Synthesis and Characterization of Pure and Indium doped SnO_2 nanoparticles By Sol-Gel Methods

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Abstract
We report simple methods to synthesize Pure Tin oxide nanostructures and Indium doped Tin oxide Nanostructures without using catalysis with less complicity. Nanosized SnO2 particles have been synthesized by a simple sol-gel method. The obtained tin oxide powder has been characterized using X-ray powder diffraction, scanning electron microscope, and DC conductivity studied. The result shows that there is the formation rutile type (tetragonal) structure in nanometric range**.** This was done by adding $SnCl_4.2H_2O$ in Ethanol and adding of HCl and NH_4OH at appropriate ratio and formed nano powder is annealed for 300°C for 2h. We also synthesized the In/SnO_2 Nanostructures by Sol-Gel method by adding 0.11 atomic % and 0.24 atomic% of Indium to SnO_2. The obtained powder is annealed at 300°C for 2h. In $(NO_3)_3$ is added to $SnCl_4.2H_2O$ to get indium doped tin oxide nanostructures. These nanocomposites are characterized by XRD, SEM, EDX and DC Conductivity was studied in the temperature range 25°C to 150°C and it was observed that conductivity of SnO_2 is increased by adding Indium dopant.

Keywords:
SnO_2, optical band gap, sol-gel, XRD, SEM, EDX, DC-Conductivity.

1. INTRODUCTION:

Materials of nanostructure have received much attention of research because of their novel properties, which differ from those of bulk materials. SnO_2 is one of the few dominant nanomaterials for nanotechnology and tin oxide belongs probably to the biggest group of one dimensional nanostructures. Tin oxide (SnO_2) has a wide direct band gap (3.6 eV) and a relative large excitation binding energy compared to thermal energy. A wide band gap has many benefits like enabling high temperature and power operations, reducing electronic noise, making sustenance in large electric fields possible and raising breakdown voltages. By proper alloying with indium or cobalt, the band gap can be tuned in the range of 3-4 eV.

Tin oxide (SnO_2) Nanoparticles are available in the form of faceted high surface area diamagnetic oxide nanostructures. Tin belongs to Block P, Period 5 and Oxygen belongs to the Block P, Period 2 in the Periodic table. SnO_2 exhibits the most splendid and abundant configurations of nanostructures that one material can form. Owing to its unique properties and potential application in solar cell, electro and photo-luminescence devices, chemical sensors and so on, SnO_2 becomes an attractive inorganic material. SnO_2 with hierarchical structure has fundamental importance to understand the growth habit of SnO_2 crystal; moreover, considering their high surface to volume ratio, they are of great physical or chemical activities in gas-sensor and photo-catalysis. Tin oxide (SnO_2) received much attention because of its unique piezoelectric properties made suitable for surface acoustic wave devices, optical fibers and up to electronic devices. Due to the high optical band gap, SnO_2 films have been used as window layers in copper indium diselenide based hetero junction solar cells to enhance the short circuit current. Another important advantage of SnO_2 is its chemical stability in the presence of hydrogen plasma which enable for use in the amorphous silicon solar cell fabrication by plasma enhanced chemical vapor deposition.

The study of one-dimensional nanostructure SnO_2 has attracted much interest owing to its low cost; it's unique electrical, optoelectronic, and luminescent properties; and its many potential applications in devices, such as solar cells, luminescent devices, and chemical detectors.

SnO_2 nanostructures have many potential applications in various fields. SnO_2 is used in solar cells, gas sensors and spintronics etc. Depending on SnO_2 nanostructure and shape there many applications. Magnetic properties of tin oxide nanoparticles are used in magnetic data storage and magnetic resonance imaging, as catalysts energy-saving coatings and anti-static coatings, as electrodes anti-reflection coatings in solar cells, in the making of gas sensors, optoelectronic devices and resistors and in the making of liquid crystal displays.

The shape of the nanostructure depends on synthesis parameters. The various shapes of SnO_2 nanostructures are nanorings, nanobelts, nanotapes, nanorods, nanowires, etc. Among these nanorods are used for gas sensing applications. There are many methods to synthesize SnO_2 nanostructures such as chemical vapor deposition, physical vapor deposition and molecular beam epitaxy,Precipitation, hydrothermal, sol-gel and spray pyrolysis. SnO_2 nanowires have been synthesized simply by heating tin oxide powders containing catalyst nanoparticles , optically pumped nanowires . The vapor–liquid–solid (VLS) mechanism is responsible for the nano-wire growth, in which a metal or an oxide catalyst is necessary to dissolve feeding source atoms in a molten state initiating the growth of nano-materials. However, sol-gel process offers several advantages over other methods, better homogeneity, controlled stiochiometry, high purity, phase pure powders at a low temperature. We use Sol-Gel technique to synthesize the SnO_2 nanostructures and In/SnO_2 nanostructures. In a sol-gel process the precursor solution is transformed into an inorganic solid by dispersion of colloidal particles in a liquid (sol) and (b) conversion of sol into rigid phase (gel) by hydrolysis and condensation reactions for various applications,

