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Fabrication of Highly Sensitive NH3 Sensor Based on Mixed $In_2O_3 – Ag_xO$ Nanostructural Thin Films Deposited on Porous Silicon

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ABSTRACT

A highly sensitive NH_3 gas sensor of mixed $In_2O_3 – Ag_xO$ nanostructure thin films deposited on porous silicon were synthesized by chemical spray pyrolysis technique. The structure of the sensor thin films is analyzed by XRD, AFM and FE-SEM techniques. The nanostructure polycrystalline thin films with average grain size between (93.56 and 57.75) nm, from AFM results. The sensitivity of the synthesized gas sensors toward 400 ppm NH_3 is obtained a high value in the low operating temperature, which ranged between (77.57%-98.66%) with low response and recovery times, ranged between (11.9-15.19) s and (8.6-25.22) s respectively. These high sensor properties are due to the porous silicon substrate.

1. Introduction:

Metal oxide semiconductors (MOS) were used in different applications such as photoelectronics and gas sensors [1-3]. To improve the MOS sensor properties, it is mixed with a metal or metal oxide of the same or different conductivity type [1, 3-5]. The nanostructural mixed metal oxides can fabricate a p-n heterojunction, which modifies the sensor surface to improve the gas adsorption at low operating temperature, then increases the sensitivity. In_2O_3 is n-type semiconductor with energy gap of 3.7 eV [6] while the Ag_xO is p-type semiconductor with energy gap ranged between (1.2-3.4 eV) [7]. When they are mixed with different Ag_xO ratio, the n-type conductivity change to p-type conductivity [6]. The sensor properties depend on many factors such as type of conductivity, nature of the substrate and grain size of MOS, etc. [4, 6, 8]. It is found that the porous silicon substrate surface increases the sensitivity and selectivity of gas sensors [1, 8], due to the effect of the surface electric charge which increases the gas interaction with the surface [3, 4, 6, 9, 10]. The detection of NH_3 which is a toxic gas, is important due to its applications in large area, such as chemical technology, medical diagnosis and refrigeration systems, etc. There are many studies on the NH_3 detection [11, 12], but the room temperature NH_3 sensors are necessary to syntheses. A few work has been carried out on $In_2O_3 – Ag_xO$ nanostructural gas sensor [9, 10]. In this study the gas sensor of mixed nanostructure $In_2O_3 – Ag_xO$ thin films deposited on porous silicon slides toward NH_3 gas are studied in order to increases the selectivity and decreases of the operating temperature of the synthesized gas sensors.

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2. Experimental Details:

Thin films of $In_2O_3 –Ag_xO$ nanostructure are deposited on porous silicon substrates by chemical spray pyrolysis technique at 400̊ C. P-type (111) oriented of porous silicon wafer formed by

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electrochemical method at 20 mA current and 25 min time used as a substrate. Thin films of pure indium oxide which mixed with silver oxide are prepared from $InCl_3$ and $AgNO_3$ aqueous solutions of (0.005 M).

The films are deposited at different mixed ratio (0%, 5%, 10%, 15%, 20%) of $AgNO_3$ solution. Deposition rate is (3 ml/min), and the period time of spraying is (5 s) with (30 s) wait alternately. Using XRD (Philips PW 1050 Å Target: Cu-Kα, Current: 20 mA, Voltage: 40 KV, Wavelength 1.541874 Å) to determine the grain size and the structural characteristics of the prepared thin films on glass. AFM (SPM-AA3000 Angstrom Advanced Inc) is used to determine the topography of the prepared thin films. FE-SEM (Leo Supra 50 VP Field Emission SEM) is used to examine selected experimental thin film of 15% Ag_xO. The sensitivity of the prepared thin films is calculated from the change of electrical resistance with operating temperature and different mixed ratio toward (400 ppm) NH_3 gas sensor.

