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Fabrication and Characterization of Gas Sensor from ZrO_2: MgO Nanostructure Thin Films by R.F. Magnetron Sputtering Technique

***Souad G. Khalil*[1]** ***Mahdi M. Mutter*[2]** ***Zainab K. Mohammed*[1]** ***Ghassan Salem*[2*]**

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Abstract:

Thin films ZrO_2: MgO nanostructure have been synthesized by a radio frequency magnetron plasma sputtering technique at different ratios of MgO (0,6, 8 and 10)% percentage to be used as the gas sensor for nitrogen dioxide NO_2. The samples were investigated by X-ray diffraction (XRD), atomic force microscopy (AFM), scanning electron microscopy (SEM), energy-dispersive X-ray (EDX) and sensing properties were also investigated. The average particle size of all prepared samples was found lower than 33.22nm and the structure was a monoclinic phase. The distribution of grain size was found lower than36.3 nm and uninformed particles on the surface. Finally, the data of sensing properties have been discussed, where they indicated that sensitivity reached 42.566% at 300 ^oC, spectral response time less than 52.2 s and recovery time 135.9 s.

Key words: Gas sensor, NO_2 gas, Plasma sputtering technique, Sensitivity, ZrO_2: MgO thin films.

Introduction:

One of the important subjects, in recent years, in the field of materials science, has been the synthesis of thin films from a metal oxide (semiconductor) that was used as a gas sensor (1). There are many studies on sensing properties for these materials especially the sensitivity and selectivity which mostly depend on semiconductor type, also, they depend on adding elements or doping and on the synthesis method (2). Moreover, theoretical studies on the conductivity of semiconductors have been availed the understanding of the nature of the works of this sensor and the investigation of their sensitivity characteristics (3). The gas sensors produced as thin films are considered attractive and are widely used in gas sensing application. Among the important characteristics for these materials are a simple structure, selectivity, fast response, fast recovery, which can be applied at room temperature in general, high stability, high accuracy, low cost, slow consumption and flexible in use as well (4). Nitrogen dioxide NO_2 is considered as one of the gases that cause pollution to the environment. This gas is dangerous on a human in case increasing its concentration more than the average rate.

[1]Departement of Physics, College of Science Woman, University of Baghdad, Baghdad, Iraq.
[2] Material Researches Directorate, Ministry of Science and Technology.
[*]Corresponding author: mahdimutter@yahoo.com

Human activities have affected the nitrogen lifecycle through extra using of nitrogen fertilization, biomass burning, and fossil fuel CO_2 combustion. This has led to an increase in the nitrogen dioxide NO_2 levels in the atmosphere (5, 6). These concentrations are on their highest levels in the urban environment and around high ways. Due to the growth in the population of urban cities, there is a need for more concerns on improving the environment and to reduce the traces of these toxic gases on human health. Thus, there must be a true consideration to the gas sensors of such gases. (7). Today the zirconium magnesia ZrO_2: MgO of nanoparticles size is considered as one of the best categories of catalysts solid. This is used as an active phase which draws the attention of many researchers because of its prosperities. It is an excellent chemical, has thermal stability high porosity, and a large surface area as well. (8). These materials have a great role in chemistry, physics, material science, and geochemistry. There is much application of these materials such as gas sensors, microelectronic devices, refractory materials, biomaterials and also in fuel cells. Therefore, there are many techniques used to prepare such material to be suitable for the application used. One of these techniques is the sol-gel methods (9-11), mechanical alloying (12). The technique used to prepare ZrO_2: MgO was by plasma spraying which is Radiofrequency (R.F) magnetron sputtering plasma technique. This technique is considered as

one of the best physical deposition methods due to its high control label on the films prepared from it, deposition stability and uniform films (13). Many researchers have studied and categorized this material. They depend on different methods in preparing such material; (14) is one of the researchers who prepared a thin film from zirconium by using Microware driven hydrothermal technique. In this technique, nanoparticles resulted in using thin films as a sensor to the oxygen gas;(15) prepared a zirconium thin film by using a conventional precipitation method as a gas sensor. He tested it with many gases such as (O_2, NO_2, C_2H_3OH, CO, H_2S, CO_2, NH_3). The thin film was more sensitive to the H_2S, (16) prepared a thin film from zirconium with SnO_2 by using co. precipitation and studied the thin film in its structural and optical characteristic. He used the thin film as a sensitive to the Methanol and Methane gases. He noticed increasing insensitivity of the thin film as per increasing of the SnO_2 ratio in the thin film (17). prepared a thin film from zirconium by using the spray pyrolysis techniques as a sensor to NH3 gas. Sensitivity shows quick response with (4S) and with a fast recovery of about 102 S. This work aims to prepare a thin film from zirconium- magnesia ZrO_2: MgO with a different doping rate of MgO (0,6, 8, 10)% as a sensor to the NO_2 gas by using R.F. magnetron sputtering plasma and studying its structural and sensitivity characteristics.

