Chapter 4

Synthesis and Characterization of ZnO Nanostructures*

This chapter primarily deals with the shape selective synthesis of novel nanostructures of ZnO namely multipods, microwires, tetrahedra, micropencils and microhexagonal cones using a modified vapor deposition method. XRD studies indicate that the microwires are (10\overline{1}0) oriented while the multipods show prominent peaks for both (10\overline{1}0) and (10\overline{1}1) miller indices. In comparison, tetrahedra structures show a biphasic mixture of Zinc and zinc oxide. The amount of oxygen in the reactant gas mixture is found to govern the final structure of ZnO. These studies reveal that multipod growth takes place via a screw dislocation mechanism while the tetrahedral and microwires grow possibly via a vapor-liquid-solid progression. Moreover, the geometry and the location of substrate are found to govern the morphology. The Si species present in the form of SiO and SiO$_2$ act as catalysts providing the nucleating sites, whereon the ZnO nanostructures grow. Further, it has been demonstrated that the micropencils grow via a vapor-liquid-solid (VLS) progression while the microhexagonal cones grow in two steps following vapor-solid (VS) and vapor-liquid-solid (VLS) mechanisms respectively.

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4.1. Introduction

Semiconducting oxide nanostructures, with a well-defined geometry and perfect crystallinity are likely to be the model materials for a systematic experimental and theoretical correlation of the fundamental electrical, thermal, optical, and ionic transport processes with dimensionality. Accordingly, ZnO nanostructures have been synthesized in various forms namely tetrapods, nanowires, nanotubes, nanosprings, prisms, etc using several methods, such as pyrolysis, chemical treatment, templated growth, thermal vapor and so on. Of the various methods adopted, thermal vapor method is the widely exploited one as it offers the advantage of low reaction time below 1h with ease of controlling key parameters, namely size, shape and morphology as also illustrated previously in chapter 2 particularly for the synthesis of SnO2 nanostructures. Moreover, it was demonstrated that the precise control over the geometry of the materials can be achieved by a simple modulation of the preparation parameters namely heating temperature and duration, nature of the substrate, type of carrier gas and oxygen flow rate. Usually, the nanostructure growth takes place via a self-catalytic process in which the precision, prediction and reproducibility, all emerge from the nature of interaction between the constituent elements.

ZnO crystallizes into the Wurtzite structure, and the polar (0001)-Zn and (000T)-O surfaces and the nonpolar (1010) surface have been objects of experimental and theoretical studies. Of these surfaces, the nonpolar (1010) surface is of particular interest from the viewpoint of surface chemistry, because the surface is terminated with the same number of O and Zn atoms, i.e., the surface is covered with both Lewis acid and base sites. Structurally, ZnO, an ionic Wurtzite crystal with a non-centro symmetry, is described schematically as number of alternating planes composed of fourfold tetrahedral-coordinated O\(^{2-}\) and Zn\(^{2+}\) ions, stacked alternatively along the c-axis. The oppositely charged ions produce positively charged (000T)-Zn and negatively charged (0001)-O polar surfaces. Recently, Wang et al. have found that the (0001)-Zn surface is chemically active in growing nanostructures, while the (000T)-O surface is smooth and inert. In an attempt to take part in the exciting nanoworld of ZnO, and to contribute to its striving challenges in particular for making field emission devices, the synthesis and characterization of ZnO have been explored in the present chapter. More specifically, we
demonstrate the successful synthesis of novel ZnO structures namely multipods, microwires, tetrahedra, micropencil and microhexagonal cones using a modified vapor deposition method. The synthesis of these low dimensional building blocks is governed by simple self-assembly processes. Thus, in order to understand the growth kinetics and to explore intellectual terra incognita further, we had carried out SEM, XRD, TEM and XPS studies of these low dimensional materials. The results of these investigations are presented below with the help of a plausible growth mechanism. Our studies indicate that the growth of multipod structure is governed by the screw dislocation propagation. In comparison, submicron wires, tetrahedra and micropencils follow VLS mechanism while microhexagonal cones grow in two steps following VS and VLS mechanism, respectively.

4.2. Experimental Aspects

4.2.1. Synthesis of multipod and tetrahedral structures

The experimental setup used for the synthesis of multipods, microwires and tetrahedral structure is shown in scheme 4.1, which is essentially similar to the one used for the synthesis of SnO$_2$ structures. However, shape selectivity was achieved by precise control over process parameters. In brief, it consisted of a tubular furnace open at one end, in which the starting material, a pure Zn metal (Latent heat of fusion, $\Delta H_f \approx 5 \times 10^8$ J m$^{-3}$) was kept in the middle. Ar was passed continuously at a flow rate of 100 ± 5 sccm with different oxygen flow rate (20% v/v for multipods and 5% v/v for tetrahedral structure) through the furnace up to 950 °C. The material was heated for 2 h, and the furnace was allowed to cool naturally with uninterrupted Ar + O$_2$ flow. The microwires were collected adjacent to the alumina boat containing the source material whereas the multipod and tetrahedral structures were collected on the alumina substrates kept near the end of tube where the temperature was between 200 and 500 °C.
Scheme 4.1. The experimental set-up used for the synthesis of ZnO nanostructures. Pure Zn metal as the starting material was heated at a temperature of 950°C. The microwires were collected adjacent to the alumina boat containing the source material whereas the multipods and tetrahedral structures were collected on the alumina substrates kept near the end of tube where the temperature was between 200 and 500 °C.

