Synthesis and Characterisation of Cupric Oxide (CuO) Doped Tungsten Oxide (WO_3) Multilayer Thick Films[1]

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ABSTRACT

This paper is focused on preparation of cupric oxide doped tungsten oxide multilayer thick film by screen printing method on alumina substrates. XRD and SEM are used to study structural and morphological properties of CuO-WO_3. The XRD pattern of (CuO-WO_3) system samples show nanocrystalline form and found the desired peaks of composites. FESEM study reveals that the grain size of nanometer order and shows nano- porous structure, which leads to exhibit large surface area, stability and highest response to gas. In present study B5 sensor (25CuO:75WO_3) is found to optimized multilayer thick film.

Keywords: *Sol-Gel Method; (CuO-WO_3); multilayer thick films; XRD; FESEM*

INTRODUCTION

Due to interesting properties and promising applications Cupric oxide (CuO) nanostructures gain interest in many applications. Nanoparticles CuO and its composite oxides have potential applications as gas sensor. As compared to bulk materials, nanoparticles of Copper oxide (CuO) show high catalytic activity and selectivity due to their large surface to volume ratio. The sensitivity and response time of CuO based sensors strongly depend on the particle size of the material [1]. With introducing changes into the procedure of its chemical synthesis, physical and micro structural properties of metal oxide can be modified. Different nanostructures of CuO like nanowire, nanorod, nanoneedle, nano-flower and nanoparticles are synthesized by using various approaches such as; Sol-Gel Combustion Route [1], Microwave Assisted Co-Precipitation Method [2],Chemical Precipitation Method [3], Simple Precipitation Method [4], Sono-chemical Method [5-7] and etc.

WO_3 films are more attractive due to their high catalytic behavior on the surface of the film. The resistance of the WO_3 increases & decreases in the presence of oxidizing and reducing gases respectively. WO_3 can be obtained in various morphological forms such as nano-wires, nano-plates, nano-sheets, nano-flowers, nano-sphere and, sub-micron porous balls. The WO_3 nano-particles or nano-crystallites have been synthesized by various techniques given below; Acid Precipitation Method [8],Hydrothermal Method [9],Reverse Micro-Emulsion-Mediated Synthesis Method [10],Sol-Gel Method [11],Calcinations Method [12] and etc.

Yu Il et al. 2010 [13] studied for gas sensing properties of CuO doped and undoped WO_3 thick films. CuO doped and undoped WO_3 thick films gas sensors were prepared using screen-printing method on alumina substrates. A structural properties of WO_3:CuO thick films had monoclinic phase and triclinic phase of WO_3 together. Artur Rydosz et al. 2014 [14] investigated results on nanocrystalline CuO and WO_3 thin films by magnetron sputtering technology. XRD, GIR, SEM and AFM methods were used to study the films phase composition, microstructure and surface topography and found to be useful in portable gas sensor applications. Nirmal Kumar et al 2018[15] was used to deposit tungsten oxide (WO_3) thin films Cupric oxide (CuO) thin films were deposited by RF magnetron sputtering. FuchaoYang et al 2018 [16] worked on acetone odor detection. With the formation of the interfacial heterojunction, the WO_3@CuO

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shows the best sensing performance. Soo-Yeon Cho et al. 2019 [17] fabricated 10 nm scale p−n heterojunction nanochannel with ultrasmall grained WO_3/CuO nanopatterns to study ethanol sensing. WO_3/CuO nanopattern was also used to study for dynamic sensing behavior for various toxic analytes such as toluene , ethanol , acetone , and ammonia. In the present work of this paper focused on synthesis of pristine nano-particles of CuO, WO_3 and Al_2O_3, and also (CuO-WO_3) mixed oxide multilayer thick films.

EXPERIMENTAL

In the present work, we have used sol-gel method (which is under liquid phase synthesis) for the synthesis of pristine nano-particles of CuO, WO_3 and Al_2O_3 [18-20]. All the chemicals used in this study were of GR grade purchase from Sd-fine, India (purity 99.99%). The chemicals are used without any further purification.

