

# CHAPTER 1:

## INTRODUCTION

The functionalized modification of solid surfaces by organic adsorbates is an eminent tool to alter electronic properties and structure of materials. Such variations are especially important in terms of their fundamental aspects as well as in their application in catalytic systems, fuel cells and sensors. The use of organic adsorbates and coadsorbates as templates for metal deposition processes has the potential to structure the surfaces in any form on mesoscopic and nanoscopic scales <sup>[1]</sup>. However finding of suitable templates is one of the future challenges for electrochemists.

One strategy is the use of self-assembled biomolecular structures as templates for metal deposition or a continuous metal coverage. The metal deposition onto chemically modified electrodes with self-assembled monolayers (SAMs) of alkanethiols is one of the extensively studied systems in electrochemistry <sup>[2-4]</sup>. Formation of organic SAMs consists, at the molecular level, of three components: an anchoring functional group, a structure-inducing region, and a head group that resides at the air-solid or liquid-solid interface.

The deposition of metal on modified electrodes with SAMs can be strongly inhibited depending on the covered adsorption places. In these investigations, the modified substrate is transferred to a separate cell containing metal adions. It was observed that the adsorption of thiols at the surface causes an inhibition in the underpotential deposition (UPD) and overpotential deposition (OPD) region even if the electrolyte contains structure-stabilizing anions. Using this property of SAMs, a patterned copper structure was produced by employing the inhibition behaviour of self-assembled monolayers (SAMs) consisting of a template of thiols with different chain lengths <sup>[5]</sup>. Also, a mask consisting of crystalline protein layers was successfully utilized to

design cuprous oxide layers <sup>[6]</sup>. But the impact of adsorbed organics is not exhaustively elucidated by inhibition effects.

The other very fundamental strategy to produce functionalized structure is the use of organic molecules, such as purine and pyrimidine bases. As different from SAMs, the size those molecules are small. The influence of adsorption states of those molecules on metal deposition can be adjusted. For example, physisorption or chemisorption of organic molecules leads to generating different kinds of surface structures <sup>[7, 8]</sup>.

In this line, certain organic additives have been exploited as levellers and brighteners in galvanic industry to produce smooth, mirror-like metal deposits for early years <sup>[9]</sup>, however, the exact mechanism of the action of organic molecules on metal deposition is still not completely understood due to the complexity as well as the nonlinearity of the interactions between adsorbates, metal substrates and metal ions. Therefore, enlightening the first stages of metal deposition on adsorbate-modified electrode is one of the starting steps to elucidate the action of organic molecules and to make predictions for the effects of definite classes of organic molecules in these processes.

Before switching to the system of the electrochemical interaction between metal-adatoms and organic molecules on an electrode, the following separate systems should firstly be stated considering the former studies:

- i) *formation of organic adlayer on electrodes,*
- ii) *metal deposition on foreign metal substrate.*

### **i) Formation of organic adlayer on electrodes**

Adsorption of organic molecules at metal electrodes has for a long time been investigated almost exclusively at the metal electrolyte interface. The interaction of organic molecules with metal surfaces is an important topic for a variety of reasons. For example, organic molecules are widely used as additives in plating baths for improving the quality of metallic coatings <sup>[9]</sup> or they are employed as corrosion inhibitor <sup>[10]</sup>. Thin films of organic molecules on metal electrodes are often used to modify the chemical nature of surfaces, aiming at tailor-made properties <sup>[11]</sup> and such films are often the basis for the development of highly selective sensors in biochemistry and environmental analytical chemistry. Besides these more technological aspects, organic molecules

on single-crystal metal electrodes have become a model system for the study of structural transitions in adlayers and for the self-assembling of molecules on surfaces <sup>[12-14]</sup>.

Large number of researchers studying photoresists, nanoelectronics, molecular recognition, electrochemistry, and biomaterials has investigated the formation of ordered organic adlayers (purines <sup>[15, 16]</sup>, pyrimidines <sup>[15, 16]</sup>, pyridine <sup>[17]</sup> and thiols <sup>[18]</sup>) on solid surfaces, mostly under nonelectrochemical conditions. Some *in-situ* and *ex-situ* surface sensitive experimental techniques as well as capacity measurements on Hg and single crystal electrodes demonstrated that several classes of organic neutral molecules can undergo a first-order phase transition at electrodes forming monolayer films <sup>[19-22]</sup>. The kinetics of this film formation generally includes nucleation and growth processes and other first-order transitions on surfaces observed. Early measurements at solid electrodes, e.g., adsorption of camphor on the basal plane of a zinc single crystal <sup>[19]</sup> and on polycrystalline tin <sup>[23]</sup>, indicated that two-dimensional phase transitions are not restricted to the liquid mercury electrode. Meanwhile several studies have been performed using single crystal electrodes, which show two-dimensional phase transitions in adsorbed organic adlayers. Such systems were thymine on Au(111) <sup>[7, 12, 14, 24-27]</sup> and Cd(0001) <sup>[28]</sup>, coumarin on Au(111) and Au(100) <sup>[29]</sup>, uridine on Au(111) <sup>[30]</sup> and uracil on Au(111) and Au(100) <sup>[20]</sup>.

