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Fabrication of Cr_2O_3: ZnO Nanostructure Thin Film Prepared by PLD Technique as NH_3 Gas Sensor

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Abstract

Chromium oxide (Cr_2O_3) doped ZnO nanoparticles were prepared by pulsed laser deposition (PLD) technique at different concentration ratios (0, 3, 5, 7 and 9 wt %) of ZnO on glass substrate. The effects of ZnO dopant on the average crystallite size of the synthesized nanoparticles was examined By X-ray diffraction. The morphological features were detected using atomic force microscopy (AFM). The optical band gap value was observed to range between 2.78 to 2.50 eV by UV-Vis absorption spectroscopy, with longer wavelength shifted in comparison with that of the bulk Cr_2O_3 (~3eV). Gas sensitivity, response, and recovery times of the sensor in the presence of NH_3 gas were studied and discussed. In the present work, we found that the sensitivity was increased upon increasing the concentration ratio from 3 to 5%wt of ZnO, whereas it was decreased again over that value. Also, we found that the sensitivity was increased when increasing operating temperature, while the response time was decreased. The optimum concentrations ratio for NH_3 gas sensitivity at 5%wt ZnO revealed sensitivity of 66.67% and response time of 14s at operating temperature of 300°C and 700mJ PLD energy.

Keywords: Cr_2O_3: ZnO Nanostructure, PLD technique, structural, optical properties. Sensitivity

تصنيع غشاء رقيق مركب من أوكسيد الكروم(Cr_2O_3) والمطعم بأوكسيد الزنك(ZnO)النانوي والمحضر بتقنية ترسيب الليزر النبضي في تطبيق متحسس لغاز الامونيا(NH_3)

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الخلاصة

تم تصنيع غشاء رقيق من أوكسيد الكروم النانوي (Cr_2O_3) المطعم بأوكسيد الزنك (ZnO) النانوي والذي تم تحضيره بتقنية ترسيب الليزر النبضي وبنسب تركيز مختلفة (9,7,5,3,0)% من أوكسيد الزنك على قواعد من الزجاج . لقد تم اختبار تأثير نسب التطعيم لأوكسيد الزنك في معدل الحجم البلوري للبنية التركيبية النانوية وتم ذلك بوساطة حيود الاشعة السينية (XRD) . وأن طبوغرافية السطح تم فحصها ومناقشتها باستخدام مجهر القوة الذرية (AFM .) وقد لاحظنا ان قيم فجوة الطاقة البصرية تتراوح بين(2.78 الى 2.50) الكترون فولت باستخدام مطياف امتصاص الاشعة (ضوء مرئي- فوق بنفسجية) وكانت تنزاح نحو طيف الاطوال الموجية الاطول عند مقارنتا مع هيكل اوكسيد الكروم (3 الكترون فولت) .تحسسية الغاز

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وزمن الاستجابة للمتحسس بوجود غاز أوكسيد النيتروجين (NH_3) تم دراستها ومناقشتها . في هذا البحث وجدنا ان التحسسية تزداد عند زيادة نسبة التطعيم (3 الى 7) % ثم تعود تتناقص فوق ذلك .افضل نسبة تركيز لأوكسيد الزنك لكي نتحسس غاز NH_3 كانت عند نسبة تطعيم 5% وقد ظهر ان اكبر مقدار للتحسسية يساوي 66,67 % وزمن الاستجابة 10ثانيه عند درجة حرارة 300 سيليزي ,وطاقة ترسيب الليزر(700ملي جول) .

Introduction

Semiconductor metal oxide received a lot of interest in recent years, because of its structure and optical, electrical, and chemical properties. Among the various semiconductor metal oxides, Cr_2O_3 is one of the successful semiconductors and broadly studied compounds due to its wide band gap (~3 eV) [1]. Cr_2O_3 has an p-type semiconductor nature at lower temperatures [2]. This kind of p-type metal oxide semiconductors with broad optical band gap may be decent candidates for many applications in gas sensors and optical storage systems [3]. Such applications of Cr_2O_3 material depends on their structure, phase, shape, size and synthesizing techniques, along with the addition of suitable dopants to them, such as zinc oxide [4]. For example, the composite of nanomaterial with large surface area to volume (lesser particle size) and high chemical actions has been an important area of active research [5]. The sensing properties of this metal oxide were proved for some flammable or deadly gases, such as NO_2 and NH_3. Advances in nanotechnology generally provide an increasing response of semiconductor metal oxides because of high surface area. Thin films of nanostructure provide high sensitivity and faster response times [6].

The average crystallite size (D) was estimated by Scherrer's equation [7], as follows.

$$D = K\lambda / (\beta \cos\theta) \qquad \text{......................1}$$

where K = 0.9 is Scherer's constant, λ is X-ray radiation's wavelength (λ = 1.54056 Å), β is the peak full width at half maximum (FWHM) in radians, and θ is the Bragg diffraction angle at which FWHM is measured.

The optical band gap energy (Eg) of the as-synthesized nanoparticles is obtained from the UV-Vis spectra by using the Tauc's relation [8]:

$$\upsilon\alpha h\upsilon = A(h\upsilon - E_g)^n \qquad \text{.................2}$$

where α represents the absorption coefficient, hυ is photon energy, A is constant (absorbance) and the exponent n = ½ for direct transition.

