Nanoscale Science – Semiconductor Nanostructures

1. MBE quantum dots

1.1 Molecular beam epitaxy

One possible technique to create nanostructures on semiconductor surfaces is molecular beam epitaxy (MBE). In general MBE is a highly controlled ultra high vacuum (UHV) technique where evaporated material in front of a semiconductor substrate results in the epitaxially crystalline growth of the substrate. This allows the production of novel materials with excellent atomic-level control of surfaces and interfaces. Under certain conditions this method offers the possibility of forming strain-induced nanoscale islands (dimension ~ 10 – 100 nm) with high crystalline quality, so-called quantum dots (QDs), which will be the topic of this lecture.

The constituent parts of a MBE chamber are shown in a schematic drawing in Figure 1: in several effusion cells the desired growing material is heated up to a temperature which generates an appropriate flux of atoms. By opening a shutter, this flux can pass the UHV chamber and reach the surface of a heated sample lying opposite to the cells. In order to avoid contamination and to guarantee that the molecules of the beam can reach the sample surface, the MBE growth should be carried out in UHV environment.

In order to control the growth process in situ, reflection high energy electron diffraction (RHEED) is utilized to determine the surface quality, the surface reconstruction and the flux rate. This analysis method uses a high energy (~ 20 keV) electron beam which strikes the sample surface at a glancing angle and is then reflected to a fluorescent screen. Because of the grazing incidence, the electron beam is scattered on the first monolayers of the sample leading to a very high surface sensitivity. Therefore the diffraction pattern on the screen gives qualitative information about the surface morphology. Besides, this method is a powerful instrument to calibrate the growth rates of the cells. If the surface is perfectly flat, the intensity of the spots in the diffraction pattern will be very high. With the beginning of the layer-by-layer growth the intensity of the spot decreases, because the steps, which are formed during the growth of the first monolayer, scatter the incoming electrons. Further growth completes the two dimensional islands to one monolayer and increases again the spot intensity, resulting in an oscillatory behavior of the intensity. Thus, the time between two maxima of this oscillation is needed to grow one monolayer. Since the geometry of the RHEED setup doesn't affect the growth process, it allows doing in situ analysis during the growth of the sample.

The low growth rate (typical growth rate: 0.1 – 1.0 ML/s) and the UHV environment make the MBE technique complex and time consuming. However, these pretended disadvantages represent also the power of this deposition method: First, MBE provides an excellent control of interfaces due to the low growth rate (abrupt changes of layer compositions and doping profiles on a atomic scale), second, the purity of the material is very high and third, the in situ control of the surface by surface characterization methods (e.g. RHEED, Auger electron spectroscopy (AES)) is possible due to the UHV.[1, 2]

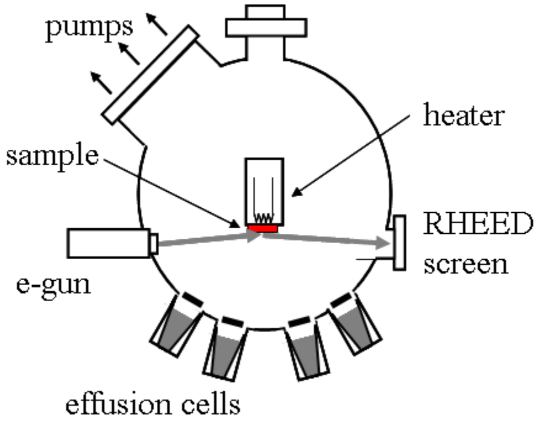

Figure 1 Schematic drawing of an UHV MBE chamber.

