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Preparation and Characterization of In_2O_3-CuO Nanocomposite Thin Films as NH_3 Gas Sensor

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Abstract

An NH_3 gas sensor was prepared from nanocomposite films of indium oxide-copper oxide mixtures with ratios of 0 , 10 , and 20 Vol % of copper oxide. The films were deposited on a glass substrate using chemical spray pyrolysis method (CSP) at 400°C. The structural properties were studied by using X-ray diffraction (XRD) and atomic force microscopy (AFM). The structural results showed that the prepared thin films are polycrystalline, with nano grain size. By mixing copper oxide with indium oxide, the grain size of the prepared thin films was decreased and the surface roughness was increased. The UV-Visible spectrometer analysis showed that the prepared thin films have high transmittance. This transmittance was decreased by mixing copper oxide with indium oxide. The direct optical energy gap ranged 3.5 - 3 eV, which was decreased with increasing copper oxide concentration. The sensitivity of the prepared gas sensor was measured towards NH_3 gas at a concentration of 71ppm with operating temperatures of 100, 150, 200, 250 and 30) °C, according to the change of sensor resistance. This sensitivity of the mixture oxides showed a value of about nine times greater than that of individual indium oxide thin films. The results of the optimum gas sensor properties demonstrated a sensitivity value of 75.06%, response time of 10s, and recovery time of 11 s, at a mixing ratio of 20% of copper oxide and an operating temperature of 200°C.

Keywords;Thin films, optical and structural properties, Nano – composite, In_2O_3 – CuO, NH_3 gas sensor.

تحضير ودراسة خصائص اغشية رقيقة لمتراكب نانوي من In_2O_3–CuO كمتحسس غاز NH_3

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الخلاصة

تم في هذا البحث تصنيع متحسس غاز NH_3 من اغشية متراكب نانوي من خليط اوكسيد الانديوم–اوكسيد النحاس بنسب حجمية (0,10,20 Vol%) من اوكسيد النحاس .الغشاء مرسب على قواعد زجاجية بأستخدام تقنية التحلل الكيميائي الحراري , بدرجة حرارة 400 °C , الخصائص التركيبية درست باستخدام تقنية حيود الاشعة السينية (XRD) ومجهر القوة الذرية (AFM) . النتائج التركيبية بينت ان الاغشية الرقيقة المحضرة متعددة التركيب ذات حجم حبيبي نانوي . عند خلط اوكسيد النحاس مع اوكسيد الانديوم ادى الى نقصان الحجم الحبيبي النانوي , وازياد خشونة السطح للاغشية الرقيقة المحضرة . ان طيف (UV–Visible spectrometer) اظهر بأن الاغشية الرقيقة المحضرة تمتلك نفاذية عالية . هذه النفاذية تتناقص مع خلط اوكسيد النحاس بأوكسيد الانديوم . ان قيم فجوة الطاقة المباشرة كانت تتراوح بين (3.5– 3)eV ،وتتناقص

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مع زيادة اوكسيد النحاس في الخليط. ان تحسسية المتحسسات المحضرة من الاكاسيد تجاه غاز الامونيا NH_3بتركيز (71ppm) , تم قياسها من خلال تغير المقاومة . ان قيم تحسسية خليط الاكاسيد اعطت قيم تحسسية اكبر مما لاوكسيد الانديوم المنفرد بحدود تسع مرات . ان خصائص المتحسس المثالية اعطت قيمة تحسسية تساوي (75.06%) وبزمن استجابة (10s) وزمن استرجاع (11 s) بنسبة خلط لاوكسيد النحاس قدرها 20% وبدرجة حرارة تشغيل $200\ ^oC$.

Introduction

Semiconductor metal oxide (SMO) has many advantages, such as low cost, easy for fabrication, low detection limits for gases, in addition to their long life, non-toxicity, and high conductivity. For these properties, it has been used in many different fields and applications, such as solar cells and gas sensors [1]. SMO has excellent sensitivity, rapid response, and long-term stability. Therefore, it has been widely used in the detection of dangerous and explosive gases in the environment [2, 3]. The enhanced sensing properties of the thin film's composite can be attributed to the p-n heterojunction contact between the semiconductor metal oxides [4]. Moreover, many attempts have been made to enhance the sensitivity and selectivity of the transparent metal oxide sensors by modifying the surface through adding metallic impurities and mixing different metal oxides [4-9]. Indium oxide (In_2O_3) is an n-type semiconductor with a wide energy gap n (3.5- 3.75 eV). Also, it has high conductivity, low resistance, and ability to modify its surface by doping or mixing with some metals [10]. CuO is a p-type semiconductor, with a narrow energy gap (1.2-1.9 eV), low cost, high catalytic activity, good electrochemical performance, and excellent response to most neutral and reducing gases [11-12]. CuO is studied as a p-type gas sensor material but not used widely as mixed oxide with n-type metal oxide semiconductors, such as In_2O_3, SnO_2, and ZnO for gas sensor applications [13]. Ammonia gas (NH_3) is highly toxic, being commonly used in agriculture, food industry, and chemical industry. In addition, it is known to be exceptionally harmful to the human body and the environment. Thus, highly sensitive detection is necessary for its monitoring [14]. Sensitivity tests for the prepared films aim to create optimal conditions for the operation of the NH_3 gas sensor [15]. The present study was designed to manufacture an NH_3 sensor from nanocomposite thin films made of a mixture of indium oxide and copper oxide deposited on a glass substrate by a simple chemical spray pyrolysis technique. The structural, optical, and sensing properties of 71 ppm NH_3 gas of the prepared films were studied.

