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Film Growth of Tetragonal SnO₂ on Glass Substrate by Dip-Coating Technique for Ethanol Sensing Applications

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Abstract: A thin film sensor based on tetragonal SnO₂ nanoparticles was fabricated by combining the sol-gel method and a dip-coating technique on a cylindrical glass substrate. The sensing material was produced through a cycling annealing process at 400 and 600 °C, using tin chloride (IV) pentahydrate as a precursor in polyethylene glycol (PEG) solution as a surfactant. Materials were characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD), revealing tetragonal phase formation with no impurities. The sensor's assembly was done with low-cost materials such as Cu electrodes, Cu-Ni tube pins, and glass-reinforced epoxy laminate as the base material. For signal variation, an adequate voltage divider circuit was used to detect ethanol's presence on the surface of the sensor. The fabricated sensor response to gaseous ethanol at its operating temperature at ambient pressure is comparable to that of a commercial sensor, with the advantage of detecting ethanol at lower temperatures. The sensor response ($S = R_a/R_g$) to 40 ppm of ethanol at 120 °C was 7.21. A reported mathematical model was used to fit the data with good results.

Keywords: sol-gel; thin film; dip-coating; SnO₂; gas sensor; semiconductor; ethanol

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1. Introduction

Evolution has given people the ability to sense around and interact with the environment. Sometimes in certain hostile conditions, it is essential to equip robots with these skills and manage to perceive, communicate, and monitor possible danger that could threaten our integrity. In robotics, perception is crucial [1], and new robots are being designed and manufactured with all kinds of sensors to emulate and improve certain deficiencies humans have. Nowadays, the importance of creating smaller sensors with high precision at a low cost is crucial. Ethanol vapor sensors are always in demand [2]. Ethanol is a transparent, volatile compound presenting a sweet smell and taste. It is one of the most utilized alcohols in industries such as health, safety, forensic laboratories, biomedical, food, transportation, and chemical industries. Therefore, its monitoring is essential, as it can cause several health problems like headaches and shortness of breath [3]. Many ethanol vapor sensors have been fabricated using different methods and substrates. For synthesis, several physical and chemical methods have been employed, such as spray pyrolysis [4], electrochemical [5], hydrothermal [6], precipitation [7], sol-gel [8,9], etc. The latter method is a low temperature and low-cost approach allowing specific control of morphology and microstructure.

Semiconductor metal oxides (SMO) are among the most researched types of chemoresistive gas sensors due to their low cost, compact size, durability, easy manufacturing, simple measuring electronics, and low detection limits. SMO sensors are sensitive to several reducing and oxidizing gases simultaneously. The interaction between these target gases causes an exchange in electrons at a particular rate affecting its resistance and producing a variable signal. These interplays improve the sensitivity sensor's response, selectivity, and response speed in SMO sensors; some methods, such as optimizing temperature during operation, morphology in bulk/surface, and doping, have been successfully tested during

the last decade [10–12]. The history of SMO sensors began with an experiment in the 1960s. For the first time, it was demonstrated that the conductivity of ZnO thin films heated to approximately 300 °C was sensitive to the traces of certain reactive gases in the atmosphere. Afterward, SnO₂ similar properties were reported with better stability [13]. SnO₂ has since become the most studied gas sensing material. It is an n-type material in its pure form with a high adsorption capacity and has interesting electrical properties thanks to its wide bandgap (3.6 eV). It is also a good candidate material for the fabrication of sensing devices due to its chemical and thermal stability in the air [14]. Different nanostructures based on SnO₂ nanomaterials have been widely studied to detect ethanol [13–18]. Many of them show an advantageous sensitivity, peculiar selectivity, and fast response and recovery speed towards gaseous ethanol. SnO₂ sensors can be manufactured in three different devices, i.e., sintered block, thick film, and thin film. The latter is known for its rapid response, low manufacturing cost, and compatibility with microelectromechanical circuits [19].

Many of the teleoperated robots reported in the literature [20,21] work with an array of sensors that need to heat at high working temperatures to detect flammable gases inside dangerous places, mines, disaster areas, and even into radioactive zones. Therefore, there is an inherent necessity to design new sensors capable of detecting traces of gases at low working temperatures to avoid the accidental autoignition of the analyte vapors. The main purpose of this research is to design a prototype sensor capable of detecting traces of ethanol gas at low temperature and, with this, improve the functionality of several robots reported in the literature, of which their main function is to localize odor source location [22].

