

Investigation of pyrolysis method for preparing CdO:In₂O₃ thin films gas sensor for NO₂ gas

The 5th International scientific Conference on Nanotechnology & Advanced Materials Their Applications (ICNAMA 2015) 3-4 Nov, 2015

Dr. Shatha Shammon Batros

Ministry of Science and Technology/ Baghdad .

Email: shathajammel@yahoo.com

Abstract

A novel CdO:In₂O₃ nano composite has been synthesized by a pyrolysis method. The prepared nano composites have been carefully characterized using X ray diffraction and atomic force microscopy. The obtained results showed that the synthesized nano composite CdO:In₂O₃ at optimum conditions has excellent grains. It was found that synthesized CdO:In₂O₃ nano composite can be used as NO₂ gas sensing to exhibit the highest sensitivity for NO₂ at 200°C. The constructed sensor showed a very low detection limit of 5 ppm .

Keywords: Thin films, crystalline structure, CdO:In₂O₃ thin films.

دراسة طريقة الرش الكيميائي الحراري لتحضير الاغشية الرقيقة من اوكسيد الكاديوم: اوكسيد الانديوم كمتحسس لغاز ثاني اوكسيد النتروجين

الخلاصة

المترابك CdO:In₂O₃ النانوي تم تحضيره بطريقة التحلل الكيميائي الحراري (PYROLYSIS) تم تقييم المترابك النانوي المحضر بدقة باستخدام حيود الاشعة السينية ومجهر القوى الذرية. النتائج المستحصلة تشير الى ان مسار تحضير المترابك CdO:In₂O₃ النانوي المستحصل عند الظروف المثالية اعطى نتائج ممتازة لاجسام نانوية يمكن استخدامها كمتحسس لغاز NO₂ واعطت افضل النتائج للتحسس عند درجة حرارة تشغيل للمتحسس تساوي 200 °C وعند نسبة تركيز للغاز قليلة و هي 5ppm.

الكلمات المفتاحية: الاغشية الرقيقة، التركيب البلوري، اغشية CdO:In₂O₃ الرقيقة

INTRODUCTION

Cadmium oxide (CdO) has been used extensively in transparent conducting oxide, solar cells [1,2], smart windows phototransistors [3], diodes [4], transparent electrodes [5], and solid state gas sensors [6] and in many other optoelectronic applications. CdO thin films exhibit high transmission in the visible and UV regions, as well as a high ohmic conductivity. Bulk CdO shows n-type conductivity mainly due to oxygen vacancies. In the recent years, many different techniques such as thermal evaporation [7] sputtering [8], solution growth [9], pulsed laser sputtering [10], activated reactive evaporation [11] and spray pyrolysis deposition (SPD) [12-14], have been used for the preparation of CdO thin film. SPD technique provides a simple route of

synthesizing thin films because of its simplicity, low cost experimental setup from an economical point of view. In addition, this technique could be used for the production of large-area thin film deposition without any high vacuum system. This method has good control over the thickness uniformity and good adherence to the substrate. It was observed that with doping by different types of metallic ions, the physical properties of CdO could be controlled for optoelectronic applications. So that doping with ions like In, Sn, Al, Sc, and Y, improves its n-type conductivity and increases optical band gap [15-18]. Surface roughness's, in homogeneity and intrinsic defects, etc. are the cause of the optical losses. From the practical point of view, these properties can severely degrade or modify the performances of a component. Overall, the structural and optical properties of the thin films depend on the method of the preparation. The properties of the films are influenced by the geometry of the experimental setup.

Nitrogen dioxide (NO₂) is one of the main harmful gases, which provokes noxious effects on environment and human health. Resistive-type sensors based on metal-oxide semiconductors have been intensively studied in the last decades due to the low cost, technological simplicity, small size, and ease of handling. Besides, thin-film gas sensors show high performance features such as high stability and fast response. Furthermore, the compatibility with micromachined structures allows sensor miniaturization, reduction of the production cost, and power consumption [19-21].