Nanosized particle or large specific surface area is essential to high performance. Among different synthesis methods for preparation of tin oxide, a sol gel method offers several advantages over other methods. As well as this method lowers the processing temperature, better homogeneity, controlled stoichiometry, and flexibility offorming dense monoliths, thin films, or nanoparticles.In this paper we presented the formation and properties ofnanosized SnO2 particles using sol-gel route. Special attention has been made to prepare the particles in the nanometric range.The complete morphology has been analyzed by SEM and EDAX.The process sol-gel method involves the use of tin tetra tetrachloride dihydrate (SnCl4.2H2O) and Ammonia water (NH4OH). The solution of tin chloride is prepared by dissolving a granule of SnCl4.5H2O in Ethanol and after some moment HCl is added and finally NH4OH is gradually added to the prepared solution of tin chloride with Continuous stirring. After some moment white precipitate of tin Hydroxide [Sn(OH)4] appears in the form of reaction product is Given below:

$$SnCl_4+4NH_4OH \rightarrow Sn(OH)_4+4NH_4Cl$$

In this reaction, excess ammonia is added to convert all tin chloride into tin hydroxide. Now, the precipitate is filtered and dried in an oven at about 200°C for 1 hr. The product obtained is tin hydroxide which is annealed at 300°C for three hours to get the tin oxide particles. The chemical reaction for the same is given below:

$$Sn(OH)_4 \rightarrow SnO_2+2H_2O$$

Indium doped Tin oxide particles are prepared by adding $In(NO_3)_3$ Solution to above solution.

2. EXPRIMENTAL:

In our experiment tin oxide nanostructure is synthesize by sol-gel techniques. Apart for synthesize of SnO_2 nanostructures we also synthesize the indium doped tin oxide nanostructures by sol-gel method.

2.1. Synthesis of SnO_2 Nanostructure by sol-gel method:

The process sol-gel method involves in synthesis of SnO_2 nanostructures.In this 4.45126gm of tin tetra tetrachloride dihydrate (SnCl4.2H2O) is dissolved in 75ml of ethanol which is taken in to beaker. The solution is placed for continuous stirring at 70°C for 1hour. After some moment 2ml of HCl is added and finally 3ml of NH4OH is gradually added to the prepared solution with continuous stirring to form white precipitate of tin Hydroxide [Sn(OH)4] appears in the form of reaction product is Given below:

$$SnCl_4 + 4NH_4OH \rightarrow Sn(OH)_4 + 4NH_4Cl$$

Now, the precipitate is filtered and dried in an oven at about 200°C for 1 hr. The product obtained is tin hydroxide which is annealed at 300°C for three hours to get the tin oxide particles. The chemical reaction for the same is given below:

$$Sn(OH)_4 \rightarrow SnO_2 + 2H_2O$$

This nano powder was characterizes by XRD, SEM, EDX and DC Conductivity.

2.2 Synthesis of 0.11 atomic % of In doped SnO_2 Nanostructure by sol-gel method.

The process sol-gel method involves in synthesis of In/SnO_2 nanostructures. In this 4.45126gm of tin tetra tetrachloride dehydrate (SnCl4.2H2O) is dissolved in 75ml of ethanol which is taken in to beaker and 8ml of $In(NO_3)_3$ is added to that solution. The solution is placed for continuous stirring at 70^{o}C for 1hour. After some moment 4ml of HCl is added and finally 7ml of NH4OH is gradually added to the prepared solution with continuous stirring to form white precipitate of Indium tin Hydroxide

Now, the precipitate is filtered and dried in an oven at about 200°C for 1 hr. The product obtained is Indium tin hydroxide which is annealed at 300°C for three hours to get the 0.11atomic % of Indium doped tin oxide. This nano powder was characterizes by XRD, SEM, EDX and DC Conductivity.

2.3 Synthesis of 0.24 atomic % of In doped SnO_2 Nanostructure by sol-gel method.

The process sol-gel method involves in synthesis of In/SnO_2 nanostructures. In this 4.45126gm of tin tetra tetrachloride dihydrate (SnCl4.2H2O) is dissolved in 75ml of ethanol which is taken in to beaker and 10ml of $In(NO_3)_3$ is added to that solution. The solution is placed for continuous stirring at 70^{o}C for 1hour. After some moment 4ml of HCl is added and finally 8ml of NH4OH is gradually added to the prepared solution with continuous stirring to form white precipitate of Indium tin Hydroxide Now, the precipitate is filtered and dried in an oven at about 200°C for 1 hr. The product obtained is Indium tin hydroxide which is annealed at 300°C for three hours to get the 0.24 atomic % of Indium doped tin oxide. This nano powder was characterizes by XRD, SEM, EDX and DC Conductivity.