4.2.2. Synthesis of micropencils and microhexagonal cones

Scheme 4.2 shows the experimental set-up used for the synthesis of ZnO structures. Pure Zn metal, (melting point = 420 °C, boiling point = 907 °C) was heated at a temperature of 950°C for 2 h in a mixed environment of argon and oxygen flowing at a rate of 100 ± 5 sccm and 20 sccm (20% v/v) respectively, on an alumina substrate kept on a commercially available aluminosilicate refractory brick substrates. The pencils were found to grow on the aluminosilicate substrate, while hexagonal cones were formed on the opposite side of the substrate kept downstream, where the temperature was between 200 and 500 °C.
Scheme 4.2. The experimental set-up used for the synthesis of ZnO micropencils and microhexagonal cones. The micropencils were collected on an aluminosilicate refractory brick substrate, while hexagonal cones were collected on the opposite side of the substrate kept downward where the temperature was between 200 and 500 °C.

4.2.3. Material characterization

FT- Raman spectra were measured with Bruker FRA106 FT-Raman instrument with Nd:YAG (1064 nm) excitation. The other characterization details like XRD, SEM, HR-TEM, XPS and TG-DTS have been already described in Chapter 2, section 2.2 and chapter 3, section 3.2.5.1.

4.3. Results and Discussion

4.3.1. Structural and morphological variation

Figure 4.1 shows the SEM and TEM images of the as-synthesized multipods. It is obvious from these images [figure 4.1(b) and (c)] that the number of arms of the multipods is between 4 and 16 and all have a common origin with varying length from 10 to 80 μm. Most of the arms have uniform width, whereas some of them end like a cone (tip apex of ~ 24 nm). In few other arms, the width suddenly narrows down in the middle to a sharp protrusion. Figure 4.1 (d) shows the TEM image of a tetrapod exhibiting an arm length between 120 and 200 nm with the fourth arm standing perpendicular. These tetrapods are smaller in dimensions as compared to those reported earlier by Surya et
al. and others. They have elucidated that the oxidation of Zn in air resulted in the formation of tetrapod nanorods only, with no nanowires. Further, a Zn self-catalytic VLS process is involved for the growth of tetrapod-like structures. Interestingly, in the present case some of the tetrapods end with a hexagonal tip suggesting that the relative growth rate of various crystal faces bounding the crystal plays a crucial role in deciding the growth mechanism.

Figure 4.1. SEM images of multipod structure collected downstream (200 - 500°C) (a) as-synthesized multipod structure, (b) an individual multipod structures with 8 arms with the tip ending into a hemispherical geometry, (c) another multipod structure wherein the sudden change in the width of the arm with narrowing tip apex is observed, (d) TEM image of tetrapod structure with smaller arm length between 100 and 180 nm; in some the fourth arm is observed perpendicular to the plane of the paper and (e) SEM image of the tetrapod with hexagonal tip apex.

Figure 4.2 shows the SEM image of the white fluffy microwires that are collected on the substrate containing Zn vapor source where the temperature is between 850 and 950°C. The wires are polydispersed in nature with width varying from 200 nm to 3 μm and the length from 50 to 200 μm. Most of the wires observed, end with a hexagonal tip as shown in figure 4.2 (c). A tetrahedral like structure is also observed along with the wires as shown in figure 4.2 (d) suggesting the initialization of multipods to be taking place at the beginning according to a vapor-liquid-solid growth model.
Figure 4.2. SEM images of the white fluffy microwires collected adjacent to source material where the temperature was between 850 and 950°C (a) as-synthesized microwires with width varying from 200 nm to 3 μm and length from 50 to 200 μm. The wires closer to the source material are bigger in the dimensions (b) and end with a hexagonal tip as can be seen in figure 2 (c). A tetrahedral like structures was also observed (figure 2 (d)) suggesting the initialization of multipods to be taking place as per the vapor-liquid-solid progression.

At a typical low O₂ flow rate of 5 sccm, the gray colored powder was collected at a temperature of 200 - 500 °C and it mainly comprises the sphere-like with diffused tetrahedral geometry structures (Figure 4.3 (a) and (b)). These structures are polydispersed in nature with size varying between 200 nm and 5 μm. Some of these are found to form a wire like geometry (Figure 4.3(c)) suggesting them to be the probable nucleating sites for the growth of wires. The gray color of the sample indicates incomplete oxidation, which is also supported by the lower oxygen content as can be seen in the EDX (Figure 4.3(d)).
Figure 4.3. (a) SEM images of tetrahedral ZnO with diffused edges collected downstream where the temperature is between 200 and 500°C, (b) isolated tetrahedra with size from 200 nm to 5 μm, (c) tetrahedra joined together to form a wire like geometry and (d) EDX of the gray colored tetrahedra emphasizing lower oxidation of Zn.

