Chapter 2

A Novel Route towards the Shape Selective Synthesis of SnO$_2$ Nanostructures: Bipyramids, Cubes and Wires

This chapter primarily deals with a novel route for preparing shape selective SnO$_2$ nanostructures like bipyramids, cubes and wires from the same precursors. Detailed characterization using various analytical techniques elucidates the role of various interactions between the nuclei of the building blocks (RuO$_2$ and SnO liquid droplets at the prevailing temperatures). The presence of an inert (carrier) gas and the amount of RuO$_2$ in the initial reaction mixture helps in gaining adequate control over these interactions at well defined temperatures. The shape dependent preferential growth directions observed in SnO$_2$ structures indicates that a control over the growth position and shape could be achieved by changing the initial positions of Ru and its concentration.

2.1. Introduction

The shape and texture of semiconducting oxides has a substantial effect on their optical\(^1\), electrical\(^2\), and gas sensing\(^3\) properties. For example, several anisotropic semiconducting nanostructures have been prepared in the form of nanowire superlattices (group III-V and group IV materials). Further, photoluminescence, electrical transport and electroluminescence measurements of single-nanowire show the unique photonic and electronic properties of these superlattices, suggesting potential applications ranging from nano-barcodes to polarized nanoscale LEDs.\(^4\) These architectures display new properties and enrich the selection of nano-building blocks for electrical, optical, and sensing device construction.\(^5\) Hence an accurate control over the particle size and shape offers new application possibilities facilitating to enmesh desired characteristics in next generation materials. Tin oxide, as a wide band gap semiconducting oxide attracts an awesome interest due to its distinctive electrical, optical and thermal properties. Two unique characteristics, i.e., the variation in valence state and oxygen vacancy make tin oxide indispensable for a variety of applications including many smart and functional devices. Consequently, in a short span of last few years, various forms of tin oxide namely microwires\(^6\), nanowires\(^7\), nanotubes\(^8\), nanobelts\(^9\), and nanodiskettes\(^10\), have been synthesized using diverse techniques of thermal evaporation, laser ablation, carbothermal reduction, solution precursor route, etc. All these studies clearly show that reduced dimensionality causes a radical change in the density of states highlighting the prominence of surface effects. Besides size and shape dependent behavior, the doping of these materials preserving the structural integrity, can also provide a far more favorable means of tailoring their properties due to their aspect ratio induced changes in the electronic structure. Doping is particularly significant in the field of electronics as illustrated in examples, like the one for constructing the contacts whose conductivity can be tailored by controlling the level of doping. Moreover, new functionality, such as emissive or rectifying junctions, can also be introduced into the nanostructure by anisotropic growth with compositional variations.\(^5\) Thus, specific shape of the particles and the asymmetric interaction patterns on their surface could induce orientation specific exchanges at lower dimensions.
Among the various methods adopted for the synthesis of SnO$_2$ nanostructures, thermal vapor method is the widely exploited as it offers various advantages like low reaction time below 1h and the precise control of geometry of the materials by a simple control over the reaction parameters viz. heating temperature and duration, nature of substrate, carrier gas and oxygen flow rate.Usually, nanostructured growth takes place via a self-catalytic process in which the precision, prediction and reproducibility all emerge from the nature of forces between the constituent elements. The method based on the vaporization of oxide materials at high temperature requires a complex apparatus with good vacuum, precise control of temperature and gas flow and the products are generally collected at the downstream end onto a substrate or at the inner wall of alumina or quartz tube.

Because of its unique change in conductance upon the adsorption of gases, tin oxide, a wide band gap semiconductor (3.6 eV) is a promising candidate towards miniaturized, ultrasensitive chemical sensors. The characteristics of tin oxide like the presence of cations with mixed valences and adjustable oxygen deficiency enables tuning of their structure and properties. For example Meyyappan et al. have shown the synthesis of In-doped tin oxide nanowires using a carbothermal reduction followed by a catalyst mediated heteroepitaxial growth. The doping or compositional changes in nanowires can be controlled by pre-evaporation in a way similar to that in metalorganic chemical vapor deposition (MOCVD). Although several other procedures for synthesizing pristine nanowires have been recently demonstrated, the preparation of doped SnO$_2$ has not been reported so far, despite its tremendous significance in nanotechnology.

In this chapter, we describe a simple synthetic procedure for the shape selective preparation of several dissimilar types of tin oxide structures including bipyramids (a double tetrahedron with a common plane, which is a natural habitat of rutile RuO$_2$ and SnO$_2$), cubes and wires using chemical vapor deposition employing RuO$_2$ as a promoter/nucleating agent. In order to understand the growth kinetics and to explore intellectual terra incognita further, we had carried out X-ray diffraction (XRD), Thermogravimetric/differential thermometric analysis (TG-DTA) and x-ray photoelectron spectroscopy (XPS) of these low dimensional structures. The results of these
investigations are presented below with the help of a plausible model describing the growth mechanism. In particular, the texture coefficient values of all the structures, indexed to a tetragonal lattice, exhibit amazing variation in the preferred orientation with respect to their shapes. Although, XPS data indicate that wires and cubes have a strong SnO₂ type signal, bipyramids interestingly exhibit both SnO and SnO₂ signals and a correlation of the binding energy helps in understanding the growth kinetics of such submicron structures. More significantly, the results suggest that the bipyramids are formed due to the vapor-solid process (VS) while wires and cubes are formed by the vapor-liquid-solid (VLS) progression. In addition, the present study indicates the key role of RuO₂ as an important nucleating agent in promoting the growth of low dimensional structures of SnO₂.