In this context, our work deals with gas-sensing properties of thin films of (CdO) (In₂O₃) mixed oxide for NO₂ detection. Spray pyrolysis technique was selected to prepare the oxide films since it is an inexpensive and simple technique, which allows obtaining a wide range of nano structured oxides with high surface area.

Experimental

CdO:In₂O₃ thin solid films were prepared using the spray pyrolysis technique (Figure 1), which is a versatile technique that can be used to produce thin solid films. With this method the particle's size can be easily controlled by changing the concentration in the starting solution and the atomization parameters.

Chemical spray pyrolysis is one of the major techniques used to deposit a wide variety of materials including metal or alloy oxides. Generally, spray pyrolysis deposition system which is mainly consists of the following four sections: (a) the reactants and carrier gas assembly connected to the spray nozzle at the entrance of the reaction chamber, (b) the reaction chamber in which there is a resistive heater used to heat the substrate to the required temperature for thin film deposition, (c) the temperature controller that monitors the deposition temperature and controls the desired substrate temperature and (d) the exhausting gas module. The substrate temperature was measured using a K-type thermocouple to an accuracy of ± 1 K. The film were prepared on clean glass substrates, the slides first cleaned in distilled water in order to remove the impurities and residuals from their surfaces, followed by rinsing in chromatic acid (for two day), to introduce functional groups called nucleation and /or epitaxial centers, which formed the basis for layer films growth. Then the samples were washed repeatedly in deionized water, and finally put in ultrasonic agitation with distilled water for 15 min then dried. 0.1M CdO:2%In thin films were prepared from solutions of cadmium acetate

Cd(CH₃COO)₂·2H₂O diluted with methanol and distiller water in the ratio 1:1 and doping CdO solution in a ratio of (2%) with 0.1 M from mixture of InCl₃ and water distiller. The deposition of CdO:In thin films 0.1M molar concentrations were carried by spraying an aqueous solutions onto a heated glass substrates at (350±10°C). The optimized deposition parameters such as spray nozzle substrate distance (29cm), spray time (5s) and the spray interval (50s) were kept constant. The pressure of the carrier gas (N₂) was 4 mbar. The crystalline structure of the films was confirmed by X-ray diffraction (XRD, Shimadzu, DIFRACTOMETER / 6000,) with Cu K α radiation $\lambda = 1.5406\text{\AA}$).

Film thickness was measured after evaporation by optical interferometer method, using He-Ne Laser $\lambda = 0.632 \mu\text{m}$ and the thickness were determined using the formula:

$$d = \frac{\Delta x \lambda}{x 2} \quad \dots (1)$$

Where d is the thickness of sample, x is fringe width, Δx is the distance between two fringes and λ is the wavelength of He-Ne laser light, and its values are 400 ± 10 nm. AFM analysis is also studied for the sample by using atomic force microscopy (AFM), model A2000.

Sensor construction and test

In this research, glass substrates (2.5 cm × 2.5 cm × 0.2 cm), prepared with an inter digitized electrodes were used as sensing device. Fig. 1(a,b) shows the sensor configuration. The homogenous thin films as sensing layer was tested. Silver paste was used to fix two contact wires. The thickness of the thin films film was measured to be 400 ± 10 nm. For sensor test, the sensor chip (Fig. 1) was inserted into the isolated box which filled by N₂ gas. The temperature of sensor chip was adjusted in 135°C and a constant voltage of 60 V was applied by a power supply instrument into the two output wires of sensor chip. Finally, NO₂ gas was injected into the box. Internal atmosphere of the box was circulated by a small fan to make a homogenous gas. After stabilizing, the current of sensor circuit was determined by a high sensitive galvanometer. The determined current was related to the electrical resistance of the sensor. The sensor resistance was related to the NO₂ concentration in the box.

