Study of Some Properties of SnO₂ Thin Film

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ABSTRACT

In this paper thin films of Tin oxide SnO_2 was prepared by spray pyrolyess method on glass and pure silicon substrates at deposition temperature(300,400,500) C°, from Tin chloride at concentration(0.1 M) .

The films thickness were about 0.1 ± 0.02 µm and Atomization rate was about (1 nm/s).

The test was done on prepared film by XRD and optical microscopy addition to sensitivity to nitrous oxide gas at different test temperature (25, 50, 75,100) C°.

Result shows that the crystallization increased by increasing deposing temperature and the sensitivity increased by rising the gas concentration or temperature.

Keyword: SnO_2, thin film, gas sensor, spray pyrolyess, NO_2 gas, XRD.

دراسة بعض الخواص لغشاء Sno₂ الرقيق

الخلاصة

تم في هذا البحث تحضير اغشية من اوكسيد القصدير SnO_2 على قواعد من الزجاج و السليكون النقي بطريقة الرش الكيميائي الحراري و بدرجات حرارة ترسيب بلغت C° (300,400,500) لمادة كلوريد القصدير و بتركيز (0.1M) .

سمك الاغشية كان حوالي µm 0.02 ± 0.1 و معدل التذرية (1 nm/s) .

تم اجراء الفحوصات لهذه الاغشية المحضرة و منها XRD و التصوير المجهري بالاضافة الى الحساسية لغاز اوكسيد النتروز NO_2 عند درجات حرارية اختبارية مختلفة (25,50,75,100 C°).

أظهرت النتائج زيادة في التبلور مع زيادة درجة حرارة الترسيب (درجة حرارة القواعد)علاوة على زيادة الكشفية مع زيادة تركيز الغاز و درجة الحرارة.

INTRODUCTION

It is noticeable wide variety in applications of SnO_2 thin film like; flat panel display, opto-electronic applications photovoltaic solar cells, gas sensor etc [1, 2]. It is also recognized that semiconductors layered films technology, in reducing production costs, should rapidly expand high-scale commercialization.

Despite the excellent achievements made with the earliest used materials, it is also predicted that other materials may, in the next few decades, have advantages over these front-runners. The factors that should be considered in developing new materials include: band gaps matching the solar spectrum, low-cost deposition/incorporation methods, abundance of the elements, non toxicity and environmental concerns. Transparent conducting oxides as ZnO, SnO_2 as well as doped oxides could be good alternative candidates.

SnO_2 films can be fabricated by means of a number of techniques such as sputtering, chemical vapor deposition (CVD), spray pyrolysis, thermal evaporation and sol gel [3].

Tin oxide was used as hydrogen gas and carbon monoxide sensor is desired to detect incomplete combustion, the early stages of fire [3, 4], Furthermore the ability to detect NO_2 and propane [5, 6].

The goals of this paper is to fabrication SnO_2 thin film by evaporation technique , and study some of their properties and sensitivity.

SnO_2-based gas sensors have been extensively used to analyse gases. Well known advantages include their low costs and high sensitivities; well known disadvantages concern their lack of stability and selectivity .In practical applications, several attempts are usually made to overcome their disadvantages, by, for example, using chromatographic columns to separate the components, by operating at different temperatures, by choosing different burning-in procedures, dopants, measuring frequencies, etc. .For common applications of pattern recognition (PARC) and multi-component

analysis (MCA) of gas mixtures, arrays of sensors are usually chosen which operate at constant temperature. In these cases a lack of selectivity and therefore overlapping sensitivities of different sensors is of advantage [7].

EXPERIMENTAL WORK

The work include steps;

The first step: preparation of SnO_2 film from an aqueous solution of Titanium chloride (SnCl4). The concentrations was (0. 1 M),the acidity was maintained to be 4-5 pH during spraying .The preparing of the thin film is made by spray pyrolysis technique. The spraying apparatus was manufactured locally in the university laboratories. In this technique, the prepared aqueous solutions were atomized by a special nozzle glass sprayer at heated collector glass fixed at thermostatic controlled hot plate heater.

