Fabrication and Characterization of Tri Metal Oxides by Chemical Spray Pyrolysis Technique as a Gas Sensor

Farhad M. Othman* Alaa A. Abdul-hamead** Noor M. Ali***

* Department of Materials Engineering / University of Technology
** Email: fmok4@yahoo.com
*** Email: adr.alaa@yahoo.com

(Received 4 January 2016; accepted 18 May 2016) http://dx.doi.org/10.22153/kej.2016.05.007

Abstract

In this research tri metal oxides were fabricated by simple chemical spray pyrolysis technique from (Sn(NO$_3$)$_2$.2H$_2$O, Zn(NO$_3$)$_2$.6H$_2$O, Cd(NO$_3$)$_2$.4H$_2$O) salts at concentration 0.1M with mixing weight ratio 50:50 were fabricated on silicon substrate n-type (111) (with & without the presence of grooves by the following dimensions (20 µm width, 7.5 µm depth) with thickness was about (0.1 ±0.05 µm) using water soluble as precursors at a substrate temperature 550 ºC±5, with spray distance (15 cm) and their gas sensing properties toward H$_2$S gas at different concentrations (10,50,100,500 ppmv) in air were investigated at room temperature which related with the petroleum industry. Furthermore structural and morphology properties were inspecting. Experimental results show that the Zn$_2$SnO$_4$ and Cd$_2$SnO$_4$ thin films were achieved from the used salts and samples gas sensitivity which improved with the presence of substrate grooves. Which make the sensor suitable for the detection of lower concentrations of hazard H$_2$S gas in the petroleum industry.

Keywords: Zinc stannate, cadmium stannate, gas sensor, ternary metal oxides, spray pyrolysis, pollutant gases, gas sensitivity, XRD.

1. Introduction

Zero and one dimensional nano-structures of binary semiconducting oxides (2-6 and 4–6 oxides, for example, SnO$_2$, ZnO and TiO$_2$ have pulled attention from their interesting properties and potential use in assorted applications, for example, gas sensors, photograph catalysis and sun powered cells. In any case, with active examination in nano technology, there is an earnest requirement for extraordinarily outlined semiconductors to better match the properties of developing materials. This has prompted a restored attention for ternary oxide semiconductors (2–4–6 oxides) of the structure AII$_2$BIVO$_4$, for example, cadmium stannate (Cd$_2$SnO$_4$), prominently known as Tin Cadmium oxide (CTO), and zinc stannate (Zn$_2$SnO$_4$), which is called Tin Zinc oxide (ZTO). Zn$_2$SnO$_4$ is recognized for having high electron mobility, high electrical conductivity, and appealing optical properties that makes it reasonable for an extensive variety of utilizations in sunlight based cells, sensors for the recognition of moistness and different burnable gasses, negative electrode material for Li-ion battery and as a photo catalyst for the corruption of natural contaminations. Contrasted with binary oxides, the tri oxides like Zn$_2$SnO$_4$ are synthetically more steady making them perfect for applications including compelling conditions [1].

Metal oxide semiconductors based sensors are mainstream for distinguishing ignitable gasses at low concentration levels, attributable to the lower generation costs, high sensitivity and long haul steadiness. The material attributes and size effects of metal oxides have been investigated for its potential in detecting applications. The
prevalent detecting mechanisms depend on changes in electrical resistance of metal oxide semiconductors because of ion sorption of gases regions on their surfaces. The charge exchange process actuated by surface responses decides the resistance of the metal oxide. At the point when worked in the encompassing, oxygen gets ion osorbed on the surface of the metal oxide, prompting an adjustment in resistance created by a misfortune or addition of surface electrons as a consequence of adsorbed oxygen responding with the objective gas. In the event that the metal oxide is a n-sort semiconductor, the resistance increments in the nearness of oxidizing gasses, for example, nitric oxide (NO), nitrogen dioxide (NO2), ozone (O3) while lessening gasses like carbon monoxide (CO), methane (CH4) prompts a decrease in resistance. The opposite is valid for p-sort metal oxides. The greatness of progress in electrical resistance gives a direct measure of the convergence of the objective gas present [2].

