ACETONE DETECTION USING THIN TUNGSTEN OXIDE (WO_3) FILM BASED GAS SENSOR

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Acetone being a volatile organic compound is found in human breath. Non-invasive breath analysis for detection of diabetes has gained remarkable attention for the past few years. Human breath has ample of volatile organic compounds pertaining to numerous diseases in the body. Acetone in breath has been proven to be an important biomarker for diagnosis of diabetes through breath. Here, tungsten oxide (WO_3) thin films of nanometer thickness have been used for this purpose. The detector films are sputtered over silicon dioxide layer and corresponding connections are made over the film to measure the resistance change. Acetone, being a reducing gas, reduces the resistance of the film as it comes in contact. Different concentrations in parts per million (ppm) have been tested on these nanometer films having thickness of 100 nm over a chip size of 5 mm x 5 mm, as low as 1.2 ppm. Optimum temperature has also been computed to be 300 ^{o}C. The topography of film has been characterized by atomic force microscopy (AFM) and a mean grain size of 24.1 nanometers has been observed.

Keywords: Tungsten oxide, thin films, gas sensor.

Introduction

Non-invasive breath analysis techniques have drawn considerable interest of the researchers lately. Several diseases can be detected through breath exhaled by humans, viz. diabetes, liver diseases, pulmonary tuberculosis, breast cancer, lung cancer, renal disease, acute asthma, rheumatoid arthritis, etc. These diseases are detected through the volatile organic compounds present in human breath. Lately, various biomarkers have been identified pertaining to different diseases, for instance, acetone for diabetes, carbonyl sulphide, carbon disulphide, isoprene for liver diseases, pentane for rheumatoid arthritis [1-3]. Breath analysis has attracted many researchers because of its numerous advantages, viz. sample collection is an easy task, breath is a less complex mixture in comparison to other fluids available in the body such as urine or blood, etc. [4].

Breath is a mixture of nitrogen, oxygen, carbon dioxide, water and inert gases. The remaining small fraction consists of more than 1000 trace volatile organic compounds with concentrations ranging from parts per million (ppm) to parts per trillion (ppt) by volume [5]. Breath analysis plays a vital role in detection of diabetes, taking acetone as a biomarker into account. Thus, this technique can be treated as an alternative to blood analysis [6, 7]. Acetone, the biomarker for type I diabetes, has considerably low concentration in human breath. For a healthy individual, the concentration ranges from 0.22 to 0.80 ppm whereas for a person suffering from diabetes, it exceeds 1.8 ppm [6-8]. Metal oxide based sensors have gained importance lately for detection of diabetes through breath. Various thin films have been tested for this purpose, viz. WO3 [9], TiO2 [10], ZnO [11]. Tungsten oxide (WO3) is one of the most versatile semiconducting thin films for gas detection because of its good electrical and optical properties, in addition to its wide band gap, non-toxic nature and availability in nature. Like other metal oxide films, the sensing mechanism of WO3 involves adsorption of gas molecules, reaction with ionosorbed oxygen species and electron extraction processes [9, 12].

Tungsten oxide undergoes phase evolution with varying temperatures with the stable crystalline phases being triclinic, monoclinic, orthorhombic and tetragonal. It has been reported that the dipole moment of the sensed gas molecules on the surface of WO3 affects the sensitivity. As a result, it was found that ε-WO3 favours polar molecules as compared to γ-WO3 [12].

The aim of the current study is to detect low levels of acetone on as-deposited tungsten oxide thin films of nanometer thickness. The experimental set up and the consecutive results have been discussed in upcoming sections.

Experimental

A. Preparation of film

After standard cleaning procedures of n-type silicon wafers, silicon dioxide was thermally grown as an electrical isolation layer having a thickness of 1 micron. WO_3 thin films were deposited by reactive ion sputtering maintaining a ratio of 80-20 % of argon and oxygen gas respectively. The process was optimized so as to achieve the thickness of 100 nanometers. The fabricated devices were diced having a size of 5 mm x 5 mm. The chips were then wire bonded with conducting epoxy at two points to carry on the gas sensing procedure.

B. Characterization of film

The topography of sensing film was characterized using atomic force microscopy (AFM). The measurements have been performed after the deposition process. The thickness of thin film was measured using a DEKTAK surface profiler.

C. Gas sensing setup

The gas sensing setup comprised of a vacuum chamber connected to mass flow controller for controlling the air flow, a bubbler containing acetone to expose the film with acetone vapours, corresponding voltage source/pico-ammeter for providing the desired voltage to the film and measuring the current so as to compute the resistance changes.

Results and discussion

The film thickness has been computed as nearly 1000 Angstroms, i.e., 100 nanometers using the DEKTAK surface profiler (Fig.1).