2.2. Experimental Section

2.2.1. Materials

Tin (II) oxide and Ruthenium oxide were used as received from the Aldrich (99.99%), while acetone and ethanol (AR grade from Merck) were used after further purification; deionised water (16 MΩ) from Milli-Q system was used for all experiments.

2.2.2. Experimental Set-Up

Scheme 2.1 shows the experimental set-up used for the synthesis of nanowires and nanobipyramids. It consists of a tubular furnace open at one end, in which the starting material, a mixture of SnO and RuO₂ in a weight ratio of 1:0.2 was kept in the middle of the furnace. Ar was passed continuously at a flow rate of 100 ± 5 sccm (standard cubic centimeter) through the furnace upto 950°C. The material was heated for two hours and the furnace was allowed to cool naturally with uninterrupted Ar flow. The cubes and nanowires were grown on an alumina boat kept in the middle of the furnace while a nanobipyramidal structure was collected on the alumina substrates kept near the end of tube where the temperature was between 200°C and 500°C.
2.3. Structural and morphological characterization

2.3.1 X-ray diffraction

XRD was carried out on a Rigaku, D/Max IIIIB diffractometer using Cu-Kα radiation from a rotating anode x-ray generator operating at 30 kV and 15 mA at room temperature. Diffraction patterns were collected at a step of 0.02° (2θ) using a fixed Cu-Kα radiation. The background was subtracted with the linear interpolation method.

The preferred orientation of the crystallographic planes was estimated by performing the Harris analysis\textsuperscript{18}. The texture coefficient $P(hkli)$ and the preferred orientation of the $(hkli)$ planes were conferred by the following relationship,

$$P(hkli) = \frac{I(hkli)}{I_0(hkli)} \left\{ \frac{1}{n} \sum I(hkli)/I_0(hkli) \right\}^{-1}$$  \hspace{1cm} (1)

for $i = 1, 2, 3... n.$

where, $I(hkli)$ is the diffraction intensity of the $(hkli)$ plane of the sample under investigation, $I_0(hkli)$ is the intensity of the $(hkli)$ plane of the standard sample and 'n' is the number of reflections present.
2.3.2. Scanning electron microscopy (SEM) and Energy dispersive X-ray analysis (EDAX)

The surface morphology was characterized by a Lieca Stereoscan 440 model SEM with a Kevex model EDAX system. For comparative studies, the energy of the electron beam was kept constant while analyzing all the samples. The micrographs of the samples were recorded with a 20 kV electrical high tension and 25 pA camera attached on the high-resolution recording unit.

2.3.3. High-resolution transmission electron microscopy (HRTEM)

TEM images were taken with a JEOL Model 1200 EX instrument equipped with a field emission gun at an accelerating voltage of 200 kV, magnification 389,000× and the coefficient of spherical aberration 1.35 mm. As the nanowires were large, they could be picked up on a Cu grid directly by sliding over the “as-deposited” wires. The images were digitized in the size of 256 × 256 pixels with a pixel size of 0.03994 nm and thus atomically resolved images were possible. Images were stored in the computer after digitization and power spectra were calculated so that structural analysis such as interplanar distances, angle between planes could be determined.

2.3.4. X-ray photoelectron spectroscopy (XPS)

XPS measurements were carried out on a VG MicroTech ESCA 3000 instrument at a pressure of >1 × 10^{-9} Torr (pass energy of 50 eV, electron takeoff angle 60°, and overall resolution ~1 eV using monochromatic Mg Ka (source, hν = 1253.6 eV). The core level spectra of the C 1s and S 2p orbitals were recorded with an overall instrumental resolution of ~1 eV. The alignment of binding energy (BE) was carried out using Au 4f BE of 84 eV as the reference. The X-ray flux (power 70 W) was kept deliberately low to reduce the beam-induced damage. The Spectra were fitted using a combined polynomial and Shirley type background function.\textsuperscript{19, 20}

2.3.5. Thermogravimetric and differential thermal analysis (TG-DTA)

TG-DTA was carried out in the temperature range 323-1173 K under N\textsubscript{2} flow at a heating rate of 5 K/min on a Perkin-Elmer thermal analyzer.
2.4. Results and Discussion

