One-Dimensional Nanomaterials (Contd…)

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

Vapor (Solution)-Liquid-Solid (VLS or SLS) growth

Fundamental aspects of VLS and SLS growth

- In the **VLS** growth, a second phase material, commonly referred to as either impurity or catalyst, is purposely introduced to direct and confine the crystal growth on to a specific orientation and within a confined area.
- **A** catalyst forms a liquid droplet by itself or by alloying with growth material during the growth, which acts as a trap of growth species. Enriched growth species in the catalyst droplets subsequently precipitates at the growth surface resulting in the one-directional growth.
- Wagner *et al.* first proposed the VLS theory over 40 years ago to explain the experimental results and observations in the growth of silicon nanowires or whiskers that could not be explained by the evaporation-condensation theory.

Wagner summarized the requirements for the VLS growth 30 years ago, which are still valid in today's understanding:

1) The catalyst or impurity must form a liquid solution with the crystalline material to be grown at the deposition temperature.

2) The distribution coefficient of the catalyst or impurity must be less than unity at the deposition temperature.

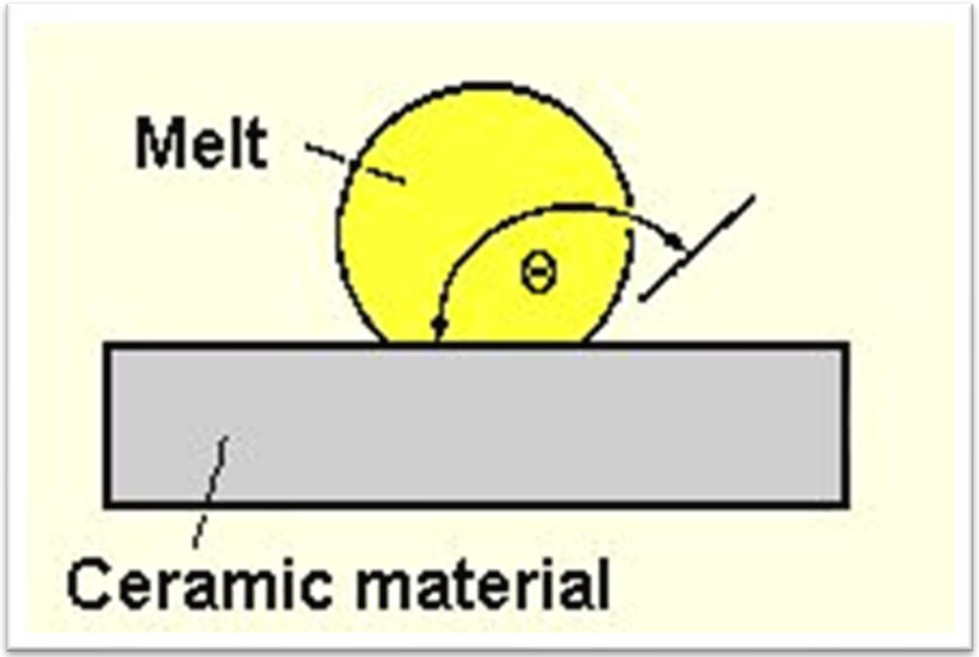
3) The equilibrium vapor pressure of the catalyst or impurity over the liquid droplet must be very small. Although the evaporation of the catalyst does not change the composition of the saturated liquid composition, it does reduce the total volume of the liquid droplet. Unless more catalyst is supplied, the volume of the liquid droplet reduces. Consequently, the diameter of the nanowire will reduce and the growth will eventually stop, when all the catalyst is evaporated.

4) The catalyst or impurity must be inert chemically. It must not react with the chemical species such as by-products presented in the growth chamber.

