International Journal of Scientific Research in Engineering and Management (IJSREM)
Volume: 06 Issue: 06 | June - 2022 Impact Factor: 7.185 ISSN: 2582-3930

A Co-operative Synthesis Approach to Prepare Tin Oxide Thin Films by Thermal Evaporation, Muffle Furnace Technique and Its Glucose Sensing Applications

Radhip N R*[1], Dr.Prashant V Joshi, Dr.N. Pradeep[2]

[1]School of Electronics and Engineering, REVA University, Bengaluru, India
[2]Department of Nano Science and Technology, Mount Carmel College, Bengaluru, India

radeepnr@mccblr.edu.in, prashanthvjoshi@reva.edu.in, pradeepzax@gmail.com

Abstract

Tin Oxide/Dioxide material plays an important role in many applications such as solar cell, sensors, optical devices and electronic devices. Tin oxide/dioxide films were thermally grown on glass substrates by the thermal method of pure metallic tin powder on glass substrates with 100nm thickness at 300°C substrate temperature for glucose sensing. An aluminium electrode was used as the contact on top of the thin films. It was used to detect the various glucose concentrations (50,100,150,200, 250 & 300) mg/dL at room temperature. The films were annealed at different temperatures and investigated for oxidation, physical and structural properties. The surface properties were studied by scanning electron microscopy and atomic force microscopy. Different elements of oxide films were recorded by energy dispersive X-ray (EDAX). For structural analysis, X-ray diffraction measurements were carried out and electrochemical workstation was used to analyse the glucose ($C_6H_{12}O_6$) sensing. It was found to be the SnO_2 film at 500°C temperature shows a better response than the other films and this was obtained as a biomedical sensor.

Keywords: Tin oxide, Muffle furnace, Thermal evaporation, Glucose sensor.

Introduction

Transparent conducting oxides have been widely used in different areas due to their many useful properties such as wide band gap (3.6eV) material with intrinsic n-type semiconductor characteristics and high transparency in the visible range. Literature survey reveals that, Stannic oxide prepared by different low dimensional Nanostructures such as nanotubes, nanowires, nanoribbons [1], Nanoplatelets [2], Springs, Rings and Spirals [3], Nanosheets [4], Nanobelts [5], quantum dots [6]. Owing to the interesting properties of different dimensional leads to the preparation of tin oxide nanostructures by various techniques of hydrothermal synthesis [7]. Various methods for the preparation of tin thin films are employed such as thermal deposition, chemical vapour deposition, DC/RF sputtering, sol-gel methods [8] and hydrothermal route [9].

Glucose sensing has received attention in the field of clinical analysis and diagnosis to detect glucose concentration due to the advantages of high sensitivity and excellent robustness than micro glucose sensors. Here, we prepared tin oxide thin film by thermal evaporation. Generally, tin oxide thin films were prepared by evaporation of tin powder and simultaneously supply of oxygen into the chamber using e-beam and sputtering techniques, etc. The novelty of this work is preparing a tin thin film on the substrate by thermal evaporation and then by annealing inside the muffle furnace to get tin oxide/dioxide thin films by different temperature. This study helps the researcher to form a thin film on a new route. To the best of our knowledge, this cooperative synthesis technique to prepare tin oxide thin film has not been done before. This is the first report to prepare tin oxide thin film by Cooperative synthesis technique. The prepared tin oxide films

International Journal of Scientific Research in Engineering and Management (IJSREM)
Volume: 06 Issue: 06 | June - 2022 Impact Factor: 7.185 ISSN: 2582-3930

used to produce glucose sensor with an aluminium contact electrode. The produced films were examined by various techniques such as morphology studies by using Scanning Electron Microscope (SEM), elemental composition through Energy Dispersive X-Ray (EDAX) and structural studies by Atomic Force Microscopy (AFM).

Materials and Methods

The glucose ($C_6H_{12}O_6$) sensing device was achieved by the three-step method.

Step1**:** Sn (Tin) thin films were prepared by the thermal method, the pure metallic tin powder used as source powder, at a substrate temperature of 300°C on a borosilicate glass substrate, before placing into the chamber, cleaned with ultra sonicator for 15 minutes. High purity metallic tin powder was placed into the boat, the chamber was pressure was evacuated to $5X10^{-5}$ mbar. The film thickness was maintained at 100nm.