The fabrication process and assembly are just part of a broader scope to develop sensors, as mentioned by Qader et al. [23] and Sethi et al. [24]; portable, suitable for bedside use, able to detect other volatile organic compounds, such as those found in the exhaled breath of people with respiratory diseases, and even the developing of wearable biosensors attached to the human body capable of detecting human biomarkers in sweat as mentioned by Nasiri et al. [25] and Tai et al. [26]. Thus, the research in this work is trying to follow the World Health Organization guidelines on being “affordable, sensitive, user-friendly, rapid, robust, equipment-free, and deliverable to end-users” [27].

Section 2 details the synthesis using hydrated tin (IV) chloride (SnCl₄·5H₂O) as the starting material of the thin film with its deposition through the dip-coating technique. It also presents the mechanical and electrical assembly of the fabricated sensor. Section 3 describes a study on the morphology characteristics and electrical properties of SnO₂ thin film prepared by the sol–gel technique on a glass surface with an average grain size of only 13.05 nm. X-ray diffraction (XRD) analysis showed the crystallinity structure. Scanning electron microscopy (SEM) was used to study the surface morphology. The film's gas sensing properties were measured by resistance changes under a steady flow of 10, 20, and 40 ppm concentration ethanol at 120 °C. The results were compared with one type of commercial sensor. A mathematical model was used to fit the sensor's response. Finally, Section 4 presents conclusions and future work.

2. Materials and Methods

2.1. Materials

Tin (IV) chloride pentahydrate (SnCl₄·5H₂O), citric acid (C₆H₈O₇), ammonium hydroxide (NH₄OH), and polyethylene glycol (PEG, Mw = 1450 Da) were purchased from Sigma-Aldrich. The chemicals used for the synthesis preparation were of analytical reagent grade and were used as received from the manufacturer without further purification.

2.2. Sample Preparation

The sol–gel method was used to prepare SnO₂ nanoparticles. In a normal synthesis process, 50 mL of a 0.5 M SnCl₄·5H₂O was mixed with 50 mL of a 0.5 M citric acid solution and stirred for 15 min. Then, 50 mL of a 2% (w/v) aqueous PEG solution stirred beforehand for 60 min was added to the tin chloride and citric acid solution and mixed for 15 min.

Concentrated ammonium hydroxide (NH_4OH) was finally added dropwise until pH 11 was reached, and the mixture turned into a distinctive milky whitish color.

2.3. Film Growth of Tetragonal SnO_2

The sensor was fabricated using a cylindrical hollow glass substrate rinsed in acetone and isopropanol, and dried. The pre-cleaned substrate was dipped into the white sol-gel solution for 5 min under constant stirring using a withdrawal speed of 3 cm/min. The substrate was coated inside and outside of the tube. The substrate was dried at 110 °C for 1 h in air and afterward at 400 °C for 10 min inside a furnace before being dipped into the sol-gel solution again. The process was performed six times in total. After the sixth iteration, the sample was heated at 600 °C for 1 h. A homemade machine was used to control the withdrawal speed and submersion time. The sol-gel and dip-coating method's reproducibility and uniformity were verified through SEM analysis for three different sensors.

2.4. Characterization

X-ray diffraction was carried out on a Miniflex 600 Powder X-ray Diffractometer (Rigaku, Monterrey, Mexico). The measurements were performed with a source voltage of 30 kV using a Cu cathode ($\text{K}\alpha$) as a source at a wavelength of 1.54 Å. The diffraction patterns were from 20° to 80° with a step of 0.05° and a scanning rate of 2°/min. No specific sample preparation was required. Scanning electron microscopy (SEM) images were taken by an EVO MA25 field-emission scanning electron microscope (Zeiss, Monterrey, Mexico), operating at an acceleration voltage of 30 kV. The particle's size was determined using a Zetasizer Nano Zs (Malvern Instruments, Malvern, UK) at 25 °C.