Figure 4.4 shows the SEM images of the micropencil structures. As can be seen (figure 4.4(a)) the substrate is uniformly coated with ZnO micropencils throughout its surface suggesting the high density of the freshly grown micropencils. Figure 4.4(b) shows the EDX of the micropencil exhibiting a strong signal corresponding to Zn and O. The intensity ratios among the Zn, O and Si peaks suggest that the Si content in the micropencils is approximately 0.61 atom%. Figures 4.4 (c) and (d) show slightly enlarged images of the micropencils revealing its clear features. It is observed that the micropencils have a hexagonal shank, with width varying between 0.8 and 1.2 μm and the shank terminates with a tapering end whose diameter is less than 100 nm. The tapering tip interestingly extends to a length of 300 to 600 nm, with a tip apex of less than 100 nm.
Figure 4.4. (a) SEM images of the micropencil structure grown on the aluminosilicate refractory brick substrate, (b) EDX of the micropencils exhibiting a strong signal corresponding to Zn and O, (c) and (d) shows the enlarged SEM of the micropencils.

Figure 4.5 shows the SEM images of the 'as grown' ZnO microhexagonal cones; the hexagonal structures emerge from the surface of the substrate. Indeed, the structure resembles an upside down cone ending into a hexagonal disc. The hexagonal cones are poly dispersed in nature with a size varying from 1 to 80 μm (figure 4.5(b)); the number of edge to all structures is fixed to six. Moreover, the edge length varies randomly from 3 to 20 μm. The six side surfaces and the base of the hexagonal cones appear smooth with a small depression at the center. Figure 4.5(d) shows the EDX recorded for hexagonal cones. The intensity ratio among the Zn, O and Si peaks suggests that the Si content in the microhexagonal cones is approximately 9.11 atom%.
Wurtzite zinc oxide has a hexagonal structure (space-group \textit{C6mc}) with lattice parameters, $a = 3.2496$ and $c = 5.2065$ Å (JCPDS Card No. 36-1451). The XRD patterns of the (a) microwires, (b) commercial ZnO (Aldrich 99.99\% pure), (c) multipod, and (d) tetrahedra structures are shown in figure 4.6. The peaks of multipods and microwires match well with those of commercial ZnO; however, intensity of the peaks differs from the bulk, due to the larger number of planes along the long axis of the pods and the wires as compared to that across the diameter. On the other hand tetrahedral structure show additional peaks, which could be attributed to signals from sub-oxides (ZnO$_x$, $x<1$) due to the incomplete oxidation. Interestingly, the microwire is found to be (10\textit{I}0) oriented with lattice parameters $a = 3.242(3)$ Å and $c = 5.201(2)$ Å, matching well with similar structural data for commercial sample, while, multipod shows a prominent signal for both (10\textit{I}0) and (10\textit{I}1) miller indices with lattice parameters $a = 3.239$ (3) and $c = 5.199$ (3) Å.

*University of Pune, Feb 2006*
Figure 4.6 The XRD patterns of the (a) microwires, (b) commercial ZnO, (c) multipod and (d) tetrahedra structure. The * in the plot corresponds to the signal arising from Zn metal.

The XRD patterns of (a) commercial ZnO (Aldrich 99.99% pure), (b) micropencils and (c) microhexagonal cone structures are shown in figure 4.7. The peaks match well with those of commercial ZnO; however, the peak position are shifted towards higher 2θ values attributed to the incorporation of Si species into the ZnO matrix. The intensity of the peaks also differs from that for the bulk due to the larger number of planes along the long axis of the structures as compared to that across the diameter.\(^{14}\)

Figure 4.7. XRD patterns of (a) commercial ZnO (Aldrich 99.99%), (b) micropencils and (c) microhexagonal cones.
For ZnO nanostructures, the quantum confinement effect is expected below 20 nm, and the absorption edge will be shifted to a higher energy when the particle size decreases. In the present case the tips of multipod structures observed is less than 20 nm and hence it is expected to have an increase in the band gap. Accordingly, the band gaps of the ZnO samples are studied by UV-vis diffuse reflectance spectroscopy (DRS). The Kubelka-Munk function, \( F(R) = \frac{(1-R)^2}{2R} \), is used to determine the band gap by analyzing the DRS results. Figure 4.8 shows the plots of \( F(R) \) vs. wavelength of ZnO structures. Band gap is defined by the extrapolation of the rising part of the plot to the X-axis (dotted line in Figure 4.8). The band gaps of commercial ZnO, microwires, and multipods are, 3.10(3) eV (400 nm), 3.15(3) eV (394 nm) and 3.13(3) eV (396 nm), respectively. These values suggest that band gap does not change significantly with the formation of multipods or microwires of ZnO.