3. Results and Discussion:

3.1. Structural properties:

The XRD pattern of nanostructure pure In_2O_3 and mixed with silver oxide of (5, 10, 15, 20) Vol % ratio, thin films deposited on glass substrate are shown in figure (1). The pattern shows a polycrystalline nanostructure of films with cubic In_2O_3 of plans (211), (222), (400), (440) and (541) according to the card no. (44-1087), with preferential plane of (222) the result is in agreement with Saryia et al [13]. The crystal size is calculated from Debye – Scherrer relation [14], the average crystalline size for In_2O_3 equal to (17.37 nm). When mixing Ag_xO with In_2O_3 the peaks do not change but their intensity are increased, that means the In_2O_3 crystallinity increased after mixing the Ag_xO with it, as shown in Fig. 1. Silver oxide gives many component oxides as monoclinic AgO with plane (310), Ag_2O_2 with plane (200) and orthorhombic Ag_3O_4 with plane (400) according to the card no. (43-1038, 22-0472 and 40-0909) respectively. At 10% Ag_xO mixed ratio the hexagonal compound $InAg_3$ with plan (002) appears. The average crystalline size of the mixed films increased from (19.01 nm) for 5% mixed ratio to (23.81 nm) for 10%, then decreased to (17.91 nm) for 20% ratio. The presence of the two phases Ag_xO and In_2O_3 in films refer to find the composite nature [9]. The results of XRD are in agreement with another authors results [3, 9, 15].

Fig. 2 shows the AFM image in two and three dimensions for the nanostructural thin films of pure In_2O_3 and mixed Ag_xO deposited on a porous silicon substrate to determine the surface topography of the prepared films.

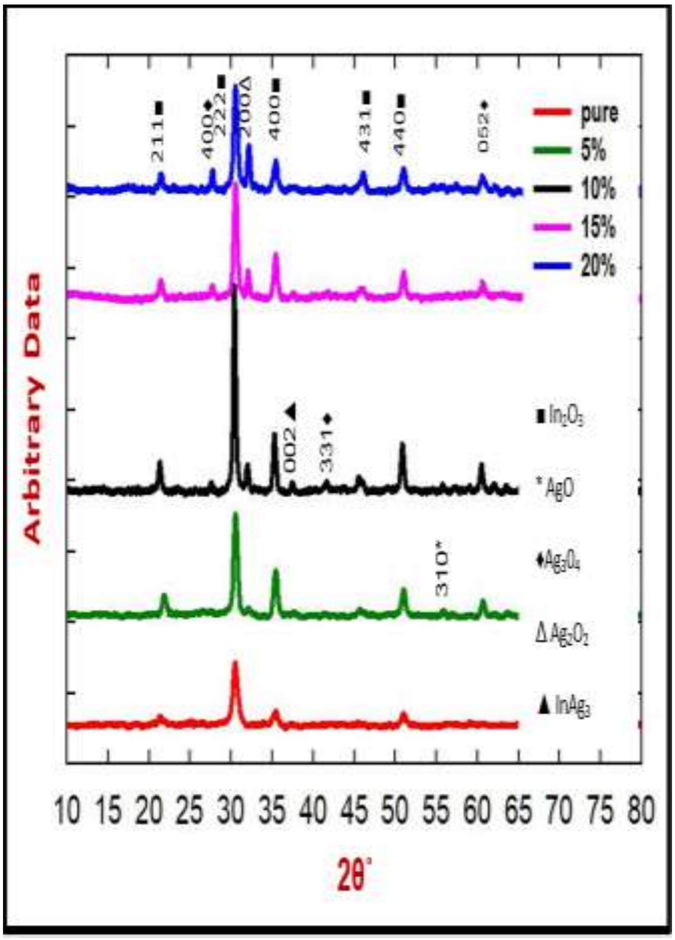


Fig. 1: The XRD patterns of mixed $In_2O_3 – Ag_xO$ thin films deposition on glass substrate.

Pure In_2O_3 surface shows its homogeneous and large grains as shown in Fig. 2, which is due to the aggregation of In_2O_3 grains because the nucleate centers which has created porous silicon. The average grain size of In_2O_3 (93.56 nm), roughness (3.23 nm) and RMS (4.25 nm) as shown in table (2). After mixing with Ag_xO the structure becomes composite, that causes the decrease of the grain size, roughness and RMS, this decrease continues until 15% mixed ratio of Ag_xO to reach (57.75 nm). The shape of grains becomes a mixture between sphericity and elliptical shape for three first mixed ratios as shown in Fig (2). The grain size of 20% ratio increased to (85.3 nm), the roughness and RMS are increased to become (3.89 nm), (4.5 nm) respectively, as shown in table (1).

The Film of 15% Ag_xO mixed ratio deposition on porous silicon wafer is examined by FE-SEM as shown in Fig. 3.