From the time of Julia et al.[3] (1995) the improvement of new materials like tri oxide semiconductors, for example, Cadmium Stannate (Cd3SnO4), Galium doped ZnO, Aluminum doped ZnO and Zinc. Tin Oxide are being investigated effectively. There are a wide range of strategies to combine ZTO, for example, physical vapor statement (PVD), concoction vapor testimony (CVD), fire pyrolysis, laser-removal, circular segment release, sol-gel strategy, aqueous technique. what's more, solvo-warm techniques [4].MA Jin et al.[5] prepared Zn-Sn-O films deposited on Polypropylene adipate (PPA) organic substrate by R.F. magnetron sputtering and characterization of the films is investigated. Spray pyrolysis technique can control of sizes and states of crystal structures .structures is essential as it might influence their electrical and optical characteristics. The physical characteristics of ZTO rely on upon the technique utilized for production. Aqueous development is an appealing and moderately straightforward technique, since crystal growth happens at gentle temperatures and pressure. This strategy is getting to be a standout amongst the most vital devices for developed material handling, especially inferable from its favorable circumstances in the preparing of materials for a wide assortment of innovative applications, for example, hardware, optoelectronics, catalysis production and bio photonics. The variety of morphology and crystallinity of hydrothermally, incorporated ZTO with the variety of pH of the precursor solution [6]. Also, there are other applications for TCOs ; liquid crystal displays; anti-static coatings; corrosion resistant coatings; ohmic contacts to surface-radiating lasers; ohmics contacts to light discharging diodes; ohmic contacts to photodetectors; Schottky contacts to photodetectors; and heat mirrors for vitality productive windows and lights [7].

Termary oxides give more prominent adaptability to tune the substance properties of the materials by changing the arrangements thus synthetic sensitivity [8].Transition-metal oxides and their compounds have some extraordinary physical properties. In spite of their expansive band holes (>3 eV), which makes them straightforward under ordinary conditions, they can manage a high convergence of carrier electrons with a high mobility [9]. TCO films have better bond and lessened film thickness that diminishes the quantity of interconnects and decreases fabricating costs [10]. Expanding prerequisites for natural checking, open security, household wellbeing, space makes, air-quality, medicinal analysis, identification of touchy lethal gasses and sensor systems have driven to developing enthusiasm for superior gas sensor. It is understood that the gas reaction, selectivity and reaction and recuperation time are the three most essential parameters in planning semiconductor metal oxide gas sensor [11]. At last, it must be indicated that one dimensional nanostructures semiconducting oxides have pulled in extraordinary consideration as of late because of their exceptional properties in appreciation of hardware and optics. Among them, parallel oxides, for example, ZnO and SnO2 have been centered around for the most part, yet ternary oxides, which may demonstrate better characteristics, are still less considered [12].

The goal of this work is to fabricating different semiconductor-based Tri metal oxide gas detector of two mixed film by spray pyrolysis technique , and study some of their structural. properties and sensitivity to some pollutant gases.

2. Experimental

The work includes the following steps:

The First Step:
- Preparation of an aqueous solutions at (50:50)% equal salts ratios with purity 99.9% from
1- Tin with zinc nitrate (Sn(NO3)2.20 H2O, Zn(NO3)2.6 H2O))
2- Tin with cadmium nitrate (Sn(NO3)2.20 H2O, Cd(NO3)2.4 H2O)
The concentration was (0.1 M), the acidity was maintained to be ≈6 pH during spraying. The spraying apparatus was manufactured locally in the university laboratories. In this technique, the prepared aqueous solution was atomized by a special 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 cm³/sec) at room temperature.
- The silicon substrate (0.6 mm thickness) temperature was maintained at 550 °C during spraying. Grooves were done on silicon substrate via mechanical notch instrument, the dimensions were 7.5 µm depth, 20 µm width, number of grooves were 10 separating by 0.1 mm as shown in Fig.1 thickness was (0.1) µm.
- 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 (15 ±1 cm) the volume of spray solution was 25 ml, number of spraying (20), time between two spraying (10 sec).
- The spray of the aqueous solutions yield the following chemical reactions [13,14]:

\[
\begin{align*}
\text{Sn(NO}_3\text{)}_2.20\text{H}_2\text{O} + 2\text{Zn(NO}_3\text{)}_2.6\text{H}_2\text{O} & \rightarrow \text{Zn}_2\text{SnO}_4\downarrow + 6\text{NO}_2\uparrow + \text{O}_2\uparrow + 32\text{H}_2\text{O}\uparrow \quad (1) \\
\text{Sn(NO}_3\text{)}_2.20\text{H}_2\text{O} + 2\text{Cd(NO}_3\text{)}_2.4\text{H}_2\text{O} & \rightarrow \text{Cd}_2\text{SnO}_4\downarrow + 6\text{NO}_2\uparrow + \text{O}_2\uparrow + 28\text{H}_2\text{O}\uparrow \quad (2)
\end{align*}
\]

- The Second Step: Spraying the solution on the substrate at temperature (550 ±5 °C) [16,17,18].
- The Third Step: Annealing samples, by using furnace(type Nabertherm) at temperature 550°C for (30 min) and cooling inside furnace.
- The Forth Step: Inspections which include:
  1- X-ray diffraction: It was taken by diffractometer type with radiation CuKα (λ=1.5406 Å). This inspection was carried out in Iraqi geological survey board Ministry of industrial and mineral, with continuous scanning.
  2- Scanning Electron Microscopy (SEM): The SEM study 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).The setting was done in Nanotechnology & Advanced Materials Research Center at University Of Technology.
  3- Atomic Force Microscopy (AFM): It 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.
  4- Optical Microscope: It was taken to determine the dimensions of grooves with magnification of 100µm. The inspection was done in Nanotechnology & Advanced Materials Research Center at University Of Technology.
  5- Gas-sensing: The gas-sensing experiments were carried out by introducing the thus prepared devices into a home-made test cell, which was consist of a cylinder with cover to restrict prepared gas.