3 Results:

3.1 Synthesize of SnO_2 Nanostructures by sol-gel method:

For synthesis of SnO_2 nanostructures, 4.45126gm of tin tetra tetrachloride dihydrate (SnCl4.2H2O) is dissolved in 75ml of ethanol which is taken in to beaker. The solution is placed for continuous stirring at 70^{o}C for 1hour. After some moment 2ml of HCl is added and finally 3ml of NH4OH is gradually added to the prepared solution with continuous stirring to form white precipitate of tin Hydroxide [Sn(OH)4] appears in the form of reaction product is Given below:

$$SnCl_4 + 4NH_4OH \rightarrow Sn(OH)_4 + 4NH_4Cl$$

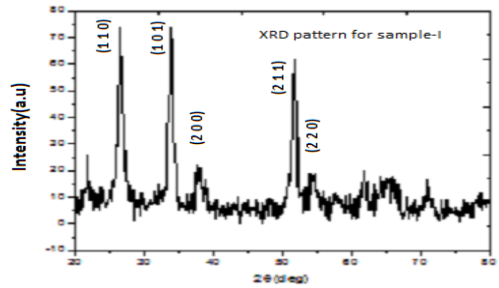
Now, the precipitate is filtered and dried in an oven at about 200°C for 1 hr. The product obtained is tin hydroxide which is annealed at 300°C for three hours to get the tin oxide particles. The chemical reaction for the same is given below:

$$Sn(OH)_4 \rightarrow SnO_2 + 2H_2O$$

This nano powder was characterizes by XRD, SEM, EDX and DC Conductivity.

XRD-Analysis:

The figure shows that the XRD pattern of the SnO_2 nanostructures.



The results obtained confirm and show that the synthesized SnO_2 nanostructures are in tetragonal structure. Peaks are observed at 26.48^o, 33.74^o, 37.80^o, 51.56^o and 54.53^o corresponding to the (h k l) values of (1 1 0), (1 0 1), (2 0 0), (2 1 1), (2 0 0) respectively. The lattice parameters were in good agreement with JCPDS card number 77-0452, having lattice parameters a=b=4.755A^o, c=3.199 A^o and angles $\alpha = \beta = \gamma = 90^o$. The crystallite size is calculated from Scherrer's formula,

$$D = \frac{k*\lambda}{\beta*Cos\theta}$$

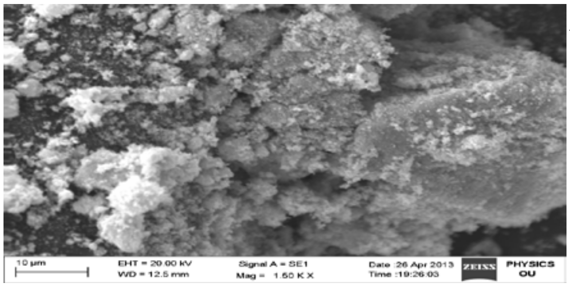
Where D – is the average crystallite size of the particle, λ – is the wavelength of the electron beam, β – is the full width at half maximum (FWHM) of the peak and θ is the Bragg's angle of diffraction.

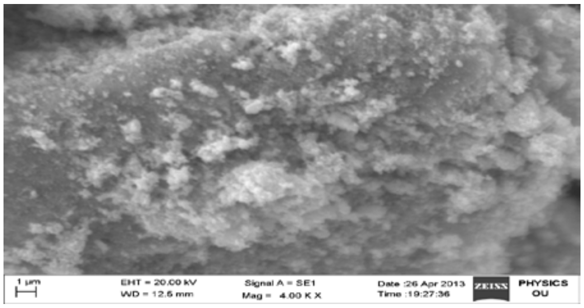
Position2θ in degree	**FWHM(β) in degree**	**FWHM(β) in radian**	**θ in degree**	**θ in radian**	**D = $\frac{k*\lambda}{\beta*Cos\theta}$**
26.487	0.756304	0.0132	13.2353	0.2310	10.7865
33.740	0.853707	0.0149	16.8907	0.2948	9.7213
37.808	0.687549	0.012	25.8346	0.4509	12.8325
Total,∑D=33.3404 **Average=11.11nm**					

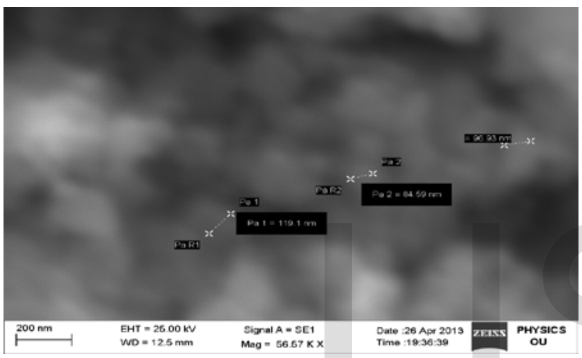
The above table shows that Crystallite size calculation from XRD data for SnO_2 nanostructures the average crystallite sizes of samples (pure SnO_2) synthesized by Sol-gel method are 11.11nm.