1.2 Thin film growth

For describing the growth of thin films the consideration of thermodynamics as well as kinetics is essential. There are different important growth parameters favoring either thermodynamic or kinetic processes. One important parameter is the surface diffusion *D*, which describes the ability of the deposited atoms to move around on the surface. This thermally activated process can be controlled via the substrate temperature during the growth. Another important parameter is the deposition rate *F* specifying the number of atoms or molecules that reach the surface per second. The ratio between *D* and *F* plays a key role during deposition. For a small ratio the absorbed atoms cannot reach the surface potential minima, because the number of impinging atoms per time interval is too high. Then the growth process is controlled by kinetic mechanisms (e.g. growth of metallic structures on metallic substrates). By contrast a small deposition rate relative to diffusion results in a system which is close to thermodynamic equilibrium (e.g. molecular self assembly on metallic substrates). In between these two extreme cases one can also find systems where thermodynamics as well as kinetics play an essential role (e.g. Stranski-Krastanov quantum dots)[3].

During the deposition of thin films different growth modes can occur depending on the change of the total energy $\Delta\gamma$ of a surface before and after deposition. $\Delta\gamma$ can be described by the following equation:

$$\Delta\gamma = \gamma_F + \gamma_{S/F} - \gamma_S$$

γ_F is the film surface energy, γ_S is the substrate surface energy and $\gamma_{S/F}$ is the interface energy between the substrate and the film. This equation characterizes the interaction between the substrate and the adsorbates. Two limiting cases can be considered: First, the interaction between the substrate and the adatoms is much higher than the interaction between the adatoms among each other, i.e. $\Delta\gamma < 0$, resulting in a layer–by–layer growth mode or **Frank–van der Merwe** growth. Second, if the adatoms are more strongly bound to each other than to the substrate ($\Delta\gamma > 0$), three dimensional islands will form on the surface. This is called island growth or **Volmer–Weber** growth. An intermediate case is the **Stranski–Krastanov** growth mode, which is described in the next chapter.

1.3 Stranski–Krastanov semiconductor quantum dots

1.3.1 The growth of Stranski–Krastanov quantum dots: from pyramids to domes

The Stranski–Krastanov growth mode is a well-established method for the fabrication of semiconductor quantum dots. The epitaxial growth of two lattice mismatched systems can lead to the formation of three dimensional islands. During the first period the growth is determined by a high adatom substrate interaction leading to the wetting of the surface ($\Delta\gamma < 0$). However after reaching a critical thickness of the film the layer–by–layer growth becomes unfavorable, because of an increased strain between the substrate and the film induced by different lattice constants. As a consequence three dimensional islands occur on the surface whose shape, size and composition are strongly influenced by the growth parameters, that means by the interaction of thermodynamic and kinetic processes. The two most famous systems are Ge on Si (001) (lattice mismatch ~ 4 %) and InAs on GaAs (001) (lattice mismatch ~ 7 %).

The change of the Gibbs free energy of a lattice mismatched system during the growth of an island can be described by the following expression:

$$E_{total} = E_{strain} + E_{surf}$$

The strain energy E_{strain} is always negative ($E_{strain} = -\alpha \cdot V$) whereas the surface energy $E_{surf} = \beta \cdot V^{2/3}$ makes a positive contribution to the total energy. The coefficients α and β describe the island shape, the free energy of the surface, the Poisson ratio and shear modulus of the substrate[4]. The fact that the signs of the two terms E_{strain} and E_{surf} are different results in a change of the slope of E_{total} with decreasing volume. At a certain critical volume V^* the change of E_{total} becomes negative ($\partial E_{total} / \partial V < 0$). That means that any further increase of the volume leads to a reduction of the free energy after a critical energy barrier E^* has to be overcome. As a result, islands with a volume $V > V^*$ grow while in the opposite case ($V < V^*$) islands are not stable (see Figure 2).

