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Fabrication of Metal Oxide Sensor for Hydrogen Sulfide Sensing Applications

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Abstract: Metal oxide nanomaterials were synthesized via Horizontal Vapor Phase Crystal Growth deposition. Fabricated crystals were characterized using SEM and EDX spectroscopy and were installed in a circuit complete with mini gas chamber where the target gas at varying quantity was allowed to interact with the sensing surface. The sensitivity of the fabricated prototype was tested to hydrogen sulfide (H_2S) gas using voltage analysis. Voltage measurements were made to study the response of the metal oxide crystal to the molecules of Hydrogen Sulfide gas. Results denote that the synthesized Tin Oxide nanomaterial sensor substrate is more sensitive and responsive to H_2S gas compared to the Zinc Oxide sensor substrate.

Key Words: metal oxide; nanosensors; hydrogen sulfide; horizontal vapor phase crystal growth deposition; fabricated crystals.

1. INTRODUCTION

1.1. *Hydrogen Sulfide*

Hydrogen Sulfide (H_2S) is a colorless gas at room temperature which emits a very foul odor similar to a rotten egg. It is usually present in the environment as a contaminant; It naturally occurs in petroleum, bodies of stagnant water, waste water treatment and in volcanic gases. It can be found in the body when organic matter containing sulfur breaks down in the digestive tract. H_2S gas can also be made by mixing a strong cleaning agent, usually a toilet bowl cleaner, and a sulfur bath soap.*(Reedy, SJ., July 2011)*

This gas has a wide variety of applications specifically in medical and food industry. To name some, Hydrogen Sulfide acts as a biomarker to different lung diseases (*Huber, F., et. al, 2017*); it is also an indicator of the freshness of poultry products and quality of wine in the market. *(J. Koskela, et. al, 2015; T. Rajamäki, et. al, 2016)* However, the detection process is crucial since this gas is toxic and emits a foul odor which eventually can damage the ability of a person to smell. Studies have shown that a normal person should only have an exposure of 5 parts per million (5 ppm) within 10 hours. *(Berahman, M., 2015)* Exceeding the given concentration would lead to olfactory fatigue in which a person can permanently lose the ability to smell. A study by J. Pla- Tolós et. al (2016) shows detailed presentation of the exposure limits to Hydrogen sulfide as suggested by different organizations. Consequently, the problem leads to the development of electronic nose nanosensors.

1.2. Metal-oxide Nanosensors

Nanostructured metal oxides offer a great potential for energy and environmental applications including gas sensing due to large surface area, low cost, and low toxicity.(*Das, S., July 2014)* Its gas sensing capabilities is reported due to its sensitive conductivity changes upon gas reaction and adsorption, nonetheless much innovative science needs discovery, and new fabrication techniques must be

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explored in this type of material by exploiting strategies in the field of material science and nanotechnology. The use of chemical and bio-functionalized gas sensors is important in many aspects such as personal safety and security, detection and diagnosis of pollutants and poisons, health, semi-conductor processing, agriculture, and automotive and aerospace industries. *(Bancolo, F, 2011; Cadena, G., 2007)*

Many studies have reported of gases such as volatile organic compounds (VOCS) that can be used as biomarkers in various sensor applications. Certain types of gases that pose health risk (i.e. Hydrogen Sulfide) must be detected to avoid injury or livestock kill. In all cases, detection of these gases poses significance to both the individual and the community.

However, much sensory analysis is very expensive and not always practical. Developing sensing materials that is fast and reliable is needed in many applications. The devices that need to be developed must not only be robust, portable, and compact but also have high sensitivity, selectivity and reversibility in ambient temperature conditions with low manufacturing cost. With the characteristics mentioned above, nanostructured metal oxide gas sensor substrate was applied in real time gas detection.

This research study aimed to develop a metal oxide nanomaterial gas sensor for a non-contact rapid detection. The response of the metal oxide sensors to hydrogen sulfide was determined through impedance and voltage measurements.