Scanning Electron Microscopy

The surface morphology was observed from SEM images with different magnifications. The SEM images of SnO_2 nanostructures which were synthesized by sol-gel method



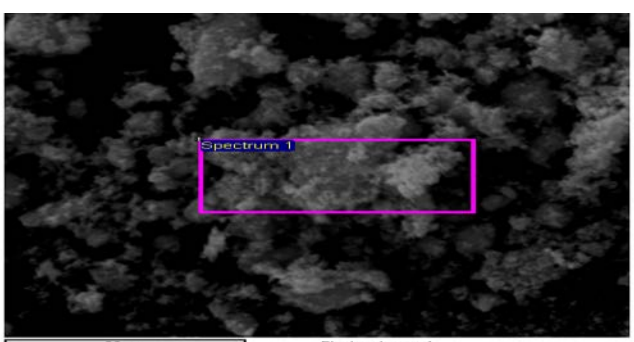


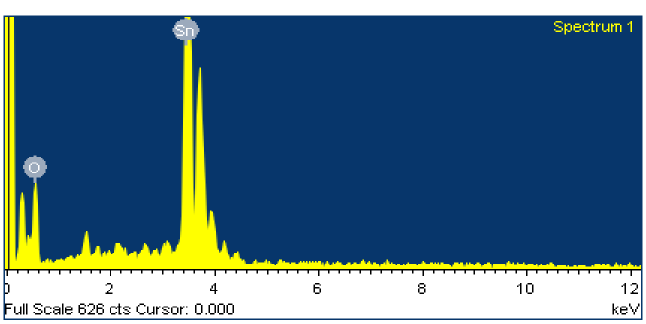


From the above SEM images we can infer that the as synthesized SnO_2 nanostructures exhibit crystalline morphology, particles are agglomerated and are non-porous.

Energy Dispersive X-ray spectrometry:

The elemental composition percentages of Nano powders were obtained from EDX pattern. The EDX spectrums of SnO_2 nanoparticles synthesized by Sol-gel method are shown in below figures respectively.





Element	Weight%	Atomic%
O K	45.11	85.91
Sn L	54.89	14.09
Totals	100.00	

The above table shows the elemental composition of elements in SnO_2 nanostructures prepared by sol-gel method.

DC-Conductivity:

Electrical conductivity or specific conductance is the reciprocal of electrical resistivity, and measures a material's ability to conduct an electric current. It is commonly represented by the Greek letter σ (sigma), Its SI unit is siemens per metre (S/m) and CGSE unit is reciprocal second (s−1).

The temperature (T) and corresponding resistance(R) values are taken from the experiment and further the resistivity and conductivity is measured from the following formulas.

The electrical resistivity (ρ) is defined as:

$\rho = RA/l$

Where R is the electrical resistance of sample (measured in ohms, Ω)

A is the area of the specimen (measured in square meters, m^2).

l is the thickness of the pellet(measured in meters, m)

Conductivity (σ) is defined as the inverse of resistivity and it is defined as

$\sigma = 1/\rho$

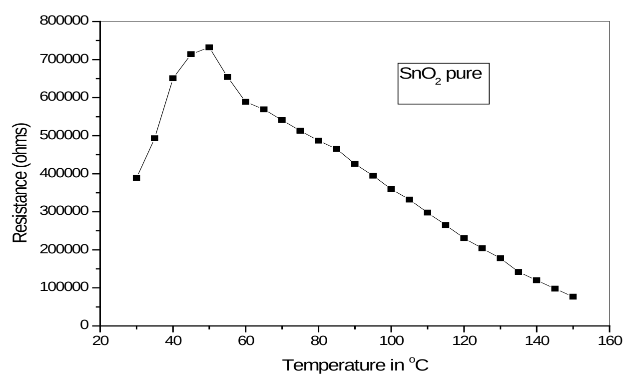
Conductivity has SI units of Siemens per meter (S/m).

Thickness and radius of the pellet is calculated by using screw gauge as given below:

Thickness (l) of the pellet=0.00135m

Radius of the pellet(r) =0.006025m

The below figure shows the variation between Resistance and Temperature. It indicates that indicates that initially resistance increases up to 50^0C and after gradually decreases



The temperature (T) and corresponding resistance(R) values are taken from the experiment are show in below Table

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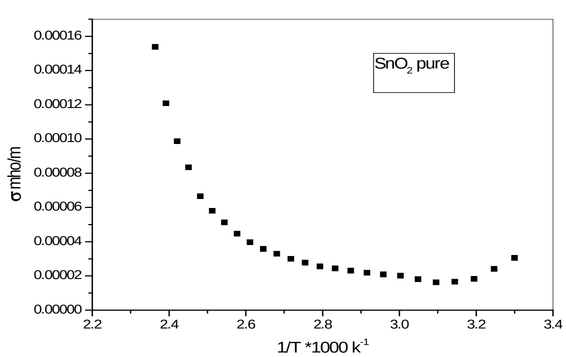
Temperature (^{O}C)	Resistance(MΩ)
30	0.389
35	0.493
40	0.651
45	0.714
50	0.732
55	0.654
60	0.589
65	0.569
70	0.541
75	0.513
80	0.487
85	0.465
90	0.426
95	0.395
100	0.36
105	0.332
110	0.298
115	0.265
120	0.231
125	0.204
130	0.178
135	0.142
140	0.12
145	0.098
150	0.077

The below Figure shows the variation of conductivity. It indicates that the conductivity gradually increases above the transition temperature