Sensing measurements are carried out by measuring the R_a resistance of thin films in air resistance (R_g) in the presence of NH_3 gas. Evaluating gas sensitivity (S%) and response time (S) for reducing gas can be obtained from equations 3 and 4, respectively.

$$S\% = \left|\frac{R_g}{Ra}\right| \quad \% \qquad \text{...........................3}$$

$$S = \left|\frac{R_g}{Ra} - 1\right| \qquad \text{.......................4}$$

In this paper, we present the results of studying Cr_2O_3 doped with ZnO to find probability and optimal conditions for PLD of nano-crystalline films on glass substrate. The crystallite size, morphology, and optical properties of the as-synthesized Cr_2O_3 doped with ZnO nanoparticles are investigated and discussed. The thin films prepared are studies for the sensing properties to NH_3 gas.

Experimental Part

Un-doped Cr_2O_3 films and those with different doping concentrations of ZnO (3, 5, 7 and 9 %wt) with high purity (99.99%) were pressed less than 6-8 Ton to form a target product with 2 cm diameter and 0.5 cm thickness. The films were deposited by Nd:YAG laser Second Harmonic Generation, with a laser wavelength of 1064 nm, on glass substrates at room temperature and oxygen pressure of 0.01 to 0.5 mbar. Pulse laser depositions energy was 700mJ and the frequency of laser pulse was 6 Hz, with about ~2cm distance between the target and the substrate. The laser beam was focused on the target inside the chamber in 45^o angle. The glass substrates were cleaned by ethanol and thereafter rinsed with distilled water in an ultrasonic device. The crystalline structures of the as-synthesized nanoparticles were characterized through XRD r (model D_2 PHASER BRUKER, power diffraction systems, Germany) with Cu-K_α radiation (λ=1.54056 Å), voltage = 40 kV, current = 30 mA, and scanning 2θ range of 20^o to 80^o. Morphological images of the thin film surfaces were measured using an AFM (SPM, Model AA3000, Angstrom Advanced Inc, USA) which can provide information about average diameter , root mean roughness (RMS) and average roughness. The wavelength range of the optical absorbance spectrum (190–1100) nm was recorded by spectrophotometer (SHIMADZU UV-1800, Japan).

RESULTS AND DISCUSSION

Structural Properties

The X-ray diffraction patterns of the as-deposited nanoparticles are shown in Figure-1.

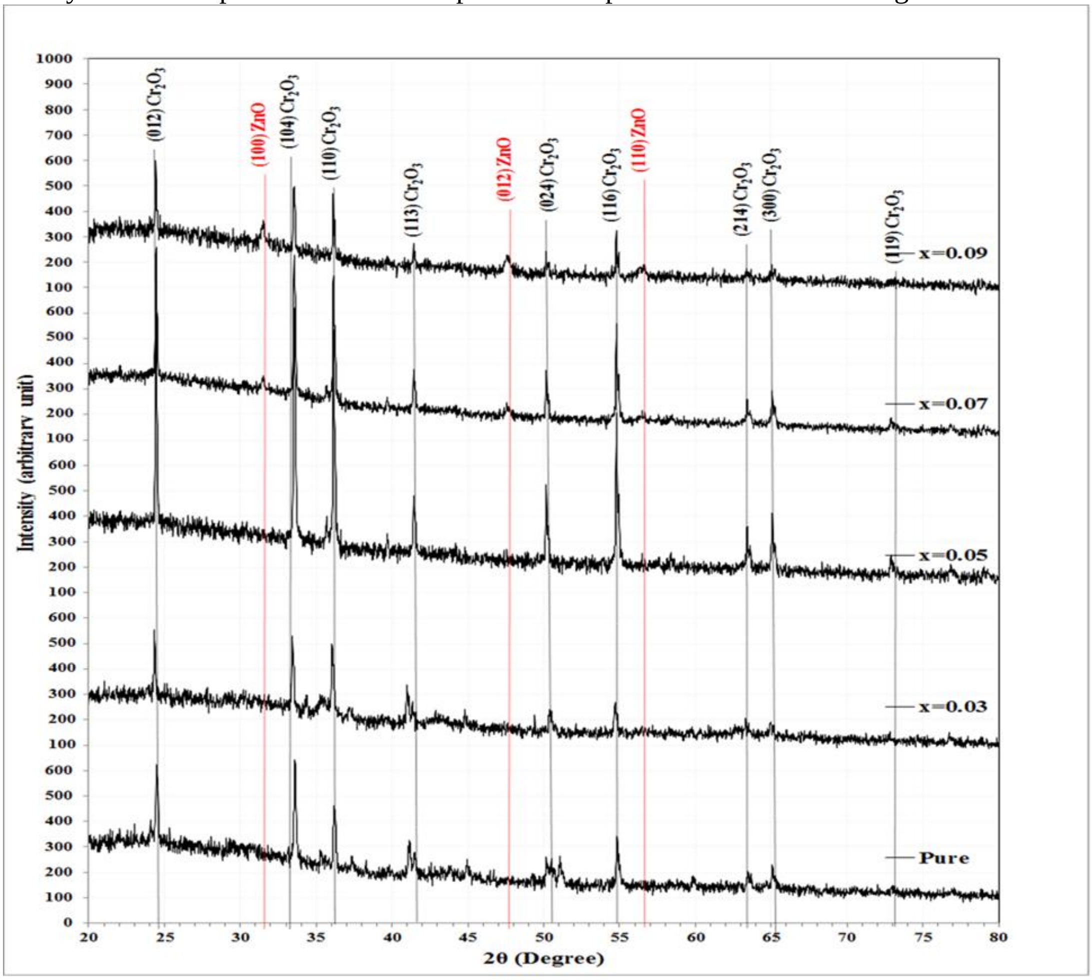


Figure 1-XRD patterns for Cr_2O_3:ZnO thin films with different ratio.