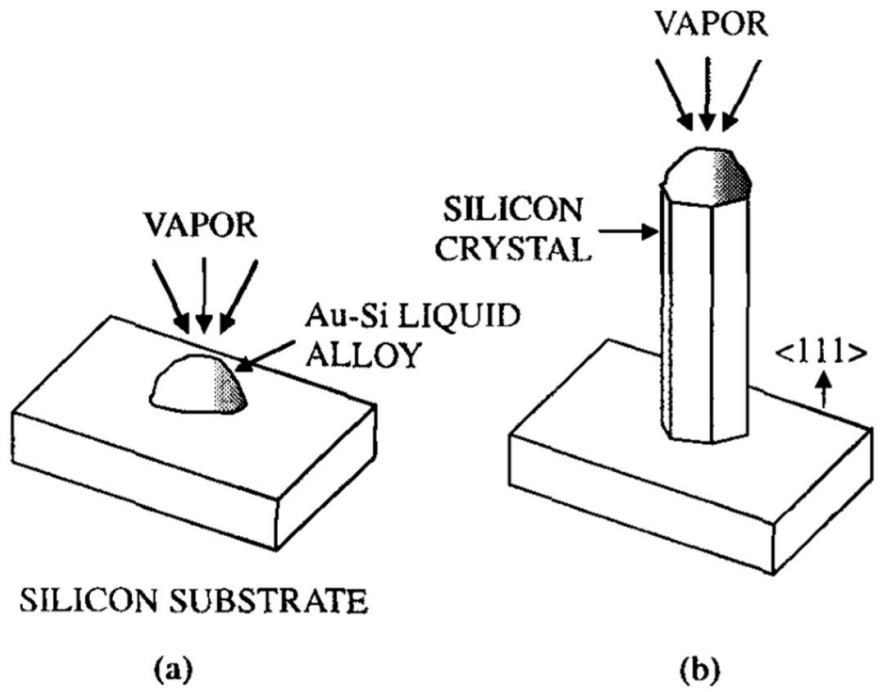
5) The interfacial energy plays a very important role. The wetting characteristics influence the diameter of the grown nanowire. For a given volume of liquid droplet, a small wetting angle results in a large growth area, leading to a large diameter of nanowires.

