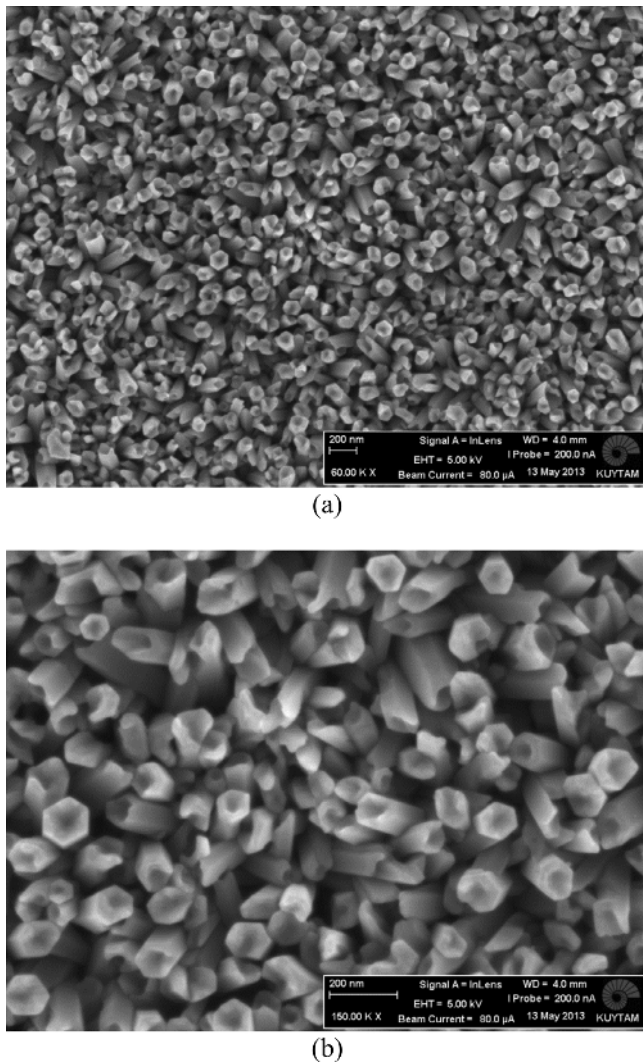
(a)

(b)

Fig. 5. The top SEM images of ZnO nanotube coated Ni microcantilever with different magnifications ((a) 60,000× and (b) 150,000×).

Fig. 6. Phase versus time graphs for microcantilever devices exposure to different DEA concentrations. DEA detection of ZnO nanorod coated – uncoated Ni microcantilever (a) and ZnO nanotube coated microcantilever (b).

