

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

The 5th International Scientific Conference for Nanotechnology and Advanced Materials and Their Applications (ICNAMA 2015) 3-4 Nov.2015

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 لأكسيد الانديوم المشوب بالقصدير بطريقة sol-gel ورسبت الاغشية على زجاج كوارتز بطريقة الغمر، تم تشويب العينات بنسب (5، 10 و 15%) 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 bixbyte structure with lattice parameter of 10.117Å°. Also, indium oxide is an important and distinguished transparent conducting oxide (TCO) [2].

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].

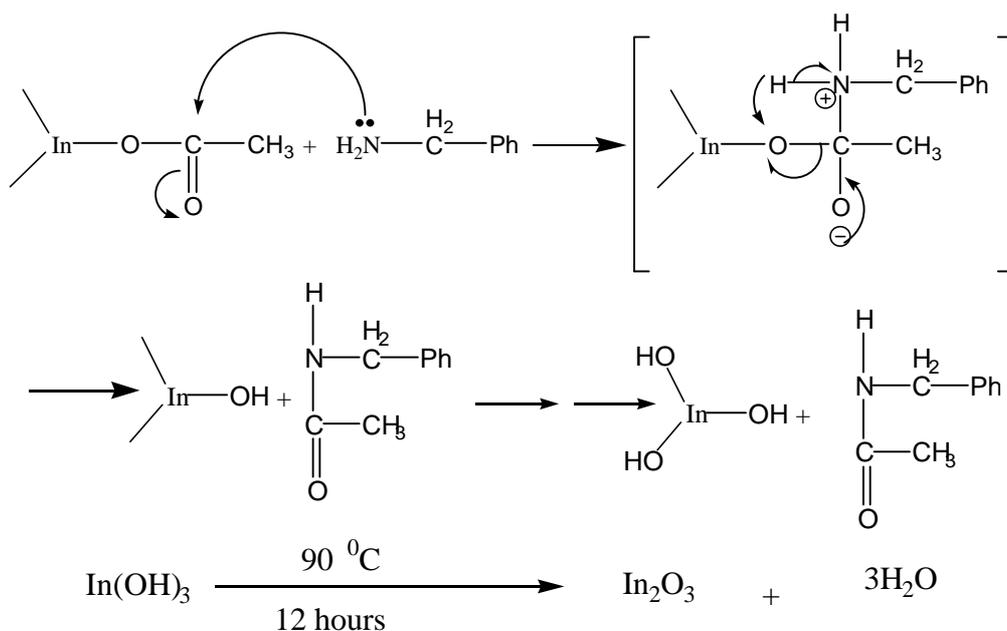
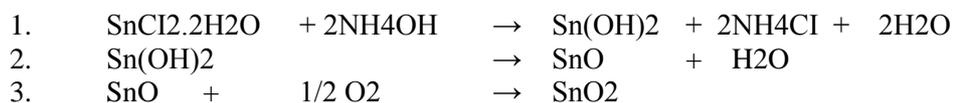


Figure (1) Suggested mechanism of reaction between indium acetate and benzylamine

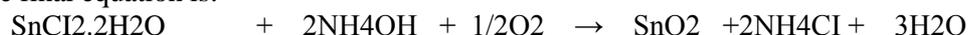
Preparation of Tindioxide (SnO₂) nanoparticle:

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]:



The final equation is:



Thin Film deposition

ITO thin films (5, 10 and 15%, SnO₂: In₂O₃ 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 In₂O₃ 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-Scherrer'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 2θ = 21.5662, 30.6535, 35.3847 and 51.0946 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 51.110, 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 51.140), 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 concentration 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).

