Chapter 4

Effect of temperature on particle size of nanocrystalline $SnO_2$ during synthesis and sintering

4.1 Introduction

In $3^{rd}$ Chapter an attempt was made to control the particle size of tin oxide powder by varying the precipitation, sedimentation and reaction time. The results of previous chapter clearly indicated the fact that the particle sizes remained invariant under the different precipitate separation techniques. In Chapter-1 as we have discussed that in the nanomaterials based gas sensors particle size is very important parameter that controls the sensing response; so in this chapter we have followed slightly different approach to reduce/control the particle size of nanocrystalline $SnO_2$ powder. In this work we have carried out precipitation of nanocrystalline $SnO_2$ at different temperatures and then treated them at different elevated temperatures.

The change in the reaction temperature will certainly influence the morphology and structure of nanomaterials because particle morphology is strongly de-

\textsuperscript{0}Some work out of this chapter was published in the journal \textit{Sensors and Actuators B: Chemical} (143 (2009) 226-32) in the paper entitled “Influence of synthesis and calcination temperatures on particle size and ethanol sensing behaviour of chemically synthesized SnO$_2$ nanostructures”
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dependent upon the supersaturation which in turn is dependent upon the solution temperature [Cao (2004)]. The heat treatment such as sintering has a predominant effect upon the grain growth. The reduction in the overall surface energy is the true driving force for the grain boundary enlargement and consequently the particle size increases as a function of the temperature. Sintering is the consolidation of a powder by means of prolonged use of elevated temperatures, which are, however, below the melting point of any major phase of the material. It facilitates the movement of atoms or molecules through the mechanism of mass transport that may be lattice diffusion, surface diffusion or evaporation-condensation and results in the grain growth which has detrimental effect on the properties of the material [Anderson et al. (2002)].

An overview of work on nanostructured SnO$_2$ ethanol sensor of various researchers has been taken into due consideration. The survey reveals that different sophisticated techniques have been used to synthesize and vary nanostructure sizes [Xu et al. (1991), Ivanovskaya et al. (2001), Lee et al. (2001), Panchapakesan et al. (2001), Comini et al. (2002), Li et al. (2002), Kennedy et al. (2003), Ivanov et al. (2004), Ying et al. (2004), Joshi et al. (2006), Neri et al. (2006), Pourfayaz et al. (2008), Zhang et al. (2008), Chen et al. (2009), Wang & Liu (2009)]. We have tried to vary nanoparticle sizes by changing reaction temperature of starting chemical species, which is quite novel and relatively simple technique. In this chapter different permutations and combinations of reaction and sintering temperatures have been tried to synthesize SnO$_2$ powder samples. Gas sensors using each sample have been fabricated and their sensing response have been studied as function of particle size.

4.2 Synthesis of nanocrystalline SnO$_2$ powder at different reaction temperatures

Nanoparticles of tin dioxide powder were prepared through fine crystallization in liquid phase. The detailed preparation procedure is as follows (technique is almost similar to the method mentioned in Sec. 3.2). Ammonia water at 25°C (room temperature) was added slowly to the 0.2M solution of SnCl$_4$ and precipitate of tin hydroxide was produced. The material produced was separated
from rest of the liquid by filtering, which follows drying at 120°C. To investigate the effect of heat treatment on the morphology and sensing characteristics of tin dioxide powder, the material produced was divided into three parts and each part was sintered for 3 hrs in air at 400, 600 and 800 °C, respectively. In the present study we wanted to devise some method to control the particle size by simple technique. To put forward this idea, in the other experiments the reactions during crystallization in liquid phase were carried out at 5 and 50 °C instead of room temperature. The powder samples synthesized at these temperatures were also divided into three parts and subjected to similar heat treatments as mentioned in the first experiment. In this way nine different samples of powder produced by different procedures were obtained. The crystal structure of the materials produced was characterized by powder X-ray diffraction (XRD\(^1\)) using Cu K\(_\alpha\) radiation with Shimadzu (Model XRD-7000) Diffractometer system. Morphologies and sizes of material particles were analyzed by transmission electron microscope (TEM\(^2\)) with Morgagni 268, operating at 80 kV.