6) For a compound nanowire growth, one of the constituents can serve as the catalyst.

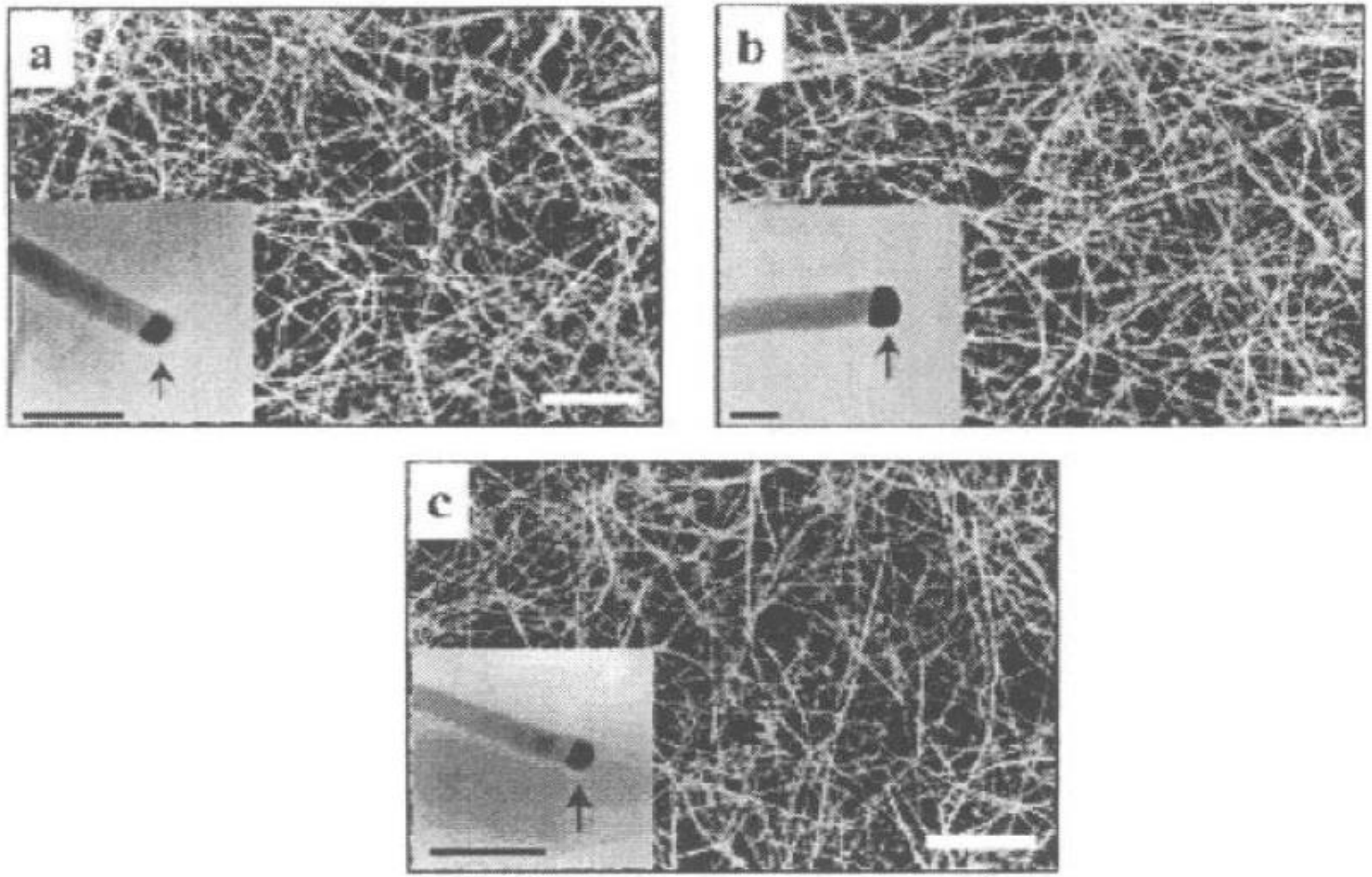
7) For controlled unidirectional growth, the solid-liquid interface must be well defined crystallographically. One of the simplest methods is to choose a single crystal substrate with desired crystal orientation.