2.4.1. Shape Selective Synthesis: Bipyramids, Cubes and Wires

2.4.1. Bipyramids

SnO$_2$ in the cassiterite phase belongs to the P4$_2$/mnm space group and has a ditetragonal bipyramid type of symmetry. The number of macrocrystal habits observed is approximately $10^{14}$. Figure 2.1 shows typical micrographs of RuO$_2$ doped SnO$_2$ nanobipyramidal structures, which also reveal their natural habitat. Upon heating the reaction mixture (RuO$_2$: SnO) containing 0.1 wt. fraction of RuO$_2$ at 950°C for 2h, nanobipyramids are deposited on the alumina substrates that are kept in the temperature range of 200-500°C (Figure 2.1 a-g). No other structure is interestingly found in this region implying high shape selectivity of the process. Interestingly, two types of bipyramids are observed, one where the pyramid ends with a tip and the other where a small separation is present between the two opposite triangular planes, suggesting a deviation from the perfect square geometry to be a nearly rectangular one. The bipyramids are polydispersed with size varying between 100 and 800 nm. Although most of them are located flat with another end at the backside, base of the bipyramid is thin with varied dimensions suggesting the growth process to be initiated from the base, from both sides and growing further, leading to a pyramid like geometry at the end. Some of them lie in different orientations as shown in Figure 2.1f, confirming the bipyramidal nature of the structures. The TEM analysis further confirms that the bipyramids are not monodispersed in nature. Steps at the edge of the structure suggest the growth mechanism to be starting from the edge of cubical structure that is formed prior to the bipyramidal structure. Selected area electron diffraction (SAED) exhibits a kikuchi pattern that can be attributed to the uneven thickness of the structure and the orientation being not parallel to the incident beam. This is, perhaps, due to the electrons that are first scattered inelastically and then elastically from a thick crystalline sample, forming a system of kikuchi lines.
As explained in section 1.5.1, the rutile structure of pure SnO₂ is 6:3 coordinated and the bonding between atoms has a relatively strong ionic character. The tetragonal unit cell contains two Sn and four O atoms. Perpendicular to the surface in the [110] direction, the rutile structure is built up from neutral stacked layers of three alternating planes (O), (2Sn+2O), and (O) with nominal ionic charges of 2-, 4+ and 2- respectively in the surface unit cell. The termination of the SnO₂ (110) called a stoichiometric surface with these three planes is possible. Removal of the topmost bridging-oxygen atom results in the reduced (110) surface, which is the case in the nanobipyramidal structure.

2.4.2. Cubes

In case of samples with a low wt. % of RuO₂ in the starting material, non-uniform cubical structures are grown on the substrate containing the reaction mixture (Figure 2.2). However, with an increase in the RuO₂ percentage in the starting material, the cubes get...
slowly transformed into nanowires implying Ru playing a crucial role as a promoter for 1D growth of SnO₂ nanowires. Two types of cubes are observed (RuO₂ - 1wt %), one with similar upper and lower surface having dimensions of \(a = b = 10-20 \mu m\) and \(c = 1-3 \mu m\) and detailed analysis suggests that the cubes are porous in nature with a diffused boundary. Moreover, the extent of porosity varies from cube to cube that can be attributed to the non-homogeneity of RuO₂ in the starting material. Further, the cubical edges are likely to be formed first, followed by there filling to give a complete cubical morphology. The other cubical structure has one surface slightly shorter than the opposite surface, called a biscuit shape, which in the present case accounts nearly 10% of total structures. Interestingly, no such structure formation is observed when experiments are carried out under similar conditions with pure SnO and RuO₂ alone, which further confirms the role of RuO₂ as a nucleating aid.

Figure 2.2. SEM images of SnO₂ cubes synthesized at 950°C with 1 wt.% of RuO₂ in the reaction mixture; (a-d) show general images while (e and f) reveal biscuit shape.

2.4.3. Wires

Figure 2.3 shows typical images of the "as-synthesized nanowires" formed by heating the reaction mixture containing 20 wt. % RuO₂. Most of the wires appear rather straight, exhibiting smooth sidewalls and detailed examination shows that the wires have
diameter between 100-900 nm and length of the order of <1 mm, indicating an aspect ratio of ~1000 (Figure 2.3b). This large length of the wire is particularly significant in the field of electronics for making the contacts whose conductivity can be tailored by controlling the level of doping. It is also seen that some of the wires are transformed to a highly porous structure consisting of interconnected nanocrystallites (~5 nm diameter) due to the incomplete 1D growth, further supporting the role of Ru as a nucleating agent (Figure 2.3c). As these nanowires are large, they can be easily picked up on a Cu grid directly by sliding over the 'as-synthesized' wires on alumina substrates. Figure 2.3d shows the TEM image of RuO$_2$ doped SnO$_2$ nanowires. The wires are not, however, monodispersed in nature with diameter varying between 100-900 nm. A liquid droplet equilibrated with the RuO$_2$ and SnO$_2$ vapors is likely to form first under the reaction conditions directing the growth of SnO$_2$ into nanowires. Figure 2.3f shows the SAED and most of the wires exhibit a kikuchi pattern like that of the nanobipyramid structure implying the higher crystallinity.

![Figure 2.3](image)

Figure 2.3. Morphology of as-synthesized nanowires; formed by heating the reaction mixture containing 20 wt. % RuO$_2$ (a) photograph, (b and c) SEM images and (d) TEM images of nanowires; (e) the rounded tip is clearly seen in the TEM image of a single wire; (f) SAED pattern of a single wire of diameter 300 nm.
2.5. Structural and morphological characterization

Figure 2.4 depicts the XRD patterns of different forms of SnO$_2$ nanostructures along with the commercial SnO$_2$ (Aldrich 99.99%) powder. The presence of characteristic SnO$_2$ peaks, indexed to a tetragonal lattice, without any RuO$_2$ or mixed oxide, indicates single-phase formation. One peak corresponding to Al (200) can also be identified which is attributed to the aluminium sample holder used in XRD system. A comparison of the relative intensities of samples with their standard values indicates the existence of a shape dependent preferential growth in different planes. Interestingly, in bipyramids, cubes and wires, the preferential growths are in (101), (110) and (211) crystal directions respectively. (Table 2.1) We propose that such different shapes are triggered by the presence of RuO$_2$ along with metallic tin droplets acting together as nucleating aids. When all the SnO grains initially are embedded in RuO$_2$, the growth is supposed to trigger through a liquid droplet at those prevailing temperature (>500 °C). This liquid droplet is composed of higher RuO$_2$ and lower SnO concentrations, and is likely to generate the reaction conditions directing the growth of SnO into wires, cubes and bipyramids.