### 4.3 Sensor fabrication and testing method

Thick films of all the powders were deposited on alumina substrates; resulting in nine different sensor samples. The detailed description of deposition method followed has been explained in Sec. 2.4. Interestingly all the nine samples didn’t require any binder for fabricating the sensors; this is one of the preliminary indication that the powders have particle sizes within nanoscale regime.

The fabricated sensors were now subjected to ethanol vapours at different temperatures such as 200 to 400°C to find out optimum operable temperature of the sensor. The detailed description of the sensor testing unit has been explained in the Sec. 2.5, following which the sensors were also tested for different ethanol concentrations at optimum operating temperature. We repeatedly carried out observations of the sensor’s response at the optimum operating temperature for known volume of ethanol to test the sensors for long term stability.

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\(^1\)XRD was carried out at Physics Department, Guru Nanak Dev University, Amritsar

\(^2\)TEM investigations were done at SAIF, All India Institute of Medical Sciences, New Delhi
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4.4 Results and Discussions

4.4.1 Structural Characterization

Plots of X-ray diffraction\(^1\) data of tin dioxide samples prepared at 5, 25 and 50°C and calcined & sintered at 400, 600 and 800°C are shown in Fig. 4.1-4.3. The diffraction pattern in all the plots are in agreement with the standard X-ray diffraction peaks, which confirmed that the synthesized materials were $SnO_2$ of the tetragonal geometry.

![XRD plots of SnO\(_2\) samples](image)

**Figure 4.1:** XRD of $SnO_2$ powder synthesized at 5°C and sintered at 400, 600 and 800°C.

The crystallite size $D$ was estimated from the peak width with Scherrer’s formula, $D = K\lambda/\beta \cos \theta$, where $\lambda$ is the X-ray wavelength, $\beta$ is the full width at half maximum (FWHM) of a diffraction peak, $\theta$ is the diffraction angle, and $K$ is the Scherrer’s constant. The calculated crystallites sizes are comparable with the TEM results given in Table 4.1 which confirmed the particle growth with sintering and calcination temperature.
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Figure 4.2: XRD of $SnO_2$ powder synthesized at 25$^\circ$C and sintered at 400, 600 and 800$^\circ$C.
Figure 4.3: XRD of SnO$_2$ powder synthesized at 50°C and sintered at 400, 600 and 800°C.
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4.4.2 Effect of Reaction Temperature

The images represented in Figs. 4.4-4.12 are TEM\(^2\) micrographs of \(SnO_2\) synthesized at 5, 25 and 50\(^\circ\)C and calcined & sintered at 400, 600 and 800\(^\circ\)C.

![TEM of SnO\(_2\) powder synthesized at 5\(^\circ\)C and sintered at 400\(^\circ\)C.](image)

**Figure 4.4:** TEM of \(SnO_2\) powder synthesized at 5\(^\circ\)C and sintered at 400\(^\circ\)C.

Tin dioxide particles synthesized at 5, 25 and 50\(^\circ\)C, followed by sintering/calcination at 400\(^\circ\)C yielded particles of average sizes of 2, 10 and 5 nm, respectively. It is evident that particles of \(SnO_2\) synthesized at 5 and 50\(^\circ\)C are smaller than those prepared at 25\(^\circ\)C.

These results may be explained by the nucleation and growth of particles in a solution. Particle morphology is influenced by the factors such as supersaturation, nucleation and growth rates, colloidal stability, recrystallization and aging process. Generally, supersaturation, which is highly dependent on solution temperature, has a predominant influence on the morphology of the precipitates. A highly supersaturated solution possesses high Gibbs free energy. The tendency of a system to lower its Gibbs free energy is the driving force in the processes of nucleation and growth of particles. The relation between Gibbs free energy change
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**Figure 4.5:** TEM of $SnO_2$ powder synthesized at $5^\circ C$ and sintered at $600^\circ C$.

**Figure 4.6:** TEM of $SnO_2$ powder synthesized at $5^\circ C$ and sintered at $800^\circ C$. 
Figure 4.7: TEM of SnO$_2$ powder synthesized at 25°C and sintered at 400°C.

Figure 4.8: TEM of SnO$_2$ powder synthesized at 25°C and sintered at 600°C.
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**Figure 4.9:** TEM of SnO$_2$ powder synthesized at 25°C and sintered at 800°C.