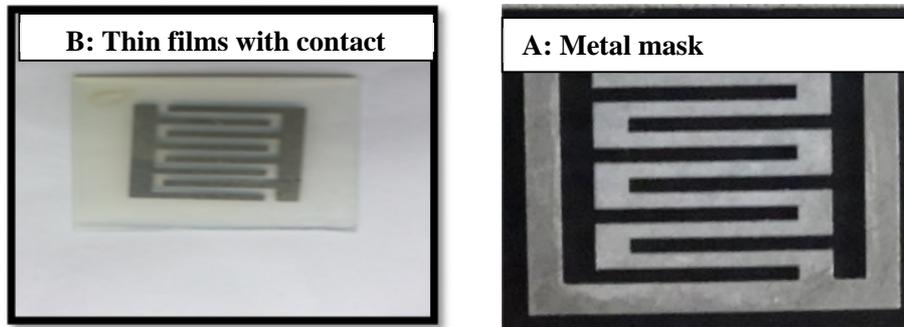


Figure (1) (A,B) scheme of used sensore device

Results and Discussion

Structural properties

Figure 2 shows the X ray diffraction (XRD) patterns of the prepared CdO:2%In film of molar concentrations (0.1M). The pattern show polycrystalline of cubic CdO structure (NaCl structure) and CdO:In films are composed of crystallites of CdO and In₂O₃ (JCPDS Card 2010). XRD shows neither the formation of CdO and In₂O₃ nor mixed phases. It can be clearly seen that the film is preferentially orientated along (222) crystallographic directions, and this is in agreement with the result obtained by others on film prepared by sputtering [22], vacuum evaporation [23] and spray pyrolysis [24]. In figure (3:A,B), a typical 5×5 μm² sized AFM image of CdO:In₂O₃ film surface is shown. The film crystallites are well shape and uniform in size. It was observed, from 2D, 3D image that, the films exhibit a surface columnar morphology, which can be a consequence of crystalline preferential orientation. AFM images indicate that the used preparation conditions of the films are more favorable to obtain sample with excellent shape as it shown in figure (4). The Granularity cumulation distribution chart and the distribution pattern of CdO: In₂O₃ grain size of the sample are shown in figure (5), (6) which deals that the grain size are about ~125 nm .

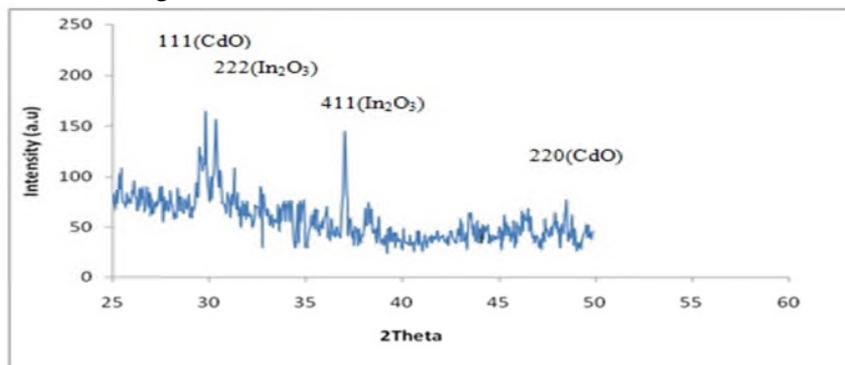


Figure (2) The X ray diffraction (XRD) patterns of the prepared CdO: In₂O₃ thin films

Table (1): The structural properties of CdO:In₂O₃ thin films

Sample	2θ (deg)	D (Å)	I / I ₀	FWHM (deg)	Identification with (hkl)
CdO:In ₂ O ₃ 3	29.8248(CdO)C	2.9932	44	0.262	111
	30.3733(In ₂ O ₃)C	2.9404	50	0.220	222
	37.0240(In ₂ O ₃)C	2.4261	56	0.205	411
	48.5733(CdO)C	1.8728	28	0.366	220