Air was used as a carrier gas to atomize the spray with the help of an air blower. The substrate temperature was maintained at 300,400,500 °C during spraying.

Atomization rate was about(1 nm/s) with (0.5 ml/min) of flow rate. The distance between the collector and spray nozzle was kept at (5 cm.) The spray of the aqueous solution yields the following chemical reaction [6]:

$$SnCl_4\,(s) + O_2\,(g) \longrightarrow SnO_2 \downarrow + 2Cl_2\,(g) \uparrow \quad \dots \quad (1)$$

The second step: preparing specimens substrate with dimension(7.5*2*0.3 cm) for glass and (1*1 *0.2) cm³ for Si.

The third step: deposition of the thin film by spraying the solution on the surface of glass and pure Si and at three different temperatures (300,400,500°C).
The Forth step : is the measurement which include:
1-TiO$_2$ thickness was calculated from the relation below, and it was found to be about 0.1µm[7]:

$$t = \Delta m / \rho'.A \qquad\qquad ...(2)$$

Where Δm is the mass changes of the substrate before and after deposition ,ρ' is theoretical density of TiO$_2$ film and A is substrate area .
2- X-ray diffraction with diffractometer type CuKα ($\lambda = 1.5406$ Å), the scanning speed was 3%. .To determine the (a- lattice constant) from X-ray spectrum were using the following formulas were used [8]:

$$1/d^2 = [h^2 + k^2 + l^2] / a^2 \qquad\qquad ...(3)$$

3- Atomic Force Microscopy (AFM) of type (CSPM-AA3000, Angstrom Advanced Inc. USA) at the Nanotechnology and Advanced Materials Research Center / the University of Technology, can be used to characterize information on the structural morphology of the film.
4- The gas-sensing experiments were carried out by introducing the thus prepared devices into a home-made test cell, which was consist of beaker or cylinder with cover to restrict as in Figure (1) , the gas was obtained from reaction the acid and base solution to liberate the wet ammonia gas as explain in the following equation:

$$Cu + 4HNO_3 \longrightarrow Cu\,(NO_3)_2 + 2H_2O + 2NO_2\,(g) \uparrow$$
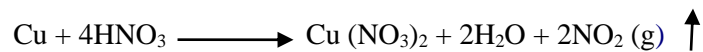
The ranges of the serial dilutions were (0.001-0.01) M, and mixer with same concentration of the base solution was fixed at 10ml, the same concentration of NO$_2$ gas was expected to be produced. The nitrous oxide NO$_2$ gas-sensing properties were determined at room temperature by measurement of the D.C. electrical conductive of the samples were exposed for various concentration of the NO$_2$ gas (10, 50,100ppm).
To evaluate the sensor sensitivity we used initial value ($\Delta R/R0$)[9].

RESULTS AND DISCUSSION
Showed the results of X-ray diffraction and clear increase in the values of the peaks with the increase in the deposition temperature because increasing regularity the structure and also a convergence with the standard values (ASTM card No. 33-1374) with cubic system, as we can see in Figure (2). Better crystallized when temperatures prepare 500 C^o, be more appropriate in terms of the peaks. Also lattice constant of SnO$_2$ is shown in Table (1), the stander value is 4.9255 A°.
Figure (3) shows the AFM image of the surface of the SnO$_2$ film deposited at 400C^o . This degree has been chosen heat among the degrees that have been deposition of in

order to be a clear idea of the topography of films when temperature their vicinity, Roughness average was(1.52 nm) and average diameter(31.01 nm) .

    Figure (4) shows the relation between gas concentration (ppm) and resistance R (Ω). We find in general form the resistance decrease with increasing concentration of nitrous oxide gas.

While in Figure (5) decreased the time required to respond with increase concentration. And Figure (6) Sensitivity of SnO_2 thin film increases with temperature testing, due to Increase the response with temperature [10, 11].

