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TMT4320 Nanomaterials, fall 2015

EXERCISE 8 - SOLUTION

PROBLEM 1

a) A typical VLS process starts with the dissolution of gaseous reactants into nanosized liquid droplets of a catalyst metal, followed by nucleation and growth of single-crystalline rods and then wires (figure 1A). The 1D growth is mainly induced and dictated by the liquid droplets, the sized of which remain essentially unchanged during the entire process of wire growth. In this sense, each liquid droplet serves as a soft template to strictly limit the lateral growth of an individual wire. As a major requirement, there should exist a good solvent capable of forming liquid alloy with the target material, ideally they should be able to form eutectic compounds (figure 1B).

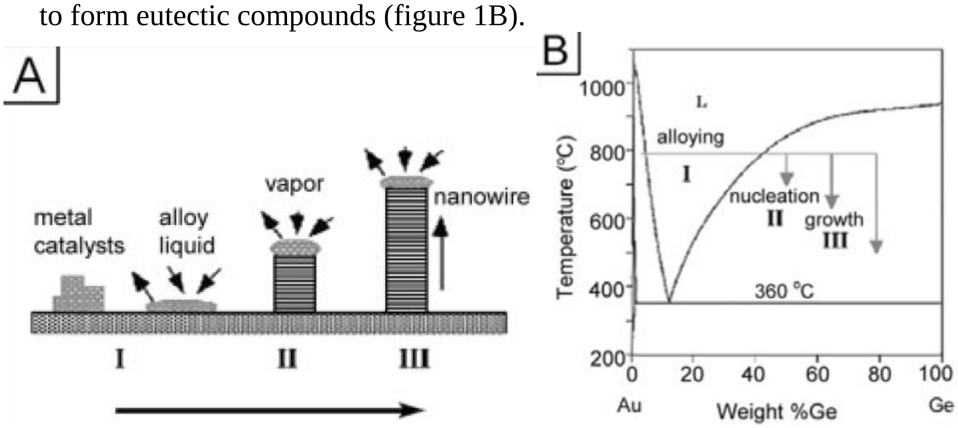


Figure 1: A) Schematic illustration showing the growth of a nanowire via the vapor-liquid-solid mechanism. B) The binary phase diagram between Au and Ge, with an indication of the compositional zones responsible for alloying, nucleation, and growth of Ge nanorods.

The vapor pressure of the precursor in the system has to be kept sufficiently low that secondary nucleation events will be completely suppressed.

Both physical methods (laser ablation, thermal evaporation, and arc discharge) and chemical methods (chemical vapor transport and deposition) have been employed to generate the vapor species required for the growth of nanowires, and no significant difference was found in the quality of nanowires produced by these methods.

b) The VLS method is a widely used method for generating 1D nanostructures from a rich variety of inorganic materials that include:
- Elemental semiconductors (Si, Ge, and B)
- III-V semiconductors (GaN, GaAs, GaP, InP, InAs)
- II-VI semiconductors (ZnS, ZnSe, CdS, CdSe), and
- Binary oxides (ZnO, MgO, SiO_2)

c) It seems to be impossible to apply the VLS method to metals and ternary oxides.

One of the challenges faced by the VLS process is the selection of an appropriate catalyst that will work with the solid material to be processed into 1D nanostructures:

- The catalyst must form a liquid solution with the crystalline material to be grown at the nanowire growth temperature.
- The solid solubility of the catalyzing agent must be low in the solid and liquid phases of the substrate material.
- The interfacial energy between the catalyst droplet and the growing nanowire is very important. A small wetting angle results in a large growth area, leading to a large diameter of the nanowires.

The problem of applying the VLS method to metals is probably mainly because of the similarities between the catalyst metal and the metal to be produced into nanowires. Most of the metals form solid solutions or intermetallic phases such that the phase diagram is much more complex than the phase diagram in figure 1B.

The problem of applying the VLS method to ternary oxides such as perovskites (general formula ABO_3) and spinels (general formula AB_2O_4) is mainly because of two reasons:

- The precursors for the ternary oxides are much more complex, containing two types of metal cations, which make the control of growth conditions more challenging. For instance, the solubility of the two metal cations in the metal catalyst can vary, which can make it very challenging to obtain a material with a desired stoichiometry.
- Lack of suitable metal catalyst which forms a eutectic solution with the ternary oxide without reacting with it.

d) The most general method to produce 1D nanostructures is the template filling method, which can be used for almost all types of materials (also metals and ternary oxides). A template with 1D porous channels is filled with a solution, dispersion or melt containing the desired material or precursors. After a drying/crystallizing/annealing step (or several steps) the template can be removed (if necessary), obtaining free 1D nanostructures.