The gas was obtained from reaction solution to rising predicted gas. Pollutant gas that prepared H₂S gas as will be explained in the following reaction equation [14]:

\[
\text{FeS} + 2\text{HCl} \rightarrow \text{H}_2\text{S} \text{ (g)} \uparrow + \text{FeCl}_2 \quad \ldots (3)
\]

The gases-sensing properties were determined which exposed to various concentrations of the gases (10, 50, 100, 500) ppm. The sensor response was defined using the following equation[15]:

\[
\text{Sensor response (\%)} = \frac{[(\text{Ra}−\text{Rg})/\text{Ra}]}{100}\% \quad \ldots (4)
\]

Where

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

Fig. 1. Dimensions of grooves.
3. Results and Discussion

3.1. X-Ray Results

The result of X-ray diffraction which represent mixing ratio for precipitation films on Si substrates are shows in Figs.(2, 3). In Fig.2 the XRD patterns result of Sn_{0.5}:Zn_{0.5} salt mixed shows match with standard value in (JCPDS card No. 24-1470) for prepared Zn_{2}SnO_{4}, with polycrystalline film type with a cubic system oriented (311) at 100% was grown, no characteristic peaks for any other impurities were observed, suggesting sample have high purity. Lattice parameter was calculated \( a=8.666\,\text{Å} \). In Fig.3 the XRD patterns result of Sn_{0.5}:Cd_{0.5} salt mixed shows match with standard value in (JCPDS card No.34-0982) for Cd_{2}SnO_{4}, with polycrystalline film type also a cubic system oriented (311) at 100% was grown, no characteristic peaks for any other impurities were observed, suggesting sample have high purity. Lattice parameter was calculated \( a=9.088\,\text{Å} \).

<table>
<thead>
<tr>
<th>Table 1, Results data of XRD Zn_{2}SnO_{4}/ Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Comp.</td>
</tr>
<tr>
<td>Zn_{2}SnO_{4}</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Silicon</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 2, Results data of XRD Cd_{2}SnO_{4}/ Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Comp.</td>
</tr>
<tr>
<td>Cd_{2}SnO_{4}</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Silicon</td>
</tr>
</tbody>
</table>

Where
\( \theta \)_{ST}: Standard angle (degree)
\( \theta \)_{M}: Measured angle (degree)
I_{ST} %: Standard intensity of peaks (CPS)
I_{M} %: Measured intensity of peaks (CPS)
hkl: Miller indices
3.2. SEM Results

Figs. 4 and 5 show the results of Zn$_2$SnO$_4$ and Cd$_2$SnO$_4$ respectively. In Fig. 4 the surface of Zn$_2$SnO$_4$ shows monolithic structure contains some grain on top layer at a uniformly distributed that agree with what W.H. Zhang and W.D. Zhang found [16], The morphology of the grains was roughly spherical in shape[17]. In Fig. 5 it can seem that the surface of Cd$_2$SnO$_4$ contain cavities and craters that due to spraying droplets and process falling on the surface in circles after evaporation leave these craters that agree with V. Krishnakumar [18].

3.3 AFM Results

AFM is powerful technique to investigate the surface morphology at nano to microscale. The surfaces of the films are shown in Figs.(6,7) 2 and 3D of the surface, the roughness of Zn$_2$SnO$_4$ surface was 9.69nm while in the Cd$_2$SnO$_4$ surface was 13.41nm, This difference depending the nature of material. From AFM test also it can seem that Zn$_2$SnO$_4$ Avg. Diameter:100.44 nm and in Cd$_2$SnO$_4$ was Avg. Diameter:93.74 nm. As a technique spray pyrolysis regularity were clear on the top surface. However irregularities in the film surface (top view) from the spray technique, which benefited tremendously for the gas sensing properties [19].
3.4. Gas Sensitivity

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. For the investigation of the gas sensing properties of the oxide films, the optimum operation gas temperature should be fixed initially. Figs.(8,9) it can see that increasing the response of sensor by increased gas concentration on the one hand and un increased in response toward \( H_2S \) gas,Which resulted in change oxides consisting as it was see in AFM and SEM results. In the presence of \( H_2S \) in air the sample’s resistance decreases due to a Red/Ox process[20,21]:

\[
\begin{align*}
\text{b} \ H_2S_{(\text{gas})} + 3\text{O}^{-a}_{(\text{ads})} & \rightarrow \text{b} \ \text{SO}_2_{(\text{gas})} + \text{b} \ H_2O_{(\text{gas})} + 3\text{a} \ e^{-} \\
\end{align*}
\]

where:

\( H_2S_{(\text{gas})} \) : is the \( H_2S \) molecule in the gas phase,

\( \text{O}^{-a}_{(\text{ads})} \) : an atomic or molecular form of chemisorbed oxygen.