![Figure 4.8](image_url)

Figure 4.8. Plot of \( F(R) \) vs. wavelength of (a) commercial ZnO, (b) multipod, (c) microwires and (d) tetrahedral structure, calculated from diffused reflectance spectra of these structures. The Kubelka-Munk function was calculated using \( F(R) = \frac{(1-R)^2}{2R} \), where \( R \) is reflectance (a.u).
The band gap variation with size is more prominent with structures having dimension less than 20 nm. For example, Kanaev et al. have observed the variation in the band gap of ZnO as a function of size of ZnO particles. They observed a shift in band gap from 3.48 eV to 3.75 eV for ZnO nanoparticles having dimensions between 3 and 5 nm.\textsuperscript{15}

Coupling between electronic and vibrational excitations plays an important role in semiconductor materials because of its significant influence on the optoelectronic properties of semiconductors, e.g. the transport processes, the energy relaxation rates of excited carriers and linear or nonlinear optical absorption. Moreover, the electric field within materials correlates to Coulomb interaction with the exciton and the strength of electron-phonon coupling will be enhanced if the wavelength of the phonon vibration is close to the spatial extent of the exciton. Accordingly, Raman scattering was performed (Figure 4.9) at room temperature to investigate the vibrational properties of the multipod ZnO. Since the wurtzite structure of ZnO belongs to the space group $C_{6v}(P\bar{6}3mc)$, one primitive cell includes two formula units, with all of the atoms occupying $2b$ sites of symmetry $C_{3v}$. Group theory predicts the existence of the following optic modes: $(A_1 + 2B_1 + E_1 + 2E_2)$ at the $\Gamma$ point of the Brillouin zone; $B_1$(low) and $B_1$(high) modes are normally silent; $A_1$, $E_1$, and $E_2$ modes are Raman-active; and $A_1$ and $E_1$ are both Raman and infrared-active\textsuperscript{10}. Thus, $A_1$ and $E_1$ are split into longitudinal (LO) and transverse (TO) optical components. The peak at 330 cm$^{-1}$ can be assigned to the second order Raman scattering arising from zone-boundary phonons $2-E_2$(M) of ZnO, while the peak at 436 cm$^{-1}$ corresponds to $E_2$(high). Another broadened peak around 585 cm$^{-1}$ is contributed to the superimposition of $A_1$(LO) and $E_1$(LO), which are associated with the existence of some nonstoichiometric defects, such as oxygen vacancy, interstitial zinc or their complexes.
Figure 4.9. Raman spectrum recorded for ZnO multipod at room temperature. The peaks at 330, 436 and 585 cm\(^{-1}\) could be assigned to the second order Raman scattering arising from zone-boundary phonons \(2E_2(M)\) of ZnO, \(E_2\) (high) and to the superimposition of \(A_1(LO)\) and \(E_1(LO)\) respectively.

An analysis of the electronic state of the material is also of particular importance to understand the growth kinetics and hence XPS studies were carried out on all these structures. Consequently, Figure 4.10 shows the deconvoluted C1s peak for commercial ZnO, multipod and tetrahedral structures. 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 4.1. Figure 4.11 shows the deconvoluted O1s peak for all the structures. For commercial ZnO, tetrahedral and multipod structures, the peaks at BEs of 530.2, 530.6 and 530.3 eV can be attributed to the O1s, while the peaks at binding energies of 531.8, 532.7 and 532.1 eV are attributed to the adsorbed oxygen species and Zn suboxides.
Figure 4.10 The core level spectra for C1s for different forms of ZnO (a) commercial ZnO (Aldrich 99.99%) powder, (b) tetrahedral and (c) multipods structure. The spectra were fitted using a combined polynomial and Shirley type background function.

Figure 4.11 The spectra for O1s for different forms of ZnO (a) commercial ZnO (Aldrich 99.99%) powder, (b) tetrahedral and (c) multipod structure. The spectra were fitted using a combined polynomial and Shirley type background function.
Table 4.1. A comparison of relevant binding energy positions of Zn, C and O present in different structures of ZnO.

<table>
<thead>
<tr>
<th>Species</th>
<th>Chemical Species</th>
<th>ZnO- aldrich B.E. (eV)</th>
<th>Multipods B.E. (eV)</th>
<th>Tetrahedra B.E. (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>1s</td>
<td>285</td>
<td>285</td>
<td>285</td>
</tr>
<tr>
<td></td>
<td>adsorbed</td>
<td>287.8</td>
<td>287.8</td>
<td>288</td>
</tr>
<tr>
<td>Zn</td>
<td>2P$_{1/2}$</td>
<td>1044.7</td>
<td>1044.8</td>
<td>1044.8</td>
</tr>
<tr>
<td></td>
<td>2P$_{3/2}$</td>
<td>1021.7</td>
<td>1021.7</td>
<td>1021.8</td>
</tr>
<tr>
<td>O</td>
<td>1s</td>
<td>530.2</td>
<td>530.6</td>
<td>530.3</td>
</tr>
<tr>
<td></td>
<td>adsorbed</td>
<td>531.8</td>
<td>532.7</td>
<td>532.1</td>
</tr>
</tbody>
</table>