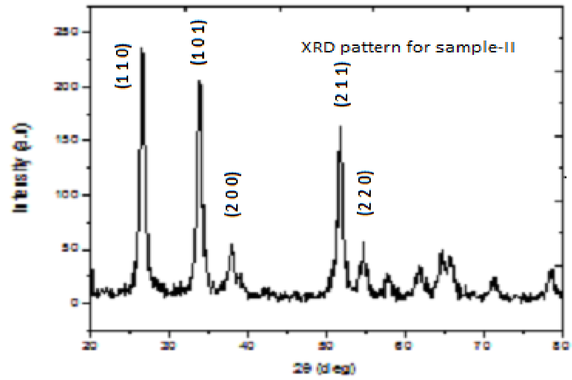


3.2Synthesis of 0.11 atomic % of In doped SnO_2 Nanostructure by sol-gel method

For In/SnO_2 nanostructures,4.45126gm of tin tetra tetrachloride dihydrate (SnCl4.2H2O) is dissolved in 75ml of ethanol which is taken in to beaker and 8ml of $In(NO_3)_3$ is added to that solution. The solution is placed for continuous stirring at 70^{o}C for 1hour. After some moment 4ml of HCl is added and finally 7ml of NH4OH is gradually added to the prepared solution with continuous stirring to form white precipitate of Indium tin Hydroxide Now, the precipitate is filtered and dried in an oven at about 200°C for 1 hr. The product obtained is Indium tin hydroxide which is annealed at 300°C for three hours to get the 0.11atomic % of Indium doped tin oxide. This nano powder was characterizes by XRD, SEM, EDX and DC Conductivity.

XRD-Analysis:

The figure shows that the XRD pattern of the In/SnO_2 nanostructures obtained by sol-gel method



The obtained results confirm and show that the synthesized In/SnO_2 nanostructures are in tetragonal structure. Peaks are observed at 26.58^{o}, 33.87^{o}, 37.95^{o}, 51.77^{o} and 54.76^{o} corresponding to the (h k l) values of (1 1 0), (1 0 1), (2 0 0), (2 1 1), (2 2 0) respectively. The lattice parameters were in good agreement with JCPDS card number 88-0287, having lattice parameters a=b=4.737A^{o}, c=3.185 A^{o} and angles α = β = γ = 90^{o}. The crystallite size is calculated from Scherrer's formula,

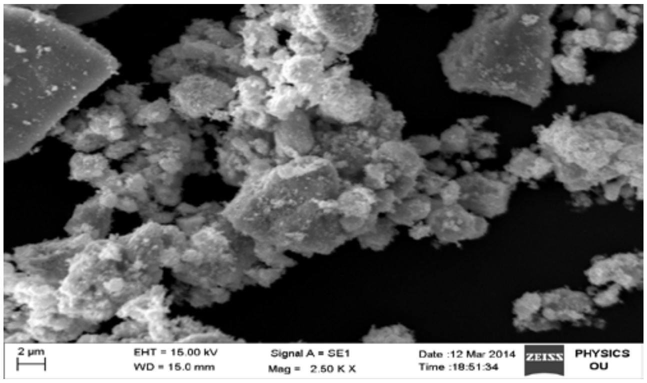
$$D = \frac{k*\lambda}{\beta*Cos\theta}$$

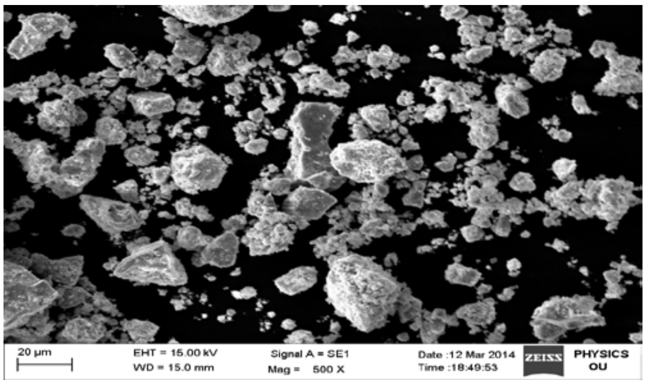
Where D – is the average crystallite size of the particle, λ – is the wavelength of the electron beam, β – is the full width at half maximum (FWHM) of the peak and θ is the Bragg's angle of diffraction.

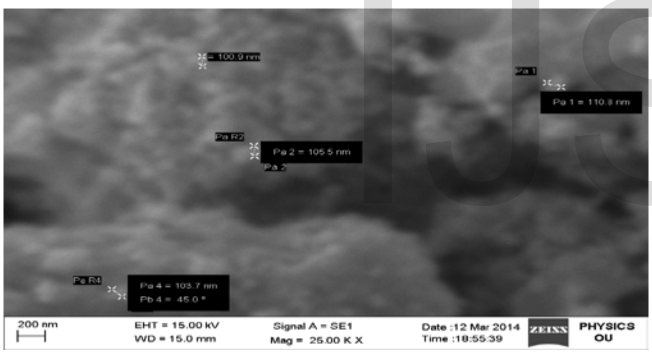
Position2θ in degree	FWHM(β) in degree	FWHM(β) in radian	θ in degree	θ in radian	D = $\frac{k*\lambda}{\beta*Cos\theta}$
26.589	0.7122	0.0124	13.294	0.2315	11.483
33.877	0.7042	0.0122	16.938	0.2952	11.874
37.956	0.6752	0.0117	18.978	0.4513	13.164
Total ∑D=36.522 Average=12.17 nm					