![XRD patterns](image)

Figure 2.4. XRD patterns of different forms of SnO$_2$ (a) bipyramids, (b) wires, (c) cubes and (d) commercial SnO$_2$ (Aldrich 99.99%) powder exhibiting single-phase formation.
Table 2.1. The texture coefficient values for the different structures calculated using Harris analysis (equation 1)

<table>
<thead>
<tr>
<th>Sr. No</th>
<th>Planes</th>
<th>Texture Coefficient value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Wires</td>
</tr>
<tr>
<td>1</td>
<td>(110)</td>
<td>1.807</td>
</tr>
<tr>
<td>2</td>
<td>(101)</td>
<td>2.305</td>
</tr>
<tr>
<td>3</td>
<td>(200)</td>
<td>0.681</td>
</tr>
<tr>
<td>4</td>
<td>(211)</td>
<td>2.619</td>
</tr>
</tbody>
</table>

The lattice constants (Table 2.2) of all these interesting structures are further determined to understand the strain dependent properties. As depicted in Table 2.2, larger lattice parameters are observed for bipyramids ($a = 4.750(3)$ Å and $c = 3.199(3)$ Å) as compared to that of commercial SnO$_2$ powder ($a = 4.730(1)$ Å, $c = 3.183(1)$ Å) although, no marked variation in the lattice parameters, interestingly, is observed for cubes and wires. The unit cell volume for the structures as revealed in Table 2.2 shows that for wires and cubes there is no dramatic variation while for bipyramids an increase in the cell volume by 1.3 % is observed. The $a/c$ ratio, which is a measure of lattice distortion, does not show any effective variation implying the stability of the structures.

Table 2.2. Values of lattice constant, $a$ (Å) and $c$ (Å), $a/c$ ratio, crystallite size (nm) calculated using the Scherer equation; the cell volume ($\text{Å}^3$) is also indicated in the last column.

<table>
<thead>
<tr>
<th>Sr. No</th>
<th>Lattice Parameters</th>
<th>Bipyramids</th>
<th>Wires</th>
<th>Cubes</th>
<th>SnO$_2$-aldrich</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$a$ (Å)</td>
<td>4.750(3)</td>
<td>4.728(3)</td>
<td>4.733(1)</td>
<td>4.730(1)</td>
</tr>
<tr>
<td>2</td>
<td>$c$ (Å)</td>
<td>3.199(3)</td>
<td>3.183(3)</td>
<td>3.181(1)</td>
<td>3.183(1)</td>
</tr>
<tr>
<td>3</td>
<td>$V$ (Å$^3$)</td>
<td>72.2(1)</td>
<td>71.1(1)</td>
<td>71.29(4)</td>
<td>71.23(3)</td>
</tr>
<tr>
<td>4</td>
<td>$a/c$ ratio</td>
<td>1.484</td>
<td>1.485</td>
<td>1.487</td>
<td>1.486</td>
</tr>
<tr>
<td>5</td>
<td>Crystallite size (nm)</td>
<td>50.26</td>
<td>46.94</td>
<td>62.80</td>
<td>57.1</td>
</tr>
<tr>
<td>6</td>
<td>Uniform strain (110)</td>
<td>$6.08 \times 10^{-3}$</td>
<td>$-7.75 \times 10^{-3}$</td>
<td>$3.08 \times 10^{-3}$</td>
<td>-</td>
</tr>
</tbody>
</table>

Analysis of the effect of dopant molecule on the electronic state of host material is of particular importance to understand the growth kinetics and hence XPS studies were carried out on all these structures. Accordingly, Figure 2.5 shows the deconvoluted
C1s peaks for all the structures of SnO₂. In all the cases representing XP spectra, the hollow circles denote the original data and solid lines represent the fitted curves and the deconvoluted individual peaks of different species present in the sample. All the binding energy positions of the elements are listed in Table 2.3. For commercial SnO₂, the spectrum can be deconvoluted into three peaks at 285, 286.9 and 289.1 eV corresponding to C1s, and adsorbed carbon species respectively. No signal corresponding to Ru is observed for commercial SnO₂ and cube samples, while for wires and bipyramids the peaks at 282.0 and 282.8 eV respectively confirm the presence of Ru in the submicron structures. These peaks can be attributed to the thermodynamically stable oxide i.e., RuO₂, signifying the binding energy of Ru 3d₅/₂ corresponding to Ru⁴⁺.²¹

Figure 2.5. The deconvoluted C1s peaks for all the structures of tin oxide (a) commercial SnO₂ (Aldrich 99.99%) powder, (b) wires, (c) cubes and (d) bipyramids.
Table 2.3. All the binding energy positions of the element present in different submicron structures of tin oxide.