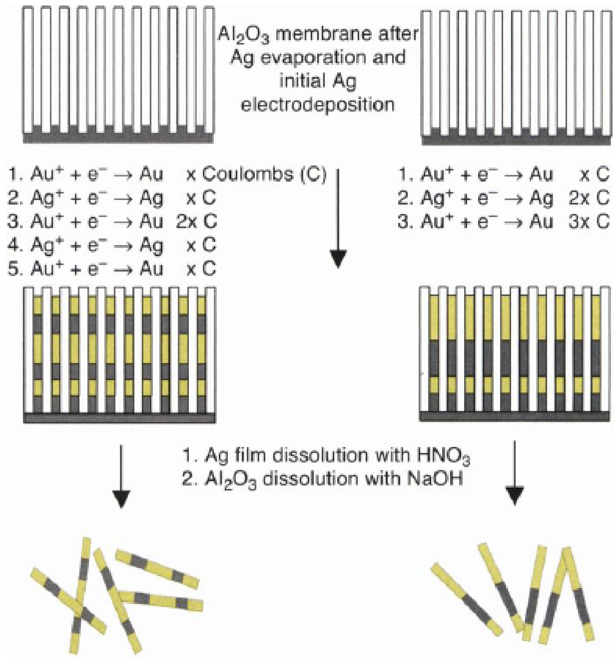
Typical templates are nanoporous anodic aluminum oxide (alumina) and track-etched polymers. The alumina template can be removed by dissolving in NaOH solution, while polymer templates are removed by annealing in air or oxygen to burn away the polymer.

PROBLEM 2

a) How to make barcoded nanorods:

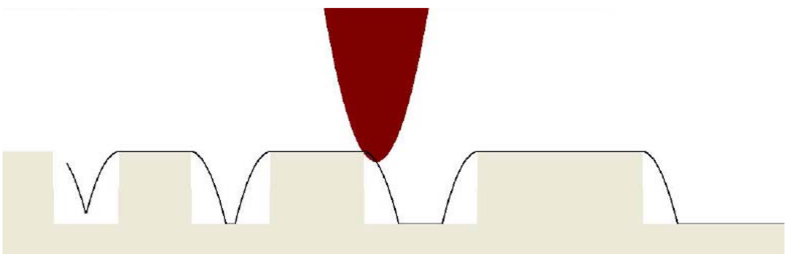
- A thin metal film is evaporated onto one side of the membrane, and serves as the electrode to initiate electrochemical deposition of metals within the nanochannels.
- The template is then immersed into a metal salt bath and an electrical potential is applied. The metal deposition begins at the metal contacts at the bottom of the channels by reduction of the metal ions.
- The length of the metal segment scales directly with the number of coulombs of electricity passed.
- The metal backing is dissolved using an appropriate acid, for instance HNO_3 for Ag.
- The alumina membrane is dissolved using sodium hydroxide, giving free-standing nanorods.

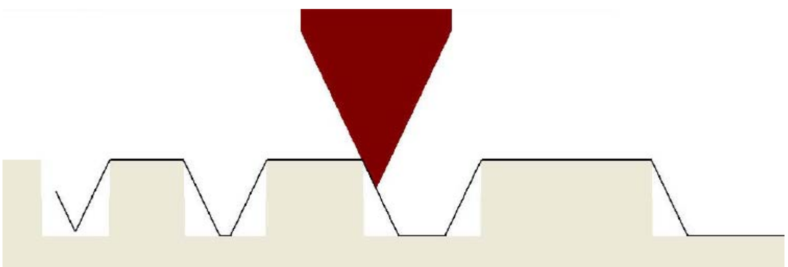
b) The bath can be switched between baths with different metal salts to grow different segments. See the figure below.

