

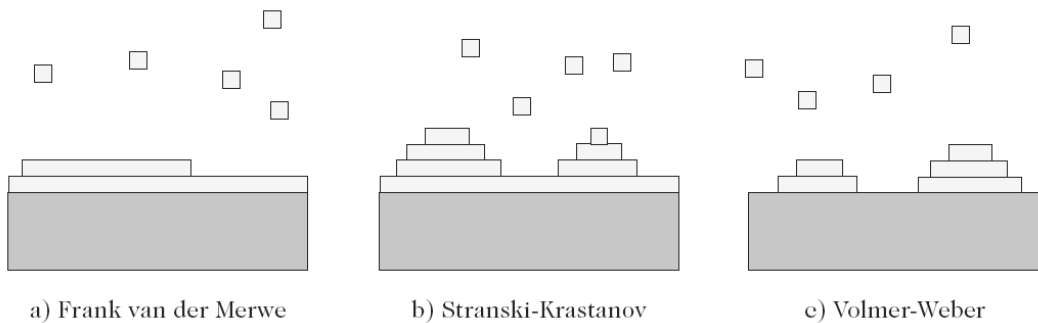


TMT4320 Nanomaterials, fall 2015

## EXERCISE 9 - SOLUTION

### PROBLEM 1

a) The three growth modes for growth on a substrate:



Frank-van der Merwe (layer-by-layer): In the layer-by-layer mode a new layer only begins when the previous one has been completed, and the successive layers tend to spread out.

Stranski-Krastanov (intermediate growth mode): Begins with two-dimensional growth and then continues by three-dimensional growth. In this case, the overall interaction energy between the adsorbed atom and the film varies significantly with the thickness of the deposited film, and this transition can be quite abrupt in many pairs of metallic or semiconductor systems after the deposition of just a few monolayers.

Volmer-Weber (island): In the island growth mode small clusters nucleate directly on the surface of the substrate and the atoms tend to bind to each other rather than to the substrate.

b) How do the interface energy and the surface energies of the substrate and the adsorbate influence the morphology of the growing structures?

Depending on the balance of free energies  $\gamma$  in the adsorbate, the substrate, and the interface between the two, three basic growth modes are possible. If

$$\gamma_{\text{substrate}} > \gamma_{\text{adsorbate}} + \gamma_{\text{interface}},$$

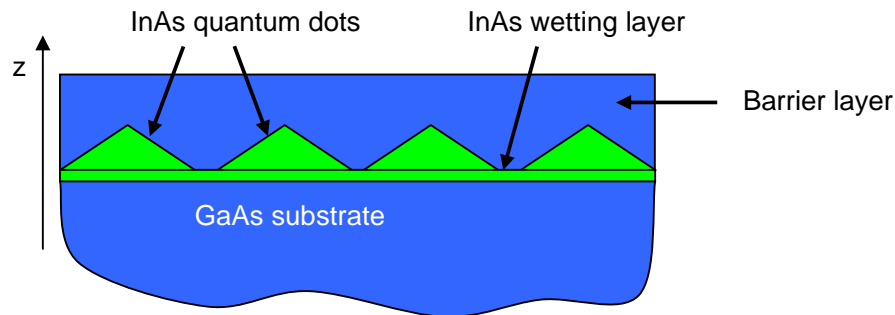
the first layer will tend to wet the substrate. Concerning subsequent growth, there are two possible situations: either the arriving atoms form further layers and the growth is then said to occur layer-by-layer or by the Frank-van der Merwe mode; or the free energy of the substrate has already been reduced (and/or the energy due to the lattice mismatch comes into play) and the growth continues in the form of islands on this first layer (Stranski-Krastanov mode). If the energy balance is such that

$$\gamma_{\text{substrate}} < \gamma_{\text{adsorbate}} + \gamma_{\text{interface}},$$

the adsorbate will form 3D islands directly (Volmer–Weber mode). It is commonly observed if a reactive material is deposited on an inert substrate, e.g., a transition metal on a noble metal or an oxide.

- c) Which growth mode is observed in the growth of InAs quantum dots on GaAs by molecular beam epitaxy? Is this growth mode ideal for the use of quantum dots in intermediate band solar cells?

InAs quantum dots on standard GaAs grow by Stranski-Krastanov growth. The quantum dots are situated on top of a wetting layer (see figure below).

