Abdulrahman and Alias Iraqi Journal of Science, 2021, Vol. 62, No. 11, pp: 3858-3870
DOI: 10.24996/ijs.2021.62.11.7

ISSN: 0067-2904

Synthesis and Characterization of a Nano $(CdO)_{0.94}$:$(In_2O_3)_{0.06}$ / Si gas Sensor

H.A.Abdulrahman and, M.F.A.Alias*
Department of Physics, College of Science, University of Baghdad, Baghdad, Iraq

Received: 22/8/2020 Accepted: 10/2/2021

Abstract
In this work, a $(CdO)_{0.94}$:$(In_2O_3)_{0.06}$ film was developed on a glass substrate using Q- switching pulse laser beam (Nd:YAG; wavelength 1064 nm). The quantitative elemental analysis of the $(CdO)_{0.94}$:$(In_2O_3)_{0.06}$ thin film was achieved using energy dispersive X- ray diffraction (EDX). The topological and morphological properties of the deposited thin film were investigated using atomic force microscope (AFM) and field emission scan electron microscopy (FESEM). The I-V characteristic and Hall effect of $(CdO)_{0.94}$:$(In_2O_3)_{0.06}$ thin films were used to study the electrical properties. The gas sensor properties of the film prepared on n-Si were investigated for oxidization and reduction gases.

Keywords: Gas nanosensors, $(CdO)_{0.94}$:$(In_2O_3)_{0.06}$ thin film, morphological properties, electrical property and pulsed laser deposition technique.

تصنيع ودراسة خصائص المتحسس الغازي للمركب النانوي $(CdO)_{0.94}$:$(In_2O_3)_{0.06}$)

هاجر عبد الستار عبد الرحمن , ميسون فيصل احمد الياس*
قسم الفيزياء , كلية العلوم , جامعة بغداد , بغداد , العراق

الخلاصة
في هذا العمل تم تحضير اغشية $(CdO)_{0.94}$:$(In_2O_3)_{0.06}$ والمرسبة على ارضية زجاجية باستخدام تقنية الليزر النبضي (ليزر الندميوم- ياك , بطول موجي 1064 نانومتر).تم تحليل العناصر الكمية للأغشية المحضرة باستخدام مطيافية تشتت الطاقة بالأشعة السينية . تم دراسة الخصائص السطحية للأغشية المرسبة باستخدام مجهر القوة الذرية المجهر الالكتروني الماسح . خصائص التيار – الفولتية وتأثير هول لاغشية اوكسيد الكادميوم مع اوكسيد الانديوم بنسبة 6 % تم استخدامها لدراسة الخصائص الكهربائية . تم دراسة خصائص المتحسس الغازي للاغشية المحضرة والمرسبة على ارضية سليكونية من النوع السالب باستخدام غازين احداهما مؤكسد والاخر مختزل .

Introduction

In recent years, transparent thin films of conductive oxides (TCOs), such as PbO , CdO, ZnO, SnO_2, In_2O_3, and MoO_3, of semiconductor materials have been used in various applications, including transistors, optical storage devices, gas sensors, phototransistors, and photo-thermal and photovoltaic converters [1,2]. Most of the studies related to transparent conducting metal oxides were performed on anion deficient (oxygen deficient) materials and, hence, always produced n-type conductors [3, 4]. It is well known that high carrier mobility (μ_H) is essential for manufacturing TCOs with good electro-optical properties [5].

*Email: may20131313@yahoo.com

The preparation of thin films of nanometeric size is important because of their potential applications in various science and technology fields, such as electronics, optics, space, aircraft and other industries [6, 7]. Nanofilms are different from those made of either the bulk materials or single atoms [8]. These oxide films showed an extraordinary important because of their potential applications in electronics, gas sensing, and photonic devices [9].

Cadmium oxide (CdO) film is an n-type that belongs to the II - VI group, with face center cubic crystal structure (FCC) (rock-salt crystal structure) [5].

The CdO film is one of the most promising TCO semiconductors due to its high electrical conductivity and high carrier concentration, which make it useful for various applications, such as photodiodes and gas sensors [10, 11]. It is well know that the electrical properties of CdO films can be improved by the movement of interstitial cadmium atoms and oxygen vacancies [12].

Indium oxide (In_2O_3) is a significant translucent conducting oxide of intrinsic semiconductor. It has a considerable chemical stability and high electrical conductivity. Therefore, it is used for the fabrication of many types of devices, such as liquid crystal displays (LCD), light emitting diodes (LEDs), solar cells, gas sensors, and anti- reflective coatings [13- 15].

Indium oxide is an n-type degenerate semiconductor with a cubic bixbyite structure [16-18]. Many researchers over the last few years have demonstrated that the metal–oxide–semiconductors can be widely used as sensors to detect various gases. The sensing properties of sensors need to be enhanced to achieve excellent selectivity with fast response and recovery time to detect low concentrations of materials in the environment [10].

In this study, the topology, morphology, and electrical and gas sensing properties of a nano $(CdO)_{0.94}$: $(In_2O_3)_{0.06}$ film prepared by pulsed laser deposition technique were investigated.

Materials and Methods

A pellet was prepared from 94 wt% CdO and 6 wt% In_2O_3 powders (Sigma Eldritch; 99.98 purity) with dimensions of 9 mm diameter and 5 mm thickness. Thin film of $(CdO)_{0.94}$:$(In_2O_3)_{0.06}$ was prepared using pulsed laser deposition technique with 600 mJ energy. The Nd:YAG laser of 1064 nm wavelength was operated at 6 Hz repetition rate and 7 ns pulse duration. The target-to-substrate distance was 2 cm.

The quantitative elemental analysis of the $(CdO)_{0.94}$:$(In_2O_3)_{0.06}$ thin film was examined using energy dispersive X-ray (EDX) (DeyPetronic Co.) which provides information about the composition of the prepared films. The topological surface analysis was carried out by using atomic force microscope (AFM) (AA3000 Scanning Probe Microscope SPM, tip NSC35/AIBS, Angstrom Ad-Vance Inc).

Field emission scanning electron microscopy (FESEM) is equipped with energy-dispersive produce by MIRA3 model-TE-SCAN, (DeyPetronic Co.), was used to provide morphology and elemental information.

The electrical properties of the prepared $(CdO)_{0.94}$:$(In_2O_3)_{0.06}$ film were studied using the measurements of I-V characteristics and Hall effect. The I–V measurement was taken in the dark and in room light at room temperature (RT) using a system that consists of a Keithley source meter, which is used as the electrode contact material for the film. Two strip contacts were made by the deposition of aluminum on the prepared film surface, using the thermal evaporation technique. The film contact configuration had 1 cm length and 1cm width. Silver paste was used to fix the two contact wires.

Two main parameters were taken into account throughout the fabrication of $(CdO)_{0.94}$:$(In_2O_3)_{0.06}$ /n-Si gas sensor, namely the response and recovery time. The testing system for the proposed gas sensor consisted of cylindrical stainless steel test chamber. It has an inlet for allowing the tested gas to flow in, along with an air admittance valve to allow the flow of atmospheric air after evacuation. A multi-pin feed through was used at the base of the chamber to allow the electrical connections to be established to the hot plate heater, K-type thermocouple, and sensor electrodes. A PC-interfaced digital multimeter (UNI-T UT81B) and a laptop PC were used to record the variation of the sensor resistance when exposed to the mixing ratios of air-NO_2 or H_2S gas at various operating temperatures (RT,323, 373, 423, and 473 K).