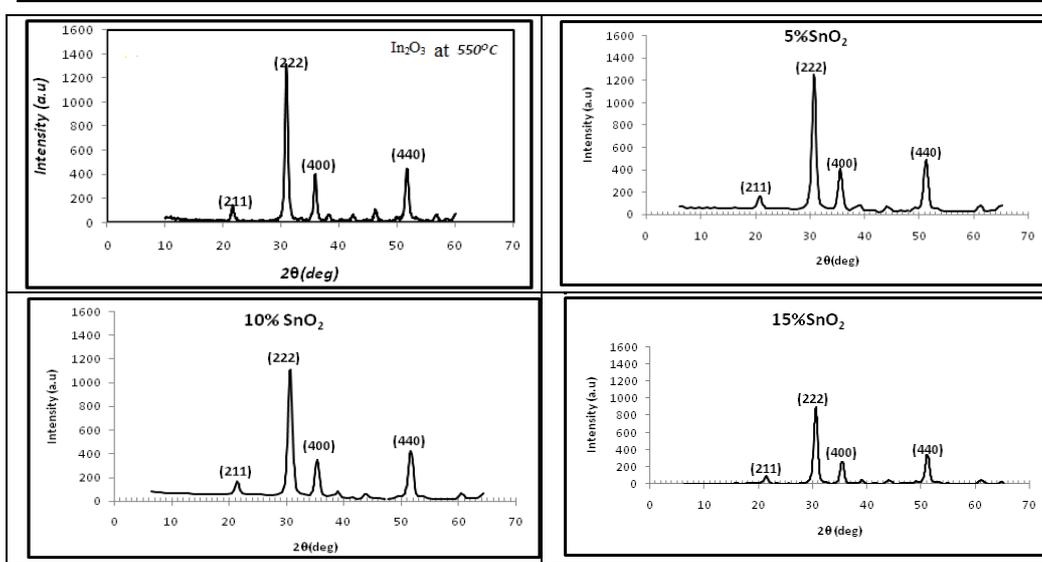


Figure (2): XRD pattern of In₂O₃ and ITO nanoparticles with doping concentration 5, 10, 15 % annealed at 550 °C

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 (Å)	D (Å)
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
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