Materials and Method:

Pure materials have been used, they are: zirconium made by Changsha snatch Co, China, with purity of greater than >99.94 %, magnesia made by Nanjing Nanotechnology, China, with purity of 99.9%. They were mixed with (0, .6, 8, 10)% of MgO of zirconium weight. Four targets have been made ZrO_2 pure, ZrO_2: 6% MgO, ZrO_2: 8% MgO and ZrO_2: 10% MgO. The diameter of the track was 5 cm and (3 mm) in thickness and was compressed with a Hydraulic pressure of (10 tons). Then they were under the sintering process for the target with the heat of 850 ^oC for two hours. Then they were dealt with by grinding and polishing. The films are precipitated on a glass substrate after being cleaned by distilled water, alcohol and ultrasonic. Finally, they were cleaned by using special cleaner soft paper. The dimension was ($20\times25\times1.5$ mm^3). The kind of systems used to prepare thin films was (Compact Research Coater-600 Tor) CRC, an American product. The vacuum pressure was $2\text{-}3\times10^{-5}$Torr. The sputtering pressure was about$(6\text{-}6.9)\times10^{-3}$Torr. The gas used in sputtering was Argon. The conditioning process of the system was100-watt power for 2 hours and 100 ℃ substrate temperature, the films were under heat processing for two hours with degrading from 450^{o}C to 200^{o}Cat time 20 min. Structural properties were made by using X-ray diffraction. The device used was Shimadzu-6000. The target is Cu, wavelengths λ=1.5406 ^{o}A, current 300A, voltage 40 Kv, the range of angle (10-80) degree. The atomic force microscopy (SPM Nitegra NT. MDT). The scan electronic microscopy was type JEOL, JSM-67001 and the systems used for sensing properties (home-built) with a heater of (1500 watt), Fig.1, shows the diagram of the system used to measure the sensitivity of gas.

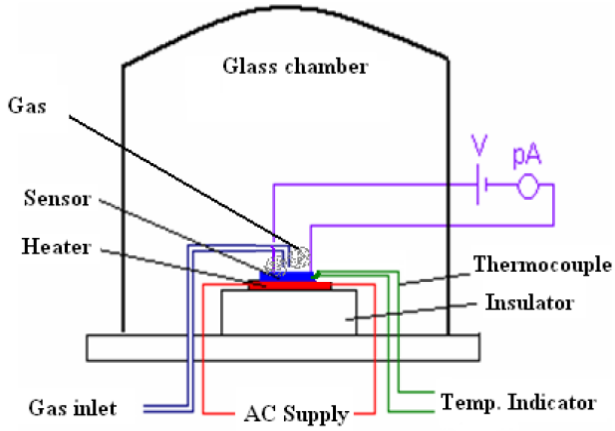

Figure 1. Schematic diagram of the sensing system used in test samples

Results and Discussion:

Figure.2, shows XRD pattern of the ZrO_2: MgO films annealing at 450^{o}C, after comparison with cart (JCPPs. No. 00-049-1746) for zirconium and with cart (JCPPs. No. 01-075-0417). For magnesia, the diffraction pattern shows that all the films prepared have a multi-crystal- structure except the sample ZrO_2 pure which is mono-crystalline and the structural crystalline was of monoclinic phase. The common direction for crystallization was (120) plane. The peaks showed in addition to the peak prominent, direction (211) and (240) in the planes film ZrO_2: MgO. It is well known that the prominent direction for crystallization of the same material depends on the preparation methods and the preparation conditions. The crystallization process is directed towards the nucleus that has rapidly grown which crystalline in a certain direction more than other direction of the nucleus that is having a slow growing, through the phase diffraction we noticed that the structural crystalline of ZrO_2 films has been affected by the dropping process of MgO clearly(18, 19). This happened with the stable structure of all the prepared films in a monoclinic structure. We also noticed that there were little changes in the peak position of the diffraction patterned. This happened due to the

smaller ionic diameter of the plain atoms than the Ionic diameter of zirconium atoms. Consequently, there would be special plains for then inside the structural crystalline of ZrO_2. This, in return, leads to a shift of the peaks in the crystalline structure. We also noticed that the peak flux decreased with the increasing full-width values in the middle of the great utmost (FWHM). The values increased from 0.1771 to 0.4447 for all rates. This means that the crystalline degree of ZrO_2 films decreased with the increasing the doping rates. Table (1) shows the structural parameters calculation of ZrO_2: MgO. They have been calculated depending on a special formula (equation) of the crystalline structure (20).

Table 1. crystalline structural parameters calculation

Samples	2θdeg.	FWHM deg.	$d_{hkl}A^o$	β (rad)	I	I/I_o	Hkl(planes)
ZrO_2 pure	31.6137	0.177	2.8279	0.0031	83	0.83	120
ZrO_2:6%MgO	31.7027	0.2668	2.820	0.0047	80	1.57	120
	43.8210	0.2516	1.201	0.0021	60	1.21	211
ZrO_2:8%MgO	31.7027	0.1779	2.820	0.0031	80	4.09	120
	43.8340	0.101	2.106	0.0071	30	2.01	211
	66.2135	0.3558	1.410	0.0062	42	3.50	240
ZrO_2:10%MgO	31.6137	0.1779	2.827	0.0031	80	1.24	120
	43.7103	0.4447	2.069	0.0078	27	0.415	211
	66.125	0.255	1.607	0.0061	50	2.40	240