microcantilever were manually kept constant as 100 s for exposure to VOCs and 150 s for cleaning with dry air. As seen in Fig. 6a, while the Ni microcantilever without the nanostructures showed nearly constant phase, ZnO nanorod coated Ni microcantilever showed a repeatable change corresponding to the changes in the gas concentration. After the base line phase reached a steady state value in 5 sccm (Standard Cubic Centimeters per Minute) dry air flow, the device was exposed to 5000 ppm DEA at the same flow rate and the phase of the device decreased sharply for a few seconds and then the decrease in the phase slows down. When DEA is desorbed and removed with dry air flow, the phase increased rapidly and then the increase in the phase slows down and then the phase almost recovered to the base line. Subsequent changes in the DEA concentrations also showed similar behavior and the changes with time in the subsequent experiments are shown in Fig. 6a. Response time is defined as the time required for the phase of the nanostructure coated microcantilever to reach 90% of the total change in the phase when exposed to VOC gas. Recovery time is defined as the time required for the phase of the nanostructure coated microcantilever to return 90% of the baseline when cleaned with dry air. The response and the recovery times were measured as approximately 80 s and 120 s for the nanorods coated microcantilever exposure to 5000 ppm DEA respectively.
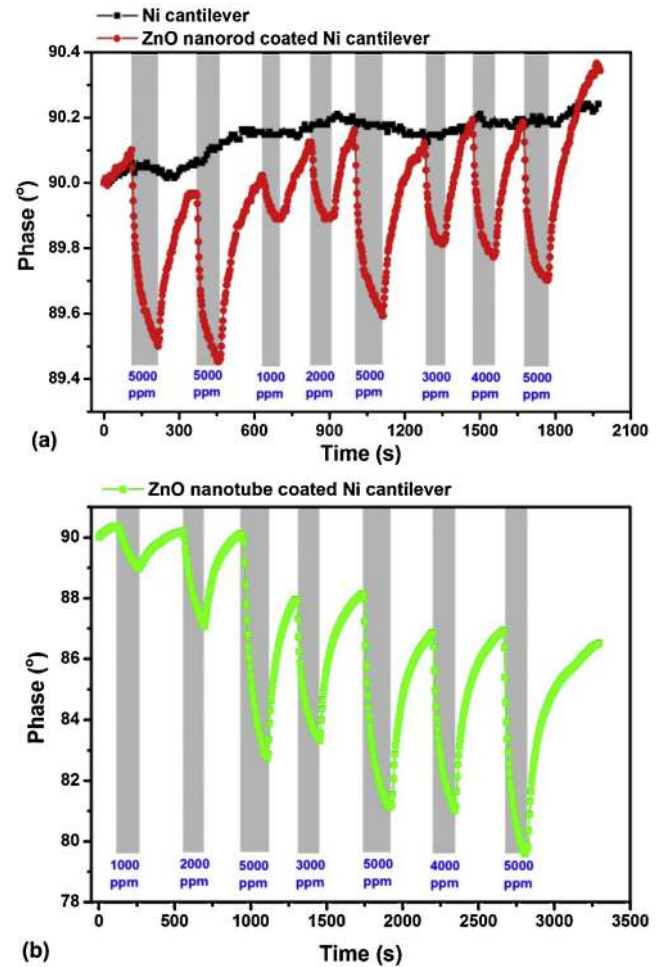
VOC gas testing cycles for ZnO nanotube coated microcantilever sensor were manually implemented with constant exposure time (~150 s) and constant purge time (~300 s). Similarly to the behavior of ZnO nanorods coated microcantilever sensor, the phase of ZnO nanotube coated microcantilever device decreased with exposing to DEA and increased with purging by dry air flow for all the measured concentration ranges as seen in Fig. 6b. After the base line phase reached a stable value in 5 sccm dry air flow, ZnO nanotube coated microcantilever device was exposed to 1000 ppm DEA at the same flow rate and the phase of the device decreased sharply and then the decrease in the phase slows down. When DEA removed with dry air flow, the phase increased rapidly and then the increase in the phase slows down. The phase of ZnO nanotube coated microcantilever device did not recovered in purging time of 300 s and the phase is shifted. The response time was measured as approximately 120 s for the nanotubes coated microcantilever exposure to 5000 ppm DEA. The phase variation of both ZnO nanotube and nanorods coated Ni microcantilevers devices increased with increasing concentration of DEA as given in Fig. 6. While ZnO nanotube and nanorod coated Ni microcantilevers device exposed to 5000 ppm DEA, the phase variations of these devices were measured as approximately 7.5° and 0.6°, respectively.

The phase variation of the ZnO nanostructure coated microcantilever depends on the number of VOC molecules adsorbed on the surface of the ZnO nanostructures. All fabricated microcantilevers sensors were the same with respect to the resonant frequency,
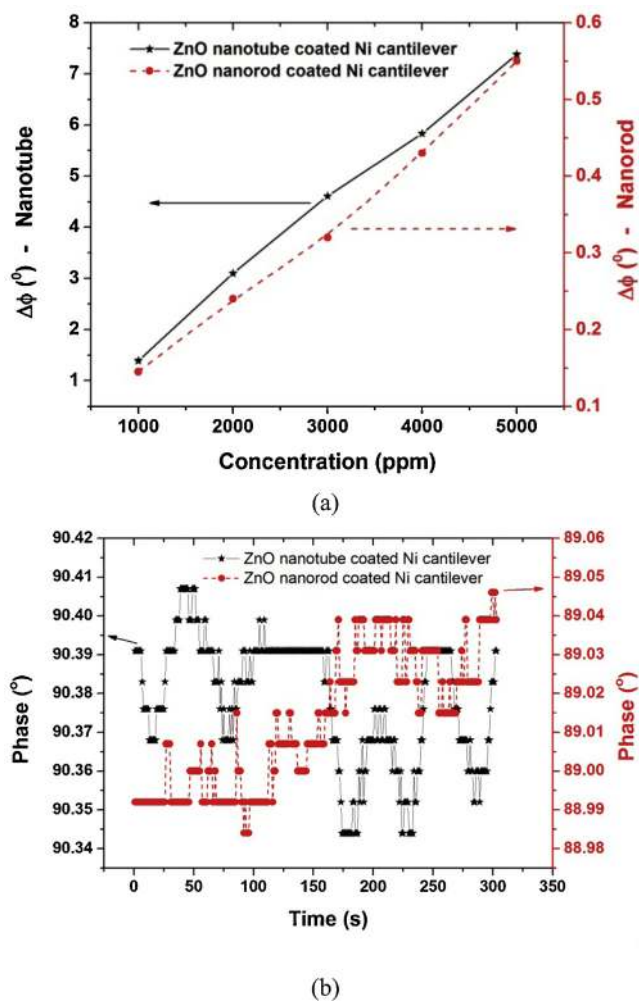
Fig. 7. (a) The concentration dependence phase change for ZnO nanotube and nanorod coated microcantilever sensor. (b) The phase versus time graph of ZnO nanorods and nanotubes coated microcantilevers in 5 sccm dry air flow for phase stability. The sensitivities ($\Delta\phi/C$) of the nanotube and the nanorod coated microcantilevers devices are about 1.2 m°/ppm and 0.11 m°/ppm respectively.

