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EFFECT OF ADDITIVES ON GRAIN SIZE AND AMMONIA SENSING PROPERTIES OF SPRAYED PURE AND CuO MODIFIED ZnO THIN FILMS

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*Nanocrystalline pure and CuO doped ZnO thin films were prepared using spray pyrolysis technique. The zinc nitrate (*0.1 *M) and copper chloride (*0.1 *M) were used as starting precursor. These films were characterized by XRD, SEM and EDAX to observe structural, microstructural properties and elemental analysis respectively. It is observed that the average grain size was found to decrease from* 190 *to* 90 *nm, as the doping wt % of copper chloride in zinc nitrate solution goes on increasing. The sensing performances of pure and doped films were tested. The sensitivity goes on increasing with decreases in grain size (increase of copper chloride in zinc nitate solution). The maximum sensitivity of S =* 35 *at* 400 *°C was found for films prepared from* 10 *wt % of copper chloride.*

Keywords: *GRAIN SIZE CONTROL, ZINC OXIDE, THIN FILMS, AMMONIA SENSOR, SPRAY PYROLYSIS.*

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1. INTRODUCTION

Among the various materials ZnO is the most promising semiconductor to detect the toxic and hazardous gases [1]. As gas sensing material, it is one of the earliest discovered and most widely applied oxide gas sensing material [2]. It is particularly applicable to gas sensors because of it's typical properties such as resistivity control over the range 10^{-3} to 10^5 Ω·cm, high electrochemical stability, non toxicity, abundance in nature, etc. [3]. It crystallizes in a wurtzite structure and exhibits n-type electrical conductivity [4]. The use of ammonia gas sensors has increased in many areas of technology. Electrolytic method is normally used for the detection of ammonia. However this method is being replaced by semiconducting oxide devices. The detection of ammonia gas in the device is done by sensing the hydrogen produced by decomposition of ammonia. Semi-conducting oxides such as ZnO, SnO_2 and TiO_2 with additives like $CuCl_2$, Al and Cr_2O_3 are used as ammonia sensors [5-9].

This article deals with preparation procedure of thin films of pure and CuO doped ZnO by spray pyrolysis technique and their gas sensing performance. Studies were carried out and the results are presented on the variation of sensitivity with different operating temperatures. The results are interpreted in terms of conclusions.

2. EXPERIMENTAL

2.1 Preparation of solution

Commercially available AR grade zinc nitrate and copper chloride were used as precursors to obtain pure and CuO doped ZnO thin films.The solution was prepared in deionized water. The reaction mixture was formed after adding the aqueous solutions in appropriate quantity after well steering.

2.2 Preparation of Pure ZnO thin film

Thin films of pure ZnO were prepared using following procedure. 0.1 M aqueous solution of $Zn(NO_3)_2$ was prepared in deionised water. The solution was filled in a spray gun. This solution was allowed for spraying onto heated glass substrate at constant temperature of 350 °C. The sample was referred as S0.

2.3 Preparation of CuO doped ZnO thin films

Different wt % of CuO was doped into ZnO by adopting following procedure. The 0.1 M solutions of water soluble zinc nitrate and copper chloride prepared in deionised water. The stock solutions to be sprayed were prepared by mixing zinc nitrate and copper chloride in the proportion of : 99 : 1, 95 : 5 and 90 : 10. Each solution was filled in a spray gun and was allowed to spray onto heated glass substrate at constant temperature 350 °C. Zinc nitrate and copper chloride would be decomposes and pyrolyzed to obtain Zn_xCu_{1-x} ($x = 0.99, 0.95, 0.9$). Thus the thin films with different wt % of CuO were obtained. The thin film samples were referred as S1, S2 and S3 respectively.

2.4 Anneling of pure and dopped thin films

The prepared pure and modified thin films were fired at 500 °C for 60 minute for complete oxidation.