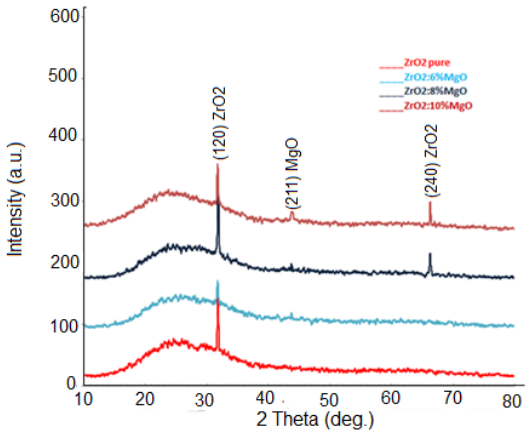

Figure 2. Diagram of XRD for all prepared samples of ZrO_2: MgO at annealing with 450 ºC for two hours.

The scan electron microscopy technique is used to determine the exact size, the shape, and particles distribution as well as the crystalline structure. Figure.3, shows images of samples for ZrO_2: MgO. The image shows homogeneity in a uniform distribution grain and the particles have spherical shapes with other different shapes. The particles size mean for ZrO_2 pure was 28.26 nm, ZrO_2 6% MgO was 23.21 nm, ZrO_2 8% MgO was 33.22 nm and for the ZrO_2: 10% MgO was 18.44 nm. In Fig.3, there is a slight difference between the sample ZrO_2: 6% MgO and the sample ZrO_2: 8% MgO have less conglomeration for some particles though there is a uniform surface. This because of the slight difference in some operating conditions in which no control for the researcher is due. As a result, we have such a slight difference in the images.

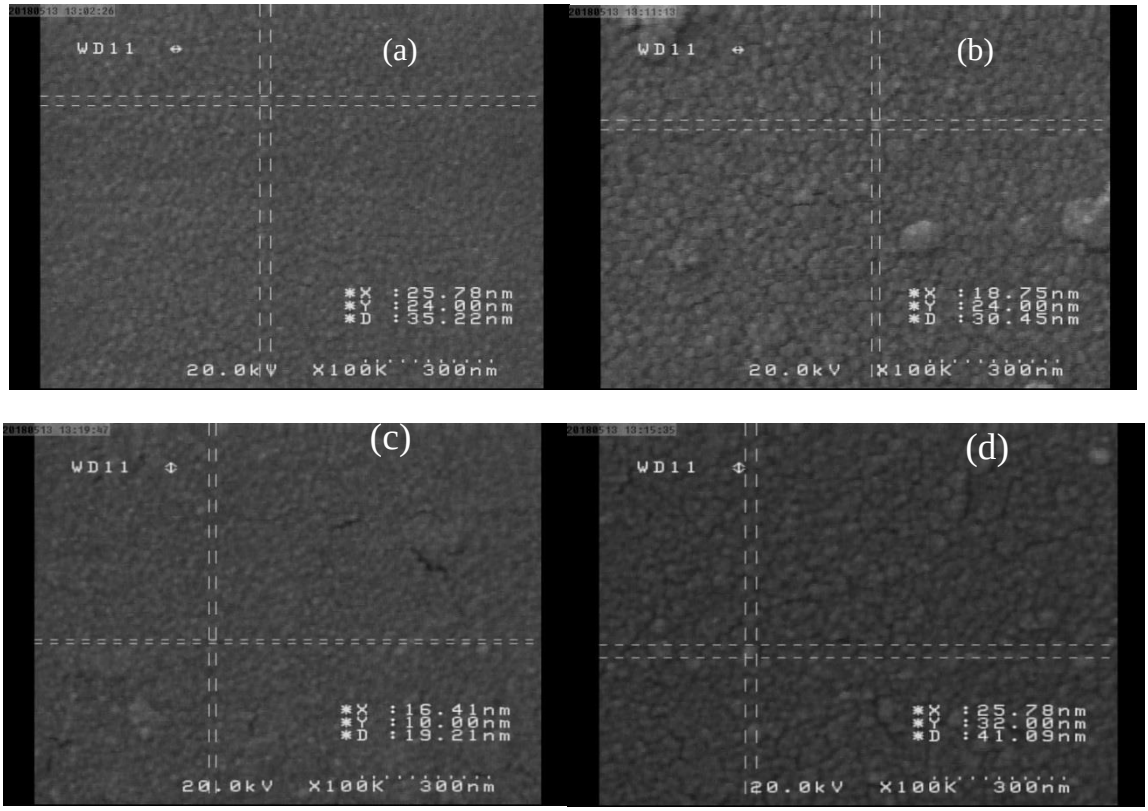

Figure 3. SEM image of ZrO_2:MgO, (a) ZrO_2 pure, (b) ZrO_2:6%MgO, (c) ZrO_2:8%MgO, (d) ZrO_2:10%MgO.