Step 2: The prepared tin thin films was kept inside the muffle furnace. The thin film was annealed at various temperatures (300°C, 400°C, 500°C, 600°C) at one-hour duration.

Step 3: Aluminium interdigitate electrode was coated on the prepared tin oxide thin film using a thermal evaporation technique for glucose sensor device. This device was used to analyse the Glucose sensing for different concentrations of 50,100,150,200, 250 and 300mg/dL. The sensor was analysed by using the electrochemical workstation (CHI604D) instrument.

Result and Discussion

Scanning Electron Microscope (SEM) studies

Fig: 1 shows the surface morphology studies of SnO and SnO_2 thin films on glass substrate using muffle furnace were investigated through scanning electron microscopy images. The tin oxide particles were scattered and irregularly arranged with nearly spherical shapes shown in figs. (A) - (E). All films are an agglomeration of the particles occurred with irregular shapes of films and diameter ranging from 50nm to 100nm size. When the annealing temperature increased, the surface of the films was relatively uniform and dense particles formation was found. The crystals in film grown at 600°C were a lenticular shape as shown in fig. (E).

Energy Dispersion X-ray (EDAX) analysis

The EDAX analysis was done for as-deposited and annealed films and it is shown in fig.2 it reveals the presence of various ingredients like C, N, O, Si, Au, Na, Mg, Sn and Ca. The SnO and SnO_2 was confirmed by EDAX analysis of the films. fig.2 (A), (B) & (C) is for as-deposited SnO thin film shows the Oxygen atomic percentage nearly same as tin atomic percentage. Fig.2 (D) & (E) is for as-deposited SnO_2 thin film shows the Oxygen atomic percentage twice that of as tin atomic percentage and a low percentage of C(Carbon), N(Nitrogen), Si (SiO_2), Na (Albite), Mg (MgO) and Ca (Calcium) ingredients are from glass and Au(Gold) from sputtering deposition. The Sn and O deposition is confirmed the Atomic percentage and weight percentages. Atomic and weight percentage were given in the insert table for all different temperature EDAX images. The data confirmed the presence of tin and Oxygen in all films.

Atomic force microscopy (AFM) studies

Fig.3 shows the three-dimensional atomic force microscopy (AFM) images. The parameters of prepared tin film and different annealing temperatures values were tabulated and are shown in table 1. It is concluded from Table 1, the average roughness values increased from without annealing of tin film to high temperature annealed at 600 °C. This variation is due to the formation of a cluster of tin oxide particle in high temperature. This result is similar to the SEM images.

The grain size was found samples of annealed different temperature were determined using XRD with Cu Kα radiation. The XRD patterns shown in fig.4 demonstrated that the deposited films were orthorhombic and tetragonal crystal structure of SnO and SnO_2 respectively. XRD data is presented in Table 1 represents the peaks at 2θ: 30.72, 31.8, 44.4.55.3, 62.2, and 64.2 represents a tetragonal crystalline phase of SnO and table 2 shows the peaks at 2θ:43.5, 51.2, 55.5 which represents Orthorhombic crystal structure of Sno_2 Crystallite size and lattice strain have been determined in the table (2-4) according to equation [10,11]. The SnO and SnO2 grain size increased as the annealing temperature was increased. We calculated the grain size (table shown) of films grown at various annealing temperatures by using the Scherrer equation (1)

$$D=0.9\lambda/\beta\cos\theta \qquad (1)$$

Where D is the crystallite size, λ is the X-ray wavelength, β is the full width at half maximum of the diffraction peak, and θ is the Bragg diffraction angle of the diffraction peaks. Inter planar spacing, grain size, lattice strain was found for the SnO and SnO_2 structures. When 2θ values are increasing the grain size was increasing. Other structural parameters were shown in table2. Tin oxide structural parameters were shown in Table3.

The intermediate annealing temperatures, between substrate temperatures 300ºC and annealed temperatures from 300ºC to 600ºC at **one** hour, peaks of the SnO and SnO_2 grain size was analysed. For all different annealing temperature interplanar spacing, grain size, lattice strain was found, almost all **were** in the same size.