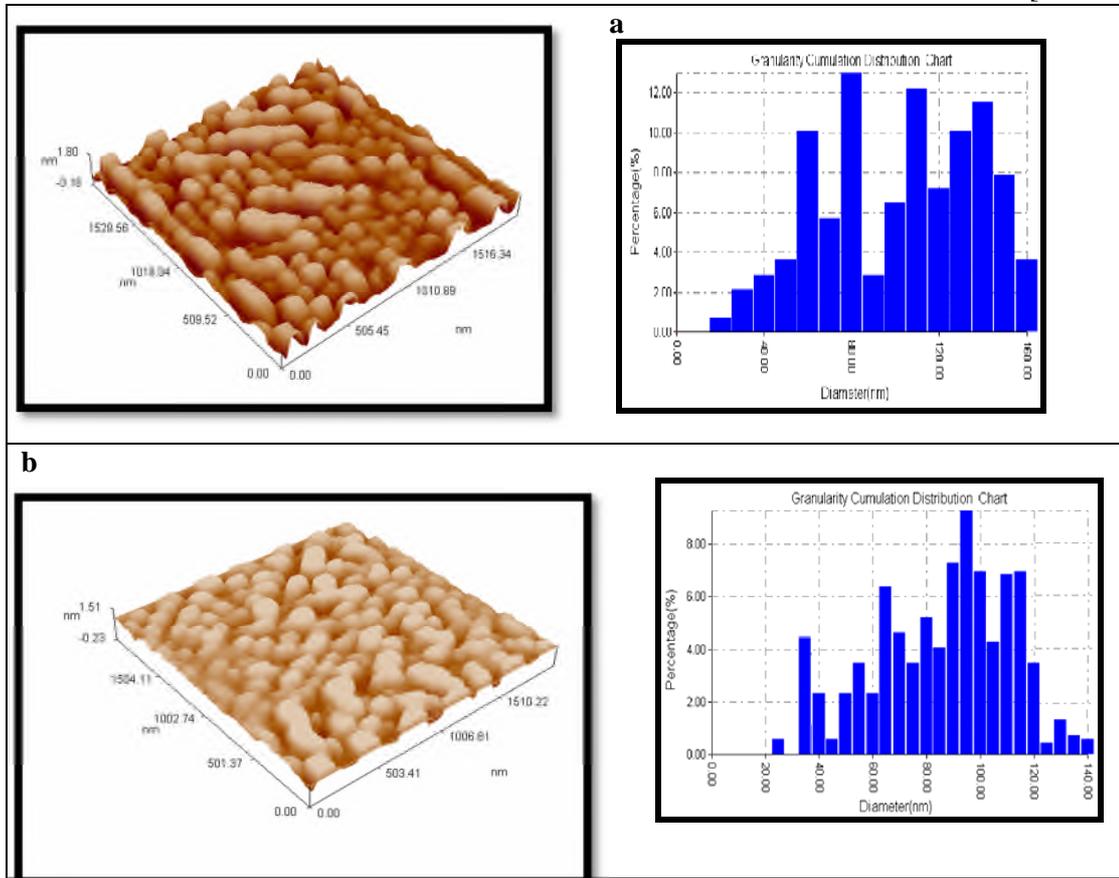


Figure (3): 3-D AFM image and Granularity cumulation distribution chart annealing at 550 C of: (a) In₂O₃ and (b) In₂O₃ doped with 15% SnO₂

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.

