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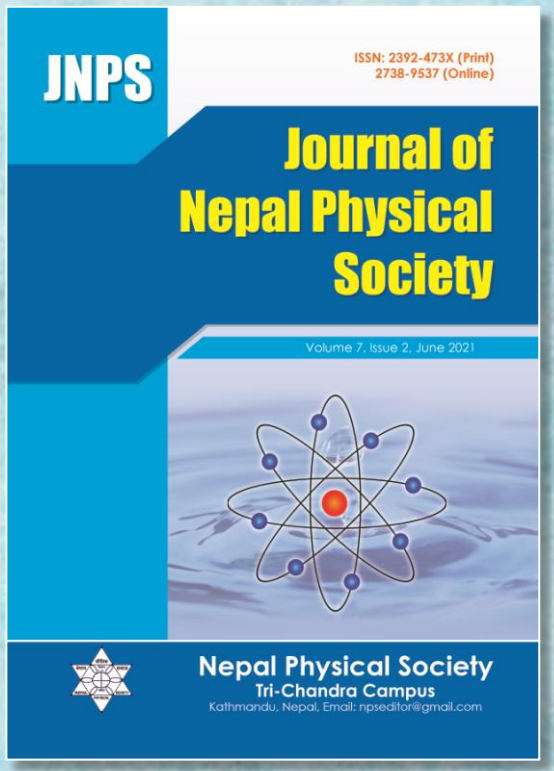

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Preperation of Thin Film of Tin Oxide (SnO_2) by Spray Pyrolysis Method and Study its Application as Gas Sensor

R. Chalise, P. K. Thakur,* J. J. Nakarmi and S. P. Shrestha
Central Department of Physics, Tribhuvan University, Kirtipur, Kathmandu, Nepal
*Corresponding Email: pk_thakur12@yahoo.com

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ABSTRACT

In this article SnO_2 thin films have been deposited onto glass substrates by Spray Pyrolysis Method. Tin chloride dihydrate ($SnCl_2.2H_2O$) and Copper nitrate ($Cu(NO_3)_2.3H_2O$) were used as source of Sn and Cu respectively. The structural, optical and gas sensing properties of Undoped and copper doped by (vol. %) SnO_2film have been investigated. XRD of film shows structure of films. Also result so obtained from XRD spectroscopy shows that these layers have the tetragonal polycrystalline tinoxide structure. The optical transmission was found to decrease with addition of copper as dopant on SnO_2 with the addition of Cu except for 5% Cu-Doped. The reponse of these layers have been investigated for different concentrations of butane gas by static gas sensing system. The results of this investigation show that the Cu-Doped SnO_2 nanostructure layer compared with the pure SnO_2 nanostructure layer has showed the better response for butane gas. Among Cu-Doped SnO_2 thin film layer 4% (by vol.) copper doped thin film layer has showed higher response toward the Butane gas with less response and recovery time than other films.

Keywords: Spray Pyrolysis, SnO_2Thin Film, Gas sensing.

1. INTRODUCTION

Transparent and conducting oxides (semiconductors) have been extensively studied because of their novel properties and wide range of applications including architectural windows, polymer-based electronics, etc.SnO_2 has wide band gap(3.6 eV) and called n-type semiconductors, the most frequently used as a sensitive material for gas sensor.tinoxide (SnO_2) is one of the most widely used materials for gas sensor application because of its ease of fabrication and its special properties such as chemical and thermal stability, natural non-stoichiometry, high sensitivity, low cost, fast response and good ability to absorb oxygen[1].

The structure of SnO_2 in its bulk form is tetragonal rutile with lattice parameters of a = b = 4.737 Å and c = 3.185Å [2]. However, in thin film form, depending on the deposition technique, its structure can be polycrystalline or amorphous.

There are various methods such as chemical vapour deposition, sol gel, spray pyrolysis, Spin Coating, electron beam evaporation, vapour deposition, thermal evaporation and magnetron sputtering, etc. for the preparation of pure or doped.

