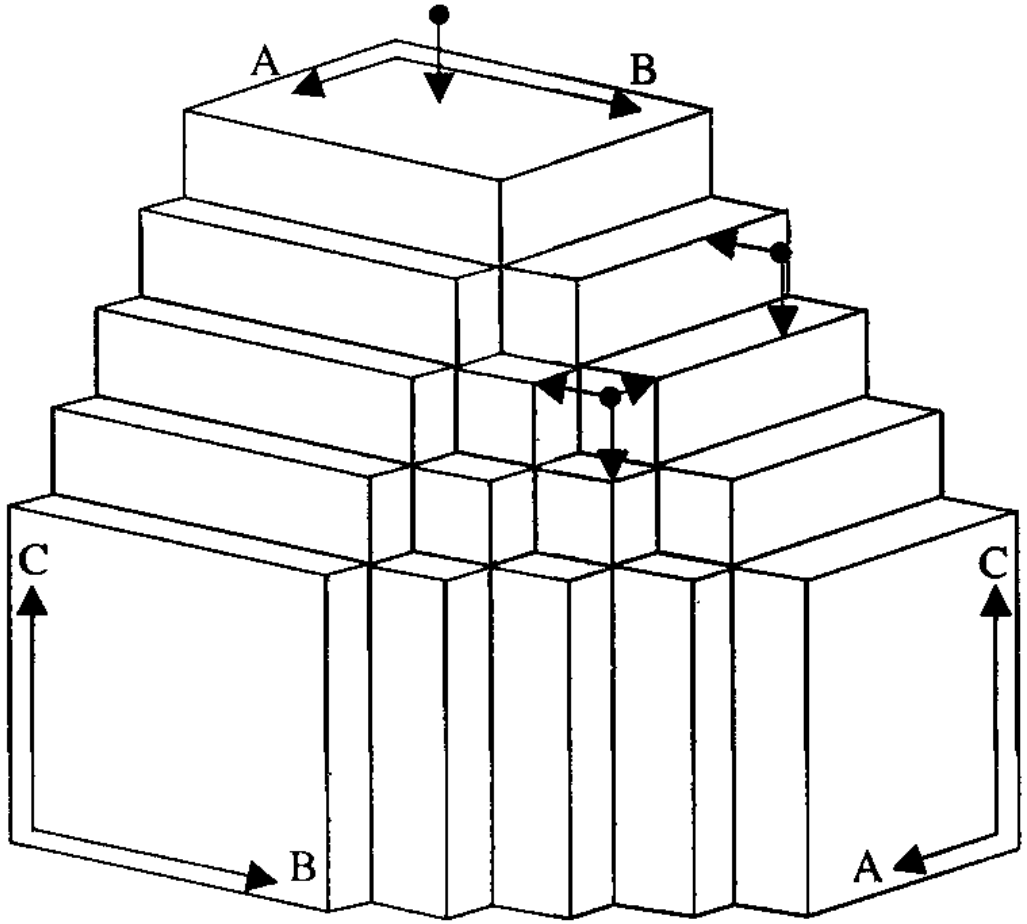
One-Dimensional Nanomaterials (Contd…)

(Ref: Guozhong Cao; Nanostructures & Nanomaterial: Synthesis, Properties & Applications)

- PBC theory offers a different perspective in understanding the different growth rate and behaviour in different facets.
- Let us take an example of simple cubic crystal to illustrate Periodic Bond Chain (PBC) theory as shown in following figure:



Schematic illustrating the PBC theory. In a simple cubic crystal, {100} faces are flat surfaces (denoted as F-face) with one PBC running through one such surface. {110} are stepped surfaces (S-face) that have two PBCs, and {111} are kinked surfaces (K-face) having three PBCs. [P.Hartman & W.G.Perdok, Acta Crystal, 8, 49 (1955).]

- According to PBC theory, {100} faces are flat surfaces (denoted as F-face) with one PBC running through one such surface.
- {110} are stepped surfaces (S-face) that have two PBCs.
- {111} are kinked surfaces (K-face) that have three PBCs.
- For {110} surfaces, each surface site is a step or ledge site, and thus any impinging atom would be incorporated wherever it adsorbs.
- For {111} facets, each surface site is a kink site and would irreversibly incorporate any incoming atom adsorbed onto the surface.
- For both {110} and {111} surfaces, the above growth is referred to as a random addition mechanism and no adsorbed atoms would escape back to the vapour phase.
- It is obvious that both {110} and {111} faces have faster growth rate than that of {100} surface in simple cubic crystal.
- In general, S-faces and K-faces have higher growth rate than F-faces.
- For S- and K-faces, growth process is always adsorption limited. Accommodation coefficients on both types of surfaces are unity, all impinging atoms are captured and incorporated into the growth surface.
- For F-faces, accommodation coefficient varies between zero (no growth at all) and unity (adsorption limited), depending on the availability of kink and ledge sites.