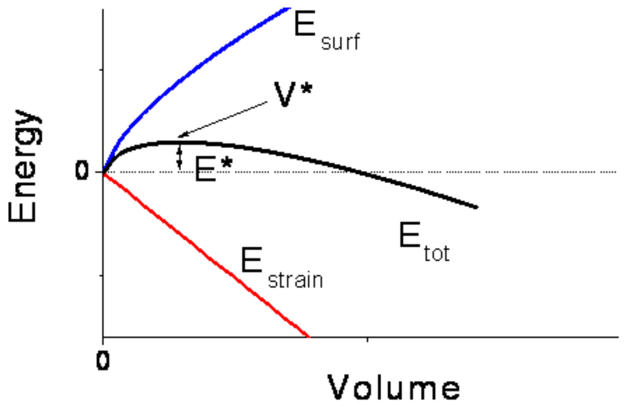

Figure 2 The change of the Gibbs free energy E_{tot} (= E_{strain} + E_{surf}) in dependence on the volume (black curve); islands with a critical volume V^* that have overcome a critical energy barrier E^* continue to grow.

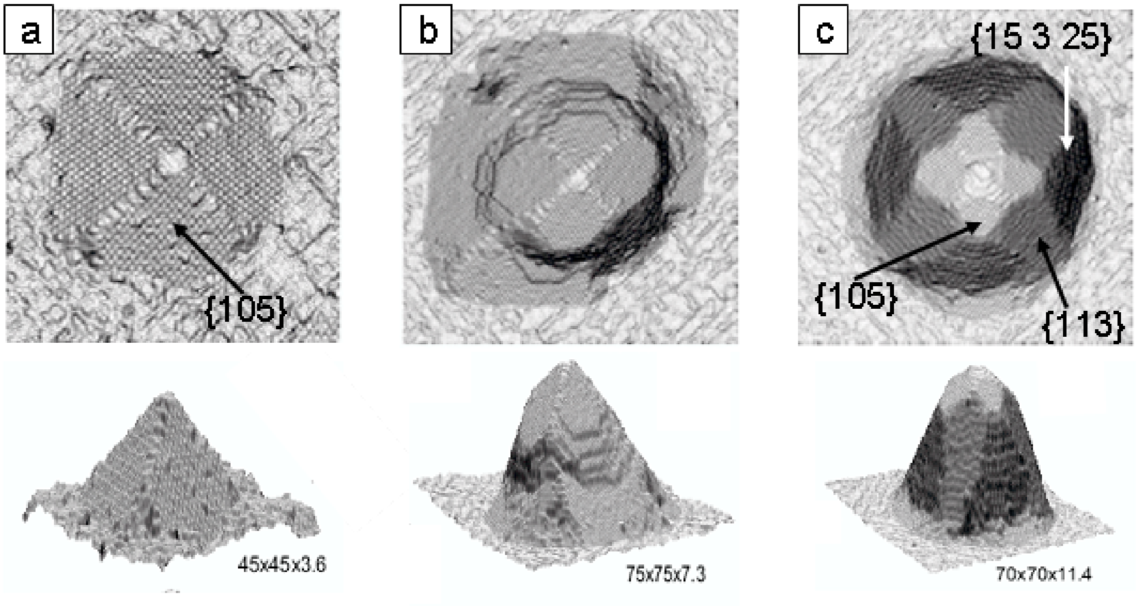

Figure 3 STM images and 3D views illustrating the transition from pyramid to dome during the growth of Ge/Si (001) quantum dots; (a) shows a pyramid, (b) a transition dome and (c) a dome, image scales are in nm.[7]

But besides the growth of the islands after a critical amount of material is deposited, also a shape transition from small shallow pyramids to steeper multi – faceted domes takes place. This can be described by a phase diagram for the island shape as a function of volume and surface energy[5, 6]. The shape change of semiconductor quantum dots was mainly studied by high resolution scanning tunneling microscopy (STM).

Concerning the Ge/Si (001) system three different basic types of islands evolve over time: pyramids, transition domes and domes, which are shown in Figure 3.

They can be distinguished by their facets. Whereas the pyramids are made up of shallow {105} facets, the domes consist of {105}, {113} and {15 3 25} facets. Additionally also intermediate types of islands can be found, so–called transition domes, which have incomplete facets. It could be shown that the pyramids grow from top to bottom. At a certain critical volume incomplete facets are formed. The bunching of the steps at the end of these facets leads to a steeper dome facet[8]. This can be nicely seen in the 3D views of Figure 3.