Figure 4.12 shows the spectra for Zn signals for all the samples. Interestingly, both the multipod and the tetrahedral structures show two peaks at B.E. of 1044.8 and 1021.7 eV that can be attributed to the Zn 2p$_{1/2}$ and Zn 2p$_{3/2}$ signals, respectively. Using the atomic sensitivity factors the ratio of Zn:O is calculated using the relation

$$\frac{\text{Zn} \ (2p_{3/2})}{\text{O} \ 1s} = \frac{I_{2p}}{I_o} \times \sigma_o \sigma_{2p} \times (K.E_{2p}/K.E_O)^{1/2}$$

where, $I_{2p}$ is the area under the curve of deconvulated Zn2p$_{3/2}$, $I_o$ is the area under the curve of deconvulated Zn2p$_{1/2}$, $\sigma_o$ and $\sigma_{2p}$ are the atomic sensitivity factors for O(2.85) and Zn(9.29) respectively and K.E$_{2p}$ and K.E$_O$ are the kinetic energies of the electron of Zn and O respectively. The ratio of Zn:O varies from 1:1.01 for commercial ZnO, 1:0.74 for multipods to 1:0.4 for tetrahedra. The gray color of the tetrahedral structures suggests the presence of Zn suboxides.
Figure 4.12. The separate Zn 2p\textsubscript{3/2} and Zn 2p\textsubscript{1/2} signals for Zn in (a) commercial ZnO (Aldrich 99.99%) powder, (b) tetrahedral and (c) multipods structure. The spectra were fitted using a combined polynomial and Shirley type background function.

Figure 4.13 shows the deconvoluted C1s peak for commercial ZnO and freshly prepared micropencils and microhexagonal structures. All the binding energy positions of the elements are listed in Table 4.2. For commercial ZnO, micropencil and hexagonal structures, the peaks at binding energy of 285 eV can be attributed to the C1s, while the peaks at binding energies of 288.6, 287.6 and 287.1 eV could be attributed to the adsorbed carbon species.
Figure 4.13. The deconvoluted C1s peak for (a) commercial ZnO, (b) micropencils and (c) hexagonal structures. The spectra were fitted using a combined polynomial and Shirley type background function.

Table 4.2. All the binding energy positions of the element present in different ZnO structures

<table>
<thead>
<tr>
<th>Species</th>
<th>Chemical Species</th>
<th>ZnO- Aldrich</th>
<th>Microhexagonal Cones</th>
<th>Micropencils</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>1s adsorbed</td>
<td>285</td>
<td>285</td>
<td>285</td>
</tr>
<tr>
<td>Zn</td>
<td>2P_{1/2}</td>
<td>1044.7</td>
<td>1047.5</td>
<td>1045.4</td>
</tr>
<tr>
<td></td>
<td>2P_{3/2}</td>
<td>1021.7</td>
<td>1024.5</td>
<td>1022.3</td>
</tr>
<tr>
<td></td>
<td>1s adsorbed</td>
<td>530.2</td>
<td>530.2</td>
<td>530.6</td>
</tr>
<tr>
<td>O</td>
<td>lattice oxygen of ZnO/ SiOx</td>
<td>-</td>
<td>535.1</td>
<td>533.9</td>
</tr>
<tr>
<td>Si</td>
<td>2P_{3/2}</td>
<td>-</td>
<td>-</td>
<td>102.8</td>
</tr>
<tr>
<td></td>
<td>2P_{1/2}</td>
<td>-</td>
<td>105.1</td>
<td>-</td>
</tr>
</tbody>
</table>
Figure 4.14 shows the deconvoluted O1s peak for all the ZnO structures under investigations. For commercial ZnO the peak at binding energy of 530.2 eV can be attributed to the O1s, while the peak at binding energy of 531.8 eV is attributed to the adsorbed oxygen species. In case of micropencil and hexagonal cones, the oxygen peak can be deconvoluted in three different signals corresponding to the O1s, adsorbed oxygen and lattice oxygen of ZnO/SiO$_x$.

![Figure 4.14](image)

Figure 4.14. The deconvoluted O1s XPS peak for (a) commercial ZnO, (b) micropencils and (c) hexagonal structures. The spectra were fitted using a combined polynomial and Shirley type background function.

Figure 4.15 shows the spectra for Zn signals for all the samples. Interestingly, for both the micropencils and the hexagonal structures the two peaks corresponding to Zn 2p$_{1/2}$ and Zn 2p$_{3/2}$ levels, respectively are found to be shifted towards higher binding energy side and could be attributed to the incorporation of Si into the ZnO matrix. The ratio of Zn:O calculated using the atomic sensitivity factors and relation (1), varies from 1:1.01 for commercial ZnO, 1: 0.3 for micropencils to 1: 1.1 for hexagonal cones.
Figure 4.15. The deconvoluted Zn 2P XPS peaks for (a) commercial ZnO, (b) micropencils and (c) hexagonal structures. The spectra were fitted using a combined polynomial and Shirley type background function.

