Development of NO2 gas sensor using Sn-doped ITO nanoparticles prepared by Sol-Gel method

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Dr. Saryia D. Al-ALgawi
Applied Sciences Department, University of Technology/Baghdad
Email: Sarya algawi @yahoo.com
Dr. Rashed T. Rasheed
Applied Sciences Department, University of Technology/Baghdad
Sahar Zeyad Tareq
Applied Sciences Department, University of Technology/Baghdad

Abstract

In this work In2O3 and Sn-doped ITO nanoparticles were prepared by sol-gel method and deposited on quartz substrate by dip coating technique at different doping concentration of (5, 10 and 15%). The samples were annealed at 550 oC at constant time (60 min). X-ray analysis confirmed the formation of polycrystalline cubic phase that decreases in crystalline size with increasing doping concentration. The optical properties of Sn-ITO nanostructure thin film were studied. The transmittance was measured in the wavelength range of (300nm to 1100 nm) for all thin films. The sensitivity towards NO2 gas was measured, when In2O3 was doped with Sn at different concentrations.

Keywords: ITO, Sn-doped, NO2 gas sensor, Sol-Gel method.

تطوير متحسس لغاز NO2 باستخدام القصدير ضمن جزيئات نانوية من ITO المحضرة بواسطة طريقة Sol-Gel

الخلاصة

في هذا العمل تم تحضير جسيمات نانوية لاوكسيد الانديوم المشوب بالقصدير بطريقة sol-gel ورسبت الاغشية على زجاج كوارتز بطريقة الغمر،تم تشويب العينات بنسب (5، 10 و15%) ثم لدنت بدرجه حرارة (550) لمدة (60 دقيقة). اكدت فحوصات حيود الاشعة السينية تكون الطور المكعبي متعدد البلورات ولوحظ نقصان الحجم الحبيبي بزيادة نسب التشويب. تم دراسة الخصائص البصرية للاغشية المحضرة، قياس النفاذية لمدى الطول الموجي من (300 الى 1100) وتحسسية الاغشية لغاز NO2 المشوبة بالقصدير عند تراكيز مختلفة.

INTRODUCTION

Metal oxide nanoparticles such as indium oxide (In2O3) and indium tin oxide (ITO) have unique characteristics such as good conductivity, high optical transmittance over the visible wavelength region, excellent adhesion to substrates, chemical stability and photochemical properties [1]. Indium oxide is a wide band gap n-type semiconductor with direct band gaps of 3.75 eV. Indium oxide has cubic bixebyte structure with lattice parameter of 10.117A˚. Also, indium oxide is an important and distinguished transparent conducting oxide (TCO) [2].

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2412-0758/University of Technology-Iraq, Baghdad, Iraq

Gas sensors play an important role in detecting, monitoring and controlling the presence of dangerous and poisonous gases in the atmosphere at very low concentrations [3-5]. Nanostructured semiconductor gas sensors are highly sensitive and dependable, and have a performance/price ratio as good as to that of microelectronic components [6-8]. It is well known that the physicochemical properties which control gas adsorption on the surface of a semiconductor can significantly influence its electrical conductivity [9,10].

Experimental Procedure

Preparation of Indium Oxide (In2O3) Nanoparticles.

Indium oxide nanoparticles were synthesized through the aminolysis reaction of indium acetate in the presence of benzylamine in bottom round flask. We suggest that the substitution reaction took place between the acetate group of In(CH3COO)3 and the -NH2 group of benzylamine, to form In(OH)3. After reaction, white In(OH)3 powder was separated through centrifugation, rinsed in ethanol, and dried in a vacuum oven at 90 °C for 12 h. The suggested aminolysis mechanism is shown in figure (1) [11].

