Aldehyde Gas Detection using Nanostructured ZnO-based Gas Sensor fabricated via Horizontal Vapor Phase Growth Technique

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Abstract. Detection of aldehydes such as pentanal, hexanal, octanal, and nonanal are studied with the use of nanostructured zinc oxide (ZnO) as sensing element. ZnO nanowires synthesized at optimized growth parameters using horizontal vapor phase growth (HVPG) technique was used due to its unique properties in gas sensing applications. Scanning Electron Microscope (SEM) and Energy Dispersive X-Ray (EDX) were used to verify the growth of ZnO nanowire structures. Further characterization using Source Meter was used to measure its resistance and resistivity based on the I-V graph. The sensor substrate wire set-up is connected to the Source Meter for resistance measurements as exposed to the different gas concentration of aldehydes. Gas sensing measurements were done at the static headspace gas concentration of the identified aldehydes. The sensor response of nanostructured ZnO-based gas sensor towards different gas concentrations ranges from 5.84\% to 38.08\%. Response time varies but it was observed that octanal gas has the longest response while pentanal has the fastest response.

1. Introduction

Aldehydes are compound commonly found in the atmosphere as air pollutants emitted by factories and industrial facilities. Aldehydes undergo a variety of reactions that lead to many different products such as organic aldehydes that are readily oxidized to give carboxylic acids. When exposed to air, aldehydes can form peroxy acids and finally carboxylic acids [1]. Aside from its presence in the atmosphere, aldehydes are also found in human body and exhaled in breath as indicators of underlying diseases [2]. Exhaled breath is largely composed of oxygen, nitrogen and carbon dioxide and contains very low concentration of various volatile organic compounds (VOC). Breath contains a few of exogenous VOC which is a result of external contamination from cigarette smoke, pollution and through ingested food or drinks. However, many of the VOC detected in exhaled breath are endogenous substances that originate from the physiological processes that occur in the body such as pentanal, hexanal, octanal, and nonanal [3,4,5].

Equipment and tools most commonly used in measuring the component of exhaled breath are gas chromatography (GC), laser-absorption spectroscopy and chemical gas sensors. GC coupled with various detection methods such as mass spectrometry (MS), flame ionization detector (FID) and ion mobility spectrometry (IMS) were used in various researches in the identification and quantification of breath components [6,7,8]. In comparison, other devices such as chemical gas sensors offer several advantages such as portability, low power consumption and low-cost production. The most common types of chemical gas sensor that are used in gas sensing are polymers, quartz microbalance sensor, acoustic wave device and metal oxide semiconductors. Most of these relies on the adsorption of gases into the sensing device which causes change in mass, vibration, conductivity or color thus a change in its output [9,10,11]. Moreover,
chemical gas sensor which employ metal oxide semiconductors has had considerable impact to researchers for its wide range of sensing properties which can be synthesize using variety of techniques [12]. Among the various nanostructured metal oxide that are used in gas sensing, ZnO is widely used in gas sensing application for its excellent sensing properties [13].

Using horizontal vapor phase growth technique (HVPG), ZnO nanowires were synthesized and fabricated as sensing element to detect the identified aldehydes: pentanal, hexanal, octanal, and nonanal. Characterization method was used to identify the surface morphology of the grown nanostructured ZnO using Scanning Electron Microscopy (SEM) and to verify its elemental composition using Energy Dispersive X-Ray (EDX). Furthermore, electrical characterization using Keithley Source Meter was used to investigate the sensor's properties such as response, sensitivity, response time and recovery time through IV-curve analysis and resistance change as gaseous chemicals from the prepared VOC interact with the sensing element.

2. Methodology

ZnO nanomaterials was synthesized using HVPG technique at optimized growth parameters based on previous studies yielding dense nanowire formations at a particular zone of a quartz tube [14, 15, 16]. After the deposition process, the quartz tube is allowed to cool down at room temperature followed by mechanically cracking the walls of the tube to retrieve sections of deposited ZnO nanomaterial. The surface morphology of ZnO samples is viewed using SEM. With EDX, the captured images of ZnO nanomaterial are analyzed to determine its elemental composition. Resistance and resistivity of the substrate is measured using Keithley 2450 Source Meter as reference for gas sensing application. Resistance can be computed following Ohm’s Law R=V/I considering that the I-V graph of ZnO nanomaterial shows an ohmic resistor. Resistivity of the material is computed following the Van der Pauw technique.

Pentanal (97%), hexanal (98%), octanal (99%), nonanal (98%) were purchased from Sigma-Aldrich. Amber tinted bottles of different volume capacities were used as container of the aldehyde solution to attain the desired headspace gas concentration and protect the solution from visible light radiation to prevent some form of chemical reaction due to the high volatility nature of the aldehyde. Different concentration levels of aldehyde headspace gas are attained using phase ratio of the volume of the bottle vs. volume of the aldehyde solution. For very low concentration, larger vials were used as container for small volume of aldehyde solution such that a 200ml bottle with 0.01ml of aldehyde solution produced 0.06ppm or 60ppb of headspace gas concentration. This is to reach the cut-off value for cancer recognition of 0.02ppm-1.2ppm as reported by Fuchs et al. (2010). The prepared aldehyde solution is stored for at least 1 day to allow headspace gas to saturate.