- In a VLS growth, the process can be simply described as following as sketched in Fig. The growth species is evaporated first, and then diffuses and dissolves into a liquid droplet. The surface of the liquid has a large accommodation coefficient and is therefore a preferred site for deposition.
- Saturated growth species in the liquid droplet will diffuse to and precipitate at the interface between the substrate and the liquid. The precipitation will first follow nucleation and then crystal growth. Continued precipitation or growth will separate the substrate and the liquid droplet, resulting in the growth of nanowires.
- In general, a high temperature and a vacuum are required in the growth of nanowires by VLS method.



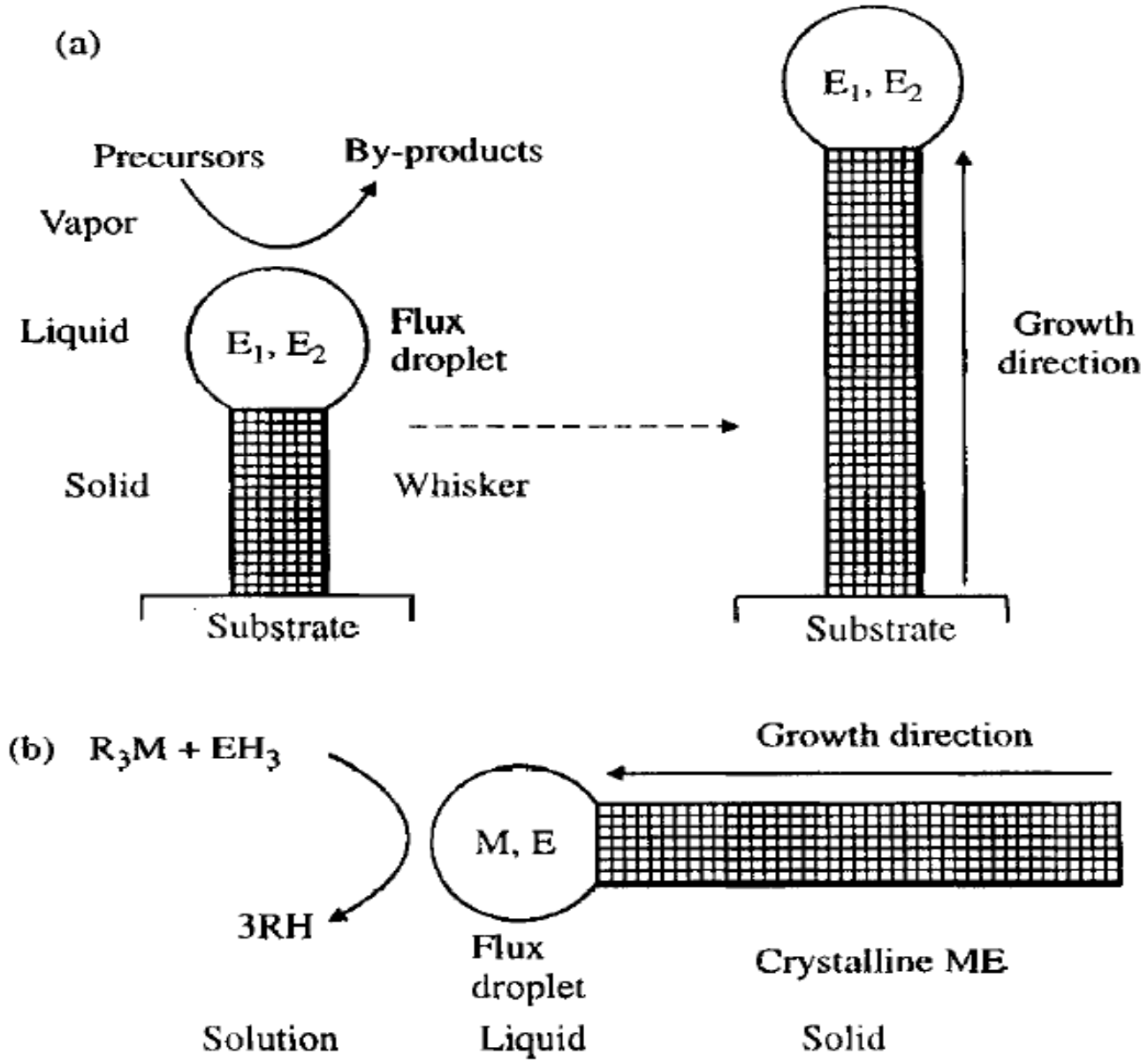
Schematic showing the principal steps of Vapour-Liquid-Solid growth technique: (a) Initial Nucleation, and (b) Continued Growth



Field-emission SEM images of compound semiconductor nanowires grown by VLS method: (a) GaAs, (b) GaP, and (c) $GaAs_{0.6}P_{0.4}$. The scale bars are 2µm.

[Ref.: X.Duan and C.M.Lieber, Adv. Mater. 12(2000)298]

- An alternative method called solution-liquid- solid **(SLS)** growth method was developed by Buhro's research and first applied for the synthesis of InP, InAs and GaAs nanowires with solution-phase reactions at relative lower temperatures (≤203°C).
- SLS method is very similar to VLS theory; Fig. compares the similarities & differences between these two methods.
- Nanowires were found to be polycrystalline or near-single-crystal with a diameter of 10-150 nm and a length of up to several micrometers.
- Let us take the growth of InP nanowires as an example to illustrate the SLS growth process. Precursors used were typical organometallic compounds: $In(t\text{-}Bu)_3$ and PH_3, which were dissolved into hydrocarbon solvent with protic catalyst such as MeOH, PhSH, Et_2NH_2, or $PhC0_2H$.
- In the solution, precursors reacted to form In and P species for the growth of InP nanowires with the following organometallic reaction, which is commonly used in chemical vapor deposition
- $In(t\text{-}Bu)_3 + PH_3 \rightarrow InP + 3(t\text{-}Bu)H$ Indium metal functions as the liquid phase or catalyst for the growth of InP nanowires. Indium melts at 157° and forms liquid drops. It is postulated that both **P** and **In** dissolve into the In droplets and precipitate to form nanowires of InP. The growth direction of InP nanowires was found to be predominated by <1 1 1>, similar to that with VLS method.



Comparison of the similarities of differences between VLS (a) and SLS (b) growth techniques.