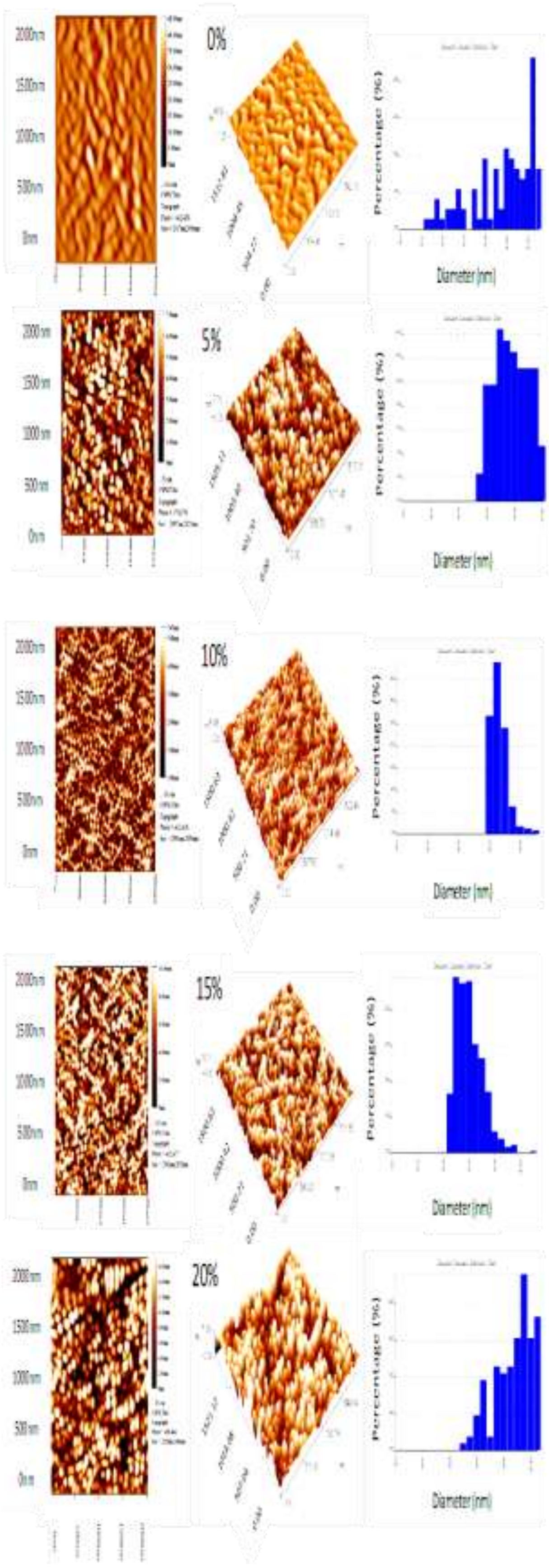


Fig. 2: AFM images of $In_2O_3 – Ag_xO$ thin films at different mixed ratio deposition on porous silicon substrate.

Table 2: AFM measurements of prepared In_2O_3 – Ag_xO thin films deposition on porous silicon substrate.

Mixed ratio %	Roughness Average (nm)	Root mean square (nm)	Average grain size (nm)
0	3.23	4.25	93.56
5	1.46	1.74	75.83
10	1.06	1.21	63.96
15	2.25	2.65	57.75
20	3.89	4.58	85.30