active area and quality factor. So, the change in mass due to the adsorption of VOC gas molecules on ZnO nanostructures primarily depends on the surface area of the ZnO nanostructures. ZnO nanotube has higher surface area and subsurface oxygen vacancies than that of ZnO nanorods. Thus more VOC molecules are adsorbed on the ZnO nanotubes with the increase in the surface area.

The sensing properties of the ZnO nanostructure coated microcantilevers sensor can be assessed by determining the sensitivity, which is defined as

$$\text{Sensitivity} = \frac{\Delta\phi}{C} \qquad (5)$$

where $\Delta\phi$ is the phase variation that defined as $\Delta\phi = \phi_{gas} - \phi_0$ and C is VOC concentration. The sensitivities of the nanotube and the nanorod coated microcantilevers devices are 1.2 m°/ppm and 0.11 m°/ppm respectively. The sensitivity of the nanotubes coated on the cantilever were shown to be more than 10 times better than that of the nanorods, which can be referred as a result of a larger effective surface area with higher surface-to-volume ratio of the nanotubes. Previously, for resistive and quartz crystal microbalance based mass sensitive gas sensors it is observed that the increase in the effective surface reaction sites causes high sensor response and fast responding kinetics (high sensitivity and low response time) [42–50]. On the other hand, there is literature available that report
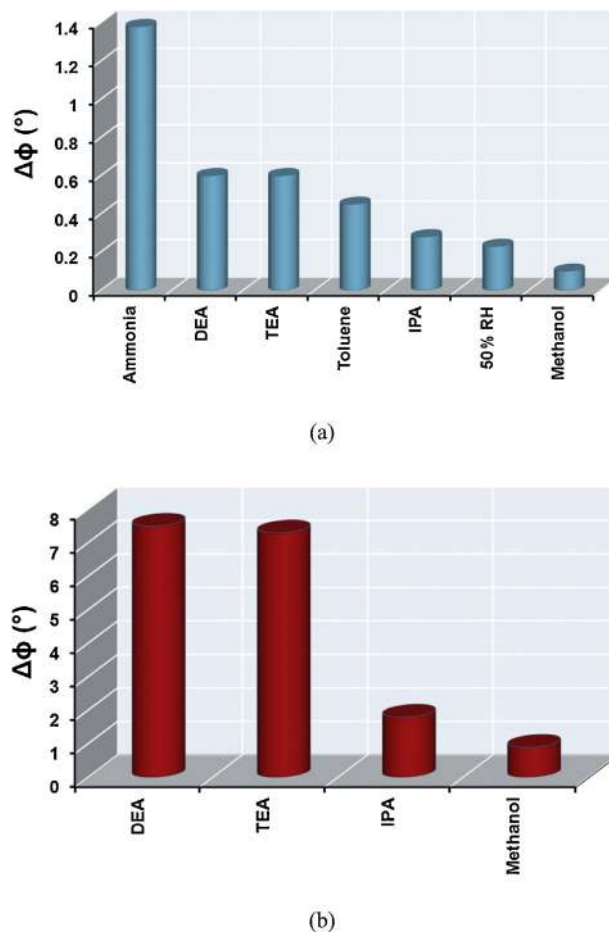