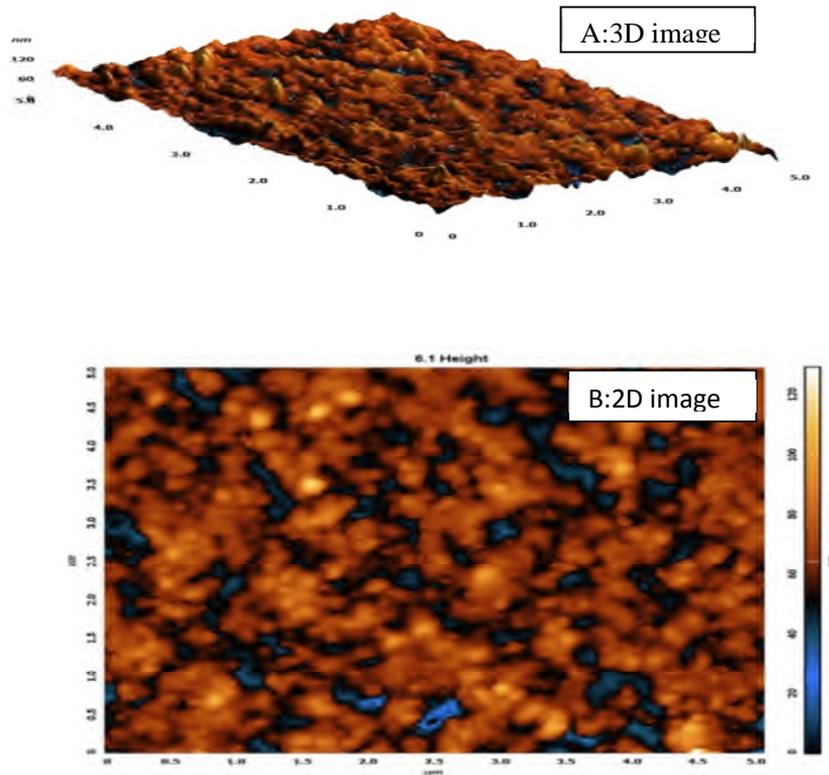


Figure (3(A,B)) AFM micrographs characteristic of CdO: In₂O₃ thin film

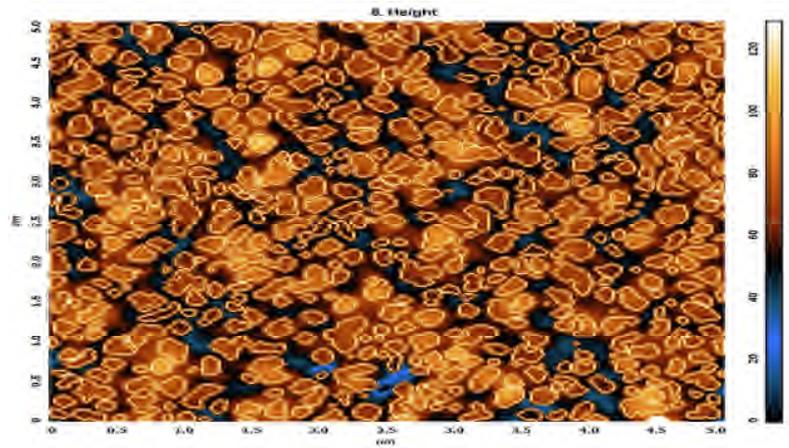


Figure (4) The shape of CdO:In₂O₃ grains

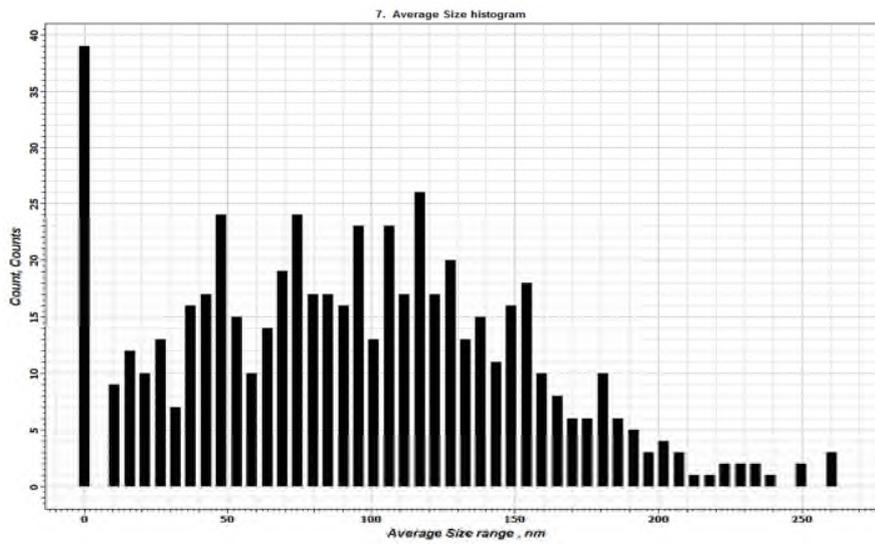


Figure (5) Granularity cumulation distribution chart of CdO:In₂O₃ sample