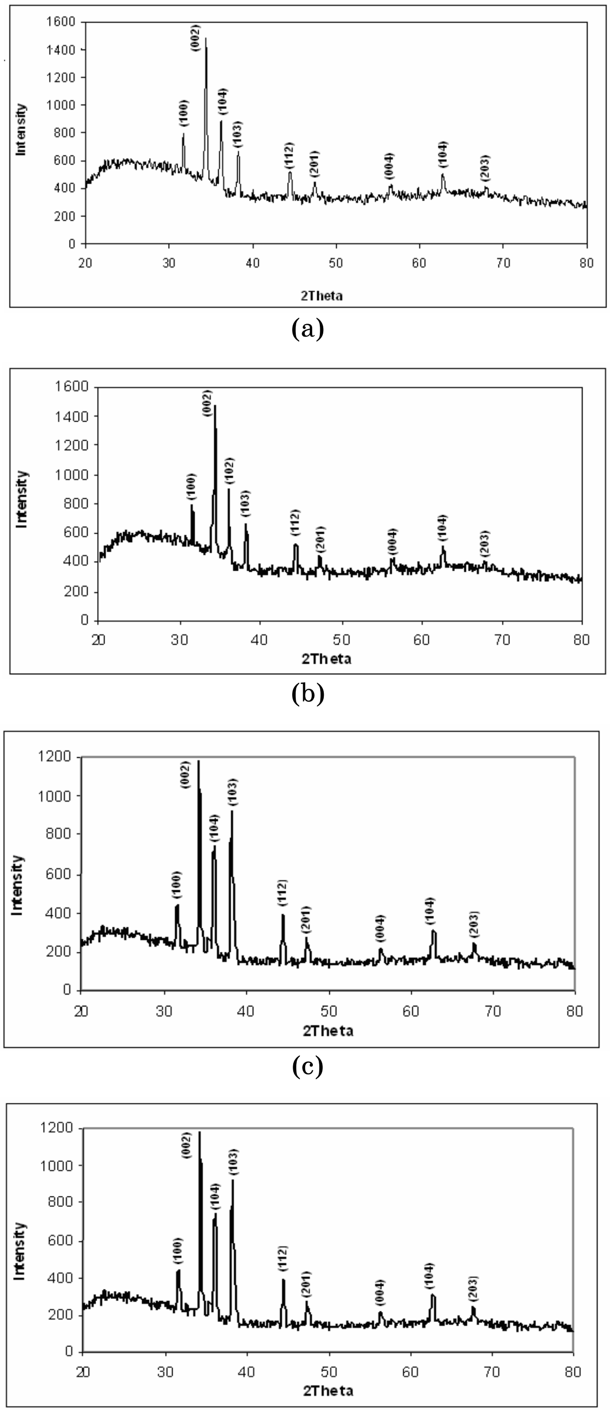
2.5 Characterizations

The surface morphology of the thin films were studied using scanning electron microscope (JEOL JSM-6360 A). The quantitative elemental analysis of the thin film was carried out by computer controlled energy dispersive X-ray analyzer attached to the scanning electron microscope. The structural properties of the thin films were studied with X-ray diffractogram (Philips PW 1730) using Cu K α radiation ($\lambda = 1.5418$ Å) The electrical and gas sensing characteristics were measured using a indigenous static gas sensing system.

3. RESULTS AND DISCUSSION

3.1 Structural analysis using XRD

The structure of the films was analyzed with X-ray diffractogram (RIGAKU DMAX 2500) using CuK_α radiation with a wavelength 1.5418 Å.



(a)

(b)

(c)

(d)

Fig. 1 – X – ray diffractogram of samples: S0 (a), S1 (b), S2 (c), and S3 (d)

Fig. 1 a through Fig. 1 d are the X-ray diffractograms of pure ZnO, and CuO doped ZnO thin films (with $CuCl_2$ 1 ml, 5 ml, 10 ml) respectively. The observed peaks are matching well with ASTM reported data of pure ZnO. There are no prominent peaks of CuO associated in XRD pattern. It may be due to smaller wt % of CuO in comparison with ZnO. It reveals from XRD that the films are polycrystalline in nature. The average grain sizes as determined from Scherer formula and presented in Table 1. The d-values of as prepared films were compared with standard values and presented in Table 2.