<table>
<thead>
<tr>
<th>Species</th>
<th>BE (eV)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>SnO$_2$-Aldrich</td>
</tr>
<tr>
<td>C1s</td>
<td>285</td>
</tr>
<tr>
<td></td>
<td>286.9</td>
</tr>
<tr>
<td></td>
<td>289.1</td>
</tr>
<tr>
<td>Ru 3d</td>
<td>-</td>
</tr>
<tr>
<td>Sn 3d</td>
<td>486.6</td>
</tr>
<tr>
<td></td>
<td>495.1</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>O 1s</td>
<td>530.7</td>
</tr>
<tr>
<td></td>
<td>532.5</td>
</tr>
<tr>
<td></td>
<td>(minor)</td>
</tr>
</tbody>
</table>

Figure 2.6 shows separate Sn3d$_{5/2}$ and Sn3d$_{3/2}$ signals for the Sn present in these structures. Commercial SnO$_2$, freshly prepared wires and cubes all exhibit two prominent peaks with a symmetric Voigt profile corresponding to the binding energies of Sn3d$_{5/2}$ and Sn3d$_{3/2}$ respectively. However, the presence of Sn$^{2+}$ cannot be ruled out because the energy of Sn3d$_{5/2}$ for SnO is very close to that for SnO$_2$ (0.7 eV). The peak to peak separation of Sn 3d peaks for commercial SnO$_2$ is 8.48 eV while for wires and cubes, this amount to 8.48 and 8.79 eV respectively. For the bipyramids, four peaks at the BE of 484.5, 487.3, 493.5 and 496.6 eV are observed corresponding to metallic Sn and SnO$_2$ 3d levels respectively. The binding energy difference between the Sn$^{4+}$ and Sn$^0$ is 2.2 eV as in accordance with the literature values. The broadening on the higher binding energy side of the peak can be attributed to the doping effect.
Figure 2.6. The separate Sn3d\textsubscript{5/2} and Sn3d\textsubscript{3/2} signals for Sn in (a) cubes, (b) commercial SnO\textsubscript{2} (Aldrich 99.99\%) powder (c) wires and (d) bipyramids.

Figure 2.7 depicts the spectra for O1s signal. For the commercial SnO\textsubscript{2}, freshly prepared wires and cubes, the O1s major peak maxima occurs at BE of 530.7, 530.3 and 530.5 eV respectively and are attributed to the lattice oxygen in the SnO\textsubscript{2} crystal structure.\textsuperscript{23} The existence of other minor peaks can be attributed to the adsorbed oxygen species. In case of bipyramids, the broad peak can be deconvoluted into three peaks at BE of 529.6, 532.1 and 534.0 eV corresponding to the oxygen of RuO\textsubscript{2}, SnO\textsubscript{2} lattice and the adsorbed oxygen respectively. Analysis of the difference between the energies of the Sn3d\textsubscript{5/2} (E\textsubscript{1}) and O1s (E\textsubscript{2}) electronic levels characterizing the Sn-O bond energy suggests that the incorporation of Ru in the SnO\textsubscript{2} matrix does not cause any noticeable change in the \(\Delta E\) value for wires and cubes. In contrast, for bipyramids the change in the \(\Delta E\) value is 0.9 eV as compared to that of commercial SnO\textsubscript{2}, suggesting that Ru species in the bipyramidal structures alter the Sn-O bond energy. This is in accordance with the results of Rumyantseva et al., where they have observed a shift in \(\Delta E\) when Ru is present in 1.1-1.2 at. \%, thus further confirming the incorporation of Ru\textsuperscript{4+} into the Sn\textsuperscript{4+} positions changing the Sn-O bond energy.\textsuperscript{22} Moreover, RuO\textsubscript{2} evaporates at low temperature compared with the SnO and hence during the synthesis of bipyramids, vapors are likely to have excess of RuO\textsubscript{2} which are relocated through the carrier gas to the substrates kept downwards. Consequently, the substrate is left with lower concentration of Ru on its surface that acts as nucleating centers for the growth of wires and cubes. Thus, RuO\textsubscript{2} in its initial position acts as nucleating centers for the anisotropic growth that continues due to the self-catalyzed growth process in Sn-O system.

\textit{University of Pune, Feb 2006}
Moreover, the values of the relative intensity of adsorbed oxygen are dependent on the grain size - smaller the grain size is, higher is the intensity of the adsorbed oxygen peak. Thus a comparison of the relative adsorbed oxygen peak intensities of all the structures suggests that the grain size decreases from cubes to bipyramids to wires further supporting the conclusions derived from the XRD results.

![Figure 2.7. The spectra for O1s for different forms of SnO2 (a) commercial SnO2 (Aldrich 99.99%) powder, (b) wires, (c) cubes and (d) bipyramids.](image)

**2.6. Effect of reaction composition, temperature, time and carrier gas**

In order to understand the role of RuO₂, further experiments were carried out with and without different weight percentage of RuO₂ in the starting material. The presence of RuO₂ in the reaction mixture leads to the transformation of cubical structure into deformed porous structure. With increase in RuO₂ percentage, there is an increase in the number of nucleating sites leading to the formation of small nanobelts or nanowires with smaller aspect ratios. The deformity in cubical structure, nanowire percentage and their aspect ratio, all are found to increase with the amount of Ru content. At higher weight percentage (2 wt%), nearly 80% of material contains nanowire with few cubes.
and small irregular shaped granules. With further increase upto 2.2 wt% the total yield of nanowires is increased to 90%.