Figure 4.16 shows the spectra for the Si signals for both the micropencil and microhexagonal structures. Interestingly, for ZnO pencils, peak at binding energy of 102.8 eV is observed that could be attributed to the signal from Si\(^{2+}\) (2P\(_{3/2}\), SiO). However, in the case of microhexagonal cones, signal at the BE of 105.1 eV could be attributed to the Si\(^{4+}\) (2P\(_{1/2}\), SiO\(_2\))\(^{16}\). The appearance of Si peaks further suggests that Si acts as a nucleating aid and probably gets incorporated into the ZnO matrix.

Figure 4.16. The deconvoluted Si XPS peak for (a) micropencils, (b) microhexagonal structures.
4.4. Plausible Growth Mechanism

4.4.1. Thermogravimetric and Differential Thermal Analysis (TG-DTA)

In order to understand the growth kinetics, Thermogravimetric and differential thermal (TG-DT) analysis of the Zn metal was performed under similar environment for the synthesis of these remarkable ZnO microstructures (Figure 4.17). Upto 300 °C, a weight loss of 1.08 wt% attributed to the evaporation of impurities like adsorbed moisture is observed. With a further increase in temperature upto 650 °C, the observed weight loss of 1.4 % could be attributed to the slow evaporation of Zn. However, from 650 °C to 730 °C, a small weight gain (0.94 wt%) due to the conversion of Zn to ZnO species is seen. On the contrary, above 730 °C, a sharp loss of about 10.3 wt % is seen, which could be assigned to the evaporation of Zn species. At this temperature, Zn metal gets transformed into a liquid droplet and with a further increase in temperature, a weight gain of about 2 wt% observed subsequently could be attributed to the conversion of Zn species to ZnO. Thus, with increase in the temperature, Zn metal transforms into liquid droplets with a small loss of Zn species, as per the equation

\[
\text{Zn}(l) \rightarrow \text{Zn}(g), \quad \Delta G_0 = +114,200 - 96.99T \text{ J mol}^{-1}
\]

\[
\text{Zn}(l) + \frac{1}{2}\text{O}_2 = \text{ZnO}(s), \quad \Delta G_0(\text{ZnO}) = -355,970 + 107.53T \text{ J mol}^{-1}
\]

A negative value for \( \Delta G \) in equation (2) indicates that the reaction can proceed spontaneously without external inputs, while a positive value in equation (1) indicates that it will not proceed spontaneously and will require higher energy (temperature).

This liquid droplet subsequently grows into a ZnO layer consisting of large grains on which several nucleating sites are generated. On this site several ZnO nuclei selectively grow along the crystallographic orientation of ZnO grain due to the strong epitaxial relation between them\(^17\). Continuous feeding of Zn vapor and oxygen into the favorable nucleating sites will lead to vertical growth of ZnO structures possessing the same direction of c-plane to the ZnO grain as per the VLS progression.

\[
\text{Zn}(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{ZnO}(s)
\]
The process can be understood by looking at the Ellingham diagram of ZnO.

Figure 4.17. TGA-DTA curve of the source material i.e., Zn metal used for the synthesis

4.4.2. Ellingham Diagram of ZnO

The stability of materials at high temperature has been traditionally introduced through plots of the standard free energy of reaction ($\Delta G_0$) as a function of temperature, commonly called Ellingham diagrams. Such diagrams can help to visualize the relative stability of metals and their oxidized products. The values of $\Delta G_0$ on an Ellingham diagram are expressed as kJ/mole to normalize the scale and be able to compare the stability of these oxides directly, i.e. the lower the position of the line on the diagram, the more stable is the oxide.

For a given reaction ($2\text{Zn} + \text{O}_2 = 2\text{ZnO}$) assuming that the activities of Zn and ZnO are taken as unity, the following equations can be used to express the oxygen partial pressure at which the Zn metal and oxide coexist, i.e. the dissociation pressure of the oxide:

$$P_0^{\text{Zn}/\text{ZnO}} = e^{-\Delta G_0^0/RT}$$

(4)

Zn metal and volatile oxide species are important in the kinetics of high temperature and six types of oxidation phenomena were identified:
(a) At low temperature, diffusion of oxygen and metal species
(b) At moderate and high temperatures, a combination of oxide film formation and oxide volatility
(c) At moderate and high temperatures, the formation of volatile metal and oxide species at the metal-oxide interface and transport through the oxide lattice and mechanically formed cracks in the oxide layer
(d) At moderate and high temperatures, the direct formation of volatile oxide gases
(e) At high temperature, the gaseous diffusion of oxygen through a barrier layer of volatilized oxides
(f) At high temperature, spalling of metal and oxide particles

Figure 4.18. Plot of the free energy of formation of ZnO vs. temperature. This can be used to predict the temperatures at which a metal is stable and the temperatures at which it will spontaneously oxidize. For temperatures at which the free energy of formation ($\Delta G_0$) of the oxide is positive, the reverse reaction is favored and the oxide will spontaneously decompose to the metal.  