- The above theories enable us to understand that why some facets in a given crystal grow much faster than others.
- However, facets with fast growth rate tend to disappear, i.e. surfaces with high surface energy will disappear.
- In thermodynamically equilibrium crystal, crystal with lowest surface energy will survive as determined by Wulff plot.
- Therefore, formation of high aspect ratio nanorods or nanowires entirely based on different growth rates of various facets is limited to materials with special structures.
- In general, other mechanisms are also required for continued growth along with the axis of nanorods or nanowires, such as defect-induced growth and impurity inhibited growth.
- For anisotropic growth, a low supersaturation is required.
- Ideally, concentration is higher than equilibrium concentration (saturation) of growth surface, but equal or lower than that of other non-growth surfaces.
- Low supersaturation is required for anisotropic growth.
- Medium supersaturation supports bulk crystal growth.
- High supersaturation results in secondary or homogeneous nucleation leading to formation of polycrystalline/powder.

Evaporation-Condensation (EC) Growth

- In 1955, Sears was the first to explain the growth of mercury whiskers (Nanowires with diameter ~ 200 nm, length~1-2 mm) by axial screw-dislocation induced anisotropic growth.
- Mercury whiskers/nanowires were grown by simple evaporation-condensation method.

  Condensation Temperature: -50°C under vacuum.

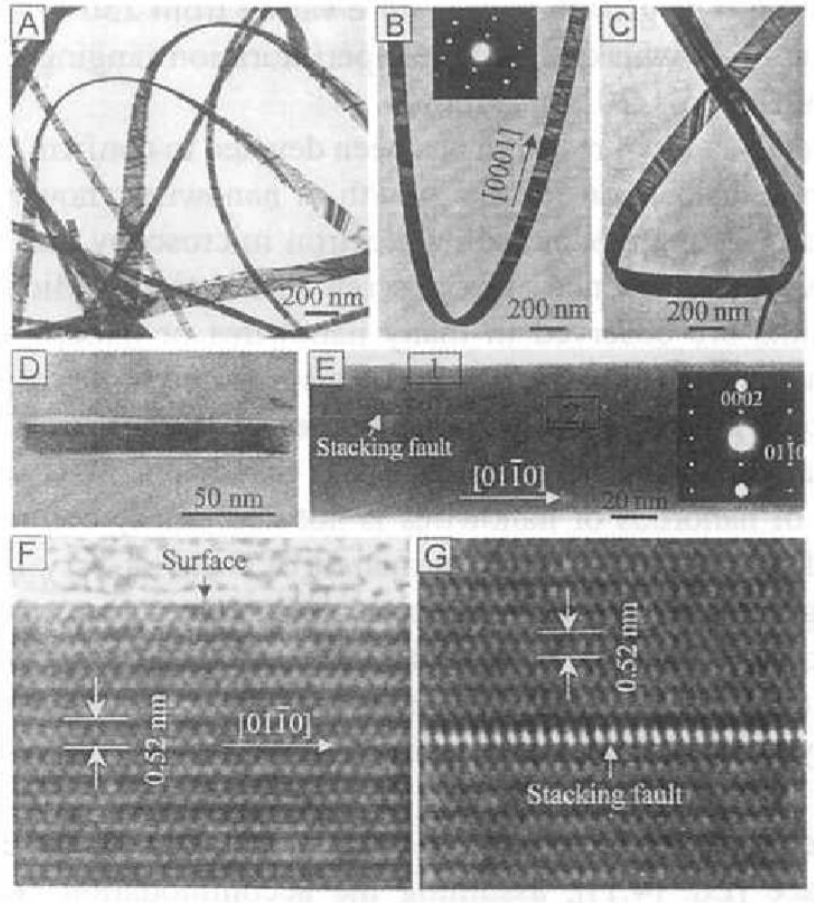
  Axial Growth Rate: 1.5 µm/sec under supersaturation of 100 (Ratio of pressure over equilibrium pressure).
- It was found that whiskers/nanowires remained at constant radius throughout the axial growth.
- It implies that there was no/negligible lateral growth.
- Sears, further demonstrated that fine whiskers of other materials Zn, Cd, Ag, CdS could be grown by EC method.
- Experimental conditions varies from material to materials. For. e.g.
- Growth temperature varied from 250°C for Cd to 850°C for Ag whiskers, with supersaturation ranging from ~2 for CdS to ~20 for Cd.