Table 1 *– Dependence of grain size with $CuCl_2$ dopping level*

Sample No.	Solution in ml			Grain Size (nm)
	$Zn(NO_3)_2$	$CuCl_2$	Total	
S0	100	0	100	190
S1	99	1	100	138
S2	95	5	100	110
S3	90	10	100	90

It is clear form Table 1 that, the average grain size was found to decrease from 190 to 90 nm, as the doping wt % of copper chloride in zinc nitrate solution goes on increasing.

Table 2 *– Comparision of observed and standard d values of pure and CuO doped ZnO thin films with different wt % of $CuCl_2$*

Sr. no.	Standard	Pure ZnO		CuO doped (1.27 %)		CuO doped (8.56 %)		CuO doped (9.66 %)		*hkl*
	d(Å)	*d*(Å)	*I*(a.u.)	*d*(Å)	*I*(a.u.)	*d*(Å)	*I*(a.u.)	*d*(Å)	*I*(a.u.)	
1	2.81	2.81	792	2.81	792	2.81	475	2.81	475	100
2	2.6	2.6	1481	2.6	1481	2.6	947	2.6	947	2
3	2.47	2.47	890	2.47	890	2.47	692	2.47	692	104
4	1.91	1.91	664	1.91	664	1.91	899	1.91	899	103
5	1.62	1.62	509	1.62	509	1.62	451	1.62	473	112
6	1.47	1.47	440	1.47	440	1.47	246	1.47	264	201
7	1.4	1.4	431	1.4	431	1.4	273	1.4	273	4
8	1.38	1.38	502	1.38	502	1.38	303	1.38	334	104
9	1.35	1.35	391	1.35	391	1.35	243	1.35	273	210

[PDF 79-206, $a = 3.2499$ Å and $c = 5.2065$ Å], possessing hexagonal wurtzite structure. The d values of all the films were mathches well with those in the PDF for ZnO.

3.2 Elemental composition using EDAX

The wt. % of Zn, Cu, O were obtained by EDAX technique are represented in Table 3. It is clear from the Table 3 that the thin films are zinc rich and oxygen deficient and hence are non stichiometric in nature. With increase $CuCl_2$, the wt. % of Zn goes on decreasing. The thin film with 10 ml $CuCl_2$ doping was observed to be most oxygen deficient. The percentage of Zn is larger while percentage of Cu is smaller in sprayed S1, S2 and S3 samples.

***Table 3** – The composition of CuO doped ZnO thin films*

Sample No.	Mass, %					
	Cu	O	CuO	Zn	O	ZnO
S0	0	0	0	51.70	48.30	100
S1	0.66	0.61	1.27	51.42	47.31	98.73
S2	4.35	4.21	8.56	48.98	42.46	91.44
S3	5.18	4.48	9.66	48.48	41.86	90.34

3.3 Surface morphology using SEM

Fig. 2 a depicts SEM image of pure and Fig. 2 b through 2 d represents SEM images of CuO doped ZnO thin films. Fig. 2 a shows randomly distributed flat plate-like grains with shape distribution. Fig. 2 b, 2 c, 2 d depicts the microstructure of a most sensitive CuO doped films (with $CuCl_2$ 1 ml, 5 ml, 10 ml) consisting of smaller spherical grains of Cu doped ZnO. The spherical grains may be due to large number of Cu – nucleation centers. The texture of sample S3 is seems to be relatively better than the pure ZnO sample S0. The sample S3 is expected to be more porous, giving larger effective area for the gas to react and in turn higher sensitivity may be expected. Image in Fig. 2b shows relatively larger spherical/elliptical shaped grains. Grain size is becoming more and more spherical, and numbers of grains are increasing with the increase of CuO percentage in the composition as evidenced from Fig. 2d. Atomic radius of Cu^{+2} is smaller than Zn^{+2}. Larger the number of Cu^{+2} ions, larger would be the nucleation centers. The feed would therefore, be divided and this would result into larger number of grains with smaller size and spherical shape.