Results and Discussion

The results of the quantitative elemental analysis of the $(CdO)_{0.94}$:$(In_2O_3)_{0.06}$ thin film are shown in Figure 1, which were deduced from data measured by using the EDX technique. The values of the constituent elements of the prepared film were 8.0, 12.6, and 79.4 wt.% for In, O, and Cd, respectively. No other elemental peaks appeared in the EDX spectrum, which indicates the high purity of the prepared thin film [19]. It can be observed that oxygen deficiency may enable the sample to adsorb a large amount of oxygen species, which is one of the reasons of the improved electrical conductivity of the films [20].

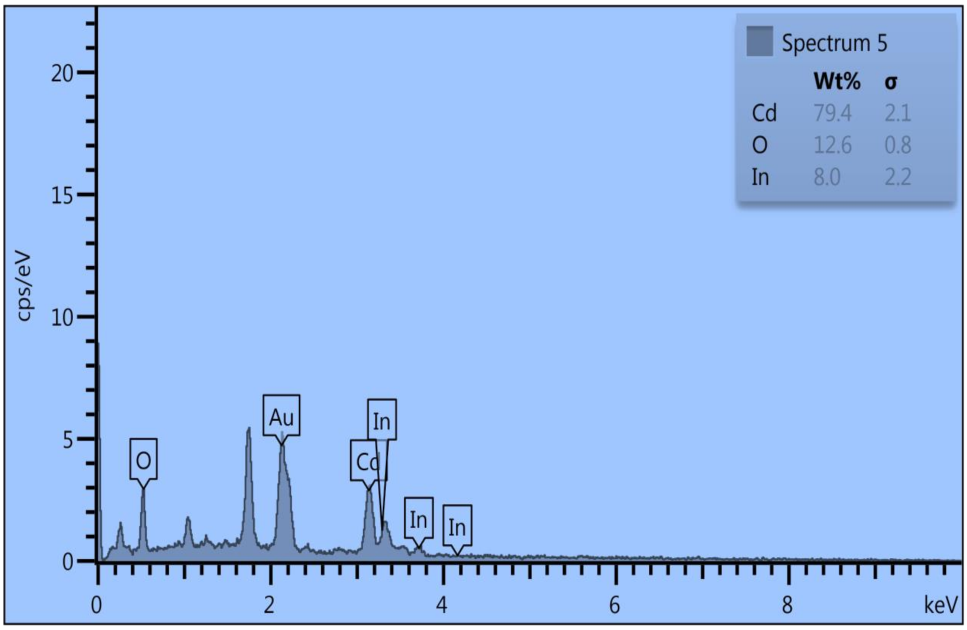


Figure 1-Quantitative elemental analysis of $(CdO)_{0.94}$:$(In_2O_3)_{0.06}$ thin film

The nanostructured $(CdO)_{0.94}$:$(In_2O_3)_{0.06}$ thin film were topologically characterized using the atomic force microscope technique. Figures 2 (a and b) show the two and three-dimensional images, respectively, whereas Figure 3 presents the distribution of granularity accumulation of the prepared $(CdO)_{0.94}$:$(In_2O_3)_{0.06}$ thin film deposited on a glass substrate at room temperature. One can observe clearly that the film exhibits a granular structure, distributed almost homogeneously on the surface. The small spherical grain agglomerates are uniformly distributed in shape and size along the film surface. Also, one can notice that the film possesses a high grain density distribution with tightly packed grains [7]. The fine topology and roughness of the film were observed by other researchers [10].

The root mean square (RMS), roughness, peak to peak, and average grain size values for the $CdO_{0.94}$: $In_2O_{0.06}$ thin film were found to be 25.1nm, 21.2nm, 101.1nm, and 88.7 nm, respectively. It is clear that the prepared film has a high roughness value, indicating that it possesses a high specific surface area of the sensing material (maximum roughness). This outcome usually has positive effects on the gas-sensing performance [10].

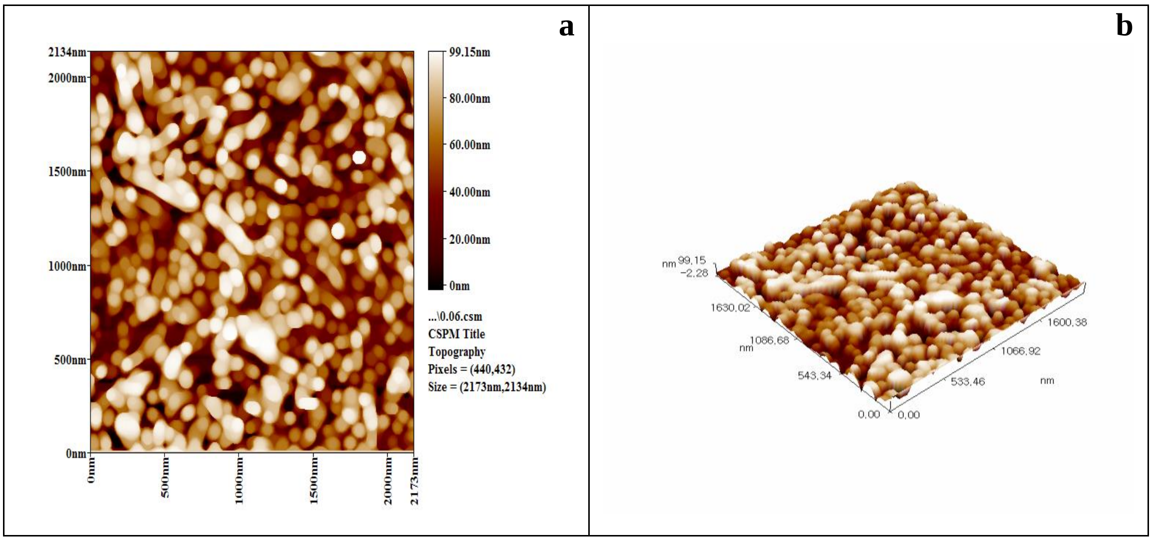


Figure 2-AFM images for $(CdO)_{0.94}$:$(In_2O_3)_{0.06}$ thin film a-2D image, b- 3D image.

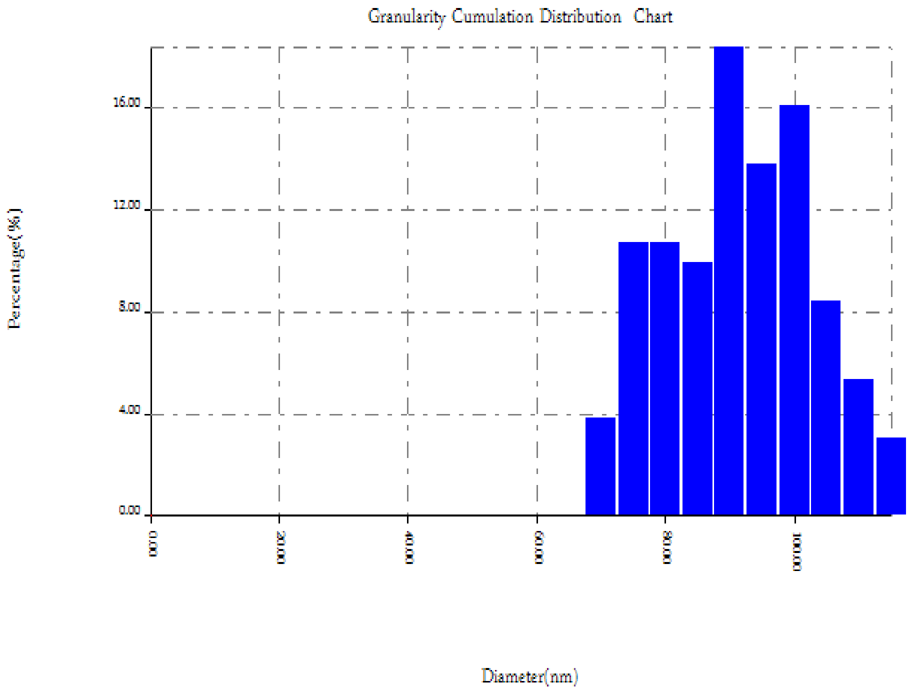


Figure 3- Granularity accumulation distribution for $(CdO)_{0.94}$:$(In_2O_3)_{0.06}$ thin films.