2.5. Sensor Fabrication and Measurements

To mechanically assembly the sensor, Cu electrodes, rings, and wires (1 mm of diameter and 4 mm length) were situated at each end of the glass tube, and inside a Ni-Cr coil was used to change the heating current for temperature control by adjusting the heating voltage (Figure 1a). The electrodes were connected to several Cu-Ni tube pins to ensure stability and to keep them immobilized during the measurement. The pedestal was manufactured with a glass-reinforced epoxy laminate material (FR4 base) to avoid heating while sensing target gases through a range of temperatures, as shown in Figure 1b. Then, the sensor was re-heated at 120 °C for one month to observe its signal behavior. The operating temperature was tuned and supplied by an external voltage source. The resistance of the sensor was calculated by manufacturing a voltage divider. The electrical components are presented in the circuit diagram in Figure 1c. V_c is the circuit input voltage, V_h is the heating voltage, and V_{out} is the output voltage passing through the reference resistance. The sensor resistance values were determined through the variation of V_{out} . The homemade experimental box containing the sensor is presented in Figure 1d. Finally, Figure 1e shows a general view of the experimental setting with the main components.

Figure 1. (a) General illustration of the fabricated sensor; (b) the sensor's support assembly; (c) the electrical circuit for the sensor device; (d) the homemade experimental container for the sensor and the circuitry; (e) view of the experimental setting with the main components.

The gas sensing properties were measured at room temperature conditions. All gas sensing measurements were performed at different operating temperatures in an acrylic rectangular homemade box testing device (one half-liter volume). During the gas sensing tests, a given amount of analyte (gaseous ethanol) and a humid airflow were injected into the test chamber. Only dry air was introduced to recover the sensor after a new equilibrium was reached. The relative humidity during measurements was about 48%. The sensor response ($S = R_a/R_g$) to the target gas is defined as the ratio of resistance in the air (R_a) over reducing gas (R_g). The required time to reach 90% of its saturation after injecting the detected analyte was the response time; meanwhile, the recovery time was for the sensor to return to 10% above the original resistance value in the air after releasing the gas [28–30].

3. Results and Discussion

3.1. Structural and Morphological Analysis

The phase purity of the sensor was determined by the XRD pattern. The obtained peaks in the XRD test corresponds with the typical values of lattice parameters $a = 4.738 \text{ \AA}$ and $c = 3.187 \text{ \AA}$ (JCPDS file No. 41-1455) for SnO_2 . All diffraction peaks have been identified by the XRD software, which corresponds to the tetragonal crystal structure. Figure 2 presents the XRD patterns of the SnO_2 thin film growth.

Figure 2. XRD patterns of the sensor.

The peaks indicate the polycrystalline nature of the SnO_2 . The indexed peaks with the highest intensities were: (110), (101), and (211). The Debye–Scherrer equation (Equation (1)) was used to estimate average crystallite sizes [31]:

$$D = \frac{0.89\lambda}{\beta \cos \theta} \quad (1)$$

where λ is the X-ray wavelength, β is the full width at half maximum, and θ is the corresponding angle. The values of the crystallite sizes were 12.6, 12.9, and 13.7 nm, respectively, with a mean size of 13.05 nm. Besides, the crystallinity in the samples can be confirmed by the sharp and well-defined diffraction peaks, and the purity is assured with no other material peaks. Characteristic peaks of different forms of SnO_2 were not detected. The results reveal that the SnO_2 nanoparticles show a well-developed tetragonal single-phase.

According to Ahlers et al. [32], grains smaller than approximately 30 nm within the layers with a high degree of porosity show a significant increase in sensor response because their size allows the penetration of gases into the thin film-sensitive layers.

The film's morphology has the shape of a forest of randomly oriented flakes, as shown in Figure 3a. In a closer look at Figure 3b, random paths are presented everywhere, which means an increase in reaction areas due to the high porosity. The cracks on the surface are due to the stress created during annealing and, according to Yeh et al. [33], are presented in multi-layer samples, particularly in those using a sol–gel synthesis. In Figure 3c, inside the small gaps between the formed crystals, there are more flakes below. This formation may be due to the multiple dip-coating processes creating a fractal-like structure shown in Figure 3d. The average size of these flakes is around 10 μm wide. The thickness of the sensitive film was determined by SEM analysis and was found to be 5 μm .

Figure 3. SEM images of the SnO_2 thin film layer deposited on the glass substrate at different resolutions—each red square indicates a zoom in on the next image: (a) 20 μm ; (b) 10 μm ; (c) 5 μm ; (d) 1 μm .

3.2. Gas Sensing Experiments

The widely used commercial sensor MQ3 gives a range from 0 to 1023 as an analog to digital converter (ADC), and it was taken as a reference for the experiments performed in this research. It is essential to mention that the MQ3 gives a mapping signal (inset in Figure 4), and such a signal was converted to resistance, as shown in Figure 4.

Figure 4. MQ3 signal in terms of $\text{k}\Omega$ after being converted.