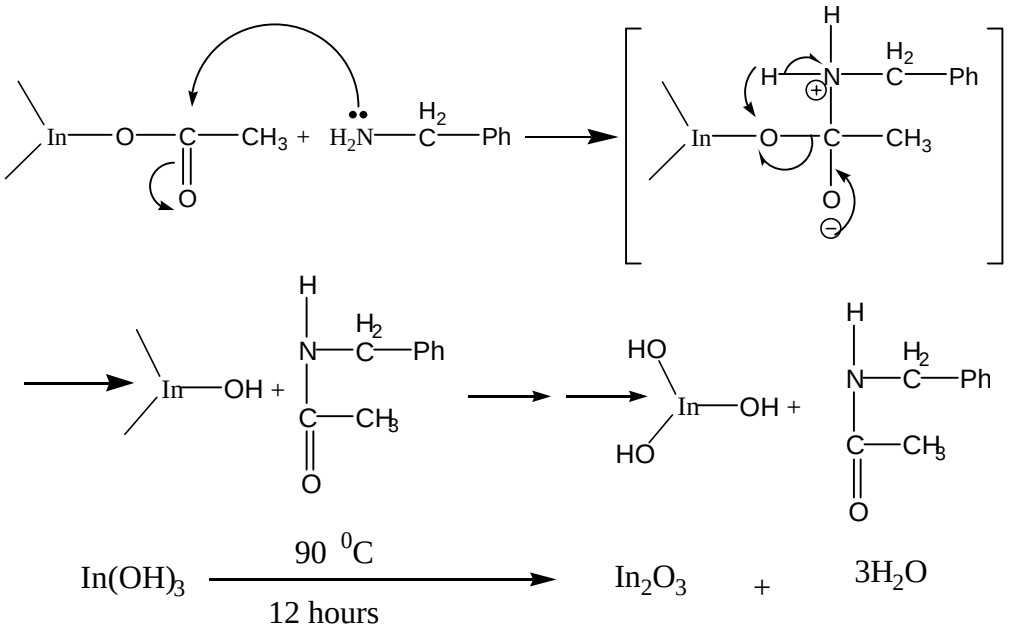

Figure (1) Suggested mechanism of reaction between indium acetate and benzylamine

Preparation of Tindioxide (SnO_2) nanoparticle:

Tin dioxide nanoparticles were prepared by dissolving stannous chloride dihydrate (SnCl2.2H2O) in (20 ml) of absolute ethanol. The solution was stirred with a magnetic stirrer for 30 min in a beaker until it became colorless. Ammonium hydroxide was added drop wise (one drop in 30 second) to the solution until the final

solution reaches a pH value of about 8. The mixture was filtered in a centrifuge, washed with a small portion of deionized water and then the precipitate was dried under vacuum at 90 °C for 3 hours. This has resulted pale yellow precipitate powder of tin dioxide of 1g weight (75% yield). The general suggested reaction between stannous chloride dihydrate and ammonium hydroxide solution are [12]:

1. $SnCl_2.2H_2O + 2NH_4OH \rightarrow Sn(OH)_2 + 2NH_4Cl + 2H_2O$
2. $Sn(OH)_2 \rightarrow SnO + H_2O$
3. $SnO + 1/2\ O_2 \rightarrow SnO_2$

The final equation is:

$$SnCl_2.2H_2O + 2NH_4OH + 1/2O_2 \rightarrow SnO_2 + 2NH_4Cl + 3H_2O$$

Thin Film deposition

ITO thin films (5, 10 and 15%, SnO_2: In_2O_3 mole ratio) were deposited by dip coating technique. Quartz substrates were dipped in the prepared solution and withdrawn at (1 cm / sec.) rate. The substrate stayed in the sol for 60 sec., and was subsequently dried for 5 min at 100°C. The procedure necessitated 8-15 dipping to achieve 200 nm thick films.

Results and Discussion

X-Ray Diffraction (XRD)

According to the JCPDS card no: (6-416), figure (2) indicates a polycrystalline cubic doped In_2O_3 structure. The ITO nanoparticles show high intensity diffraction peak in (222) plane, increasing in FWHM is a result to decreases in the main grain size according to Debye-Scherer's equation which is given by:

$D = 0.9\ \lambda / (\beta \cos\theta)$

Where

D is the grain size, λ is the X-ray wavelength, β is the diffraction peak at FWHM, and θ is the diffraction peak position [13]. The diffraction pattern of ITO nanoparticles; doped to 5 wt% and annealed at 550 □C illustrate four diffraction peaks located at 2□ = 21.5662, 30.6535, 35.3847and 51.0946o which correspond to (211), (222), (400) and (440) planes. When doped by 10 wt%, four different peaks located at (211), (222), (400) and (440) appear at 2Θ=¬ 21.585, 30.6622, 35.4085 and 51.11 o, respectively. With 15 wt% doping, newer four peaks located at (211), (222), (400) and (440) appear at (2Θ=¬ 21.602, 30.6895, 35.5559 and 51.14o), respectively [14].

