Electrochemical Deposition of Silver Oxide Nanostructure for CO_2 Gas Sensing Application

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Abstract:

High-quality 3D silver oxide nanostructures (Ag_2O) were deposited in the form of nanocrystals on n-type Si using silver nitrate with low-cost and easily controlled technique, which is electrochemical deposition (ECD). Ag_2O has unique potential applications for CO_2 gas sensor. The manufacture of a high-performance CO_2 gas sensor can be achieved based on Ag_2O nanoparticles and growth conditions, such as annealing temperature of the samples produced. Images of Field Emission Scanning Electron Microscope (FESEM) showed Ag_2O nanoparticles in the form of crystals at different annealing temperatures. High crystallization was achieved with a low level of defects of Ag_2O nanostructures prepared at room temperature on Si for the sample annealed at 600 ºC. The XRD pattern showed that the prevailing peak is at (111). The real-time of start/stop was measured with and without CO_2 gas applied to a sensor manufactured based on Ag_2O nanostructures prepared, response time, recovery and sensitivity (3.8, 4.3 and 37.7%), respectively.

Keyword: Silver oxide nanostructures, electrochemical deposition (ECD), thermal vacuum machine, sensitivity.

الترسيب الكهروكيميائي لهياكل اوكسيد الفضة النانوية وتطبيقها في استشعار غاز ثاني اوكسيد الكاربون

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الملخص:

تم ترسيب هياكل أوكسيد الفضة النانوية ثلاثية الأبعاد عالية الجودة (Ag_2O) في شكل بلورات نانوية على n-type Si باستخدام نترات الفضة $AgNH_3$ بتقنية منخفضة التكلفة ويمكن التحكم فيها بسهولة ؛ الترسيب الكهروكيميائي (ECD). تمتلك Ag_2O النانوية تطبيقات محتملة فريدة لمستشعر غاز ثاني أوكسيد الكاربون. ويمكن تحقيق تصنيع مستشعر غاز ثاني أوكسيد الكاربون عالي الأداء استنادًا إلى جسيمات Ag_2O النانوية واعتمادًا على ظروف النمو مثل درجة حرارة التلدين للعينات المنتجة. أظهرت صور المجهر الإلكتروني الماسح للانبعاث المجالي (FESEM) جسيمات Ag_2O النانوية على شكل بلورات تحت التلدين المختلفة. وتم تحقيق تبلور عالي مع مستوى منخفض من عيوب الهياكل النانوية Ag_2O المحضرة في درجة حرارة الغرفة على Si للعينة الملدنة عند 600 ºC، وأظهر نمط XRD أن الذروة السائدة عند (111). وتم قياس تبديل التشغيل/ الإيقاف في الوقت الفعلي مع وبدون غاز ثاني أوكسيد الكاربون المطبق على مستشعر مُصنَّع استنادًا إلى الهياكل النانوية Ag_2O المحضرة وزمن الاستجابة والاسترخاء والحساسية 3.8 و4.3, 37.7%.

الكلمات المفتاحية: هياكل اوكسيد الفضة النانوية، الترسيب الكهروكيميائي، نظام التفريغ الحراري، التحسسية.

Introduction

Ag_2O particles have attracted considerable attention due to their extensive properties and uses in photovoltaic (PV) cells and gas sensors for their high chemical sensitivity to gases [1, 2]. Ag_2O is a transparent p-type semiconductor with a simple cubic structure. It is used in different ways, including the deposition of thermal oxidation of silver membranes [3], thermal evaporation [4], and the electrochemical deposition method employed in the current study [5]. When depositing Ag_2O on Si, the membranes are heated for 60 min at varied temperatures (500,550,600,650 ºC), respectively. The synthetic and surface characteristics of deposited samples and their changes are studied through changing the temperatures. This is to obtain the best membrane with appropriate structure, reduce the lattice asymmetry of crystals, and improve sensor performance for detecting CO_2 gas with measuring the highest sensitivity at the lowest time of response and recovery.