Figure.4 shows a distribution chart of average grain size distribution for the surface of the sample (grain size for samples surface). We notice that the average of the grain size for samples surface ZrO_2 pure is of 13.2 nm and we notice that the distribution is nearly uniform, the sample ZrO_2: 6% MgO the average grain size was 14.7 nm, the sample ZrO_2: 8% MgO the average grain size was 29.5 nm and the rate of the last sample ZrO_2:10% MgO was 36.3 nm. Note that the average grain size represented the average particle size on the surface of the samples, which was calculated in parameters of the AFM image. The quantities elemental analysis of the films prepared from ZrO_2: MgO and annealing at 450 ^oC for all samples have been done by using an energy dispersive spectrum as shown in Fig.5, which shows the quantities elemental composition at thin films analysis. Table (2) shows the weight and atomic percentage of the positive ions Mg, Zr and the negative ion O. The proportion was different for the samples prepared. The proportions were not in equity due to differences in mixing percentages. The mixing of zirconium is a matrix. The EDX analysis shows thin films purity of ZrO_2: MgO and the raw materials purity used in preparing these films. There was no phase except for the preparation elements.

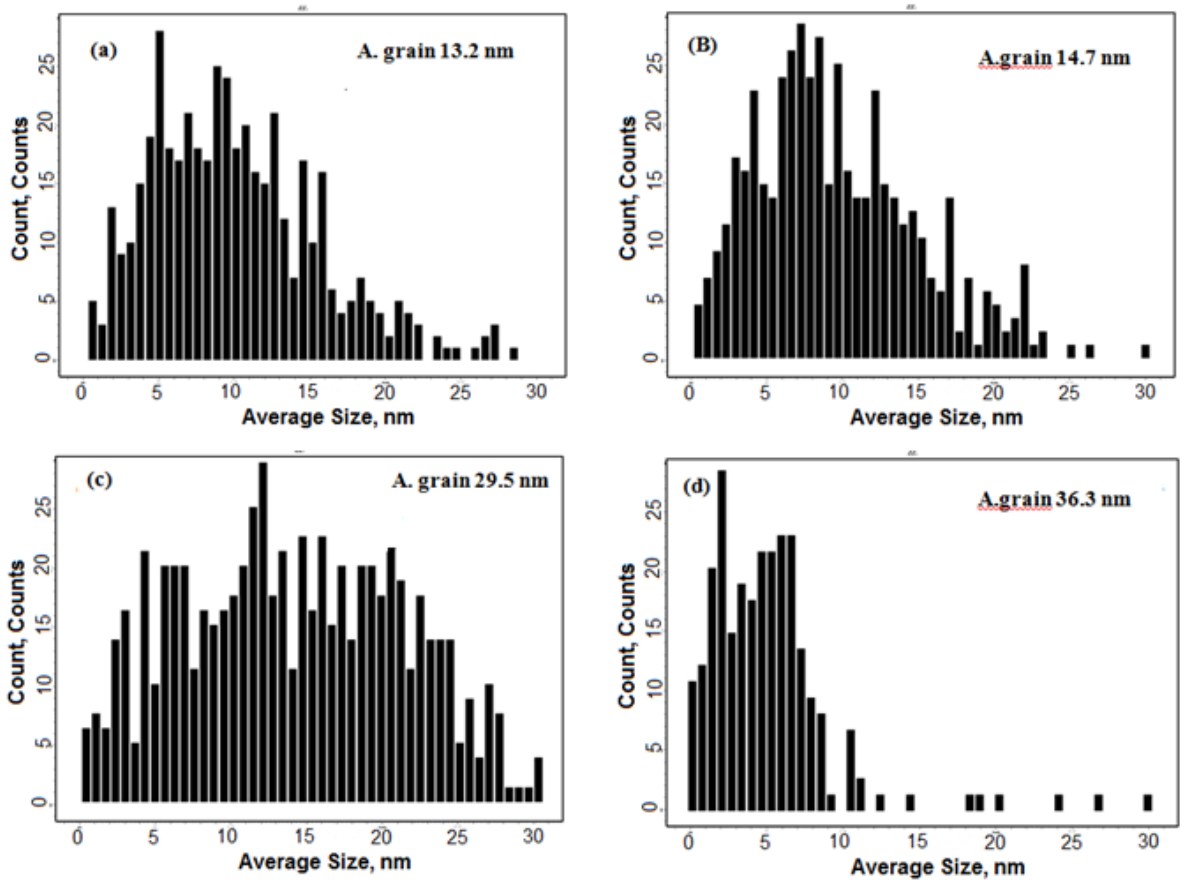

Figure 4. Corresponding histograms of the surface particle size distribution for ZrO_2: MgO thin films: (a) as deposited, (b) ZrO_2:6%MgO, (c) ZrO_2:8%MgO and (d) ZrO_2:10%MgO., Where A: average distribution grain size, SD: stander diffusion.

Table 2.energy dispersive X-ray analysis results of ZrO_2:MgO, (a) ZrO_2 pure, (b) ZrO_2:6%MgO, (c) ZrO_2:8%MgO, (d) ZrO_2:10%MgO

Samples	Element	Energylevel	WeightPercentage %	AtomicPercentage %	Error
ZrO_2 pure	O	K	71.3	93.4	11.3
	Zr	L	28.7	6.6	2.9
ZrO_2:6%MgO	O	K	54.6	79.1	12.3
	Mg	K	13.4	12.7	15
	Zr	L	32	8.1	2.8
ZrO_2:8%MgO	O	K	57.4	18.1	11.9
	Mg	K	12.1	11.3	16.5
	Zr	L	30.5	7.6	2.9
ZrO_2:10%MgO	O	K	64.5	82.3	10.4
	Mg	K	15.9	13.3	13.6
	Zr	L	19.6	4.4	2.9