Field emission scanning electron microscopy (FESEM) images of the prepared $(CdO)_{0.94}$:$(In_2O_3)_{0.06}$ thin film are shown in Figure 4. It is clear that the particles are in the nano-size with a spherical structure. They are uniformly distributed and highly agglomerated in nature, due to the aggregation or overlap of smaller particles. The highest particle size is 183.1 nm , whereas the lowest is 24.56 nm [21].

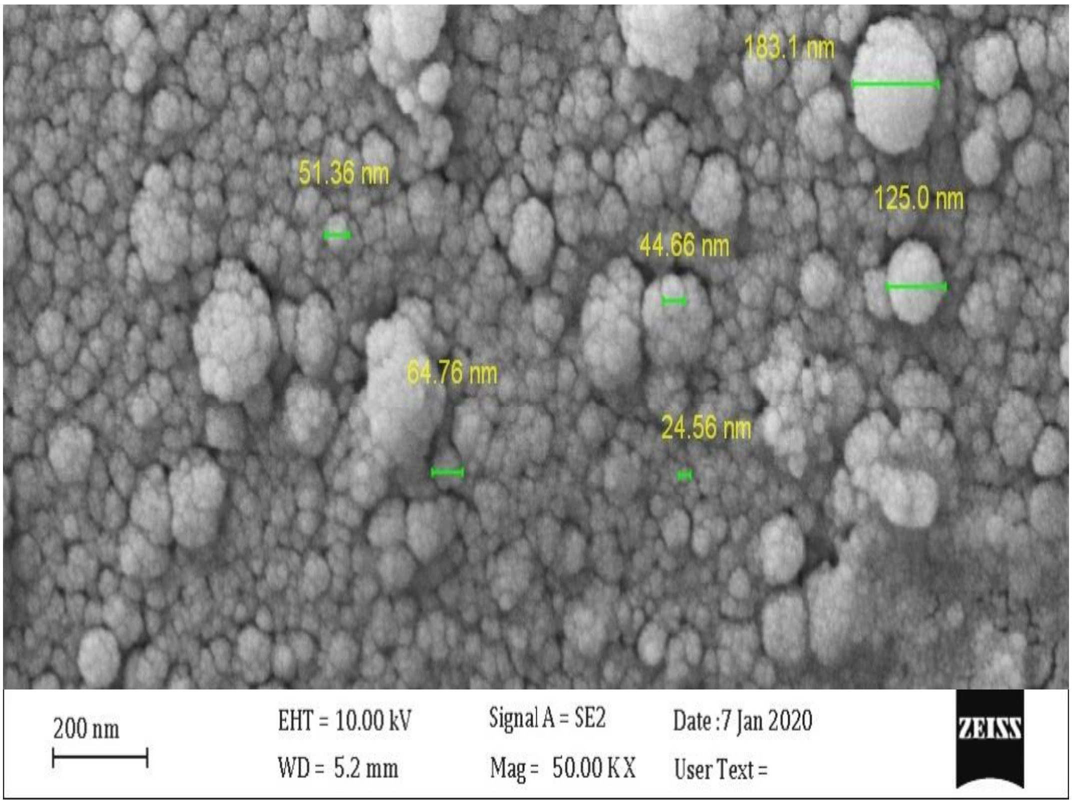


Figure 4-FESEM images for $(CdO)_{0.94}$:$(In_2O_3)_{0.06}$ thin film.

I–V measurement of the prepared $(CdO)_{0.94}$:$(In_2O_3)_{0.06}$ film was recorded in the forward and reverse bias at RT in the dark and room light, within a voltage range of 1.0 to -1.0 V, as displayed in Figure 5. As shown in this figure, the relation between the current and the applied voltage is linear, and nearly symmetrical in nature. This indicates that aluminum forms Ohmic contacts for the $(CdO)_{0.94}$:$(In_2O_3)_{0.06}$ thin film . This result is in line with other publications [22].

Hall coefficient (R_H), carrier concentration (n_H), carrier conductivity, and Hall mobility (μ_H) were calculated from the measurement of Hall effect for the $(CdO)_{0.94}$:$(In_2O_3)_{0.06}$ thin film deposited on a glass substrate. The n_H and μ_H values for the prepared film were calculated by using the following relations [23]:

$$n = 1/eR_H \quad \text{....(1)}$$

$$\mu_H = \sigma R_H \quad \text{....(2)}$$

where e is the electronic charge and σ is film conductivity.

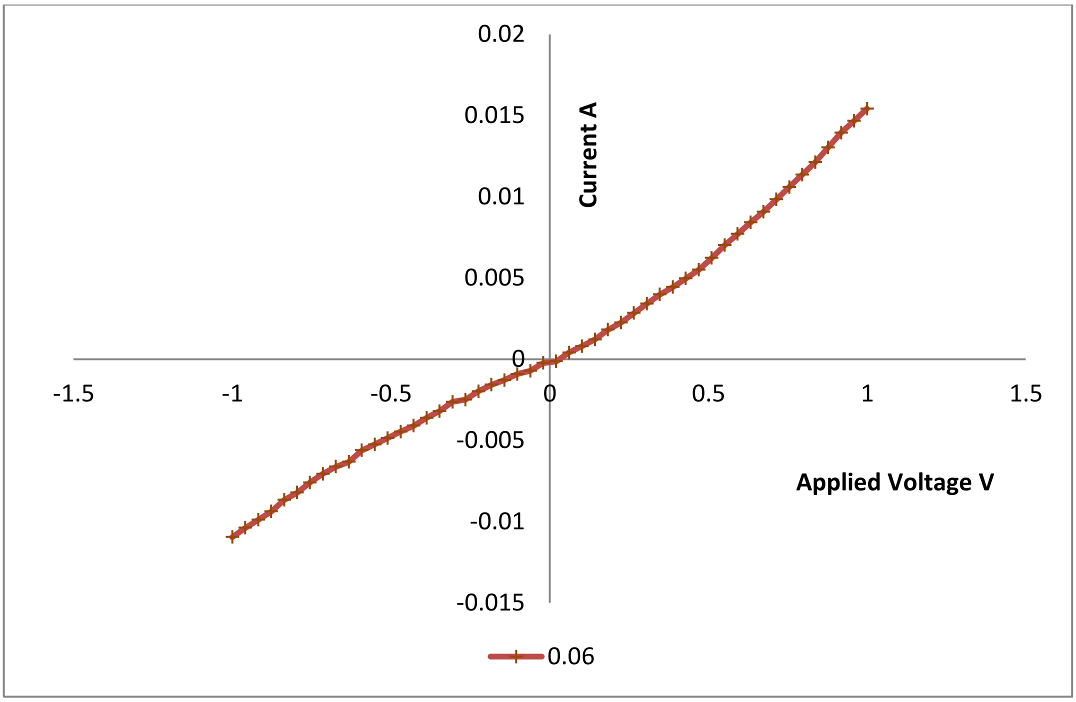


Figure 5- I-V characteristics of $(CdO)_{0.94}$:$(In_2O_3)_{0.06}$ thin film.