CONCLUSIONS

    Gas detector can be prepared from SnO_2 film on pure silicon and be acceptable sensitivity at room temperature and be appropriate for applications.

REFERENCES

[1]. Lee, B. , "Effect of process parameters on the characteristics of indium tin oxide thin film for flat panel display application", Thin Solid Films, Vol. 302, (1997)Issues 1–2.

[2]. Bauer, C.; Boschloo, G., Mukhtar, E. & HagfeldtA ,"New Guide to Thermally Optimized Doped Oxides Monolayer Spray-Grown Solar Cells: The Amlouk-Boubaker Optothermal Expansivity" , J. Phys. Chem., A., (2001). B 105.

[3]. Salehi, A. ,"Selectivity enhancement of indium-doped SnO2 gas sensors", Thin Solid Films ,Vol.416 (2002) .

[4]. Salehi, A., "A highly sensitive self heated SnO_2 carbon monoxide sensor", Sensors and Actuators B 96 (2003).

[5]. Madler, L., Roessler A., Pratsinis S., Sahmb T., Gurlo A. , Barsan N., Weimar U.,"Direct formation of highly porous gas-sensing films by in situ thermophoretic deposition of flame-made Pt/SnO2 nanoparticles", Sensors and Actuators B114 (2006).

[6]. Kim, K. and Chun J. ,"XRD study of SnO2 prepared by chemical vapour deposition", thin solid film ,Vol.141(1986) (1).

[7]. Hyodo, K., "Preparation of porous tin dioxide powder by ultrasonic spray pyrolysis and their application to sensor materials", Sensors and Actuators, B: Chemical, Vol.133,2008 (1).

[8]. Heili, A. ,"Gas identification by modulating temperatures of SnO_2-based thick film sensors", Sensors and Actuators B 43 (1997) .

[9]. Ueda, T., Katsuki S., Takahashi K., Narges H.A., Ikegami T., Mitsugi F., "Fabrication and characterization of carbon nanotube based high sensitive gas sensors operable at room temperature, Diamond & Related Materials vol.17(2) (2008).

[10]. Andio, M., Browning P., Morris P. A., " Akbar Comparison of gas sensor performance of SnO_2 nano-structures on microhotplate platforms", Sensors and Actuators B: Chemical,Vol.165,(2012) Issue 1.

[11]. Zhou, Li Z, Y.," Versatile nanobead-scaffolded N-SnO₂ mesoporous microspheres: one-step synthesis and superb performance in dye-sensitized solar cell, gas sensor, and photocatalytic degradation of dye", J. of Materials Chemistry A ,Issue 3, (2013).

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Table (1) Lattice constant of SnO₂.

