


Carbon Monoxide Gas Sensing Characteristics Dependent on Morphological Properties of Ternary Oxide ($\text{SnO}_2/\text{ZnO}/\text{TiO}_2$) Nanolayers

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ABSTRACT

Mixed oxide nanolayer gas sensors were produced by Sol-Gel spin coating method. The morphological and gas sensing properties of thin films were studied in detail. The Atomic Force Microscopy (AFM) was used for analyzing the morphological properties of the thin film. Also electrical properties of the $\text{SnO}_2/\text{ZnO}/\text{TiO}_2$ thin films were investigated by using current-voltage (I-t) characteristics measurement. Finally, the Carbon Monoxide sensing property of the each fabricated $\text{SnO}_2/\text{ZnO}/\text{TiO}_2$ thin films were investigated and discussed in this study.

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1. Introduction

There are various types of gases inside the atmosphere. Some of the gases are vital for livings but many others are harmful. The concentration of any gas must be under controlled in living atmosphere. For example, gas concentration of O_2 must between 80 ppm and 105 ppm in living atmosphere. Same like O_2 under controlled humidity is also important for the livings. Air cleaners with air-quality sensor are using for safety in some facilities. Because harmful gases must be at fairly low levels. CO, which is an odorless and invisible gas, is considered as one of the most harmful gases for all living things. Therefore, it is extremely important not to breathe carbon monoxide and measure the amount of CO in the environment[1].

The gas sensor industry is emerging day by day. metal oxide based gas sensors are the most remarkable ones among these gas sensors. It is known that metal-oxides are sensitive to various gases at different temperatures. This sensing mechanism of the gas sensors are related to the point defects in the bulk structure and the reaction of the oxygen in the gas phase. Changing the atmospheric pressure creates this effect. At low temperature (below 90°C) the

variation of the conductivity of $\text{SnO}_2, \text{TiO}_2$ and ZnO depends on the adsorption and desorption[2].

Semiconductor based gas sensors are usually metal oxide based. The electrical resistance of the material changes as a result of the absorption of gas molecules by the surface layer. This Change in electrical resistance usually depends on the amount of gas molecules. The sensitivity of such Metal oxide based gas sensors can be increased by various methods. The most important of these is additive or use of various metal oxide mixtures[3].

Zinc oxide, gas sensor especially due to its stable behavior in electrical properties has found wide place in applications. In the use of ZnO structures as a sensing layer, sensor performance[4]. The main method of measuring the structure of the nano or thin film created is the measurement of the change in conductivity. SnO_2 is commonly used in this field[5]. Interaction between gas and metal-oxide is fast enough when the temperature 100°C . Electron interaction between the conduction band of the metal-oxide and adsorbed gas molecules is too fast to not affect to the kinetic interaction. Another of the metal oxides commonly used in gas sensor studies[6] It is titanium dioxide. In TiO_2 -based sensors, the sensing mechanism is can be explained by changes in resistance. Detection mechanism; of oxygen

entering the structure (atomic or molecular structure) injecting electrons into the structure, or electron from the structure works in the form of pulling. The temperature is another important parameter for metal-oxide gas sensors[7]. Gas sensing property is typical for most of the gas sensor. Sensitivity increases directly proportional to the temperature. Then at a certain temperature sensitivity is maximum value. We can say that a gas sensor has the maximum sensitivity at this maximum value. Thus each of the metal-oxide gas sensors have their own operating temperature. When the activation energy of the chemical reactions high, the sensor response is limited by the rate of the chemical reaction[8]. At a certain temperature range, reaction rate and diffusion rate get equal and at this temperature range the sensor response get its maximum value[9]. The material cannot sense the gas except its operating temperature effectively [10].

In this study; The morphological and gas sensor properties of the triple metal oxide thin film obtained were investigated. On the surface of the prepared thin film, with the help of electrodes created by evaporation of Ag, their sensitivity to low amounts of CO gas was investigated at high temperature.