Scanning Electron Microscopy:

The surface morphology was observed from SEM images with different magnifications. The SEM images of In/SnO_2 nanostructures which were synthesized by sol-gel method are shown in figures

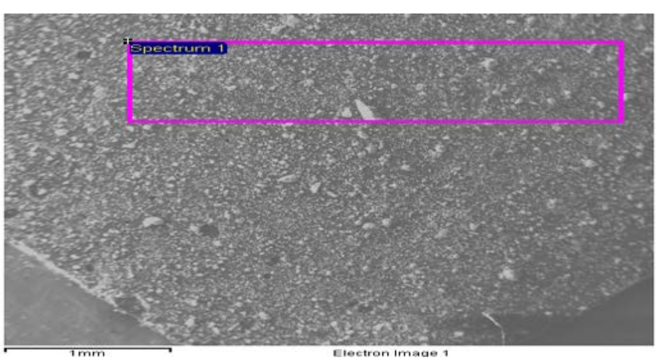


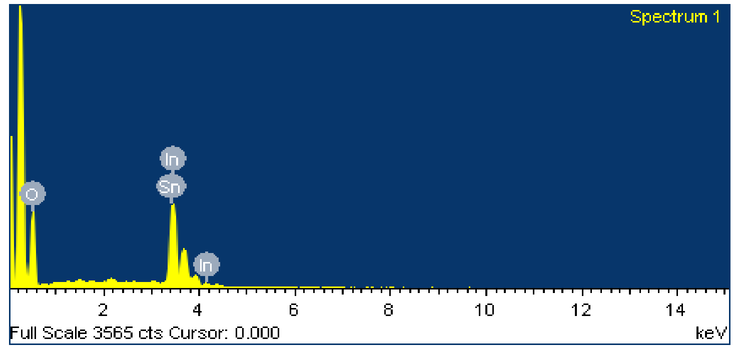




Energy Dispersive X-ray spectrometry:

The elemental composition percentages of Nano powders were obtained from EDX pattern. The EDX spectrums of SnO_2 nanoparticles synthesized by Sol-gel method are shown in figure respectively.





The above table shows the elemental composition of elements in In/SnO_2 nanostructures prepared by sol-gel method.

Element	Weight%	Atomic%
O K	47.72	87.91
In L	1.42	0.11
Sn L	50.86	11.98
Totals	100.00	

DC-Conductivity:

Thickness and radius of the pellet is calculated by using screw gauge as given below:

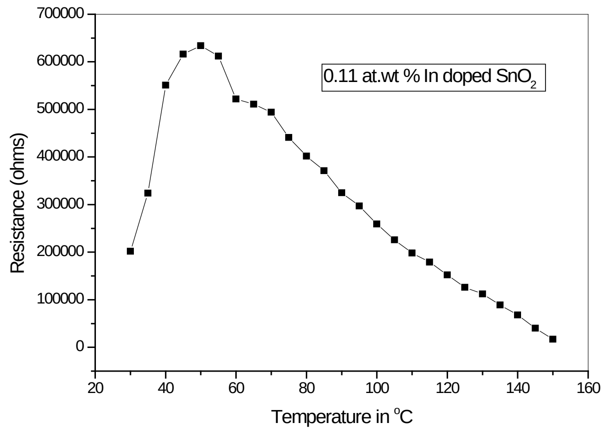
Thickness (*l*) of the pellet=0.00189m,

Radius of the pellet(r) =0.00633m

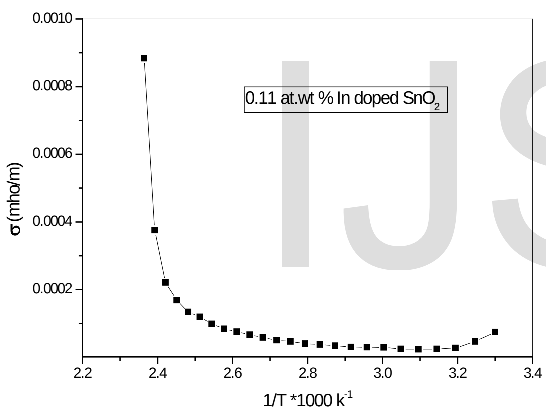
The temperature (T) and corresponding resistance(R) values are taken from the experiment are show in Table

Temperature (^{o}C)	Resistance(MΩ)
30	0.202
35	0.324
40	0.551
45	0.616
50	0.634
55	0.612
60	0.522
65	0.511
70	0.494
75	0.441
80	0.402
85	0.371
90	0.325
95	0.297
100	0.259
105	0.226
110	0.198
115	0.179
120	0.152
125	0.126
130	0.112
135	0.089
140	0.068
145	0.04
150	0.017

The below Figure shows the variation between Resistance and Temperature. It indicates that initially resistance increases up to 50 ^{O}C (Transition temperature) and after this gradually decreases.