As shown in figure (2) the intensity of (222) peak decreases with increasing doping concentration. Also it is noticed that the FWHM increases and main grain size decreases with increasing doping consternation as reported in the publication [15]. The values of the FWHM and the main grain size of the samples are given in the Table (1).

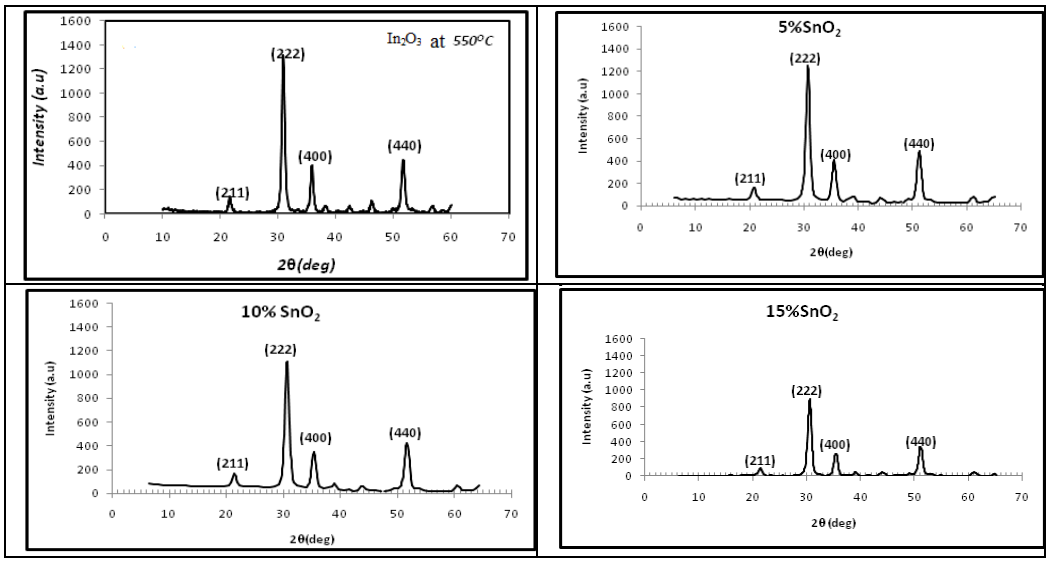

Figure (2): XRD pattern of In_2O_3 and ITO nanoparticles with doping concentration 5, 10, 15 % annealed at 550 °C

Table (1): The obtained result of the XDR for ITO nanoparticles at 5, 10 and 15% at annealing temperature 550°C.

Doping concentration	θ (deg)	hkl	FWHM (β)	Grain Size (nm)	Lattice constant (A)	D (A)
SnO_2 5 %	21.602	211	0.66	11.82495	10.06469	4.108892
	30.6895	222	0.668	11.47004	10.07972	2.909763
	35.5559	400	0.639	11.84009	10.08748	2.521871
	51.14	440	0.65	11.02624	10.09185	1.784004
SnO_2 10 %	21.585	211	0.662	11.78956	10.07252	4.11209
	30.6622	222	0.6781	11.211	10.08848	2.912292
	35.4085	400	0.6484	11.67324	10.12812	2.532031
	51.11	440	0.692	10.35832	10.09737	1.78498
SnO_2 15 %	21.5662	211	0.752	10.3789	10.0812	4.115632
	30.6535	222	0.924	8.292905	10.09127	2.913099
	35.3847	400	0.771	9.817679	10.13472	2.533679
	51.0946	440	0.802	8.938173	10.10021	1.785482

Films Morphology

Surface morphology by Atomic Force Macroscopic (AFM)

The surface morphology of In2O3 and ITO nanoparticles was analyzed using atomic force microscope. Figure (3) shows a typical three dimensional AFM image

and granularity cumulation distribution chart of In2O3 and ITO nanoparticles. The average grain size was (70-60 nm). The AFM results a decreasing grain size with doping; due to substitution of larger (In) anion with smaller (Sn) anion which [16-18 .[