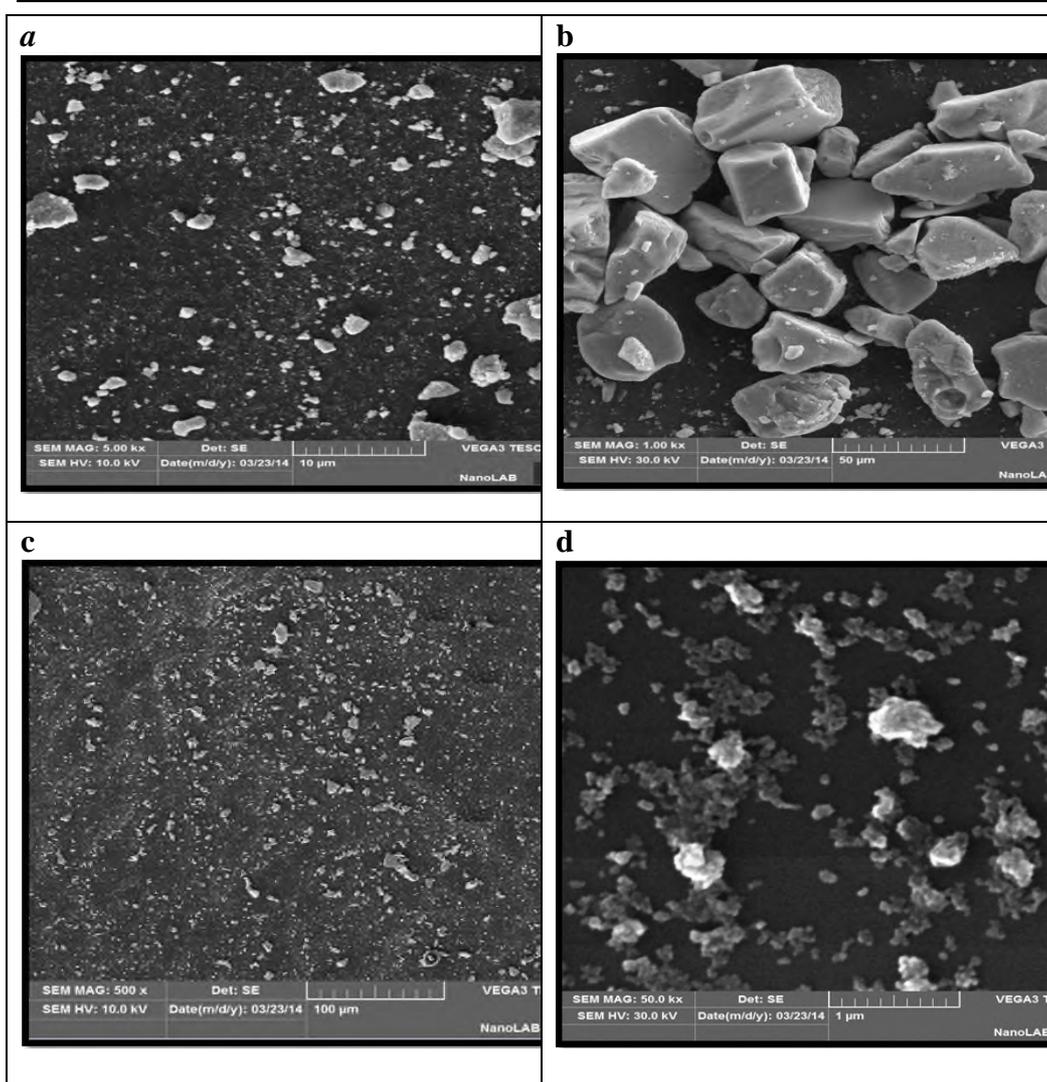


Figure (4): SEM image for In₂O₃ nanoparticles: (a) as-prepared,(b) annealing at 550 °C, and ITO nanoparticles doped with 15% SnO₂:(c) as-prepared, (d) annealing at 550 °C.

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].

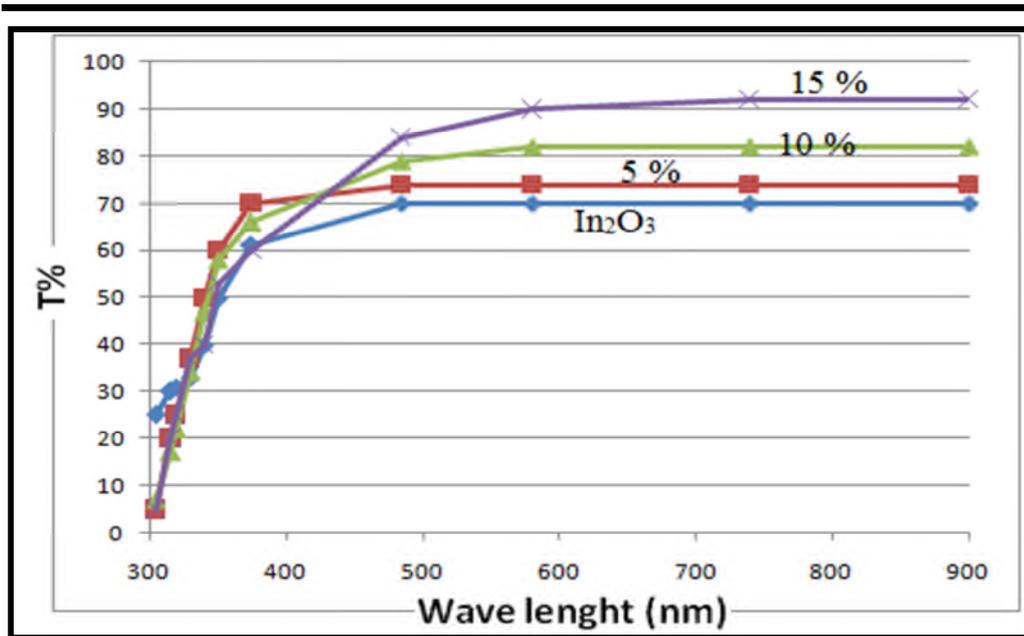


Figure (5): UV-VIS transmittance spectra of In₂O₃ thin films and In₂O₃ at different doping concentration (5, 10 and 15 %).

