

Chapter 2

Theoretical Basics

In this chapter I will summarize some basics for growth modes of heteroepitaxial films on substrates including the origin for the appearance of facets. Furthermore, I will explain the importance of the anisotropy of the electronic work function of metals (Smoluchowski effect [Smo41]) for the interfacial stability between ionic adlayers and stepped metal substrates.

2.1 Growth Modes

The growth mode of heteroepitaxial films is influenced by two parameters: The total surface free energy per unit area and the lattice constants of the substrate and the film. For the determination of the growth mode the surface free energies of the substrate γ_{sub} , of the interface γ_{int} , and of the film γ_{film} are important. Bauer [Bau58] described three growth modes close to thermal equilibrium, which depend on the relationship between these three contributions to the total surface free energy. The different modes are schematically plotted in Figure 2.1.

1. Layer mode (Frank-van der Merwe)

For this mode, the sum of the film and interface free energy is smaller than the substrate free energy: $\Delta\gamma = \gamma_{film} + \gamma_{int} - \gamma_{sub} \leq 0$. In this growth mode the adsorbate is forming a complete monolayer before a second layer starts on top of the first.

2. Island mode (Volmer-Weber)

For this mode, the sum of the film and interface free energy is larger than the substrate free energy: $\Delta\gamma = \gamma_{film} + \gamma_{int} - \gamma_{sub} > 0$. In this growth mode the adsorbate is forming 3-dimensional islands instead of a complete layer.

3. Layer plus island mode (Stranski-Krastanov)

For this mode, $\Delta\gamma$ changes its sign with increasing film thickness. The surface free energy

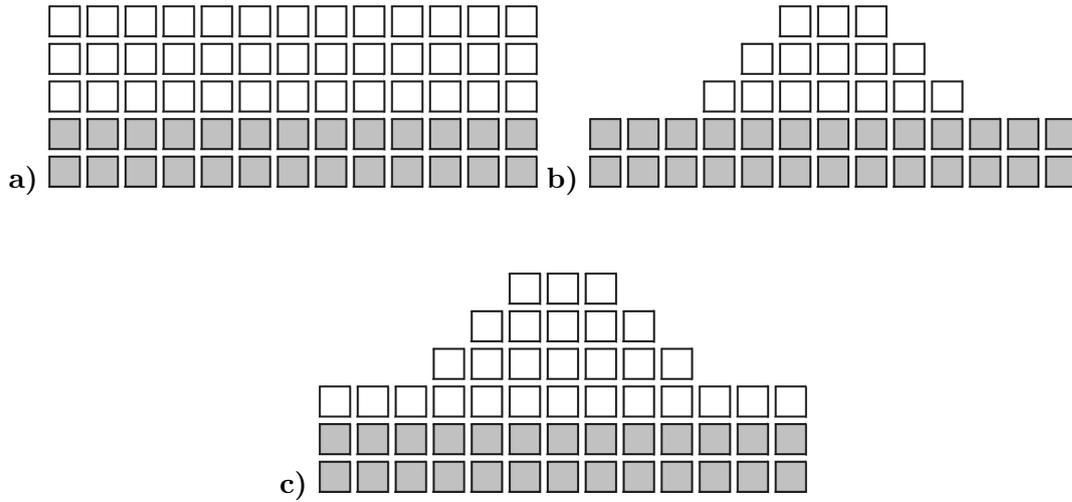


Figure 2.1: Heteroepitaxial growth modes close to thermal equilibrium [Bau58]

- a) layer mode (Frank-van der Merve)
- b) island mode (Volmer-Weber)
- c) layer plus island mode (Stranski-Krastanov)

γ_{film} can be increased for thicker films due to an increased contribution of mismatch-induced strain. For thin films $\Delta\gamma$ is smaller than zero, which results in layer growth, but for thicker films $\Delta\gamma$ becomes larger than zero, and island growth occurs.

For the creation of perfect, flat, and smooth films the layer growth mode is the preferred case.

The growth modes described above refer to conditions close to the thermal equilibrium. However, most growth processes are more or less far from thermal equilibrium. Therefore meta stable growth modes are possible. Henzler [Hen93] explains 4 modes, where the lattice constants of the substrate and the adsorbate play an important role (cf. Figure 2.2).

1. Floating mode

The substrate has a low corrugation, that means that a deposited adatom has nearly the same binding energy for all sites on the surface. Then the lattice constant is nearly unchanged compared with the bulk value, no strain appears.

2. Pseudomorphic mode

The substrate shows a stronger corrugation, and the film is gaining energy by adapting the lattice constant of the substrate. This mode occurs especially for thin films, and/or for small misfits between film and substrate. The film is under strain.

3. Dislocation mode

For the previously described mode for thicker films the strain is becoming too large, and

