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Sol-Gel Synthesis and Characterization of SnO_2- PPy Multilayer Thick Films[1]

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ABSTRACT

The aim of this study is focused on preparation of tin oxide doped with polyporrole multilayer thick film by using base as a alumina substrates. The structural and morphological properties reported, XRD patterns show nanocrystalline form with desired peaks of composites and SEM 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 and found (92SnO_2:8 PPy) sensor multilayer thick film as optimised sensors

Keywords: *Tin oxide; polyporrole; multilayer thick films; XRD; SEM*

INTRODUCTION

Tin oxide (SnO_2) is the most used sensing material in commercially sensor devices for toxic gases detection [1]. It is well known that the sensing properties of SnO_2-based material depend on its chemical and physical characteristics, which are strongly dependent on the preparation conditions, dopant and grain size. This implies that the synthesis of the sensing material is a key step in the preparation of high-performance MOS gas sensors. SnO_2 powders and films can be prepared by a variety of synthesis methods [2-5]. This paper focused on synthesis of pristine nano-particles of SnO_2, ppy and Al_2O_3 and also (SnO_2- ppy) multilayer thick films with Al_2O_3, as base material.

EXPERIMENTAL: PREPARATION OF MATERIALS

The methods of synthesis of nano-particles can be broadly classified in the three categories namely, liquid phase synthesis, gas-phase synthesis and vapour-phase synthesis . In the present work, we have used sol-gel method for the synthesis of pristine nano-particles of SnO_2, Al_2O_3 and PPy [6].

Preparation of Tin Oxide (SnO_2)

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. Stannous chloride dehydrates ($SnCl_2.2H_2O$), Ammonia solution and deionized water were used during reaction. The conducting silver paint (Sigma Aldrich Chemical, USA) is used to form electrodes.

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In preparation of SnO_2, 2g (0.1 M) of stannous chloride dehydrate ($SnCl_2.2H_2O$) is dissolved in 100 ml water. After complete dissolution, about 4 ml ammonia solution is added to above aqueous solution with magnetic stirring. Stirring is continued for 20 minutes. White gel precipitate is immediately formed. It is allowed to settle for 12 hrs. Then it is filtered and washed with water 2-3 times by using deionized water. The obtain precipitate were mixed with 0.27 g carbon black powder (charcoal activated). The obtained mixer is kept in vacuum oven at 70 ºC for 24 hours so that the mixer gets completely in to dried powder. Then this dry product was crushed into a find powder by grinder. Now obtained product of fine nanopowder of SnO_2 was calcinated at 700^0C up to 6 hours in the auto controlled muffle furnace (GAYATRI Scientific, Mumbai, India.) so that the impurities from product will be completely removed.

Preparation of Polypyrrole (PPy)

The method used for the preparation of polypyrrole is chemical polymerization. Powder polypyrrole was prepared with 4.290 (high) weight ratio of pyrrole (Py) monomer/oxidant ($FeCl_3$). During the synthesis, concentration of $FeCl_3$ was kept constant and methanol was used as a solvent.

The Py monomer, anhydrous iron (III) chloride ($FeCl_3$) and methanol were used as received for synthesis of PPy. The solution of 7 ml methanol and 1.892 g $FeCl_3$ was first prepared in round bottom flask. Then 8.4 ml Py monomer was added to ($FeCl_3$ + methanol) solution with constant stirring in absence of light. The amount of Py monomer added to the solution (1/2.33 times of $FeCl_3$) was in such a way to get maximum yield [7].

The polymerization of Py, which was suppressed in a solution, progressed rapidly due to an increase of oxidation potential caused by evaporation of solvent. In the polymerization reaction of Py, it was observed that as soon as the Py monomer was added to the solution, the colour changed to dark green/black. There was an increase in temperature of the solution during the start of reaction, which showed that it is an exothermic reaction [8]. The reaction was carried out at room temperature for 4 hrs. The final precipitated polymer was filtered by a conventional method. The polymer was washed with distilled water several times till the filtrate obtained was colourless. To remove last traces of un-reacted pyrrole and remaining ferric and ferrous chloride formed due to polymerization, it was then washed with methanol.

