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Synthesis and characterization of silver oxide nanoparticles prepared by chemical bath deposition for NH3 gas sensing applications

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Abstract

Nano-silver oxide thin films with high sensitivity for NH_3 gas were deposited on glass substrates by the chemical bath deposition technique. The preparations were made under different values of pH and deposition time at 70^o C, using silver nitrate $AgNO_3$ and triethanolamine. XRD analysis showed that all thin films were polycrystalline with several peaks of silver oxides such as Ag_2O, AgO and Ag_3O_4, with an average crystallite size that ranged between 31.7 nm and 45.8 nm, depending on the deposition parameters. Atomic force microscope (AFM) technique illustrated that the films were homogenous with different surface roughness and the grain size ranged between 55.69 nm and 86.23 nm. The UV-Vis spectrophotometer showed that the optical direct energy gap ranged between 1.66 eV to 2.12 eV. The silver oxide thin film gives a high sensitivity of 70.12 for NH_3 gas at 75°C operating temperature. This study shows that different types of silver oxides can be prepared by the CBD techniques, with the nanostructure to be used in gas sensors and optoelectronic applications.

Keywords: Silver oxide Nano-particles, chemical bath deposition, NH_3 gas sensing, Structural properties.

تصنيع ودراسة خصائص أغشية نانوية لأوكسيد الفضة المحضرة بطريقة الترسيب بالغمر الكيميائي لتطبيق متحسس غاز NH_3

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الخلاصة

تم ترسيب أغشية أوكسيد الفضة النانوية على شرائح زجاجية بتقنية الترسيب بالغمر الكيميائي. حضرت الأغشية بدوال حامضية PH وبأزمان غمر متغيرة وبدرجة حرارة محلول تساوي C °70، باستخدام نترات الفضة ($AgNO_3$) و TEM (Triethanolamine). أظهر فحص الأشعة السينية للأغشية المحضرة بأنها من النوع متعدد التبلور وبعدة قمم تعود لعدة أنواع من أكاسيد الفضة Ag_2O, AgO and Ag_3O_4 وبمعدل حجم بلوري يتراوح بين 31.7 nm الى 45.8 nm بالأعتماد على معلمات الترسيب. تقنية مجهر القوة الذرية AFM بينت بأن الغشاء متجانس وبخشونة سطحية متغيرة وأن الحجم الحبيبي يتراوح بين 55.69 nm و86.23 nm. القياسات البصرية بمطياف UV-vis أظهرت بأن فجوة الطاقة البصرية تتدرج قيمتها بين 1.66 eV الى 2.12 eV. إن أغشية أوكسيد الفضة أعطت تحسسية عالية لغاز NH_3 بمقدار 70.12%

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بدرجة حرارة تشغيل 75° C. إن هذه الدراسة بينت أنه بالإمكان تحضير عدة أنواع من أكاسيد الفضة بطريقة الترسيب بالغمر الكيميائي وبتركيب نانوي لاستخدامها كمتحسسات غاز ولتطبيقات الإلكترونيات البصرية.

1- Introduction

Silver oxides are semiconductors of a band gap that ranges between 1.2 and 3.4 eV [1], depending on the stoichiometries and deposition techniques. Silver oxide materials are used as gas sensors because of their sensitivity toward gases, stability, non-toxicity, low-cost, and other properties [2-4]. Also, silver oxides can be used in optoelectronic applications [5-7]. The oxygen vacancies in the silver oxide play an important role in the mechanisms of conduction [8]. Thus, silver oxide thin films are regarded as a new set of transparent conducting oxide of P-type thin films. Ammonia is a toxic gas present in the atmosphere and in chemical laboratories, petrochemicals, etc. Recently, the use of ammonia gas sensors was investigated by many researchers [9-13]. The synthesis of silver oxide thin films can be achieved by various techniques [2, 14-16]. Among these techniques is the chemical bath deposition method [3, 14], which is the simplest way to deposit nanometal oxides thin films. The structural, morphological and optical properties of the deposited films can be controlled by varying the deposition time, pH of the solution, and temperature of the bath.

