



# Chapter 1

## General Introduction

For a long time thin films have been relevant for technological progress in many fields. In heavy industry, metals are coated by thin films or receive special treatment so that thin films grow for corrosion protection. In optics, thin films are used to custom tune transmissivities and reflectivities of optical devices. Some solid state lasers require systems of layered thin films to achieve the desired optical emission. Without layers of different materials, most semiconductor devices would not be possible and vital physical effects as giant magneto-resistance (GMR) [1, 2, 3] would have never been discovered. However the various applications of thin films also have different definitions to what a thin film is and what surface properties it needs. For corrosion protection and isolation, it is sufficient that the film isolates the metal from the surrounding atmosphere. Here, the surface prop-



erties are only relevant if the isolation or corrosion protection are in reactive surroundings. For optics on the other hand, the surface and interfaces are relevant as they effect the reflectivity and transmissivity. However, the films are of sufficient quality if the defects are of smaller order than the order of the wavelength. Especially for surface quality a decent and thorough polishing would be sufficient to achieve the necessary surface roughness and quality for most optical applications. For semiconductor devices, the quality of the films has a much higher importance as single defects can massively influence the electronic properties of devices. For heterolayers in solid state lasers, the homogeneity of the layers has to be at least one order better than those for optical applications.

In physical sciences, many effects have been discovered that change or have properties that change as a function of film thickness. Some examples are thermal conductivity in hetero systems (thermal boundary conductance) of thin films which can depend on the film thickness according to the atomic mismatch model (AMM) [4, 5] or the diffuse mismatch model (DMM) [4, 6, 7, 5] which also depends on the quality of the interface at coverages of a few monolayers. As a second example, the conductivity of various materials can change between insulator, semiconductor and metal as the coverage is changed also in the region of a few monolayers [8, 9, 10, 11, 12, 13, 14]. As a more recent example, new material properties and fascinating effects can occur as layers reach only single layer thickness. These effects can differ so much from the bulk properties that they are considered a different material as it is the case for Carbon and Single Layer Graphene. Here, even a second layer changes the properties from

metal to semiconductor as the interaction of two graphene layers leads to the opening of a band gap, even though it is rather small [14].

However, not only film thickness has a strong influence on properties of structures. Also the lateral dimensions can lead to quantum state effects and thereby manipulate the properties of structures as they are used for plasmonic devices [15, 16, 17, 18, 19, 20]

Various approaches and techniques have been taken in the past to investigate film structure and properties. Here, we use a new technique to study surface diffusion and combine it with SEM and SPA-LEED. Our technique is based on either photoemission or reconstruction based contrast in real-time surface sensitive microscopy using either a Low Energy Electron Microscope (LEEM) or a Photoemission Electron Microscope (PEEM).

Part I deals with the basics. First, general basics are presented in Ch. 1. In Ch. 2, the experimental setups are presented. Chapter 3 deals with the special characteristics of Si and Si surfaces.

Part II contains results on Ag growth especially the Island formation on Si(1 1 1).

In Part III, any results involving diffusion and diffusion anisotropy are presented.

Part IV contains the conclusions and outlook as well as the appendix.

## 1.1 Nucleation and Growth

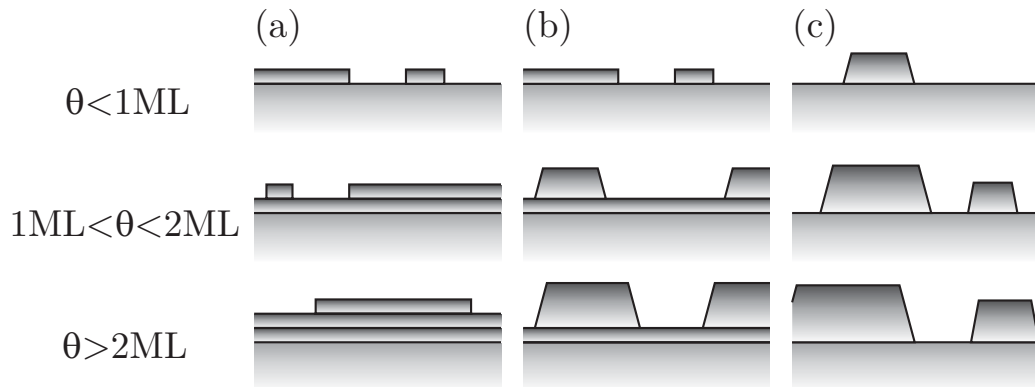


Figure 1.1: Schematic representation of the three crystal growth modes: (a) layer by layer or Frank-van der Merwe, (b) layer plus island, Stranski-Krastanov, (c) island or Vollmer-Weber mode.  $\theta$  represents the coverage in monolayers (ML)

The considered thin film deposition situation is a special case of epitaxial growth. The term *epitaxy* is used for the growth of a crystalline layer upon (*epi*) a crystalline substrate, while the crystalline composition and orientation of the substrate impose an order (*taxis*) on the orientation of the deposited layer [21, 22]. An epitaxial system has therefore two parallel contact planes of the two crystal structures and parallel crystallographic directions within these planes. The direction the epitaxial layer forms is selected by the constraint to minimize the interface energy which results from the mismatch between the two crystal structures. If a film material different from the substrate material is used, and this is the only case considered in this work, the

term hetero epitaxy is used. In general, three different modes of crystal growth are widely accepted for growth near the thermodynamic equilibrium. The growth modes are illustrated in Fig. 1.1 according to Bauer [23].