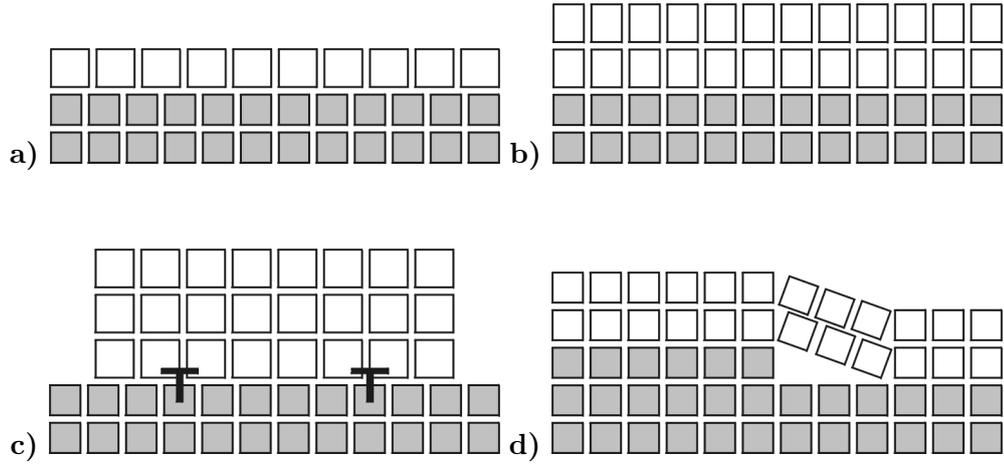


Figure 2.2: Heteroepitaxial growth modes considering the atomic arrangement of the first monolayer [Hen93]

a) floating mode, b) pseudomorphic mode, c) dislocation mode, d) carpet mode

the film relaxes by the formation of dislocations at the interface. These could be for instance the incorporation of steps in the substrate.

4. Carpet mode

For this mode the film has to accommodate distortions, like steps, in the substrate. If there is sufficient high binding between the substrate and the adsorbate, a coherent film is formed. This film bends over step edges.

The growth process can also be influenced by the directional anisotropy of the surface free energy of a crystal [Zan88]. In certain cases, the total energy of the system can be lowered by the reorganization of the initially flat surface into an assembly of facets with different orientations. Although the total surface area is increased, the total energy is decreased in these cases. The directional anisotropy of the surface free energy can be further increased by adsorbates [MNP⁺99]. Furthermore, in the case of a film with a lattice mismatch, a facet formation can be driven by the attempt to relieve the strain. The energetically driven faceting process is kinetically limited, that means for the formation of the facets a sufficient mobility of the substrate surface atoms is necessary. This mobility is increased if the substrate material is at elevated temperatures.

For the investigated Cu and Ag surfaces, the mobility of kink atoms starts at temperatures around 300 K. Since the used stepped surfaces have uniaxial surface geometry, their adatom mobility is highly anisotropic. Stoltze [Sto94] calculated activation energies for the diffusion of adatoms using effective medium theory. The expected result is that the activation barrier is smaller if the adatom diffuses along a step instead of over a step.

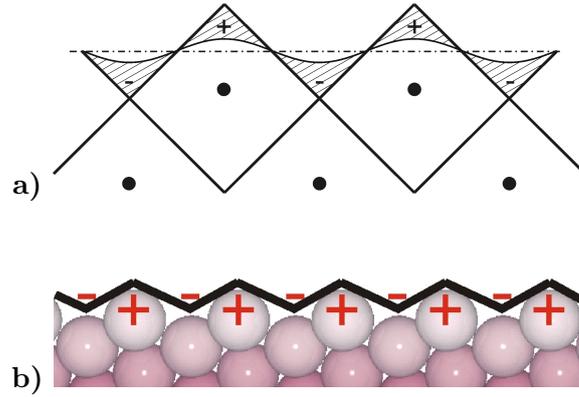


Figure 2.3: Charge modulated metal surfaces

a) charge distribution of a sc(110) oriented metal surface [Smo41]

the zigzag line corresponds to the corrugation of the surface; the wavy line represents the equilibrium charge distribution

b) a charge modulated fcc(311) metal surface in side view; the positive charges are located on top of the intrinsic rows, whereas the negative charges are in the troughs

2.2 Smoluchowski Effect

In the following I will describe a surface phenomenon related to the anisotropy of the electronic work function of metals introduced in Smoluchowski's pioneering theoretical work from 1941 [Smo41]. The effect is called **Smoluchowski effect**.

The Smoluchowski effect is a redistribution of the electron cloud on a metal surface with a strong corrugation. Figure 2.3a shows this smoothing effect. The surface corrugation is represented by the zigzag line. The kinetic part of the total energy of the electrons can be written in a simplified form as: $E_{kin} = \frac{\hbar}{2m} \int |\nabla\Psi|^2 d\vec{r}$. A higher gradient in the charge density leads to a higher kinetic energy. To lower the kinetic energy, the charge distribution is smoothed out, which is represented by the wavy line in Figure 2.3a. The charge redistributes from the “hills” into the “valleys” formed by the surface atoms. In this way there arises a net positive charge on the “hills” and a negative charge in the “valley”. This charge distribution depends strongly on the corrugation of the surface. For a close-packed surface like fcc(111) this smoothing mechanism has not a big effect, whereas the surface charge distribution of an open surface like sc(110) or a stepped surface like fcc(311) is effected strongly by this mechanism. The consequence of this behavior is an anisotropy of the work function of such stepped surfaces, which was experimentally verified by STM [JIH⁺98].

The growth systems investigated in this work take advantage of the Smoluchowski effect which induces an enhanced substrate/adsorbate interaction. The substrate surface orientations

used in this work, (211), (311), (221), and (532), all correspond to stepped or kinked surfaces. Due to the Smoluchowski effect there is a charge corrugation on these surfaces, which builds up stripes of positive and negative charge on the stepped surfaces (e.g. for the (311) orientation see Figure 2.3b). The electrostatic dipoles associated with the steps and kinks interact by means of Coulomb forces with the ionic adlayer. The latter correspond to the ionic insulators NaCl and KCl in the present study. A strong and localized binding between the ionic insulator and the underlying charge modulated substrate is obtained if the lateral charge modulation matches with the characteristic spacing of ions in the ionic film.