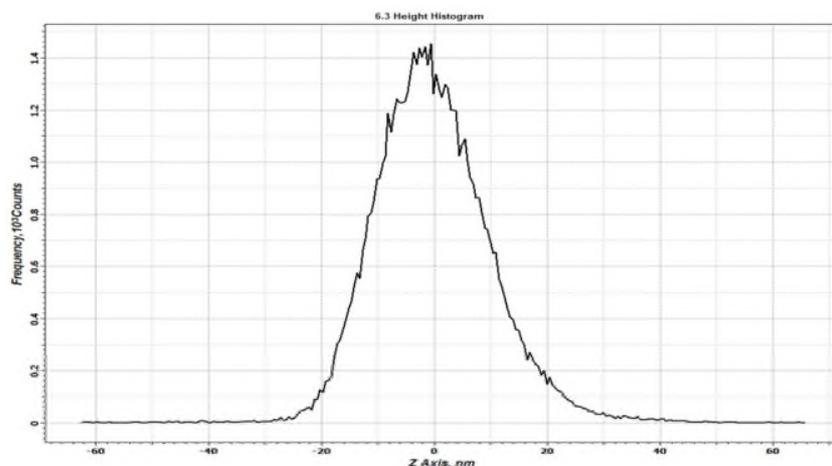


Figure (6) The distribution patterns of the grain size for CdO: In₂O₃

Figure (7) shows the resistance of sensor with time at different operation temperature. Our results show increasing in the resistance values with increasing operation temperature.