2. Experimental Details

Nano thin films of indium oxide pristine and the mixture of thin films of indium oxide– copper oxide were deposited with different volumetric ratios of copper solution (0, 10, 20 Vol. %), using the chemical spray pyrolysis technique. The materials' solutions were prepared from indium chloride ($InCl_3$) with a purity of 97% (supplied by CDH) and copper chloride ($CuCl_2.2H_2O$) with a purity of 98 % (BDH chemicals Ltd Poole, England). The molarity of solutions was 0.01 M. The slides were cleaned with detergent water and ethanol using an ultrasonic bath for 10 minutes. The solutions were sprayed automatically on a glass substrate at 400^oC using comprised air of 1 bar as a gas carrier at a period time of spraying of 5 s and (20 s) wait alternately, with a deposition rate of 2.5 ml/min. The optical method was used to determine the thickness of the prepared films, which ranged 250-320 nm. The optical and structural properties were studied using UV-Visible spectrometer, XRD, and AFM. The sensitivity properties of the sensor toward NH3 gas were measured at a concentration of 71 ppm and different operating temperatures.

3. Results and discussion

3.1 Structural properties

Figure-1 shows the X-ray diffraction of the prepared films having a polycrystalline structure with nanocrystalline size. The single indium oxide films have several crystalline peaks of (211), (222), (400), (431), (440), (622) at the diffraction angles 2q = (21.43, 30.51, 35.37, 45.5, 50.92, 60. 56º), respectively. The predominant peak is at (222) with a cubic structure, in accordance to the card (JCPDS 01-088-2160), which is in agreement with the results reported by Zhi-HongMaa *et al*. [10] and Wojtyła *et al*. [16]. The results also showed that, when adding 10 and 20 % of copper oxide to indium oxide, the predominant peak shifts to the larger angles and the previously appeared peak (431) was missing. Also, there is no compound between the two oxides, which indicates the formation of the composite between the two oxides. The crystalline size was calculated using the Debye- Scherer equation. It was found that the addition of copper oxide leads to a decrease in the crystal size as compared with individual indium oxide thin film, as shown in Table-1.