In this work, the chemical bath deposition method was used to deposit silver oxide thin films on a glass substrate at different pH and dipping time. Structural, optical and sensing properties were investigated.

2- Experimental Details

In this study, the used substrate is glass slide. Prior to deposition of silver oxide, the substrate was scratched using chromic acids with water (20%) for 24 hoursand washed with a detergent solution in an ultra-sonic system. Silver nitrate ($AgNO_3$) solid (0.0787 g) was dissolved in 5 mL of distilled water. Then, triethanolamine ($C_6H_{15}NO_3$), commonly known as TEM (the complexing agent), was added drop by drop with continuous stirring until the solution became colorless. The solution volume was completed to 40 mL with 0.01 M. The pH of the solution was increased by adding nitric acids dropwise. The glass slides were placed in the beaker vertically with a constant temperature bath of (70^{o} C), for different dipping times (25, 35 and 45 min) and different pH values(9, 10, 11). Then, the coated slides were removed from the bath, rinsed in a distilled water, and dried by hot air. The film thickness was determined by the optical interference method. The structure of the prepared thin films and the crystallite size were determined by XRD technique (Philips PW 1050 Å Target: Cu-Kα, Current: 20 mA, Voltage: 40 KV, Wavelength: 1.541874 Å). Topography and roughness of the surface of the deposited films were determined by atomic force microscope AFM (SPM-AA3000 Angstrom Advanced Inc). Optical properties of the prepared thin films were examined using UV-Visible spectrophotometer sp-8001 in the wavelength range of 300-1100 nm at normal incidence of light. The gas sensing of silver oxide films was calculated by measuring the change in electrical resistance toward 400 ppm NH_3 gas at different working temperatures and pH solution values. Table-1 shows the sample number and the deposition conditions for the prepared thin films.

Table 1-The sample number with preparation conditions of the prepared nano-silver oxide thin films at 70°C

Sample No.	PH value	Deposition Time (t min)	Thickness nm
1	9	35	298.7
2	10	35	248.9
3	11	35	211.6
4	10	25	261.4
5	10	45	323.6

3. Results and Discussion

3.1. Structural studies

The XRD patterns of nanocrystal silver oxides are shown in Figure-1. The films are polycrystalline with many peaks related to Ag_2O, AgO and Ag_3O_4 silver oxides. Ag_2O is a cubic structure of plane

200 and a hexagonal structure with plane (003), corresponds to the card No. 43-0997 and 42-0874, respectively. While AgO is of a monoclinic structure with plane 023 according to card No. 43-1038. The peak intensities of all oxides were increased at pH of 10 (sample 2) as well as with increasing the deposition time (sample 5), as shown in Fig. 1. This may be due to the silver oxide nucleation which has effects on the crystallinity. The average crystallite size was estimated using the Debye-Scherrer formula [7]:

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

Where λ is the wavelength of X-ray radiation, K is a dimensionless constant with a value of 0.9, often called the shape factor, 2θ is the diffraction angle in degrees, and β is the full width at half maximum (FWHM) of the diffraction peak. The average crystalline size ranged from 32.84 nm to 37.27 nm, as shown in Table-2.

Table 2- XRD and AFM measurements of the prepared silver oxide films

Sample No.	XRD	AFM		
	Crystallite size (nm)	Roughness Average (nm)	Roughness Root mean square (nm)	Average grain size (nm)
1	36.39	0.85	0.99	74.04
2	35.14	4.03	4.65	71.45
3	32.84	3.11	3.63	86.23
4	37.27	4.64	5.35	55.69
5	33.63	1.71	2.02	67.02