Glucose Sensor characteristics

Table 5 shows six glucose concentrations spread across the sample. The tested glucose concentration was 50, 100, 150, 200, 250 and 300mg/dL.Change in resistance was measured for all the annealed temperature samples. The resistance of the sample at different glucose concentration and using double distilled water the TDS level 5 was taken [12-14]. Table 5 shows the sensing behaviour of without annealing of tin film at different annealed temperatures of thin-film samples. All different concentration of the solution was dropped on the sample and resistance were measured.

From the table, we observed that the resistance was almost same in all concentration for without annealing thin film. Annealed at 300ºC, 400ºC and 600ºC temperatures the resistance are constant in all concentration. Annealed at 500ºC temperature shows a considerable response to the glucose. This is due to the formation of SnO_2 film. At 600ºC temperature the film form big clusters particles. This make discontinues glucose formation on the sample, this makes again the samples was non-sensing behaviour. This concludes the sample is smoother and helps the sensing behaviour [15].

Conclusion

The tin metal powder was thermally evaporated on the glass substrate in $5x10^{-5}$ mbar vacuum at 300ºC substrate temperature and it was found that annealed temperature has a significant impact on crystal structure to form the SnO and SnO_2 thin films. The properties of the films were analysed. Elemental values were obtained from EDAX results. The X-ray diffraction pattern of the Tin thin films corresponded to the diffraction peak typical of SnO and SnO_2 and the rutile phase of SnO with Orthorhombic crystal structure and SnO_2 with tetragonal crystal structure were studied. Morphological characteristics of SnO and SnO_2 Nanocrystalline thin films are relatively uniform and dense particles formation was found. These results reveal that tin oxide/dioxide thin films can be prepared without oxygen gas. It was done using thermal evaporation and muffle furnace technique only, this creates a new path of preparation of tin oxide/dioxide thin films. Finally, the glucose sensor was made using SnO_2 thin film. From the results, it was found to be the SnO_2 film at 500°C temperature shows favourable response than the other films for glucose ($C_6H_{12}O_6$) detection.

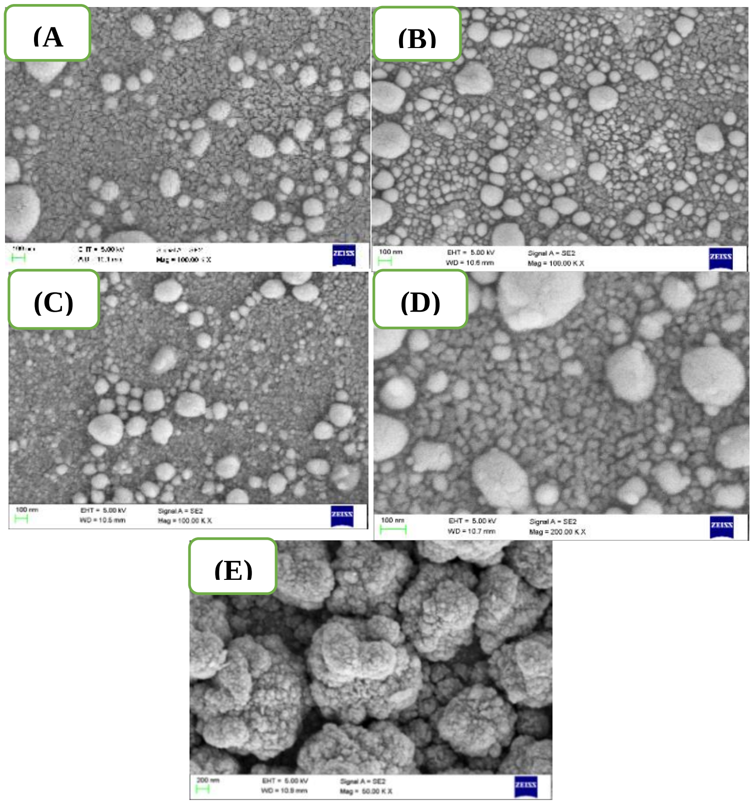

Fig.1 shows Surface analysis of Tin Oxide films for different annealing temperatures (A) without annealing of tin film, (B) Annealed at 300°C, (C) 400°C, (D) 500°C and (E) 600°C for one hour.