2. METHODOLOGY

2.1. Preparation of Raw Materials

A. Metal-oxide sensors

Fifty milligrams (50 mg) of the bulk powder of 99% purity and 5microns grain size obtained from MERCK was weighed and placed into clean closed- end quartz tubes. The said reaction tube was then evacuated using a thermionic high vacuum system decreasing the pressure to about 10^{-6} torr. The tube was then be fully sealed by annealing to a length of 15 cm. With the bulk material in the sealed tube, exposure of the researchers to the metal oxide powders during curing is prevented. The horizontal vapor phase crystal growth technique (HVPG) was used in the fabrication of the SnO_2 and ZnO nanomaterials

B. Hydrogen Sulfide Gas

The gas is prepared using 22 g of Zinc sulfide (ZnS) powder and 500 mL of Hydrochloric acid (HCl) with a concentration of 6M. The hydrochloric acid is then placed in an Erlenmeyer flask covered with a rubber cork with a rubber tubing connected to a large container of water as shown in Figure 1. Zinc sulfide powder is then mixed to the acid and was immediately contained. Mixing the powder and the acid would create the reaction which eventually produces the hydrogen sulfide gas.

$$ZnS_{(s)} + 2\,HCl_{(aq)} \rightarrow H_2S_{(g)} + ZnCl_{2\,(aq)}$$

Collection of the gas was done using a 5-mL syringe.

Figure 1. Set-up for the fabrication of Hydrogen Sulfide (H_2S) gas

2.2. Fabrication of Nanomaterial

The sealed quartz tubes were placed in a Thermolyne horizontal tube furnace and were cured. The furnace was programmed at a ramp time of 40 minutes, at a growth temperature of 1200 °C, and at 8 hours growth time. To enhance the morphology of the synthesized crystals external magnetic field was applied at the end of the quartz tube as shown in Figure 2. This follows the horizontal vapor phase crystal growth technique (HVPG).

To create a temperature gradient that is necessary for the growth of the nanomaterials, the tube was inserted halfway through the furnace and was monitored by a type-K thermocouple. After the set time for curing, the set up was allowed to cool down to room temperature.

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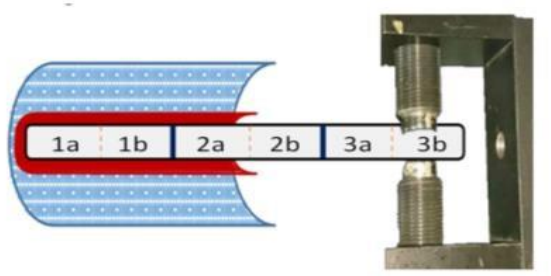


Figure 2. A diagram of quartz tube inserted halfway through a horizontal tube furnace.

2.3. Characterization

The deposits on quartz tube fragments were characterized using the Scanning Electron Microscope (SEM) and Energy Dispersive X-Ray Spectroscopy (EDX). SEM was used to determine the morphology of the nanomaterials present on the fragments of the quartz tube and on the substrate as shown in Figure 3.1. a and 3b. The elemental composition was determined using EDX as shown in Figure 3.2. a and b.

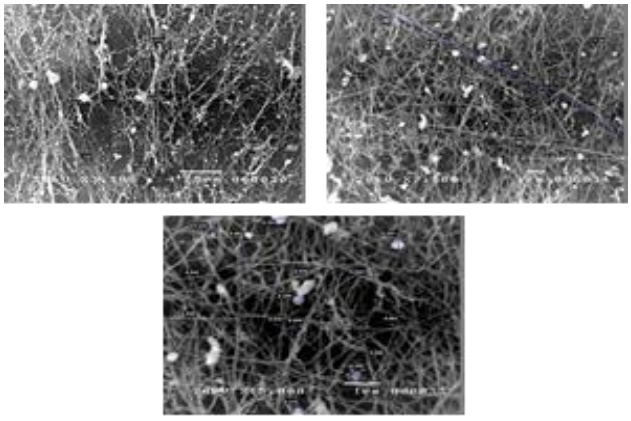


Figure 3.1.a. SEM images of fabricated Tin Oxide (SnO_2) nanomaterial.