2. MATERIALS AND METHOD

The solutions required to form nano-layers were prepared using the sol-gel process. Solutions to form the mixture were prepared for equal molar ratios in separate containers. Tin (II) Chloride ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$), Zinc Acetate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) and Titanyl Acetylacetonate ($\text{TiC}_{10}\text{H}_{14}\text{O}_5$) were used as starting material for the preparation of each solution, respectively. 2-methoxyethanol was used as solvent and MEA (monoethanolamine) was used as stabilizer. These prepared solutions were grown on the microscope glass by sol-gel spin coating technique. The microscopy glasses prepared in the specified size were cleaned ultrasonically with acetone, ethylalcohol and de-ionized water, respectively. The substrates, whose cleaning process was completed, were finally dried with N_2 gas. Ag electrodes were formed on the surface of the ternary nano-layers to determine gas sensitivities. These electrodes were obtained using the thermal evaporation method (Fig.1.). With the help of electrodes formed on the surface of the film, current changes in parallel with the change in the gas rate in the environment were followed and the use of the sample as a gas sensor was tested. The process steps of gas sensor production are schematized in Fig. 2.

In order to examine the morphological characteristics of thin films, 2D and 3D images of the surfaces were taken with PARK SYSTEM (XE-100E) AFM (Atomic Force

Microscope). Gas sensitivity measurements were taken at room temperature with a specially designed experimental setup using the electrometer (KEITHLEY 6517A). Schematic representation of the experimental setup in which measurements are made is given in Fig. 3.

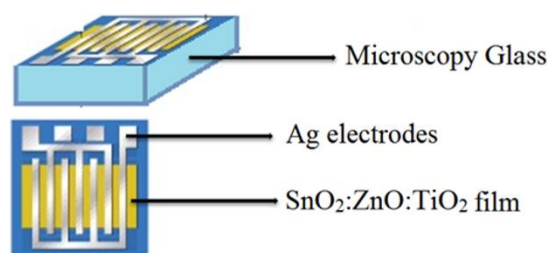


Figure 1. The metal contact prepared for gas sensor

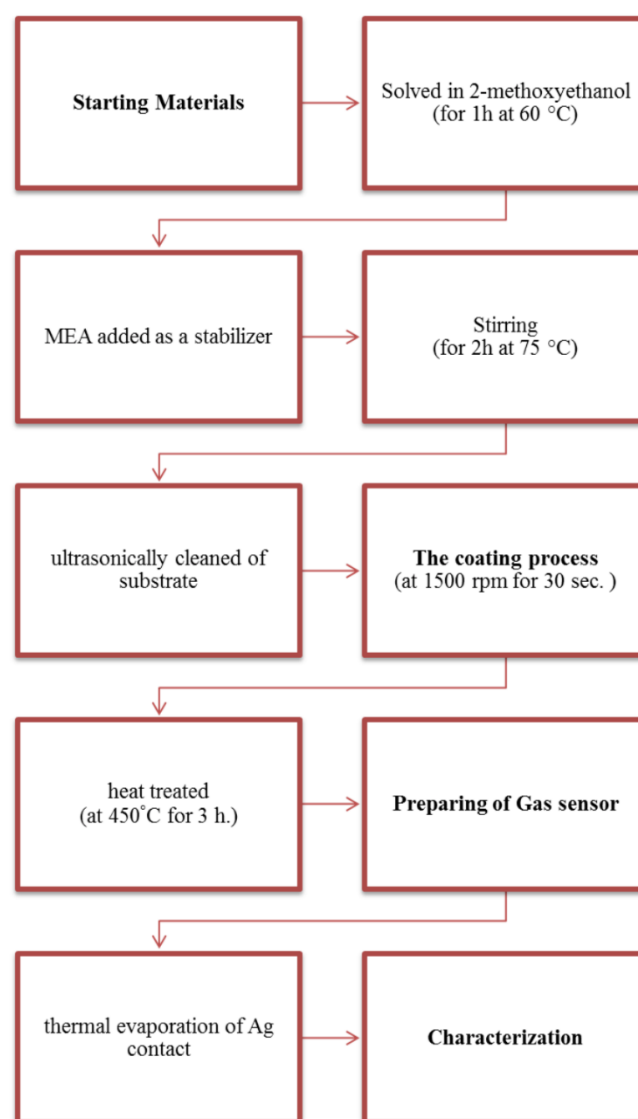


Figure 2. Gas sensor production scheme

3. RESULT AND DISCUSSION

Atomic force microscopy (AFM) photographs were taken to examine the surface morphology of the prepared ternary nanolayers and the images taken are shown in Fig. 4a, b and c. Images of the prepared ternary oxide nanolayers were taken in the dimensions of $40\mu\text{m} \times 40\mu\text{m}$, $5\mu\text{m} \times 5\mu\text{m}$ and $1\mu\text{m} \times 1\mu\text{m}$. In AFM images, nanostructured grains and their combination fibers are outstanding[11]. It is seen that the grain size of the prepared film is nano and the fibers are at the micron level[12]. Due to the large size of the fibers,