Synthesis of Cupric Oxide (CuO)

In a cleaned round bottom flask, the aqueous solution of CuCl:6H_2O (0.2 M) was prepared. After addition of 1 ml of glacial acetic acid to above aqueous solution it was heated to 100°C with constant stirring. 8 M NaOH was added to above heated solution till its pH attains a value of 7. After this process immediately the color of the solution turned from blue to black and the large amount of black precipitate was obtained. The obtained precipitate was centrifuged and washed 3-4 times with de ionized water. The obtained powder was kept in vacuum oven at 70^0C for 24 hours so as to gets completely dried powder of CuO.

Synthesis of Tungsten Oxide (WO_3)

For Synthesis of WO_3 particles were simply precipitation method was used. Firstly, Sodium tungstate (Na_2WO_4) salt (6.59 gm) was dissolved in (200 ml) de-ionized water. Then in to the sodium tungstate solution 10 ml of hydrochloric acid (HCL) was added dropwise with continuous stirring. After the stirring for 5 hours of this mixed solution, the precipitates were allowed to settle for 1 day at room temperature. The precipitate was filtered using a filter paper. Then precipitate was washed many times by de-ionized water until pH reached to 7. The washed precipitate was dried at 100^0C in an oven for 1 hour and further the precipitates were passed from calcination processes in muffle furnace at 500^0 C for 4 hours to get WO_3 powder.

Synthesis of Alumina (Al_2O_3)

All chemicals used were analytical grade. Aluminium chloride, $AlCl_3$ (MOLYCHEM), 25% NH_3 solution (QUALIGEN Fine Chemicals) and polyvinyl alcohol (PVA) were used as raw materials for the synthesis of aluminium oxide nanoparticles. 1M alcoholic $AlCl_3$ solution was prepared, followed by addition of 25% ammonia solution. The resulting solution turned to a white sol. This was followed by the addition of PVA (0.5M). The solution was stirred continuously using a magnetic stirrer until it became a transparent sticky gel. The gel was allowed to mature for 24 hours at room temperature. The resultant gel was heat treated at 100°C for 24 hours which led to the formation of light weight porous materials due to the enormous gas evolution. The dried gel was, then calcined at 1000°C for 4 hours and finally, the calcined powders were crushed using mortar and pestle to get the fine homogeneous dense powder of Alumina (Al_2O_3).

Fabrication of Sensors

Three series of the samples prepared were CuO:WO_3 with Al_2O_3 base of multilayer sensors. The different combinations are shown in tables 1.

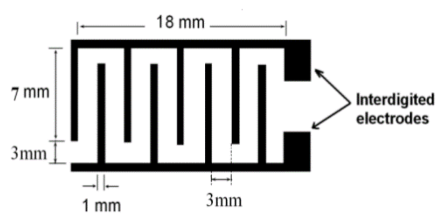
Table 1 Samples Codes of Series: CuO: WO_3/Al_2O_3/GP

Sample Code	Composition of CuO (mole %)	Composition of WO_3 (mole %)
B1	5	95
B2	10	90
B3	15	85
B4	20	80
B5	25	75
B6	30	70
PC	100	0
PW	0	100

Out of various methods of sensors preparation, the screen-printing (thick film technology) is most widely used. Screen-printing is the transfer of pastes though a fabric screen onto a substrate.

Multilayer preparation

Fig. 1 (a), and 1(b) show fabrication of interdigited electrodes, actual photographs of interdigited electrodes respectively.



(a)

(b)

Fig. 1 (a) Fabrication of interdigited Electrodes (b) Actual photograph of interdigited electrodes