Equations (2) and (3) [34] were used for the latter signal flipping, where ADC is the digital value, V_C is the circuit voltage (5 V), V_{RL} is the voltage generated from the sensor in the test area, and R_L is the resistance reported from the datasheet with $\text{k}\Omega$ unit. As observed, the resistance (R_S) goes down when the reducing gas is present, and just for convenience, $R_{g(T)}$ is the resistance value depending on temperature. It was decided to flip

the resistance (R_F) so that the signal increases as the ethanol increases, using Equation (4), and resulting in Figure 5.

$$VRL = \frac{ADC - V_C}{1023} \quad (2)$$

$$R_S = \frac{V_C - VRL}{VRL} \times R_L \quad (3)$$

$$R_F = -R_S - R_{g(T)} \quad (4)$$

Figure 5. MQ3 flipped signal.

This flipping procedure was performed for all the experimental data of this research, described in the next paragraphs.

A set of experiments were conducted to measure the fabricated sensor minimum resistance in cleanroom air and the maximum resistance at several concentrations of ethanol (10, 20, and 40 ppm) at 120 °C, as shown in Table 1.

Table 1. Minimum and maximum sensor resistance in clean air (R_a) and ethanol (R_g).

Concentration (ppm)	Time (s)
10	$R_a = 29.6 \pm 0.7$ $R_g = 194.0 \pm 0.6$
20	$R_a = 11.9 \pm 0.3$ $R_g = 50.7 \pm 0.8$
40	$R_a = 30.52 \pm 0.5$ $R_g = 220.1 \pm 0.5$

To determine the repeatability, a series of three runs were taken for each concentration. The experiment was conducted as follows: (i) the equipment was run for three and a half minutes just with room air to get a stable signal, (ii) the alcohol vapors and the room air were mixed in a small chamber, and (iii) then introduced into the testing chamber allowing the mixture to flow for three minutes; (iv) then the flow of ethanol vapors was stopped, and just air was allowed to flow for 5 min to achieve desaturation. This cycle was repeated up to four times for each of the three runs to observe how repeatable the signal was. At the end, there were 12 curves for each combination of temperature and concentration.

The raw data acquired from the sensor in which the reducing gas decreases the resistance of the material is presented in Figure 6a, and the ratio for the flipped signal ($S = R_g/R_a$) is shown in Figure 6b.

Figure 6. (a) Raw data from the sensor in which the reducing gas clearly decreases the material's resistance; (b) flipped signal of the three runs of experiments with the average signal obtained out of them.

As shown in Figure 7a, the response increases with temperature until a maximum value is reached and then apparently decreases. Figure 7b presents the sensor behavior versus ethanol concentration ranging from 5 to 40 ppm at different temperatures. The response increase with concentration, and particularly the best performance is at 120 °C at 40 ppm.

Figure 7. (a) The sensor response of the thin film fabricated sensor at 40 ppm gaseous alcohol (b) at different temperatures and concentrations; (c) the dynamic cycle response at 120 °C compared to the MQ3 (200 °C); (d) dynamic response of the fabricated sensor at different concentrations.

The fabricated sensor was compared in resistance terms with an MQ3 type commercial gas sensor, as shown in Figure 7c. After four reversible cycles, the manufactured sensor revealed excellent repeatability. It is important to get lower temperatures, looking for an improvement in the fabricated sensor's behavior versus other commercial sensors working at higher temperatures. The differences in response between 100 and 120 °C are slightly different; the latter shows better performance, but the former has good stability and good repeatability at an even lower temperature. This temperature variation is translated into lower power consumption allowing it to be considered an optimum temperature for future reference. It is crucial to mention that the MQ3 type commercial gas sensor works in its ideal sensing temperature, which is 200 °C, and the dynamic response is slightly more significant than the sensor presented in this work. It is evident from the image that the fabricated sensor signal at 120 °C has good behavior. The main comparison with the MQ3 is its excellent behavior and selectivity to ethanol and observing how the fabricated sensor is going to act between experiments. Both sensors respond almost immediately and almost simultaneously, which indicates that the fabricated sensor has excellent selectivity to ethanol as well, and it seems to get better with the increase in temperature.

Additionally, the response at different operating temperatures and concentrations is shown in Figure 7d. When ethanol is present, the fabricated sensor has similar behavior but with a different response at every temperature. The difference in response could be attributed to thermal diffusion within. After the gas is flushed out from the testing box chamber, the sensor returns to its initial condition.