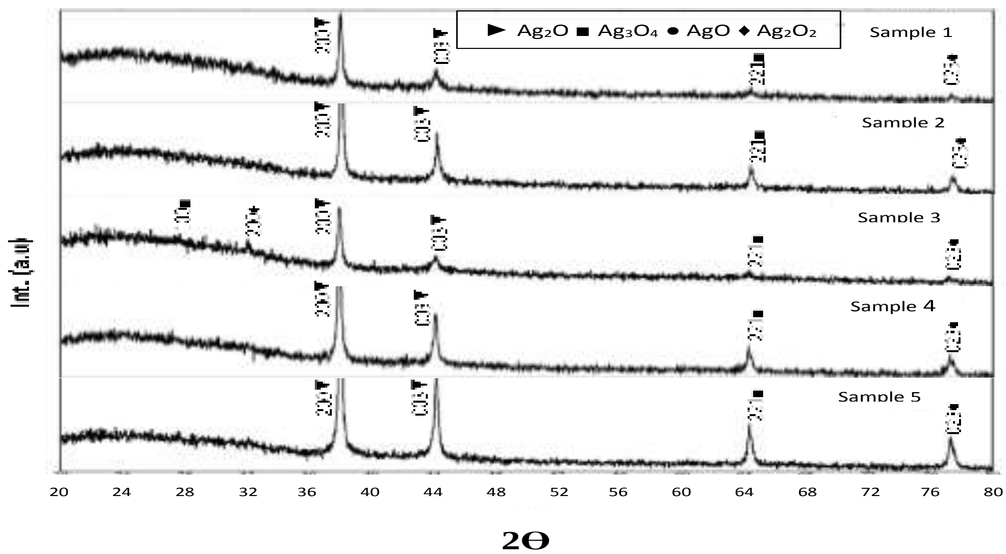

Figure 1-The XRD patterns of the deposited nano-silver oxide thin films.

The AFM images of the prepared nano-silver oxide and size distribution are shown in Figure-2. The roughness and the grain size of the film surface were dependent on the preparation parameters (PH and t). The values of grain size, average roughness and RMS roughness are shown in Table-2. The average grain size ranged between 55.69 nm and 86.23 nm depending on the deposition parameters. The roughness of the prepared nano-silver oxide thin films changed between rough and smooth, related to the kinetic of films growth. These rough and smooth films can be used in different applications. The rough film can be used in the gas sensors (sample 4) while the smooth film is used for example in the optoelectronic applications (sample 1).