For the InAs/GaAs (001) system a similar shape transition takes place. For small islands shallow {137} facets are energetically more favorable, while the larger islands are multifaceted domes ({110}, {111} and $\{\bar{1}\bar{1}\bar{1}\}$)[9]. The transition occurs in an analogous way as for the Ge/Si (001) system: the incomplete growth of the {137} facets of the pyramids leads to the formation of steeper facets.

1.3.2 The influence of growth parameters

As already mentioned above the growth process is highly determined by the competition between thermodynamic and kinetic processes, and therefore by the selected growth parameters. This strong influence of the parameters gives the possibility to manipulate the properties of quantum dots; what is an essential issue for applications.

In the following text the effect of some important growth conditions on the InAs/GaAs (001) system will be described very shortly.[10, 11]

Amount of deposition:

Since a detailed description of the influence of the amount of deposition was already given in the last chapter, only a short summary will be shown in this paragraph. The amount of material, which is deposited, is responsible for the evolution of two dimensional layer–by–layer growth to three dimensional island growth coming along with the a shape transition. Typically, at the beginning of the growth process only small terraces are formed followed by the formation of two–dimensional islands during further deposition. The additional increase of the amount of material on the substrate induces the growth of quantum dots and finally the development of dislocations and a non–uniform size distribution of the dots, because of a rearrangement of the atoms from the two–dimensional islands to the quantum dots.

InAs growth rate:

With a decreasing InAs growth rate the density of the quantum dots decreases and the average height of the dots increases. Furthermore a smaller flux leads to improved size uniformity. The reason for that behavior is that the arriving atoms have enough time to move around the surface to find an energetically favored place. In other words the growth conditions are close to thermodynamic equilibrium.

Substrate temperature:

Decreasing the substrate temperature has a similar effect as increasing the growth rate, which leads to a higher density of quantum dots with a smaller size. At an increased temperature the surface diffusion length of the adsorbed atoms is higher and the atoms are more mobile.

Additionally, a lot of further parameters could be discussed, which also influence the shape, the size and the composition of the quantum dots, e.g. the selected As–flux or growth interruptions after the formation of the quantum dots. More details can be found in the literature.

By means of an appropriate choice of these growth parameters one can tune (in a certain range) the optical and electronic characteristics of the dots. That means that for example for larger quantum dots the confinement energy is smaller and therefore these dots emit at a higher wavelength.

1.3.3 Overgrowth of quantum dots

In order to get an optical active system it is necessary to overgrow the MBE quantum dots with a large band gap material (usually the same as the substrate material). This is required to passivate the surface states, which are typically located in the band gap and lead to non radiative recombination of the charge carriers. Furthermore, another advantage of this capping layer is that the discontinuity in the band diagram acts as a trap for the charge carriers which can then recombine by emitting light. But the effects of the capping layer on the morphology of the dots are not as harmless as it had been assumed before the first systematic studies on the influences of the capping process were performed.[12, 13] It changes the morphology and also the composition of free standing quantum dots, because this process is again combined with strain release, segregation and intermixing of the atoms. As a consequence the optoelectronic properties become modified. Thus the investigation and understanding of this growth process is an essential issue to control their properties.

The development of InAs/GaAs (001) quantum dots for increasing GaAs capping layer thickness was investigated by scanning tunneling microscopy measurements. Two regimes can be clearly distinguished whereas also the GaAs flux rate plays an important role. While in the first regime (regime I) a back transition can be observed independent of the used GaAs flux, the dots show a completely different evolution path in the second regime (regime II) in dependence on the selected GaAs flux. In the following paragraph the two regimes will be described in detail:

In regime I strong modifications occur: the dots shrink drastically and material starts to accumulate around the islands. This process is explained in the following way: The arriving Ga atoms don’t find favorable adsorption places on the InAs islands, because of the high lattice mismatch of InAs and GaAs. This is why they accumulate around the islands where the lattice parameter is similar to GaAs. At the same time In atoms diffuse from the top of the islands to the base and intermix with Ga to release elastic strain by alloying. Thus the islands’ heights decrease. High resolution scanning tunneling microscopy images reveal that in this regime a backward transition from domes to pyramids takes place indicating thermodynamic equilibrium conditions. This can be studied by analyzing so–called facet plots of the STM images (seeFigure 4). Facet plots are histograms of the surface gradient of an STM image; i.e. each spot of this plot represents a facet. While in the facet plot of the as grown quantum dot (see Figure 4, image on the left side) bright spots appear on the positions which correspond to the {101} facets (typically for domes), the {137} spots (typically for pyramids) become more and more bright by increasing the amount of capping material. This back transition leads to the general conclusion that the shape of the islands is determined by a composition dependent critical volume.

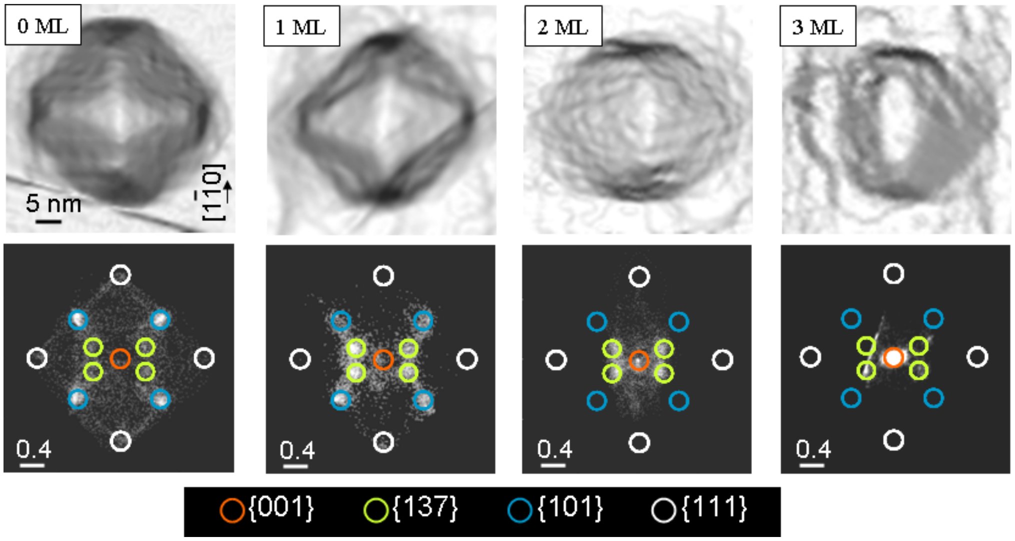

Figure 4 Development of InAs/GaAs (001) islands during overgrowth with GaAs (0 ML, 1 ML, 2 ML and 3 Ml; from left to right) and corresponding facet plots.

In regime II the influence of the GaAs flux becomes apparent. At low fluxes (e.g. 0.08 ML/s) the true overgrowth of the islands starts which proceeds by the disappearance of the facets and the elongation of the structures, because of a preferential surface diffusion along the $[1\bar{1}0]$ direction. That means that in regime II no strong shape changes are observed anymore for the low GaAs flux rate. By contrast, at high flux rates (e.g. 0.6 ML/s) structures with a rhombus base and a small hole in the center develop.[14-16] The reason for this different behavior is explained in the following way: At the beginning of regime II the Ga atoms which are exactly deposited on the quantum dot diffuse away from the center of the dot to the ridges forming a small depression in the center. This happens at the low and the high flux rate. While the system has enough time to smooth the surface in order to minimize its surface extension at the low flux, this surface diffusion is almost suppressed at the high flux leading to the enhancement of the existing surface modulations. This demonstrates again that the consequences of growth close to thermodynamic equilibrium and growth governed by kinetic processes are quite different. A very similar shape transition can be observed by the Ge/Si (001) system. Besides the importance of these investigations for understanding the optoelectronic properties of quantum dots, they demonstrate that the shape of the islands is mainly determined by their volume and their composition.