\( e^{-} \) : an electron release, that is injected into the conduction band of the semiconductor.

\( \text{SO}_2_{(\text{gas})}, \ H_2O_{(\text{gas})} \) : the molecular reaction products desorbed from the surface.

Hydrogen sulfide is a Bronsted acid, i.e. heterolytic cleavage of the (S- H) bond is quite easy, especially in the formation of new donor-acceptor bonds. An increase in \( H_2S \) adsorption on the surface of Tri metal oxides can be achieved with the introduction of modifiers that increase the electron-donor ability of surface basic centers (oxygen anions).

Growth of acidity of the \( \text{Zn}_2\text{SnO}_4 \) and \( \text{Cd}_2\text{SnO}_4 \) surface has the opposite effect causing difficulties for a heterolytic break of the (H-S) bond in the \( H_2S \) molecule and a decrease of the \( H_2S \) adsorption.

It can be observed that sensors of Tri metal oxides show response at the same operating temperature in the range from (10 – 500) ppmv, with the maximum response about 60% to 70.61% for \( \text{Zn}_2\text{SnO}_4 \) at(10) ppmv without grooves respectively, and for \( \text{Cd}_2\text{SnO}_4 \) the maximum response about 83% to 85.61% at(10) ppmv without grooves respectively.

For the change in electrical resistance of the metal oxide, there are numerous conceivable responses; the most generally acknowledged response that prompts changes in electrical resistance is the adsorption of gasses on the metal oxide surface. Adsorption is only a surface impact and smaller scale structured metal oxides have high surface to volume proportion, which upgrades this impact Metal oxide gas sensors enhance their affectability and reaction/recuperation time because of nanocrystalline nature of the material related.
Fundamentally, the changes are a result of the high surface region to volume proportion and littler crystallite size contrasted with ordinary microcrystalline materials[22].

4. Conclusion

1- Preparing gas sensor with two oxides form of (\(\text{Zn}_2\text{SnO}_4\), \(\text{Cd}_2\text{SnO}_4\)) on silicon substrates to detect \(\text{H}_2\text{S}\) gas at different concentrations.
2- Mixing Two types of salts used to fabricate two types of Tri metal oxide compounds with different responses toward \(\text{H}_2\text{S}\) gas at different concentrations.
3- Homogenous surface of thin films and crystalline structures; , and cubic for both tri oxides \(\text{Cd}_2\text{SnO}_4\) and \(\text{Zn}_2\text{SnO}_4\) respectively.
4- \(\text{Cd}_2\text{SnO}_4\) showed the highest response rate for all testing gases at the best possible time.

5. References


تصنيع و توصيف اكاسيد ثلاثية معينة بتقنية الرش الكيميائي الحراري كمتحسس غازي

فرهاد محمد عثمان*، آلاء علاء الدين**، نور محمد علي***

البريد الالكتروني:**
fmok4@yahoo.com
adr.alaa@yahoo.com
materialenginee38@yahoo.com

الخلاصة

في هذا البحث حضرت اكاسيد ثلاثية بطرية الرش الكيميائي الحراري السليتة من املاح (تترات الفسفور والزنك والكادميوم) بتركيز (0.1M) وينسب خطط وزنية 50:50 على قاعدة من السيليكون من النوع (n) باتجاه (111) (وجود ووجود الحروف بالأعداد الآتية: عرض 7.5μm، عمق 20μm، وضغط 0.1±0.05 μm). أستخدم الماء منباً بدرجة حرارة ترسب بلغت 550 ºC ± 5ºC ومسافة رش (15 cm) ككشف للغاز البتراكرز مختلفة. في الياء ودرجة حرارة العرق ودرجة المرتبة بالصناعات الغازية (10,50,100,500 ppmv) ثم تشخيص التحليل والهيدولوجيا سطح الأغشية المحضرة بواسطة أحساسات جودة الأشعة السينية. المجهر الإلكتروني الماسح ومجهز القوة الذري لها. أظهرت النتائج أن أغشية الأكاسيد المحضرة من الأملاح المستخدمة في وحدة الغازات تحسنت وجود الحروف على العلاج والتي تجعل من الكشف مماسياً للكشف التراكز القليل من غاز H2S الخطر في الصناعة الغازية.