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:

$$S = \frac{(R_g - R_a)}{R_a} * 100 \%$$

Where; R_a and R_g 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 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.

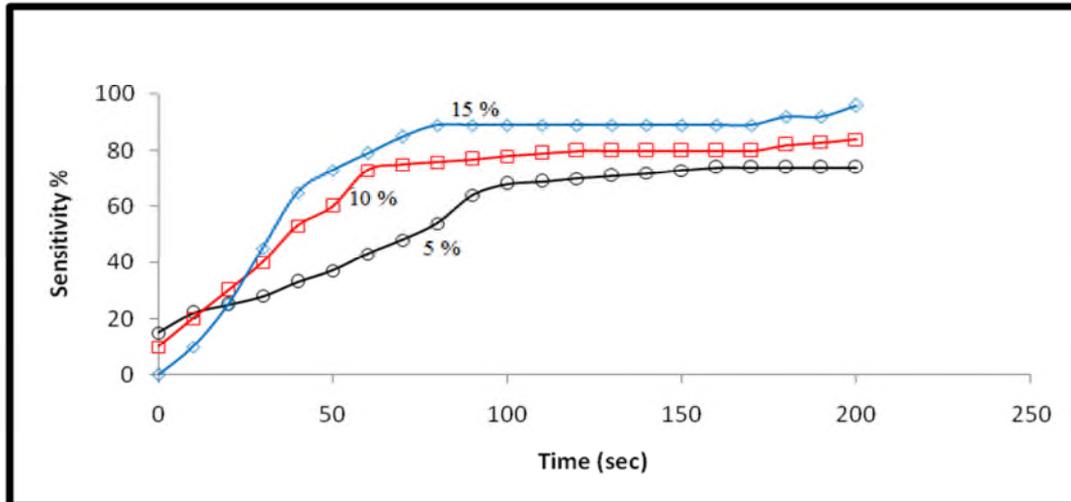


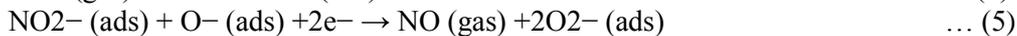
Figure (6): Sensitivity of In₂O₃ doped SnO₂ films for NO₂ gas

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:



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]:



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.

References

- [1] S. Jei Hong and J. In Han. "Fabrication of Indium Tin Oxide (ITO) Thin Film with Pre-Treated Sol Coating", Journal of Korean Physical Society, Vol. 45, No. 3: 634-637(2004).
- [2] P. K. Biswas, A. De, L. K. Dua and L. Chkoda. "Surface characterization of sol-gel derived indium tin oxide films on glass", Indian Academy of Science, Vol. 29, No. 3: 323-330(2006).
- [3] H. Woo Kim and Y. Il Kim. "Characteristics of Indium-Tin-Oxide Nanoparticles Prepared by Controlled Chemical Coprecipitation Method", Bull. Korean Chem. Soc., Vol. 29, No. 9 (2008).
- [4] V. Golovanov, C. C. Liu and A. Kiv, D. Fuks "Micro fabricated one-electrode In₂O₃ and Fe₂O₃-In₂O₃ Composite Sensors", Computer Modelling and New Technologies, Vol. 13, No. 2: 68-73(2009).
- [5] F. Quarantaa, R. Rellaa and P. Siciliano "Preparation and characterization of nanostructured materials for an artificial olfactory sensing system", Elsevier Science, Vol. 84: 55-59(2002).
- [6] M. Ivanovkaya "Gas-sensitive properties of thin film heterojunction based on In₂O₃ nanocomposites", Elsevier Science, Vol. 7031: 1-9(2003).
- [7] M. A. Flores Mendoza and R. Castanedo Pérez "Cadmium oxide, indium oxide and cadmium indate thin films obtained by the sol-gel technique", Elsevier, Vol. 518: 1114-1118(2009).
- [8] L. Korösi, S. Papp and S. Beke "Highly transparent ITO thin films on photosensitive glass: sol-gel synthesis, structure, morphology and optical properties" Springer, Applied Physics, VOL. 107: 385-392 (2012).
- [9] N. B. Ibrahim and H. Baqiah "High Transparency Iron Doped Indium Oxide (In_{2-x}Fe_xO₃, x = 0.0, 0.05, 0.25, 0.35 and 0.45) Films Prepared by the Sol-gel Method", Sains Malaysiana, Vol. 42, NO. 7: 961-966(2013).
- [10] W. Y. Chung. "Preparation of indium oxide thin film by spin-coating method and its gas-sensing properties", Elsevier, Vol. 46: 139-145(1998).
- [11] M. Z. Ahmad, J. Chang, A. Z. Sadek, and et al., Non-aqueous synthesis of In₂O₃ nanoparticles and its NO₂ gas sensing properties. IMCS- The 14th International Meeting on Chemical Sensors. 1060-1063(2012).
- [12] N. Saravanan, S. Ponnusamy, Shri Prasad S and et al. Synthesis and Characterization of SnO₂ Quantum Dots, International Journal of ChemTech Research, Vol. 6, No. 1: 600-603(2014).
- [13] A. Solieman "Effect of sintering temperature on the structural, optical and electrical properties of sol-gel derived indium oxide thin films", Sol-Gel Sci Technol, Vol. 60: 48-57(2011).