The below Figure shows the variation of conductivity. It indicates that the conductivity gradually increases above the transition temperature



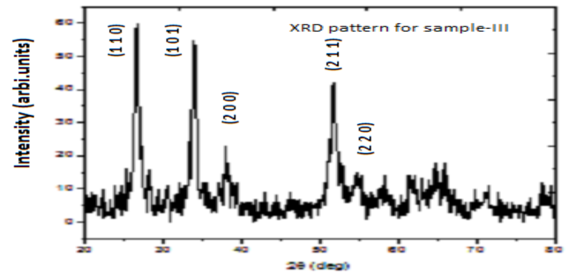
3.3Synthesis of 0.24 atomic % of In doped SnO_2 Nanostructure by sol-gel method:

For In/SnO_2 nanostructures,4.45126gm of tin tetra tetrachloride dihydrate (SnCl4.2H2O) is dissolved in 75ml of ethanol which is taken in to beaker and 10ml of $In(NO_3)_3$ is added to that solution. The solution is placed for continuous stirring at 70^{o}C for 1hour. After some moment 4ml of HCl is added and finally 8ml of NH4OH is gradually added to the prepared solution with continuous stirring to form white precipitate of Indium tin Hydroxide

Now, the precipitate is filtered and dried in an oven at about 200°C for 1 hr. The product obtained is Indium tin hydroxide which is annealed at 300°C for three hours to get the 0.24atomic % of Indium doped tin oxide. This nano powder was characterizes by XRD, SEM, EDX and DC Conductivity.

XRD-Analysis:

The figure shows that the XRD pattern of the In/SnO_2 nanostructures (sample-III) obtained by sol-gel method



The results obtained confirm and show that the synthesized In/SnO_2 nanostructures are in tetragonal structure. Peaks are observed at 26.54^{o}, 33.80^{o}, 37.88^{o}, 51.67^{o} and 54.65^{o} corresponding to the (h k l) values of (1 1 0), (1 0 1), (2 0 0), (2 1 1), (2 2 0) respectively. The lattice parameters were in good agreement with JCPDS card number 88-0287, having lattice parameters a=b=4.745A^{o}, c=3.193 A^{o} and angles α = β = γ = 90^{o}. The crystallite size is calculated from Scherrer's formula,

$$D = \frac{k*\lambda}{\beta*Cos\theta}$$

Where D – is the average crystallite size of the particle, λ – is the wavelength of the electron beam, β – is the full width at half maximum (FWHM) of the peak and θ is the Bragg's angle of diffraction.

Position2θ in degree	FWHM(β) in degree	FWHM(β) in radian	θ in degree	θ in radian	D = $\frac{k*\lambda}{\beta*Cos\theta}$
26.542	0.5786	0.0101	13.271	0.2315	14.098
33.808	0.6130	0.0107	16.904	0.2955	13.540
37.887	0.8307	0.0145	18.943	0.4509	10.620
				Total ∑D=38.259 **Average=12.75 nm**	

Scanning Electron Microscopy:

The surface morphology was observed from SEM images with different magnifications. The SEM images of In/SnO_2 nanostructures which were synthesized by sol-gel method are shown in figures\\

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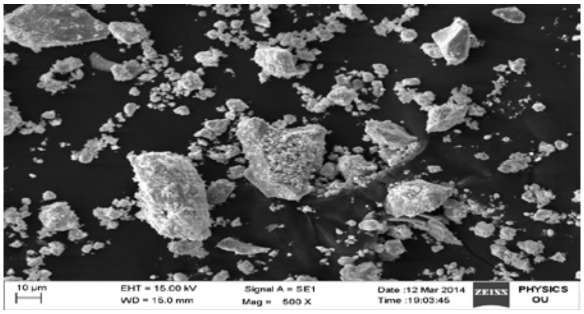
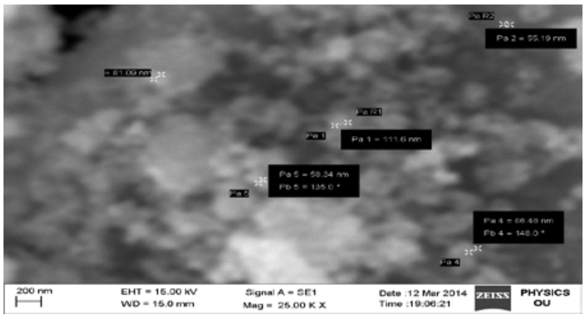
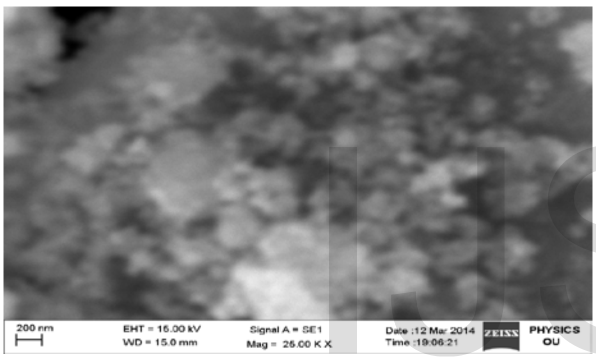
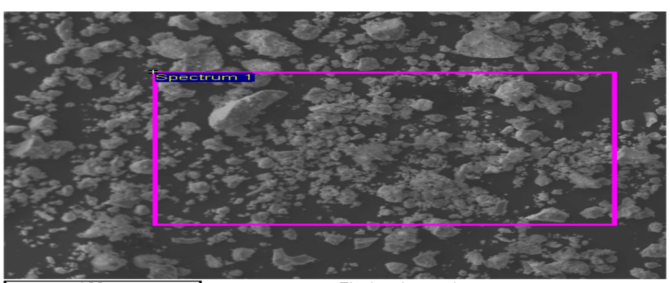


