Gas sensing using Tri-metal oxides for breathe analysis

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Abstract. This article describes the use of a semiconductor gas sensor for disease diagnosis that may potentially serve as diagnostic tool handheld breath analyzer to provide detection device. Tri metal oxides were fabricated by a modified chemical spray pyrolysis technique by the mixing of tungsten and tin salts composition at (1:1, 3:1) respectively, with a concentration of (0.1M). The substrate used was silicon n-type at a temperature (500 °C ±5), with spray distance (25 cm). Structural properties, including x-ray diffraction XRD, scanning electron microscopy SEM and atomic force microscopy AFM, were examined. Moreover, the gas sensing property toward nitrous oxide NO₂ gas at a concentration of (10) ppm in air was investigated. Experimental results show formation of tri-metal oxide film (α-SnWO₄) with wire and rods structures were achieved from the used salts, which make the sensor suitable for the detection of nitrous oxide levels in the exhaled human breath.

Keywords: disease diagnosis, breath analysis, bio marker, tri metal oxides, semiconductor gas sensor.

1. Introduction
The exhaled breath of human is a mixture of a variety of distinctive components, such as oxygen, carbon dioxide, nitric oxide and more than a few volatile organic compounds (VOCs). These breath elements are either exogenous or endogenous. Exogenous indicate the molecules which have been taken inner via the procedure of inhalation, from the source such as air or meals thus, nor has any diagnostic value. And, the endogenous molecules are those, which are created by the metabolic process. Metabolic system is a set of lifetime sustaining chemical reactions inside the cells of living organisms. From here, the endogenous molecules have a diagnostic value [1]. And therefore, the change in concentration of those molecules is a signal of the existence of disorder or alter in metabolic process. For instance, acetone is a marker of the diabetes; nitric oxide is a marker of the asthma and airway inflammation. In the equal way, on the rise in the concentration of ammonia in an exhaled human breath is a marker of existence of kidney disease [2]. Figure 1 summarizes possible breath markers and their usual concentrations in healthy people (green bars) in contrast to these at some stage in disorder (gray bars) [3].
Figure 1. Breathe markers and their common concentrations for healthy and unhealthy people [3].

Semiconducting metal oxide (SMOX)-primarily based sensors are an desirable choice for application in breath test tools due to the fact it is inexpensive, durable, compact, exhibit excessive sensor responses, and allow for real-time measurements. Tungsten trioxide (WO$_3$) is the second one maximum generally used semiconducting metallic oxide in gas sensors (SMOX)-primarily based sensors are small, robust, less expensive and sensitive, making them tremendously attractive for handheld transportable clinical diagnostic detectors. WO$_3$ is mentioned to reveal high sensor responses to numerous biomarkers determined in breath, e.g., acetone, ammonia, carbon monoxide, hydrogen sulfide, toluene, and nitric oxide [4]. Also Tungsten trioxide is one of the most multipurpose semiconducting thin layer for gas sensing due to its desirable electrical and optical characterization besides its broad band gap, nature is non-poisonous and obtainable in natural. Like other metal oxide layers, the sensing process of WO$_3$ includes adsorption of gas molecules, reaction with ion absorbed oxygen species and electron extraction processes. Tungsten oxide go through Phase transition with changing temperature with the steady crystalline phases being triclinic, monoclinic, orthorhombic and tetragonal. The dipole moment of the sensed gas molecules on the surface area of WO$_3$ influences the sensitivity, and it was observed that α-WO$_3$ had favors polar molecules as in contrast to γ-WO$_3$ [5, 6]. Both Tin Oxide (SnO$_2$) and Tungsten trioxide (WO$_3$) are popular materials in the semiconductor gas-sensor area and have observed purposes in industrial sensor devices. A combination of these substances in the structure of the compound SnWO$_4$ used to be first stated in 1972. Alpha form of stannous tungstate is stable at low temperature below 670 °C, it is n-type semiconductor with diamagnetic characterize has orthorhombic crystal structure and a dark-red color. Both metal atoms have distorted octahedral oxygen coordination's as in SnO$_2$ and WO$_3$, and in the α-SnWO$_4$, structure the SnO$_2$ tin shows in divalent form, Sn$^{2+}$ [7, 8].

This paper concentrate on detect nitrous oxide gas level in human breath by way of using metal oxide semiconductor gas sensor to investigate the possibility of the existence of renal disease that may potentially serve as a primary diagnosis tool handheld breath analyser.

2. Experimental

Preparation of an aqueous solutions of tungsten and tin salts at two composition are summarized in table 1, the concentration was (0.1 M), and the acidity was maintained to be ≈6 pH during spraying. In this technique, the prepared aqueous solution was atomized by double sprayer nozzle glass at a heated silicon substrate fixed at thermostatic controlled hot plate heater, air was used as a carrier gas to atomize the spray solution with the help of an air compressor with pressure (7 bar), air flow rate (8 cm$^3$/sec). The silicon substrate (n-type Si$_{100}$) at thickness (0.6 mm), atomization rate was (1 nm/s) with (2.5 ml/min) of feeding rate. The distance between the spray nozzle and substrate was kept at (25 ±1 cm) the volume of spray solution was (20 ml), number of spraying (20), time between two spraying (2 min), and spraying the solution on the substrate at temperature (500 ±5 °C), then annealing samples, by using furnace (type Nabertherm) at temperature 600°C for (1hour) and cooling inside furnace.
Table 1. The mixing percentages of salts.