Further, to understand the effect of temperature on nanowire growth kinetics, several experiments were designed and performed with the optimized reaction mixture (2.2 wt%, RuO$_2$). Accordingly, Figure 2.8 shows the SEM images of these samples prepared at different temperatures from 800-950°C for 2 h. Remarkably, only cubes are observed for temperatures as low as 800°C, identical to the products obtained when pure SnO is heated at 1150°C, thus supporting our assertion of the role of RuO$_2$ as a promoter for growth. As the temperature increases from 800°C, some nanowires with no smooth sidewalls along with cubes are formed indicating incomplete oxidation. With a further increase in temperature, both yield of nanowires and their aspect ratio are found to improve. For example, at a temperature of 950°C, nearly 90% of all the samples are in the form of nanowires, implying this temperature to be optimum for nanowire formation. It is interesting to note that the results obtained both by increasing the amount of RuO$_2$ and the temperature variation are identical pointing out to the optimum temperature of 950°C and with 2.2 wt% RuO$_2$. These results clearly demonstrate the importance of temperature and the amount of RuO$_2$ in the reaction mixture, as crucial factors, which govern the final shape, aspect ratio and yield.

Figure 2.8. SEM images of sample prepared with 2.2 wt% RuO$_2$ in SnO heated at different temperature (a, b) 800 (c, d) 850 (e-g) 900 and (h) 950°C.
Additional experiments carried out for different time intervals with the above reaction mixture provide further insight into the growth mechanism and these results are in accordance with the results obtained by varying the temperature and RuO$_2$ content. For example, when the reaction is deliberately stopped after five minutes, only the deformed cube like geometry is observed as shown in figure 2.9 while an increase in the duration enhances the amount of nanowires. In addition, the quality as well as the aspect ratio increases leading to a complete nanowire growth by the end of 2 h. During the initial growth, grains of about 100-250 nm are first formed, which attach to themselves forming a long chain of interconnected structure. Subsequently, more number of grains coalesces with time to form a nanowire with a higher aspect ratio and the number of grains taking part in the nanowire formation decides the final shape and the aspect ratio.

![Figure 2.9](image)

Figure 2.9. SEM images of samples prepared with 2.2 wt% RuO$_2$ in SnO heated at 950°C for different time interval (a) 5 min, (b) 30 min, (c) 60 min, (d, e) 90 min and (f) 120 min.

After optimizing the reaction composition, temperature and time, we proceeded further to study the effect of carrier gas. Figure 2.10 shows the SEM images of samples heated in different environments of N$_2$ and O$_2$ by keeping all the other process parameters identical. Interestingly, only cubical structures are formed in O$_2$ environment although structures are somewhat distorted with plenty of non-uniformity in shapes implying the importance of Ar environment during the nanowire formation. However for the case of N$_2$ as a carrier gas, nanowires are formed along with distorted cubes,
although the yield of total nanowire is 10%, which is still small compared to the case of synthesis under Ar. This shows that removal of $O_2$ by Ar to cause negligible oxygen partial pressure plays a very crucial role in deciding the yield and quality of the nanowires.

![SEM images](image)

Figure 2.10. SEM images of sample prepared with 2.2 wt% RuO$_2$ in SnO heated in different environment of (a-b) $O_2$ and (c-d) $N_2$. From the images it is clear that the yield of wires using both $O_2$ and $N_2$ is less as compared with Ar.

### 2.7. A Plausible Growth mechanism

In order to understand the growth kinetics, SEM images (figure 2.11(a-d)) were taken at different areas on the surface of the "as-synthesized" nanowires. At the edge of the substrate as shown in Figure b, c and d, a large number of nanowires are found to grow on a single wire resembling a fractal growth common in nature. Initially all the SnO grains are assumed to be covered from all sides by RuO$_2$ and the growth is supposed to take place through a liquid droplet composed of more of RuO$_2$ and less of SnO vapors, which is likely to form first under the reaction conditions directing the growth of SnO into nanowires. The oxygen partial pressure is sufficient for the formation of SnO$_2$. When the length of the wire grown is sufficiently high, it breaks off from the central main wire, which is supported by figures c and d (taken from different distances from the periphery, approaching towards the center). In the central region, no branched network is observed and interestingly all the nanowires exhibit smooth edge and appear rather straight. Thus
the growth process is assumed to be initiated at all points as indicated by the traces of branched network appearing at the end. This signifies the important role of Ru as a nucleating aid during the formation of nanostructures.

![SEM images of SnO$_2$ nanowires](image)

Figure 2.11. SEM images of SnO$_2$ nanowires (a-d) taken at different distances from the periphery approaching the center of alumina substrate.