A highly crystalline nature was observed in the spectrum for the as-deposited thin films, whereas the lattice referred to hexagonal axes [9]. It was observed that the crystalline size in planes (012), (104) and (110) was increasing when increasing the concentration from 3 to 7 wt%, while it was decreased over that value. New peaks were observed in the XRD image for a material which represents zinc oxide when concentration ratios of 7 and 9 wt% were used at planes of 100, 012 and 110 in the hexagonal phase, as show in Figure-1. The restrained quantity of ZnO atoms exists due to the effect of ZnO doping decreasing peak intensity of Cr_2O_3 nanoparticle due to an interstitials sharing the oxygen with Cr atoms and hence recede the crystallinity size , a result which is in agreement with that reported by Mohanapandian [10].

Morphological properties

Three-dimensional images and the distribution of granularity accumulation for Cr_2O_3:ZnO at the used different concentration ratios of ZnO deposited on glass substrate, with dimensions of 2.5×2.5 cm^2, are demonstrated in Figure-2.The grain size was increased when increasing the concentration ratio of ZnO from 3 to 7 % wt, whereas it was decreasing over that value. The images of AFM displayed that all films were of a granular structure. The granular films showed a greater surface area, which is decent for thin film gas interaction and results in higher sensitivity, where the sensitivity of gas has a proportional relationship with the thin film roughness, which is in agreement with the results of Deshpande [11].

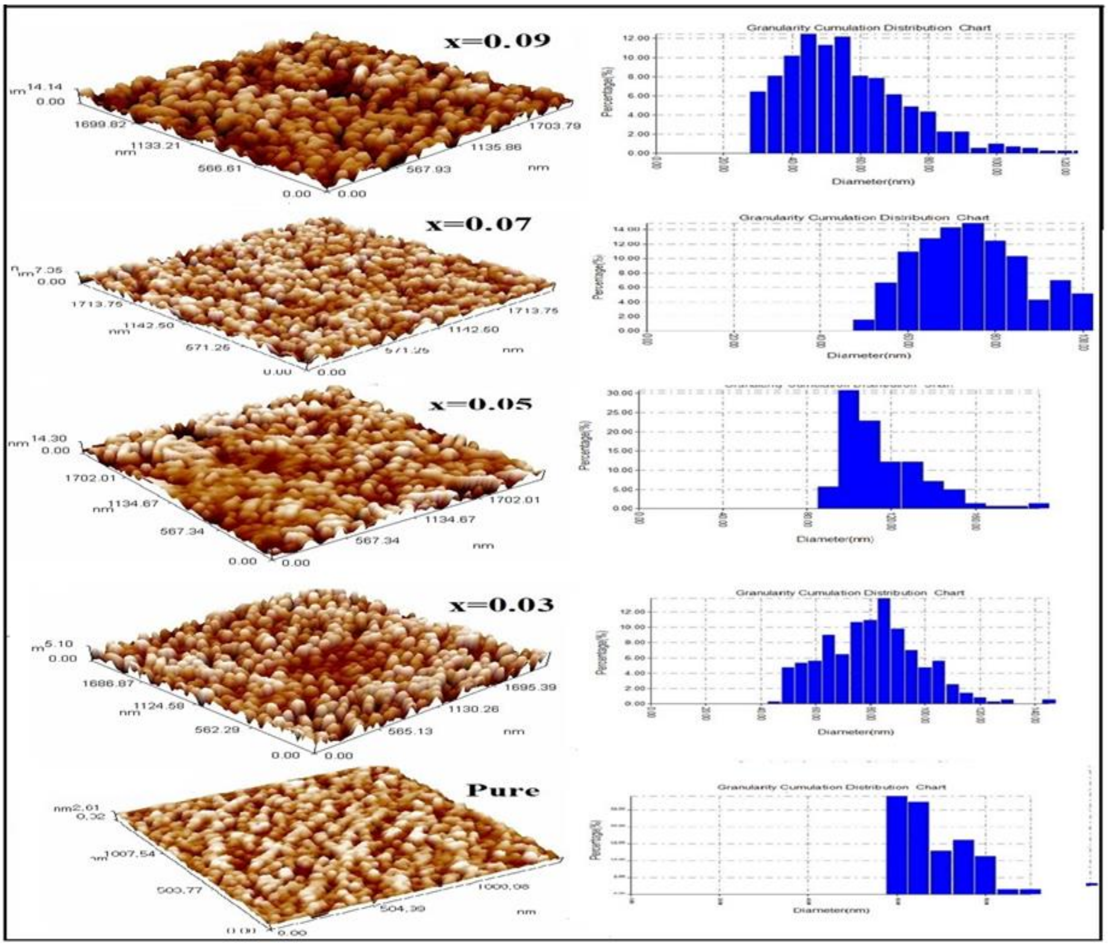


Figure 2- AFM image and the chart of grain density distribution for Cr_2O_3:ZnO thin films.