Figure 1.1 (a) shows the layer by layer or Frank-van der Merwe growth mode, where a new layer is only nucleated after all previous layers are completed. This growth mode occurs when the deposited atoms or molecules are more strongly bound to the substrate than to each other. Figure 1.1 (c) shows the island or Volmer-Weber growth mode where islands are formed and layers are not completed. Islands can, however, grow in both vertical and lateral directions. Figure 1.1 (b) shows the layer plus island or Stranski-Krastanov growth mode where one or more layers are completed before the film roughness increases and islands are formed. This is thus an intermediate case of the other two growth modes. The growth modes can be distinguished according to the balance between the surface free energy  $\gamma_D$  of the deposit, the surface free energy  $\gamma_S$  of the substrate, and the interface free energy  $\gamma_{int}$ . If

$$\gamma_S > \gamma_D + \gamma_{int}, \quad (1.1)$$

the energy balance requires that the area the adsorbate uses is maximal and the atomic layer will grow smoothly in the layer by layer growth mode. If on the other hand

$$\gamma_S < \gamma_D + \gamma_{int}, \quad (1.2)$$

the energy balance requires a minimum of the adsorbate covered area. Therefore, 3-dimensional islands are formed and grow

predominantly in height. However, for most scenarios in heteroepity, in the initial stages of layer by layer growth, the deposited material will be strained and elastic energy will build up. Therefore, Eq. 1.1 will eventually break down after a certain number of layers are grown. The chemical influence of the substrate is vastly screened by the additional layers and the surface free energies  $\gamma_D$  and  $\gamma_S$  are close to identical in the  $n$ -th layer. The elastic influence of the substrate remains and therefore is  $\gamma_{int} > 0$ . This inevitably leads to the case of Eq. 1.2 and therefore Stranski-Krastanov growth as illustrated in Fig. 1.1 (b). The elastic energy can be decreased by the implementation of various crystal defects as for example dislocations if the formation energy is reached before the layer by layer growth collapses.

The early stages of thin film growth involve various steps between the arrival of particles on the surface and nucleation (see Fig. 1.2) and therefore various exchanges of kinetic, vibrational and potential energy. The kinetic energy of an atom arriving on the surface is usually of the order of  $\sim 0.1$  eV if the atom was created by evaporation [22]. As an atom approaches the surface, it is accelerated by the surface potential. In order to stick to the surface the atom has to dissipate a considerable amount of energy to place it below the adsorption energy  $E_{ad}$  in the order of 1 eV so that the atom has not enough energy to escape again. The probability of this to occur is then called the *sticking coefficient* of the atom. Once an atom has been adsorbed, it is called an adatom and the next relevant energy scale is the activation energy of surface diffusion of a few tenths of an eV, which is usually smaller than the adsorption energy. Therefore, in the

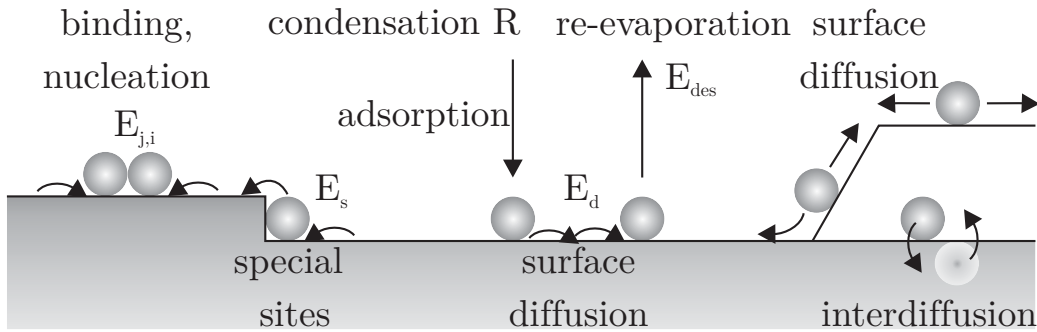


Figure 1.2: Illustration of various possible surface processes occurring during the early stages of thin film growth. This illustration is not exhaustive.

event that a sufficiently efficient transfer of energy from adsorbing atoms to the surface has not taken place, freshly adsorbed adatoms can have enough kinetic energy to move over the surface (see Fig. 1.2) even if the thermal energy of the substrate is not sufficient for diffusion which is then called transient mobility [24]. Of course other atomistic processes are also possible once an atom is adsorbed on a surface. Most of these processes are illustrated in Fig. 1.2.

If we assume a gas pressure  $p$ , the molecular weight  $m$ , the Boltzmann constant  $k_B$  and temperature  $T$ , the rate of arrival  $R$  is given by

$$R = \frac{p}{\sqrt{2\pi mk_B T}}.$$

Independent of the origin of the arriving atoms, this leads to a density of atoms or molecules on the surface with a number density  $n_1(t)$  with a total number of diffusion sites  $N_0$ . This



leads to the adatom concentration  $\theta = n_1(t) / N_0$  in the residual adatom gas. These adatoms can diffuse freely as described in section 1.2 until they are lost in one of several processes. These processes include nucleation of clusters, attachment to already existing clusters, re-evaporation, attachment to special sites as kinks, steps and other crystal defects, or dissolution into the substrate. For the following description, we will neglect the latter two processes as they are not present at a perfect crystal surface. Each of these processes will be dominated by characteristic times, which if the process is thermally activated are linked by characteristic frequencies and activation energies. The characteristic time for re-evaporation for example is the mean desorption time  $\tau$  which is given by

$$\tau = \frac{1}{\nu} \exp\left(\frac{E_a}{k_B T_s}\right), \quad (1.3)$$

where  $T_s$  is the substrate temperature and  $\nu$  is the characteristic surface vibration frequency. Some other characteristic energies are the diffusion energies  $E_D$ , binding energy of small clusters of size  $j$  ( $E_j$ ) until the critical nucleus size  $i$  ( $E_i$ ) is reached. When larger clusters can decay onto the surface or desorb directly, the associated energies will also become important.