the surface roughness value of the sample is also high, which is a desirable situation for gas sensors[13]. Because as surface roughness increases, the effective surface area will increase, it will be exposed to more gases and the number of gas molecules attached to the surface will increase[14]. This confirms that the sensor property of the sample produced depends on morphology.

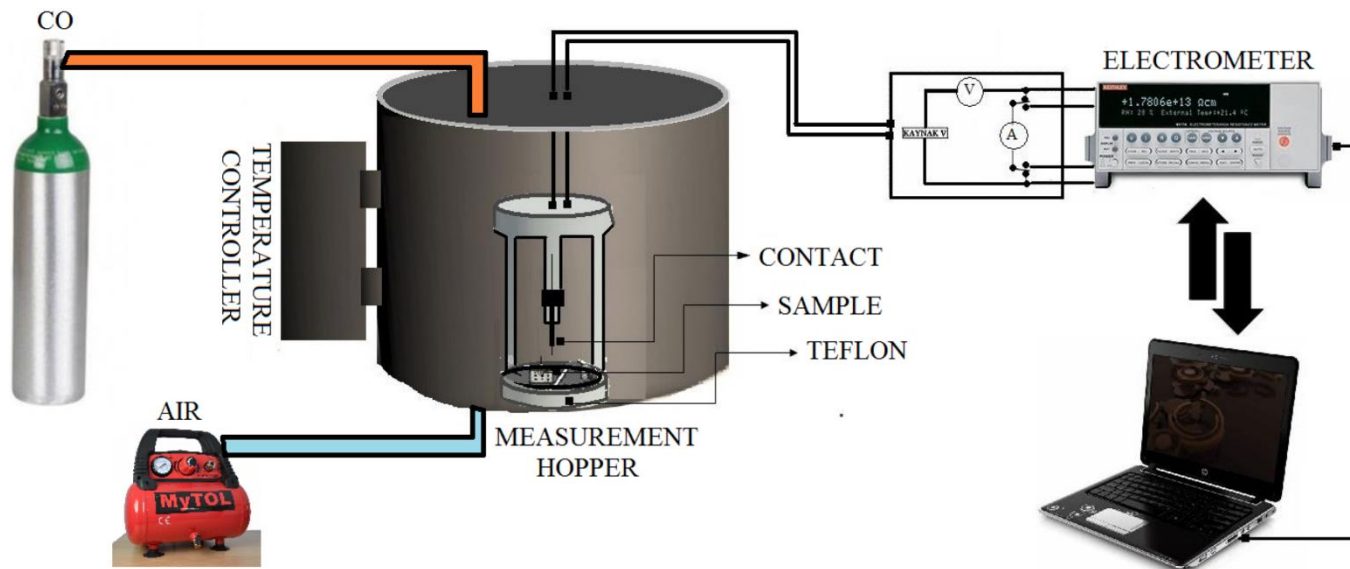


Figure 3. Schematic of gas flow system

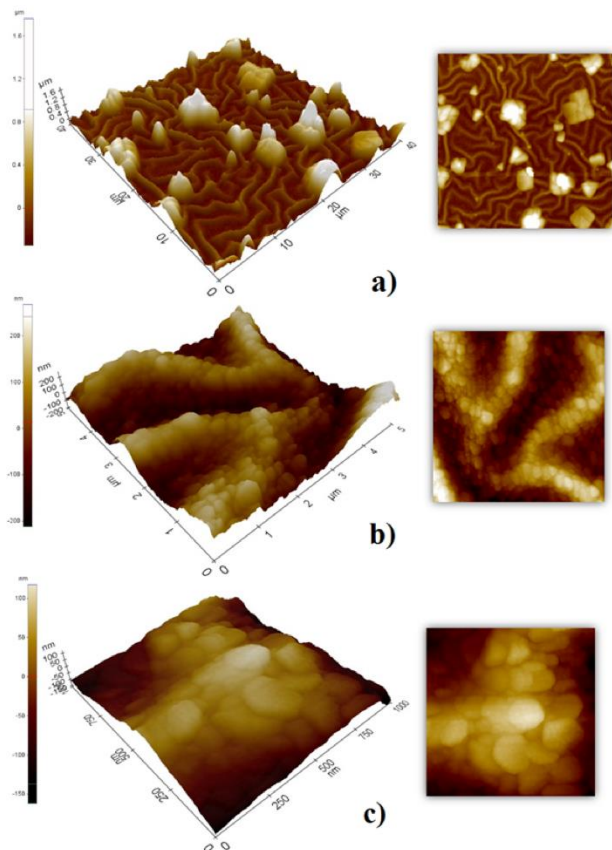


Figure 4: AFM Micrographs of Ternary Oxide ($\text{SnO}_2\text{:ZnO:TiO}_2$) Nanolayers a) $40\mu\text{m} \times 40\mu\text{m}$, b) $5\mu\text{m} \times 5\mu\text{m}$ and c) $1\mu\text{m} \times 1\mu\text{m}$ (Left 2D-view and Right 3D-view)

The working principle of thin film gas sensors is explained by measuring the electrical resistance change depending on the amount of carrier electrons on the surface according to the amount of gas in the environment [15-18].

The gas sensitivity measurement of the prepared samples was calculated with the following formula [10]:

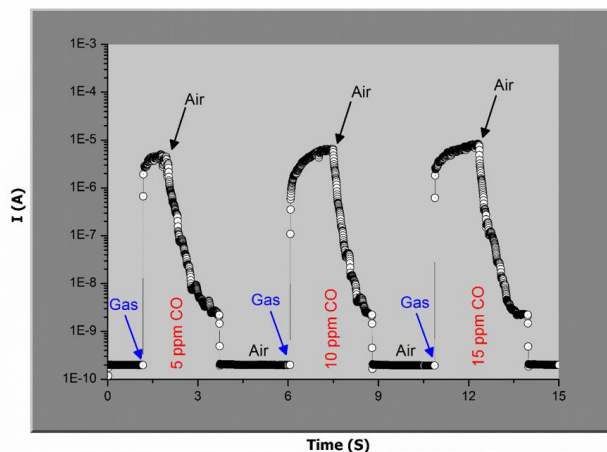


Figure 5: The variation of I-t in the sample with the CO gas in different amounts.

$$S = \frac{I_g - I_h}{I_h} \quad (1)$$

defined as the current change ratio. Where, I_a is the current of a sample measured in air environment and I_g is its current measured in gas environment. The thin film prepared as a sensor was exposed to carbon monoxide gas in different proportions (5 ppm, 10 ppm and 15 ppm). The responses of the prepared sensor to different amounts of CO gas are shown in Fig. 5. as Current (I) / Time (t) graph. It is seen that the prepared nanomaterial gas sensor of ternary oxide reacts to the CO gas and the sensor response changes depending on the increasing CO concentration. This is because when the sample surface is exposed to gas, the gas molecules are adsorbed onto the sensor surface because of a physical interaction between the surface and the gas molecules [19-22]. The energy released as a result of the interaction of oxides forming the surface with CO provides sufficient energy for the electrons to leap into the transmission band, thereby increasing the conductivity of the sensor. When air is given to the environment, the carrier density is decreased and the resistance is increased due to the oxygen adsorbed by the grains on the surface.

4. CONCLUSION

The ternary oxide nanolayers were successfully produced by sol-gel spin coating process and annealed at 450 °C. The main object of the study was the investigating the carbon monoxide response of the device by different gas concentration of CO. It was observed that the morphological properties is definitely effected on the gas sensing property of a ternary metal-oxide semiconductor thin film gas sensors. By increasing the gas concentration, the sensitivity or gas response of the fabricated gas sensor increase in direct proportion. The study showed that ternary oxide nanolayers (SnO₂:ZnO:TiO₂) was sensitive to CO gases in the air and positive results were obtained.

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