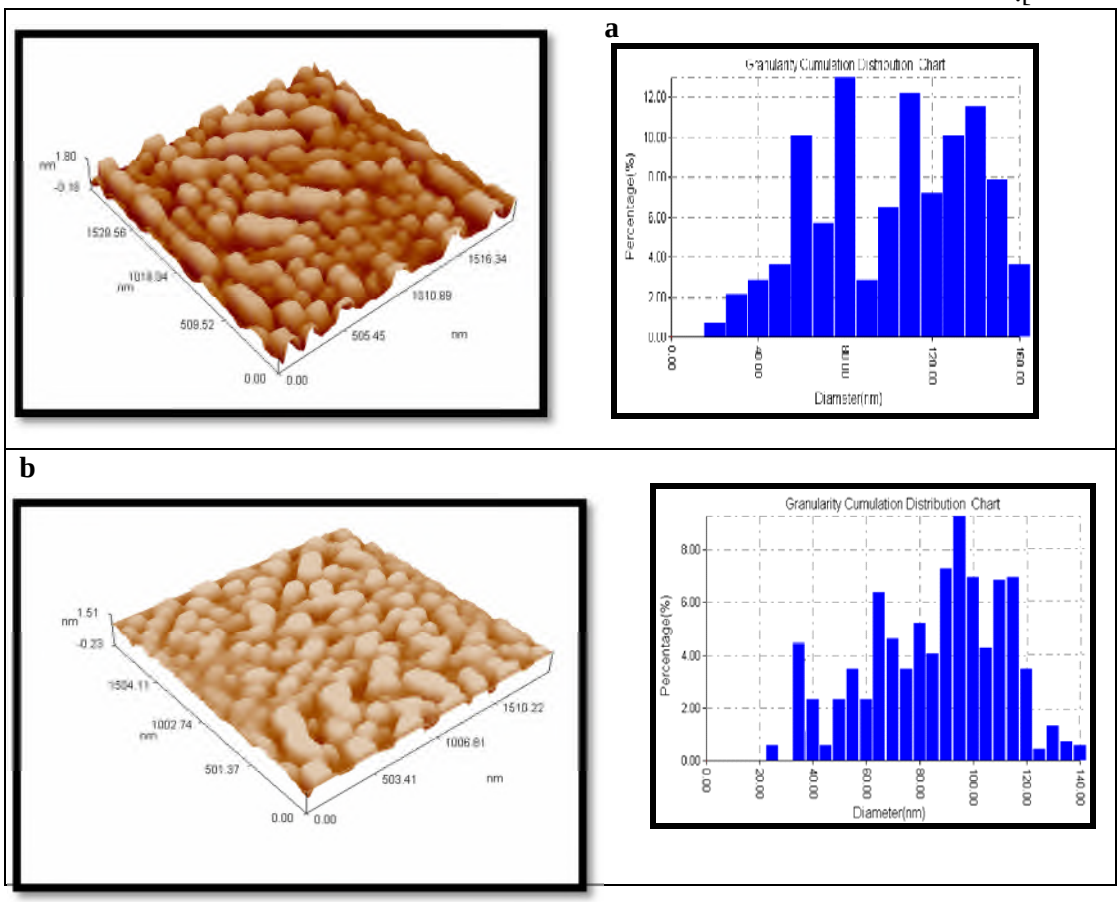

Figure (3): 3-D AFM image and Granularity cumulation distribution chart annealing at 550 C of: (a) In2O3 and (b) In2O3 doped with 15% SnO2

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Surface Morphology by (SEM)

The SEM images of the In2O3 and ITO nanoparticles doped with 15% SnO2 (with and without annealing) prepared by sol–gel methods have been shown in Figure (4). As seen, nanoparticles have been grown as individual clusters with a few agglomerates over the surface, also it shows a cube structure which has not completely formed, this may be due to the agglomeration of simpler units of In2O3 cubes over the bigger cubes of In2O3 as shown in Figure (4). The size of the cube depended upon the agglomeration of the particles during the reaction period.