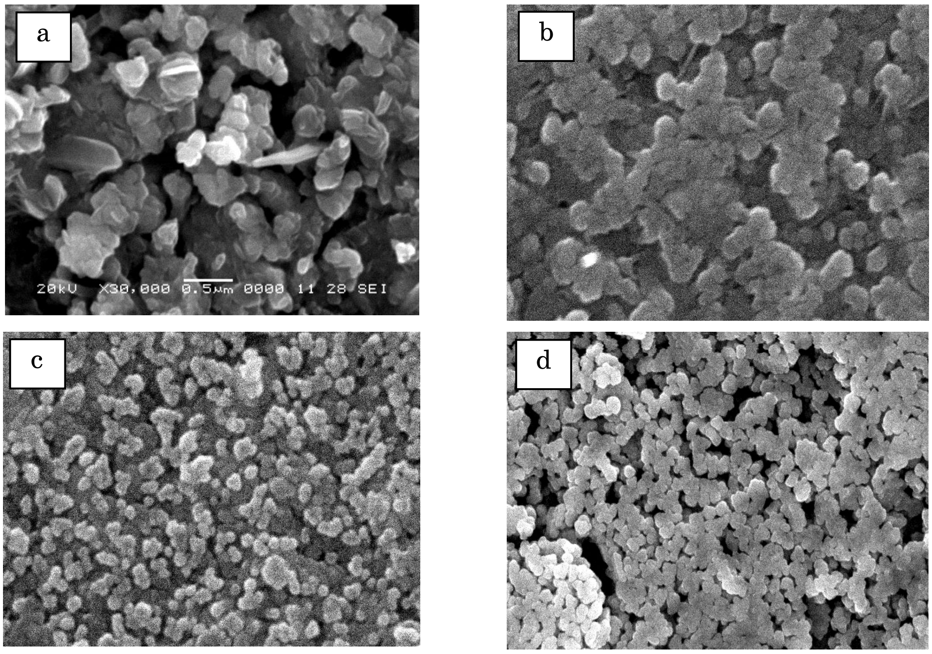


***Fig. 2** – SEM images: S0 (a), S1 (b), S2 (c), and S3 (d).*

4. GAS SENSING CHARACTERISTICS

Gas response, selectivity, response time and recovery time are the important characteristics in gas sensing. Gas response is defined as the ratio of change in conductance of a sample on exposure to a test gas to the conductance in air. The gas response can be written as

$$S = \frac{Ga - Gg}{Gg} = \frac{\Delta G}{Gg}$$

Where Gg and Ga are the conductance in the presence of test gas and in air respectively. Selectivity can be defined as the ability of a sensor to respond to a certain gas in the presence of other gases. Response time is defined as the time needed for a sensor to attain 80 % of maximum change in conductance upon the exposure to a test gas, while recovery time as the time taken by a sensor to get back 80 % of the original conductance in air [11].

4.1 Sensitivity of pure and CuO doped ZnO films to NH_3 gas

Fig. 3 depicts the variation of gas response with operating temperature of CuO doped ZnO thin film for LPG, H_2, CO_2, C_2H_5OH, NH_3, Cl_2 gases. It is clear from figure that the nature of gas responses is similar for all gases. The response of NH_3 gas goes on increasing with operating temperature, reaches to maximum at 400 °C and decreases with the further increase of operating temperature. CuO misfits would favour more oxygen ions to be adsorbed on the film surface. More the oxygen ions adsorbed, more electrons would be removed from the surface. This would make the film more resistive before exposure of NH_3 gas. On exposure of NH_3 gas, it would be oxidized and all the abstracted electrons would be returned back to material giving high conductivity. Smaller conductivity before exposure and larger conductivity after exposure of NH_3 gas would give higher gas response. The sensitivity of pure ZnO was observed to be smallest against the response of all the doped samples.