- Subsequently, lot of research was devoted to confirm the presence of axial screw dislocation for growth of nanowires; however in most cases, various techniques including electron microscopy and etching, all failed to reveal the presence of axial screw dislocation.
- Micro-twins and stacking faults are observed in many nanowires/nanorods grown by EC method and are responsible for anisotropic growth.
- Many other researchers revealed no axial defects at all in the grown nanorods and nanowires.
- It is obvious that growth of nanorods/nanowires is not necessarily controlled by presence of micro-twins.
- Though formation of twins is very important in determining final crystal morphology.
- Such an anisotropic growth is also not possible to explain by means of anisotropic crystal structures.
- More work is needed to understand the growth of nanowires & nanorods by evaporation-condensation method.
- Another issue is that observed growth rate of nanowires exceeds the condensation rate calculated by equation used for flat surface, assuming the accommodation coefficient as unity.

$$J = \frac{\propto \sigma P_0}{\sqrt{2\pi mkT}}$$

- It simply means that growth rate of nanowires is faster than all the growth species arrived at growth surface.
- To explain enhanced growth rate of whisker/nanowire, a dislocation-diffusion theory was proposed as mentioned below:
- In this model, it was proposed that the depositing materials at the tip are originated from two sources.
- Direct condensation of growth species from vapour, and;
- Migration of adsorbed growth species on side surfaces to the growth tip.
- However, an adatom migrating over an edge from side surfaces to growth surface on the tip is unlikely, since the edge serves as an energy barrier for such migration.
- Wang and co-workers reported growth of single crystal nanobelts of various semiconducting oxides, simply by evaporating desired commercially available metal oxides at high temperatures under vacuum of 300 torr and condensing on an alumina substrate, placed inside same alumina tube furnace, at relatively lower temperatures.
- The oxides include zinc oxide (ZnO) of wurtzite hexagonal crystal structure, tin oxide (SnO_2) of rutile structure, indium oxide (In_2O_3) with C-rare-earth crystal structure, cadmium oxide (CdO) with NaCl cubic structure.

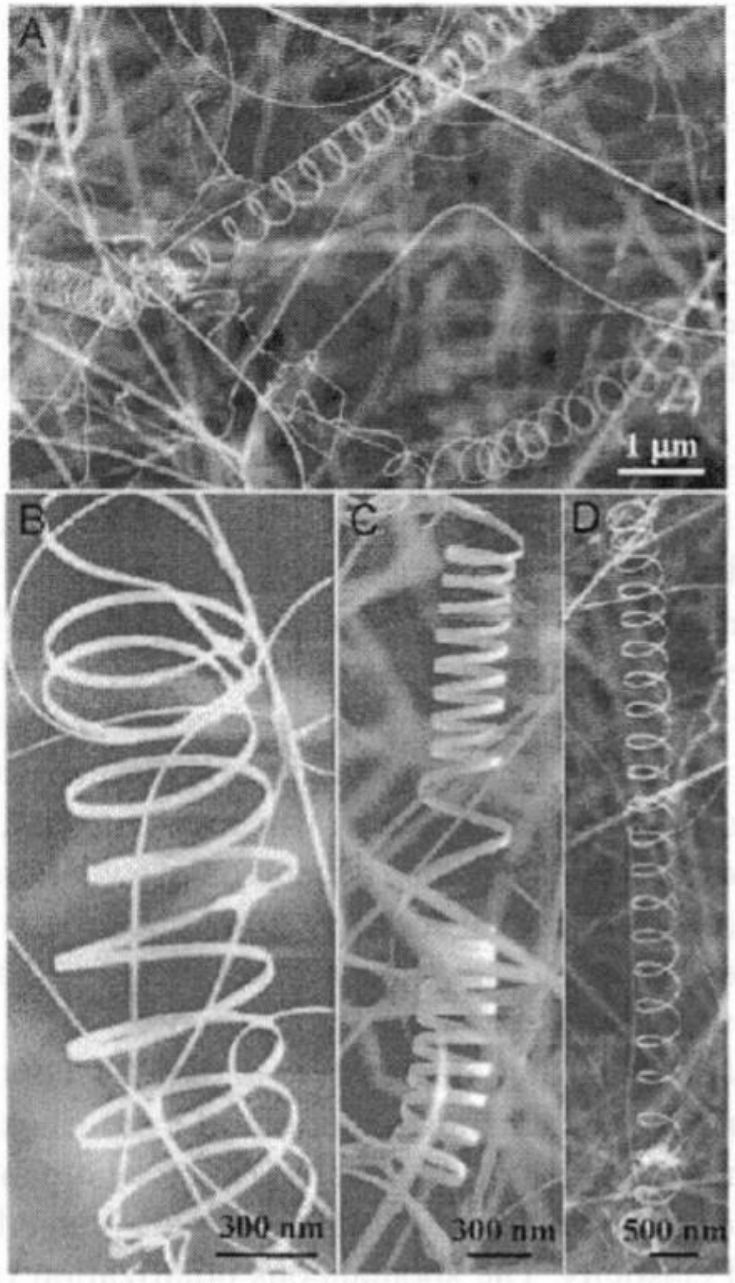
- We will focus on growth of ZnO nanobelts. Similar phenomena were found in all four oxides.
- Following figure shows SEM and TEM pictures of ZnO nanobelts.
- Typical thickness: 10-30 nm, width-to-thickness ratios: ~5 to 10, Growth directions: [0001] and [0110].