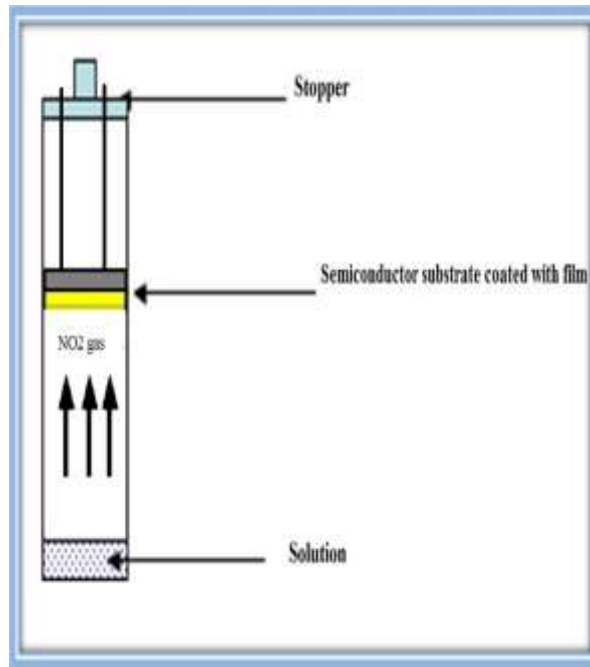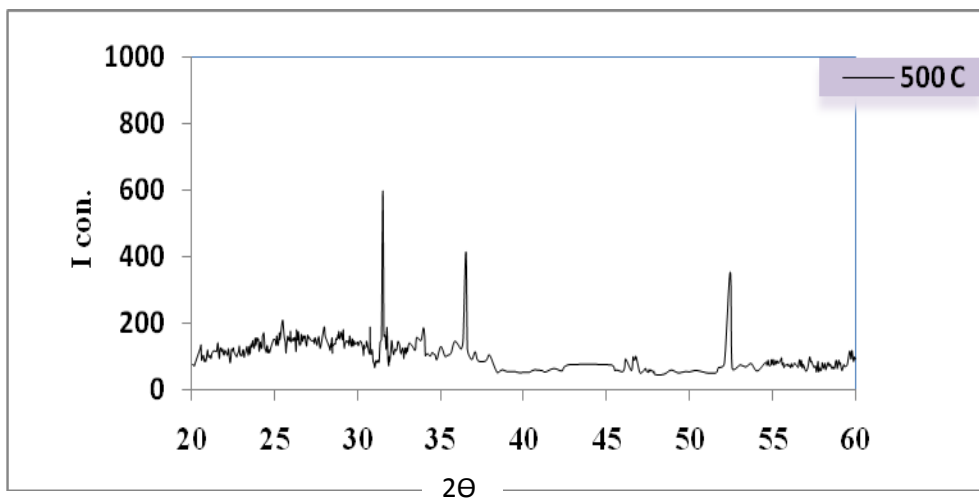| Temp. C°	a A°
300	4.9304
400	4.9274
500	4.9167

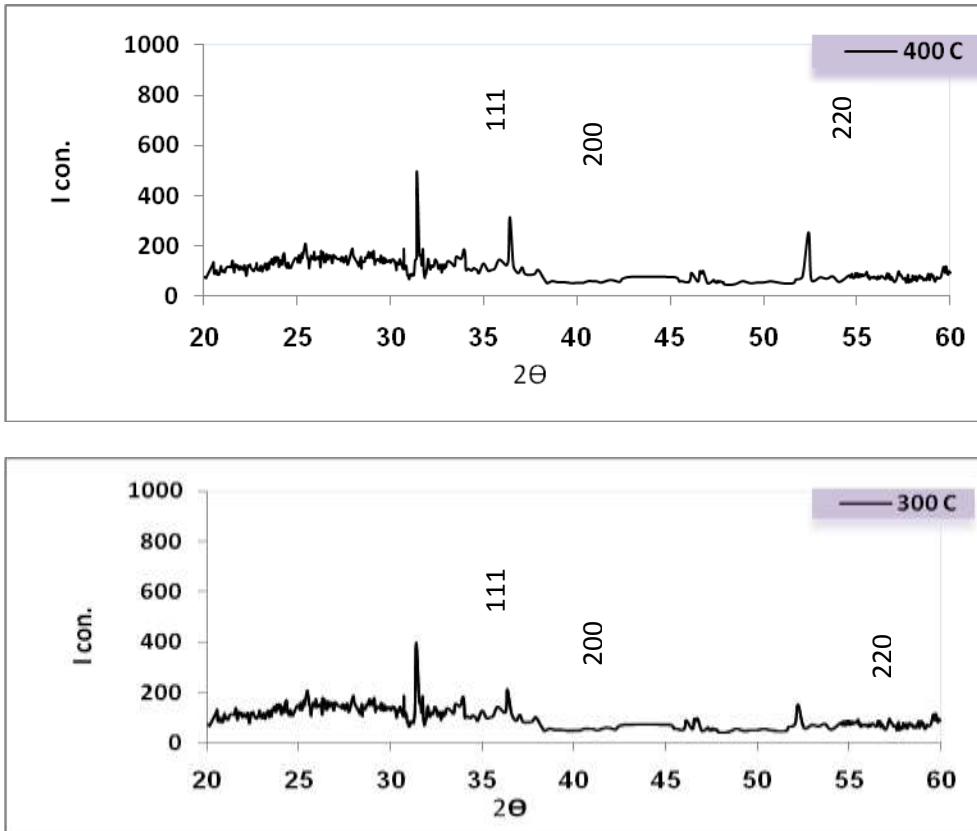**Figure (1) D.C. electrical conductive.**