**Figure 4.10:** TEM of SnO$_2$ powder synthesized at 50°C and sintered at 400°C.
Figure 4.11: TEM of \(SnO_2\) powder synthesized at 50\(^\circ\)C and sintered at 600\(^\circ\)C.

Figure 4.12: TEM of \(SnO_2\) powder synthesized at 50\(^\circ\)C and sintered at 800\(^\circ\)C.
4. EFFECT OF TEMPERATURE ON PARTICLE SIZE OF NANOCRYSTALLINE SnO$_2$ DURING SYNTHESIS AND SINTERING

<table>
<thead>
<tr>
<th>Sintering Temp. ($^\circ$C)</th>
<th>Reaction Temp. ($^\circ$C)</th>
<th>Average Particle Size from TEM (nm)</th>
<th>Crystallite Size from Scherrer’s formula (nm)</th>
<th>Optimum Operating Temp. ($^\circ$C)</th>
<th>Sensing Response for ethanol (120 ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>5</td>
<td>$\sim$ 02</td>
<td>3.78</td>
<td>250</td>
<td>14</td>
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<tr>
<td></td>
<td>25</td>
<td>$\sim$ 10</td>
<td>6.67</td>
<td>350</td>
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<td>50</td>
<td>$\sim$ 5</td>
<td>4.42</td>
<td>250</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>600</td>
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<td>22.14</td>
<td>250</td>
<td>4.6</td>
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<tr>
<td></td>
<td>5</td>
<td>$\sim$ 15</td>
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<td>6</td>
</tr>
<tr>
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<td>$\sim$ 32</td>
<td>34.56</td>
<td>350</td>
<td>4</td>
</tr>
</tbody>
</table>

Table 4.1: Comparison between sensing response and crystallite sizes of SnO$_2$ at different synthesis parameters.

per unit volume, $\Delta G_v$, and supersaturation is given by the following equation:

$$\Delta G_v = -\left[\frac{kT}{\Omega}\ln\left(\frac{C}{C_o}\right)\right] = -\left[\frac{kT}{\Omega}\right]\ln(1 + \sigma) \quad (4.1)$$

where $C$ is the concentration of the solute, $C_o$ is the equilibrium concentration or solubility, $k$ is the Boltzmann constant, $T$ is the temperature, $\Omega$ is the atomic volume and $\sigma$ is the supersaturation defined by $(C - C_o)/C_o$ as reported by Cao (2004). Without supersaturation (i.e. $\sigma = 0$), $\Delta G_v$ is zero, and no nucleation would occur. It is clear from the relation that $\Delta G_v$ can be significantly increased by increasing the supersaturation for a system. Now the supersaturation is temperature as well as rate of reaction dependent. At low temperature (5$^\circ$C in present study) a higher supersaturation leads to large reduction in Gibbs free energy. This energy reduction appears as an increased surface energy favouring continued nucleation with smaller sizes. An increased temperature to 25$^\circ$C leads to the increased solubility and hence reduced supersaturation of the solution and as a consequence large size particles were obtained. The high temperature (50$^\circ$C in present study) favours a fast hydrolysis reaction and results in the high super-
saturation, a large $\Delta G_v$, which in turn leads to the formation of a large number of small nuclei.

### 4.4.3 Effect of sintering temperature

Figs 4.4-4.12 represent the TEM images of the prepared $SnO_2$ powders; they clearly indicate the agglomeration and represent the particle size growth under the influence of sintering. The average particle sizes observed at different calcination conditions are given in Table 4.1 Evidently the sintering temperature promotes enlargement of grain boundaries and consequently particle size increases as a function of sintering temperature. Macroscopically, the reduction of total surface energy is the driving force for sintering and microscopically, the differential surface energy of surfaces with different surface curvatures is the true driving force for mass transport during sintering.

