Preparation and Characterization of Mixed In$_2$O$_3$–Ag$_x$O Nanostructure Thin Films on porous silicon as NH$_3$ High Gas Sensor

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Abstract. Mixed nanostructured thin films composed of In$_2$O$_3$ – Ag$_x$O, were synthesized on glass and porous silicon to produce NH$_3$-gas sensor. The films’ structure of the sensor was analyzed by XRD and AFM. The results obtained that polycrystalline nanostructure thin films were prepared. The optical properties indicate that the transmission and the energy gap were decreased with the increase in Ag$_x$O ratio. The sensor conductivity changed from n-type for In$_2$O$_3$ up to 10 Vol% Ag$_x$O to p-type with mixed oxides. The synthesis gas sensor gives sensitivity toward 40 ppm NH$_3$ gas at different temperatures (50, 100, 150 and 200) °C. The maximum sensitivity of mixed films on porous silicon for 15% Ag$_x$O ratio is 94.13% with a response time of 11.85 s and a recovery time of 20 s. Porous silicon improves the sensitivity of the prepared sensor by a factor of two with respect to the sensor over the glass. The good sensor properties of In$_2$O$_3$ – Ag$_x$O nanostructure mixed oxide at a low temperature indicated as highly efficient NH$_3$ gas sensor.

Keywords: In$_2$O$_3$-Ag$_x$O thin films, NH$_3$ gas sensor, nanostructure, mixed oxides, Porous Silicon.

1. Introduction
Thin films of transparent conducting oxide (TCO) were used in many applications such as optoelectronics and gas sensors [1, 2]. The wide band gap of TCO gives transparency to the spectrum of the visible region, while the conductivity is due to the oxygen vacancies. The n-type or p-type TCO is used in gas sensor applications with attractive properties [1, 3, 4]. The doping of transparent conductor oxide with metal or metal oxide of the same conductivity or with different conductivity enhances the sensor properties [3-5]. The nanostructure materials are unique with useful properties for the gas sensor which gives a large surface area to the volume [6], for this reason, many researchers were given high attention for it. The energy gap of an n-type In$_2$O$_3$ is 3.7 eV [7], while the p-type Ag$_x$O has energy of (1.2-3.4 eV) [8]. The mixed of these two oxides have exhibited a new composite with conductivity changed from n-type to p-type depending on the Ag$_x$O ratio [7], also the addition of Ag metal to the In$_2$O$_3$ is given suitable properties for gas sensor applications [1, 9-11]. Also adding silver oxide to indium oxide make narrowing of its energy gap, which contributes in the gas sensing properties enhancement comparing with the pure indium oxide [12]. Porous silicon is an interesting material because it has 3D-structure, where it is very important for the attractive energy of sensors [13]. Also, porous silicon can affect the surface phase composition due to the storage and the time of the storage of pure-Si [14]. Therefore, the use of porous silicon as a substrate for the gas sensor is very interesting material. The objective of the present study is to investigate the dependence of structural, optical and NH$_3$ gas sensing properties on the nanostructure films of mixed In$_2$O$_3$ – Ag$_x$O layers.
deposited on glass and on porous silicon, to understand the effect of mixed oxides and porous silicon on the NH$_3$ sensing properties.

2. Experimental Details
Nanostructure of In$_2$O$_3$ – Ag$_2$O thin films was deposited by chemical spray pyrolysis on glass and on porous silicon slides at 400°C. An electrochemical method is used to form a porous silicon layer on a p-type (111) oriented with 20 mA current and time of 25 min. Single In$_2$O$_3$ and mixed with Ag$_2$O thin films prepared from (0.005 M) aqueous solutions of InCl$_3$ and AgNO$_3$ with a ratio of (0, 10, 15) Vol % of AgNO$_3$ solution. The time period of spraying was (5 s) followed by (30 s) wait intervals at 3 ml/min deposition rate. Structure and the grain size of the prepared thin films were determined by the XRD technique (Philips PW 1050 Å Target: Cu-K$_\alpha$, Current: 20 mA, Voltage: 40 KV, Wavelength 1.541874 Å). The surface topography and roughness of prepared thin films were determined by AFM (SPM-AA3000 Angstrom Advanced Inc). The optical transmission and energy gap of the films were examined by using (UV-Visible spectrophotometer sp-8001) in the range 300-1100 nm wavelength. The 40 ppm NH$_3$ gas sensing of the prepared sensor was calculated due to the change in electrical resistance with different mixed ratios and operating temperatures.