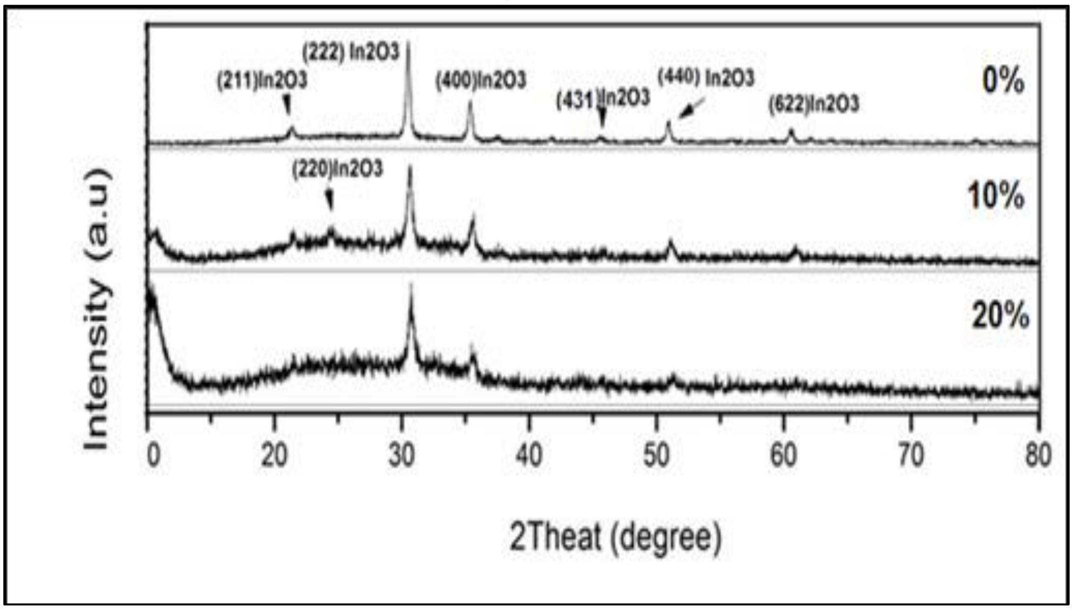

Figure 1- The X-ray diffraction of the prepared films

Figure-2 shows the atomic force microscopy (AFM) images of the prepared thin films. The results show that indium oxide has an average grain size of 107.5 nm and average roughness of 3.13 nm. Adding 10 and 20 % copper oxide to indium oxide leads to a decrease in the grain size to 82.25 nm and 45.27 nm, respectively, along with an increases the roughness and the root mean square, as shown in Table-1. The shape of the grains changes from spherical and elliptical at 10 % copper oxide to spherical at 20 % copper oxide, due to the nanocomposite formation of the mixed films, as shown in figure 2. This behavior corresponds to the XRD result and an agreement with that described by Suhai *et al*. [5] and Sofi *et al*. [17].

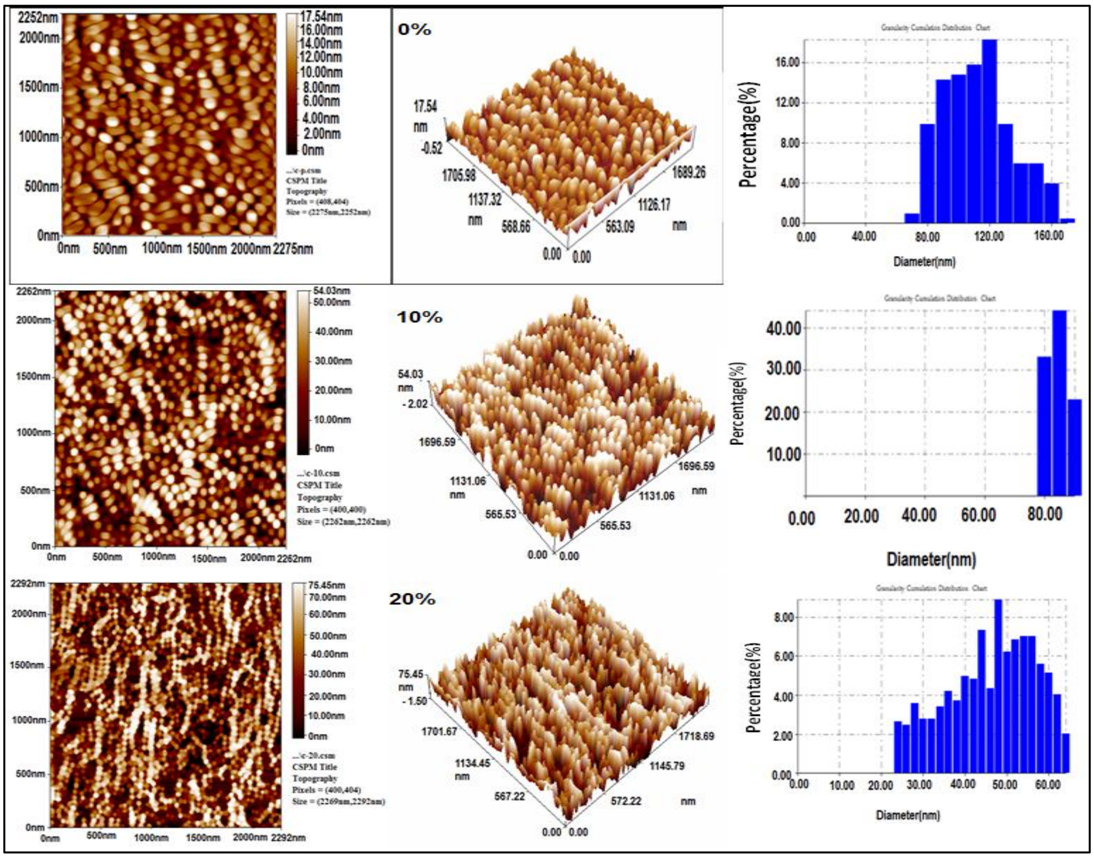

Figure 2-AFM images of the prepared films

Table 1-The values of crystalline size, grain size, average roughness, and root mean square of the prepared films

Sample content	Oxide type	XRD	AFM		
		Crystal size			
		D (nm)	Roughness (nm)	Root mean square(nm)	Grain size(nm)
100% $InCl_3$	In_2O_3	27.9	3.13	3.84	107.5
$90\%InCl_3+10\%CuCl_2$	In_2O_3+CuO	16.27	14.2	16.4	82.25
$80\%InCl_3+20\%CuCl_2$	In_2O_3+CuO	22.16	19.2	22.2	45.27

3-2. Optical properties

Optical examinations of the prepared indium oxide-copper oxide mixture showed a high transmittance within the wavelengths of visible light, as shown in Figure-3. The transmittance of the prepared individual indium oxide films reached 74% at a wavelength of 650nm, as shown in Figure-3. The transmittance was decreased to 66% at 20% of copper solution and a wavelength of 650nm. The reason for the decrease in transmittance after adding copper oxide is the high absorption of copper oxide within the visible wavelengths, which corresponds to the small value of the optical energy gap. These results have good agreement with those of Mahdi *et al*. [5].