[Ref.: T.J. Trentler, K.M. Hickman, S.C. Goel, A.M. Viano, P.C. Gobbons, and W.E. Buhro, Science 270(1995)1791]

Stress-Induced Recrystallization

- Application of pressure on solids at elevated temperatures is known to result in the growth of whiskers or nanowires with diameters as small as 50 nm.
- It was demonstrated that the growth rate of tin whiskers increased proportionally with the applied pressure and could be four orders of magnitude when a pressure of 7,500psi was applied. The growth of such nanowires or whiskers is based on a dislocation at the base of the whisker and the growth proceeds from the base and not from the tip.

Template Based Synthesis

- Template-based synthesis of nanostructured materials is a very general method and can be used in fabrication of nanorods, nanowires and nanotubules of polymers, metals, semiconductors and oxides.
- Various templates with nanosized channels have been explored for the template growth of nanorods and nanotubule.
- The most commonly used and commercially available templates are anodized alumina membrane, radiation track-etched polymer membranes.
- Other membranes have also been used as templates such as nanochannel array glass, radiation track etched mica, and mesoporous materials, porous silicon by electrochemical etching of silicon wafer, zeolites and carbon nanotubes.

Requirements of Template Based Synthesis:

1. template materials must be compatible with the processing conditions. For example, an electrical insulator is required for a template to be used in electrochemical deposition.

2. Depositing materials or solution must wet the internal pore walls.

3. Synthesis of nanorods or nanowires, the deposition should start from the bottom or one end of the template channels and proceed from one side to another However, for the growth of nanotubules, the deposition should start from the pore wall and proceed inwardly. Inward growth may result in the pore blockage, so that should be avoided in the growth of “solid” nanorods or nanowires.

4. Easiness of release of nanowires or nanorods from the templates and of handling during the experiments.

Deposition Techniques for Template-Based Synthesis:

1. *Electrochemical deposition.*

2. *Electrophoretic deposition.*

3. *Template filling.*

    (i) *Colloidal dispersion filling.*

    (ii) *Melt and solution filling*

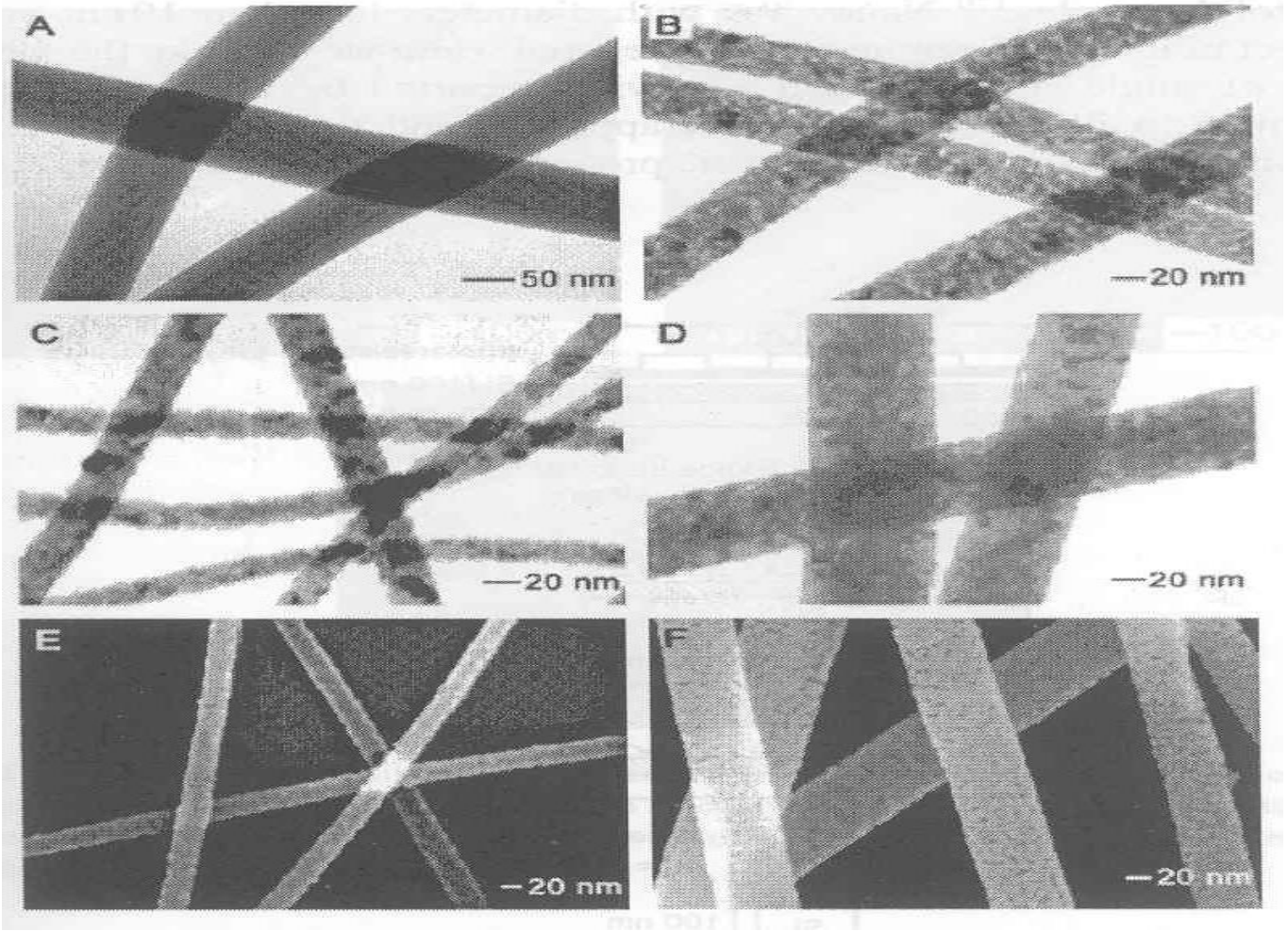
    (iii) *Chemical vapor deposition*

    (iv) *Deposition by centrifugation*

ELECTROSPINNING

- Electrostatic fiber processing
- Developed for ultrathin polymer fibers
- Uses electrical forces to produce polymer fibers with nanometer scale diameters
- Electrospinning occurs when the electrical forces at the surface of a polymer solution or melt overcome the surface tension and cause an electrically charged jet to be ejected.

- When the jet dries or solidifies, an electrically charged fiber remains.
- This charged fiber can be directed or accelerated by electrical forces and then collected in sheets or other useful geometrical forms.
- 30 polymer fibers produced (Dia 40-500 nm) successfully produced by Electrospinning
- The morphology of the fibers depend on the process parameters
- Recent results are also applicable for
    - Ultrathin organic-inorganic hybrid fibers
    - Porous anatase titania nanofibers made by ejecting an ethanol solution containing both poly vinyl pyrrolidone and titanium tetra-isopropoxide through a needle under strong magnetic field resulting in formation of amorphous TiO_2/PVP composite nanofiber



[A} TEM image of TiO_2/PVP composite nanofibers fabricated by electrospinning an ethanol solution that contained 0.03 g/mL. PVP and 0.1 g/ mL $Ti(OP_r^i)_4$. (B) TEM images of the same sample after it had been calcined in air at 500°C for 3 hrs. (C, D) TEM images of nanofibers made of anatase that were prepared under the same conditions except that the precursor solution contained (C) 0.025 g/mL and (D) 0.15 g/mL, $Ti(OP_r^i)_4$ respectively. (E, F) High-magnification SEM images taken from the samples shown in C and D, respectively. No gold coatings were applied to the samples for all SEM studies.