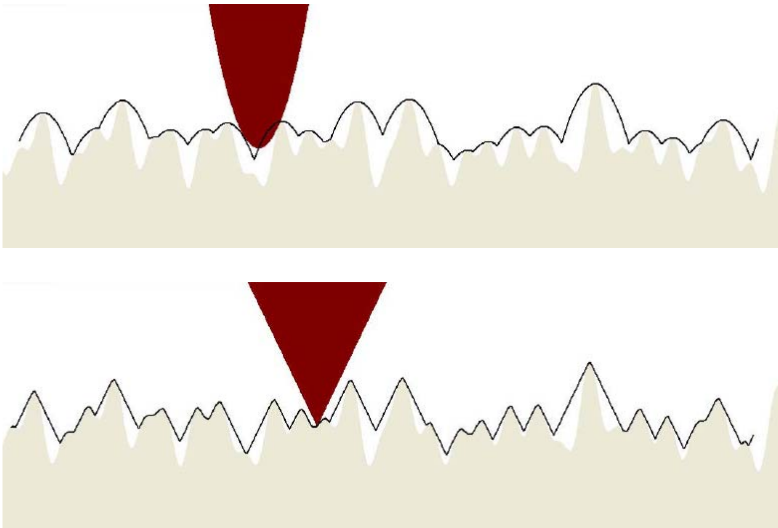


PROBLEM 3

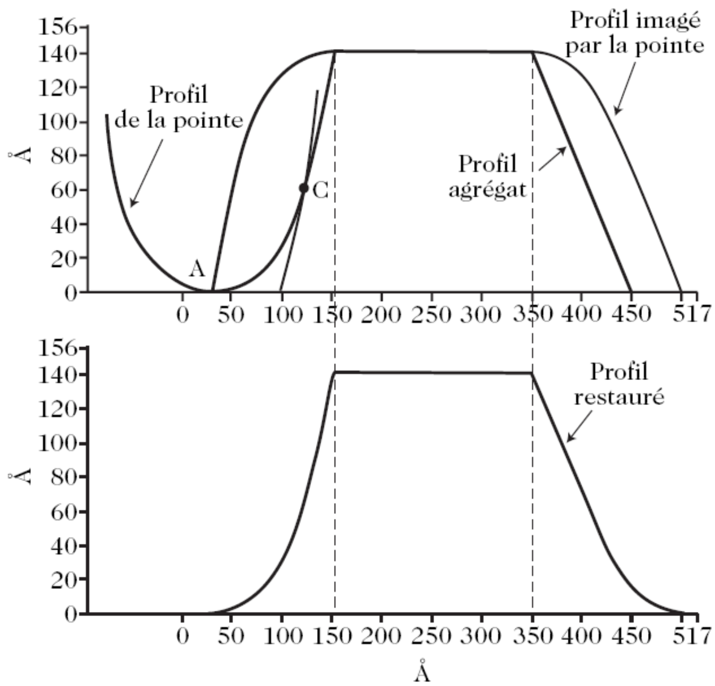
a) The four linescans are shown below:





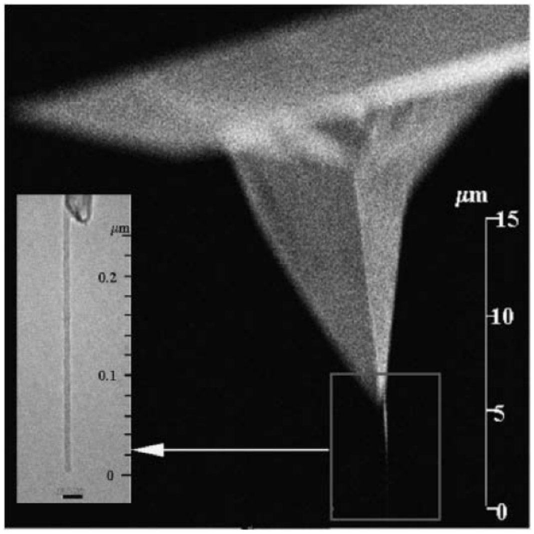


b) If the shape of the tip is known the images can be partly corrected. On the corrected profile, information has been lost at the base of the particle, up to a height equal to the radius of curvature of the tip. See the figure below for a reconstruction of a structure with sloping sides.



For stepped surfaces such as in figure 1a in the exercise, the 100% correct profile cannot be obtained because the aspect ratio of the tip needs to be extremely high to obtain the exact profile during a scan. However, by reconstruction one will obtain a more correct profile than without reconstruction.

c) The convolution effect can be minimized by increasing the aspect ratio (length/diameter) of the tip. One solution is to fix a multiwalled nanotube at the end of a standard tip (see figure below). The nanotube is fixed either by sticking it on, or by growing it directly on, the standard tip by catalyst-assisted chemical vapor deposition. These tips considerably enhance the resolving power of such instruments compared with standard tips, because their very small radius of curvature allows one to overcome the problem of convolution of the tip with the imaged object. Such tips are already commercially available.



Tip of an atomic force microscope with a multiwalled nanotube stuck onto it. *Insert*: TEM image of the nanotube.