Values of maximum and average RMS roughness were 3.55 and 2.98 nm, respectively, at 5% wt doping, as shown in table 1. The increases in roughness of thin films may be due to the presence of several hillocks, which are faceted and distributed randomly on the relatively smooth structure densification of the deposition processes [12].

Table 1-Average Diameter, Average roughness and RMS roughness for Cr_2O_3: ZnO thin films

ZnO Ratio %	Average Diameter (nm)	Average Roughness (nm)	RMS roughness (nm)
0	65.89	0.455	0.558
3	78.32	1.22	1.41
5	82.54	2.98	3.55
7	89.14	1.65	1.83
9	53.47	2.99	3.5

Optical properties

Figure-3 shows that the transmission spectra of different concentration of ZnO-doped Cr_2O_3 nanoparticles were decreased with the increase in the concentrations ratio, whereas they were increased with increasing wavelength.

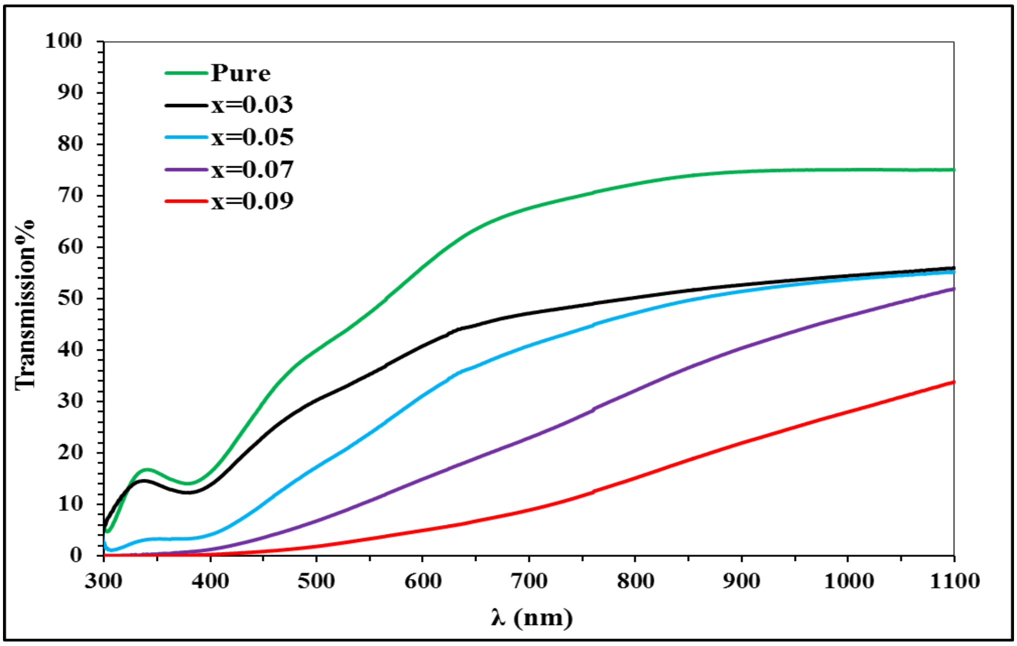


Figure 3-Transmission spectra of un-doped Cr_2O_3 and Cr_2O_3: ZnO thin films as a function of wavelength

The spectra show a higher absorption coefficient in the wavelength of 360 nm, as shown in Figure-4, which was increased when increasing the concentration ratio from 3 to 9% wt. The absorption coefficient was decreased with increasing wavelength.

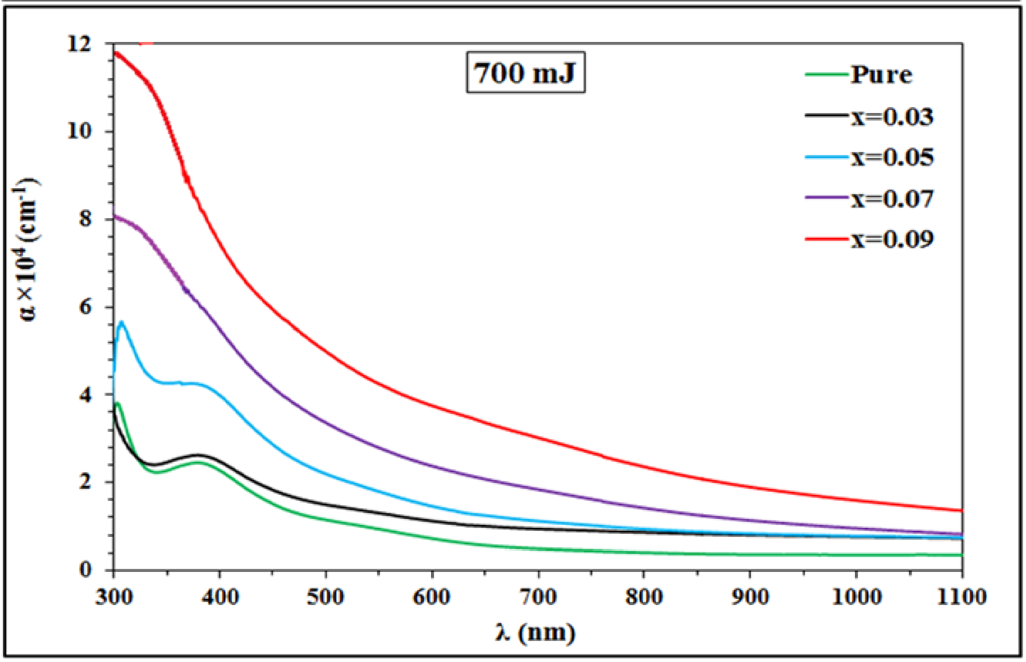


Figure 4-The relation between the absorption coefficient and wavelength for un-doped Cr_2O_3 and Cr_2O_3: ZnO thin films

Figure-5 shows the relation of $(\alpha h\upsilon)^2$ versus hυ, where the extrapolation of the linear portions of the curves to the hυ axis results in Eg.