The direct optical energy gap of the prepared films was calculated from the relationship between the energy values of the photon hv and $\alpha hv2$, as shown in Figure-4. The value of the direct energy gap for In_2O_3 was equal to 3.5 eV. Then, it was decreased with increasing copper oxide concentration to 3.3eV) for 10%, and to 3 eV for 20%. The decrease in the direct energy gap value of the mixture In_2O_3-CuO films together with the increase in the ratio of copper oxide concentration occurred due to the small energy gap value of copper oxide.

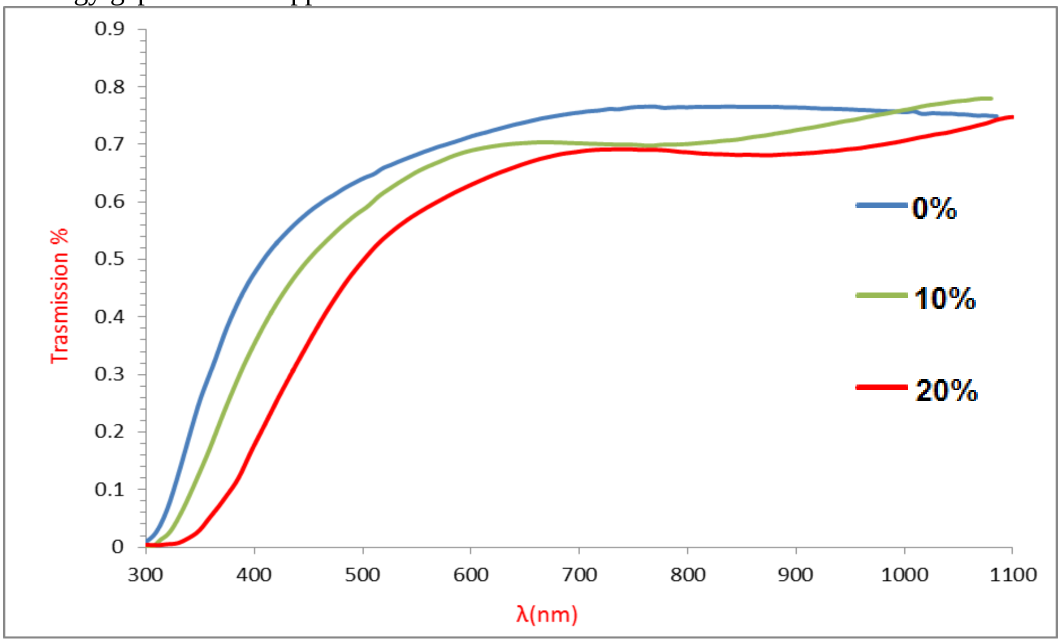

Figure 3-The transmittance spectrum values of In_2O_3:CuO thin films deposited on glass substrate .

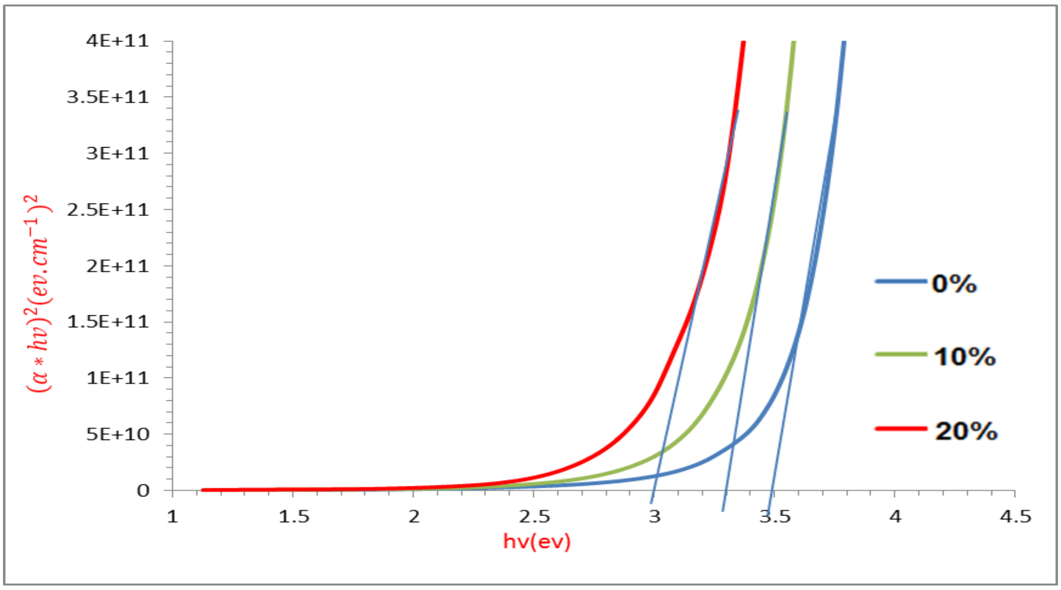

Figure 4-The energy gap values of In_2O_3:CuO thin films deposited on glass substrate.