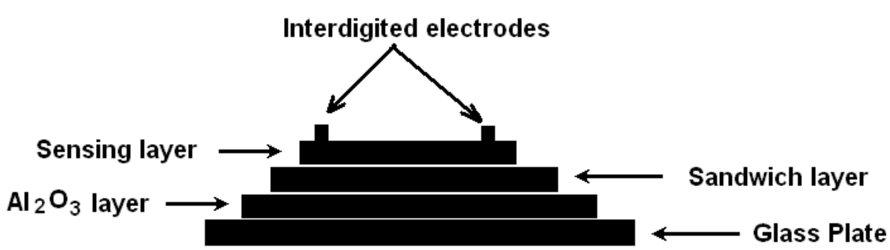


Fig.2 Design of multilayer Sensor

On clean glass plate, Al_2O_3 was deposited by using screen-printing technique and it was used as base of the sensor. On Al_2O_3, the sample layers were prepared. Finally on the top, Interdigited electrodes were fabricated [21] using conducting silver paste as shown in the Fig. 1(b). Design of multilayer sensor is shown in Fig. 2.

Preparation of Samples of Series: CuO: WO_3 / Al_2O_3/GP

The obtained product of fine nanopowder of CuO and WO_3 are used for fabrication of thick films sensors by using screen-printing technique. For this, the different X mole% CuO powder (X = 05, 10, 15, 20, 25, 30) was mixed thoroughly with different X mole% of WO_3 (X = 95, 90, 85, 80, 75, 70) along with Al_2O_3 base on glass plate (GP) substrate the aid of acetone by using the mortar and pestle. The sample codes, mole% of powder, and thickness are listed in the Table 2**.** The mixed powder of CuO : WO_3system was further calcinated at temperature 800°C for 5hrs. in the autocontrolled muffle furnace (*Gayatri Scientific, Mumbai, India.*) After, the calcinations again uniformly mixed the powder using the grinder.

Table 2 Thickness of Multi-layers for Series: CuO: WO_3 / Al_2O_3/GP Gas Sensors.

Sample Code	Composition	Thickness (x 10^{-4} cm)		
	Layers:----	Upper Layer(1)	Al_2O_3 Layer(2)	Total (1+2)
	Upper /Al_2O_3/Glass plate (GP)			
B1	05CuO:95 WO_3/ Al_2O_3/GP	4.1	29.3	33.4
B2	10CuO:90 WO_3/ Al_2O_3/GP	3.8	28.5	32.3
B3	15CuO:85 WO_3/ Al_2O_3/GP	2.6	29.7	32.3
B4	20CuO:80 WO_3/ Al_2O_3/GP	3.9	28.8	32.7
B5	25CuO:75 WO_3/ Al_2O_3/GP	4.9	28.1	33
B6	30CuO:70 WO_3/ Al_2O_3/GP	4.1	30.2	34.3

RESULTS AND DISCUSSION

XRD of CuO &WO_3 Nanomaterial and their dopings

The average crystallite size was calculated by Debye-Scherer's equation with the help of XRD patterns as shown in figure 3. The strong and sharp peak of CuO observed at 37° position with (1 1 1) indicates that the sample is having high crystalline quality, and it is in the structure of monoclinic with lattice parameters a = 0.4685 nm, b = 0.3532 nm, and c = 0.5121 nm, which is good agreement with JCPDS card number 88-2341. The average crystalline size was obtained 27 nm from Debye-Scherer's equation, $D = \frac{K\lambda}{\beta\cos\theta}$

Where, D = nanoparticles crystalline size, K = Scherrer constant (0.98), λ = wavelength and β denotes the full width at half maximum (FWHM).

As shown in figure 3. spectra, main peak, in case of pure WO_3, is observed at 23.21° and this peak corresponds to the plane (0 2 0) of WO_3 in monoclinic structure (JCPDS Card No.3-1124) with 100% intensity. The other peaks of WO_3 mainly correspond to the crystalline planes (0 2 2), (1 4 0), (2 2 2), (0 4 2), matching well with the monoclinic structure of WO_3. This manifested that the WO_3 is well crystallized. As compared with diffraction peaks of WO_3, those of CuO are wide and weak due to small grain sizes [22]. From table 3., it is seen that the sample 25CuO:75 WO_3 has small crystalline size.