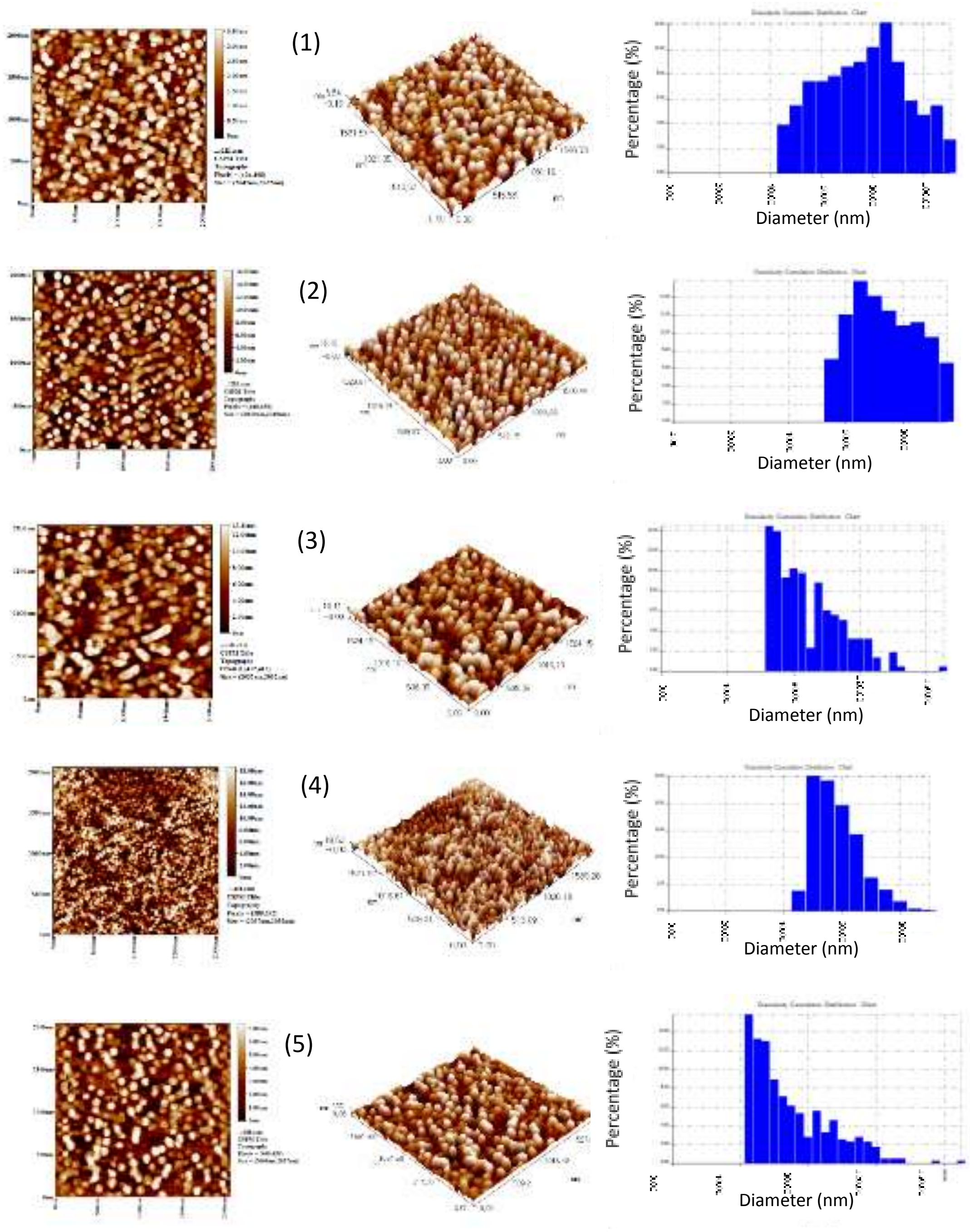

Figure 2-AFM images of silver oxide thin films at different preparation parameters.

3.2. Optical Studies

Figure-3 shows the optical transmission of the nano-silver oxide thin films prepared at different bath parameters. The transmission increased with the increase of bath temperature and pH values. The roughness of the surface film increases the interaction of electromagnetic radiation with film surface, while the reflectivity increases with the increase of surface smoothing. Hence, the film of higher roughness gives good transmission compared with the high smooth surface, as shown in Figure-3, due to the increase in grain size. This includes that, at higher pH, transmission thin films are obtained, which may be used as transparent conducting oxides [17]. The direct optical energy gap (E_g) was evaluated from the plot of $(\alpha h\nu)^2$ versus $h\nu$, as shown in Figure-4. The values of E_g for different preparation parameters are shown in Table-3. From this table, it can be observed that the energy gap value ranged between 1.66 eV and 2.08 eV, which denotes that the films are a mixture of silver oxides.

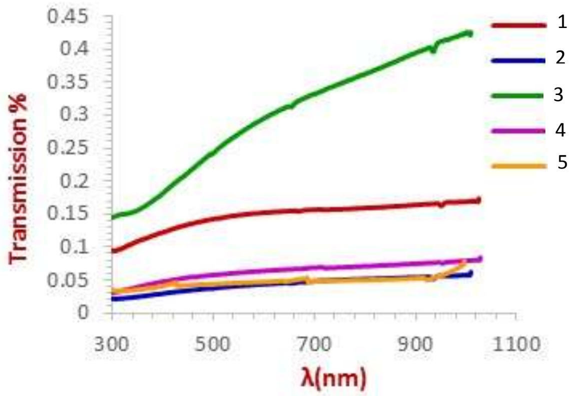

Figure 3- Optical transmission spectra of the prepared nano-silver oxide thin films at different preparation.