Samples	Roughness average S_a	Valley depth S_v	Peak height S_p	Peak valley height S_y
Without annealing of the tin film	5.2456nm	-31.738nm	30.823nm	62.561nm
Annealing at 300°C	5.4726nm	-48.523nm	43.335nm	91.858nm
Annealing at 400 °C	4.6832nm	-41.199nm	36.926nm	78.125nm
Annealing at 500 °C	8.6269nm	-93.994nm	192.87nm	286.87nm
Annealing at 600 °C	25.179nm	-102.23nm	975.34nm	1077.6nm

International Journal of Scientific Research in Engineering and Management (IJSREM)
Volume: 06 Issue: 06 | June - 2022 Impact Factor: 7.185 ISSN: 2582-3930

Table 1 shows Roughness average S_a, Valley depth S_y, peak height S_P, peak valley height S_y

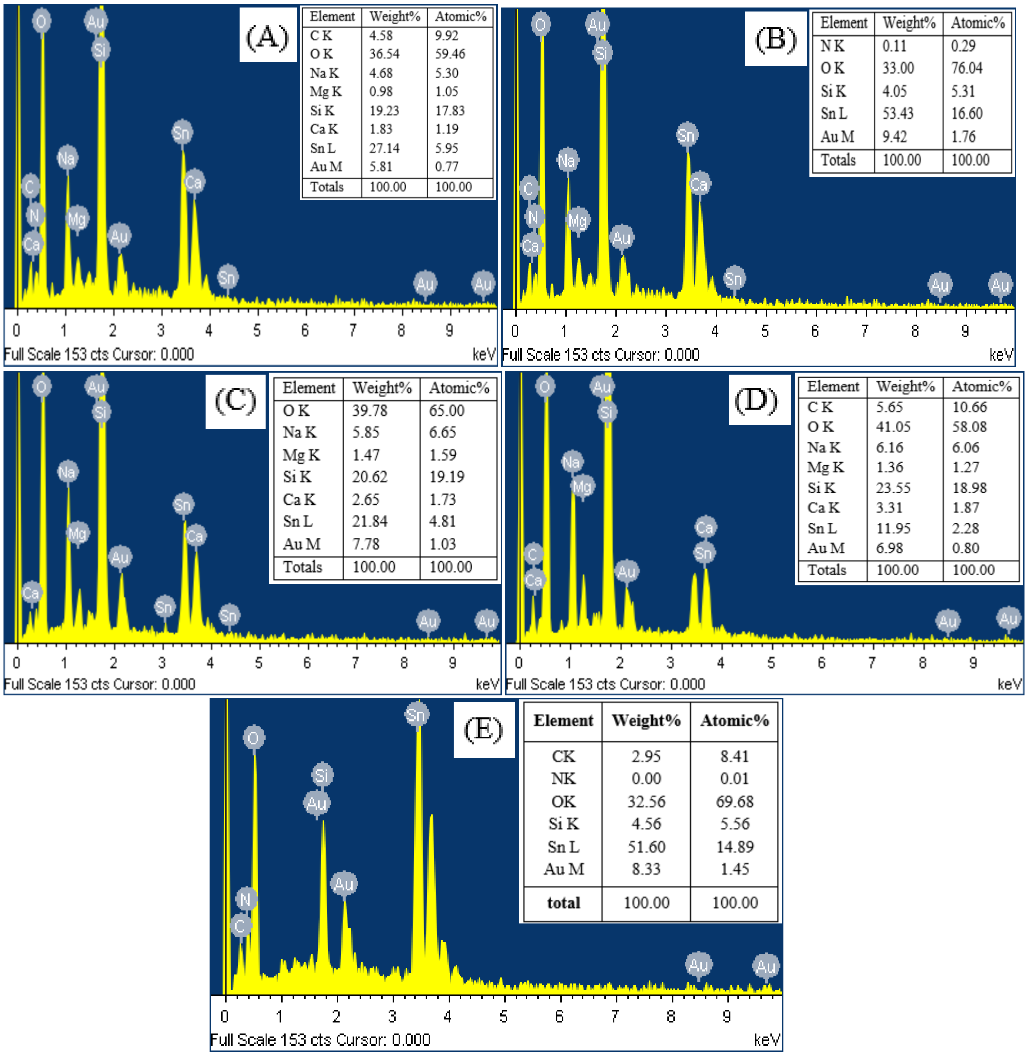

Fig.2 shows EDAX analysis of Tin Oxide films for different annealing temperatures, (A) without annealed of tin film, (B) Annealed at 300°C, (C) 400°C, (D) 500°C, (E) 600°C for one hour.