3-3. Gas sensor characteristics

The sensitivity of individual indium oxide and that mixed with copper oxide films toward 71ppm of NH_3 gas was calculated through the following relationship [7]:

$$S\% = \frac{R_a - R_g}{R_a} \times 100\% \qquad \text{-----------(1)}$$

where Ra and Rg are the electrical resistance values of the sensor in air and gas, respectively. Figures-(5, 6, 7) show the change in the electrical resistance of the sensor with the gas reaction time at different temperatures. Figure-5 shows the change in the electrical resistance verses time of indium oxide sensor towards NH3. Ammonia gas is one of the reducing gases, while indium oxide is considered an n-type semiconductor. Exposing this sensor to ammonia gas leads to a decrease in the electrical resistance value for the sensor from which the sensitivity was calculated, and its value was (4.92%), while the response time was 12s and the recovery time was14 s at an operating temperature of 100^{o}C. Also, there was no response to the sensor at room temperature and when the operating temperature was increased to 250^{o}C. The sensitivity was equal to 5.47% while the response time was equal to 4s and the recovery time was equal to 10s. When mixing a proportion of 10% copper solution, the sensitivity reached8.81%), the response time was 20s and the recovery time was 11s at an operating temperature of 200 ^{o}C . By observing the results, it is concluded that the sensor is thermally activated, as the reaction between the surface of the sensor and ammonia gas increases with increasing temperature. The mixing ratio of 20% of the copper solution clearly led to an improvement in the sensitivity of the sensor, the response time, and the recovery time. The sensitivity of the sensor at 20% of copper solution reached 15.18%, with a response time of 20s and a recovery time f 8s, at an operating temperature of 100^{o}C. When the operating temperature was increased to 200^{o}C, the sensitivity increased to 75.06%, while the response time was 10s and recovery time was 11 s, as shown in Table-2.

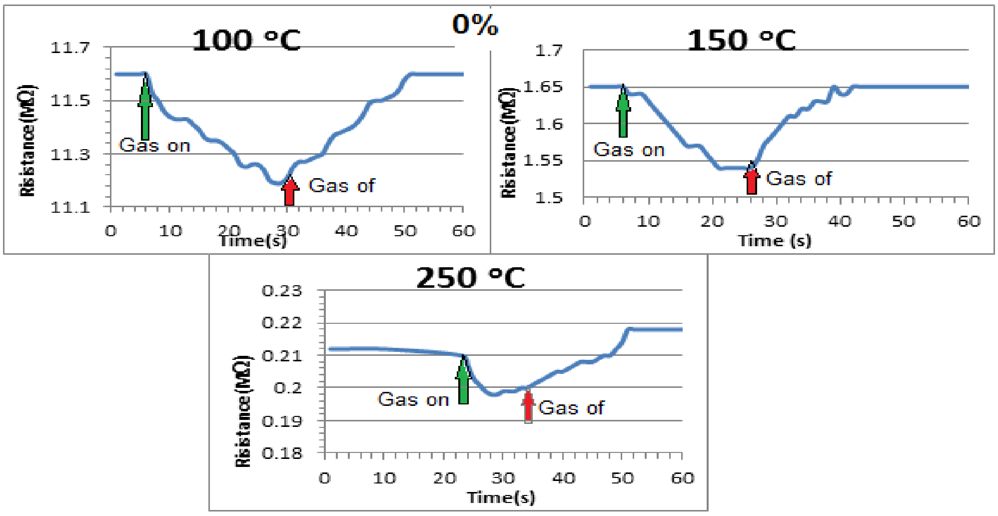

Figure 5-The change in electrical resistance with time for indium oxide films deposited on glass towards NH_3 gas at a concentration of 71 ppm.

