Also for epitaxial growth we observe characteristic growth scenarios. For growth determined by energetics (not too far from equilibrium) we distinguish three growth modes according to Bauer:

- Frank - van der Merwe : 2D, layer-by-layer
- Volmer - Weber : 3D, crystallites
- Stranski - Krastanov : 2D followed by 3D

See Fig. 6.7 Why we observe these growth modes will be discussed in the following chapter

8.2 Nucleation

The concept of nucleation is of fundamental importance. Therefore we spend the time and consider first homogenous nucleation. Consider a supersaturated vapor which forms liquid droplets. Initially we have vapor only:

$$G_S = n^g \cdot \mu^g$$

If we form a droplet of radius r we have

$$G_E = (n^g - n^\ell) \mu^g + n^\ell \mu^\ell + 4\pi r^2 \gamma$$

Then $\Delta G = G_E - G_S = -n^\ell (\mu^g - \mu^\ell) + 4\pi r^2 \gamma$

or $\Delta G = -\frac{4}{3}\pi r^3 \cdot \frac{1}{v^\ell} \cdot \Delta\mu + 4\pi r^2 \gamma$; $\Delta\mu = kT \ln \frac{P}{P_0}$

This corresponds to situation I in Fig. 6.8. The size of the critical nucleus is defined by

$$\frac{\partial \Delta G}{\partial r} = 0 = -4\pi r^2 \cdot \frac{1}{v^\ell} \Delta\mu + 8\pi r \gamma$$

$$\Rightarrow \quad r^* = \frac{2\gamma v^\ell}{\Delta\mu}$$

and the height of the nucleation barrier is given by

$$\Delta G^* = \frac{16\pi}{3} \cdot \frac{\gamma^3 v^{\ell 2}}{\Delta\mu^2}$$

Note that the size of the critical nucleus r^* is the one for which the vapor pressure of the droplet matches the supersaturation

$$\Delta \mu = \frac{2 \gamma v^\ell}{r^*}$$

In conclusion, for a phase transition there is a nucleation barrier, which can be only surmounted by fluctuations. The nucleation barrier decreases with increasing supersaturation. The nucleation rate I is essentially determined by the probability, that the systems displays a fluctuation in Gibbs free energy of magnitude ΔG^* : $P \sim e^{-\frac{\Delta G^*}{kT}}$

Let us now consider heterogeneous nucleation, i.e. nucleation of a condensed phase in the presence of a substrate. Again we will work in the liquidlike approximation, neglecting for now effects of anisotropy in γ. Close to equilibrium, the balance of surface and interface energies for the condensation of a liquid phase on a solid substrate from the vapor is given by Young's equation

$$\gamma^{sg} = \gamma^{\ell s} + \gamma^{\ell g} \cos \theta$$
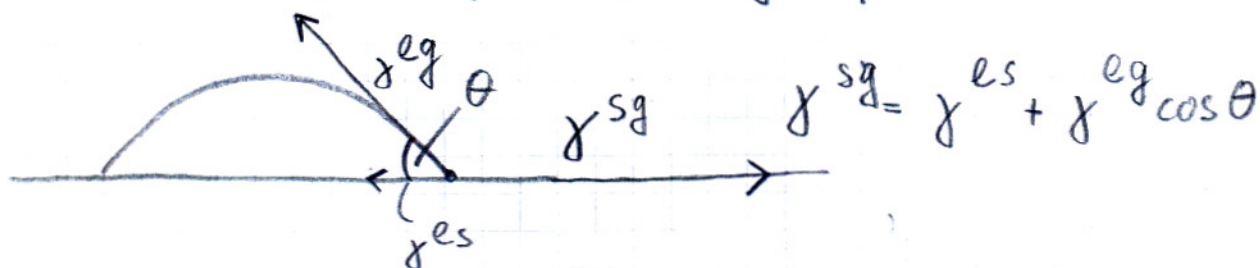
For this situation we obtain

$$\Delta G = - n^\ell \Delta \mu + (\text{droplet surface}) \, \gamma^{\ell g} + (\text{interface}) \, (\gamma^{\ell s} - \gamma^{sg})$$