$\Delta G$ of reaction (kJ/mol)

$\Delta G$ of reaction (kJ/mol)

Temperature (°C)

Figure 4.18. Plot of the free energy of formation of ZnO vs. temperature. This can be used to predict the temperatures at which a metal is stable and the temperatures at which it will spontaneously oxidize. For temperatures at which the free energy of formation ($\Delta G_0$) of the oxide is positive, the reverse reaction is favored and the oxide will spontaneously decompose to the metal.
From the plot (Figure 4.18) it is clear that between 423 °C and 911 °C, Zn and O species coexists with standard free energy change of \( \Delta G_0 \) (J) = \(-355,890 + 107.5 T \) (K).

### 4.4.3. Growth Mechanism

The structure of ZnO can be simply described as a number of alternating planes composed of tetrahedrally coordinated \( O^{2-} \) and \( Zn^{2+} \) ions, stacked alternatively along the c-axis. The important characteristic of ZnO is the polar surfaces, the most common being the basal plane. The oppositely charged ions produce positively charged \( Zn-(0001) \) and negatively charged \( O-(0001) \) surfaces, resulting in a normal dipole moment and spontaneous polarization along the c-axis. In ZnO, a VLS process is presumed to control the formation of various nanostructures. The nanostructure formation takes place via a self-catalyzed process. The growth habit of a crystal is related to the relative growth rate of various crystal faces bounding the crystal, which is mainly determined by the internal structure of a given crystal as well as is affected by the growth conditions. The appearance of porous hemispherical tetrahedra condensed on the inner wall close to the open end of the tube suggests the formation of liquid droplets in the initial stages, which are carried away by the carrier gas to the substrates kept downstream. This further emphasizes, that the tetrahedra follows the VLS progression.

To understand the growth kinetics further, the reaction was quenched after 15 and 30 min, respectively and the SEM studies were carried out. A sphere like tetrahedral are observed on the inner wall (figure 4.19(a)) of the thin layer like droplet, while on the upper side of the thin wafer (figure 4.19(b)) large number of needle like features with protruding tip ending into cones similar to multipod arms are observed. Figure 4.17(c) reveals the enlarged image of the area showing the needle like protrusion on the surface of the droplet wafer. A large number of wires (figure 4.19 (a)) are also formed at the edge of the solidified liquid droplet by the self-catalyzed growth mechanism on the ZnO nuclei. These wires have a uniform diameter although; the aspect ratio is small (<30) suggesting incomplete growth. For the reaction quenched after 30 m, a large number of nanowire (figure 4.20) is found protruding out of the thin vapor. At the substrate, along with the microwires, a structure resembling the tetrahedral morphology appears although the arm lengths are not sufficiently grown. Upon increasing the time duration or the
oxygen flow rate (10 sccm) due to further oxidation, the concentration of oxygen in the droplets increases. The tetrahedral planes formed at the initial stage acts as nucleating sites where ZnO then deposits resulting in the growth of oriented ZnO structures. The tetrahedra formed at the substrate fuse together to form wires further confirming the process to follow the vapor-liquid-solid progression. Further, the sharp conic tip and the abrupt change in the width of the arms of multipod suggest the screw dislocation mechanism governing the tip morphology\textsuperscript{19}. The spiral plane perpendicular to the screw dislocation line possesses a step as a low-energy site for growth. The growth rate along the dislocation line is then much faster than that of radial direction, which results in the 1-D morphology. Thus the multipod growth is initiated by the VLS mechanism and the screw dislocation governs the final structure/tip morphology.

Figure 4.19. SEM images of the Zn droplets (globular thin wafer slightly yellowish in color) formed after quenching the process after 15 min, (a) globular or spherical Zn droplets seen on the inside wall of the droplet, (b) large number of conical tips protruded out of the surface of the molten droplet, spherical drops is also observed detached from the sharp needles, suggesting the growth via a VLS progression. Large number of wires is also observed protruding out of the surface of the thin wafer.
4.4.4. Effect of Substrate and Temperature