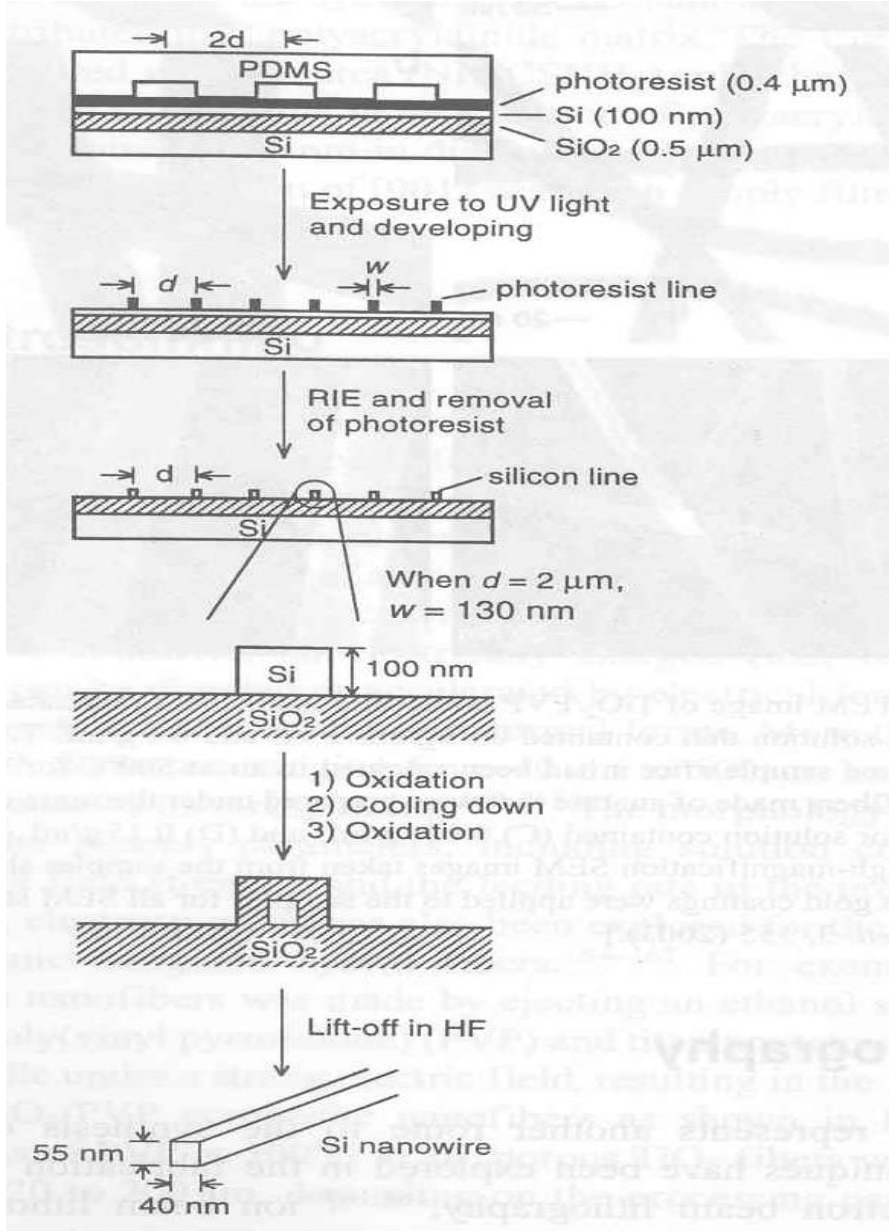
[Ref.: D.Li and Y.Xia, Nano Lett. 3(2003)555]