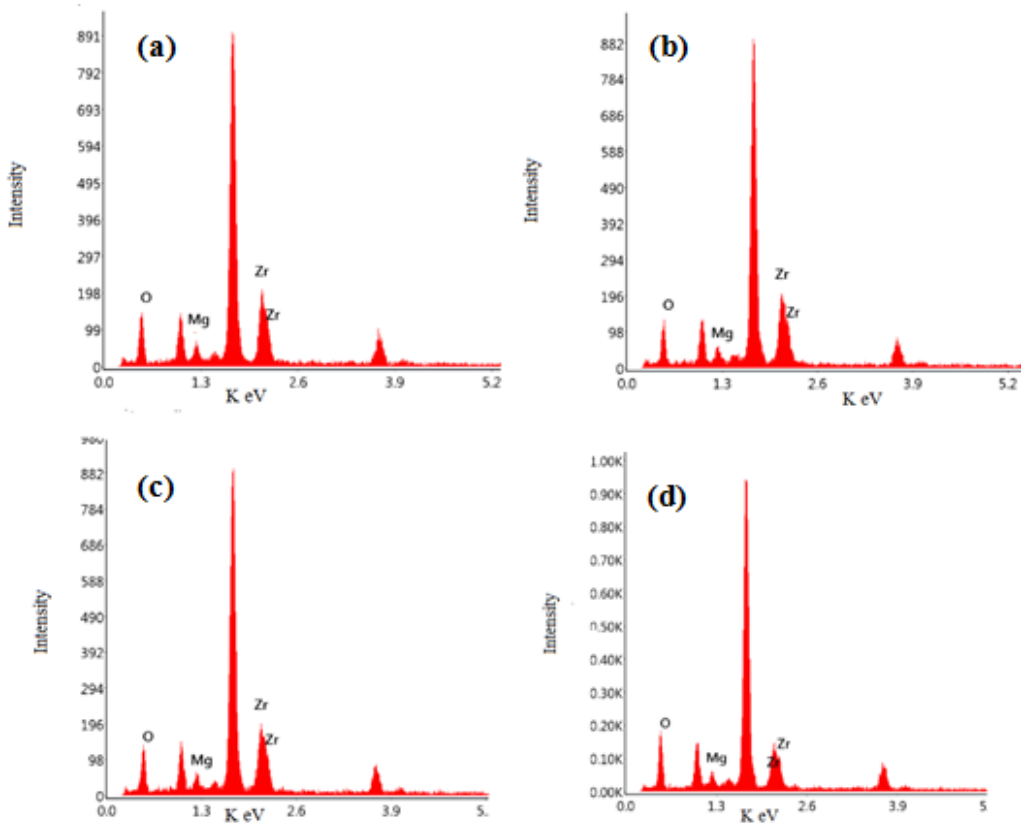

Figure 5. The typical EDX spectra of the ZrO_2:MgO, (a) ZrO_2 pure, (b) ZrO_2:6%MgO, (c) ZrO_2:8%MgO, (d) ZrO_2:10%MgO.

The surface morphology and roughness of films prepared have been chosen by using AFM. Figure.6, show that the images were of three dimensions for the films prepared ZrO_2: MgO which were under processing heating at 450 ^oC. The scanning process with (2×2) μm of films surfaces for all samples shows that the distribution of grain size has been increased from 13.2 nm to 36.3 nm with the increasing of doping ratios by using magnesia. Table (3) summarizes the results of the AFM image. This increase in the roughness surface can be back to calescence of films particles due to heat processing and this is clearly shown in Figure (7) of ZrO_2 pure sample and ZrO_2: 10% MgO without heat processing where notice that the roughness and the root mean square RMS of the ZrO_2 pure sample were 0.436 nm and 0.573 nm respectively and the ZrO_2: 10% MgO sample was 0.87 nm and 1.461 nm respectively. This means that the increase happened after the heat processing for the prepared sample.