The polymer, obtained in powder form was dried first at room temperature for a few hours and then finally dried in an oven kept at 80^0C for 5-6 hrs. This polypyrrole is then used for active layers of Semiconductor Gas Sensors.

Preparation of Alumina (Al_2O_3)

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.

Fabrication of Sensors

Three series of the samples prepared were SnO_2: PPy with Al_2O_3 base of multilayer sensors. The different combinations are shown in tables 1.

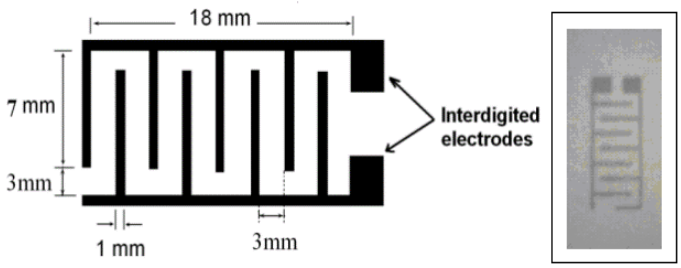
Table 1 Samples codes of series : SnO_2: PPy

Sr. No.	Sample codes	SnO_2 (mole %)	PPy (mole %)
1	F1	100	00
2	F2	98	02
3	F3	96	04
4	F4	94	06
5	F5	92	08
6	F6	90	10

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

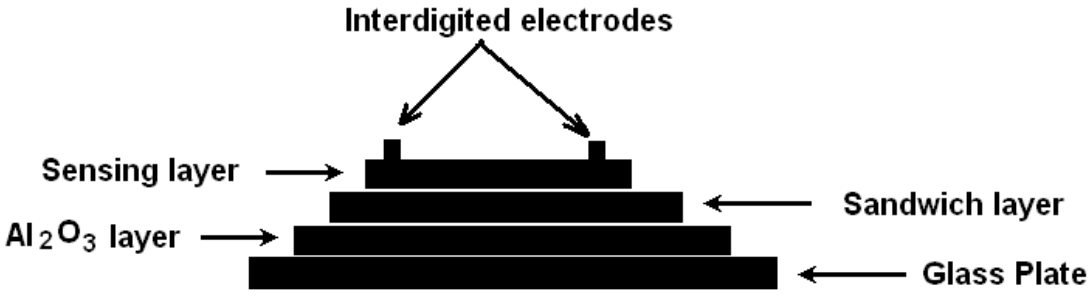


Fig.2 Design of multilayer Sensor

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 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 SnO_2: PPy/Al_2O_3/GP

The obtained product of fine nano-powder of SnO_2 and PPy are used for fabrication of thick films sensors by using screen-printing technique. For this, the SnO_2 powder was mixed thoroughly with different X mole% of PPy (X = 2, 4, 6, 8,10) 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 SnO_2:PPy system was further calcinated at temperature 800°C for 5hrs. in the auto controlled muffle furnace (Gayatri Scientific, Mumbai, India.) After, the calcinations again uniformly mixed the powder using the grinder

Table 2: Length, Width and Thickness of Multi-layers in SnO_2: PPy/Al_2O_3/GP gas sensor

Sample Code	Doping mole % Layers: Upper/ /Al_2O_3/ Glass plate (GP)	Upper layer length (cm)	Upper layer width (cm)	Thickness (x 10-4 cm)		
				Upper Layer (1)	Al_2O_3Layer (2)	Total (1+2)
F1	SnO_2/ Al_2O_3/GP	3	1.5	5.1	26.4	31.5
F2	98 SnO_2:2 PPy/ Al_2O_3/GP	3	1.5	3.1	34.2	37.3
F3	96 SnO_2:4 PPy/ Al_2O_3/GP	3	1.5	2.8	35.1	37.9
F4	94 SnO_2:6 PPy/ Al_2O_3/GP	3	1.5	3.4	32.6	36.0
F5	92 SnO_2:8 PPy/ Al_2O_3/GP	3	1.5	3.0	35.5	38.5
F6	90 SnO_2:10 PPy/ Al_2O_3/GP	3	1.5	3.6	32.3	35.9
F7	PPy/ Al_2O_3/GP	3	1.5	1.9	48.4	50.3