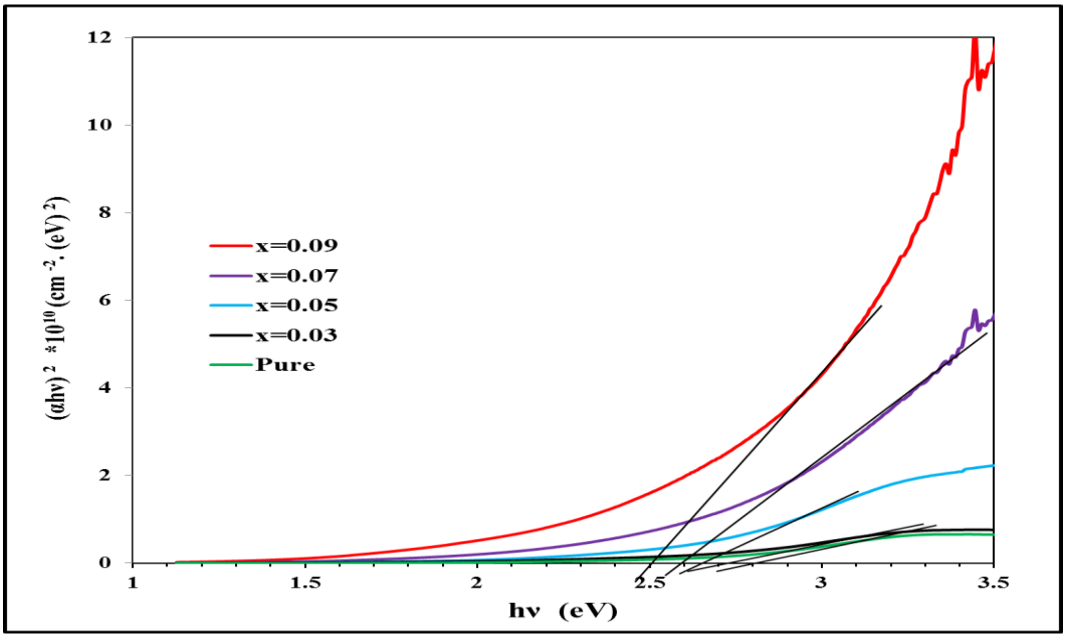


Figure 5-Optical energy gap for Cr_2O_3: ZnO thin films at different ratios of ZnO

The estimated transmissions (T) and absorption coefficient (α) at a wavelength of 550 nm and the values of the energy band gap (Eg) are given in Table-2.

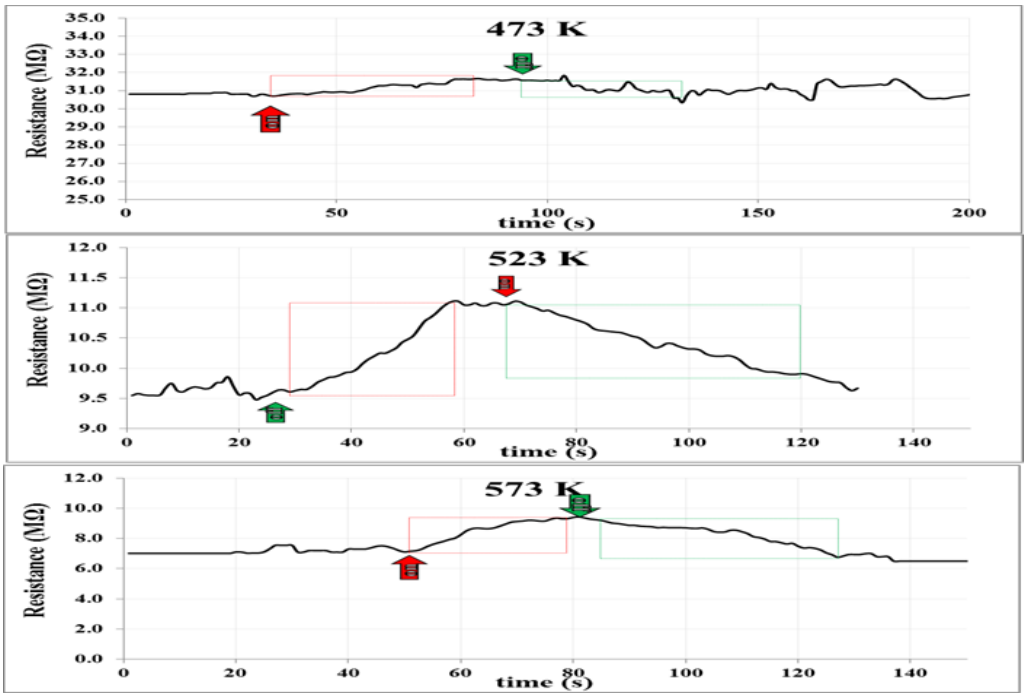
Table 2- energy gap for Cr_2O_3: ZnO thin films