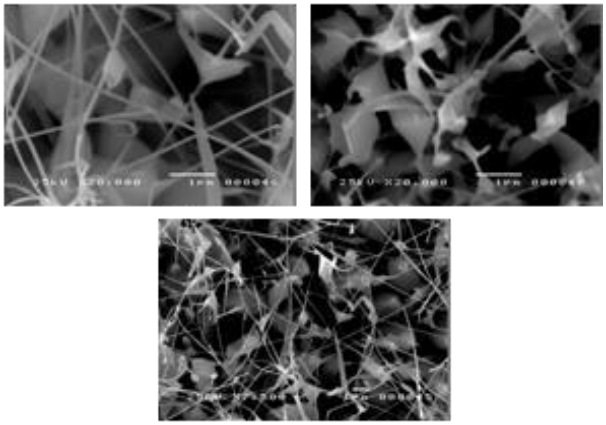
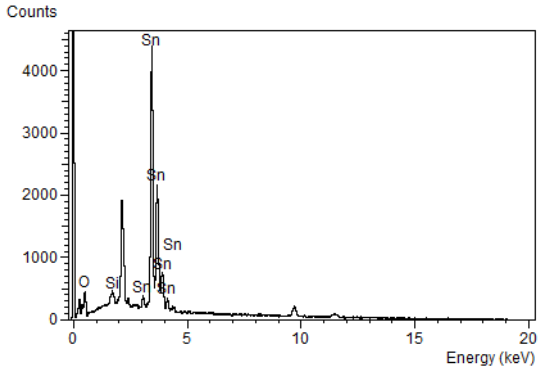


Figure 3.1.b. SEM images of fabricated Zinc Oxide (ZnO) nanomaterial



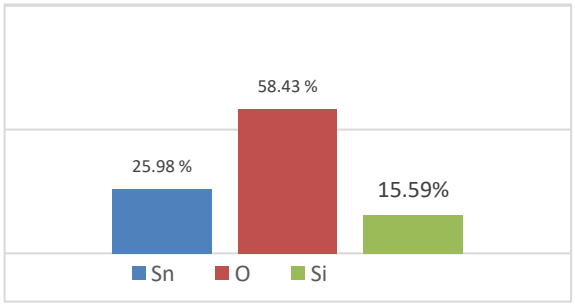


Figure 3.2.a. Elemental Composition of Tin Oxide (SnO_2) nanomaterial.

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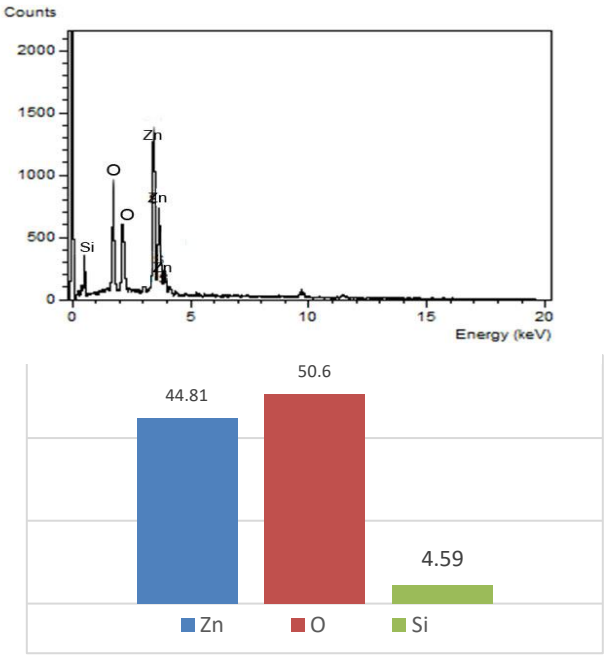

Figure 3.2.b. Elemental Composition of Zinc Oxide (ZnO) nanomaterial.