Experimental Method

Ag_2O was deposited on Si, where Si samples were cleaned by immersing them in Hcl for 5 min with concentration of 95%. After that, they were immersed in ionic water and placed in diluted methanol CH_3OH for 5 min. Then, they were washed with ionic water and immersed in absolute ethanol C_2H_5OH for 5 min and the sample was washed with distilled water and then dried. Ag_2O solution was prepared using 0.894 gm of $AgNH_3$ with molarity of 0.1% and placed in 50 ml of distilled water with constant stirring. The deposition process on Si was for 1hr and then the sample was placed in the electric oven for 60 min at a temperature of 500 ºC to oxidize it and get the Ag_2O membrane. The depositions process was repeated for three samples using the same time with different temperatures (550, 600, 650 ºC), respectively. The synthetic properties were studied by using X-ray diffraction (XRD) machine with copper radiation (Cu- radiation), with voltage of (40 kV) and current of (30 mA). The structural characteristics of the material surface were studied using field emission scanning electron microscope (FESEM). In order to design a gas sensor, the junction of a metal-semiconductor-metal (MSM) was done and AL was deposited on Ag_2O in thermal vacuum machine to obtain the Schottky diode using Fingers pattern where each electrode contained five fingers with a thickness of 230 µm, length of 3.3 mm and the distance between each two fingers was 400 µm. After depositing AL, the sensor was annealed at 450 ºC for 5 min. For obtaining CO_2 gas sensor, AL was deposited with a thickness of 200 nm. Therefore, the highest sensitivity was measured for samples at the lowest time of response and recovery.

Results and Discussion

Figure (1) shows (FESEM) images of Ag_2O samples regularly distributed on Si. The images demonstrate a difference in the order and distribution of particles as temperatures increase. The particles are in a crystallike shape of a regular size with decreased distances between them. When the temperatures change from 500 ºC to 550 ºC, there appears a combination of large and small particles. However, the best results are obtained at 600 ºC and 60 min, which corresponds to XRD results in figure (2).

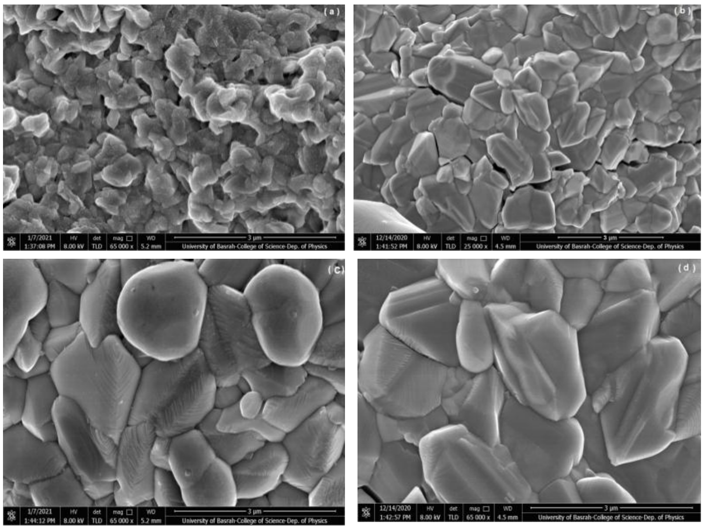

Figure 1: FESEM images of Ag_2O structures deposited on n-type silicon (111) and annealed for 1hr at temperatures of a) 500 ºC, (b) 550 ºC, (c) 600 ºC, (d) 650 ºC