The response (τ_{res}) and recovery (τ_{rec}) time is presented in Table 2. According to the results, the response time is affected by temperature and concentration. Furthermore, the recovery time is affected by temperature but not so much by concentration. The response time describes the time needed for the fabricated sensor output signal to reach 90% of its saturation value after the ethanol gas is introduced into the atmosphere. The recovery time is the time taken for the sensor output signal to drop to 90% of its saturation value after the ethanol gas is off, reaching a recovery to within 10% above its initial value in air. The best response/decay time for the fabricated sensor is at 100 and 120 °C. The recovery time is affected by temperature, increasing with lower temperatures.

Table 2. Sensor response/recovery time of the fabricated sensor.

Concentration (ppm)	τ_{res} (s)	τ_{rec} (s)
5	53	220
10	53	223
20	47	271
40	47	272

The mathematical model presented by Villarreal et al. [1] has a complete ventilation system with start, rise, sample, and decay periods. They proposed the use of a closed chamber with the shape of a dog's nose. The rise and decay periods in their work were used to fit the fabricated sensor's signal at different operating temperatures as a first approach in finding an adequate model that explains the acquired curve's behavior. Figure 8a shows the mathematical model fit to the MQ3 sensor. Meanwhile, Figure 8b shows the mathematical model applied to 40 ppm at 120 °C. The results showed differences that were impossible to overlap one into another in the data. This apparent drift is explained due to the main differences in the composition of the sensors.

Figure 8. The mathematical model proposed by Villarreal et al. [1] applied to the (a) MQ3 sensor and; (b) fabricated sensor, respectively.

As can be observed, the model does not fit the experimental data properly. Therefore, there is a need for a different mathematical model based on the phenomenological description of the interactions between ethanol and the SnO_2 film, e.g., one model that can explain certain discrepancies in the rise and decay stages better than the latter model. Moreover, the complexity of the sensing phenomenon is compounded by several steps: (i) several chemical reactions are taking place inside the substrate, (ii) the diffusion, adsorption, desorption of the chemical species, and (iii) the tortuosity followed by the molecules strongly related to the porosity and morphology created by the dip-coating process. The steps stated above must be reviewed to propose a model able to fit the experimental data.

3.3. Sensor Stability

Measurements were taken for 30 consecutive days to ensure repeatability and stability by the fabricated sensor. The gas sensing measurements for gaseous ethanol at 40 ppm at their optimum working temperature (120°C) every five days indicate accurate results and are shown in Figure 9. The results present apparent drift over time; decreasing in the response may be because the sensor was under monitoring every day with an excessive test proving every bad aspect or variation in the signal or due to the Cu electrodes' possible oxidation. The sensor presents 0.5% of drift over 30 days. This parameter will be enhanced in the future improvement of the sensor. Furthermore, a calibration procedure, such as the one mentioned by Khameneian et al. [35], will be established to assure its adequate functionality in long periods.

Figure 9. Stability of the fabricated sensor at 40 ppm gaseous ethanol concentration for 30 days at the optimum working temperature (120°C).

4. Conclusions

A thin film SnO₂ sensor was fabricated through dip-coating using a synthesized sol-gel technique. The coating was done on a glass substrate and contained tetragonal crystals with an average size of 13.7 nm and as flake aggregates. The resulting circuit was established using copper electrodes. The sensor response to 40 ppm of ethanol at 120 °C was 7.21.

The fabricated sensor was able to detect low ethanol ppm levels at lower temperatures compared to the commercial one and with a conductivity similar to those reported in previous studies. The electrical response of the sensor is very promising for practical applications. The knowledge gained on the fabrication method and assembly process provides essential information for the future development of a prototype to identify volatile organic compounds present in the exhaled breath of people with certain diseases.

The methodology used in this research proves to be a low cost and easy way to fabricate new sensors. The high molecular weight surfactant (PEG, MW = 1450 Da) turned out to be a good choice to get crystals with an average size of 13 nanometers. The lower detection temperature reduces the autoignition problem and eases the sensor's integration into teleoperated robots' electronic circuitries since less dissipation of heat is required. A published mathematical model was applied to the signal obtaining a good fitting.

Future work should study the influence of humidity, lower concentrations, and several temperatures, as well as the detection, by gas chromatography, of the subproducts due to the oxidation of ethanol. This information will be very helpful to improve the adsorption and desorption parameters the model requires for the identification of volatile organic compounds.

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