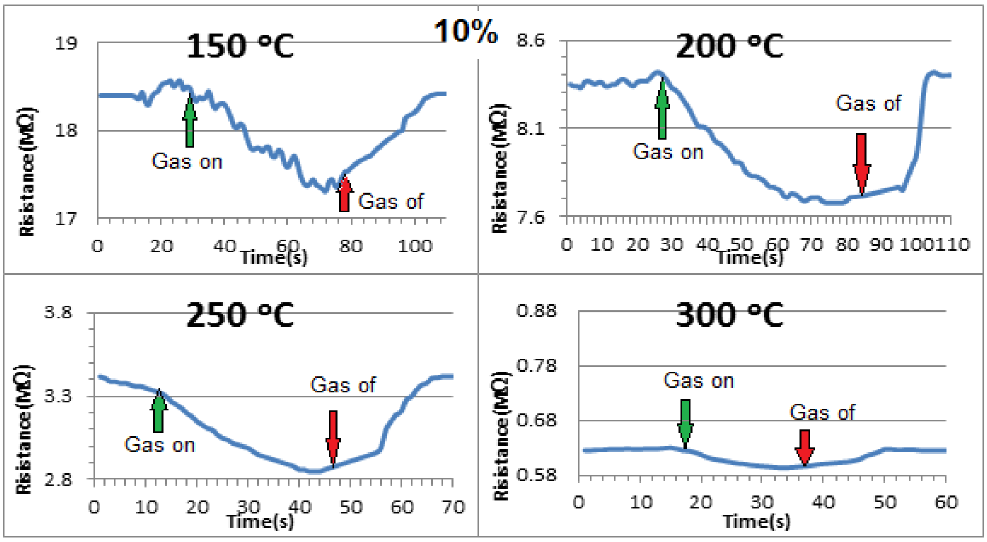

Figure 6-The change in electrical resistance with time for 90% In_2O_3:10%CuO mixture deposited on glass towards NH_3 gas at a concentration of 71 ppm.

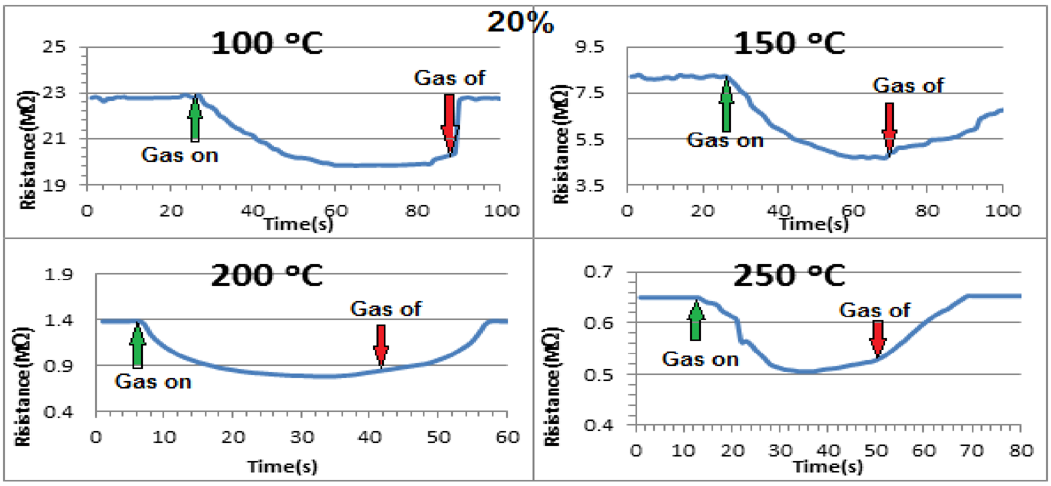

Figure 7-The change in electrical resistance with time for 80% In_2O_3:20%CuO thin films deposited on glass towards NH_3 gas at a concentration of 71 ppm.

Table 2-The values of the sensitivity, the response time, and the recovery time for the mixture of In_2O_3-CuO films deposited on glass toward NH_3 gas at a concentration of 71ppm.

$CuCl_3$%	Sample	Operating Tem. C^o	Sensitivity %	Response Time (sec)	Recovery Time (sec)
0	In_2O_3	100	4.92	12	14
		150	6.62	10	12
		250	5.47	4	10
10	CuO+In_2O_3	150	6.55	28	16
		200	8.81	20	11
		250	13.22	16	10
		300	6.07	12	6
20	CuO+In_2O_3	100	15.18	20	8
		150	72.95	16	12
		200	75.06	10	11
		250	10.69	9	8

Figure-8 shows the sensitivity change of the prepared films at different operating temperatures. From the observation of the figure we conclude that the optimal sensitivity of the prepared films to NH_3 gas was at the mixing ratio of 20% of copper oxide. The reason is the contact p-n heterojunction between CuO and In_2O_3. Also from Figure-8, it is observed that the optimum operating temperature was decreased from 200 ^oC for 0% and 10% to 180 ^oC for 20% mixing ration. This means that the optimum mixing percentage between oxides is 20%, which led to improving the sensitivity properties of the thin film.