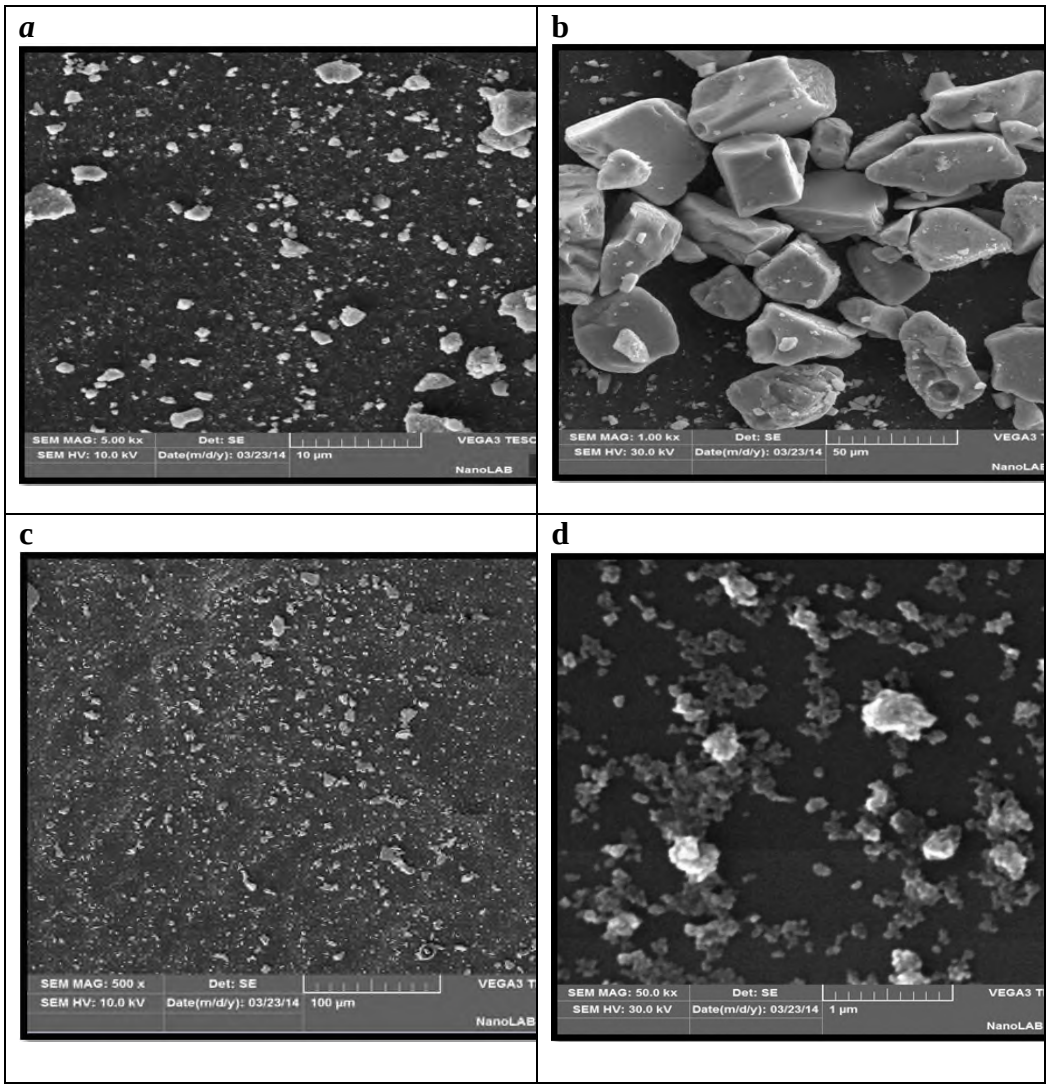

Figure (4): SEM image for In2O3 naoparticles: (a) as-prepared,(b) annealing at 550 OC, and ITO naoparticles doped with 15% SnO2:(c) as-prepared, (d) annealing at 550 OC.