3. Results and Discussion
3.1. Structural properties
The XRD patterns of single In$_2$O$_3$ nanostructured thin film and mixed with silver oxide at different concentrations of (10, 15) Vol % are shown in Figure 1. The Figure obtained that the films are polycrystalline in structure with cubic In$_2$O$_3$ of plans (211), (222), (400) and (440) according to the card no. (44-1087), with a preferential plane of (222) which agreement with Saryia et al [15]. The average crystallite size according to Debye – Scherrer [16] of In$_2$O$_3$ equal to (13.11 nm) as shown in Table 1. The indium oxide peaks after mixed with silver oxide do not change their angle explicitly but increased their intensity, which means that increased the crystallinity of In$_2$O$_3$ with mixing by Ag$_2$O as shown in Figure 1. The silver oxide gives peaks related to the monoclinic AgO with a plane (310), AgO with a plane (200) and orthorhombic Ag$_5$O$_3$ with a plane (400) according to the card no. (43-1038 and 40-0909) respectively. Also, there is a hexagonal compound of InAg$_3$, with a plane (002) at a 10% silver oxide ratio. The crystallite size at the mixed film of 10 Vol % equal to (23.81 nm) and for 20% is (17.91 nm). The presence of two phases In$_2$O$_3$ and Ag$_2$O in the films confirms that a composite nature is found [9]. The XRD results are agreement with other results [9, 10, and 17]. The surface topography of nanostructure In$_2$O$_3$ thin films and of mixed with silver oxide is determined by AFM technique as shown in Figure 2. The image of the prepared thin films in two and three dimensions obtained that the surface of In$_2$O$_3$ film is rough. This means that the crystals’ growth is vertical to the surface with long grains [18]. The average roughness of In$_2$O$_3$ film is equal to (29.0 nm) and the root mean square roughness (RMS) is equal to (33.5 nm), while the average grain size is (65.62 nm), as shown in Table 2. The rough film exhibits a high surface area, which enhances the gas sensor properties. The mixed silver oxide with indium oxide by 10% decreases the grain size to (47.12 nm) as shown in Figure 2 and Table 2. Also, the roughness and the RMS values are decreased to (16.9 nm), (19.6 nm) respectively. The 10% ratio gives a good crystallinity and a good morphology as shown from XRD and AFM results. The increasing of Ag$_2$O ratio to 15% change grains shape to a spherical shape with a grain size of (54.15 nm) and average roughness of (19.2 nm), with RMS equal to (22.1 nm). These results agree with Raad et al [17] results. The decreasing of the average roughness of In$_2$O$_3$ by adding Ag$_2$O explained that the silver oxide makes a composite with In$_2$O$_3$ surface that decreases the vertical growth.

The mixed In$_2$O$_3$ – Ag$_2$O thin films, which deposited on porous silicon gives a very smooth surface compared with deposited on glass slides as shown in Figure 2 and Table 2. While the grain sizes are in the same range of the glass substrate. The value of roughness and of the RMS for 10% and 15% deposited on porous silicon are equal to (1.21 nm), (1.05 nm) and (2.13 nm), (2.35 nm) respectively.
Figure 1. The XRD patterns of mixed In2O3 – AgxO thin films.

Table 1. The XRD measurement for mixed In2O3 – AgxO thin films.

| Ag,O ratio % | 2theta (Exp.) | d_hkl Exp.(Å) | d_hkl Std.(Å) | FWHM (°) | G.S. (nm) | hkl | Syst. | phase |
|--------------|----------------|----------------|----------------|--------|---------|------|-------|-------|
| 0            | 21.44          | 4.143          | 4.134          | 0.7632 | 10.60   | 2 1 1 | Cubic | In2O3 |
|              | 30.49          | 2.931          | 2.923          | 0.6722 | 12.26   | 2 2 2 | Cubic | In2O3 |
|              | 35.36          | 2.537          | 2.532          | 0.6270 | 13.31   | 4 0 0 | Cubic | In2O3 |
|              | 51.00          | 1.790          | 1.790          | 0.5413 | 16.27   | 4 4 0 | Cubic | In2O3 |
|              | 21.30          | 4.170          | 4.134          | 0.3484 | 23.23   | 2 1 1 | Cubic | In2O3 |
|              | 27.57          | 3.235          | 3.221          | 0.2643 | 30.98   | 4 0 0 | Orthorhombic | Ag2O3 |
|              | 30.40          | 2.940          | 2.951          | 0.3514 | 23.45   |      | Cubic | In2O3 |
|              | 31.98          | 2.798          | 2.808          | 0.3502 | 23.62   | 200  | Monoclinic | AgO   |
|              | 35.27          | 2.544          | 2.532          | 0.3690 | 22.61   | 4 0 0 | Cubic | In2O3 |
|              | 37.46          | 2.400          | 2.395          | 0.2432 | 34.52   | 0 0 2 | Hexagonal | InAg3 |
|              | 41.59          | 2.171          | 2.180          | 0.4348 | 19.56   | 3 3 1 | Orthorhombic | Ag3O4 |
|              | 45.67          | 1.986          | 1.986          | 0.6551 | 13.17   | 431  | Rhombohedral | In2O3 |
| 10           | 50.84          | 1.795          | 1.796          | 0.3817 | 23.06   | 440  | Monoclinic | In2O3 |
|              | 60.48          | 1.530          | 1.531          | 0.3854 | 23.88   | 052  | Hexagonal | Ag3O4 |
|              | 21.43          | 4.145          | 4.071          | 0.3847 | 21.04   | 2 2 0 | Orthorhombic | Ag3O4 |
|              | 30.53          | 2.927          | 2.904          | 0.4026 | 20.47   | 222  | Monoclinic | In2O3 |
|              | 32.08          | 2.790          | 2.791          | 0.3039 | 27.22   | 200  | Monoclinic | Ag2O2 |
|              | 35.41          | 2.534          | 2.532          | 0.4025 | 20.74   | 4 0 0 | Cubic | In2O3 |
|              | 45.86          | 1.978          | 1.985          | 0.6199 | 13.93   | 4 3 1 | cubic | In2O3 |
| 15           | 50.99          | 1.790          | 1.790          | 0.4392 | 20.06   | 440  | Cubic | In2O3 |
|              | 60.62          | 1.527          | 1.527          | 0.5190 | 17.75   | 0 5 2 | Monoclinic | Ag3O4 |
Table 2. XRD and AFM measurements of prepared In2O3 – AgxO thin films.