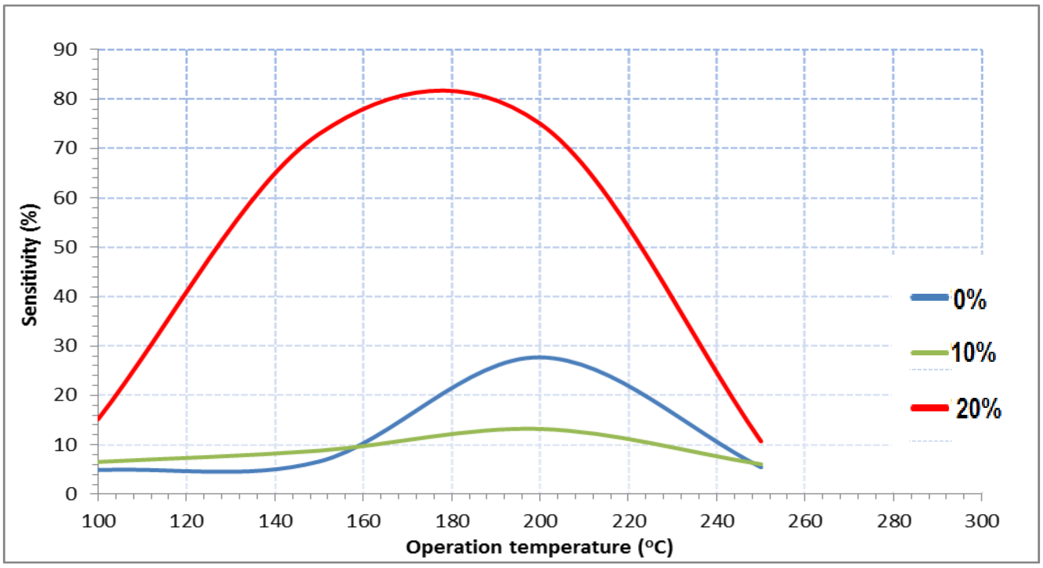

Figure 8- The sensitivity change with the change in the operating temperature of the In_2O_3-CuO thin films

The sensitization mechanism for most of the semiconducting metal oxides works on the principle of changing the conductivity of the sensor materials due to the interaction between the gas and the oxygen ions adsorbed on the surface ($^-O_2$, O^- , O^{2-}), which appears when the sensor is exposed to atmospheric oxygen. This leads to the formation of an area of depletion as a result of extracting electrons from the conduction band, thus increasing the barrier of sensor and thereby increasing the sensor resistance [18]. When the sensor is exposed to ammonia gas (NH_3), the gas reacts with oxygen ions and the electrons are released to the conduction band, which leads to a decrease in the electrical resistance of the sensor, according to the following equations [19]:

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

$$2NH_{3(ads)} + 3O^-_{(ads)} --\rightarrow N_2 + 3H_2O + 3e^- \quad \text{------------(3)}$$

This reaction requires activation energy, which means that it requires the provision of heat. For this reason, the In_2O_3-CuO mixture sensor does not obtain a response at room temperature or at lower temperatures, while the response is as high as possible when the actual thermal energy (100^{o}C) is given for the reaction, reaching to the optimum temperature. Also, we note that above this temperature, the response was decreased, due to the desorbed of oxygen ions from the surface of the sensor [7, 20-22].

4. Conclusions

The sensor was prepared at 400^{o}C from depositing indium oxide-copper oxide mixture nanocomposites film by using the chemical spray pyrolysis method. The XRD and AFM analyses were used to study the structural properties, which indicated that the prepared films are polycrystalline. They had grain size that was decreased with increasing the copper mixing ratio, while the surface roughness was increased. The optical properties were examined by using UV-Visible spectrometer and the results showed that the transmittance decreases with increasing the mixing ratio of the copper solution. The direct optical energy gap ranged between 3.5 and 3 eV and was decreased with increasing the mixing ratio of the copper solution. The sensitivity of the prepared thin films was measured towards NH_3 gas at a concentration of 71ppm. The sensitivity of the mixture showed a higher value than that for individual indium oxide, with lower response time and recovery time. The optimum sensitivity value and the operating temperature were achieved at a 20% mixing ratio of copper oxide.