2θ	(hkl) planes	Inter-Planar distances (d) in A^o	Grain Size (D)in nm	Lattice strain
30.72	(101)	2.9	21.50	0.0064
31.8	(020)	2.8	22.13	0.0060
44.4	(024)	2	21.86	0.0044
55.3	(116)	1.7	23.43	0.0033
62.2	(206)	1.5	23.64	0.0030
64.2	(225)	1.5	24.4	0.0028

International Journal of Scientific Research in Engineering and Management (IJSREM)
Volume: 06 Issue: 06 | June - 2022 **Impact Factor: 7.185** ISSN: 2582-3930

Table2 XRD analysis of SnO Nano crystallites of the tetragonal crystal structure with temperature substrate temperature 300ºC thin film, substrate temperature films annealed 300ºC for **one** hour, substrate temperature films annealed 400ºC for **one** hour.

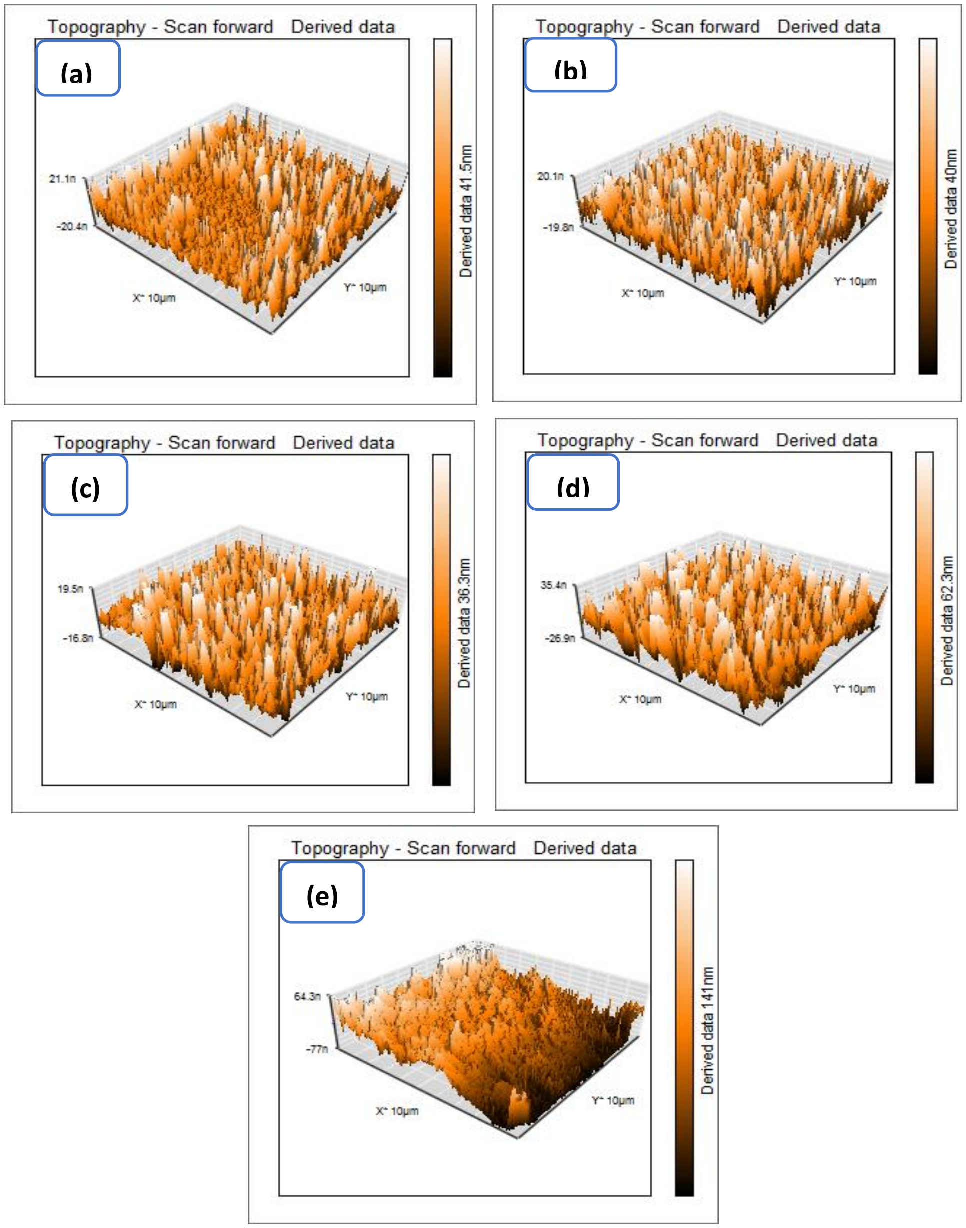