In this paper we are reporting the effect of Cu doping on the structural, optical, and electrical properties of SnO_2 films prepared by a simple spray pyrolysis technique (SPT).

Undoped and the effect of Cu doping concentration on the SnO_2 sensitivity is investigated that has not be reported in the literature as Nano-sensor.

The Cu^{2+} has smaller ionic radius than Sn^{4+}, so Cu^{2+}can be incorporated onto the SnO_2 lattice simply by replacing Sn^{4+}. This may be leading to form more oxygen vacancies, which improves chemical sensing properties of Cu-doped and SnO_2 thinfilms.

For metal oxide semiconductors, the measurable parameter is the resistance of the metal oxide, thus the sensitivity of the semiconductor is defined as the ratio of resistance of sensor in analyze gases to resistance of sensor in air as follows

$$\text{Sensor response } (S_g) = \frac{Rair-Rgas}{Rair} \times 100\% \quad ...(1)$$

Where R_{air} is the resistance of the sensor in air; and R_{gas} is the resistance of the sensor after exposure to the analyze gas. Using this definition, the sensitivity is easily calculated from the measured resistance values [3,9]. Thus, it is very convenient to compare the sensitivities in different gas environments.

Another important parameter is response time and recovery time. Response time is defined as a time taken to reach 90% of the saturation value of resistance when the sensor is exposed to be given gas. Recovery time is defined as a time taken to reach 90% of saturation value of resistance when the sensor is placed in air without any gas. For better gas sensor both response time and recovery time as small as possible [6, 8].

2. EXPERIMENTAL DETAILS

Pure SnO_2 and Cu doped SnO_2 films were deposited using an experimental set up of spray pyrolysis system as shown in fig (2.1).

Fig. 2.1: Experimental set up for Spray Pyrolysis

For the preparation of tin oxide solution, first of all we have taken hydrated stannous chloride ($SnCl_2.2H_2O$) which is about 99.9% pure and Ethanol (99.9%purity). In this experiment we have prepared the 0.08M molar Precursor solution of tin oxide by mixing ethanol and stannous chloride in required proportion and this solution is stirred on magnetic stirrer about 2 hour until the clear and homogeneous solution is obtained. To get clear solution we have added 2 to 3 drop of dilute HCL solution. For the doping of Cu on SnO_2 we have made 0.08M concentration of cupric Nitrate ($Cu(N0_3)_2.2H_20$) solution by mixing with ethanol.

Seven different solutions were prepared by mixing precursor solution and doping solution in different volume. To get different doping percentage of Cu solutions we have mixed 0%, 1%, 2%, 3%, 4%, 5% and 6% Cu Nitrate solution (by volume%) on SnO_2 solution. And these separate percentage of finally prepared solution are filtrate using whatman filter paper and kept separately around 24 hour for ageing.

LPG from cylinder is filled in glass bottle by opening the in-late valve which is controlled by tighter placed on pipe and equivalent amount of gas is injected in the gas chamber. The experiment is performed with continuous flow of LPG at the rate of 16.67 ml/sec. The gas was supplied inside the chamber of 17576ml at the rate of 16.67ml/sec for 10 seconds and then supplied cut off, such total volume of LP gas inside was 166.7ml. The concentration i.e volume ratio is calculated by using the formula, Concentration % = (Volume of LP gas/Volume of air) ×100% was approximately 0.9485% which is equivalent to 9484.5 ppm.

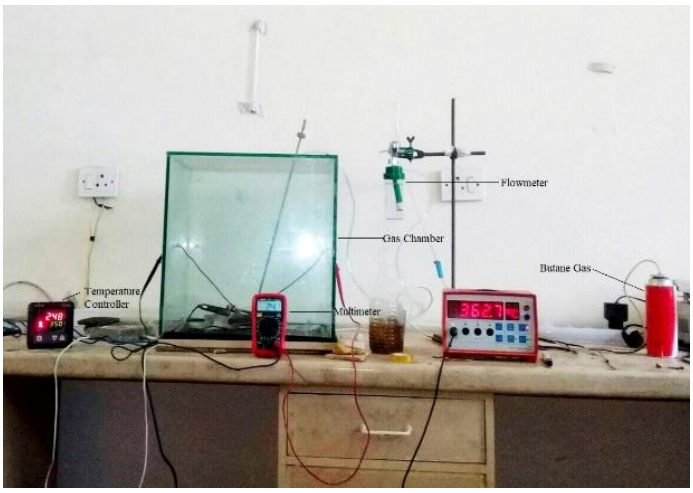

Fig. 2.2: Experimental Set-up for Gas Sensing.