ZnO ratio%	E_g (eV)
0	2.78
3	2.75
5	2.65
7	2.60
9	2.50

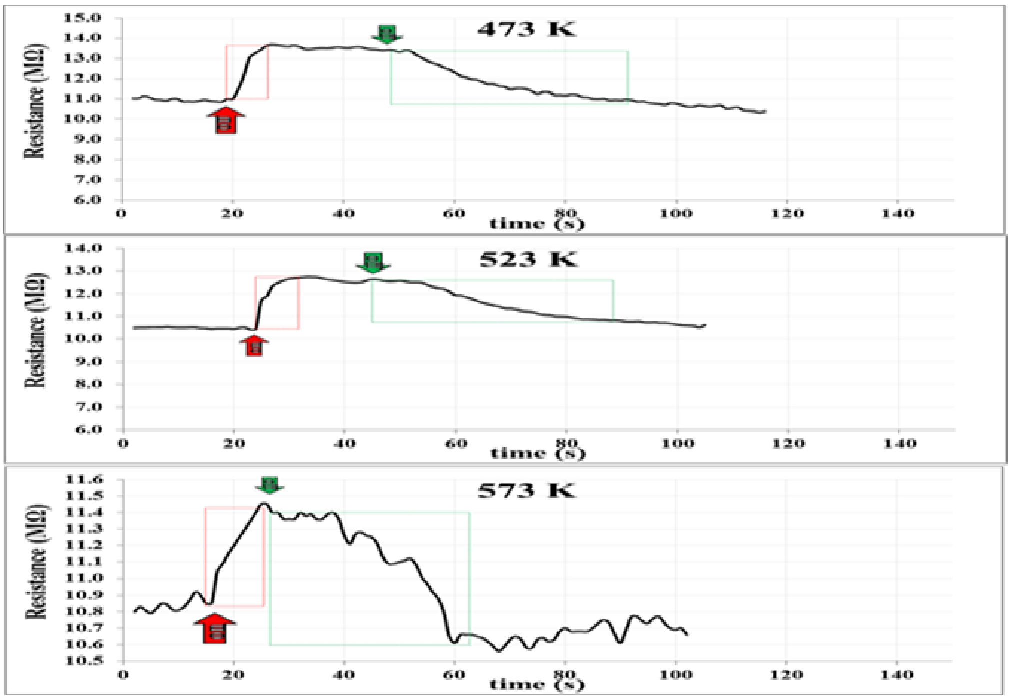
The absorption peaks showed a longer wavelength shift as the concentration of the ZnO dopant in the host Cr_2O_3 matrices increased from 0 to 9% wt, when compared with the bulk system (~3eV) [13,14]. Hence, the Eg was gradually decreased from 2.78 eV at 0 % wt to 2.50 eV at 9% wt. The observed Eg value of the pure Cr_2O_3 nanoparticles was 2.78 eV. These results are in agreement with the reported values, while showing a marginally lower value than that for the sample prepared by other techniques [15, 16].

Properties of gas sensors

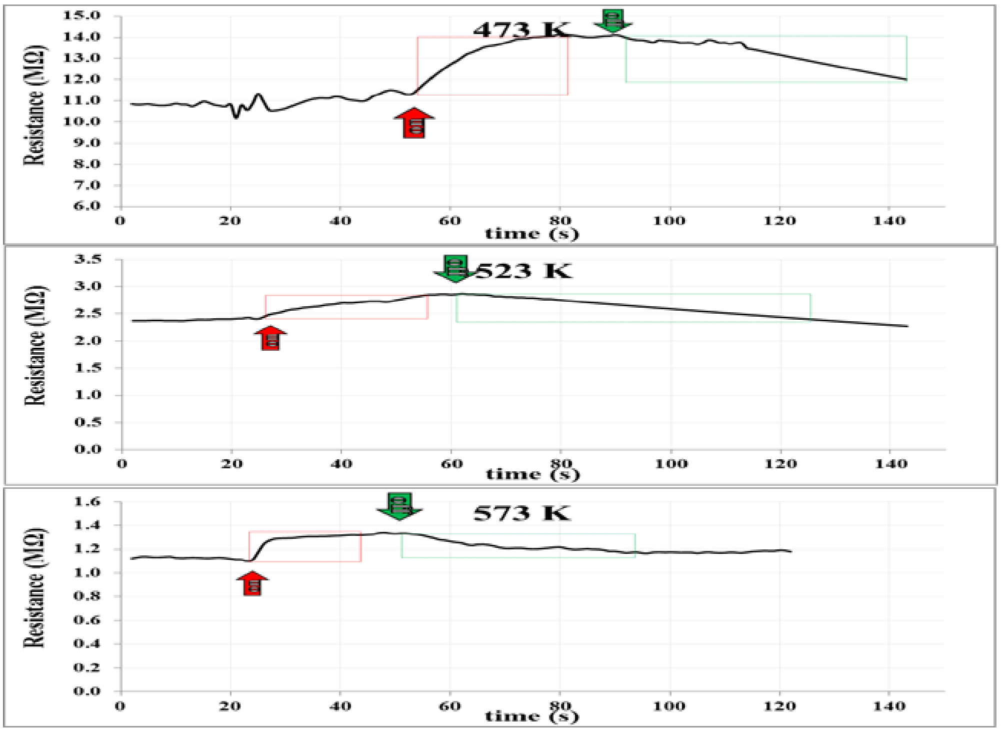
The variation in resistance for the thin films with time, after gas on and gas off, is shown in Figure-6. The resistance increasing and decreasing with time after gas on and gas off respectively of all films.