RESULTS AND DISCUSSION

X-Ray diffraction pattern of polypyrrole [9] showed that, it is amorphous in nature. In Fig. 3 XRD pattern of polypyrrole was recorded in terms of 2θ in the range 5 to 100^0. As shown in XRD pattern broad peak occurs at 29^0 and it is characteristics of amorphous nature of polypyrrole. The broad peak occurs due to the scattering of X-rays from polymer chains at the interplaner spacing. The position of maximum intensity of amorphous halos depends on monomer to oxidant ratio. The average crystallite size of polypyrrole is about 119 nm. Abroad peak is observed at about $2\theta = 29.36$ which is characteristics peak of amorphous PPy. However, the peak obtained at 29 degree matches with the value of (3.040 A^0) $FeCl_3$. The average green size determines from XRD pattern using Scherrer formula of these material is about 119 nm for PPy.

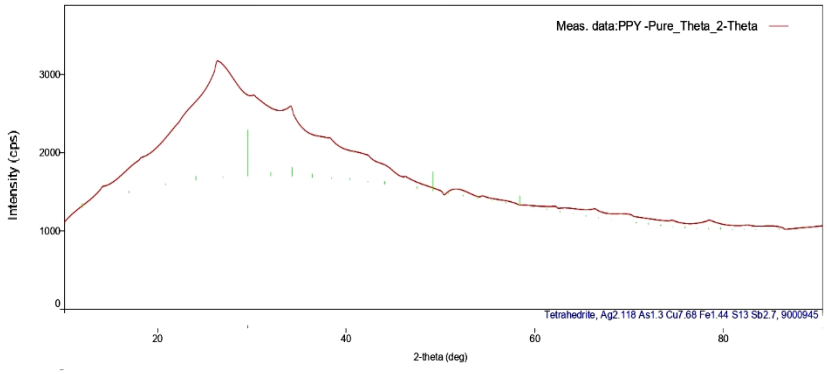


Fig. 3 XRD of Spectra of Polypyrrole

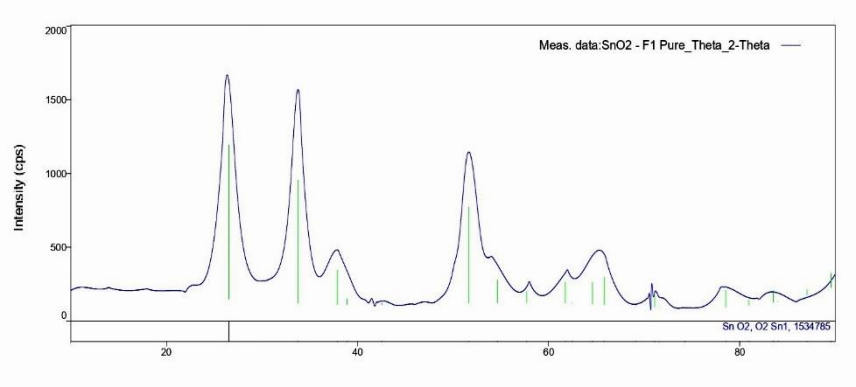


Fig. 4 XRD Pattern of SnO_2

Figure 4 shows the X-ray diffraction pattern of pure SnO_2, calcinated at 800^0C for 4-5 hours. It is recorded in terms of 2θ in the 10 to 100 ^{0}.