Sensitivity versus temperature is measured by varying temperature and find out the optimum temperature at which maximum sensitivity for different sample is obtained. Again after finding out the optimum temperature, sensitivity vs time is measured which is determined by supply of gases and cutting of gas and thus which helps to determine response and recover time of given sample at given operating temperature which can be measured by experimental set-up as shown in fig(2.2). Firstly gas was supplied into the chamber and resistance was measured until a saturation value was observed and corresponding time called response time was noted. When saturation value was reached chamber was evacuated with clean air and time required to reach saturation value of resistance called recovery time was noted again this process repeated two times for each samples at different concentration of gas passing.

3. RESULTS AND DISCUSSION

3.1 Study and analysis of structural properties of prepared thin film

In this case we have studied the XRD pattern obtained in Undoped and Cu-Doped SnO_2 thin films deposited on glass substrate. We also calculated d-spacing, average crystallite size, plane orientations from the X-ray diffraction patterns. The average crystalline size of Undoped and Cu-Doped SnO_2 is calculated by using the Scherrer's relation,

$$D = \frac{k\lambda}{\beta cos\theta}$$

Where D is average crystalline size, λ= 1.542A° (X-ray wavelength), β is the observed full width at half maximum intensity (FWHM) of the peaks, and θ is the diffraction angle [4, 7].