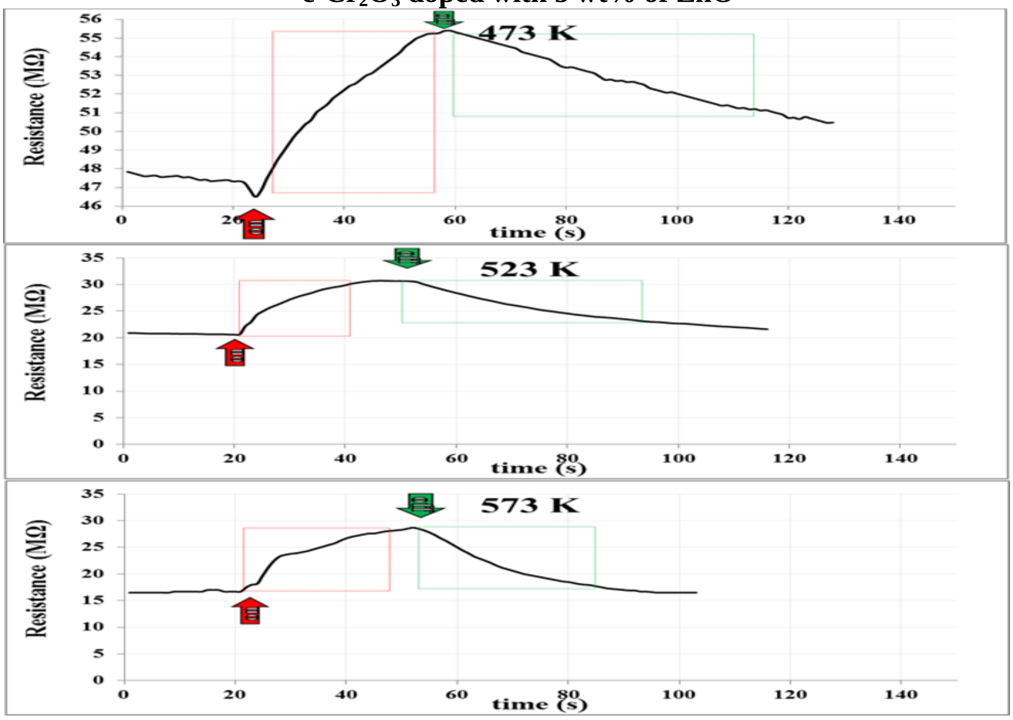
a- **Un-doped Cr_2O_3**



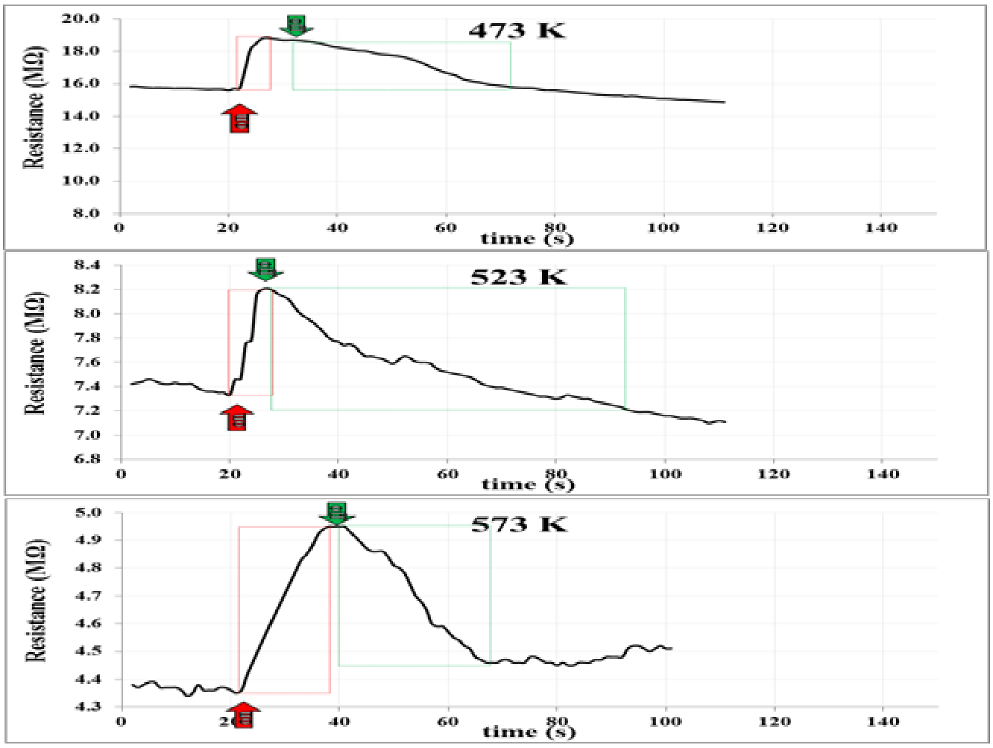
b- Cr_2O_3 doped with 3 wt% of ZnO



c-Cr_2O_3 doped with 5 wt% of ZnO



d- Cr_2O_3 doped with 7 wt% of ZnO



e-Cr_2O_3 doped with 9 wt% of ZnO

Figure-6 Variations of resistance of thin film as a function of time of three different operating temperatures for a-pure Cr_2O_3 . b-dopded with 3 wt%ZnO. c- dopded with 5 wt%ZnO . d- dopded with 7 wt%ZnO . e-. dopded with 9wt%ZnO .