In case of pure SnO_2 a main pic is observed at 26.54^0. This peak corresponding to the plane (110) of SnO_2 in tetragonal structure (JCPDS card No.1534785) with 100% intensity. The other Peak of SnO_2 mainly correspondent to the planes (101), (200), (211), (220), (310), (301) and (321).

These planes correspond to the cassiterite phase of SnO_2. Tin (IV) dioxide (II) i.e. SnO_2 has only one stable phase the so called cassiterite (mineral form) or rutile (material structure). It crystalizes in the tetragonal rutile structure with space group D^{14}_{4h} (P_{42}/mnm), which correspondence to the number 136 in the standard listening with cell parameter a=b=4.7456 A0, C=3.1930 A0 and $\alpha = \beta = \gamma = 90^0$ with c/a ratio of 0.6728.

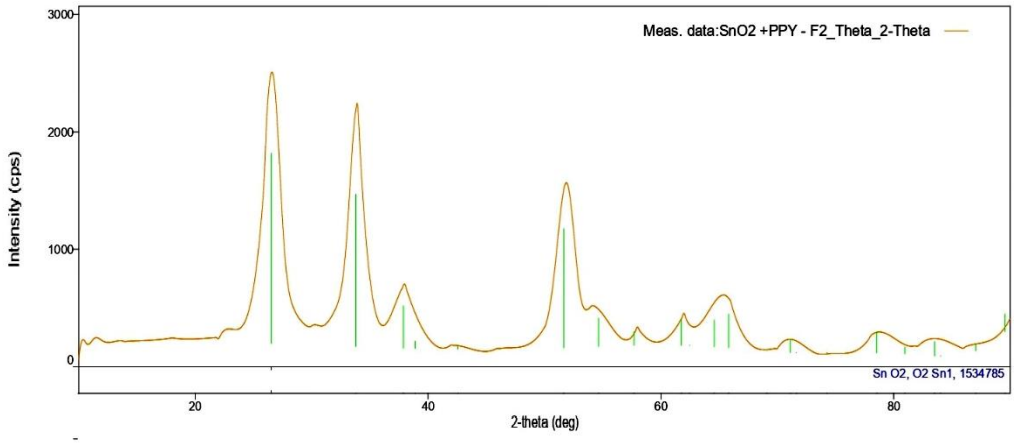


Fig. 5 XRD Pattern of $98SnO_2$:2PPy

Fig. 5. shows that the X-ray diffraction pattern of $98SnO_2$:2PPy calcinated at 800ºC for 4 to 5 hours. It is recorded in terms of 2θ in the range of 10 to 100 degree. It is observed as the doping of PPy increases, the intensity of corresponding peak increases. This peak correspondence to the plane of $96SnO_2$:4PPy (JCPDS Card no.1534785 with 100% intensity. The other peaks of $98SnO_2$:2PPy correspondence to the plane (101), (200), (211), (220), (310), (301), (321).