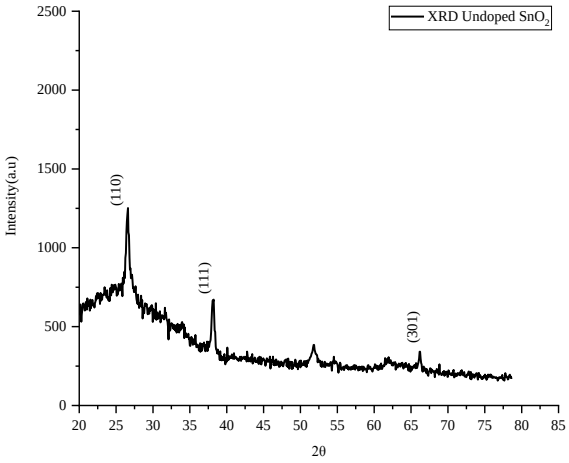

Fig. 3.1: Observed XRD pattern of Undoped SnO_2

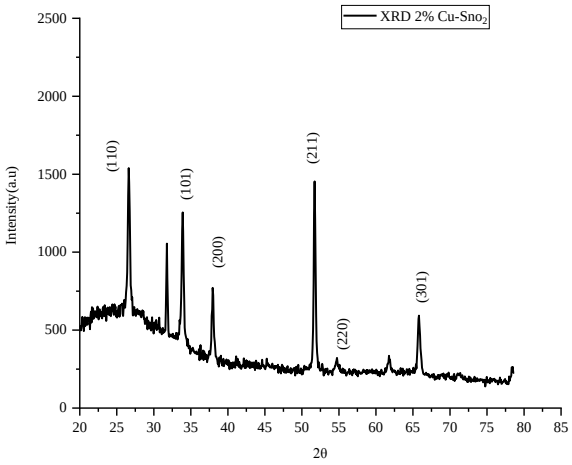

Fig. 3.2: Observed XRD pattern of 2% Cu-Doped SnO_2

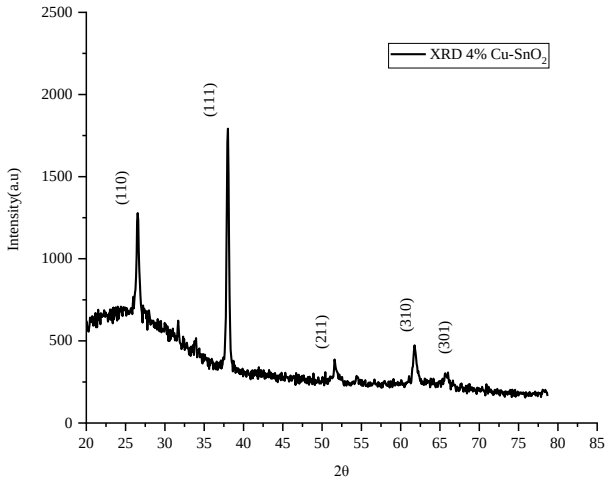

Fig. 3.3: Observed XRD pattern of 4% Cu-Doped SnO_2

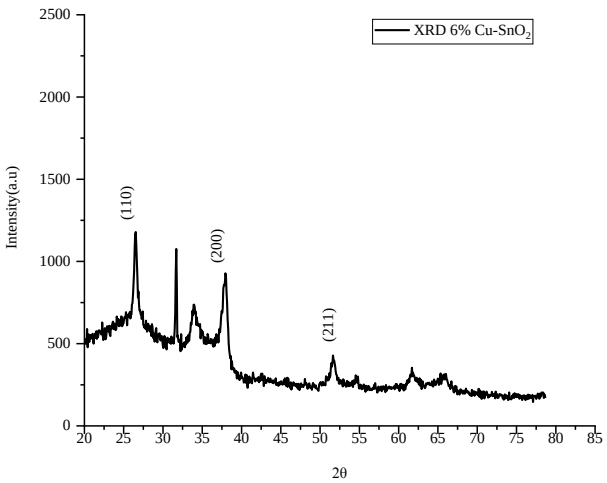

Fig. 3.4: Observed XRD pattern of 6% Cu-Doped SnO_2

Table 3.1: Observed 2θ values, Observed and JCPDS d-values, (h k l) planes, FWHM, Crystalline size (D) of A1 (undoped SnO2), A2 (2%) Cu-Doped SnO2, A3 (4%) Cu-Doped SnO2, A4 (6%) Cu-Doped SnO2 Nano structure thin film sample.

Sample	Peak position 2θ (°)	Inter planar spacing d(A°)		JCPDS Card Number	Plane (h k l)	FWHM	Crystalline size D(nm)
		Calculated value	JCPDS d value				
	26.546	3.3578	3.3556	77-0450	(110)	0.4127	0.345
A1	38.153	2.6439	2.6491	77-0450	(111)	0.2752	0.534
	66.190	1.4119	1.4174	77-0450	(301)	0.2752	0.601
	26.504	3.3603	3.3556	77-0450	(110)	0.3145	0.453
	33.772	2.6519	2.6491	77-0450	(101)	0.2970	0.488
A2	37.842	2.3755	2.3728	77-0450	(200)	0.2899	0.506
	51.597	1.770	1.7674	77-045	(211)	0.2663	0.579
	54.598	1.6795	1.6778	77-0450	(220)	0.4693	0.333
	65.688	1.4203	1.4174	77-0450	(301)	0.3699	0.447
	26.550	3.3574	3.3556	77-0450	(110)	0.3356	0.425
	38.003	2.3678	2.3131	77-0450	(111)	0.3077	0.477
A3	51.692	1.7684	1.7674	77-0450	(211)	0.6051	0.241
	61.790	1.5014	1.5006	77-0450	(310)	0.5346	0.302
	65.805	1.4192	1.4174	77-0450	(301)	1.1855	0.139
	26.501	3.3634	3.556	77-0450	(110)	0.5503	0.259
A4	37.918	2.3729	2.3728	77-0450	(200)	0.5503	0.266
	51.654	1.7696	1.7674	77-0450	(211)	0.6879	0.241

When we have calculated crystalline size as mentioned above we found that average crystalline size goes on decreasing with increasing percentage of copper doping on SnO_2 as shown in fig (3.1).