SEM and TEM pictures of ZnO nanobelts [Z.W.Pan, Z.R.Dai and Z.L,Wang, Science 291 (2001) 1947]

- No screw dislocation was found throughout the entire length of the nanobelt, except a single stacking fault parallel to the growth axis in the nanobelt grown along [0110] direction.
- Surface of the nanobelts are clean, atomically sharp and free of any sheathed amorphous phase.
- TEM analysis revealed the absence of amorphous globules on the tip of nanobelts.
- These observations imply that the growth of nanobelts is not due to the VLS mechanism.
- Growth of nanobelts cannot be attributed to either screw dislocation induced anisotropic growth, nor impurity inhibited growth.
- Nanobelts of other oxides were also synthesized by the same technique.
- It seems that shape of nanowires and nanobelts may also depend on growth temperature.
- Kong and Wang demonstrated that by controlling growth kinetics, left handed helical nanostructures and nano-rings can be formed by rolling up single crystal ZnO nanobelts.
- Phenomena is attributed to minimization of total energy attributed by spontaneous polarization and elasticity.

- Spontaneous polarization results from non-centrosymmetric ZnO crystal structure.
- In (0001) facet-dominated single crystal nanobelts, positive and negative ionic charges are spontaneously established on the zinc- and oxygen-terminated $\pm$(0001) surfaces respectively.
- Following figure shows SEM images of the synthesized ZnO nanobelt helical nanostructures.
- Typical width of nanobelts is ~30 nm.
- Pitch distance is rather uniform.
- The helixes are left handed.



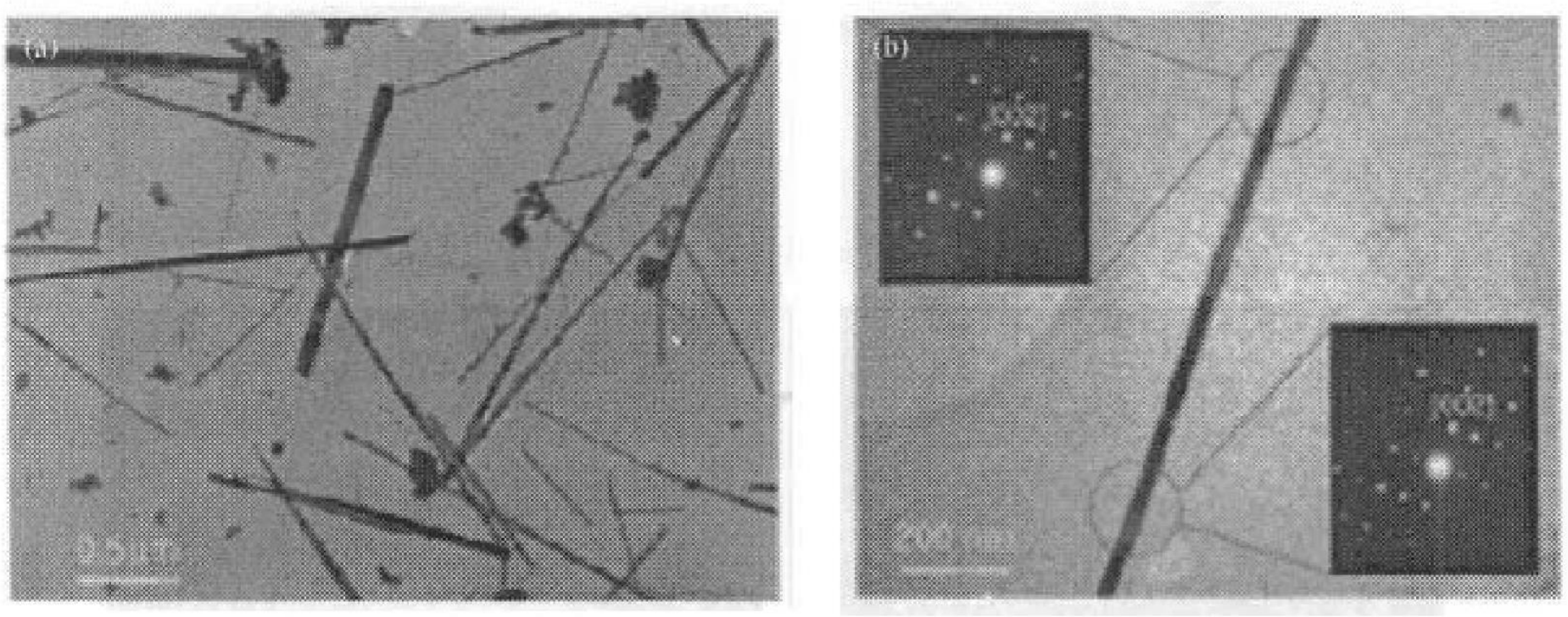
SEM images of synthesized single crystal ZnO nanobelt helical nanostructures. [X.Y.Kong and Z.L.Wang, Nano Lett. 3 (2003) 1625]