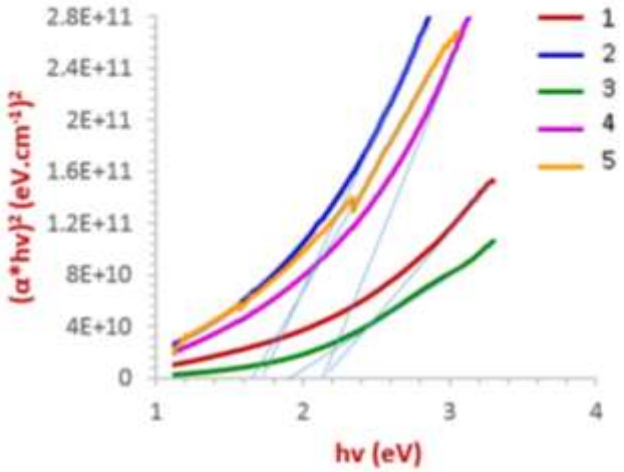

Figure 4-$(\alpha*h\nu)^2$ versus hv plot for the prepared silver oxide thin films at different preparation conditions.

Table 3-Values of energy gap of the prepared silver oxide thin films at different preparation condition

Sample No.	**Eg (eV)**
1	2.08
2	1.76
3	1.88
4	2.08
5	1.66

3.3. Gas Sensor Characteristics

The sensitivity (S%) of the prepared nano-silver oxide thin films toward 400 ppm of NH_3 gas were evaluated according to the relation:

$$S\% = \frac{R_a - R_g}{R_a} \times 100 \qquad \ldots\ldots\ldots\ldots (2)$$

where Ra and R_g are the resistance of the air and of the gas, respectively. Figure-5 shows the change of the sensitivity with time for the optimal response samples, due to the change of pH solution. The sensitivity, response time (t_{res}), and recovery time (t_{rec}) with the operating sensor temperature for all the prepared samples were determined, as shown in Table- 4. From Figure-5 and Table-4, it can be observed that the films did not sense toward 400 ppm NH_3 gas i at room temperature (25°C) . In contrast, the sensitivity increased or reached to the maximum value at 50°C. This means that the prepared sensors work at low temperatures with high sensitivity values. The change in the maximum sensitivity due to the change in pH of the solution is related to the effect of morphology, grain size and the thickness of each film. Since the sensitivity is a function of grain size, decreasing the grain size leads to an increase in the surface area, which provides more adsorption. Therefore, our prepared sensors exhibited an improved sensing performance. Wang et al. [18] showed that the high sensitivity of silver oxide gas sensor was due to the small grain size. Sample 2 exerted a low response time (0.91 sec) and a low recovery time (0.95 sec), which may be related to its good structural and optical properties.

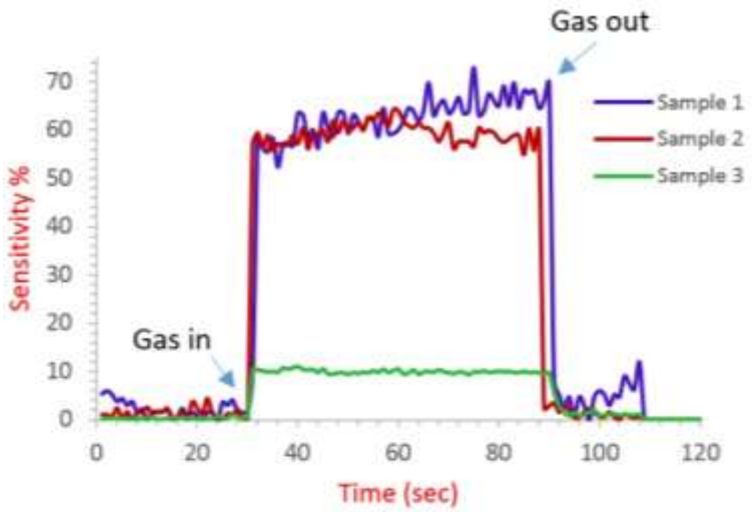

Figure 5-Sensitivity (S%) of the optimal silver oxide thin film with different operating time values toward 400 ppm NH_3 gas.