LITHOGRAPHY

Lithography is the technique for synthesis

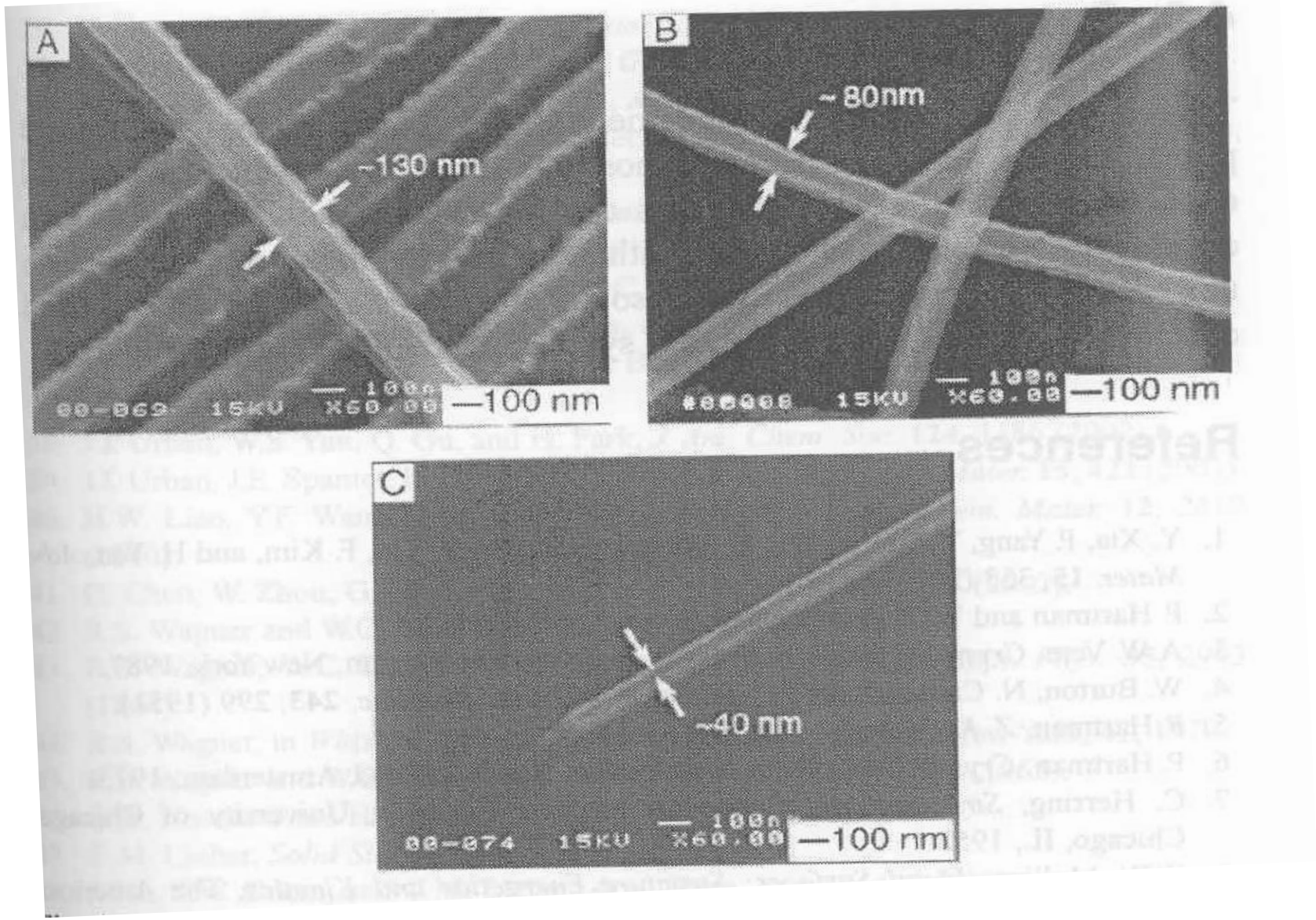
- Up to down approach
- Electron beam lithography
- Ion beam lithography
- STM lithography
- X-ray lithography
- Proxial-probe lithography
- Near-field photolithography

- Nanowires with diameters less than 10 nm and aspect ration of 100 can readily be prepared
- Example of single crystal silicon nanowire
- Nanoscale features were defined in thin film of photoresist by exposing it to a UV light source through a phase shift mask made of transparent elastomer. Such as poly-dimethyl-siloxane
- The light passing through this phase mask was modulated in the near field such that an array of nulls in the intensity was formed at the edges of the relief structures patterned on the mask.
- Therefore nanoscale features were generated in a thin film of photoresist and the pattern were transferred into the underlying substrate using a reactive ion etching or wet etching process.
- Silicon nanostructures were separated from underlying substrate by slight over-etching.



Schematic illustrating procedures used for the preparation of single crystal silicon nanowires

[Ref.: Y. Yin, B. Gates, and Y. Xia, Adv. Mater. 12 (2000) 1426].



SEM images of silicon nanostructures fabricated using such near-field optical lithography, followed by pattern transfer into silicon with reactive ion etching, oxidation or silicon at 850C in air for ~1 hr, and finally lift-off in HF solutions.

[Ref.: Y. Yin, B. Gates, and Y. Xia, Adv. Mater. 12(2000)1426].

Prof. S. K. Tripathi
Department of Physics
School of Physical Sciences
Mahatma Gandhi Central University

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