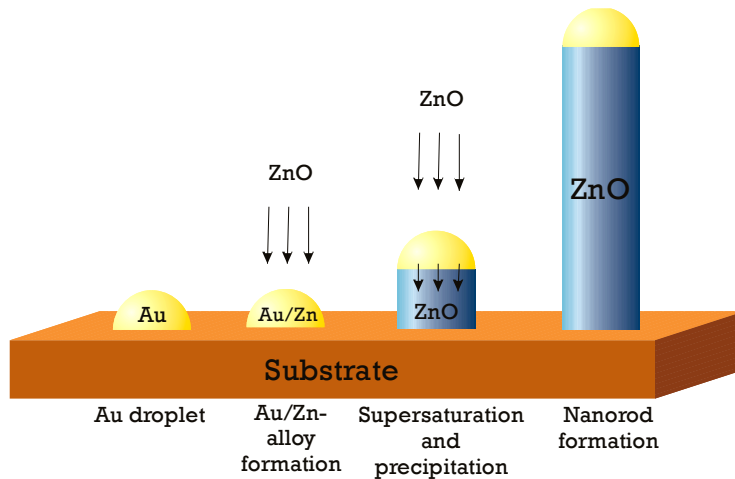


Ideally, the quantum dots should rather grow by Volmer-Weber growth to avoid formation of the wetting layer as the wetting layer hinders total separation of the quantum dots. However, in this growth mode you might encounter issues with lack of epitaxy, which leads to grain boundaries that function as recombination centers. In order to achieve this growth mode it would also be necessary to use completely different materials, with different surface properties, and these would not have the required properties for solar cell applications.

## PROBLEM 2

- a) A single crystalline Ge nanowire could be produced by utilizing the VLS (vapour-liquid-solid) mechanism. There are two methods that could potentially be used here with equally success. These are molecular beam epitaxy (MBE) and pulsed laser deposition (PLD). The first step would be to deposit a thin layer of gold (only a few nm) on a substrate. This does not need to be performed in the MBE or PLD equipment, but is usually done by sputter coating before the substrate is entered into the reaction chamber. When the substrate is then placed in the reaction chamber, it is heated to a temperature where the gold will start to melt and de-wet the surface. Small nanodroplets of gold will be produced which can act as catalyst particles for the nanowire growth. The Ge precursor can then be supplied either by evaporation by resistive heating (MBE) or by ablating a Ge target with a laser (PLD). The gold droplet will be saturated with Ge and the nanorod will start precipitating out from underneath the catalyst droplet. Growth will continue as long as the catalyst is kept in the liquid phase and precursor is supplied. The diameter of the gold particle will determine the diameter of the nanowire. See figure below for details. The figure shows growth of ZnO nanowires, but the mechanism will be the same for Ge.

The easiest way to now obtain an amorphous shell of  $\text{SiO}_2$  is perhaps to dip coat the Ge nanowires in a stable silica sol. This sol is produced by conventional sol-gel technology. It is important that the pH and degree of hydrolysis of this sol is kept sufficiently low so that a gel network can be formed rather than nanoparticles. After the nanowires have been coated they would need a slight heat treatment at 300-400 °C in order to remove excess organic components used to produce the sol.



- b) Producing a crystalline silica shell rather than an amorphous one can be achieved in at least two ways. The easiest would probably be to heat treat the core-shell nanowires obtained in part a) at a temperature where the amorphous silica would start to crystallize. However, at these temperatures the crystalline structure and morphology of the core may start to change. High temperatures may also affect the boundary between the core and the shell by silica diffusing into the Ge-matrix or visa versa. This would give a diffuse rather than an abrupt boundary.

Another method to achieve a crystalline shell could be to directly coat the nanowires while still in the BME or PLD equipment. Both types of equipment would require a solid crystalline source of  $\text{SiO}_2$  to be evaporated. If this is done after the catalyst particle is solidified, the growth will occur radially rather than axially.

### PROBLEM 3

There are a number of different ways to organize nanowires or other nanostructures on a surface. Some of the possible options have not yet been covered during lecture, but will come later on. One option that has been briefly mentioned, but not covered in detail is described below.

Patterning can be achieved by starting with a single crystalline silica substrate. Since certain crystallographic directions are more easily removed when the right etching solvent is used, this substrate can be selectively etched to produce highly ordered V-shaped grooves in the surface. The etching is usually initiated by introducing small line defects in the substrate first. Methods to achieve this will be covered in later lectures.

When the grooves are formed, a solution of dispersed nanorods can be deposited onto this patterned substrate. When the solvent is evaporated, the nanowires will align at the bottom of the V-grooves due to capillary forces and gravity. If the dispersion of nanowires is too concentrated, the nanowires may start to align on top of each other. But if the ratio of nanowires to amount of solvent is controlled at a sufficient level, it should be possible to achieve highly ordered nanowires at the bottom of the V-grooves. Some shaking or stirring may be necessary in order to prevent the nanowires from settling across the grooves, perpendicular to the direction of the grooves. The side walls of the grooves can later be removed by selective etching (reactive ion etch or some other form of etching).

Another method to achieve this type of self-assembly would be to utilize chemical recognition. This has also been briefly covered during a previous lecture. Here, parallel lines of molecules that would attract the nanowires in question can be written on the substrate. The writing can be achieved by using for example an AFM tip dipped in a solution of the wanted molecules. The molecules can also be printed on the substrate by using a premade PMMA stamp (or similar) with the desired pattern. Writing/printing using an AFM tip or PMMA stamp will be covered in later lectures.

Once the desired molecules have been written on the substrate, the nanowires dispersed in a solution are introduced onto the substrate. The nanowires will now be aligned according to the written pattern due to attractive forces between the written molecules and the nanowires.