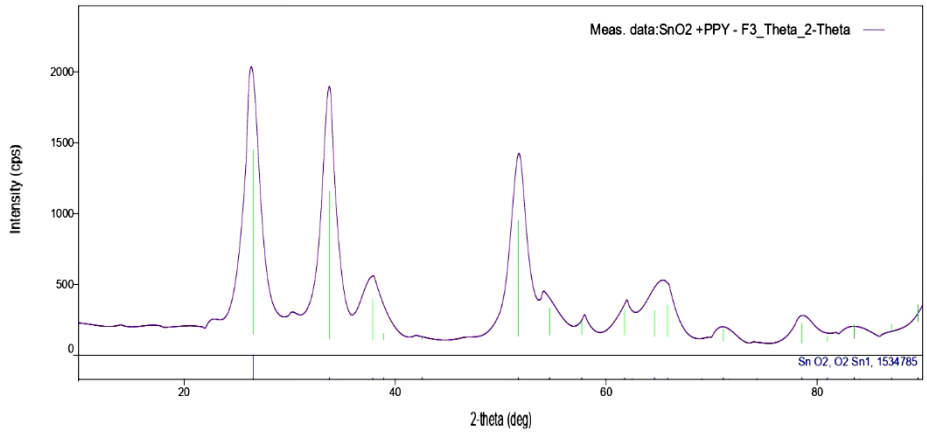


Fig. 6 XRD Pattern of $96SnO_2$:4PPy

As shown in above spectra fig.6. $96SnO_2$:4PPy main peak in case of pure SnO_2 is observe at 26.54 degree and his correspondence to the plane (110) of SnO_2 in tetragonal structure(JCPDS Card no.1534785) with 100% intensity the other pic of SnO_2 mainly correspondence to the plane (101), (200), (111) and (301).

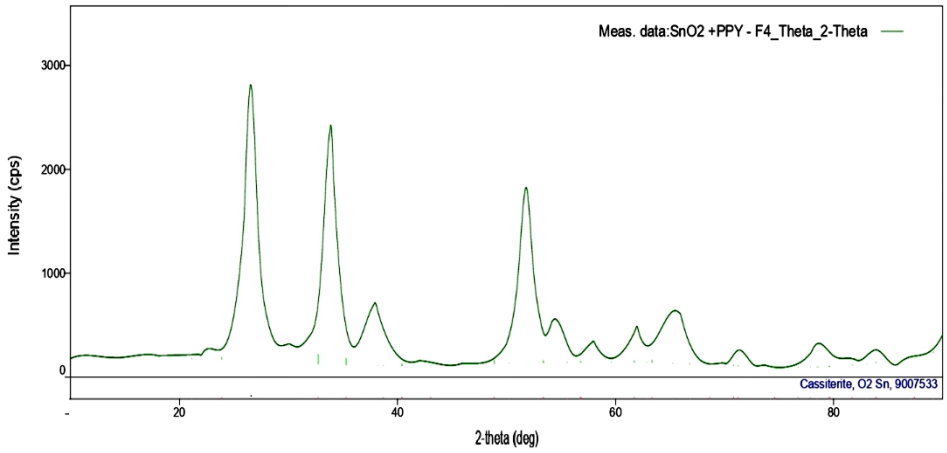


Fig. 7. XRD Pattern of $94SnO_2$:6PPy

As shown in above fig.7. $94SnO_2$:6PPy main peak [10], in case of pure SnO_2, is observed at 26.58 and this peak corresponds to the plane(110) of SnO_2 in tetragonal structure(JCPDS Card no.9007533) with 100% intensity the other peaks of SnO_2 mainly corresponds to the Planes (101), (200), (111), (211) and (301). These planes corresponds to the cassiterite phase of SnO_2.SnO_2 has only one stable phase, the so called (mineral form) or rutile (material structure) JCPDS Card no.9007533. It crystallizes in the tetragonal rutile structure with space group which corresponds to the number 136 in the standard listing with cell parameter a = b = 4.7380A, c = 3.1865A and $\gamma = \beta = \gamma = 90$ degree with c/a ratio of 0.6725.

From table 3. it is observed that average crystallite size of $94SnO_2$:6PPy doping is list as compared to the other compositions and pure materials and hence $94SnO_2$:6PPy compositions has large active surface area for sensing the gas.