| AgxO ratio % | XRD | AFM |
|--------------|-----|-----|
|              | Average Crystalline size (nm) | Roughness Average (nm) | Root mean square (nm) | Average grain size (nm) |
| 0            | 13.11 | 29.0 | 33.5 | 65.62 |
| 10           | 23.81 | 16.9 | 19.6 | 49.12 |
| 15           | 20.17 | 19.2 | 22.1 | 54.15 |
| 10-Ps        | -     | 1.21 | 1.05 | 61.24 |
| 15-Ps        | -     | 2.13 | 2.35 | 52.3  |
3.2. Optical Properties

The transmission (T) and the optical absorption of nanostructure In$_2$O$_3$–Ag$_x$O thin films were studied by UV-vis spectrophotometer. Figure 3 shows a high transmission of thin films with different silver oxide ratios. The transmission increased with wavelength to reach a nearly constant value for each Ag$_x$O ratio in the visible region which ranged between 56% to 64% at 600 nm wavelength as shown in Table 3.

The direct band gap ($E_g$) of the prepared nano-thin films of In$_2$O$_3$–Ag$_x$O at different silver oxide ratios, was calculated as shown in Figure 4 and Table 3. The energy gap values decreased with the increase of silver oxide ratio from 3.5 eV for In$_2$O$_3$ to 3.2 eV for 15% Ag$_x$O thin film due to the mixing of In$_2$O$_3$ (3.5 eV) with Ag$_x$O of lower energy gap ranged between (1.2-3.4 eV) [8]. The transmission factor in the visible region and the energy gap values have an effect on the conductivity of the gas sensor due to the change of gas interaction with metal oxide semiconductor surface, which enhances the sensor properties.

![Figure 3. Optical transmission spectra of In$_2$O$_3$–Ag$_x$O thin films at different mixed ratio.](image1)

![Figure 4. $(\alpha^*h\nu)^2$ versus h\nu plot for In$_2$O$_3$–Ag$_x$O thin films at different mixed ratio.](image2)

| Ag$_x$O ratio | $E_g$ values (eV) | Transmission% at $\lambda$=600 nm |
|---------------|------------------|----------------------------------|
| %             |                  |                                  |
| 0             | 3.5              | 56                               |
| 10            | 3.26             | 58                               |
| 15            | 3.2              | 60                               |
3.3. Gas Sensing Properties
Gas sensing response of the nanostructure In$_2$O$_3$ – Ag$_x$O thin films with different silver oxide concentrations of (0, 10 and 15) Vol % on glass and porous silicon substrates toward 40 ppm NH$_3$ gas were studied. The sensitivity (S %) of the films with gas reaction time for different operating temperatures are showed in Figure 5. Also, the response time ($t_{res}$) and recovery time ($t_{rec}$) are determined in Figure 5. The maximum sensitivity value of In$_2$O$_3$ is increased with operating temperature range (50˚C-200˚C) to give the maximum value of 3.53% at 50˚C with $t_{res}$ and $t_{rec}$ of 2 s, 0.54 s respectively. While at mixed films of 10% Ag$_x$O, the sensitivity increased to 45.55% at 50˚C with $t_{res}$ and $t_{rec}$ 16 s and 0.68 s respectively. The maximum value of a mixed film of 15% Ag$_x$O is decreased to 23.27% at 50˚C with a fast response time and recovery time of 1.06 s and 1.25 s respectively. This result obtained that the mixed films of 10 Vol% Ag$_x$O give the best sensitivity compare with In$_2$O$_3$ films by about 14 times greater than a single film, and about 7 times for 15% mixed ratio. The increasing sensitivity for mixed oxides than for In$_2$O$_3$ single oxide is related to the p-n junction between In$_2$O$_3$ and Ag$_x$O, which produces an electron depleted layer leading to an increase in the sensor response [1]. The difference in the sensitivity value may be related to the conducting type of the mixed films, which are changed from n-type to a p-type as indicated from Hall Effect experiment Table 4. The interaction of NH$_3$ gas with n-type semiconductor different from with p-type semiconductor.