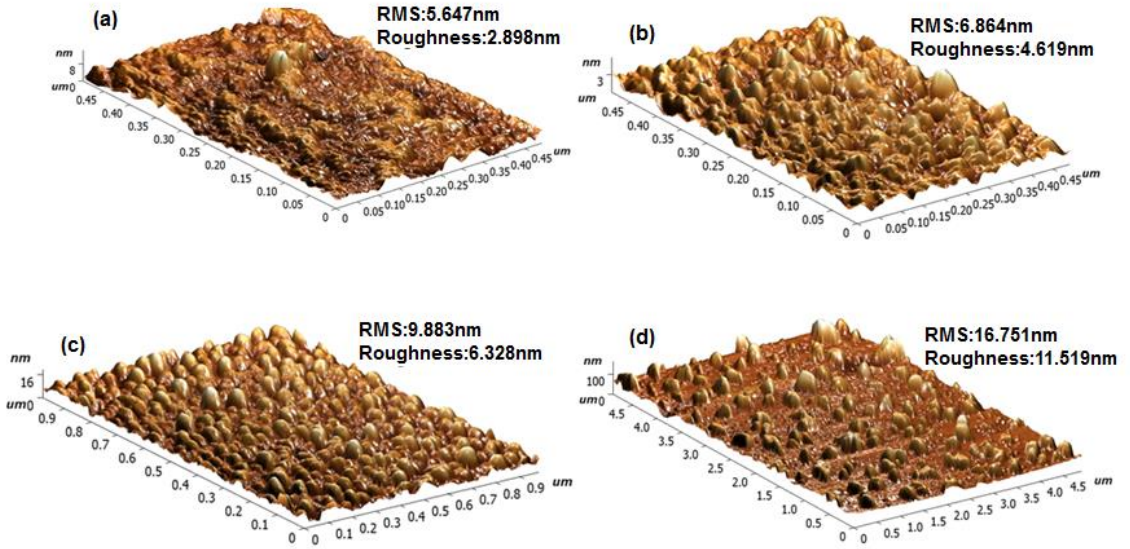

Figure 6. 3D AFM image of ZrO_2:MgO, (a) ZrO_2 pure, (b) ZrO_2:6%MgO, (c)ZrO_2:8%MgO, (d) ZrO_2:10%MgO

Table 3. Parameters of AFM image

Samples	Roughness nm	RMS nm	Distribution of grain size nm
ZrO_2	2.898	5.647	13.2
ZrO_2:6%MgO	4.619	6.864	14.7
ZrO_2:8%MgO	6.328	9.883	29.5
ZrO_2:10%MgO	11.519	16.751	36.3

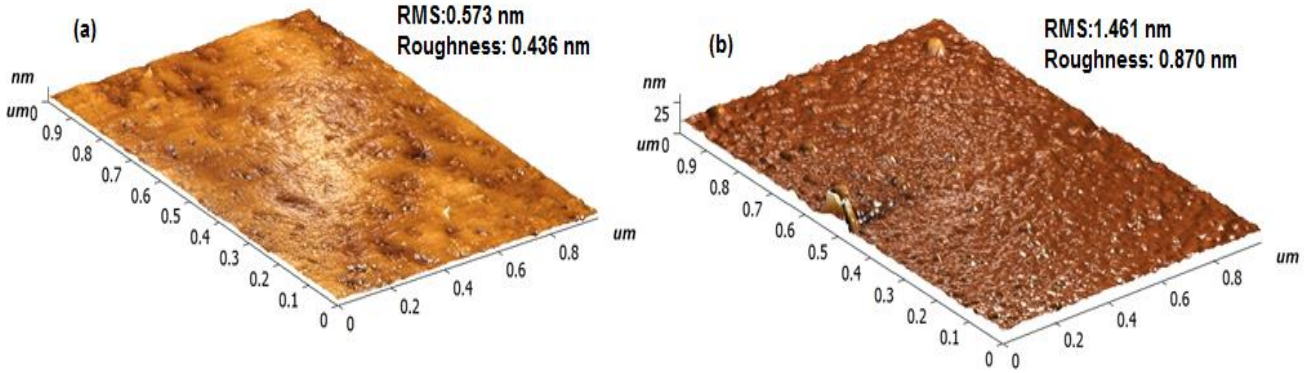

Figure 7. AFM image of ZrO_2: MgO without annealing, (a) ZrO_2 pure, (b) ZrO_2:10%MgO.

We could define gas sensing as the ratio in changing the conductivity of the sensor when exposing the target gas into sense conductivity in the air this lead to the equation:

S%=Gg-Ga/Ga …… (1)

Where Ga: the conductance of the sensor in air, Gg: the conductance in presence of target gas. Figure.8 represents the response to NO_2 gas. The ZrO_2: MgO is considered as a semi-isolated material at room temperature but at more than 200^{o}C heat there is increasing in conductivity. We could see decreasing in this response except for the ZrO_2: 6% MgO and ZrO_2: 8% MgO in which we have the most sensitivity was at 270^{o}C. This may be due to increasing films uniform in these samples. The addition of MgO to ZrO_2 leads to increase the thermal stability and then increases the stability in the electric conductivity properties. For there more, the MgO increase the surface area of ZrO_2, this is an important feature of gas sensors (20). Table (4) shows sensitivity values for all samples. When comparing our results with (G.Pratap, et al) (15), we see that through increases in operating temperature to 300^{o}C but we have got sensitivity up to 39.1% in comparator 2.2% of results by G. par tap. Response time which is defined as the time needed to vetch 90% of sense resistance from most sense resistance when exposed to the target gas. It was calculated in the samples prepared. As well as, the recovery time is defined as a time drop bake to 10% of the resistance when the sensor is placed in clean air value in the air. Figure.9, shows the response time and recovery time of the sensors prepared from ZrO_2: MgO. Table (5) shows response values and recovery values for all sensors. From Fig.9, and Table (5). We show the recovery time and response are different from each sensor and we could say that is due to the homogeneous in mixing the raw materials in preparing the target used in sputtering when preparing samples.