Hall measurement showed that the prepared film has a negative Hall coefficient, i.e. it has n-type charge carriers. This might be due to the fact that CdO has defects, such as interstitial cadmium atoms and oxygen vacancies. These defects can be easily ionized and the electrons induced by this process can contribute to the conduction of electricity, causing the film to act as an n-type semiconductor [10, 24]. The carrier concentration of $(CdO)_{0.94}$:$(In_2O_3)_{0.06}$ film is 5.253 $x10^{19}$ cm^{-3} and the sheet concentration is 2.101 $x10^{15}$ cm^{-3}. The mobility (μ), resistivity, and conductivity values of the film were found to be 2.367 cm^2 /V.s, 5.021 x 10^{-2} **Ω**.cm, and 19.92 S.cm, respectively.

The mechanism of sensing is based on the changes in the resistance of the film, which is controlled by gas species. The sensitivity (S) of the n-type metal oxide semiconductor is defined as the ratio of difference between the surface resistance of the film in air (R_a) and test gas (R_g) to its resistance in air or gas, as shown in the following equations [7, 25]:

$$S = \left|\frac{Ra-Rg}{Ra}\right| \times 100\% \quad \text{for oxidization gases} \quad (3)$$

$$S = \left|\frac{Ra-Rg}{Rg}\right| \times 100\% \quad \text{for reduction gases} \quad (4)$$

The temperature is an important parameter for gas sensing materials and the design of the sensor. The response time (t_{res}) is defined as the time required to reach 90% of the response signal, whereas the recovery time (t_{rec}) denotes the time needed to recover 90% of the original baseline signal, as extracted using the following relations [7]:

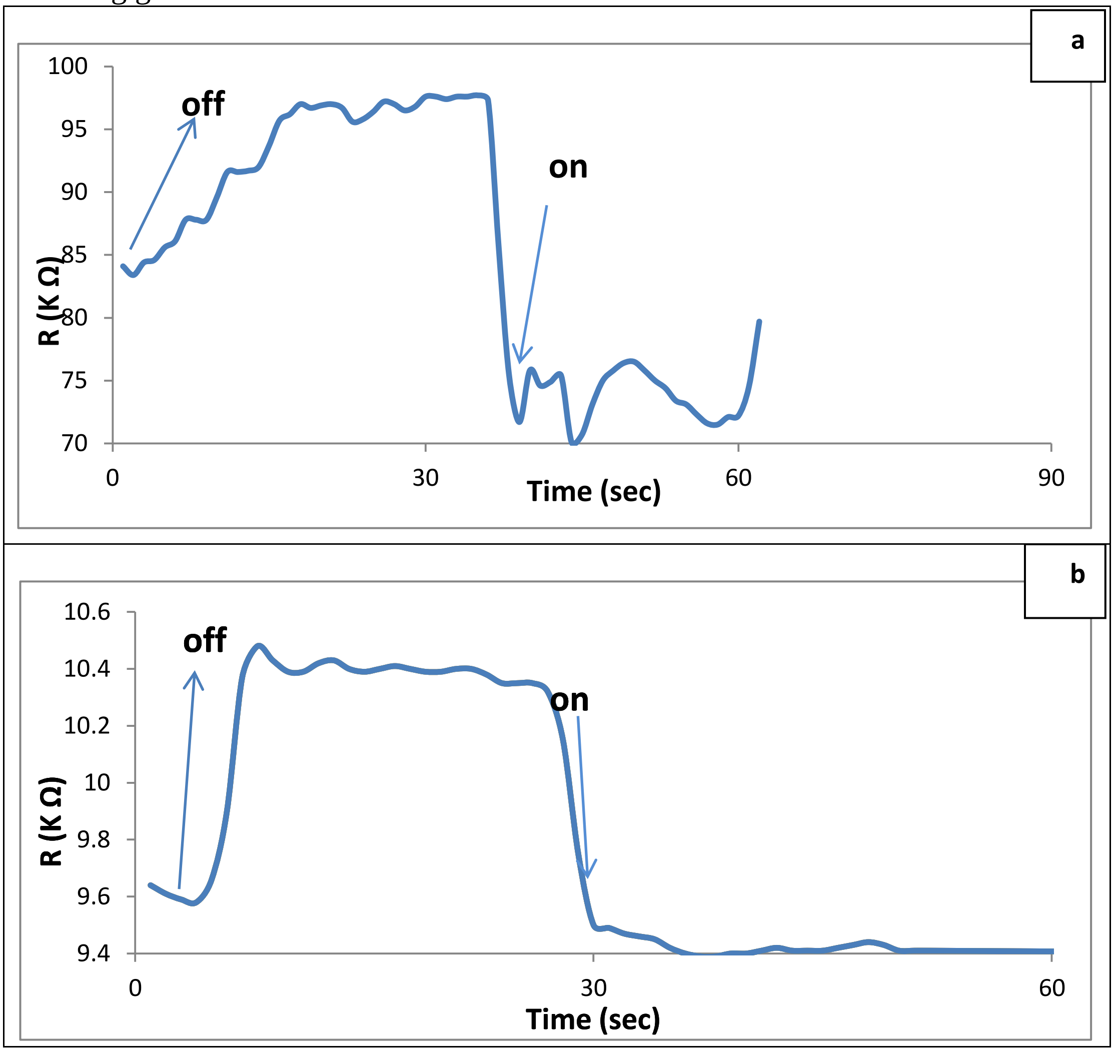
$$Response\ time = |t_{gas}(on) - t_{gas}(off)| \times 0.9 \quad (5)$$

$$Recovery\ time = |t_{gas}(off) - t_{gas}(on)| \times 0.9 \quad (6)$$

where t_{gas} (on) is the time when the gas is on and t_{gas} (off) is the time when the gas is off.

Figures 6 and 7 illustrate the sensing properties for $(CdO)_{0.94}$: $(In_2O_3)_{0.06}$ thin film deposited on n-Si substrate at different operation temperatures (RT, 323,373, 423, and 473 K) for the reducing gas (H_2S) and oxidization gas (NO_2), respectively. For the reducing gas, Figures 6a-d show a decrease in the resistance value when the gas is on, then it increases when the gas is off. For the oxidization gas, the operation is reversed, i.e. a decrease in the resistance value when the gas is off, followed by an increase when the gas is on, as shown in Figures 7 a-e. The figures show the variation of resistance as a function of time with on/off gas for

$(CdO)_{0.94}$: $(In_2O_3)_{0.06}$/n-Si sensor. Figures 8 and 9 a, b, c show the values of sensitivity, response time, and recovery time for the prepared sensor at different operation temperatures for H_2S and NO_2 gases, respectively. One can draw from these figures the best conditions that should be used to fabricate the gas sensor. Also, one should highlight the role of the operating temperature, as far as gas-sensor sensitivity is concerned, for detecting gases in the environment. The highest value of sensitivity of the prepared sensor for H_2S gas was 51.9 at 373 K operating temperature, with equal values of response and recovery time (0.9s). Whereas for the sensing of NO_2, the sensitivity value was 93.9 at RT, with 3.6 sec response time and 6.3 sec recovery time. Hence, the prepared gas sensor is more sensitive to oxidizing than reducing gases.