In order to further understand the role of RuO$_2$, we have carried out TG-DTA of these structures. Figure 2.12 depicts the thermal profiles of reaction mixtures, pure SnO and RuO$_2$ under Ar environment. Their SEM images taken immediately after TGA are also shown in order to correlate the morphology with weight loss. A gradual weight loss of 2.7 % upto 510 °C is observed for pure SnO, which could be attributed to the formation of metallic tin droplets by the disproportion reaction,

$$2\text{SnO} \rightarrow 2\text{Sn} + \text{O}_2 \quad -(2)$$

This is followed by a 7% increase in the mass upto 900 °C, owing to oxygen uptake and the formation of SnO$_2$ as per the equation:

$$\text{Sn} + \text{O}_2 \rightarrow \text{SnO}_2 \quad -(3)$$
In comparison, a total weight loss of 10% is seen for pure RuO$_2$, which could be attributed to the following reaction,

$$3\text{RuO}_2 \rightarrow \text{Ru}_3\text{O}_4 + \text{O}_2$$  \hspace{1cm} \text{(4)}

For the reaction mixture containing SnO and RuO$_2$, however, a weight loss of 1.4 % upto 520 °C (equation (2) and (4)) is observed followed by an increase in weight of about 2 % upto 800 °C. Thus the overall reaction could be expressed as

$$\text{Sn} + 3\text{RuO}_2 \rightarrow \text{Ru}_3\text{O}_4 + \text{SnO}_2$$  \hspace{1cm} \text{(5)}

The appearance of maximum at 800°C suggests the predominance of equation (4) as compared with equation (2). Thus it can be considered that metallic tin droplets are formed along with Ru$_3$O$_4$ inside the reaction chamber and at high temperature (900 °C) and low oxygen partial pressure, which serve as both catalyst and active sites for SnO$_2$ vapor adsorption and subsequent SnO$_2$ deposition with a concomitant Ru incorporation into the structure. The DTG analysis as depicted in Figure 2.12 (b) shows two peaks for pure SnO at 435 °C and 487 °C respectively, which correspond to the points of maximum slope on TG curves upto 561 °C, where the rate of weight change is minimum. The RuO$_2$ sample shows a peak around 210 °C while the reaction mixture exhibits two peaks centered at 302 °C and 465°C respectively. The SEM images taken after the TG-DTG studies for pure RuO$_2$ do not show any distinct morphological features except a large number of irregular shaped particles (Figure 2.12 (c)), although in the case of pure SnO only cubical structures are observed (Figure 12 (d, e)). In contrast, cubes with bipyramid like (Figure 2.12 (f, g)) feature and rod like geometry within (Figure 2.12 (h, i)), are observed for the reaction mixture further indicating that the bipyramid and rod structures are likely to be formed from the onset. However, being a static system, these structures grow further to attain cubical morphology along with traces of persisting bipyramids and wires. Our studies further demonstrate the significance of the amount and distribution of RuO$_2$ in the reaction mixture governing the shape selectivity during the growth process.
Figure 2.12. (a) TGA- (b) DTA curves for the reaction mixture of SnO and RuO$_2$, pure SnO and RuO$_2$ under Ar environment. The SEM images of (c) Pure RuO$_2$, (d-e) pure SnO and the reaction mixture, showing (f-g) pyramid like and (h-i) wire like geometry taken immediately after TGA-DTG studies.

Based on the above experimental results we suggest a possible model for the growth, where atomic clusters i.e. aggregates of atoms and/or molecules are in the size range from a few to thousands of the components. Their structural and electronic properties bear no resemblance either to the atoms they are composed of, or to solids or structures they can eventually grow. The growth mechanism of 1D SnO$_2$ structures prepared by thermal evaporation is very well described by the vapor-liquid-solid (VLS) model. It is assumed that metallic tin droplets act as catalysts as well as active sites for SnO$_2$ vapor adsorption and subsequent growth-deposition as confirmed by the presence of spherical particles at the tip of these structures (Figure 2.13). Initially all the SnO grains are assumed to be embedded in the RuO$_2$ and the growth process gets initiated via the evaporation of a liquid droplet comprising higher concentration of RuO$_2$ and lower SnO. SnO$_2$ and RuO$_2$ both have natural habitats of octahedral and bitetragonal symmetries, and hence the vapors are most likely to be condensed in the bipyramidal form. In addition, the fraction of RuO$_2$ still residing on the substrate, acts as a
structure-directing agent, initiating the wire growth, which is sustained by the self-catalyzed growth process. (Scheme 2.2, Figure 2.14.) The carrier gas, Ar, carries the bipyramids to the substrates kept downward stream, where the temperature varies between 200 - 500 °C. With a negligible amount of RuO₂ (6 wt. %) in the reaction mixture, the appearance of biscuit shaped cube suggests that the growth is initiated by the slow evaporation, perhaps directed upwards. As RuO₂ has higher vapor pressure the lower concentration residing on the surface is insufficient for wire formation and hence gives favorable conditions for cubical form. The sharp edge to the cubical structure is given by the wires. Thus the results propose that the bipyramids are formed due to the vapor-solid process (VS) while wires and cubes are formed due to the vapor-liquid-solid (VLS) process. The change in the flow rate does not have a noticeable effect on the morphology of cubes or wires. On the other hand, experiments carried out with different amount of RuO₂ in the reaction mixture clearly indicate that the yield of wire increases with RuO₂ content along with a decrease in the extent of cubical structures.