Fig.3 shows AFM analysis of Tin oxide films for different annealing temperatures (A) without annealing of tin film, (B) Annealed at 300°C, (C)400°C, (D)500°C, (E),600°C respectively at one hour.

Table 3 Orthorhombic crystal structure substrate temperature films annealed 500°C for 1 hour, substrate temperature films annealed 500°C for 1 hour.

2θ	(hkl) planes	Inter-Planar distances (d) In A°	grain Size in nm	Lattice strain
43.5	(210)	2.1	4.02	0.0243
51.2	(211)	1.8	9.69	0.0087
55.5	(220)	1.7	7.20	0.0108
57.5	(002)	1.6	5.92	0.0127

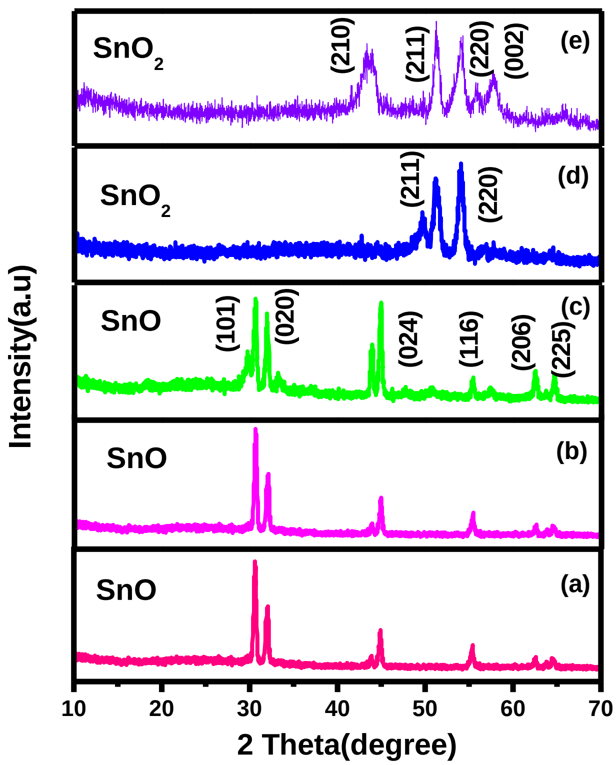

Fig.4 shows the XRD pattern for SnO/SnO_2 films prepared on a glass substrate at different temperature (a) without annealing of tin oxide thin film, (b) Annealed at 300°C, (c)400°C, (d)500°C (e) 600°C for one hour.