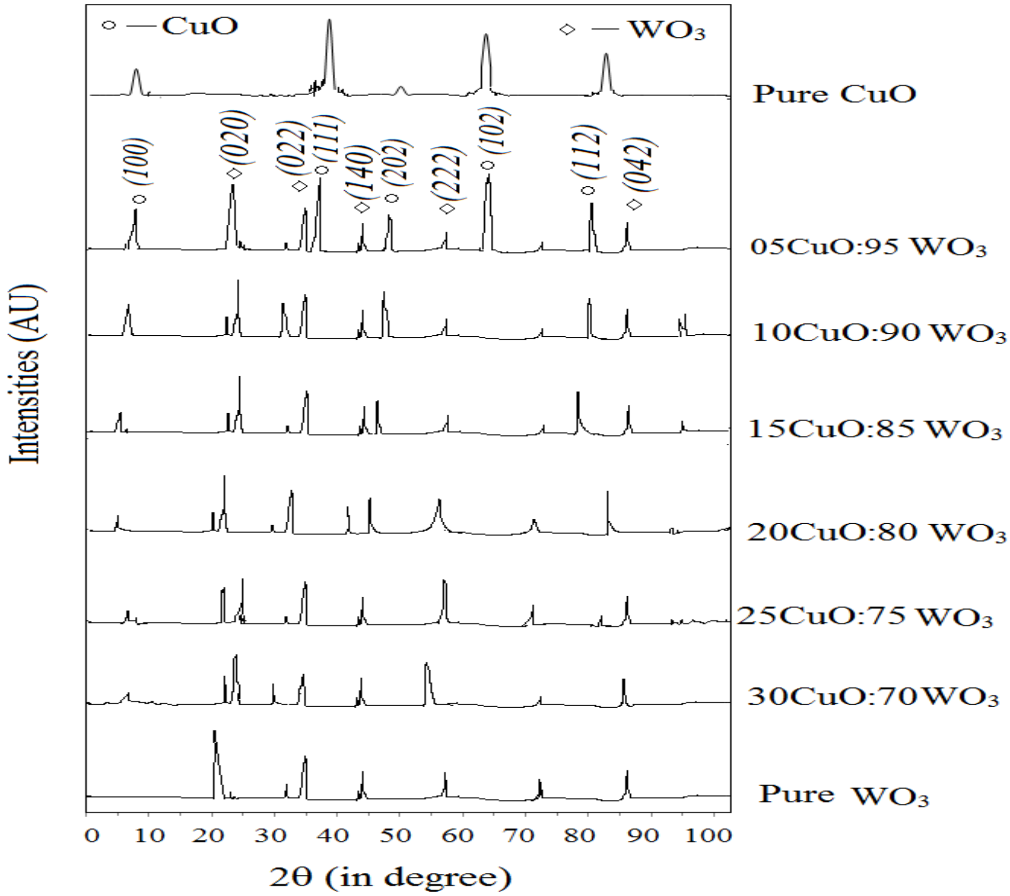


Fig.3. XRD spectra of Pure CuO, Pure WO_3 and CuO doped with WO_3 Nanomaterial

The crystallite size (D) of WO_3 and CuO doped WO_3 was calculated from Scherer's formula using FWHM and it is listed in the table 3, as below.

Table 3. Average crystallite size of WO_3 and CuO doped WO_3

Chemical Composition of CuO:WO_3 (mole %)	Maximum Intensity Peak Position (2θ) degree	FWHM (2θ) degree	Average Crystallite Size (D) in nm
05CuO:95 WO_3	28.34	0.2634	112.51
10CuO:90 WO_3	29.23	0.2112	126.67
15CuO:85 WO_3	30.65	0.2217	118.23
20CuO:80 WO_3	31.45	0.1934	109.83
25CuO:75 WO_3	**57.12**	**0.1732**	**87.72**
30CuO:70 WO_3	53.89	0.1994	105.45
Pure WO_3	23.04	0.3214	143.22

Scanning electron microscopy (SEM) Analysis

From SEM picture (figure 4 (a) to (c)), it is observed that all the samples viz. Al_2O_3, CuO, WO_3 are porous in nature. Porosity varies with sample to sample and among these material, SnO_2 showed more porosity (small size ~ 60 to 80 nm). Due to small pores size, its surface area is more [22-23] and it shows more sensing nature. Some portion of SEM picture shows some rods with fine voids over them which helps to increase sensing properties. The surface morphology of pure Al_2O_3 , CuO, and WO_3 , nano materials were studied by SEM and its picture is shown in the Fig. 4.