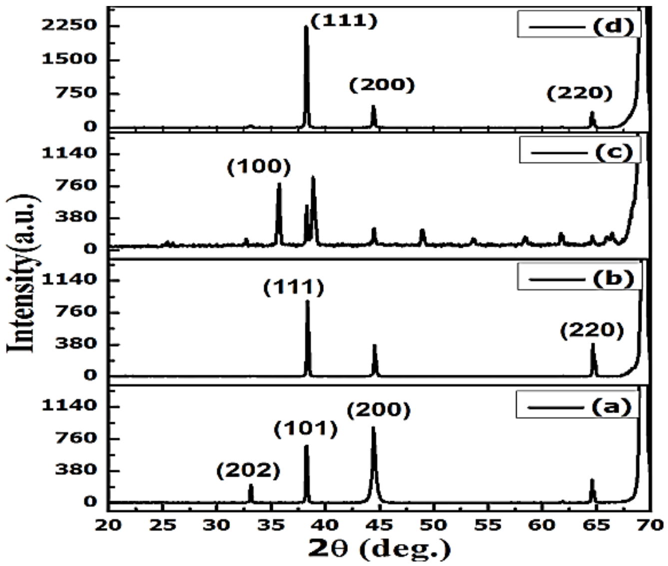

Figure 2: X-ray diffraction pattern of Ag_2O structures deposited on n-type silicon (111) and annealed for 1hr at temperatures of a) 500 ºC, (b) 550 ºC, (c) 600 ºC, (d) 650 ºC

Figure (2) presents polycrystalline membranes and peaks that clarify the type of silver oxide with cubic structure. The prevailing phase is at level (111) corresponding to JCPDS of the annealed sample at 600 °C for 60 min. The results show increased intensity of all peaks as temperatures increased. The average crystalline size (D) is measured using Debye-Scherrer equation [6]:

D = $Q\lambda$ / β $cos\theta$ ……………… (1)

Where β is the width of the curve at the mid intensity; Q is constant determined by type of material. Table (1) represents the average granular size of samples.

Table 1: The average crystalline size for all samples

Annealing temperature ºC	Average Crystalline size (nm)
500	56
550	84
600	146
650	58

The sensitivity of gas sensor, which represents the change in particle conductivity at CO_2 exposure, is calculated and can be written in terms of resistance [7,8]:

$S\ (\%) = \frac{R_{gas} - R_{air}}{R_{gas}} \times 100$ ……. (2)

Where S is sensitivity; R_{gas} is resistance measured by the presence of CO_2; and R_{air} is resistance measured in dry air.

Figure (3) shows the sensitivity of Ag_2O particle samples at 100 °C, which reveal an improvement in gas response as the annealing temperature of the implanted samples increases. The highest sensitivity of the nanocrystal-shaped-prepared samples is at a temperature of 600 ºC, which means improved CO_2 response. While the sensitivity of Ag_2O at 650 ºC and the response of CO_2 are both decreased. The sensor works with low concentrations and high sensitivity value (37.7%), time of response and recovery (tres=3.8, trec=4.3 sec) at concentration (19.5 ppm). Accordingly, sensor prepared from Ag_2O shows good sensitivity CO_2 due to its good synthetic characteristics.

Table 2: the values of response time (t_{res}), recovery time (t_{rec}) and sensitivity (S%) with changing the gas concentration for all samples

Annealing temperature ºC	Concentration (ppm)	Sensitivity (%)	Res. Time (sec)	Rec. Time (sec)
500	1.3	1	6.2	11.2
	5.0	1.2	3.9	2.1
	19.5	1.5	2.2	2.1
550	1.3	4.7	17.0	22.0
	5.0	5	10.7	9.2
	19.5	6	4.7	9.5
600	1.3	20	14.8	19.8
	5.0	33	11.7	13.3
	19.5	37.7	3.8	4.3
650	1.3	3	3.6	8.6
	5.0	4	13.3	7.6
	19.5	4.7	12.4	12.0

Figure (3) shows that the resistance increases with the increase in gas concentration, leading to increased sensor sensitivity.