3.1 Optical property of SnO_2 thin film and effect of Cu-Doping

Undoped and Cu- Doped SnO_2 films were deposited on sonicated and cleaned glass substrate by using Spray pyrolysis method. The spectral analysis were carried out by using spectrometer operated in the wavelength range of 350 nm to 1100nm.

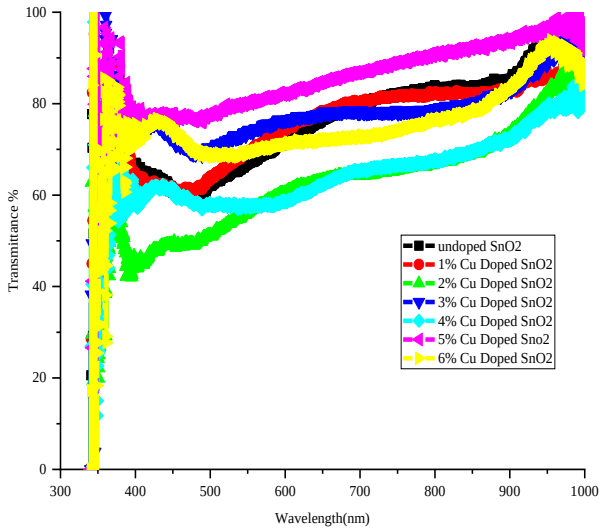

Fig 3.1.1: Showing Optical Transmittance of Undoped and 1%, 2%, 3%, 4%, 5%, 6% Cu-Doped SnO_2 thin film glass substrate sample.

From above figure (3.1.1) we have found that for every doped and Undoped sample the percentage of transmittance is increasing with increase inwavelength of UV Visible source. Highest transmittance have found on 5% Cu-Doping with all wavelength range 350nm-1000nm and lowest percentage of transmittance for 2% Cu-Doping for around 400nm and 4% Cu-Doping for around 1000nm range as shown in fig (3.2) to fig (3.4).

3.2 Electrical and Sensing properties of prepared samples towards butane gas

The resistance value of each sample before and after passing of butane gas in gas chamber was measured and sensitivity was calculated by using the relation

$S= [(R_a-R_g)\times 100]/R_a$ for n-type semiconductor

Where R_a is the stabilized resistance of sample in air and R_g is the stabilized resistance of sample in butane gas in gas chamber.

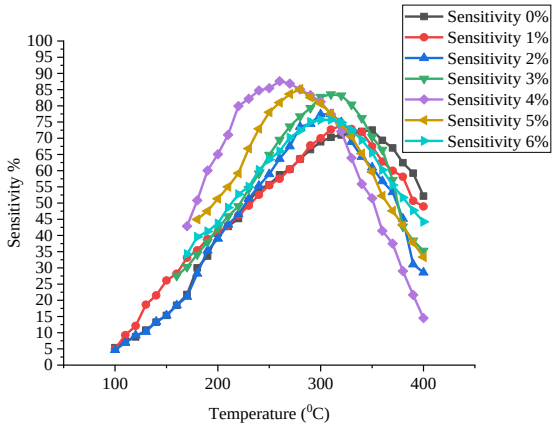

Fig 3.2.1: Sensitivity of % of Cu-Doped SnO_2 at varying substrate temperature.

From above graph (3.2.1), it is cleared that 4% Cu-Doping shows higher sensitivity 87.619% at operating temperature 260^{0}C, which is lower than the operating temperature of other gas sensor and hence it is more consistent and reliable. We found that sensitivity value at optimum temperature of respective sample goes on increasing from Undoped to 4% copper doped SnO_2 sample and beyond 4% doping concentration, the optimum sensitivity goes on decreasing which may be due to impurity band formed or heavy doping and due to collision between large number of chemisorption electron that may be released by reducing gas butane. The temperature at which highest sensitivity obtained to the analyze gas for a given sample placing on closed chamber is called optimum temperature.

