In this chapter, some basic concepts, which are useful as a guide for reading and understanding this thesis, are shown. For the sake of conciseness, however, the topics presented are of general nature and just briefly presented, rather than exhaustively. Thus, key ideas on electrode surfaces and film formation of organic molecules are presented. A more extensive explanation and literature survey can be found in refs. [18,35-39].

2.1 The Double Layer Region

When a metal is brought into contact with an electrolyte solution, an interfacial region near the metal surface (at the electrolyte side) is formed, in which its properties differ significantly than those of the bulk phase. This region is called the electrical double layer (see for instance ref. [40] for a historical survey) and its thickness usually ranges from few to hundred angstroms for a supporting electrolyte concentration from 1 to about $10^{-3}$ M [38].

The main feature of the double layer region concerns the molecular and ionic populations three-dimensionally distributed near the metal surface. In a first approximation this region has been described by Helmholtz as being equivalent to a parallel plate capacitor, where one plate is the metal surface and the other plate is composed by solvated ions present in the electrolyte. In this case, the first layer in contact with the electrode surface is composed by orientated water dipole molecules and by ions specifically adsorbed (independent of the electrode potential). The imaginary plane crossing the radius of the specific adsorbed ions is termed inner Helmholtz plane (IHP). Next to the IHP, the ions become solvated and the imaginary plane cross the center of these solvated ions. The position of these ions defines the outer Helmholtz plane (OHP) [35]. The two regions confined by the IHP and the OHP are two-dimensional (internal layer) whereas the region comprised between the OHP and the end of the double layer is a three-dimensional one dominated by thermal interactions of the species called diffuse layer as schematically given in Figure 2.1.
The study of the processes taking place at the solid/liquid interface proceeds typically by perturbing the interface and analyzing its response. When perturbing the potential across the interface, the interface is primarily disturbed due to a current that passes between the WE and the CE. Then, the ‘capacitor’ is charged and a charge-transfer, or \textit{faradaic}, process takes place, but in absence of any redox system no current flow through the interface is observed. In this case, the process is usually referred to as a \textit{non-faradaic} process. The value of the capacity for single crystal surfaces as Au in aqueous solution typically falls in the range between 20 and 80 $\mu$Fcm$^{-2}$ [41-43].

In the context of the present work, we are mainly interested in studying the interfacial properties of the gold/electrolyte interface and the impact of the adsorption of organic molecules such as thymine, adenine, guanine, bromouracil, adenosine and thymidine.

\textbf{2.2 STRUCTURE OF Au SURFACES}

Acquiring detailed information on the interfacial processes necessarily implies the use of well-defined metal surfaces. Therefore, most of the research aiming at providing a deeper understanding of interfacial processes such as adsorption, film formation and kinetics deals with single crystal surfaces instead of polycrystalline ones.
In well-characterized single crystal surfaces, the interatomic distance between surface atoms and the atoms in the bulk of the crystal differ from each other. This difference is due to an imbalance of forces at the surface because the atoms are in an asymmetric environment compared to the bulk. In order to stabilize this difference, the surface atoms undergo a lateral displacement forming different surface structures. This phenomenon is called reconstruction and it is accompanied by lowering of the surface energy [44]. This phenomena has been the subject of many studies under ultra-high-vacuum (UHV) as well as under electrochemical conditions [45-47]. Reconstruction may be thermally induced (in the solid/gas experiments), by electrode potential (in electrochemical environmental), or by adsorption of some species (in the so-called adsorption induced reconstruction [44,48], for instance. If interatomic a difference between the surface atoms and the underlying atoms takes place comparing to the bulk crystal, the phenomenon is called relaxation. In this case the structure of the surface remains the same [45]. The typical example of surface reconstruction is seen for the low-index surfaces of gold and platinum. The structure of the gold surface is shown in Figure 2.2.

The Au(111) surface reconstructs into a hexagonal-close packed (hcp) Au(111)-(5x20). This surface structure has an extend corrugation owing to the misfit between the top layer and the underlying [100] plane. As a consequence, the reconstructed Au(100) surface differs in its properties from the (111) surface [49].