Further, EDX carried out on the substrate used (refractory brick) (Figure 4.21(a)) implies that it mainly comprises of Si and Al. Among these, Si in the form of SiO$_2$ is expected to contribute for the microstructural growth. Surprisingly, when the experiments were carried out under similar conditions with Si-(100) wafer instead of aluminosilicate substrate, large number of hexagonal cones are seen originating from the substrate (figure 4.21(b)). Recently, Ajayan et al have reported the selective growth of oriented CNT’s on patterned SiO$_2$ on Si (100) substrates$^{20}$. They have observed that although there is no nanotube growth on silicon, aligned nanotubes grow readily on SiO$_2$ in a direction that is normal to the substrate surface. Similarly, in the present case, the shanks of the hexagonal cones originate from the substrate, (Figure 4.21(c)) probably from the sites containing the Si species. Moreover, the hexagonal cones resemble the micro-pyramids synthesized via strong electrostatic interactions between the ions in the melt (solvent) and the polar surfaces of ZnO$^{21}$. During the crystal growth, the polar
surfaces usually appear as growing surfaces because of their higher surface energy, exhibiting small facets even disappearing during the crystal growth. For example, in ZnO growth, the highest growth rate is usually along the c-axis and the large facets are usually \{01\overline{1}0\} and \{2\overline{1}10\} non-polar surfaces, rather than the polar \{0001\} surfaces. In contrast to the non-polar surfaces, the polar \{10\overline{1}1\} planes have a higher surface energy and usually grow too fast to be seen in the final shape of the crystal.\textsuperscript{22} Further, some of the pencil structures also exhibit a narrow pen tips on the top (Figure 4.21 (d)). Such structures have also been reported during cooling, owing to continuously decreasing zinc vapor pressure with decreasing temperature.\textsuperscript{23} Moreover, the nucleation size of the pen tips is determined by the size of the platform area of the micropencil structures. Interestingly, when additional experiments were performed using alumina substrates instead of Si-wafer, multipod structures were observed. This further signifies that the presence of Si species is crucial in governing the morphology of ZnO structures.

Figure 4.21. (a) EDX of the aluminosilicate refractory brick substrate used, (b) SEM image suggesting that the shank of the hexagonal cones originates from the substrates, (c) hexagonal cones emerging out of the Si-wafer, when the experiments were carried out in similar conditions and (d) narrow pen tips on micropencils.
Remarkably, a unique flower-like geometry is also observed on aluminosilicate substrates at lower temperature between 200 and 500 °C, as shown in figure 4.22. These structures are found to grow on a central microwire, like a tree with flowers. The flower consists of large number of nanowires originating from a single point with tapering end possessing a hexagonal structure on the tip. Some of the hexagonal structures are observed to be separate from the flower suggesting the growth of nanowires to be one of the prominent phenomena. The different length of the nanowires implies various stages of incomplete growth. Indeed, the structure resembles to the needles reported by Wang et al. with bigger dimensions. In our case, we speculate that the metallic Zn droplets are carried away to the substrate wherein the Si species present on the substrate acts as a nucleating site to grow ZnO microstructures. Moreover, during the growth process the polar planes possessing the high surface energy grow faster to give the final morphology. However, when the arms of the wires grow sufficiently long, due to the strain induced in them, the hexagonal cones detach (figure 4.22) from the central wire leading to the formation of sharp-needle like structures. For substrates kept at the middle of the furnace (950°C), the growth process is faster because of the high temperature following a VLS progression, while for the substrates kept at the lower temperature zone, the growth process is in the initial stages and hence only the hexagonal cones are observed. Further, some of the Zn vapor, evaporated from the starting material at a high temperature zone, flows and directly gets deposited on substrates at a low temperature region. At low temperature region the Zn vapors would be oxidized forming suboxides that could probably be assigned to the geometry of the substrate, which limits the amount of oxygen contributing to the reaction. Subsequently, suboxide forms liquid droplets, which in turn enhance the absorption and diffusion of Zn oxides during growth. Thus, the growth of hexagonal cones takes place via a two-step, first as per the VS mechanism where the Zn vapor at high temperature flows to low temperature and reacts with oxygen to form suboxide. Secondly, these suboxides form liquid droplets providing further nucleating sites along with SiO$_2$ for the formation of hexagonal cones and could be assigned to a VLS mechanism.
4.5. Conclusions

In conclusion, this chapter deals with the synthesis of ZnO in different morphology, namely multipods, wires, tetrahedra, micropencils and microhexagonal cones by using a simple approach of vapor deposition. XRD studies indicate that the microwires are (1010) oriented while the multipods show prominent peaks for both (1010) and (1011) miller indices. Tetrahedral structures show a biphasic mixture of Zn along with the oxide formation. Zn:O ratio calculated using XPS studies indicate that for the multipod structure there is complete oxidation. These studies reveal that the multipod growth takes place via a screw dislocation mechanism while the tetrahedral and microwires grow via a VLS progression. In case of micropencils and microhexagonal cones, XPS studies indicate that the BE of Zn species shifts to higher BE side attributed to the Si present in the matrix. Si species gets incorporated into the ZnO matrix in Si2+ (SiO) and Si4+ (SiO2) forms which play crucial role in deciding the morphology. The Si species present in the form of SiO and SiO2 acts as a catalyst providing additional nucleating sites, where ZnO nanostructures grow. It has been demonstrated that the micropencil grows via a VLS progression while the microhexagonal cones grow in two steps following VS and VLS mechanisms respectively. These results are believed to be important for controlling the growth of ZnO structures realizing their simultaneous, multidirectional growth on templates of SiO2 for various device applications.
4.6. References