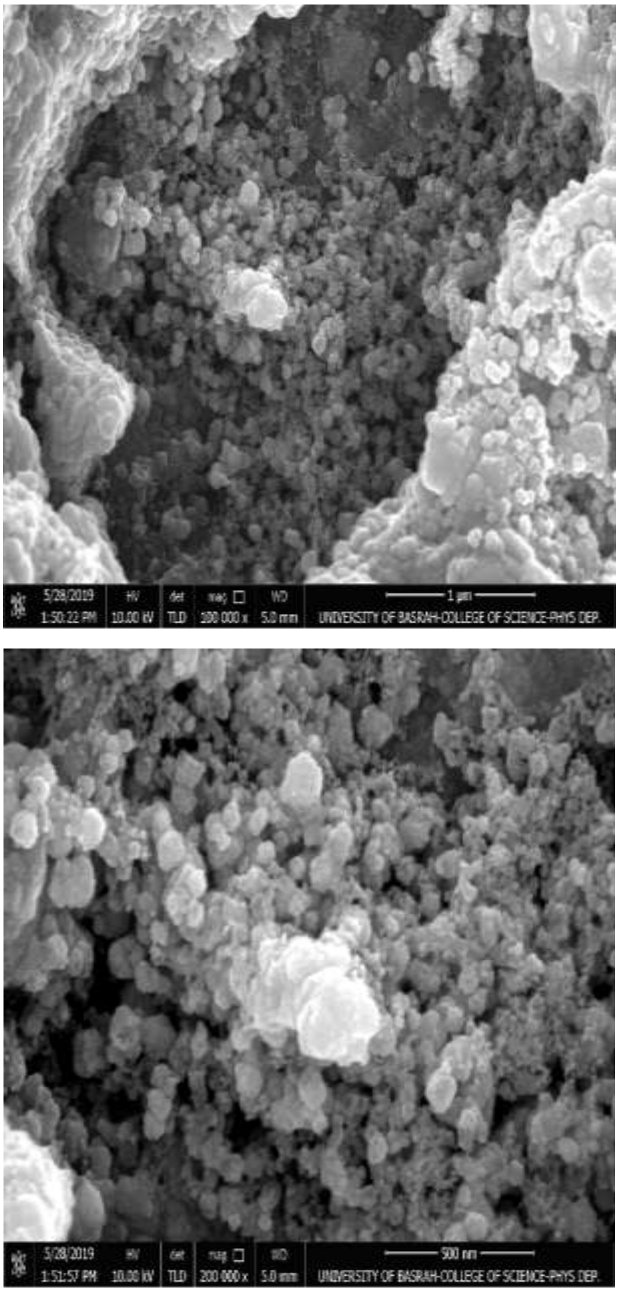
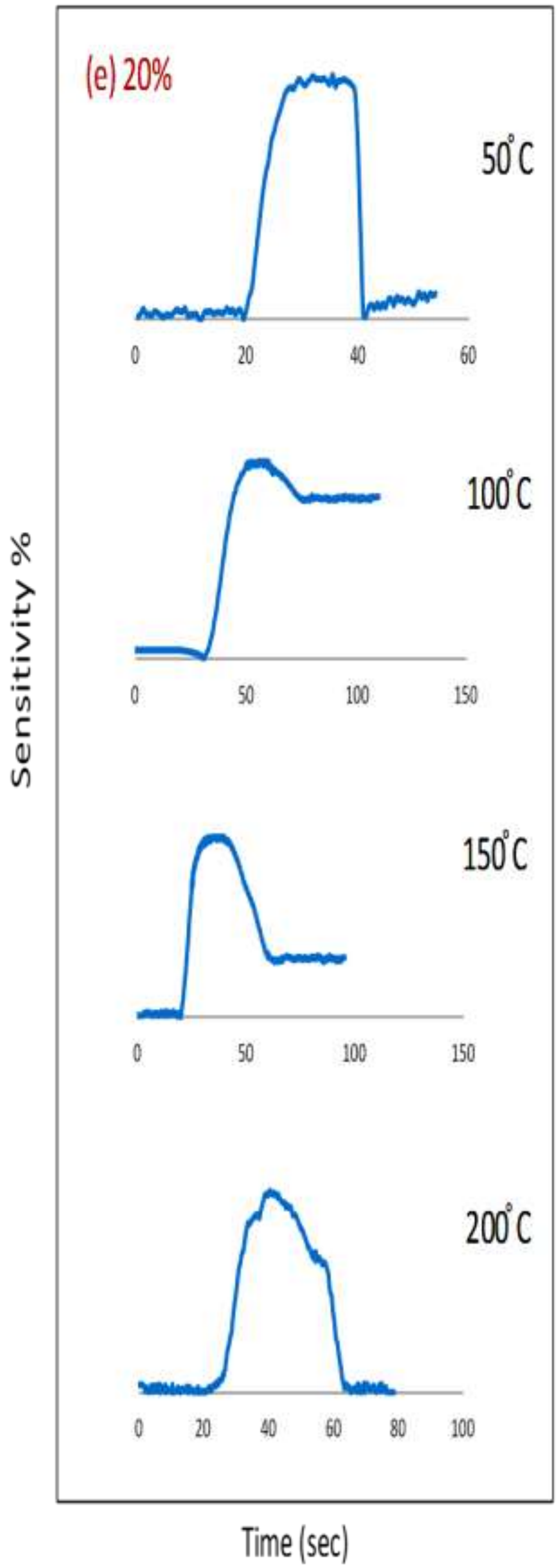


Fig. 3: FE-SEM images of In_2O_3 – Ag_xO thin films at 15% mixed ratio on porous silicon substrate.