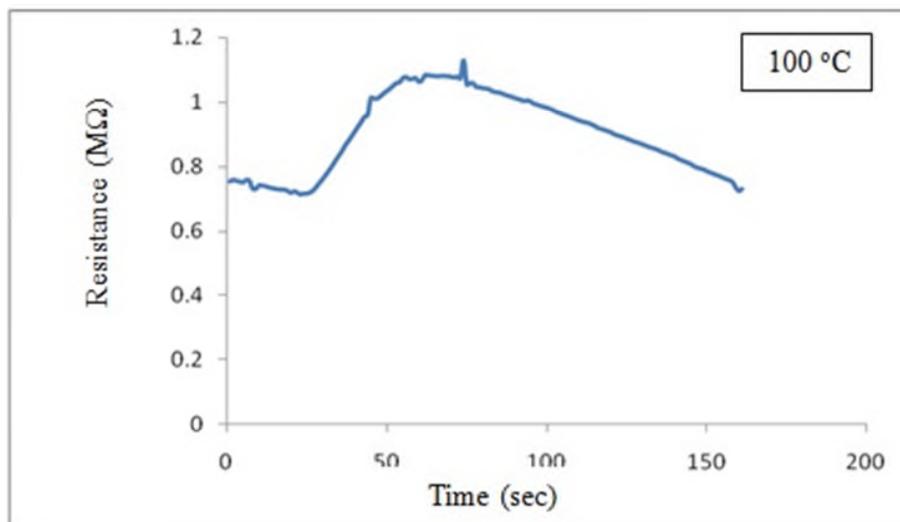
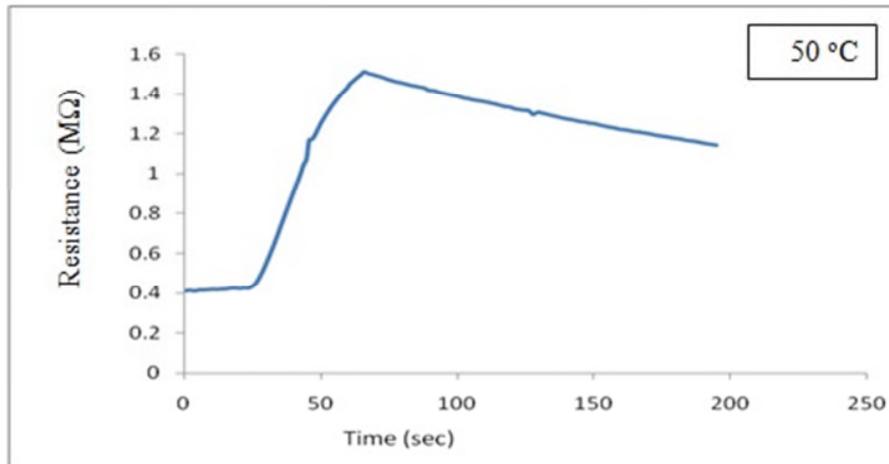
A relatively short response time and recovery time at different operation temperature was noticed at 5ppm NO₂ gas concentration. The explained behavior also predicts the response of the material to the presence of oxidizing gases, which results in an increase of the resistance. Figure 7. depicts the sensor response to NO₂ measured in the temperature interval 50 °C–300 °C for the different samples studied. The sensor response (*S*) in our case is defined as the resistance ratio, and being the sensor resistance in presence of the target gas and air, respectively. The gas concentration was fixed at 5 ppm, is observed that the sensor resistance rises in presence of NO₂ for all temperatures and a well-defined maximum on sensor response is achieved at about 200 C. The observed behavior may be understood by considering that the kinetic of the surface interaction is thermally activated and determined by the concurrence of several processes of adsorption, reaction, and desorption of previously adsorbed molecules of NO₂. At temperatures below 200° C, the sensor response change might be attributed mainly to the adsorption and/or reaction of NO₂ molecules on the solid surface according to the following mechanisms as it in [25].

The ratio of measured resistance before and after exposing the sensor surface to gas gives sensitivity [26]. Table (2) refers to the response and rapid time for sensor. The sensitivity of sensor can be calculated from the relation (2).

$$S\% = (R_{\text{air}}(\Omega) - R_{\text{gas}}(\Omega)) / R_{\text{air}}(\Omega) * 100\% \quad \dots(2)$$

Where

R_{air} , R_{gas} is resistance in air and gas the for NO₂ vapor. The sensing properties were studied at low concentrations of gases vapor (5ppm). This result obtained in that methods are promising for the preparation of sensitive and low cost gas sensor. Figure (8) shows the sensitivity to NO₂ gas with different operation temperature. The sensitivity S% increased with increasing operating temperature T.