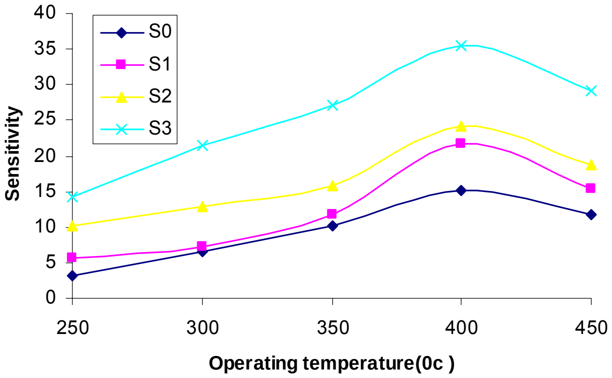


Fig. 3 *– Sensitivity of pure and CuO doped ZnO thin films to* NH_3 *as a function of temperature*

4.2 Selectivity for NH_3 against various gases at 400 °C

Fig. 4 depicts the selectivity of CuO doped sensor for NH_3 gas at 400 °C. It is clear from histogram that the sensitivity to NH_3 gas goes on increasing with the increase of CuO doping level in ZnO.

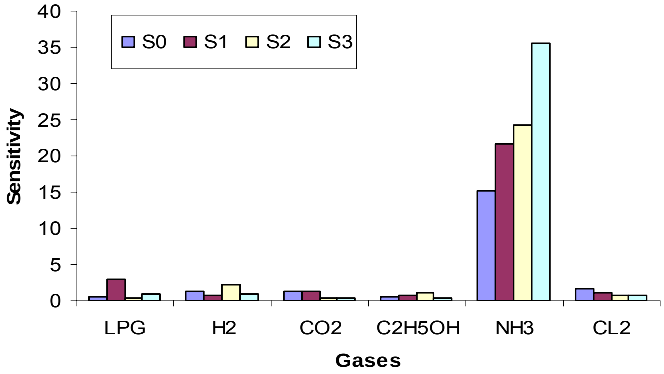


Fig. 4 *– Histogram comparing sensitivities of various gases at* 400 *°C*

5. DISCUSSION

The response to NH_3 gas would be attributed to adsorption – desorption mechanism. The ZnO is oxygen deficient. The excess zinc ions (due to oxygen vacancies) act as electron donors [13]. When reducing gas molecules like NH_3 reacts with negatively charged oxygen adsorbates , the trapped electrons are given back to conduction band of ZnO. The energy released during decomposition of adsorbed ammonia molecules would be sufficient for electrons to jump up into the conduction of zinc oxide, causing on increase in the conductivity of the sensor. An increase in operating temperature surely increases the thermal energy so as to stimulate the oxidation of NH3 given by possible reaction as,

$$2\,NH_3 + 3\,O_{ZnO} \rightarrow 3\,H_2O + N_2 + 3\,e^-$$

The reducing gas (NH_3) donates electrons to ZnO. Therefore the resistance decreases or the conductance increases. This is the reason why the gas response increases with operating temperature. The point at which the gas response reaches maximum is the actual thermal energy needed for the reaction to proceed. However the response decreases at higher operating temperatures, as the oxygen adsorbates are desorbed from the surface of the sensor [14]. In addition at high temperature the carrier concentration increases due to intrinsic thermal excitation and the Debye length decreases. This may be one of the reason for the decreased gas response at high temperature [15].

6. CONCLUSIONS

1) The pure and CuO doped ZnO thin films were successfully prepared by simple spray pyrolysis technique.
2) The average grain size was found to decrease from 190 to 90 nm, as the doping wt % of copper chloride in zinc nitrate solution goes on increasing.

3) Pure ZnO thin films are observed to be sensitive to NH_3 gas but showed poor sensitivity.
4) CuO doped ZnO sensors showed higher response to NH_3 gas as compare to pure ZnO.
5) The NH_3 response was goes on increasing with decrease in grain size.
6) Surface properties of the pure ZnO thin film could be conveniently customized (without affecting bulk properties) by doping technique.
7) The doping was observed to be an appropriate method to enhance sensitivity and selectivity to NH_3.

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