If we analyse this case in detail and enter the expressions for the droplet surface and the interface area, we find out that the radius r^* of the critical nucleus remains unchanged : $r^* = \frac{2 \gamma^{\ell g} \cdot v^\ell}{\Delta \mu}$

where r^* is only defined for $\theta > 0$. However it is evident that for $\theta < 180°$ fewer particles are necessary to form a nucleus. Consequently the nucleation barrier ΔG^* is lowered. It may be written as

$$\Delta G^*_{het} = \Delta G^*_{hom} \cdot \phi(\theta)$$

with $\phi(\theta) = \frac{1}{4}(1-\cos\theta)^2 \cdot (2+\cos\theta)$
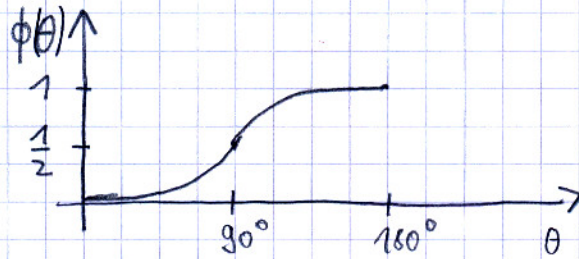
Before we consider the growth of a solid thin film on a solid substrate, we stick for a moment to the liquidlike approximation and consider the formation of a condensed phase from the vapor in dependence of surface energetics and supersaturation.

- $\theta > 0$, i.e $\gamma^{sg} < \gamma^{ls} + \gamma^{lg}$ and $\Delta\mu > 0$ (supersaturation)
  This case is similar to homogenous nucleation, but with a lowered nucleation barrier ΔG^*_{het}. It is represented by curve I in Fig. 6.8

- $\theta > 0$ and $\Delta\mu < 0$ (undersaturation). Not only that a condensed phase does not wet the substrate, a particle in the condensed phase has a higher chemical potential then in the vapor. This case is represented by curve V (dashed line) in Fig. 6.8

- $\theta = 0$, i.e $\gamma^{sg} \geq \gamma^{ls} + \gamma^{lg}$ and $\Delta\mu > 0$ (supersaturation)
  The condensed phase wets the substrate, i.e. there is no extra interface work connected with the formation of the condensed phase. Moreover each particle in the condensed phase has a lower chemical potential. This is growth without nucleation and corresponds to curve IV in Fig. 6.8

- $\theta = 0$ and $\Delta\mu < 0$ (undersaturation)
  Particles adsorbing on the substrate lower the interface energy of the system. However once the substrate surface is covered by a monomolecular layer no more interface energy is gained. As the chemical potential in the extended condensed phase is higher than in the vapor

condensation steps. This case corresponds to curve II in Fig. 6.8. Our
discussion implies that <u>adsorption always lowers the surface energy</u>

Next we consider the case of the formation of a solid crystalline – not
a liquid – condensed phase. Still we will not think precisely about
the anisotropy of surface energy. Let us assume for the moment identical
lattice parameters $a_d = a$ and $a_s = a$ (where „d" indicates deposit). The
surface and interface energies may be expressed through band strength
ψ in the picture of the Kossel crystal:

$$\gamma^{dg} = \frac{1}{2} \frac{\psi_{dd}}{a^2}$$

$$\gamma^{sg} = \frac{1}{2} \frac{\psi_{ss}}{a^2}$$

$$\gamma^{sd} = \frac{1}{2} \frac{\psi_{ss}}{a^2} + \frac{1}{2} \frac{\psi_{dd}}{a^2} - \frac{\psi_{ds}}{a^2}$$