Table 4-Values of sensitivity, response time and recovery time with respect to temperature toward 400 ppm NH_3 gas

Sample	Temp. (°C)	Sensitivity (S%)	Response Time (sec)	Recovery Time (sec)
1	25	0.00	0.00	0.00
	50	6.61	1.75	0.95
	75	70.19	10.03	1.00
	100	7.95	1.80	1.60
2	25	0.00	0.00	0.00
	50	64.83	0.91	0.95
	75	10.20	12.00	2.07
	100	1.74	1.80	0.82
3	25	0.00	0.00	0.00
	50	11.89	8.50	1.40
	75	10.68	12.00	4.30
	100	0.40	2.49	10.00

The variation of sensitivity with various operating temperatures is demonstrated in Figure-6. From this figure, it is clear that sample 2 works at pH=10 and low temperature (50°C) with high sensitivity, while sample 3 which is prepared at pH=11 works with low sensitivity at 50°C. For this reason, the optimum bath conditions for the best gas sensor are pH=10, bath temperature of75°C, and dipping time of 35 min.

The sensing mechanisms involve the action of silver oxide in trapping oxygen in the form O^- or O^{-2} on the surface, which increases the resistivity of the oxide surface. When NH_3 gas interacts with the silver oxide surface or with the adsorbed oxygen electrons that are released to the oxide surface, the surface resistance increases, as follows [10].

$4NH_3 + 3O^-_{2\,(ads)} \rightarrow 2N_2 + 6H_2O + 6e^-$ .... (3)
$2NH_{3(ads)} + 3O^-_{(ads)} \rightarrow N_2 + 3H_2O + 3e^-$ .... (4)

The reaction needs activation energy to continue, which means that it requires heat provision. For this reason, the nano silver oxide does not show a response at room temperature, unless the temperature is increased. The maximum gas response is achieved when the actual thermal energy is given to the reaction. However, the response decreases at higher operating temperature, as the oxygen adsorbates are desorbed from the surface of the sensor [19-21].

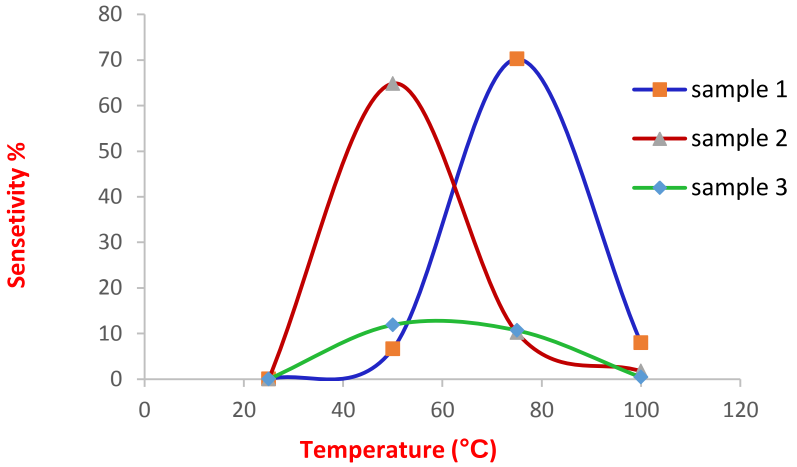

Figure 6-Changing of the sensitivity with temperature at different PH values toward (400 ppm) NH_3 gas.

4. Conclusions

Nano silver oxide thin films were prepared using the CBD technique. The films had different silver oxide structures which were Ag_2O, AgO, and Ag_3O_4, as shown from the XRD. The average crystallite size and average grain size measured by the XRD and AFM, respectively, were in the nanometer range . The optical transmittance increased with the increase in wavelength and pH. The optical energy gap depended on the pH value and the thickness of the prepared thin films. The nano-silver oxide thin films fabricated by the CBD method had a good NH_3 gas sensing properties at near room temperature (50° C), with a high sensing value and low response and recovery times. These results suggest that the prepared nano thin films can be used in gas sensor and optoelectric applications.

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