Dissolution-Condensation (DC) growth

- Dissolution-Condensation process differs from Evaporation-Condensation in growth media.
- In DC process, growth species first dissolve into solvent/solution, and then diffuse through solvent/solution and deposit onto the surface resulting in the growth of nanorods/nanowires.
- Gates et al. prepared uniform single crystal nanowires of selenium by Dissolution-Condensation methods.
- In the first step, spherical colloidal particles of amorphous selenium with sizes of ~300 nm in aqueous solution were prepared through the reduction of selenious acid with excess hydrazine at 100°C.
- Solution was cooled at room temperature and precipitate of nanocrystalline selenium with trigonal structure was obtained.
- In second step, when the solution aged at room temperature in dark, amorphous selenium colloid particles dissolved into solution, whereas selenium crystallites grew.
- In this solid-solution-solid transformation, morphology of crystalline selenium products was determined by the anisotropic growth, attributed to the one-dimensional characteristics of the infinite, helical chains of selenium in trigonal structure.

- Trigonal Se crystals were found to grow predominantly along [001] direction.
- Nanowires grown by this method were found free of defects, such as kinks and dislocations.
- Nanowires can also be synthesized using the same methods commonly used for the synthesis of nanocrystals, i.e. by decomposing of organometallic compounds in the presence of coordinating organics.
- Urban and co-workers synthesized singly crystal $BaTiO_3$ nanowires with diameter ranging from 5-70 nm and lengths up to > 10 µm, by solution phase decomposition of barium titanium isopropoxide, $BaTi[OCH(CH_3)_2]_6$.
- In a typical reaction, an excess of 30% H_2O_2 was added at 100°C to a heptadecane solution containing a 10:1 molar ratio of $BaTi[OCH(CH_3)_2]_6$ to oleic acid.
- The reaction mixture was then heated to 280°C for 6 hrs, resulting in a white precipitate composed of nanowire aggregates.
- Well isolated nanowires were obtained by sonication and fractionation between water and hexane.
- TEM images and convergent-beam electron diffraction patterns of $BaTiO_3$ nanowires are shown in next slide.

- Elemental analysis, X-ray diffraction, and electron diffraction studies indicates that grown nanowires are single crystalline perovskite $BaTiO_3$ with [001] direction aligned along wire axis.
- Diameters and lengths of grown nanowires vary substantially and no strategy is available for a controlled growth of uniformly sized nanowires.



(a) TEM images of $BaTiO_3$ nanowires, showing that the reaction produces mainly nanowires and small quantities (~10%) of nanoparticle aggregates. (b) TEM image of $BaTiO_3$ nanowire along with two convergent beam electron diffraction patterns. [J.J.Urban, J.E.Spanier, L.Ouyang, W.S.Yun, and H.Park, Adv. Mater. 15 (2003) 423.]

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