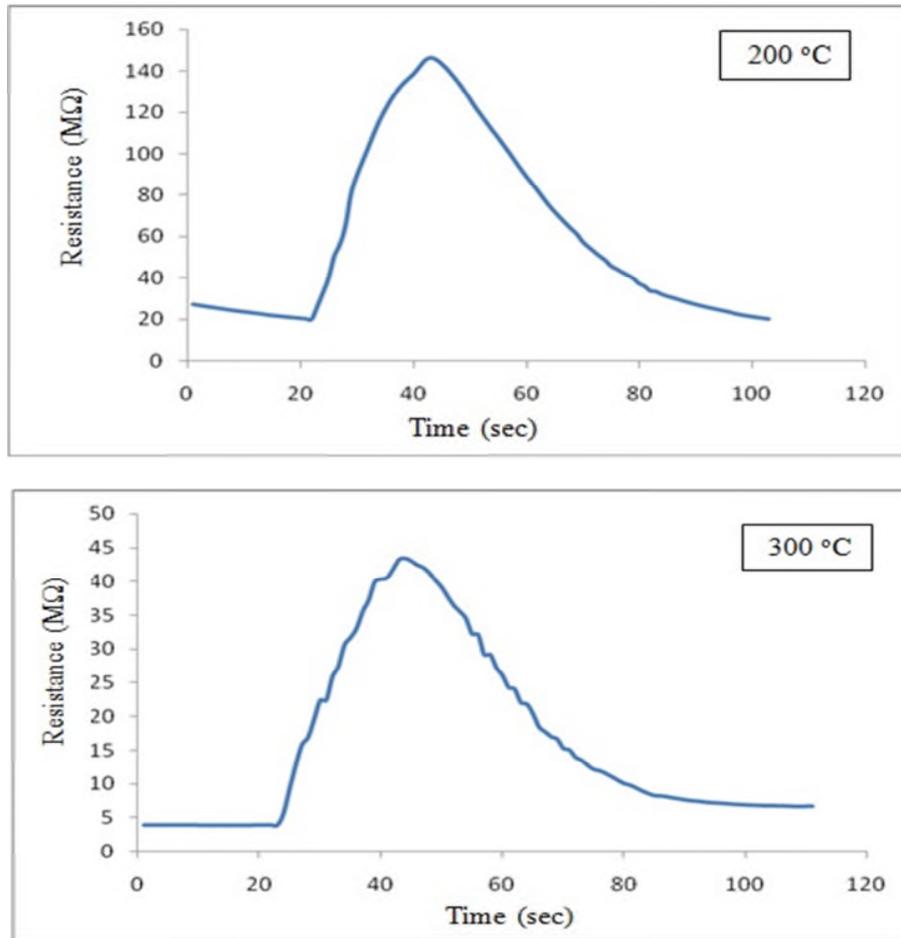


Figure (7) the resistance vs. time for different operation temperature for NO₂ gas sensor

Table (2) The CdO:In₂O₃ thin films sensor properties to NO₂ gas at different temperature

Temp(°C)	response time(sec)	recover time (sec)
50	37.8	210.6
100	32.4	79.2
200	18.9	51.3
300	18.9	50.4

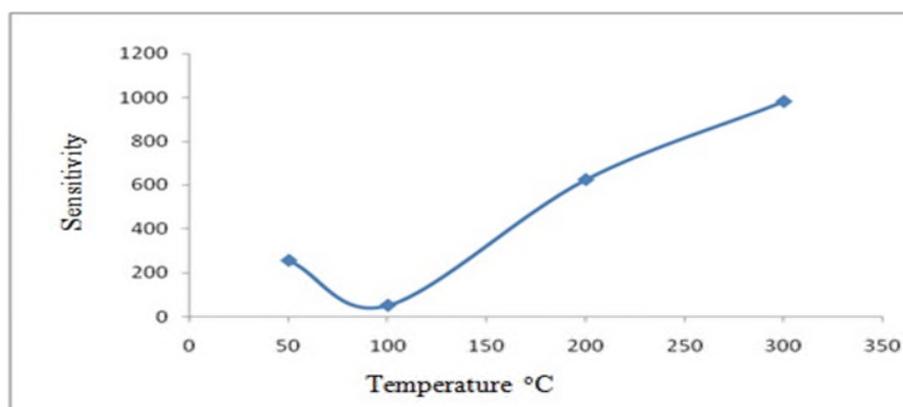


Figure (8) The sensitivity of CdO:In₂O₃ sensor for different operation temperature to NO₂ gas

Conclusions

A novel NO₂ gas sensor based on (CdO) (In₂O₃) mixed-oxide thin films deposited by spray pyrolysis has been studied. The sensor follows a typical surface-controlled gas-sensing model. A different behavior was observed when the sensor surface was exposed to exam at different temperatures. Thus, the sensor resistance reaches maximum at temperature (200°C), while it decreases with further increase of temperature to (300° C) as a consequence of different surface interaction mechanisms. The sensitivity S% increased with increasing operating temperature.