Transmission

Figure (5) shows the optical transmittance spectra of In2O3 only and In2O3doped with SnO2 at different doping concentrations. It was found that the films have high transmission at long wavelengths; reaching (95%) in the visible region. The transmittance spectra of ITO increase with increasing doping concentration; attributed to decreasing the grain size and changing the oxygen content. The transmittance decreases in the UV region, (below 350 nm), is due to the fundamental absorption of light [15, 16].

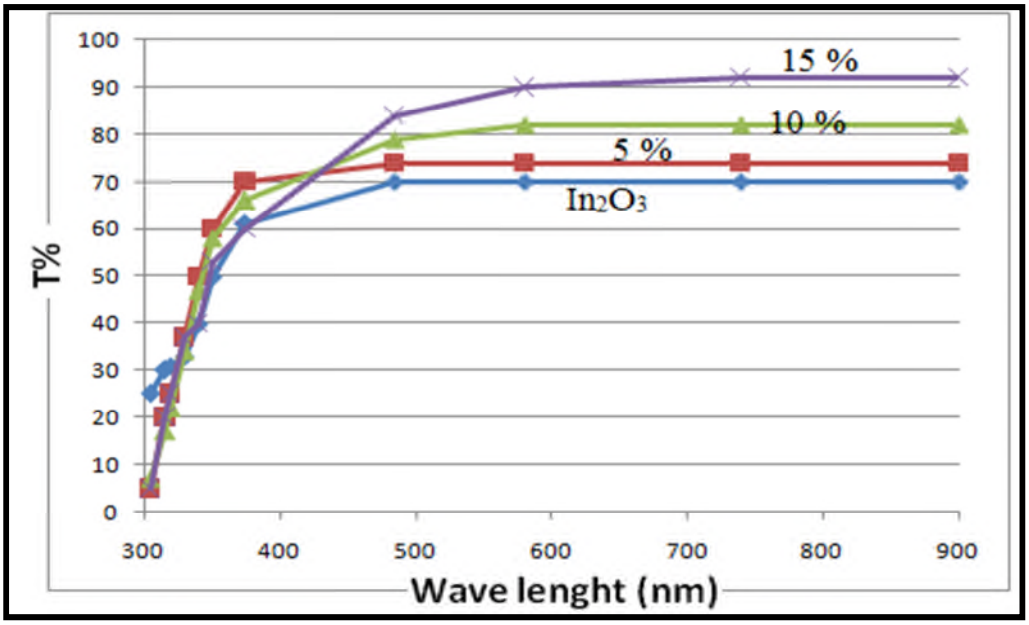

Figure (5): UV-VIS transmittance spectra of In_2O_3 thin films and In_2O_3 at different doping concentration (5, 10 and 15 %).

Sensing Properties

The sensing properties of NO2 were studied as a function of operating time using an In2O3 thin film and NO2 gas concentration of (5 ppm). The gas sensitivity of In2O3 films was calculated from measuring the resistance change of the thin films in air and in the gas. The rate of change in surface resistance in the presence of gas is measured by using equation:

$$S=\frac{(Rg-Ra)}{Ra}*100\ \%$$

Where; Ra and Rg are the resistance of films in air and in gas respectively. Figure (6) shows the gas sensitivity of SnO2 doped In2O3 on quartz substrate at different concentrations (5, 10 and 15%). The sensitivity increases with increasing the doping concentration as a result of grain size decrease. This will increase adsorption and consequently increases sensitivity [19, 20]. A maximum sensitivity of (60, 75 and 88%) was obtained to NO2 at Sn doping concentration of 5%, 10% and 15% respectively.

Where; R_a and R_g are the resistance of films in air and in gas respectively. Figure (6) shows the gas sensitivity of SnO_2 doped In_2O_3 on quartz substrate at different concentrations (5, 10 and 15%). The sensitivity increases with increasing the doping concentration as a result of grain size decrease. This will increase adsorption and consequently increases sensitivity [19, 20]. A maximum sensitivity of (60, 75 and 88%) was obtained to NO_2 at Sn doping concentration of 5%, 10% and 15% respectively.