3.2. Gas Sensing properties:

Fig. 4 shows the response of In_2O_3 – Ag_xO nanostructural thin films to (400 ppm) NH_3 gas with different mixed ratios of Ag_xO (0%, 5%, 10%, 15%, 20%) deposited on porous silicon substrate. The sensor shows a high sensitivity at all operating temperatures with sensitivity values ranged between (94.6-98), that results from porous silicon effect. Deposition of In_2O_3 on porous silicon surface creates p-n junction which increases sensor response to gas and decreases response time and recoery time, as shown in table (3). It shows that the effect of operating temperature is not clearly effect on the sensitivity values, that means the sensor doesn't need activation energy in the intraction between the gas and the surface. Which is physisorption interaction is ocure. The highest sensitivity value for the prepared sensor is (96.18) for 5% mixed ratio at (150° C). After increasing the operating temperature to (200° C) for the same ratio, desorption happened for gas and its component so the sensitivity decreased. The sensitivity value of all mixed ratios are very high with different operating temperatre, as shown in Fig. 5.



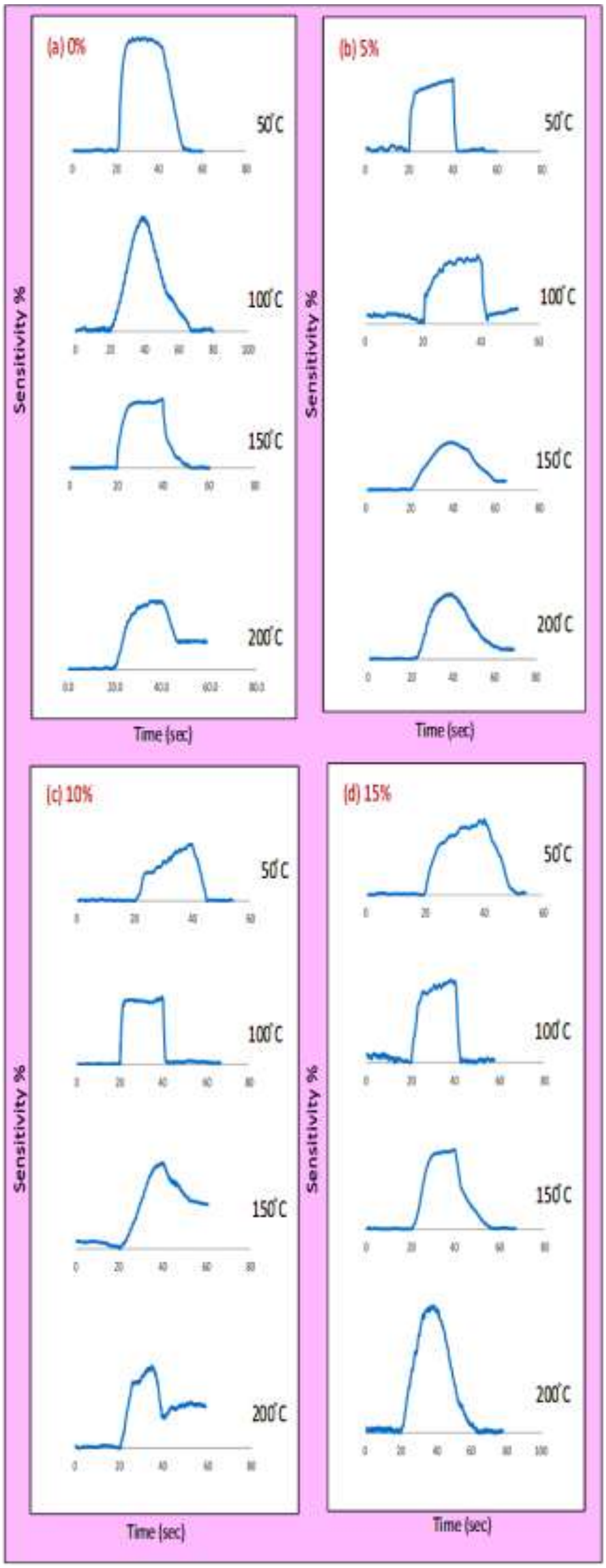


Fig. 4: Response of $In_2O_3 – Ag_xO$ thin films deposited on porous silicon substrate toward 400 ppm NH_3 gas.