2.4. *Fabrication of Gas Sensing Substrate*

The section with the highest density of nanowires and rods or 1D nanomaterial was used in the fabrication of a gas sensing substrate. The collected substrates from the set-up were sputtered with gold on both sides to serve as the electrodes with 2mm width line in the middle of the substrate exposed (Fig. 4). The nanomaterials which were not sputtered with gold will be the one to detect the target gas

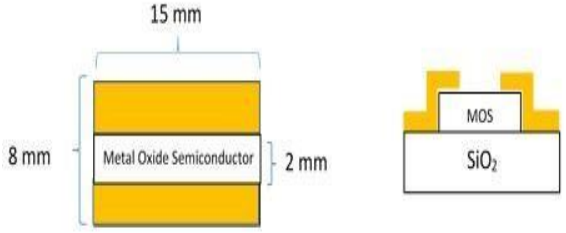

Figure 4. Sensor substrate with gold sputtered electrodes.

The circuit for the sensor was set up as shown in Figure 5.

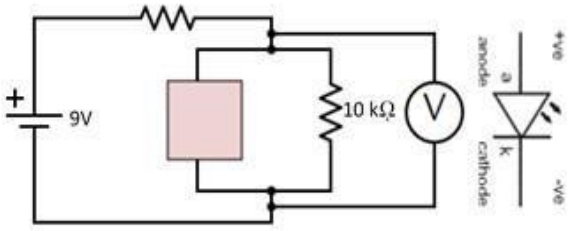

Figure 5. Circuit diagram of the gas sensing setup

An input voltage of 9V, supplied by a dry cell, was delivered to the circuit as shown in figure 3. A 10 kΩ variable resistor was used to calibrate the sensitivity of the sensor. The voltmeter on the other hand was connected to a Passport Interfaced Pasco Scientific Voltage Sensor and Data Studio. The latter was used for data-acquisition in measuring the voltage response of the sensor. The pattern in the change in the resistance of the material, which is converted to a change in voltage measurement and read via a Pasco Scientific Voltage sensor.

The circuit was housed in a 40 x 80 x 100 mm enclosure (refer to Figure 6) with a plastic chamber fasted above. The chamber housed the metal oxide nanomaterial sensor substrate so as to protect the substrate from being exposed to contaminants. This is where the analytes interact with the sensing layer. The top portion of the chamber will be connected to a plastic tube, where sample gas was introduced.

Figure 6: Sample of the fabricated prototype metal-oxide nanosensors.

The SPME fiber (50/30) µm DVB/ Carboxen/ PDMS coating) was used to absorb the gas introduced to the sensor substrate. After extraction, the SPME fiber was inserted directly at the injection port of the Gas chromatography. Peak identification was determined by comparison of the sample mass

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spectra with spectra in NIST/EPA/NIH Mass Spectral Database (Nat. Institute of Standards and tech.)

3. RESULTS AND DISCUSSION

The SEM micrographs shown in figure 3.1a showed tin oxide nanowire structures were grown while in 3.1b nanowire and nanoblade structures were grown. The synthesis of the said nanomaterials followed the HVPG technique, a thermal deposition process. Similar to the work of Das and Jayaraman (2014), the precipitation, nucleation and growth of nanostructures ensued the Vapor-Liquid-Solid (VLS) growth where a greater number and variety of deposited structures can be found at the colder regions of the tube. This suggests that temperature gradient provided the driving force in the growth of nanostructures. The formation of the nanowires is believed to be due to the presence of the external magnetic field, along with the presence of temperature gradient. The magnetic field exposure might have retarded the nucleation rate and accelerated the crystal growth favouring nanowire formation (Bastami and Entezari, 2012). The particles interconnect with each other eventually forming the nanowire like formation (Faraji et al, 2010).

The growth mechanism about the morphology enhancement of the nanowires under magnetic field is suspected to be due to a thermoelectric magneto-hydrodynamics as the flux of vaporized material interacts with the magnetic lines of force together with the presence of a temperature gradient. However, this needs further investigation and testing. It can be noted that other factors, such as the epitaxial orientation defined by the substrate, might have influenced the growth direction. EDX Spectroscopy confirms the presence of tin and oxygen for the tin oxide samples, and zinc and oxygen for the zinc oxide samples (fig. 3.2).