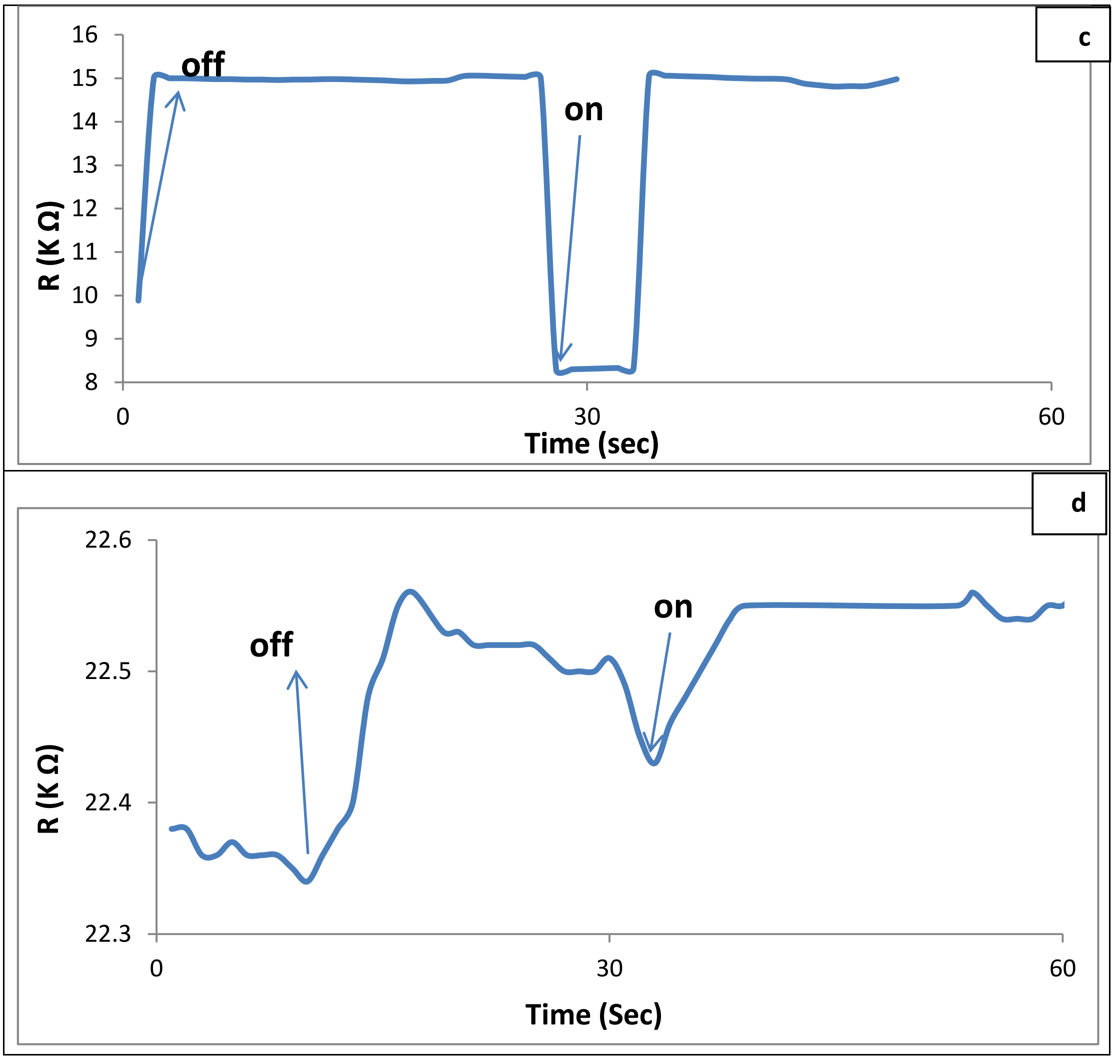
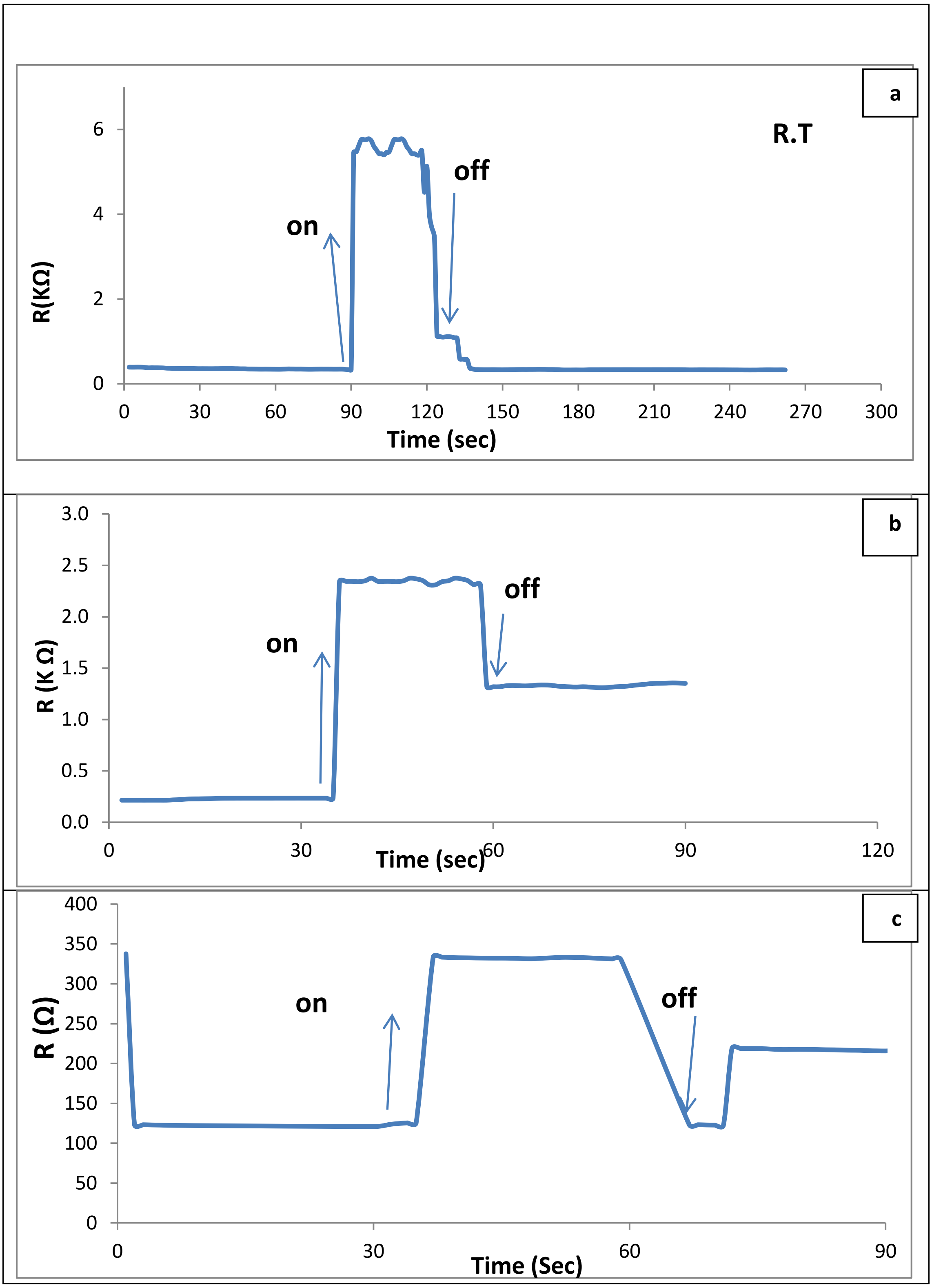