	The resistance of the sample MΩ	Water 0mg/dL MΩ	50 mg/dL MΩ	100 mg/dL MΩ	150 mg/dL MΩ	200 mg/dL MΩ	250 mg/dL MΩ	300 mg/dL MΩ
Without annealing	4.84	3.98	3.98	3.98	3.98	3.98	3.98	0.52
Annealed at 300°C	39.88	39.88	39.88	39.88	39.88	39.88	39.88	39.88
Annealed at 400°C	39.88	39.88	39.88	39.88	39.88	39.88	39.88	39.88
Annealed at 500°C	0.5	0.514	0.466	0.672	0.59	0.78	0.841	0.826
Annealed at 600°C	3.98	3.98	3.98	3.98	3.98	3.98	3.98	3.98

Table 5 shows glucose concentration and resistance

Substrate temperature (300°C) annealed	**2θ**	**Interplanar spacing (d) in A°**	**Grain Size (D) in nm**	**Lattice strain**
000°C	30.5	2.9	21.51	0.0064
300°C	30.6	2.9	21.51	0.0064
400°C	30.6	2.9	17.21	0.0080
500°C	30.6	2.9	21.51	0.0064
600°C	30.5	2.9	21.51	0.0064

Table 4 structural parameters of SnO/SnO_2 at different temperature

References:

1) Z.R. Dai,J.L. Gole,J.D. Stout, and Z.L. Wang, "Tin oxide Nanowires, Nanoribbons and Nanotubes",J.Phys.Chem.B 2002, 106, 1274-1279.
2) Yi-Zhou Zhang, Huan pang, Yanqiu Sun, Wen- Yong Lai, Ang Weil, Wei Huang, "Porous tin oxide Nanoplates as Excellent-Efficiency photoelectrodes and Gas Sensors" Int. J.Electrochem, Sci., 8(2013) 3371-3378.
3) Rusen Yang and Zhong Lin Wang, "Springs, Rings, and Spirals of Rutile- Structured tin Oxide Nanobelts", J.AM CHEM. SOC. 9 VOL.128, NO.5, 2006.
4) Yoshitake Masudal and Kazumi Kato "SnO_2 Nanosheet assembly coating on Teflon Rods",Journal of the Australian Ceramic Society Volume 48[2], 2012, 185-188.
5) Yi Cheng, Rusen Yang, Jian-Ping Zheng, Zhong Lin Wang, Peng Xiong, "Characterizing individual SnO_2 nanobelt field-effect transistors and their intrinsic responses to hydrogen and ambient gases," Materials chemistry and physics and physics 137 (2012) 373-380.
6) N. Saravanan, S. Ponnuswamy, Shri Prasad S, V. Joseph, Synthesis and Characterization of SnO_2 Quantum Dots", International Journal of ChemTech Research, CODEN (USA): IJCRGG ISSN: 0974-4290 vol.6, No.1,pp 600-603, Jan-March 2014.

7) Lin Tan, Lihong Wang and Yude Wang, Hydrothermal Synthesis of SnO_2 Nanostructures with Different Morphologies and Their Optical Properties, Journal of Nanomaterials,Volume 2011, Article ID 529874, 10 pages doi:10.1155/2011/529874.
8) Zhang G and Liu M 1999 Preparation of nanostructured tin oxide using a sol-gel process based on tin tetrachloride and ethylene glycol, J.Mater. Sci.34 3213-9.
9) Ganesh E patil, Dnyaneshwar D Kajale, Vishwas B Gaikwad and Gotan H Jain
Preparation and characterization SnO_2 nanoparticle by hydrothermal route. International Nano letters 2012, 1-5.
10) Hsyi-En Chenga, De-Cih Tiana, Kuan-Chun Huanga "properties of SnO_2 films grown by Atomic layer Deposition", Elsevier, Procedia Engineering 36 (2012) 510-515.
11) A.K.Mukhopadhyay, P. Mitra, A.P. Chatterjee, H.S. Maiti, "Tin Dioxide thin film gas sensor" Ceramics International. 2000, vol-26, pages 123-132.
12) I.Lee, N.Loew,W.Tsugawa, K. Ikebukuro, K.Sode, Development of a third-generation glucose sensor based on the open circuit potential for continuous glucose Monitoring, Biosens.Bioelectron.124-125(2019) 216-223.
13)S.Dhobale,P.Joshee,G.Deore,S.L.Laware,and S.N.Kale,Nanostructured glucose-oxidaseimmobilized SnO_2 thin films for glucose sensing,Applied physics letters 98,2011.
14) W.Joseph, Electrochemical glucose biosensors, Chem.Rev.108 (2008) 814-825.