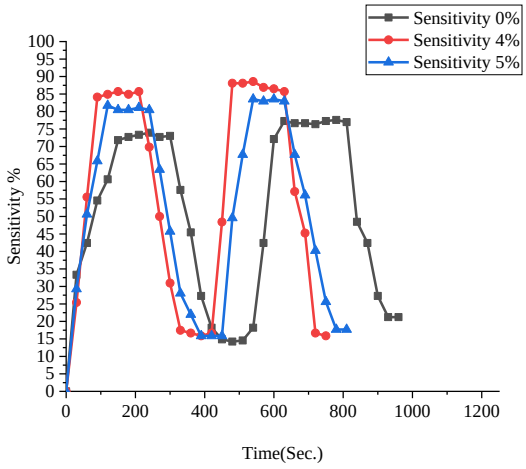

Fig 3.2.2: Combined graph for sensitivity versus time for undoped, 4%, 5% copper doped tinoxide sample.

In fig (3.2.2) Sensitivity towards analyze butane gasess greatly affected by crystalline size. Since in

this work of gas sensing, sensitivity is increase by doping of copper on SnO_2, the reason may be due to decrease in crystalline size of sample on due to the increase in doping concentration.

The butane is the major constituent (55 vol. %) of LPG. It requires high temperature to dissociate into lower alkanes. Carbon-Carbon and Carbon-hydrogen bonds are strong due to strong Vander Waals forces.

The atmospheric oxygen O_2 adsorbs on the surface of the film. When alkanes react with oxygen, a complex series of reaction takes place. Butane gas gets oxidized to CO_2 and H_2O producing extra electron on conduction band of thin film and hence increases conductivity by reducing resistance. The reaction occurring is shown below [5,10].

$O_{2\,(gas)} \rightarrow O_{2\,(ads)}$

$O_{2\,(ads)} + e^- \rightarrow O^-_{2(ads)}$

$O^-_{2(ads)} + e^- \rightarrow 2O^-_{(ads)}$

$2O^-_{(ads)} + e^- \rightarrow O^{2-}_{(ads)}$

$C_n H_{(2n+2)} + (3n + 1) O^-_{(ads)} \rightarrow nCO_2 + (n + 1) H_2O\,(g) + (3n + 1) e-$

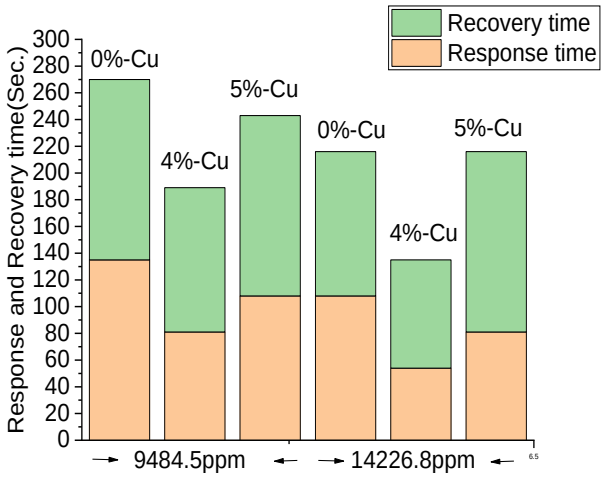

Fig 3.2.3: Bar-graph showing Response and RecoveyTime

Table 3.2: Showing response and recovery time for 0%, 4%, 5%, Cu-Doped SnO_2 sample.