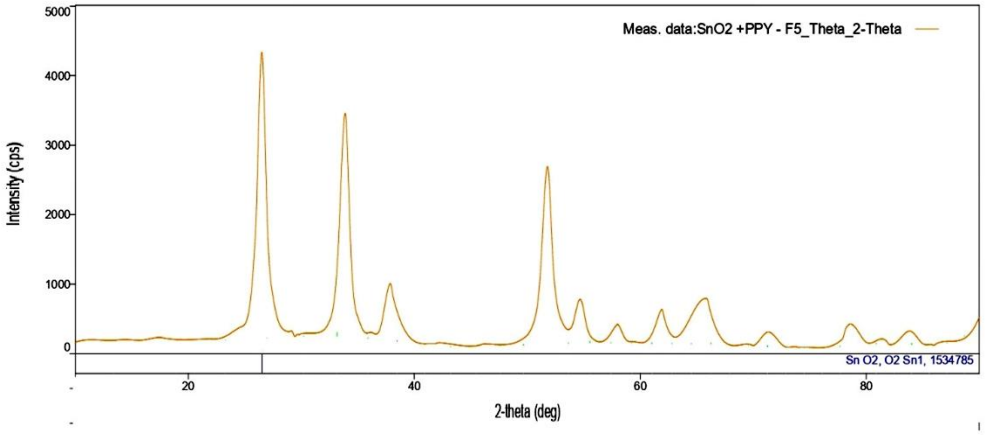


Fig. 8. XRD Pattern of $92SnO_2$:8PPy

Fig 8. $92SnO_2$:8PPy XRD spectra of doping of SnO_2:PPy, incase of pure SnO_2 is observed at 26.54 degree and this peak corresponds to the plane (110) of SnO_2 and PPy in bixbyite phase (JCPDS Card No. 1011264) with 2θ=33.16, d-value is 2.699 with 100% intensity peak of SnO_2 and PPy mainly correspond to the Planes (220), (310) and (301).

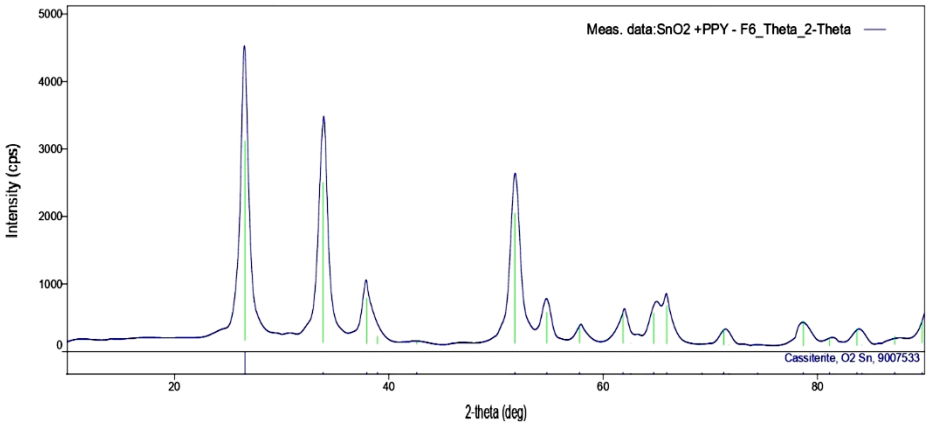


Fig. 9. XRD Pattern of $90SnO_2$:10PPy

Fig. 9. as shown in above spectra of doping of SnO_2 and PPy main peak is observed at 26.58^0 and this corresponds to the plane (110) of SnO_2 in tetragonal structure (JCPDS Caed No. 9007533) with 100% intensity. The other peak of SnO_2 and PPy Mainly correspondec to the planes (110), (101), (112) and (301). These planes correspondence to the casseterities phase of SnO_2 (JCPDS Card No. 9007533). In fig 9. it is observed that XRD pattern contains 8-10 peaks. These are prominent peak of SnO_2. The (hkl) values are obtained by using 2θ and d- values from XRD pattern.

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

Table 3. Average crystallite size of SnO_2, PPy and their compositions

Sr. No.	Chemical Composition of SnO_2:TiO_2 (mole %)	Maximum Intensity Peak Position (2θ) in degree	FWHM (2θ) degree	Average Crystallite Size (D) in nm
01	Pure SnO_2	26.5414	0.1338	120.68
02	98SnO_2:2PPy/Al_2O_3/GP	26.6424	0.2165	102.62
03	96SnO_2:4 PPy/Al_2O_3/GP	26.7123	0.2168	103.68
04	94SnO_2:6 PPy/Al_2O_3/GP	26.6821	0.2178	105.24
05	92SnO_2:8 PPy/Al_2O_3/GP	26.6531	0.2175	98.23
06	90SnO_2:10PPy/Al_2O_3/GP	26.7512	0.2040	110.58
07	Pure PPy	27.8710	0.1991	146.09

SEM Analysis

The surface morphology of polypyrrole [11-13] material was studied by SEM and its picture is shown in the Fig. 10.