### 4.4.4 Sensing Characteristics

Sensors fabricated with synthesized materials were exposed to 120 ppm of ethanol vapours at different temperatures to find out optimum operable temperature (shown in Figures 4.13 to 4.15) are listed in Table 4.1. In general, observations reveal that smaller particles have optimum temperature around $250^\circ C$ and as the particles grow in size and/or agglomerate, the optimum temperature shifts around $350^\circ C$. To study the effect of calcination on the sensing response of the synthesized $SnO_2$ nanoparticles, the fabricated sensors prepared with materials sintered at temperatures mentioned above were tested with fixed volume of the ethanol vapours at optimum operable temperature. The results of sensor response versus time for nanoparticles prepared at 5, 25 and $50^\circ C$ and treated at 400, 600 and $800^\circ C$ are shown in Fig. 4.16. The sensing response of samples prepared by treating at $400^\circ C$ is exceptionally better than the samples treated at 600 and $800^\circ C$. Important point to note is that no catalyst has been incorporated to improve the response of the material.

Three samples in each case were prepared and it was found that their performance was almost identical which ensured that the changes in sensing response were due to particle size variation only and not due to the variability in the fabrication process.
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Figure 4.13: Sensing response of $SnO_2$ nanoparticles synthesized at 5°C and sintered at different temperatures to 120 ppm of ethanol at different operating temperatures.
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![Graph showing sensing response of SnO$_2$ nanoparticles synthesized at 25°C and annealed at different temperatures to 120 ppm of ethanol at different operating temperatures.]

**Figure 4.14:** Sensing response of SnO$_2$ nanoparticles synthesized at 25°C and annealed at different temperatures to 120 ppm of ethanol at different operating temperatures.
Figure 4.15: Sensing response of SnO\textsubscript{2} nanoparticles synthesized at 50\textdegree{}C and annealed at different temperatures to 120 ppm of ethanol at different operating temperatures.
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**Figure 4.16:** Comparative sensing response of $SnO_2$ nanoparticles synthesized at different temperatures to 120 ppm of ethanol.
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The results were found to be reproducible as fabricated sensors were tested at regular intervals for period of 1 year. The comparison between the sensing response and crystallite size of SnO$_2$ at different preparation parameters is given in Table 4.1. Fig. 4.17 represents curve of sensing response versus crystallite sizes. The clear indication of this curve is towards the dependence of sensing response on particle/ crystallite size of the powder. It is quite evident that sensing response decreases as the particle size increases.

![Figure 4.17: Sensor response as a function of crystallite sizes at their optimum operating temperatures (120 ppm ethanol).](image)

The gradual decrease in sensing response is due to the growth of particle sizes. A high surface to volume ratio of nanostructures is believed to be one of the important parameters responsible for enhanced sensing response. As the particle size increases with calcination temperature, the surface to volume ratio decreases and consequently sensor response decreases. Nevertheless nanoparticles of smaller size have larger effective surface area which leads to enhancement in their surface activity. Moreover a large number of small particles can be accommodated on
a unit surface area. These contribute to a large number of active sites onto which gaseous species adsorb to initiate sensing process. Large particles offer less number of such sites because of obvious reasons and consequently are less sensitive.

![Sensing response of SnO$_2$ nanoparticles synthesized at different temperatures to different concentrations of ethanol.](image)

**Figure 4.18**: Sensing response of SnO$_2$ nanoparticles synthesized at different temperatures to different concentrations of ethanol.

Fig.4.17 represents the variation of sensing response of SnO$_2$ nanoparticles of different particle sizes at different concentrations of ethyl alcohol varying from as low as 50 to 1000 ppm. All the sensors were operated at their optimum temperatures, the results indicate the approximately linear responses up to 650 ppm. Above this concentration the slopes of all the curve decrease, indicating another region of linearity with different slope.

It may be mentioned here that we were able to synthesize SnO$_2$ nanoparticles, which were highly sensitive to ethanol vapours without promoters/additives.
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4.5 Conclusion

In this chapter it may be concluded that reaction temperature during synthesis of nanostructures of $SnO_2$ plays significant role in modification of the particle size. Because of moderate supersaturation at room temperature the particles grow larger as compare to those synthesized at low and high temperature due to high supersaturation. The nanoparticle’s size grows with the calcination temperature and consequently sensing response decreases. It is also found that operable temperature of sensors fabricated with small particles is lower than that of large particles. The technique mentioned in this chapter for controlling the particle size is novel and we were successful in modifying the particle sizes.