In the case of gold (110), the surface is reconstructed into the Au(110)-(1x2) “missing row”, where every second row of atom is removed (Figure 2.1 (b)) [50], which leads to the formation of narrow (111) microfacets.

For the Au(111) surface, the reconstruction leads to a Au(111)-(1x23) surface, in which is observed a compression of the atoms by about 4% in the [100] direction, causing every 23rd atom to be in register with the underlying bulk atoms. The overall change in the surface structure due to the reconstruction is relatively small compared with (100) and (110) faces, as is might be expected for faces already densely packed.

The reconstruction of the surface is removed by adsorption of atoms or molecules [47] because adsorption is energetically more favorable as a reconstructed surface. As was already mentioned, the reconstructed surfaces are more densely packed than the unreconstructed ones. That means that in the case of Au(100) the reconstructed surface Au(5x20) for example contains about 25% more atoms than for the unreconstructed one. In case of Au(111)-($\sqrt{3}$x22) the excess of atoms is about 4%. During the lifting of the reconstruction this excess
of atoms present in the reconstructed surface are expelled from the unreconstructed surface. This process causes a degree of surface roughness, which might interact or even disturb the electrochemical investigation of interest. The used single crystal in this thesis was Au(111).

(a) Au(100)

(b) Au(110)

(c) Au(111)

**Figure 2.2:** Unreconstructed and reconstructed structures for single crystal gold surface.
2.3 Adsorption of Organic Molecules on the Electrode Surface

It is well known that neutral organic molecules such as the DNA bases might adsorb on mercury and on single crystal electrodes. The adsorbates may undergo a two-dimensional, first order phase-transition forming well-ordered films [51-56]. In these adsorbates the molecules are randomly oriented forming a two-dimensional gas-like phase. The phase-transition of the adsorbate takes place by a nucleation and growth process. The formation of the condensed film by 2D nucleation and growth represent a first order phase transition in which an expanded phase is transformed in a condensed one by discontinuous change of the relative surface concentration. To make a phase-transition possible, the thermodynamics conditions are changed involving slow kinetics of aggregation. To form a condensed film, the single molecules must first aggregate to small clusters of a certain minimum size called “critical nuclei”, which originates from single molecules before expand in a new phase. As soon as the cluster formed reached the critical size, it can expand by incorporating additional molecules and form the condensed film.

The ordered condensed film may be physisorbed. By reorientation of the molecules at more positive electrode potentials, the physisorbed ordered film might undergo again a phase-transition in which another ordered film is formed. The most stable films result if the molecules forming the film are chemisorbed. Chemisorption results generally from partial charge-transfer between the surface and adsorbed molecules.

The mercury electrode is the most recommended electrode to study the kinetic of the film formation due to the low RC constant and the well defined surface, [51,57,58] however, working with solid single crystal electrode allows to investigate the structure of physisorbed and chemisorbed condensed films by scanning tunneling microscopy (STM). Therefore, providing the possibility of getting the structure of the films and a better understanding of processes associated to the formation of such films.

The phase-transition process and the resulting ordered film formation depends on parameters such as molecules concentration, temperature and electrode potential [59]. Adsorption of thymine on solid (Au, Ag) and liquid (Hg) electrode surfaces is a good example of occurring two-dimensional phase-transition and subsequent condensed film
formation. Vetterl [60] was the first to demonstrate the presence of 2D condensed monolayer films for purine and pyrimidines by the presence of the so called “pit” region in the capacity curves for Hg electrodes, often accompanied by hysteresis, which evidences the slow nature of the process. The width of the pit region depends strongly on the adsorbate concentration and temperature, as well as the nature of the electrolyte.

In electrochemical experiments, the investigation of the phase-transition kinetics is generally performed by potential step technique. In these measurements, the kinetics is analyzed by measuring the current after a potential jump from an initial potential, where the ordered film is absent, to a final potential into the region of the condensed film. The resulting transients in the I x t curves is limited by the time constant of the cell, which has to be small as possible to minimize the overlap of the double layer charging transient with that produced by the transition kinetics. This condition is obtained with high electrolyte concentration and smooth electrodes surfaces with small capacities.