References

- [1] Trindade, T., P.'Brien and N. Pickett, 2001. Chem. Mater., 13: 3843.
- [2] Sravani, C., K. Reddy, O. Md. Hussain and P.J. Reddy, 1996. J. Solar Energy, Soc. India, 1(6).
- [3] Su, L.M., N. Grote and F. Schmitt, 1984. Electron. Lett., 20: 716.
- [4] Gomez. O., A. Arias-Carbajal Readigos, 2001. J. Campos, M.T.S. Nair, and P. Nair, Mod. Phys. Lett., B 17: 609.
- [5] Lewis, B.J. and D. Paine, 2000. Mater. Res. Soc. Bull., 25: 22.
- [6] Yan, M., M. Lane, C. Kannewurf and R. Chang, 2001. Appl. Phys. Lett., 78: 02342.
- [7] Dakhel, A.A. and F. Henari, 2003. Cryst. Res. Technol., 38(11): 979.
- [8] Subramanyam, T., Uthanna K., and Sinivasulu B. , 2001. 1998. Materials Letters, 35: 214 Appl.1998. Surface Science, 169: 529.
- [9] Varkey, A.J. and A. Fort, 1994. Thin Solid Films, 239: 211.
- [10] Shagnov, I.I., B. Kryzhanovskii and V. Dubkov, 1981. Sov. J. Opt. Technol., 48: 280.
- [11] Ramakrishna Reddy, K.Sravani and R. Miles, 1998. J. Cryst. Growth, 184/185, 1031.
- [12] Uplane, M.D., P. Kshirsagan, B. Lokhande and C. Bhosale, 2000. Materials Chemistry and Physics, 64: 75.

- [13] Murthy, L.C.S. and K.Rao, 1999. Bull. Mater. Sci., 22: 953.
- [14] Kul, M., M. Zor, A. Senol Aybek, S. Irmak, E. Turan, 2007. Thin Solid Films, 515: 8590.
- [15] Freeman, A.J., K. Poepelmeier, T. Mason, R.Chang, and T. Marks, 2000. Mater. Res. Soc. Bull., 25: 45.
- [16] Ghosh, P.K., R. Maity and K. Chattopadhyay, 2004. Sol. Energy Mater. Sol. Cells, 81: 279.
- [17] Lakshmanan, T.K. and J. Electrochem, 1963. Soc., 110: 548.
- [18] Dakhel, A.A., 2008. Solar Energy, 82: 513.
- [19] S. G. Ansari, P. Borojerdian, S. Kulkarni, S. Sainkar, R. Karekar, and R. Aiyer, J. Mater. Sci., vol. 7, pp. 267–270, 1996.
- [20] B. Flietner and I. Eisele, “, Thin Solid Films, vol. 250, pp. 258–262, 1994.
- [21] B. Tofield, in Solid State Gas Sensors, P. T. Moseley and B. Tofield, Eds. Bristol, U.K.: Adam Hilger, 1987, pp. 198–238.
- [22] Chu, T.L., S. Chu, 1903. J. Electron Mater., 19: 1003.
- [23] Dakhel, A.A., 2010. Thin Solid Films, 518: 1712.
- [24] Rusu, D.I., G. Rusu, D. Luca, 2011. Acta Physica Polonica A, 119: 850.
- [25] R. Ferro, J. Rodríguez, I. Jiménez, A. Cirera, J. Cerdà, and J. Morante, IEEE SENSORS JOURNAL, VOL. 5, NO. 1, 2005, 48-52.
- [26] Rambu. A , Sirbu. D , Iftimie. N, Rusu. G , Thin Solid Films, 520, (2011) 1303-1307.