Fig. 8. A bar diagram graph for phase variation ($\Delta\phi$) of ZnO nanorods (a) and ZnO nanotubes (b) coated microcantilevers sensors exposure to different VOCs with 5000 ppm concentration and 50% RH.

lower LOD by using micromechanical biological sensors functionalized with nanostructured materials. Lu et al. [23] prepared Si nanowires array on top of a Si/SiO$_2$ bilayer thin membrane resonator by using reactive ion etching method to achieve detection of biomolecules at low concentrations and achieved the high sensitivity by the strongly enhanced total surface area-to-volume ratio of the resonator.

Fig. 7a shows the concentration dependence phase variation for ZnO nanorods and nanotubes coated microcantilever sensors. The phase variation ($\Delta\phi$) increases linearly with enhancing DEA concentration for both the nanorods and the nanotubes coated microcantilever sensors in the indicated concentration range. Fig. 7b shows the phase stability of ZnO nanorods and nanotubes coated microcantilevers for 5 min in 5 sccm dry air flow. The peak to peak phase variation in 5 min was about 0.05° for both ZnO nanorods and nanotubes coated microcantilevers. The phase stability of ZnO nanorods or nanotubes coated microcantilever was measured from Fig. 7b as 0.02° for 2 min, and the limit of detections (LOD) of the nanorod and the nanotube coated microcantilever sensors for DEA were calculated as 100 ppm and 10 ppm from the measurements in the concentration range of 1000–5000 ppm, respectively.

The selectivity of ZnO nanorod coated microcantilever was tested with ammonia, triethylamine (TEA), DEA, toluene, isopropyl alcohol (IPA), methanol and relative humidity. The phase changes of ZnO nanorods coated microcantilever to these analytes (5000 ppm) at room temperature are depicted in Fig. 8a. The higher sensor response is observed for amine groups and the highest phase

variation ($\Delta\phi$) is obtained for ammonia. ZnO nanorods coated microcantilever shows lower sensor response to IPA, methanol and relative humidity as seen in Fig. 8a. Besides, ZnO nanotubes coated microcantilevers device was tested for TEA, DEA, IPA and methanol. A bar diagram for the phase variation of the nanotubes coated microcantilevers device exposure to 5000 ppm VOC is seen in Fig. 8b and the higher sensor response is also observed for amine groups. The sensor response of the nanotubes coated microcantilevers was higher than that of the nanorods coated microcantilevers due to higher effective surface area of nanotubes. ZnO nanostructure coated microcantilevers shows higher sensor response to amine groups, but the nanostructure coated microcantilevers cannot distinguish one amine in an amine group mixture. The selectivity of metal oxide based gas sensors is a drawback due to cross response to many gas species and it is difficult to use only one metal oxide in a gas sensor. The most used method for selectivity was a sensor array contains several metal oxides which exhibit different responses to various gases. The detected gas can be determined by solving data that obtained from the sensor array with appropriate data-processing system such as artificial neural network.

4. Conclusions

We used ZnO nanorod or nanotube grown on microcantilever as a VOC gas sensor for the first time to our knowledge. ZnO nanostructures deposited on to Ni micromechanical cantilever by electrodeposition and hydrothermal methods due to obtain high effective surface area with higher surface-to-volume ratio. Gas sensing measurements were carried using a custom cartridge and a custom sensor system developed in-house that employs magnetic actuation and optical read out. The highest sensor response is observed for ammonia using the ZnO nanostructure coated microcantilevers. The sensitivities ($\Delta\phi/C$) of the nanotube and the nanorod coated microcantilevers for DEA were measured to be 1.2 m$^\circ$/ppm and 0.11 m$^\circ$/ppm, respectively. The higher sensitivity of nanotube coated microcantilevers could be explained with higher surface area and subsurface oxygen vacancies of the nanotubes and these provide a larger effective surface area. A 10 ppm sensitivity of DEA is predicted using the nanotube coated Ni cantilevers. The functionalized cantilever with ZnO nanostructures has practicable sizes and shapes and promises good potential for biological and chemical sensing applications.

Acknowledgements

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