Sample	Gas concentration insidesensing chamber(9484.5ppm)		Gas concentration inside sensing chamber(14226.8ppm)	
	Response time (Second)	Recovery time (Second)	Response time (Second)	Recovery time (Second)
0% Cu-Doped SnO_2	135	135	108	108
4% Cu-Doped SnO_2	81	108	54	81
5% Cu-Doped SnO_2	108	135	81	135

From above table (3.2) and Bar Graph in fig(3.2.3), response time is smallest for 4% Cu-Doped than for other doping concentration of copper on SnO_2. As the concentration of gas on sensing chamber increases the response time is found to be decreased which means that the prepared sample is effective for higher concentration of gas. The sensor having small response and recovery time are considered as good sensing device. From above table we can be conformed that 4% Cu-Doped SnO_2 sample is better for butane gas sensing application. We believed that it is a possible and effective route to improve the sensing performance of the thin films, as Nano-sensors.

4. CONCLUSION

We have confirmed that the resistance of tin oxide thin film goes on increasing on addition of copper as a dopant in this experimental work. From XRD analysis, we have confirmed that the prepared thin film has tetragonal primitive type of lattice cell and crystalline size of Undoped SnO_2 decrease from 0.492 to 0.259. From transmittance properties we have found that on addition of copper on SnO_2, transmittance goes on decreasing. From sensing properties, it is cleared that 4% Cu-Doped SnO_2 have strong ability toward sensing of butane gas at lowest optimum temperature at 260^0C and sensitivity is 87.61905% than other Undoped and doped sample among the work and also it is cleared

that 4% Cu-Doped SnO_2 have strong response and recovery ability toward butane gas with response time 54sec. and 81 sec. for 14226.8ppm gas.

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REFERENCES

[1] Chaisitsak, S. Nanocrystalline SnO_2:F Thin Films for Liquid Petroleum Gas Sensors. *Sensors*, **11**(7): 7127-7140 (2011).

[2] Savu, R.; Ponce, M. A.; Jonni, E.; Roberto, P.; Castro, B. M.; Cilense, M.; Vurela, J. A.; Longo, E. Grain size effect on the electrical response of SnO_2 thin and thick film gas sensors. *Materials Reasearch*, **12**(1): 83-87 (2009).

[3] Maekawa, T.; Jamaki, J.; Miusa, N.; Yamazoe, N.; Mtsushima, S. Development of SnO_2-based ethanol gas sensor. *Sensors and Actuators*, **9** (1): 63-69 (1992).

[4] Mishjil, K. A.; Chiad, S.; Mansour, H. L.; Habubi, N. F. Influence of copper doping on the structural and optical properties of sprayed SnO_2 thin film. *Journal of electron Devices*, **14**: 1170-1177 (2012).

[5] Suchea, M.; Christoulacis, S.; Moschovis, K.; Kasarakis, N. and Kiriakidis, G. ZnO transparent thin films for gas sensor applications. *Thin Solid Film*, **515** (2): 551-554 (2006).

[6] Sun, Y. F.; Liu, S. B.; Meng, F. L.; Liu, J. Y. Jn, Z.; Koung, L. J. and Liu, J. H. Metal Oxide Nanostructures and Their Gas Sensing Properties: A Review. *Sensors*, **12** (3): 2610-2631 (2012).

[7] Ramirez, F. H.; Barth, S.; Tarancon, A.; Casals, O.; Pellicer, E.; Rodriguez, J.; Rodriguez, A. R.; Morante, J. and Mathur, S. Water vapor detection with individual tin oxide nanowires. *Nanotechnology*, **18** (42): 424016 (2007).

[8] Ghimbeau, C. M.; Lumbreras, M.; Saidat, M.; Landschoot, V. and Schonman, J. Electrostatic sprayed SnO_2 and Cu-doped SnO_2 films for H2S detection. *Sensors and Actuators*, **133** (2): 694-698 (2008).

[9] Gong, H.; Hua, J. Q.; Wang, J. H.; Ong, C. H. and Jhu, F. R. Nano-crystalline Cu-doped ZnO thin film gas sensor for CO. *Sens. Actuators*, **115** (1): 247-251 (2006).

[10] Shyju, G. J.; Nagarani, S.; Roy, S. D. and Sanjeeviraja, C. Gas Sensing Properties of Semiconducting Metal Oxide Thin Films. *Archives of Applied Science Reasearch*, **4** (5): 2149- 2151 (2012).