| Salts            | Mix 1 (%) | Mix 2 (%) |
|------------------|-----------|-----------|
| (NH₄)₂WO₄        | 3         | 1         |
| SnCl₂            | 1         | 1         |

Inspections which include: X-ray diffraction was taken by diffractometer type with radiation CuKα (λ = 1.5406 Å), Scanning Electron Microscopy has been carried out by Electron Gun Tungsten heated filament, Resolution 3 nm at 30kV, Accelerating voltage 200 V to 30kV, chamber internal size: 160 mm (Japan), with Au coating for (20 sec). Atomic Force Microscopy (AFM) was taken with a digital instruments, typical data has been taken from AFM height images include root mean square (RMS) and roughness made in USA model AA3000 220V, and gas-sensing experiments were carried out by introducing the system of gas sensor used for checking film sensitivity for NO₂ includes the following parts:, a) Connection tubes, b) Pressure gauge (reader), c) A chamber manufactured locally with dimensions (20 × 20) cm contains the sample and has several holes ( hole for pump gases discharge, glass window, signal pickup) , c) Thermometer , d) The gas composition container , e) Ohm meter to measure the resistance and f) heater. The prepared film is mounted between pair of aluminum electrodes with ohmic contact inside the test chamber. The resistance of the film was monitored and recorded in air, then is recorded with NO₂ gas at (10 ppm) concentration with time. The gas was obtained from reaction solution to rising predicted gas.

The sensitivity is defined as a change in electrical resistance of the sample through exposure to gas, the sensor response was defined using the following formula [9].

\[ \text{Sensor response (\%)} = \left( \frac{R_a - R_g}{R_a} \right) \times 100\% \quad \ldots (1) \]

Where

Rₐ and Rₔ are the electric resistance in air and test gas, respectively.

3. Results and Discussion

3.1. X-ray Diffraction

Figure 2 shows XRD patterns of sample S1 can be well detected peak of orthorhombic Tin Tungsten Oxide (α-SnWO₄) with high crystalline intensity 100 % at (2θ = 28.35°) oriented (121) that match to (JCPDS No. 27-0902), and peaks of Hexagonal phase Tungsten trioxide (WO₃) has appeared in low crystalline peak intensity, that match to (JCPDS No. 033-1387). Figure 4 shows the XRD patterns of sample S2, indced presence of Cubic Tin Oxide SnO₂ with the highest intensity 100% due to its high percentage at (2θ = 31.45°) oriented (111) that match to (JCPDS No. 033-1374), and can find also peaks for (α-SnWO₄) at low intensity, that’s agree with [10], and no characteristic peaks of any other impurities were observed, suggesting that the sample have high purity.
3.2. SEM Result

The microstructure of the annealing films were examined by SEM, Figure 4 the SEM (2D-images) results of (S1) show a micro-wire of SnWO$_4$ were find with size (1-2) $\mu$m width and (5-10)$\mu$m length. These due to using double nozzle in spray system; this gives the required time for fabrications the micro-wires. In Figure 5 SEM (2D-images) of sample (S2) obtained for SnWO$_4$ and SnO$_2$. It was fond a micro-rods with size (2-3)$\mu$m width and (10-15)$\mu$m length [11].
3.3 AFM Result

AFM is powerful technique to investigate the surface morphology at nano to microscale. The surfaces of the films are shown in Figures 6 and 7, the surface were homogenous with roughness (45 nm) and average diameter (77.95 nm) with surface area ratio (24.2) for the micro-wire, and only (3 nm) with average diameter (74.40 nm) with surface area ratio (0.177) for micro-rod respectively.

![Figure 6. AFM images (a) 3D and in (b) 2D of (S1) salt mixed film.](image-url)
3.4 Gas Sensor Results

The gas detecting attributes are absolutely needy upon the response between semiconducting metal oxides and target gas. Instrument of gas-detecting includes the redox response at the metal oxide surface, prompting the adjustment in the consumption layer of the grains that at last change the electrical resistance of the metal oxide, all the compounds $\alpha$-SnWO$_4$, SnO$_2$ and WO$_3$ are n-type [10] and have energy gap (1.64 ev), (2.7 ev) and (3.1 ev) [12, 13, 14] respectively, NO$_2$ is an oxidizing gas and the value of the resistance increases with the time of the sensitivity. Figures 8 show the relation between the sensitivity and time at (10 ppm) of NO$_2$ gas at 100 °C, it can be observe the during the first ten seconds the sensitivity rise to around (50%) of their final value of sample S2, and (40%) for sample S1. Sample S2 show high sensitivity than S1 due to small energy gap of the compound ($\alpha$-SnWO$_4$) that is the major compound comparing with samples S1, where presence of WO$_3$ oxides rise the energy gap.

![Figure 7. AFM images (a) 3D and in (b) 2D of the (S2) salt mixed film.](image)

![Figure 8. Gas sensitivity of salt mixed film S1, S2 of NO$_2$ gas at temperature 100 °C.](image)

4. Conclusion

The objective of this paper is to detect the NO$_2$ gas by using Tri metal oxide semiconductor gas sensor, it can conclude that the deposition temperature is suitable to obtain ($\alpha$-SnWO$_4$), and spray pyrolysis
technique using double nozzles offer different design to microstructure and this improves the sensitivity to gases. Increasing the tin ratio has changed the shape topography and microstructure of the films oxides this is reflected in the changing proportions of the phases formed with different percentages of Tin salts, and it can conclude that sample S2 show highest value of sensitivity making it be used to preparation the biomedical detector.

5. References

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