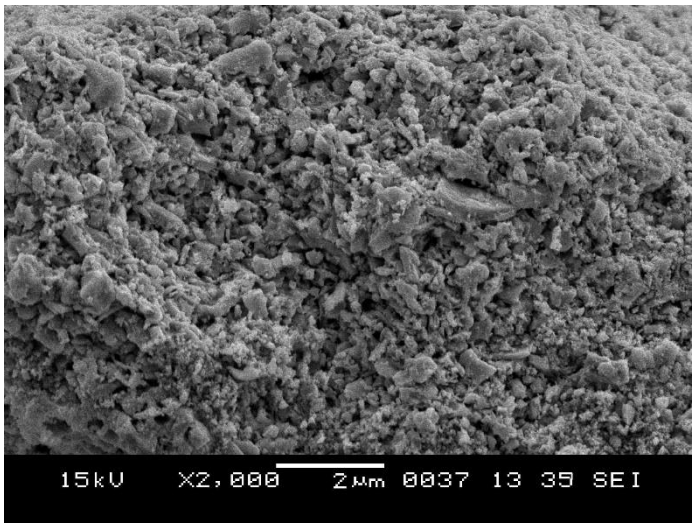


Fig. 10. SEM picture of polypyrrole

From SEM picture, it is observed that PPy is porous in nature and pore size varies from ~ 0.5 to 3 µm. Due to small pores size, its surface area is more 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.

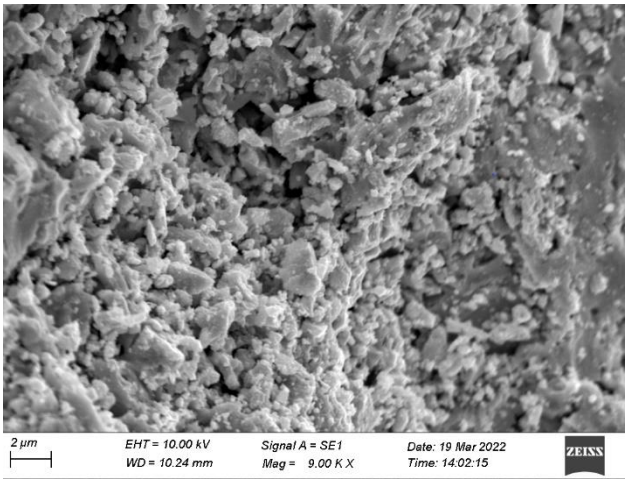
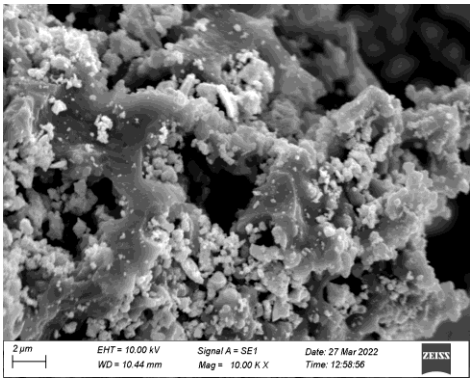
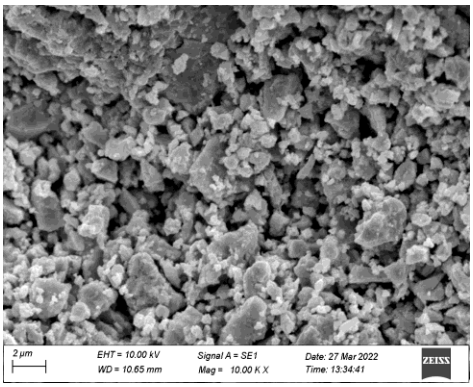