1.3.4 Quantum dot composition

In addition to the size of an island also the composition strongly influences its characteristics. The conventional experimental investigations for the stoichiometric analysis of the islands are performed with spectroscopic methods. Their disadvantage is that they average over a large area on the sample with a high number of islands. Therefore it is not possible to get a correlation between the composition and the morphology of individual dots. In order to get this information, selective chemical etching experiments are an advantageous method[17]. Thereby the sample is exposed to a reactive agent, which has a higher etching rate for one component in the sample than for the others. The etching rate of an etching solution for a specific material A is defined in the following way:

$$r_A = h_{etched} / t$$

h_{etched} is the etched height and t is the etching time. The ratio of the etching rates of two different materials A and B is called selectivity. If one assumes that $r_A < r_B$ then structures with an enrichment of component A will remain on the surface.

In order to etch Ge over Si hydrogen peroxide (H_2O_2) diluted in water or a mixture of ammonium hydroxide (NH_4OH), H_2O_2 and deionized water is used, depending on the desired selectivity of the etching process. If the etching rate is small enough, it is possible to study intermediate stages of etching by using different etching times (Figure 5). At the beginning the facets and the apex of the pyramids are attacked, which can be seen in Figure 5, (2). Further etching leads to the complete removal of the facets and the center and only the four corners remain (Figure 5, (3)). This reveals that the pyramids have Si rich corners. This observation is explained by Si intermixing processes during growth driven by surface diffusion. While the Si atoms can reach the corners of the pyramid from two sides, the edges of the pyramid can only be reached from one side. This is illustrated in the sketch on the right side in Figure 5. Therefore more Si atoms can diffuse into the corners, which results in Si enrichment. Since domes have a rounder base area, this effect is not as pronounced as it is for pyramids. It is obvious that this process also depends on the substrate temperature, which influences the diffusion lengths of the Si atoms.

As already mentioned above, the composition of the islands plays a crucial role concerning their optoelectronic properties. In order to take advantage of this, one can try to tune the composition to get the selected properties. It could be shown that e.g. an additional annealing step after the growth leads to an enhanced Ge Si interdiffusion[18]. As a consequence the bandgap and the emission energy increase.

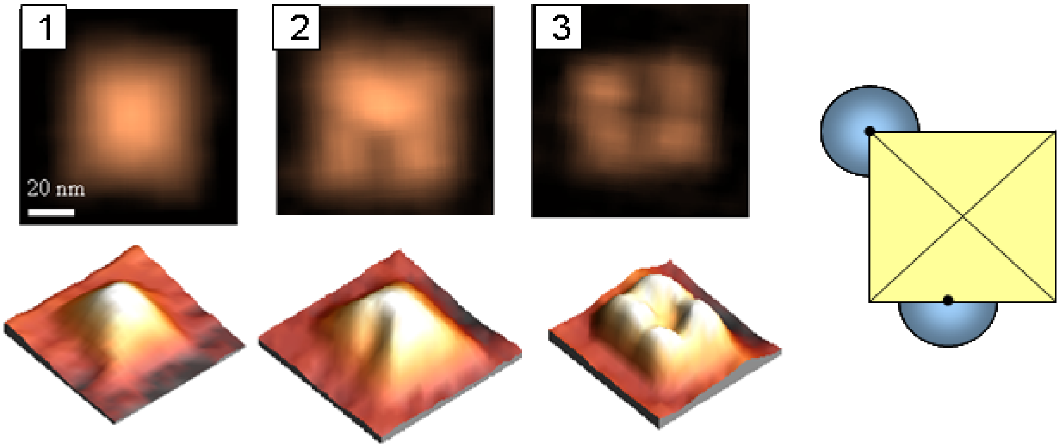

Figure 5 AFM images of the development of pyramids during etching, illustrating the Si enrichment at the corners. The sketch on the right side shows the enrichment of Si at the corners, because Si atoms can reach the pyramid from two sides. [19]

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