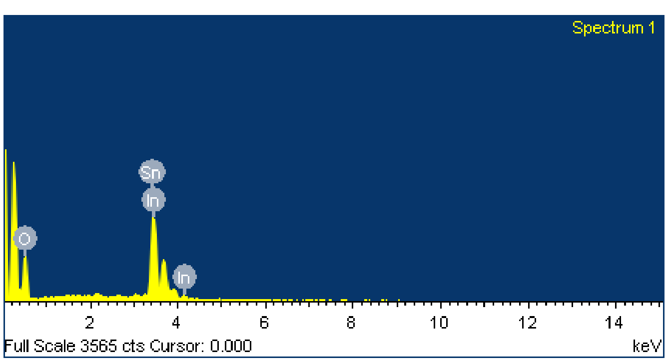




Energy Dispersive X-ray spectrometry:

The elemental composition percentages of Nano powders were obtained from EDX pattern. The EDX spectrums of SnO_2 nanoparticles synthesized by Sol-gel method are shown in figure) respectively.





Element	Weight%	Atomic%
O K	37.07	83.30
In L	2.89	0.24
Sn L	60.04	16.46
Totals	100.00	

Thickness and radius of the pellet is calculated by using screw gauge as given below:

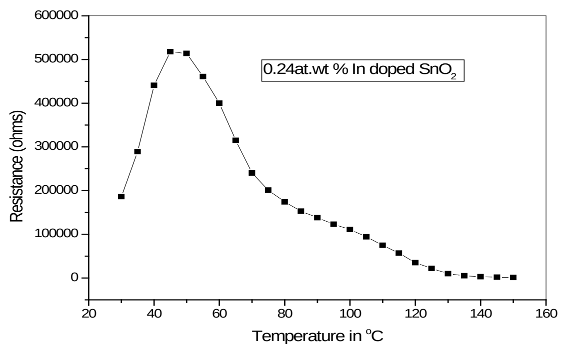
Thickness (*l*) of the pellet=0.00196m,

Radius of the pellet(r) =0.00633m

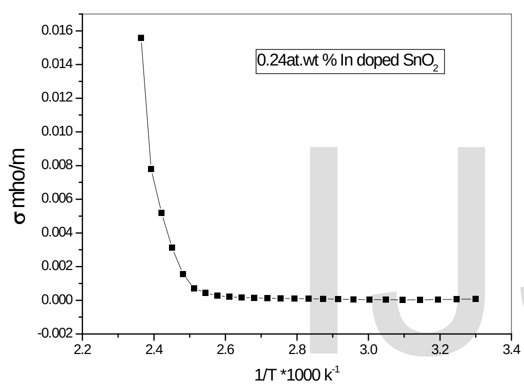
The temperature (T) and corresponding resistance(R) values are taken from the experiment are show in Table

Temperature (^{O}C)	Resistance(MΩ)
30	0.186
35	0.289
40	0.441
45	0.518
50	0.514
55	0.461
60	0.4
65	0.315
70	0.24
75	0.201
80	0.174
85	0.153
90	0.138
95	0.123
100	0.111
105	0.094
110	0.075
115	0.057
120	0.035
125	0.022
130	0.01
135	0.005
140	0.003
145	0.002
150	0.001

The below Figure shows the variation between Resistance and Temperature. It indicates that initially resistance increases up to 50 ^{O}C (Transition temperature) and after this gradually decreases



The below Figure shows the variation of conductivity. It indicates that the conductivity gradually increases above the transition temperature.



CONCULSION:

A well defined technique (sol-gel) for the synthesis of SnO_2 nanostructure has been employed. Different In/SnO_2 nanostructures are synthesized for different applications. Sol-gel technique is very simple and low cost method to synthesize the SnO_2 nanostructures. A sol-gel process offers several advantages over other methods such as better homogeneity, controlled stiochiometry, high purity etc at a low temperature. The average crystallite size of samples synthesized by sol-gel method are 11.11nm for sample-I, 12.17nm for sample-II and 12.75 for sample-III respectively are calculated from XRD data., SEM micrographs of the tin oxide nanostructures and indium doped tin oxide nanostructures have shown in the figures and the surface morphology is discussed. From the DC-Conductivity, it is observed that the conductivity increases with increasing the content of Indium in SnO_2 and the phase transition temperature in all the samples studied around $50^{0}C$.

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