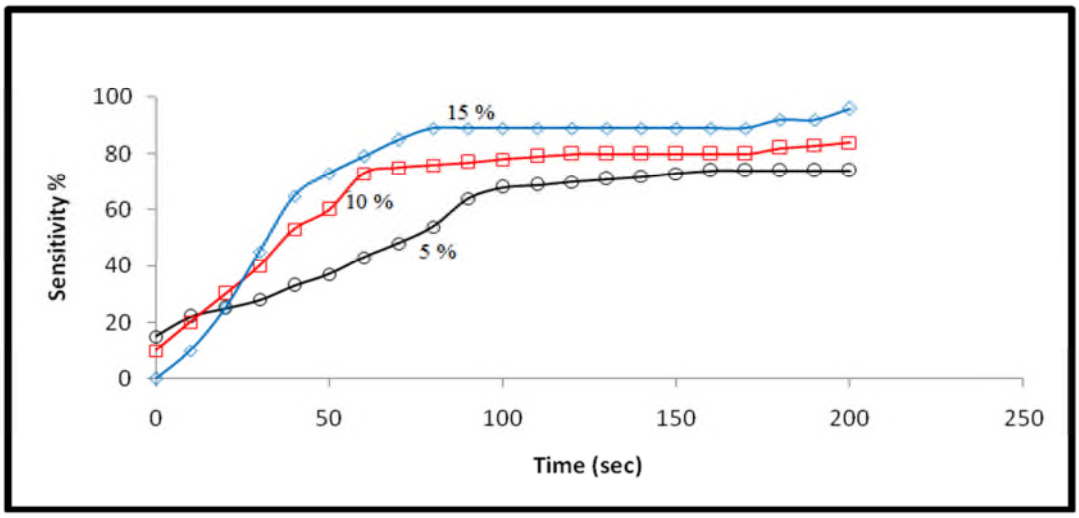

Figure (6): Sensitivity of In2O3 doped SnO2 films for NO2 gas

The sensitivity increases with doping concentration. This may be due to increasing carrier concentration which, in turn, increases the adsorption of oxygen atom and sensing gas on the surface of the thin film.

It is well known that the electrical conductivity in ITO is due to non-stoichiometric composition as a result of oxygen deficiency. The conductivity is of n-type. When the ITO sensor surface is placed in an air ambient, the oxygen molecules are adsorbed at the surface resulting in the formation of O2–, O–, O2– ions, thus decreasing the concentration of the number of charge carriers near the surface giving rise to a depletion region. When exposed to reducing gases like nitrogen dioxide vapor, mutual interaction between the reactant i.e. reducing gas and oxygen species, results in oxidation of reducing gas at the surface [21]. This oxidation phenomenon helps in the removal of oxygen ion from ITO surface resulting in decrease in the barrier height, thus increasing the conductance. During the chemisorption at higher temperature 500 OC, oxygen is adsorbed in ionic form as shown in the following reactions:

$O2\ (gas) \leftrightarrow O2\ (ads)$ … (1)

$O2\ (ads) + e^- \leftrightarrow O2^-$ … (2)

$O2^- + e^- \leftrightarrow 2\ O^-$ … (3)

When the ITO nanoparticles are exposed to NO2 gas, NO2 gas tends to react with the adsorbed O^- ions and directly accumulate on the surface of ITO nanoparticles. And its reactions are shown as below [22]:

$NO2\ (gas) + e^- \rightarrow NO2^-\ (ads)$ … (4)

$NO2^-\ (ads) + O^-\ (ads) + 2e^- \rightarrow NO\ (gas) + 2O2^-\ (ads)$ … (5)

Subsequently, the concentration of electrons on the surface of ITO nanoparticles arrays decreases and the resistance of ITO layer will increase accordingly. The adsorption of O^- ions is a very interesting and critical phenomenon in metal-oxide gas sensor, because the O^- ions tend to assist the adsorbed $NO2^-$ ions in taking the electrons from the nanoparticles arrays [23].

Conclusion

We have synthesized In2O3 and SnO2 nanoparticles by Sol-Gel method. SnO2 were doped with In2O3 nanoparticles to make ITO thin films (5, 10 and 15%, SnO2: In2O3 mole ratio) on quartz substrate by dip coating technique. The UV-VIS transmittance spectra and gas sensitivity of ITO thin films at different concentrations increases with increase doping concentration, because with increasing doping concentration the grain size decreases. Thus this will lead to increase in adsorption and increasing in sensitivity.

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