Figure 2.13. TEM image of a single wire, the spherical tip of which confirms the growth mode belonging to vapor-liquid-solid process.
Figure 2.14. SEM images of sample prepared with 2.2 wt% RuO$_2$ in SnO, illustrating the steps involved in the growth processes. A single wire, on which different wires protrude out confirming the initiation of growth in all possible directions, is clearly indicated. Black circle: Stacking of cubical structures to give wires; white circle: simultaneous growth of four wires with traces of octahedral crystals.

Scheme 2.2. Schematic illustration of the growth of bipyramids along with cubes (1 (a-c)) and wires (2 (a-c)). (1a) Evaporation of the SnO and RuO$_2$ atoms at high temperature and the formation of bipyramids, (1b) Scarcity of RuO$_2$ lead to the insufficient growth of wires with low
ambient pressure, and the main mechanism of cube growth is absorption. (1c) Formation of cubes whose envelop is given by the wires that are formed.

(2a) Evaporation of the SnO and RuO$_2$ atoms at high temperature and the formation of bipyramids. (2b) Bipyramids are taken away by the carrier gas to the substrates kept downwards and the initial growth of wires. (2c) When the ambient pressure is high, wires grow up mainly by the coalescence mechanism due to the high probability of collisions among droplet, growth process is continued further by the self catalyzed mechanism, bipyramids percentage on the surface decreases as mostly they are carried away to the substrates kept downstream.

The growth mechanism of 1D SnO$_2$ nanostructures prepared by thermal evaporation is very well described by the vapor-liquid-solid model. It is assumed that the tiny liquid metallic tin droplet acts as a catalyst as well as the active site for the SnO$_2$ vapor adsorption and subsequent deposition. The presence of spherical particles at the tip of nanostructures [tip growth mechanism] confirms the process and RuO$_2$ is assumed to play a crucial role for nucleating the nanostructure formation. With a negligible amount of RuO$_2$ in the reaction mixture, the appearance of biscuit shaped cube suggests that the growth is initiated by slow evaporation directed upwards. However, with the increase in RuO$_2$ percentage the cubes appear to be more porous and deformed further supporting the process. Initially all the SnO grains are assumed to be covered from all side by the RuO$_2$ and the growth is supposed to take place through a liquid droplet composed of more RuO$_2$ and less of SnO vapors, which is likely to form first under the reaction conditions directing the growth of SnO into nanowires. The oxygen partial pressure is sufficient for the formation of SnO$_2$. While in case of nanobipyramids the evaporation of RuO$_2$ leads to the lifting of smaller cubical structures although growth process is still in progress, leading to the formation of tip on either side resulting in a pyramid like appearance. These structures are carried by the Ar present in the system to the substrates. The randomness in the size and the orientation suggests that each nanobipyramids is isolated, formed separately and is carried away by the carrier gas. Experiments carried out with different composition of RuO$_2$ in the reaction mixture indicate that the nanowire percentage increases with increase in RuO$_2$. Moreover, it is possible to control the diameter and length of nanowires by varying the RuO$_2$ weight percentage and the duration of heating. The nature of carrier gas also has a strong influence on the yield and aspect ratio of these nanowires.
2.8. Conclusions

In this chapter, we have clearly demonstrated the shape selective synthesis of different forms of submicron sized \( \text{SnO}_2 \) bipyramids, cubes and wires using \( \text{RuO}_2 \) as a unique catalyst during chemical vapor deposition. These forms represent promising candidates for both fundamental studies of low dimensional physics and the applications in various fields like nanoelectronics, nanosensors etc. In addition, the present study indicates the key role of \( \text{RuO}_2 \) as an important nucleating agent in promoting the growth of low dimensional structures of \( \text{SnO}_2 \). Further, the XRD, TGA-DTA and XPS studies elucidate the interactions between the nuclei of the building blocks (\( \text{RuO}_2 \) and \( \text{SnO} \) liquid droplets). The presence of carrier gas and the amount of \( \text{RuO}_2 \) in the initial reaction mixture help in gaining control over these interactions. Such interactions are extremely helpful in understanding, how specific types of reactions are responsible for specific target structures, as demonstrated. Our results further signify that the growth process is governed by the kinetics. Moreover, the shape dependent preferential growth directions observed in \( \text{SnO}_2 \) nanostructures indicates that the control over growth position and shape could be achieved by controlling the initial positions of Ru and its concentration.

The importance of the present synthetic method for nanostructures lies in its selectivity and simplicity, as it neither requires a sophisticated technique nor a rigorous air-sensitive atmosphere. We believe that the present work demonstrates an ability to exert a simple control over the shape of the nanostructures. An understanding of the growth mechanism of these structures is important for both the creation of new materials as well as the fabrication of devices using these structures. Furthermore, the preparation process is easy and cost effective, as the synthesis is carried out in a tubular furnace open at one end, which does not require any controlled atmosphere and instrumentation. Consequently, we believe that this type of study concerning the shape evolution of nanocrystals will be valuable to design and develop advanced nanoscale building-block architectures for valuable applications like chemical sensors, ultracapacitors, nanoelectronic circuits, batteries and fuel cells.
2.9. References


20. The spectras were fitted using the software XPSPEAK4.1 which is available free on website www.uksaf.org/software.html#7.