The said structures are favorable for the fabrication of a gas sensor since the materials have a greater surface-to-volume ratio. Majority of the wires have a diameter below 100 nm which is similar to the description of one dimentional (1D) nanostructures (Kolmakov & Moskovits, 2004). This implies that a significant fraction of the atoms (or molecules) in such systems are surface atoms that can participate in surface reactions resulting to improved selectivity and sensitivity (Kolmakov & Moskovits, 2004).

The sensitivity of the metal oxide sensors was measured using Voltage Analysis. The sudden change of voltage reading when a chemically reactive gas is introduced to a sensor would break the stable potential barrier, thus, allowing an increase or decrease in the resistance of the material. The resistances of the metal-oxide crystals were measured with the LoadStar Power Supply with a steady current as shown in the table 1. It can be noted that tin oxide was found to have a higher initial voltage reading, correspondingly a higher initial resistance, than the zinc oxide sensor substrate. Although literature suggests that most ZnO materials have a higher resistivity, 5×10^{4}–3×10^{5} Ω-cm for undoped bulk ZnO (Polyakov et. al, 2005), as compared to SnO_2, 1-100 Ω cm for bulk SnO_2 (Ji et. al, 2013). This result could be in part due to the gold sputtering performed to create the electrodes of the sensor substrate.

Table1: Initial Resistance-Voltage measurements of Metal-oxide sensors

Metal-Oxide Sensor	Initial Current	Initial Voltage Reading	Initial Resistance
SnO_2	0.5 A	5.79 V	11.6 Ω
ZnO	0.5 A	2.14 V	4.3 Ω

The fabricated prototype is then connected to a Sparkvue Reader and data logger. Voltage reading for all setups was stabilized after 2 mins (120 s). Hydrogen Sulfide gas was then introduced into the rubber tube of the sensor and the change in voltage measurement was recorded as shown in Figures 7 and 8.

The SnO_2 sensor substrate was found to register a higher increase in voltage measurement, 0.19 V, upon introduction of a 5cc H_2S gas into the sensor substrate. The ZnO sensor substrate recorded a 0.13 V voltage increase for the same volume. Although both metal oxide sensor substrates registered a response, it can be noted however that subsequent samples (II and III) of the latter showed instability and inconsistency as to the baseline voltage and response voltage measurement, respectively, as shown in Figure 9. Although this is the case, more investigation must be carried out to verify this observation. This is not observed in all of the SnO_2 sensor substrates as the second and the third samples showed a stable baseline and consistent increase in the voltage measurement upon exposure to the analyte gas.

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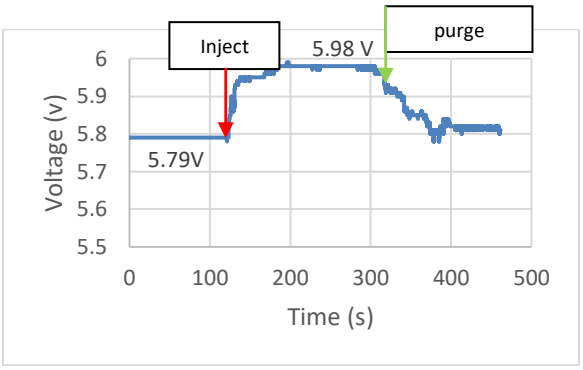

Figure 7. Response of the Tin oxide Sensor substrate (Sample I) to the introduction of Hydrogen sulfide (H_2S) and purging gas.

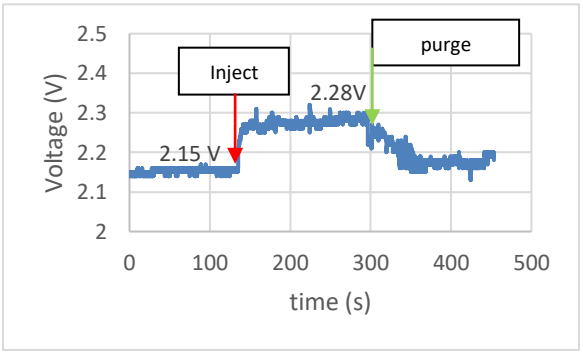

Figure 8. Response of the Zinc oxide Sensor substrate (sample I) to the introduction of Hydrogen sulfide (H_2S) and purging gas.