- $\gamma^{sg} < \gamma^{dg} + \gamma^{sd}$, i.e. non-wetting behavior and $\Delta\mu > 0$.
  The deposit will grow in form of small crystallites as the deposit
  bonds are stronger than the substrate - deposit bonds. We have again
  the case I. The growth - mode is named Vollmer - Weber growth
  and is visualized in Fig. 6.9.
- $\gamma^{sg} < \gamma^{dg} + \gamma^{sd}$, i.e non wetting behavior and $\Delta\mu < 0$
  Curve IV as before. No growth. No adsorption
- $\gamma^{sg} \geq \gamma^{dg} + \gamma^{sd}$ and $\Delta\mu > 0$ (supersaturation).
  This situation does <u>not</u> correspond to curve IV, but to curve I or II
  The reason is as follows. Consider first homoepitaxy. Then $\gamma^{sd} = 0$
  and $\gamma^{sg} = \gamma^{dg}$. Then already for the first layer the formation of
  twodimensional nuclei is necessary. Although there is no interface

energy connected with the formation of the 2D crystallite, its formation requires edge energy

↙ broken edge bond.
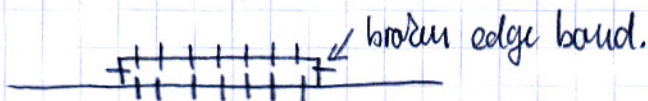
Therefore a nucleation barrier has to be surmounted, leading to case I. If however $\gamma^{sg} > \gamma^{dg} + \gamma^{sd}$, it may well be that the interface energy gain due to particle adsorption is large enough, such that nucleation is not necessary.

However, after a few layers, the chemical influence of the substrate has decayed and we are again in the situation of 2D nucleation. This situation is characterized by curve III. The corresponding growth mode is the Frank - van der Merwe growth. An example gives Fig. 6.10.

The third growth mode, the Stranski-Krastanov growth results from epitaxial misfit. If $a_s \neq a_d$ the deposit layers will be strained, resulting in elastic energy $\gamma_{el} \sim E_{eff} \varepsilon^2$, with E_{eff} being an effective elastic modulus, $\varepsilon = m$ the misfit. γ_{el} is the elastic energy per layer. Assume now the first deposited layer to wet the substrate, i.e.

$$\gamma_{(1)}^{sg} > \gamma_{(1)}^{dg} + \gamma_{(1)}^{sd} + \gamma_{el} \qquad \text{and } \Delta\mu > 0.$$

This condition may be fullfilled for a few layers. But eventually the chemical influence of the substrate dies and $\gamma_{(n)}^{sg} = \gamma_{(n)}^{dg}$ and $\gamma_{(n)}^{sd} \approx 0$. Then the elastic energy γ_{el} makes the inequality invalid and growth does not more take place layerwise. Instead it switches to crystallite formation in order to get rid of the elastic energy.

There are generally three stages of release of elastic energy:

- tetragonal distortion (already in the layerwise growth)
- formation of coherently strained islands
- introduction of misfit dislocations

Fig. 6.11.

Fig. 6.12 displays a nice false color representation of hut-clusters formed in the Stranski-Krastanov growth of Ge on Si. Figs. 6.13 and 6.14 display the sequence of growth situations observed in stranski-Krastanov growth of Si of $Si_x Ge_{1-x}$ on Si.

Starting with the wetting layer, after deposition of about 3 ML hut clusters form, which release strain energy coherently. The hut clusters are bounded by (015) facets. After a critical amount of material has been deposited the hut clusters collaps and form coherent, large dome clusters. These dome clusters are considerably deformed in their lattice. Specifically they induce also a substrate deformation. Close to coalescence coherent strain relaxation breaks down and misfit dislocations are injected, which reach down to the substrate. Eventually a relative flat, dislocated films is reached.

As shown in Fig. 6.15, in Si/SiGe multilayer growth a vertical positional alignment of island positions takes place. The reason is that the coherently strained Si/Ge islands cause an elastic distortion in the overgrowing Si. Thus right above the island the Si is strained and has a lattice parameter slightly larger than its equilibrium one. Thus at these locations upon renewed SiGe island formation less strain in these islands is necessary and for energetic reason they will preferentially form on top. As shown in Figs. 6.16 & 6.17 this mechanism leads to an improved size distribution of islands after a number of layers through two mechanisms:

- two nearby island give rise to only one strain-field minimum
- in large gaps in between islands a shallow minimum causes preferential nucleation.

This mechanisms has been brought to the ultimate in the multi-layer epitaxy of PbSe islands on $Pb_{1-x} Eu_x Te$ spacer layers.