The reason of this behavior can be attributed to the Cr_2O_3 mechanism of sensing associated to the ion sorption of gas type over the surface, leading to charge transfer between the gas and surface molecules and changes in the electrical conductance. Hence, NH_3 is reducing gas in the environment. When the gas sensor is under the ambient reducing gas, the electrons obtained from the chemical reaction in the process of forming the adsorbed oxygen ion are given back to the conduction band. For the p-type metal oxide semiconductor sensor, the electrons go to the valence band and recombine with the holes, which results in reducing the carrier concentration (holes) and an increased reduction in electrical conductance [17-18]

Figure-7 and Table-3 show that the sensitivity is increased and the response time is reduced with increasing the doping ratio of ZnO from 0 to 7 wt%. The maximum value of sensitivity was equal to 66.67% at 0.07% wt and operating temperature of 573K. Furthermore, when operating temperature was increased from 473 K to 573 K, the sensitivity was also increased, which is in agreement with the results of Starke [19].

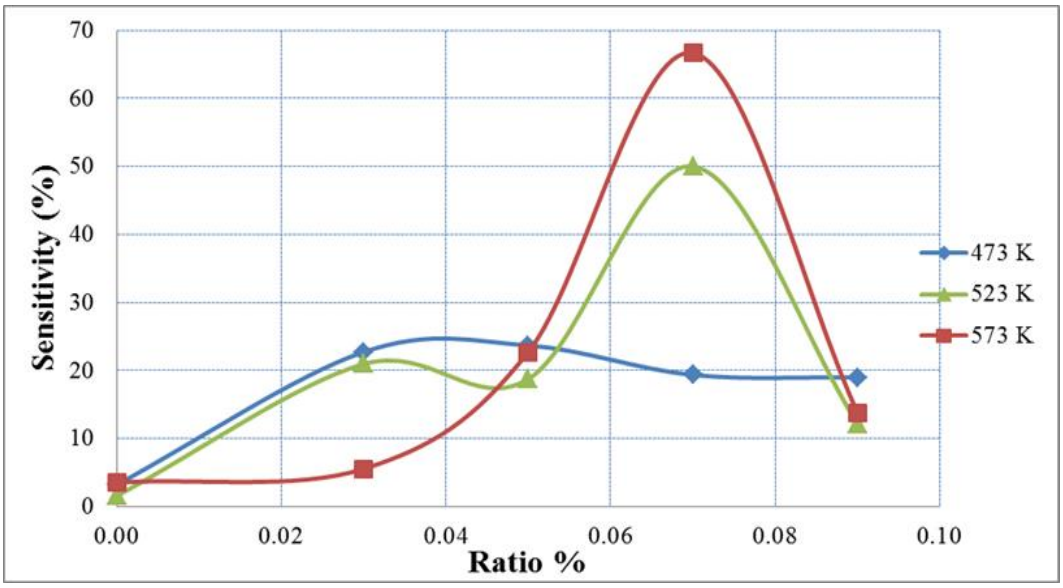


Figure 6-Variation of sensitivity for NH_3 gas with ZnO ratios at different temperatures for films

Table-3 shows the response time reduction with increasing the doping ratio of ZnO from 0 to 7% wt , while it was increased again at 9%, with 573 K, where the response time was 10s at 7% wt and 573K [20-27].

Table 3-Sensitivity, response time, and recovery time for Cr_2O_3: ZnO thin films at different operating temperatures

Temp.(K)	ZnO ratio%	Sensitivity (%)	response time (s)	recover time (s)
473	9	18.99	8.00	40.00
	7	19.35	30.00	58.00
	5	23.68	30.00	50.00
	3	22.73	9.00	40.00
	0	3.23	40.00	30.00
523	9	12.16	7.00	66.00
	7	50.00	20.00	40.00
	5	18.75	33.00	68.00
	3	20.95	8.00	48.00
	0	1.58	30.00	45.00
573	9	13.79	18.00	30.00
	7	66.67	10.00	28.00
	5	22.73	20.00	43.00
	3	5.56	28.00	41.00
	0	**3.57**	**30.00**	**40.00**

Conclusions

The characterization of structural, optical, and gas sensors properties for ZnO-doped C_2O_3 thin films were investigated in an reducing ammnia gas sensor prepared by simple and cost-effective PLD technique The XRD measurements showed that the lattice may be referred to as having a hexagonal phase with a maximum intensity for Cr_2O_3:ZnO in plane (104) at 5% wt. The AFM images of all films illustrated a granular structure. Increasing the concentration ratio of ZnO into the Cr_2O_3 resulted in an increase in the roughness of the deposited thin films, with a higher roughness at 0.05% wt doping ratio. The optical energy gap was decreased with increasing the concentrations ratio of ZnO . The 5% wt ZnO-doped Cr_2O_3 thin film had the highest sensitivity to NH_3 gas, which was 66.67% at 573 K

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