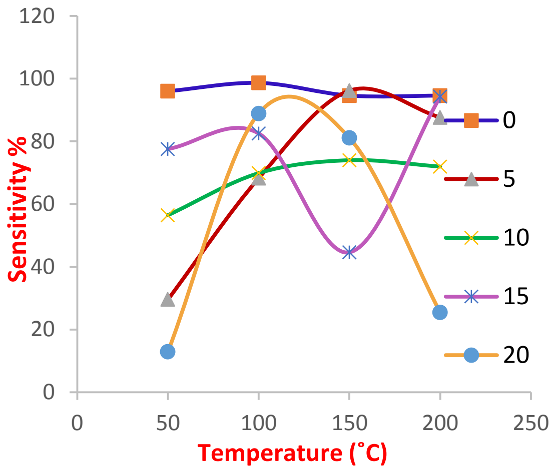


Fig. 5: Sensitivity versus temperature for In_2O_3 – Ag_xO sensors at different Ag_xO concentration on porous silicon.

Table 3: The sensitivity, response time and recovery time of the prepared sensors toward 400 ppm NH_3 with different Ag_xO concentration and at different operating temperatures.

Mixed ratio %	Temp. ℃	Sensitivity %	Response Time (sec)	Recovery Time (sec)
0	50	96	4	9.9
	100	98.66	15.29	25.22
	150	94.61	5.2	8
	200	94.59	4.53	5.7
5	50	29.56	8.9	1.4
	100	68.23	7.53	2.14
	150	96.18	14.1	18.1
	200	87.63	13	18.2
10	50	56.46	15.29	4.68
	100	69.88	1.7	1
	150	74.00	15.4	12
	200	71.96	10.8	2.9
15	50	77.57	11.9	8.6
	100	82.54	10	2.1
	150	44.62	9.1	12.6
	200	94.23	11.8	20
20	50	12.89	6.4	0.9
	100	88.90	13.4	13.6
	150	81.09	7.2	18.2
	200	25.42	16.3	22.3

4. Conclusion:

Gas sensor of mixed In_2O_3 – Ag_xO nanostructure thin films are deposited on porous silicon for gas detection. AFM analysis obtaind that the grain size depend on the Ag_xO consentration. The porous silicon substrate enhances the sensing properties to give very high sensitivity at low temperature with low respose time and recovery time. The sensitivity of In_2O_3 is not affected by operating temperature, due to the active p-n junction which formed between n-In_2O_3 and p- PsSi, to give a very high sensitivity of (98.66), while the sensitivity of the mixed sensor depends on the operating temperature due to the change of the conductivity of the mixed films from n-type to p-type to form p-p junction with porous silicon which is less active junction.

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تصنيع متحسس عالي التحسسية لغاز NH_3 من أغشية رقيقة ذات تركيب نانوي لخليط من أوكسيد الأنديوم وأوكسيد الفضة على السليكون المسامي

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الخلاصة

تم تصنيع متحسس غاز ذو حساسية عالية لغاز NH_3 من أغشية رقيقة ذات تركيب نانوي لخليط من In_2O_3 وAg_xO مرسب على قواعد من السليكون المسامي بطريقة التحلل الكيميائي الحراري. إن تركيب الأغشية الرقيقة للمتحسس فحصت بتقنيات XRD وAFM وFE-SEM. لقد وجد أن التركيب النانوي للغشاء متعدد البلورات ذات شكل قضبان نانوية بمعدل حجم حبيبي يتراوح بين (57.75-93.56 nm) من خلال نتائج فحص مجهر القوة الذرية AFM. المجهر الإلكتروني الماسح فائق الدقة FE-SEM يبين بأن الغشاء ذو تركيب نانوي وبمعدل حجم حبيبي يساوي (35 nm). إن تحسسية المتحسسات المصنعة تجاه غاز NH_3 بتركيز 400 ppm أظهرت قيم عالية وبدرجات حرارة تشغيل واطئة والتي تراوحت بين (77.57-98.66) وبأزمان استجابة واسترجاع واطئة تراوحت بين (11.9-15.19 s) و(8.6-25.22 s) على التوالي. إن خصائص المتحسس العالية تعود الى تأثير قاعدة السليكون المسامي.

الكلمات المفتاحية: متحسس غاز الأمونيا NH_3، خليط $In_2O_3 - Ag_xO$، الأغشية الرقيقة، السليكون المسامي، التراكيب النانوي.