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References

1. Kanan, Sofian M,El-Kadri, Oussama M,Abu-Yousef, Imad A,Kanan, Marsha C. **2009**. Semiconducting metal oxide based sensors for selective gas pollutant detection. *Sensors*, **9**(10): 8158-8196.
2. Liu, Chang,Gao, Hongyu,Wang, Liwei,Wang, Tianshuang,Yang, Xueli,Sun, Peng,Gao, Yuan,Liang, Xishuang,Liu, Fengmin,Song, Hongwei. **2017**.Facile synthesis and the enhanced sensing properties of Pt-loaded α-Fe_2O_3 porous nanospheres. *Sensors and Actuators B: Chemical*, **252**: 1153-1162.
3. Yang, Shuqin,Song, Zhilong,Gao, Naibo,Hu, Zhixiang,Zhou, Licheng,Liu, Jingyao,Zhang, Baohui,Zhang, Guangzu,Jiang, Shenglin,Li, Hua-Yao. **2019**. Near room temperature operable H_2S sensors based on In_2O_3 colloidal quantum dots. *Sensors and Actuators B: Chemical*, **286**: 22-31.
4. Trakhtenberg, LI,Gerasimov, GN,Gromov, VF,Belysheva, TV,Ilegbusi,OJ. **2012**. Effect of composition on sensing properties of SnO_2+ In_2O_3 mixed nanostructured films. *Sensors and Actuators B: Chemical*, **169**: 32-38.
5. Suhail, Mahdi Hasan,Al-Jumily, Hamad Saleh,Abdullah, Omed Gh. **2019**. Characterization and NO_2 gas sensing performance of CdO: In_2O_3 polycrystalline thin films prepared by spray pyrolysis technique. *SN Applied Sciences*, **1**(1): 69.
6. Nayel, Hajar H,AL-Jumaili, Hamid S. **2019**. Fabrication of Highly Sensitive NH3 Sensor Based on Mixed In_2O_3–Ag_xO Nanostructural Thin Films deposited on porous silicon. Journal of university of Anbar for Pure science, **13**(2): 40-47.
7. Al-Jumaili, HS, Jasim, MN. **2019**. Preparation And Characterization Of Zno: Sno_2 Nanocomposite Thin Films On Porous Silicon As H_2S Gas Sensor. *Journal of Ovonic Research*, **2**(1): 81-87.
8. Suhail, Mahdi Hasan**. 2017**. Preparation and characterization of mixed SnO_2: CdO thin films as gas sensor. *Iraqi Journal of Physics* (IJP), **15**(33): 28-39.
9. Li, Tian-tian,Bao, Na,Geng, Ai-fang,Yu, Hui,Yang, Ying,Dong, Xiang-ting. **2018**. Study on room temperature gas-sensing performance of CuO film-decorated ordered porous ZnO composite by In_2O_3 sensitization. Royal Society open science, **5**(2): 171788.
10. Ma, Zhi-Hong,Yu, Rui-Tao,Song, Ji-Ming. **2020**. Facile synthesis of Pr-doped In_2O_3 nanoparticles and their high gas sensing performance for ethanol. *Sensors and Actuators B: Chemical*, **305**: 127377.

11. Bhuvaneshwari, S, Gopalakrishnan, N. **2016**. Enhanced ammonia sensing characteristics of Cr doped CuO nanoboats. *Journal of Alloys and Compounds,* **654**: 202-208.
12. Highly sensitive and selective gas sensors using p-type oxide semiconductors: Overview , Highly sensitive and selective gas sensors using p-type oxide semiconductors: Overview. Sensors and Actuators B: Chemical, 2014. **192**: 607-627.
13. Srivastava, J., Gupta, Amit,Bhaskar, Anand A. **2014**. Sensing behavior of CuO-doped SnO_2 thick film sensor for H_2S detection. *Int. J. Scientific and Technology Research*, **3**(5): 266-272.
14. Li,Ching-Feng,Hsu,Chia-Yen,Li,Yuan-Yao. **2014**. NH_3 sensing properties of ZnO thin films prepared via sol–gel method. *Journal of Alloys and Compounds*, **606 .:** 27-31.
15. Yuasa, Masayoshi,Masaki, Takanori,Kida,Tetsuya,Shimanoe, Kengo,Yamazoe, Noboru. **2009**. Nano-sized PdO loaded SnO_2 nanoparticles by reverse micelle method for highly sensitive CO gas sensor. *Sensors and Actuators B: Chemical*,**136**(1): 99-104.
16. Wojtyła, Szymon,Baran, Tomasz. **2020**. Electrochemically prepared copper/indium oxides photocathode for efficient photoelectrochemical hydrogen production. *Solar Energy Materials and Solar Cells*, **206**: 110262.
17. Sofi, AH,Shah, MA. **2019**. Structural and electrical properties of copper doped In_2O_3 nanostructures prepared by citrate gel processes. *Materials Research Express*, **6**(4): 045039.
18. Kumar, Nagesh,Srivastava, AK,Nath, R,Gupta, Bipin Kumar,Varma, GD. **2014**. Probing the highly efficient room temperature ammonia gas sensing properties of a luminescent ZnO nanowire array prepared via an AAO-assisted template route. *Dalton Transactions*, **43**(15): 5713-5720.
19. Vinoth,E,Gopalakrishnan, N. **2018**. Effect of temperature on NH_3 sensing by ZnO: Mg thin film grown by radio frequency magnetron sputtering technique. in AIP Conference Proceedings. AIP Publishing LLC.
20. Jasim, Ismaail K,Ibrahim, Isam M,Alyas, Marwan K. **2018**. In_2O_3-ZnO pyramids like structure prepared by Spray-pyrolysis Technique for gas Sensing Applications. *Iraqi Journal of Science*, 67-74.
21. Zheng, Zhao Qiang,Zhu, Lian Feng,Wang,Bing. **2015**. In $_2$ O $_3$ nanotower hydrogen gas sensors based on both schottky junction and thermoelectronic emission. *Nanoscale Research Letters*, **10**(1): 293.
22. Nayel, Hajar H,AL-Jumaili, Hamid S. **2020**. Synthesis and characterization of silver oxide nanoparticles prepared by chemical bath deposition for NH_3 gas sensing applications. *Iraqi Journal of Science*, **61**(4): 772-779.