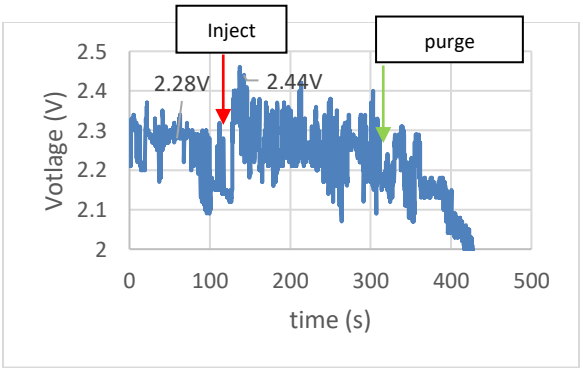

Figure 9. Response of the Zinc oxide Sensor substrate (sample II) to the introduction of Hydrogen sulfide (H2S) and purging gas

As for the SnO_2 sensor substrate, increasing the volume of the H_2S gas to 10cc increased the voltage change to +0.73 V for both the first and the second exposures (figure 10).

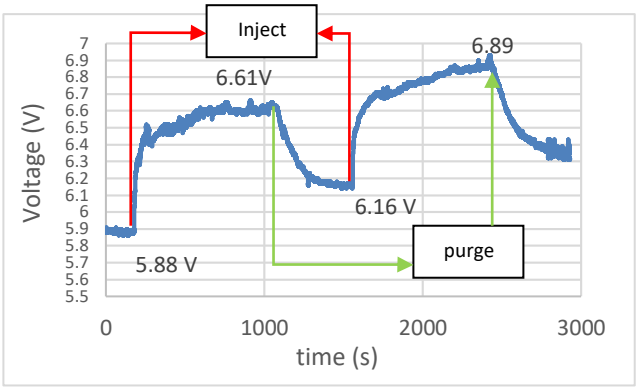

Figure 10. Response of the Tin oxide Sensor substrate (sample II) to 10cc of Hydrogen sulfide (H_2S) and purging gas.

The trapping of electrons at adsorbed molecules and band bending induced by these charged molecules are identified as the reasons for the change in the resistivity. The sensing reaction to the H_2S gas is believed to occur only on the surface of the sensing material. The application of magnetic field to the synthesis of nanomaterials has increased the defects, i.e. oxygen vacancy, and thus improved the sensitivity of the sensor even without doping. A charge depletion layer can be formed near the grain surface of SnO_2 in an oxidizing atmosphere. The electrons associated with these are drawn from the conduction band of the material leading to an increase in resistance. Given a constant current, this results to increase in voltage measurement. (Batzill, M. and Diebold, U., 2005; Bancolo, F., 2011; Liu et al, 2003).

4. CONCLUSIONS and RECOMMENDATIONS

With the presence of magnetic field, thermoelectric magneto hydrodynamics is suspected to be the mechanism for the formation of nanowires, however more investigation is needed to be carried out. The presence of the magnetic field, along with the presence of temperature gradient, was found to be responsible for the formation of the homogenized nanowires. However, the temperature gradient has a greater influence than the presence of magnetic field in the growth of the nanowires. The fabricated Tin oxide (SnO_2) substrate shows a more significant response to nanosensors at room temperature as compared to Zinc Oxide which shows instability and

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inconsistency in the succeeding trials.

Further improvement of the device is needed to be carried out. The researchers recommend using different temperature scale in analyzing the response of Tin Oxide sensor to Hydrogen Gas. Doping and addition of materials like CuO as composite, may lead to further and improved responses of the device to Hydrogen Sulfide gas. Addition of a heating element in the sensor circuit to replace the manual purging is recommended.

5. ACKNOWLEDGMENTS

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