Figure 6- Resistance vs. time for $(CdO)_{0.94}$:$(In_2O_3)_{0.06}$ /n-Si sensor for H_2S gas at different operating temperatures; a-RT, b- 323K, c- 373K, d-423K.


a
R.T
R(KΩ)
on
off
Time (sec)
b
R (K Ω)
on
off
Time (sec)
c
R (Ω)
on
off
Time (Sec)

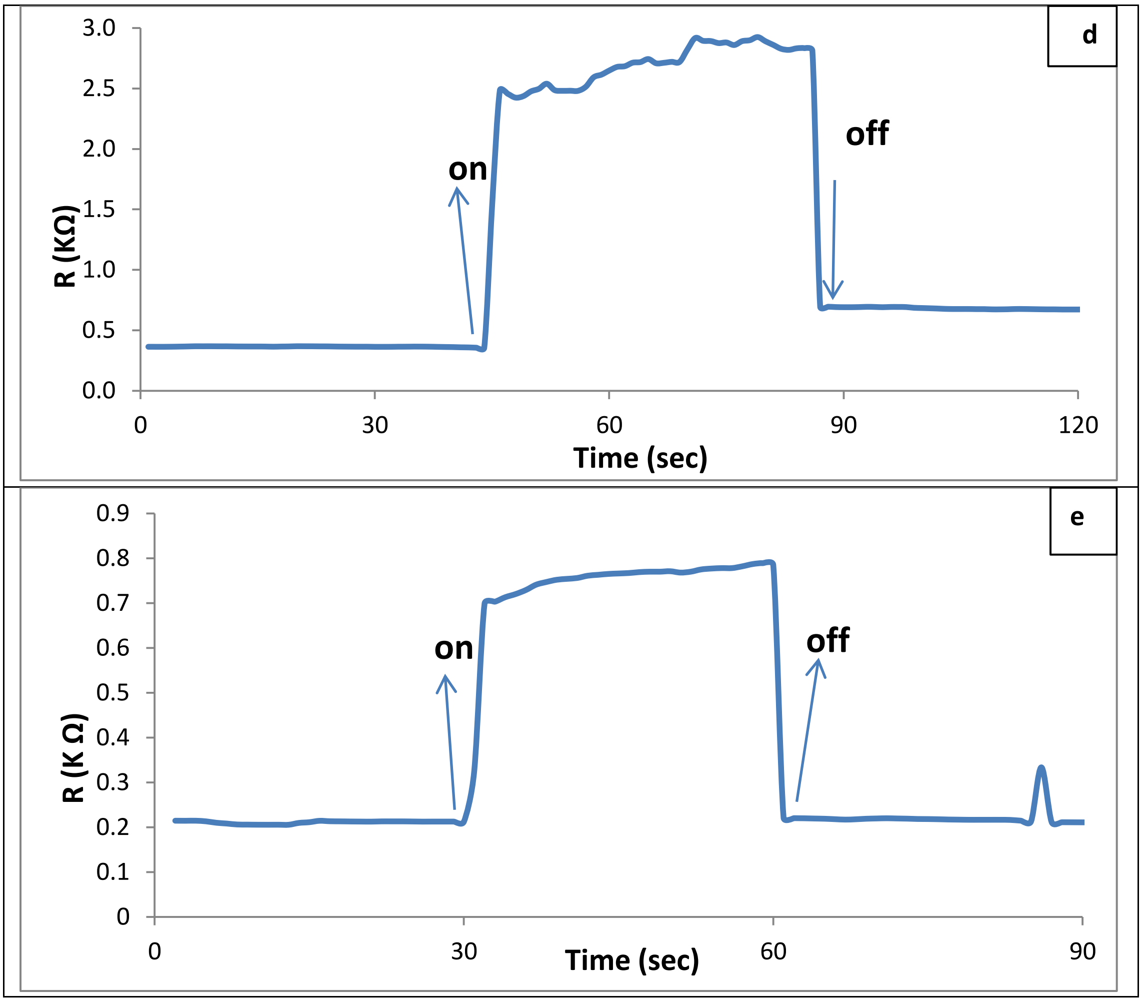
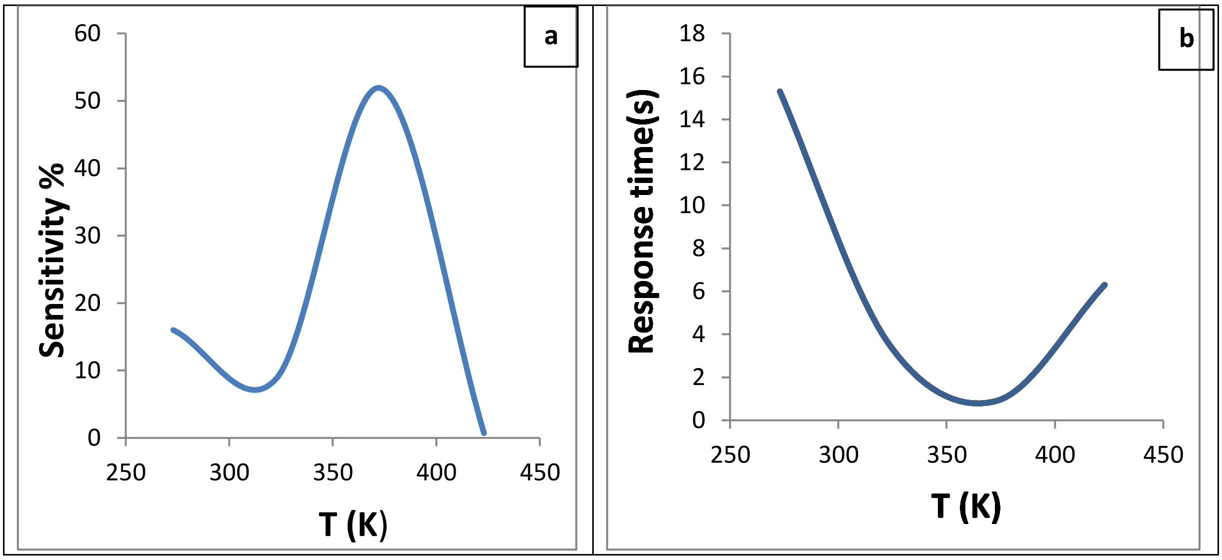


Figure 7-Resistance vs. time for $(CdO)_{0.94}$:$(In_2O_3)_{0.06}$ /n-Si sensor for NO_2 gas at different operating temperatures; a- RT, b- 323K, c- 373K, d- 423K, e -473K.