-
- [14] K. Daoudi, B. Canut and M.G. Blanchin" Tin-doped indium oxide thin films deposited by sol–gel dip-coating technique", *Materials Science and Engineering* ,Vol. 21,PP. 313–317,(2002).
- [15] P. Psuja, D. Hreniak and W. Strek" The influence of sintering temperature and Sn⁴⁺ concentration on electrical and optical properties of ITO nanocrystallites" *Journal of Physics: Conference Series*, Vol. 146: 112-120 (2009).
- [16] A. Solieman "Effect of sintering temperature on the structural, optical and electrical properties of sol–gel derived indium oxide thin films", *Sol-Gel Sci Technol*, Vol. 60: 48–57(2011).
- [17] M.-M. Bagheri-Mohagheghi" Effect of the synthesis route on the structural properties and shape of the indium oxide (In₂O₃) nano-particles", *Elsevier*, Vol.41: 1757–1762(2008).
- [18] G. Liu." Synthesis, Characterization of In₂O₃ Nanocrystals and Their Photoluminescence Property", *Int. J. Electrochem*, Vol.6: .2162 – 2170 (2011).
- [19] A. Ayeshamariam" Optical, electrical and sensing properties of In₂O₃ nanoparticles" *Materials Science in Semiconductor Processing*, Vol. 16: 686–695(2013).
- [20] R. Savu, M. Adlfo and E. Joanni," grain size effect on the electrical response of SnO₂ thin and thick film gas sensor", *Materials research*, Vol.12, NO.1.:83-87 (2009).
- [21] K. K. Makhija , R. Arabinda, R. M. Patel, U. B. Trivedi and H. N. Kapse. Indium oxide thin film based ammonia gas and ethanol vapour sensor. *Bull. Mater. Sci.*, Vol. 28, No. 1:9-17(2005).
- [22] T. V. Belysheva, L. P. Bogovtseva, E. A. Kazachkov and N. V. Serebryakova Gas- sensingproperties of doped In₂O₃ films as sensors for NO₂ in air. *J. Anal. Chem.* Vol. 58: 583–587(2003).
- [23] I. Cherng Chen, Shiu-Shiung Lin, Tsao-Jen Lin, Cheng-Liang Hsu, Ting Jen Hsueh, and Tien-Yu Shieh. The Assessment for Sensitivity of a NO₂ Gas Sensor with ZnGa₂O₄/ZnO Core-Shell Nanowires—a Novel Approach. *Sensors*, Vol. 10: 3057-3072(2010).