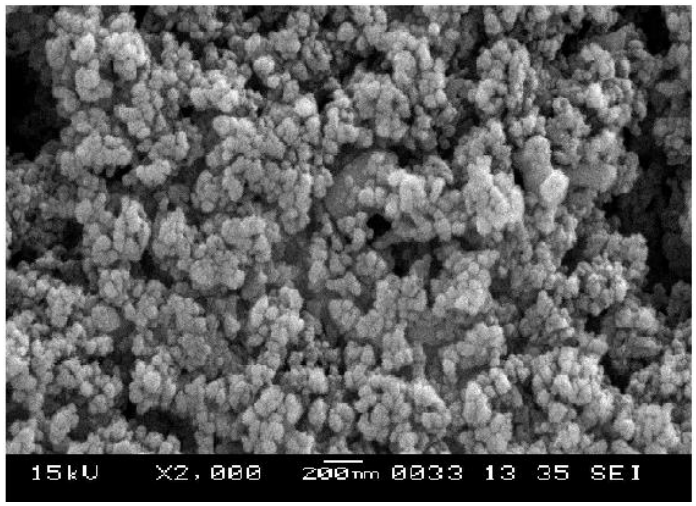


Fig. 4 (a) *SEM picture of Al_2O_3*

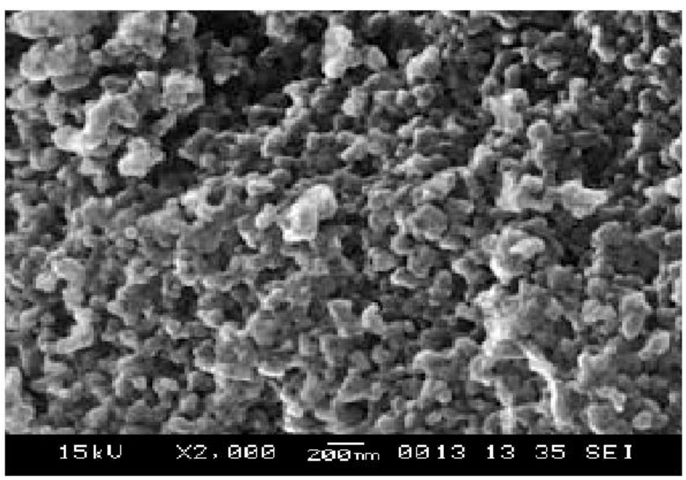


Fig. 4 (b) *SEM picture of CuO*

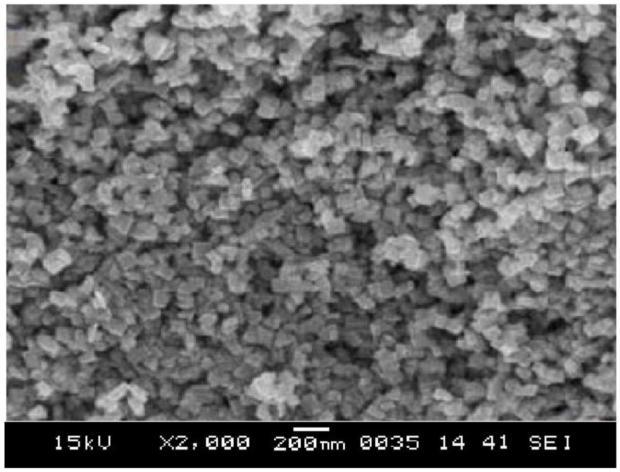


Fig. 4 (c) *SEM picture of WO_3*

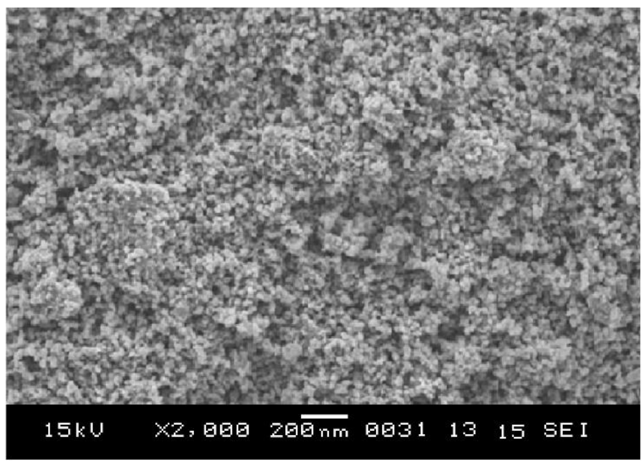


Fig. 4 (d) *SEM picture of 05CuO:95WO_3*

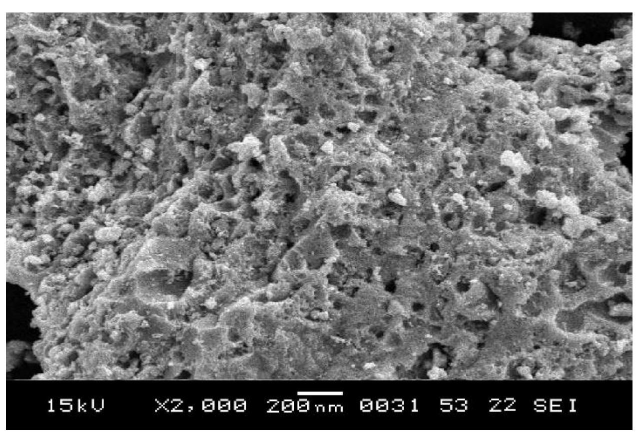


Fig. 4. (e) *SEM picture of 10CuO:90WO_3*

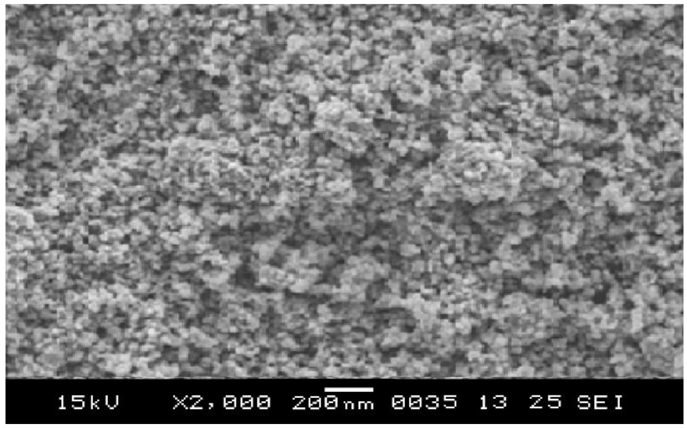


Fig. 4. (f) *SEM picture of 15CuO:85WO$_3$*

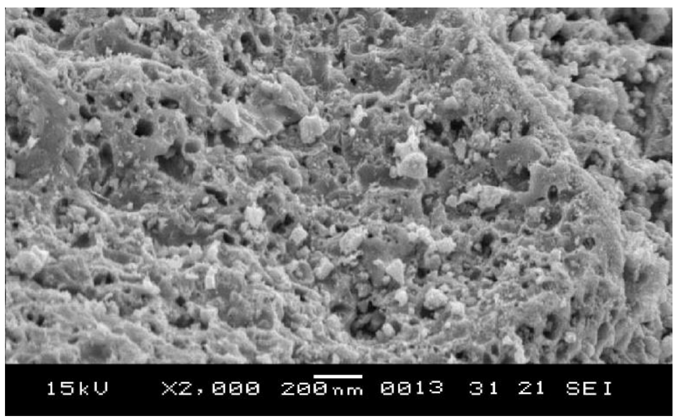


Fig. 4. (g) *SEM picture of 20CuO:80WO$_3$*

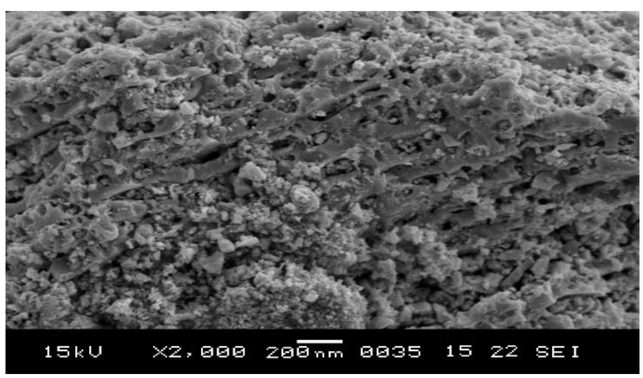


Fig. 4 (h) *SEM picture of 25CuO:75WO$_3$*

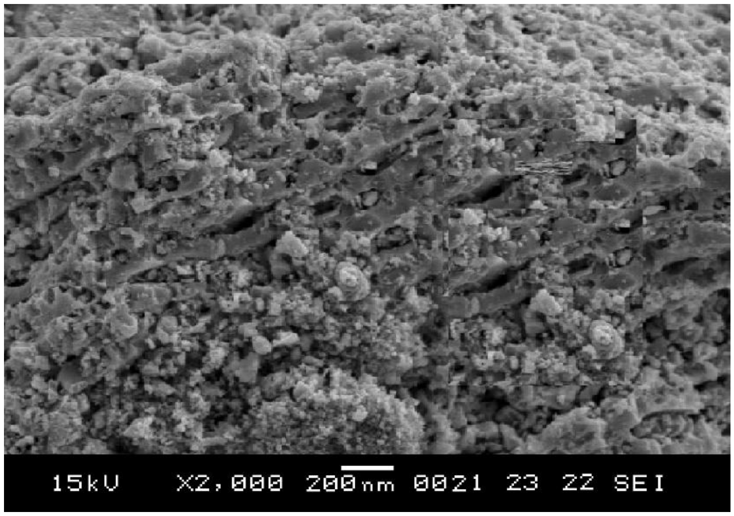


Fig. 4. (i) *SEM picture of 30CuO:70WO$_3$*

Fig. 4. SEM picture of Samples of Series CuO:WO$_3$