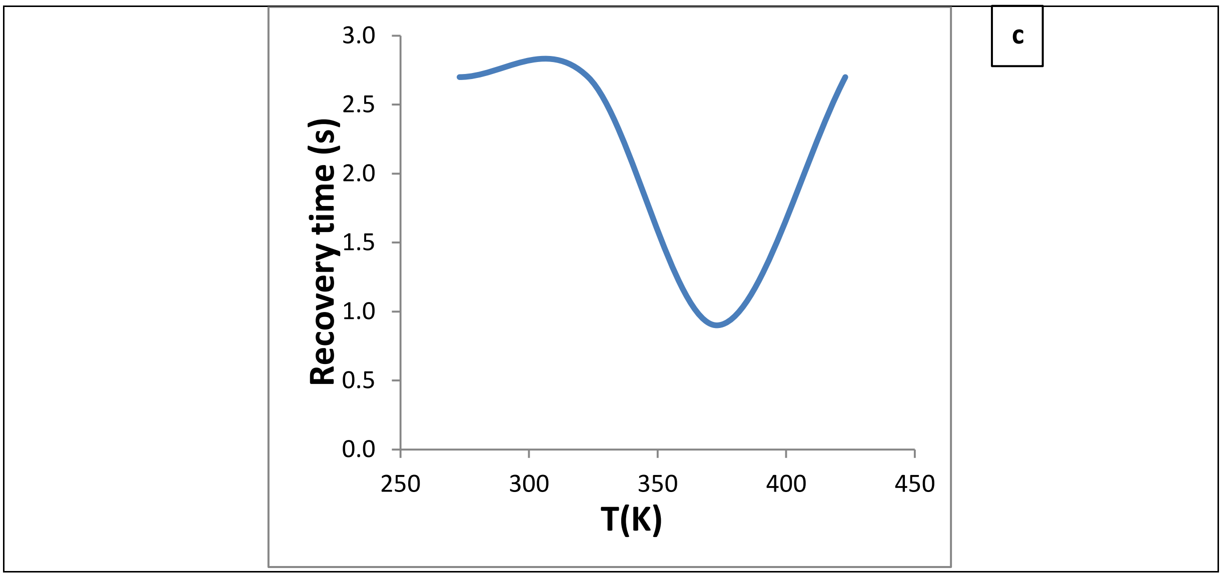


Figure 8-Variations in (a) sensitivity, (b) response time, and (c) recovery time for $(CdO)_{0.94}$:$(In_2O_3)_{0.06}$ / n-Si sensor of H_2S gas at different operating temperatures.

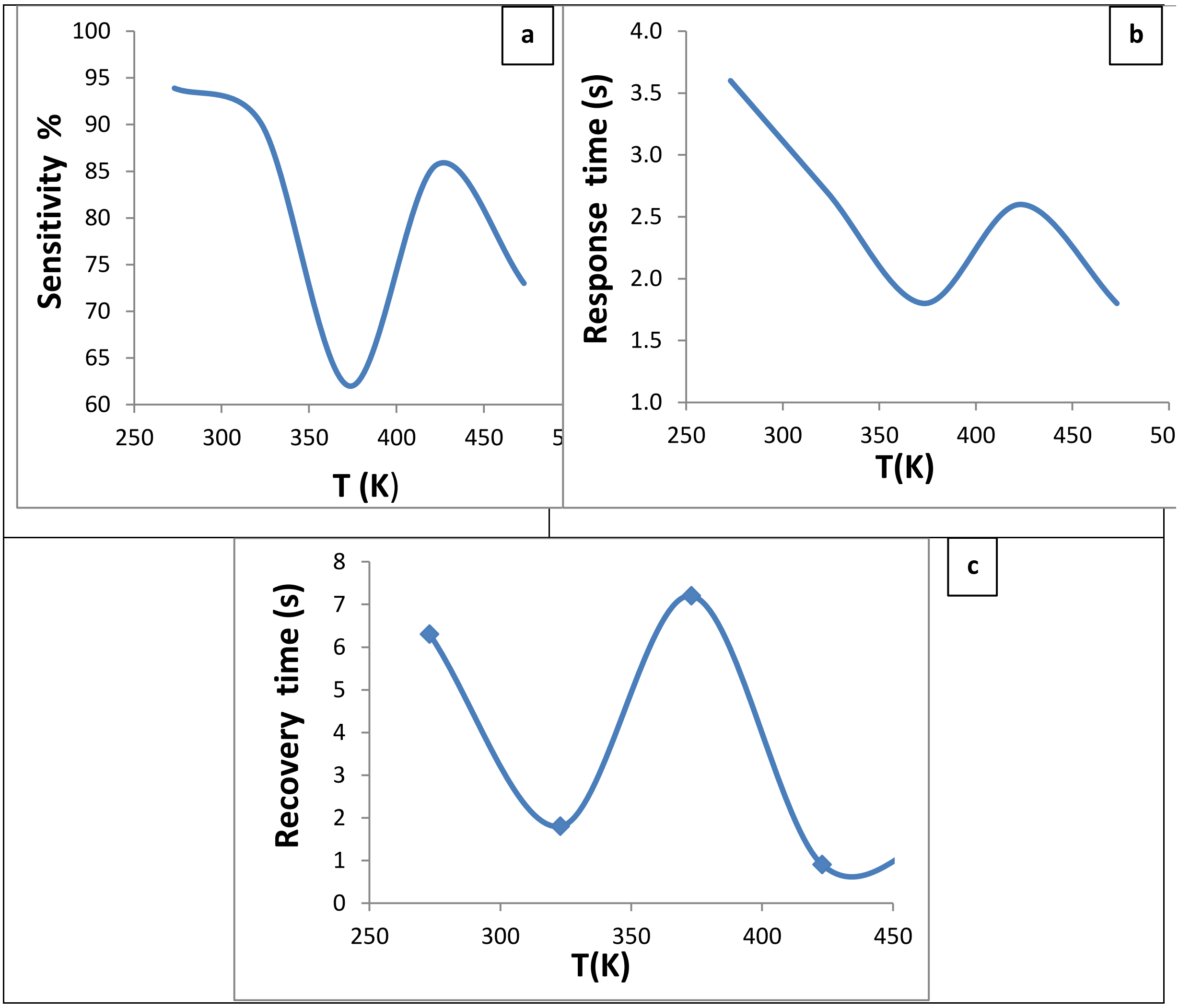


Figure 9-Variations in (a) sensitivity, (b) response time, and (c) recovery time for $(CdO)_{0.94}$:$(In_2O_3)_{0.06}$ / n-Si sensor of NO_2 gas at different operating temperatures.

Conclusions

A thin film of $(CdO)_{0.94}$: $(In_2O_3)_{0.06}$ was successfully deposited on a glass substrate using the pulsed laser deposition technique at room temperature. The quantitative elemental analysis of the film demonstrated the presence of the constituent elements of In, O, and Cd. The topology of the prepared film displayed a granular structure and an almost uniform dimension distributed over the film. The film morphological analysis showed spherical grains. Aluminum is used to form Ohmic contacts for the $(CdO)_{0.94}$:$(In_2O_3)_{0.06}$ thin film. The prepared film is n-type with 5.253 $x10^{19}$ cm^{-3} carrier concentration and low mobility. The $(CdO)_{0.94}$:$(In_2O_3)_{0.06}$/n-Si gas sensor possesses higher sensitivity for the oxidizing gas of NO_2 than that for the reducing gas of H_2S.