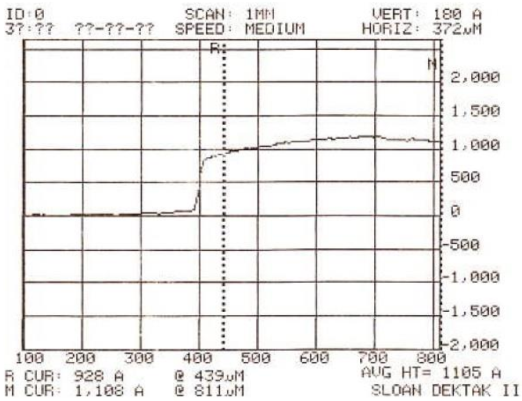

Fig. 1. Thickness measurement of sensing film by surface profiler

The AFM image of the sensing film is shown in the figure 2 with a nearly uniform topography and a mean grain size of 24.1 nanometers.

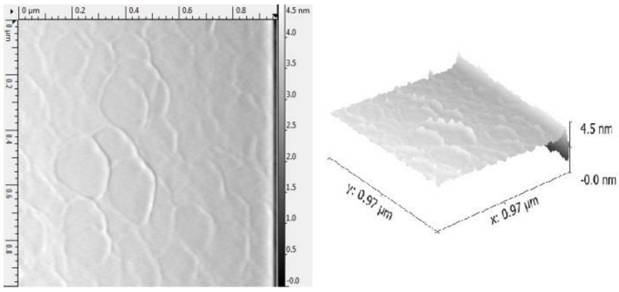

Fig. 2. Atomic force microscopy images of sensing film in 2D and 3D

The semiconductor films work at a particular temperature, i.e., the surface reactions between the sensing film and the gas to be sensed takes place at an optimum temperature. Sensitivities at different temperatures were computed so as to discover the optimum temperature. The sensitivity was calculated using the formula S= (Rf – Ri) X 100/Ri, where Rf is the final resistance obtained after the reaction with gas and Ri is the initial resistance when the sensing film is in presence of air. Fig. 2 shows the graph for optimum temperature which has been computed as 300 oC.

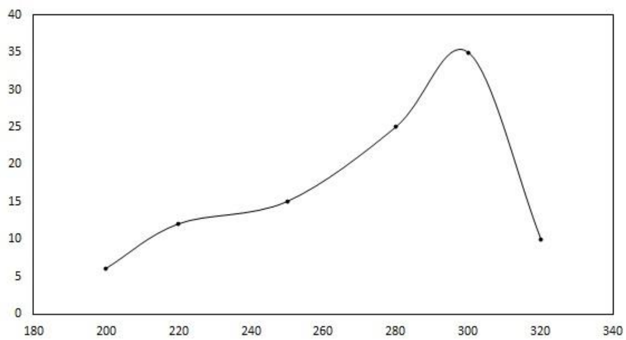

Fig. 3. Plot for calculation of optimum temperature at which sensing film operates efficiently

The sensing film creates oxygen ion species O- and O2- when in air, i.e., the WO3 film interacts with the oxygen, by transferring the electrons from the conduction band to adsorbed oxygen atoms, resulting into formation of ionic species such as O2- or O-.

$$\text{O2 (gas)} \leftrightarrow \text{O2 (adsorbed)}$$

$$\text{O2 (adsorbed) + e-} \leftrightarrow \text{O2-}$$

$$\text{O2- + e-} \leftrightarrow \text{2O-}$$

The electron transfer from the conduction band to the chemisorbed oxygen results into the decrease in the electron concentration in the film. As a consequence, an increase in the resistance of the WO3 film is observed. When the sensing film is exposed to reducing gas like acetone, the acetone vapour reacts with the chemisorbed oxygen releasing an electron back to the conduction band which decreases the resistance of the WO3 film [9].

$$\text{CH3COCH3 (gas) + OH-} \rightarrow \text{CH3CHO + CH3O-}$$

$$\text{CH3COCH3 (gas) + O-} \rightarrow \text{CH3COC+H2 + OH- + e-}$$

$$\text{CH3CHO + O (bulk)} \rightarrow \text{CH3COOH + O (vacancies)}$$

Or

$$\text{CH3COCH3 (gas) + O-} \rightarrow \text{CH3C+O + CH3O- + e-}$$

$$\text{CH3C+O} \rightarrow \text{C+H3 + CO}$$

$$\text{CO + O-} \rightarrow \text{CO2 + e-}$$

The changes in resistance were observed as the WO3 sensing film was exposed to different concentration levels of acetone up to 1.2 ppm (Fig. 4-7).