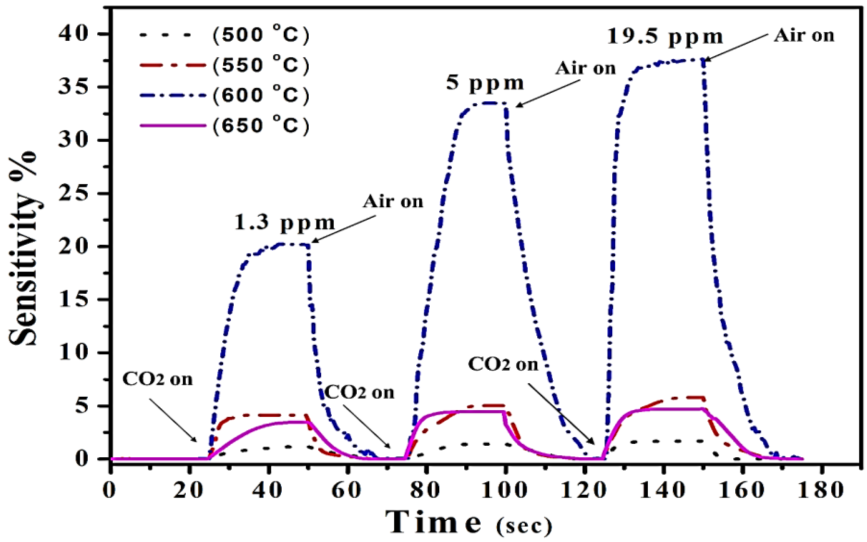

Figure 3: Sensitivity change over time for best response to patterns

Conclusion

Ag_2O was prepared from the $AgNH_3$ material using electrochemical deposition method for 60 min and annealed at different temperatures (500, 550, 600, 650 ºC), respectively. The XRD results showed that Ag_2O is polycrystalline with a cubic structure and the prevailing phase is level (111). The FESEM results demonstrated that the best regular crystalline structure of Ag_2O is at 600°C, which corresponds to the results of XRD. CO_2 sensor is also manufactured by depositing AL on Ag_2O using a thermal vacuum machine. Sensor sensitivity for membranes prepared is calculated at the best synthetic structure at 600 °C. The highest sensitivity value is (37.7%) at the lowest time of response and recovery (tres=3.8, trec=4.3 sec).

References

1. P. N. Reddy, M. Reddy, J. F. Pierson and S. Uthanna, Characterization of silver oxide films formed by reactive RF sputtering at different substrate temperatures. ISRN Optics (2014). https://doi.org/10.1155/2014/684317.
2. V. Ovchinnikov, Reduction of silver oxide film in inert gas plasma, ISBN: 978-1-61208-495-4, (2016).
3. N. R. C. Raju, K. J. Kumar and A. Subrahmanyam, Physical properties of silver oxide thin films by pulsed laser deposition: effect of oxygen pressure during growth. J. Phys. D 42(13), 135411 (2009).
4. F. Hajakbari and M. Ensandoust, Study of thermal annealing effect on the properties of silver thin films prepared by DC magnetron sputtering. Acta Physica Polonica A 129, 4 (2016).
5. Tonelli, D., Scavetta, E., and Gualandi, I., Electrochemical Deposition of Nanomaterials for Electrochemical Sensing. Sensors, 19(5), 1186. doi:10.3390/s19051186, (2019)..
6. Klug H. P. and Alexander L. E., X-ray diffraction procedures: for polycrystalline and amorphous materials. X-Ray Diffraction Procedures: For Polycrystalline and Amorphous Materials, 2nd - 99 -Edition, by Harold P. Klug, Leroy E. Alexander, pp. 992. ISBN 0-471- 49369-4. Wiley-VCH, , 1974: p. 992, May (1974).
7. A.u Takafumi, I.. Noriya and Sh. Woosuck, NO and NO_2 sensing properties of WO_3 and CO_3O_4 based gas sensors. Sensors, 2013. 13(9): p. 12467-12481.
8. L. Qingcheng, L. D., G. Shang, J. Dayong, Z. Jianxun, Q. Jieming and H. Jianhua, Room-temperature NH_3 sensors with high sensitivity and short response/recovery times. Chinese science bulletin, 59(4): p. 447-451, (2014).