References

[1] A. Rahmana , Md. Shahjahan and M. H. Khatunc, " Structural, Optical and Electrical Properties of Al Doped CdO Thin Films Deposited by Spray Pyrolysis Method" , *IOSR Journal of Applied Physics* (IOSR-JAP) , vol. 11, no. 6, pp. 9-14, 2019.

[2] N.B. Hasan and M. A. Mohammed, "XRD Investigation of $(PbO)_{1-x}(CdO)_x$ Thin Films Deposited By Spray Pyrolysis Technique" , *Journal of Babylon University/Pure and Applied Sciences* , vol. 25, no. 2, pp.544 -552, 2017 .

[3] H. Ullah , R. Rahaman and Shahin Mahmud, " Optical Properties of Cadmium Oxide (CdO) Thin Films " , *Indonesian Journal of Electrical Engineering and Computer Science* , vol. 5, no. 1, pp. 81 – 84, 2017.

[4] T. S. Almaadhede, " Structural, Optical, and Morphological Properties of the Cadmium Oxide Thin Film" , *Al-Mustansiriyah Journal of Science*, vol. 28, no. 2, pp. 179- 183, 2017 .

[5] A.A. Shehab , S. A. Maki and A. A. Salih , " The Structural and Surface Morphology Properties of Aluminum Doped CdO Thin Films Prepared by Vacuum Thermal Evaporation Technique " , *Ibn Al-Haitham Journal for Pure and Applied Science* , vol. 27, no. 2, pp. 158- 169, 2014.

[6] R. H. Bari and S. B. Patil , " Nanostructured CdO thin films for LPG and CO_2 gas sensor prepared by spray pyrolisis technique ", *International Letters of Chemistry, Physics and Astronomy* , vol. 37, pp. 31-4, 2014.

[7] A. A.Yousif and M. H. Hasan, " Gas sensitivity and morphologically characterized of nanostructure CdO doped In_2O_3 films deposited by pulsed laser deposition ", *Journal of Biosensors and Bioelectronics* , vol. 6, no. 4 , pp. 192 – 199, 2015.

[8] K. Kaviyarasu, E. Manikandan, P. Paulraj, S.B. Mohamed and J. Kennedy, "One dimensional well-aligned CdO nanocrystal by solvothermal method ", *Journal of Alloys and Compounds* , vol. 593 , pp.67–70, 2014.

[9] H.C. Kumar, R. Shilpa, SaAnanda**,** "Synthesis of cadmium oxide nanoparticles by electrochemical method: Its photo degradation effects on carboxylic acids and antibacterial behaviors" , *Journal of . Nanoscience and Nanotechnology* , vol. 5, no. 5, pp. 840–845, 2019.

[10] M.H. Suhail, H. S. Al-Jumily and O. Gh. Abdullah,"Characterization and NO_2 gas sensing performance of CdO:In_2O_3 polycrystalline thin films prepared by spray pyrolysis technique ", *SN Applied Science Springer Nature Journal*, vol. 1, pp. 69, 2018.

[11] A. T. Dahham , K. A. Aadim and N. K. Abbas, "Synthesis and fabrication of In_2O_3: CdO nanoparticles for NO_2 Gas Sensor ",*Baghdad Science Journal* , vol. 15, no. 3, pp.292 – 299, 2018.

[12] S. G. Ibrahim, " Electrical behavior of cadmium oxide thin films deposited by chemical spray pyrolysis method "*International Journal of Basic and Applied Chemical Sciences*, vol. 7, no. 1, pp.14-17, 2017.

[13] M. Girtan, H. Cachet and GI. Rusua**,** "On the physical properties of indium oxide thin films deposited by pyrosol in comparison with films deposited by pneumatic spray pyrolysis" ,*Thin Solid Films* , vol. 427, no. 1, pp.406-410, 2003 .

[14] J. Panneerdoss, J. Jeyakumar, S. Ramalingam and M.Jothibas**,** " Preparation, characterization, spectroscopic (FT-IR, FT-Raman, UV and Visible) investigation, optical and physico chemical property analysis on In_2O_3 thin films, *Journal of Theoretical and Computational Science* , vol. 2, no. 2, 2015.

[15] H.S. Kim, H.G. Na, J.C. Yang, C. Lee, and H.W. Kim, " Synthesis, structure, photoluminescence, and Ramanspectrum of indium oxide nanowires ", *Acta Physica Polonica a* , vol. 119, no. 2, pp. 143 – 145, 2011 .

[16] P.M. Babu, B . Radhakrishnaa, G.R .Venkata., P. S. Reddy P. and S. Uthanna, " Bias voltage dependence properties of dc reactive magnetron sputtered indium oxide films ", *Journal of Optoelectronics and Advanced Materials* , vol. 6, no. 1, pp.205– 210, 2004 .

[17] M. A. Fakhri and S.F. Hamza, " Nano and micro indium oxide structure prepared using laser ablation method ", *The Iraqi Journal for Mechanical and Material Engineering*, vol. 13, no. 1, pp.120 – 128, 2013.

[18] A. B. Khatibani, S.M. Rozati and Z. Bargbidi, " Preparation, study and nanoscale growth of indium oxide thin films ", *Acta Physics Polonica a* , vol. 122, no. 1, pp. 220 – 223, 2012.

[19] P. Sakthivel , R. Murugan, S. Asaithambi, M. Karuppaiah, R. Yuvakkumar and G.Ravia , " A Comparison study of two indium free alternative cadmium based TCO thin films for optoelectronic applications " , *International Journal of Advance Engineering and Research Development* , International Conference on Momentous Role of Nanomaterials in Renewable Energy Devices , vol. 5, no. 7, pp. 1-4, 2018.

[20] Sp Desai and Av Moholkar,"Concentration dependent structural, morphological and optoelectronic properties of sprayed cadmium based transparent conducting oxide " *Biomedical Journal of Scientific and Technological Research*, vol. 1, no. 6 , pp. 1637 -1646, 2017.

[21] S. Sagadevan and A. Veeralakshmi, " Synthesis, structural, and dielectric characterization of cadmium oxide nanoparticles ", World Academy of Science, Engineering and Technology *International Journal of Chemical and Molecular Engineering* , vol. 8, no. 12, pp.1492 – 1495, 2014.

[22] D.N .Chavan, V. B. Gaikwad, G. E. Patil , D. D. Kajale and G. H. JAIN, " CdO doped indium oxide thick film as a low temperature H_2S gas sensor " , *Sensors and Transducers Journal*, vol. 129, no. 6, pp. 122-134, 2011 .

[23] S. Ahmed , M. S. I. Sarker , M. M. Rahman , M. Kamruzzaman and M. K. R. Khan**,** " Effect of yttrium(Y) on structural, morphological and transport properties of CdO thin films prepared by spray pyrolysis technique" , *Heliyon* , vol. 4, no. 8, pp. 1- 16, 2018.

[24] O.A. Fahad , H.S. Al-Jumailiand M. H. Suhail, " Preparation and characterization of mixed SnO_2:CdO thin films as gas sensor ", *Iraqi Journal of Physics*, vol. 15, no. 33, pp. 28-39, 2017.

[25] R. A. Rasheed, " Characterization of ZnO:Al thin films for sensing applications" , MSC thesis , Physics Department, College of Science, University of Baghdad, 2019.