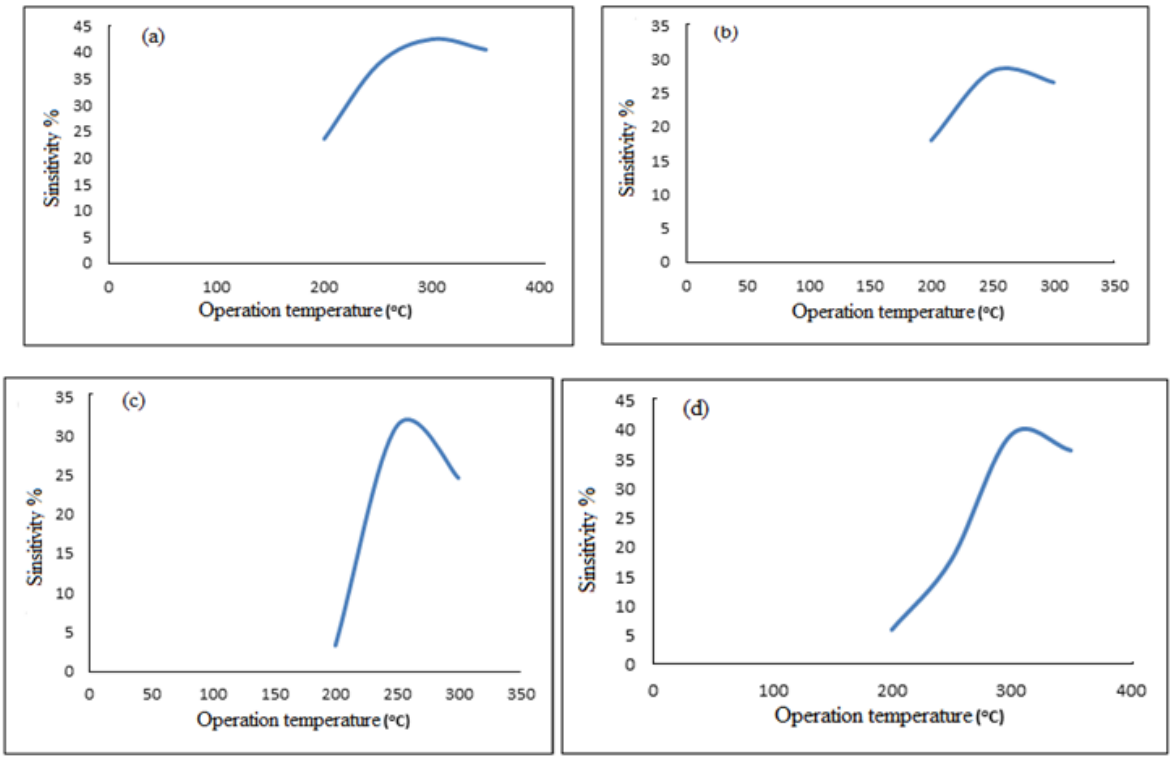

Figure 8. Sensitivity of ZrO_2:MgO for No_2 gas, (a) ZrO_2: pure, (b) ZrO_2:6%MgO, (c) ZrO_2:8%MgO, ZrO_2:10%MgO

Table 4. The sensitivity of ZrO_2: MgO thin films at operating temperature.

Sensitivity % of samples	Sensitivity% at 200 °C	Sensitivity% at 250 °C	Sensitivity% at 300 °C	Sensitivity% at 350 °C
ZrO_2 pure	23.642	37.799	42.566	40.543
ZrO_2:6%MgO	18.083	28.362	26.655	-
ZrO_2:8%MgO	3.308	31.336	24.698	-
ZrO_2:10%MgO	5.90	17.87	39.15	36.52