Table 4. Hall effect of 10% and 15% mixed ratio of In$_2$O$_3$ – Ag$_x$O thin films.

| Ag$_x$O ratio % | Conductivity type | Carrier concentration (N/cm$^3$) | Conductivity $\sigma$ (Ω.cm)$^{-1}$ | Mobility $\mu$ (m$^2$/Vs) |
|----------------|-----------------|-----------------|-----------------|-----------------|
| 10 n           | 1.39*10$^{13}$  | 1.5*10$^{-4}$   | 69              |
| 15 p           | 1.98*10$^{12}$  | 1.7*10$^{-4}$   | 536             |

Figure 6 obtained the sensitivity (S %) with the reaction time of the mixed nanostructure In$_2$O$_3$ and Ag$_x$O deposited on porous silicon with different operating temperatures. The sensitivity increased with increasing temperature to a value of 69.88% and 82.54% at an operating temperature of 100˚C for 10% and 15% concentration respectively. The value of S% for mixed oxide deposited on porous silicon is greater than that deposited on glasses by about 2-3 times.
Figure 5. The sensitivity (S %) with the reaction time of the mixed nanostructure In2O3 and AgxO deposited on glass substrate with different operating temperature.

The increasing of S% on porous silicon is due to the roughness of the porous silicon and the large internal surface area provides nucleation centers [19], which enhances the oxygen adsorption and then the sensing response [20]. The deposited mixed oxide In2O3 – AgxO thin films over porous silicon, has two interfaces are found, one between the metal oxide and the other between silicon and mixed oxide [21], these two interfaces make the surface of mixed oxide is more adsorption [21] for NH3 gas with high sensitivity in lower temperatures.

Figure 6. the sensitivity (S %) with the reaction time of the mixed nanostructure In2O3 and AgxO deposited on porous silicon with different operating temperature.
3.4. Gas Sensing Mechanism

The gas sensing mechanism of the gas sensor includes the resistance change due to the adsorption and desorption of gas molecules on the metal oxide semiconductor surface. The interaction of oxygen with the surface sensor was adsorbed as (O₂⁻, O, or O³⁻) by taking electrons from the sensor surface, which increases its resistance. When the reduced gas (NH₃) interacts with an n-type metal oxide, the gas is interacting with the adsorbed oxygen species. This interaction leads to release back electrons to the sensor surface as the following relation [22]:

\[ 4\text{NH}_3 + 3O_2^{(\text{ads})} \rightarrow 2\text{N}_2 + 6\text{H}_2\text{O} + 6e^- \]  \hspace{1cm} (3)

Related to decrease the sensor resistance, the mixed silver oxide with In₂O₃ induces compensation of the n-type carriers and by increasing Ag₂O concentration change the conductivity to p-type [1], makes p-n junction, defects, and vacancies in the films. These are enhancing the active sites for adsorption gases on the mixed metal oxide, also the nanostructure increases the amount of gas molecule adsorption. When the operating temperature increases, it leads to an increase in the desorption gas molecule from the surface which leads to a decrease the sensitivity of the sensor.

4. Conclusion

Nanostructure of In₂O₃ – Ag₂O thin films was deposited on glass and porous silicon substrates by chemical spray pyrolysis as NH₃ gas sensor. XRD and AFM technique obtained that mixed films have nanostructure with high roughness. The films give high optical transmission in the visible region and a direct band gap decreased with Ag₂O ratio. The mixed oxides sensor deposited on glass give high sensitivity of (45.55%), which greater than for single In₂O₃ sensor by about 14 times, while the mixed oxide sensors deposited on porous silicon give a maximum sensitivity of (94.23%), which greater than on glass by 2-3 times with low response and recovery times. The mixed In₂O₃ – Ag₂O oxides on glass and porous silicon enhances the sensor response toward NH₃ gas.

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