The sensor substrate with gold sputtered electrodes is connected to copper wires using silver conducting paste as contacts. Using bottle caps as the holder for the sensor substrate ensures that headspace gas does not alter drastically during the gas sensing thus retaining its concentration. The assembled gas sensor with wire setup is connected to a Keithley 2450 Source Meter for measurement of resistance during the exposure of the sensor to target gas analytes.
Gas sensing application begins by exposing the sensor to air to measure its resistance, which acts as the baseline resistance of the sensor. Following the exposure of the sensor to the target gas to measure the resistance as exposed to the gas analytes. After exposure to the target gas, a purging by means of manual heater was used to remove adsorbed gas species and obtain the initial resistance reading. Assisted heating of the sensor after exposure to the target gas allows the gas species that adsorbed on the surface of the sensor to detach at a faster rate and for the sensor to return to its baseline resistance. The gas sensing for each gas is repeated for three trials. The process is also repeated as exposed to each aldehyde solution with varied concentrations.

### 3. Results and Discussion

Nanowire formations were found in Zone 2 section of the quartz tube measuring an average diameter of 81.12nm scattered throughout the substrate. Nanowires overlapping each other appear to be thick white areas. The atomic percentage as measured from the weight percentage is 59.27% oxygen, 37.71% zinc and 3.02% gold as shown in Fig. 2. Approximately, the ratio of zinc to oxygen is 1:2. The nanowire structures and cloud-like particles were analyzed to be zinc oxide.

**Figure 2.** SEM-EDX of ZnO substrate located in Zone 2
In Fig.3, based on the current-voltage graph, ZnO substrate has a computed resistance ($R_{AB,CD}$) of $7.0 \times 10^4 \Omega$ and resistivity measurement of $5.1 \times 10^{-3} \Omega \text{m}$. The setup was done using linear sweep across a voltage from $-3\text{V}$ to $3\text{V}$ resulting to current measurement of $-36.0105 \text{nA}$ to $43.7475 \text{nA}$. It can be observed that the slope follows a straight line having a linear relationship between the measured current and the applied voltage. This indicates a connection of ohmic resistor.

Figure 4. Dynamic sensor response (resistance vs. time plot) of ZnO towards different gas concentration of a)pentanal b)hexanal c)octanal d)nonanal at room temperature.
Table 1. Summary of sensor response, response and recovery time

|        |          |          |          |        |        |
|--------|----------|----------|----------|--------|--------|
|        | Rs (kΩ)  | Rs (kΩ)  | R%       | Rs (sec) | Rs (sec) |
| 4ppm   | 81.91    | 101.86   | 24.35    | 23.07   | 14     |
| 2ppm   | 80.58    | 98.54    | 22.3     | 40.27   | 17.33  |
| 0.6ppm | 81.33    | 95.85    | 17.86    | 31.87   | 21.33  |
| 4ppm   | 83.03    | 114.65   | 38.08    | 148.67  | 25.6   |
| 2ppm   | 82.34    | 112.46   | 36.59    | 186.27  | 31.2   |
| 0.6ppm | 81.48    | 109.78   | 34.74    | 191.2   | 29.87  |
| 4ppm   | 82.92    | 108.99   | 31.44    | 301.2   | 107.33 |
| 2ppm   | 83.05    | 102.98   | 24       | 303.73  | 142.4  |
| 0.6ppm | 84.15    | 99.26    | 17.95    | 248.8   | 164.27 |
| 4ppm   | 83.19    | 89.57    | 7.66     | 94.53   | 48.27  |
| 2ppm   | 82.61    | 88.45    | 7.07     | 118.8   | 38.8   |
| 0.6ppm | 82.48    | 87.3     | 5.84     | 105.87  | 48.93  |

Generally, it can be observed that the sensor response of the ZnO for each of the target aldehyde gases decreases as the concentration also decreases. It can be observed that the resistance in air averages at almost 82kΩ with uniform distribution. The resistance in gas also diminishes as the concentration is decreased from 101.86kΩ to 95.85kΩ for pentanal, 114.65 kΩ to 109.78 kΩ for hexanal, 108.99 kΩ to 99.26 kΩ for octanal and 89.57 kΩ to 87.3 kΩ for nonanal. The response and recovery time seems to be longest in octanal gas concentrations as compared to the other aldehyde gas while pentanal gas concentrations has the fastest response and recovery time.

4. Conclusion

ZnO nanowires have been successfully synthesized using HVPG technique and used as sensing substrate to detect specific aldehyde gases. The sensing parameters such as sensor response, response time and recovery time have been characterized. ZnO nanowire-based gas sensor showed high response towards hexanal and octanal for as low as 0.6ppm headspace gas concentration. Moreover, the response time is fastest with regards to pentanal gas having a response time of 23.07 seconds while the slowest response time recorded is 303.73 seconds as a response to octanal gas. This may due to the strong smell corresponding to high volatility of pentanal gas as compare to other gases. Furthermore, the recovery time of the sensor is 14.00 seconds as the fastest with regards to pentanal gas and 164.27 seconds with regards to octanal gas. The long recovery time of the sensor with regards to octanal gas may be due to the higher resistance value of the sensor as exposed to octanal gas.

Further studies on the sensor response pattern of each aldehyde gas to fabricate sensor device which can recognize the response curve of each type of gas that is exposed to the sensor and assessment of the limit of detection of ZnO nanowire sensor towards aldehyde gas are excellent progress to enhance its sensing capabilities.
5. References

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