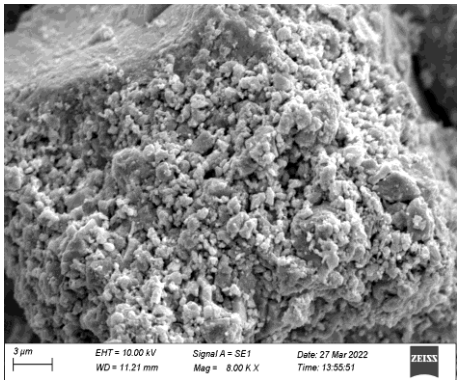
Fig. 11. SEM picture of Pure SnO_2



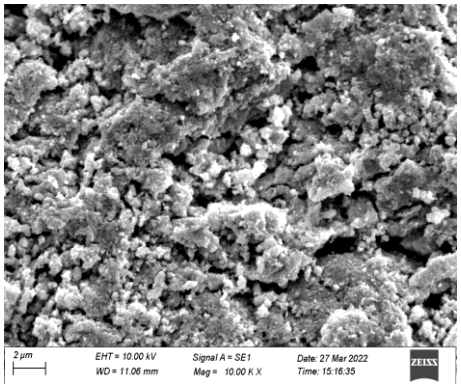
(a) SEM Picture of $98SnO_2$:2PPy



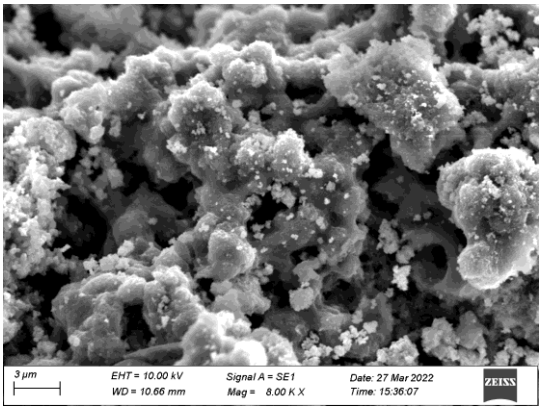
(b) SEM Picture of $96SnO_2$:4PPy



(c) SEM Picture of $94SnO_2$:6PPy



(d) SEM Picture of $92SnO_2$:8PPy



(e) SEM Picture of $90SnO_2$:10PPy

Fig. 12. SEM Picture of SnO_2:PPy Series

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

Serial No.	Pure sample and their dopings (mole %)	Codes	Average diameter of pore (nm)	No. of pores per inch
1	Pure SnO_2	F1	335	93
2	$98SnO_2$:2 PPy/ Al_2O_3/GP	F2	387	83
3	$96SnO_2$:4 PPy/ Al_2O_3/GP	F3	310	112
4	$94SnO_2$:6 PPy/ Al_2O_3/GP	F4	289	134
5	$92SnO_2$:8 PPy/ Al_2O_3/GP	F5	215	154
6	$90SnO_2$:10 PPy/ Al_2O_3/GP	F6	323	95

From table 4 the SEM pictures showed that $92SnO_2$:8PPy, compositions have more pores per inch than other compositions. Thus these three compositions have more active surface areas and exhibit more sensing nature. It is also found that average diameter of pore in case of $92SnO_2$:8PPy compositions are small as compared to other compositions. This also tends to exhibit large surface area and exhibited high response of the samples [14,15].

CONCLUSIONS

All samples show nanocrystalline form and found the desired peaks of composites and also the grain size of nano-meter order and shows nano-porous structure, which leads to exhibit large surface area, stability and highest response particularly from this study ($92SnO_2$:8 PPy) sensor was found to optimized for gas sensing applications.

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