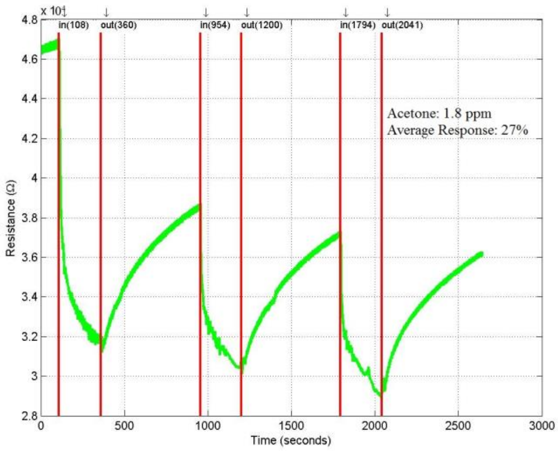

Fig. 4. Resistance changes in sensing film when exposed to 1.8 ppm of acetone at 300 ^{o}C for a particular time interval. Three cycles of exposure turned on and off are shown.

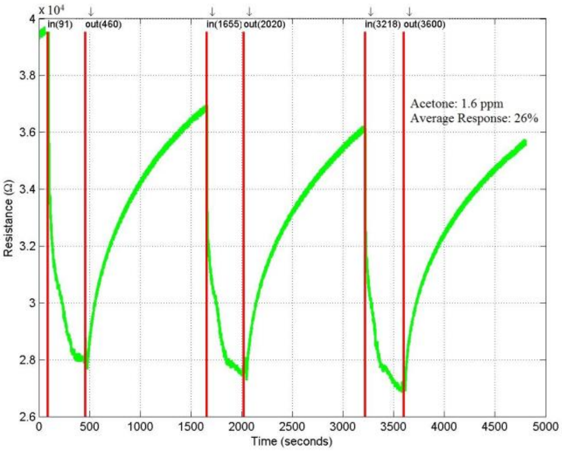

Fig. 5. Resistance changes in sensing film when exposed to 1.6 ppm of acetone at 300 ^{o}C for a particular time interval. Three cycles of exposure turned on and off are shown.

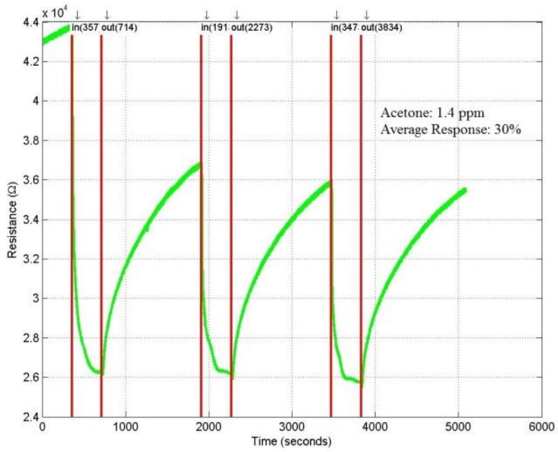

Fig. 6. Resistance changes in sensing film when exposed to 1.4 ppm of acetone at 300 ^{o}C for a particular time interval. Three cycles of exposure turned on and off are shown.

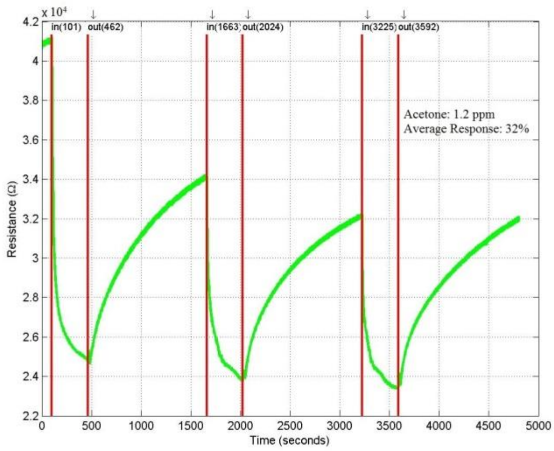

Fig. 7. Resistance changes in sensing film when exposed to 1.2 ppm of acetone at 300 ^{o}C for a particular time interval. Three cycles of exposure turned on and off are shown.

Conclusion

Diabetes detection through breath can be beneficial to many as it is a non-invasive method for diagnosis. Acetone, which has been proven to be the biomarker for diabetes, can be sensed through a particular sensing film sensitive towards acetone present in breath. An effort towards this approach has been made taking WO_3 thin films into account. The resistance of these nanometer thin films reduce when acetone comes in contact with them. This concept can contribute to detection of diabetes through breath. Here, the concentration value of as low as 1.2 ppm has been detected. The average response for different concentrations has been observed to be approximately 30%. Acetone being a reducing gas reduces the resistance of the sensing film when it comes in contact with it. There are oxygen ions developed on the surface of the sensing film. When acetone comes in contact with the film it gives the electrons back to the conduction band of sensing film, thus reducing its resistance.

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