The surface morphologies of pure Al_2O_3, CuO, WO_3, and their dopings materials were studied by SEM and its picture are shown in the figures 4. As shown in the SEM pictures, some pores are in the form of rods, some are the form of circles and some are in conical shapes [24].

Table 4. shows the average diameter and number of pores per inch of pure Al_2O_3, CuO, WO_3 and their dopings.

Table 4. **Average diameter of pore and number of pores per inch of pure samples and their dopings.**

Sample Code	Pure sample and their dopings (mole %)	Average diameter of pore (nm)	Number of pores per inch (in x 2000 magnification)
PA	Al_2O_3	95	154
PC	CuO	80	172
PW	WO_3	98	145
B1	05CuO:95WO$_3$	73	155
B2	10CuO:90WO$_3$	82	143
B3	15CuO:85WO$_3$	79	158
B4	20CuO:80WO$_3$	83	138
B5	**25CuO:75WO$_3$**	**52**	**218**
B6	30CuO:70WO$_3$	71	177

From the SEM pictures (table 4), it is observed that, Sample Code B5 i.e. (**25CuO:75WO$_3$)**, have more pores per inch (calculated for x 2,000 magnification for each composition) than other sensors. Thus, these sensors have more active surface areas and exhibit more sensing nature [24-25]. It is also found that average diameter of pore in case of Sample Code B5 i.e. (**25CuO:75WO$_3$)** are small as compared to other doping. This also tends to exhibit large surface area and exhibited high response of the samples.

CONCLUSIONS

The XRD pattern of (CuO-WO_3) system samples show nanocrystalline form and found the desired peaks of composites. FESEM study reveals that the grain size of nanometer order and shows nano-porous structure, which leads to exhibit large surface area, stability and highest response. Therefore the B5 sensor (**25CuO:75WO_3)** is found to optimized multilayer thick film sensor.

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