Organic compounds such as purines and pyrimidines interact generally weakly with the substrate surface. For these molecules, it is assumed that the ordered monolayer is stabilized due to interaction between the molecules by the development of hydrogen bonding networks. In the case of pyrimidines, it has been found that their interaction or adsorption behavior on solid electrodes can change with the applied potential. In particular, thymine, one of the simplest pyrimidine bases, has been a frequent subject of many studies due to its biochemical importance. Thymine molecules on Au(111) are known to be weakly physisorbed and flatly orientated with respect to the surface at negative potentials whereas strongly chemisorbed and vertically oriented at positive potentials <sup>[24-27]</sup>. The chemisorbed state is characterized by charge transfer from deprotonated thymine molecules to the gold surface <sup>[14, 24-27]</sup>.

## **ii) Metal deposition on foreign metal substrate**

Another large number of researchers have focused on the investigation of the structure and dynamics of metal adsorbates on solid surfaces. The adsorption and deposition of metal

atoms on foreign metal substrates represents a very attractive family of systems for study because the strong adatom/substrate bonding can control the growth behavior and the resulting structures, especially as a function of surface coverage. Particularly attractive is the study of such systems by electrochemical means, especially within the context of underpotential deposition (UPD). This refers to the electrodeposition of metal monolayer(s) on a foreign metal substrate at potentials positive of the Nernst potential. It occurs when the adsorbate adatoms are more strongly bound to the foreign substrate than to a substrate of their own kind<sup>[31]</sup>. This phenomenon has been known since the early years of this century<sup>[32, 33]</sup>, but its study has intensified only during the last two decades<sup>[34]</sup>. Current-potential data for UPD on single-crystal surfaces, obtained from cyclic voltammetry (CV) experiments, frequently display sharp current peaks. The shapes, positions, and number of these peaks depend on the substrate and the crystal plane on which the adsorption takes place, as well as on the nature of the electrolyte.

The UPD of metals provide a means of controlling the microscopic surface structure through the electrolyte composition and the applied potential. UPD is the first step in the liquid-phase epitaxial growth of metallic heterostructures. Some applications suggest that the metallic submonolayers have the ability to significantly modify the catalytic activity of a substrate<sup>[35]</sup>.

On the other hand, UPD mechanism is very complex and can be affected by a number of additional processes such as anion adsorption, surface reconstruction etc. So, only proper correlation of electrochemical and STM measurements allows a reasonable interpretation of observed changes on an electrode surface at the atomic or nanometer scale. Initially, this process was interpreted in terms of a continuous adsorption. Only later with the invention of the EC-STM, this phenomenon was treated as first order phase transition, which results in a condensation of metal phase.

The UPD of copper and silver on the low index faces of Au appears to be the most extensively studied system using both *in situ* and *ex situ* methods<sup>[7, 8, 26, 36-52]</sup>. Much has been said about the deposition of copper or silver on Au(111), but they are still most popular model systems. On the other hand, the adsorption behaviour of thymine<sup>[12, 24, 25, 53-55]</sup> and adenine<sup>[56-60]</sup> has been studied extensively by numerous people. In this thesis, the deposition behaviour of Cu and Ag on thymine or adenine modified Au(111) is presented. Besides traditional electrochemical methods, like cyclic voltammetry, chronocoulometry and alternating current voltammetry;

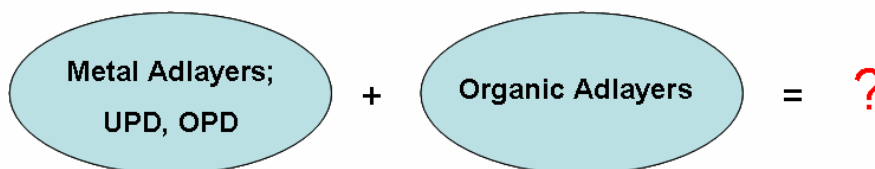
electrochemical scanning tunneling microscopy (EC-STM) and *ex situ* XPS experiments were carried out during the study.

The thesis is organized as follows. In the second chapter some key concepts necessary to understand the discussed results are presented. Chapter 3 describes the experimental aspects including the instrumentation and techniques employed. In Chapter 4 the adsorption behavior of thymine and adenine are presented. The UPD of copper or silver in the absence and the presence of thymine and adenine are displayed in Chapters 5, 6, 7. In Chapter 8 the sequential deposition of Cu and Ag is presented. A summary of the main results is given in the last chapter.

### 1.1 The aim of the study

With respect to the problems given above, the objectives of this thesis are to give some reasonable answers to the following questions.

- How can the first stages of metal deposition on adsorbate-modified electrodes be enlightened? (Fig. 1.1).
- How do neutral organic molecules (for example, thymine) influence the Cu and Ag deposition (UPD and OPD)?
- What role plays the adsorption states of metals?
- Are the influences of physisorbed and chemisorbed thymine molecules on Cu and Ag deposition different?
- Is it possible to produce a layered or a composite structure of Cu and Ag in the presence of thymine?



**Figure 1.1:** The schematic representation of the problem solved in the thesis.