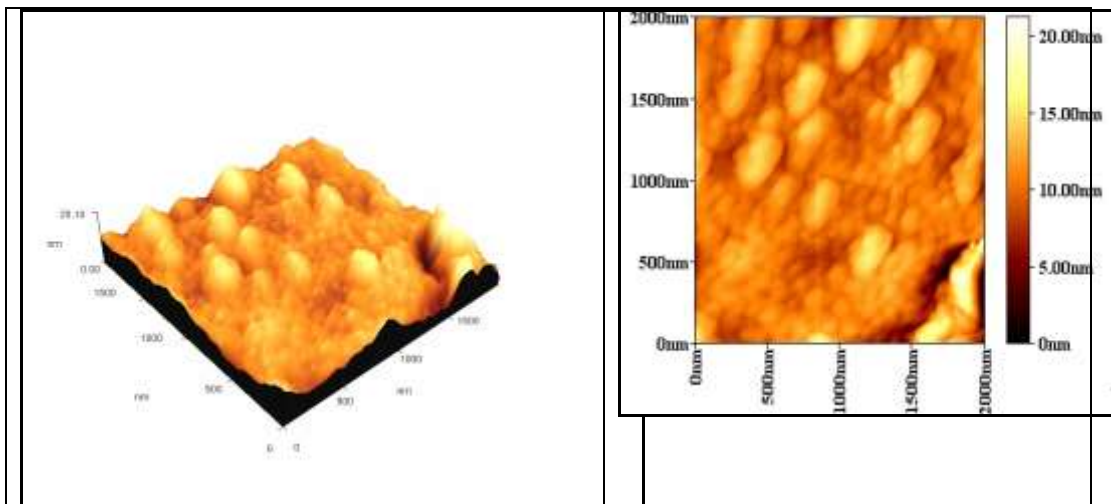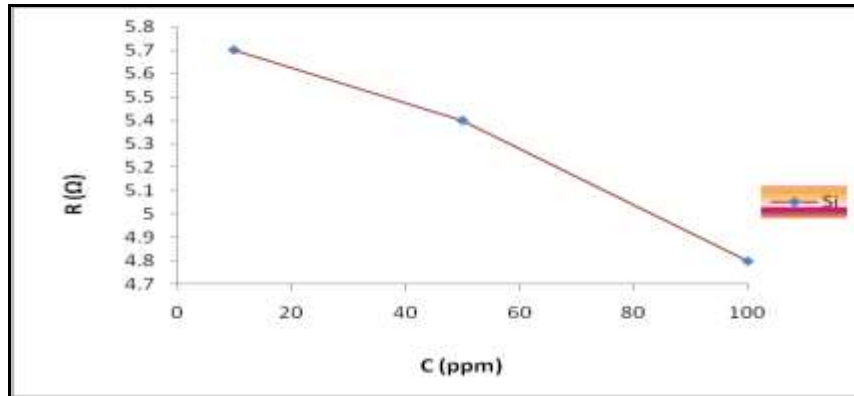**Figure (2) XRD result of SnO₂ thin film.**

Figure (3) AFM result of SnO₂ thin film.

Figure (4) Resistance of SnO₂ thin film.

| **Figure(5) Time respond of SnO₂ thin film.** | **Figure(6)Sensitivity of SnO₂ thin film.** |