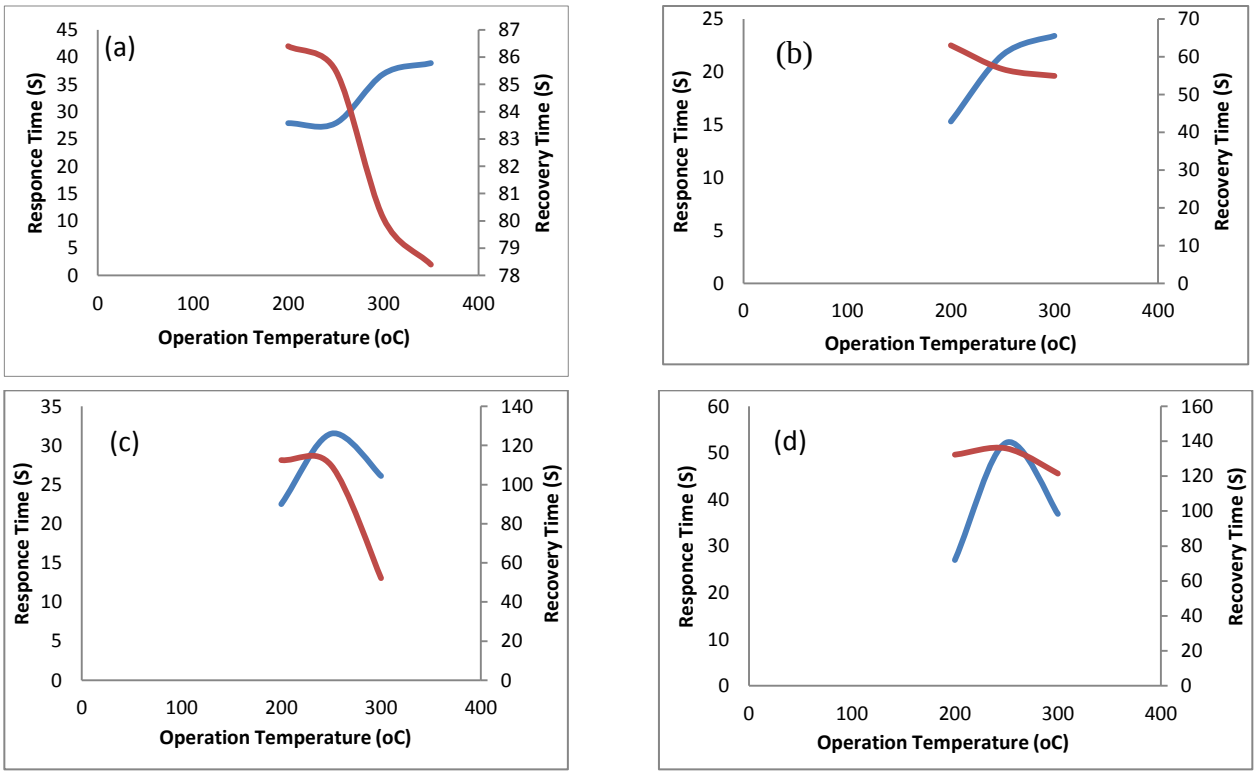

Figure 9. Response and recover time for all samples,(a)ZrO_2 pure, (b) ZrO_2:6%MgO, (c)ZrO_2:8%MgO, (d)ZrO_2:10%MgO.

Table5.The response and recovery time of all samples

Samples	Time (s)	200 °C	250 °C	300 °C	350 °C
ZrO_2 pure	response	27.9	27.9	36.9	38.9
	recovery	86.4	85.5	80.1	78.4
ZrO_2:6%MgO	response	15.3	21.6	23.4	-
	recovery	63	56.7	54.9	-
ZrO_2:8%MgO	response	22.5	31.5	26.1	-
	recovery	112.5	109.8	52.2	-
ZrO_2:10%MgO	response	27	52.2	36.9	-
	recovery	132.3	135.9	121.5	-

Conclusion:

The ZrO_2: MgO thin films, where (x=0%, 6%, 8%, and 10%) percentage of ZrO_2 weight are prepared by R.F.. magnetron sputtering plasma as a gas sensor. XRD analysis reveals the monoclinic phase of ZrO_2: MgO. The SEM image reveals that the roughly spherical particles with an average particles size of less than 33.22 nm. The AFM image shows the surface of thin films prepared homogeneous with distribution grain size is less than 36.3 nm and roughness of the surface is less than 16.751 nm. The response of ZrO_2: MgO based sensor is observed high to NO_2 gas, which it reaches as sensitive to 42.566% at 300 °C for ZrO_2 pure, 28.362% at 250 °C for ZrO_2:6%MgO, 31.336% at 250 °C for ZrO_2:8%MgO and 39.15% at 300 °C for ZrO_2:10MgO.The addition of MgO to ZrO_2 to increases the thermal stability, and then increase the stability in the electric conductance properties. As well as, the MgO increase the surface area of ZrO_2, this is an important feature of gas sensors. This is evident in the obtained results, where the operating temperature drop from 300 °C to 250 ° C when adding magnesia, this indicates a positive effect on the gas sensor.

Conflicts of Interest: None.

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تصنيع متحسس غازي من اغشية ZrO_2:MgO النانوية باستخدام تقنية الترذيذ الماكنتروني ببلازما الترددات الراديوية

سعاد غفوري خليل[1] مهدي محمود مطر[2] زينب قاسم محمد[1] غسان سالم[2]

[1]قسم الفيزياء كلية العلوم للبنات، جامعة بغداد، بغداد، العراق.
[2]دائرة بحوث المواد، وزارة العلوم والتكنولوجيا، بغداد، العراق.

الخلاصة:

الأغشية الرقيقة ذو تركيب نانوي من ZrO_2:MgO تم تحضيرها باستخدام تقنية الترذيذ ببلازما الترددات الراديوية بنسب مختلفة من MgO كانت (10,8,6,0) % لغرض الاستخدام كمتحسس غازي لغاز ثاني اوكسيد النيتروجين NO_2 .العينات المحضرة تم توصيفها باستخدام حيود الأشعة السينية XRD ،مجهر القوى الذرية AFM ،الماسح الالكتروني SEM ، تشتت طاقة الأشعة السينية EDX والخواص التحسسية تم تحقيقها أيضا. الحجم الحبيبي للعينات المحضرة وجد اقل من (33.22 nm) والتركيب البلوري كان أحادي الطور. توزيع الحجم الحبيبي على السطح كان اقل من (36.3 nm) مع تجانس في توزيع الجسيمات على السطح.أخيرا نتائج الخواص التحسسية تم مناقشتها. حيث إشارة النتائج إلى إن التحسسية الغازية وصلت إلى (42.566 %) عند درجة حرارة (300) درجة مؤية وزمن استجابة كان (52.2) ثانية مع زمن عودة (135.9) ثانية.

الكلمات المفتاحية: متحسس غازي، غاز NO_2، تقنية الترذيذ بالبلازما، الاغشية الرقيقة من ZrO_2:MgO، تحسسية.