

# Chapter 1

## Introduction

### 1.1 Crystals, surfaces and interfaces

Epitaxial films are of fundamental and technological interest. The growth mode of thin films depends both on the substrate and the adlayer properties, making the investigation of both surfaces and interfaces an important challenge in modern day surface science.

Crystalline and electronic structure are complementary properties of surfaces and thin films: only with the investigation of both characteristics is it possible to obtain a complete knowledge of the system. Such investigations form the basis of this thesis; various surface techniques have been adopted to analyse crystalline and electronic properties of a surface reconstruction and of two kinds of interfaces, a reactive and a non-reactive one.

In a crystal the position of atoms is given by the equilibrium among attractive and repulsive forces between atoms and, apart from the special case of quasi-crystals, follows a periodic order [1]. This particular order defines the crystalline structure that is a typical property of the crystal at certain physical conditions described by pressure and temperature. The knowledge of the crystalline structure of a material, determined by the crystal class and the coordination number, is important because it is derived from microscopic effects and is responsible for many macroscopic physical properties: one of the most instructive examples is represented by carbon, which crystallizes in two distinct conformations, diamond and graphite. The difference between the two crystals is due to the different bonds among the carbon atoms. The  $sp^3$  hybridization in diamond induces its tetrahedral structure, while the

$sp^2$  hybridization in graphite is responsible for its layered structure. This difference in structure is reflected in the different electrical resistance properties of diamond and graphite: the former has a large resistivity, ranging from  $10^{11}$  to  $10^{18}$   $\Omega\cdot\text{m}$  depending on the doping type, and the latter has a resistivity of about  $8 \mu\Omega\cdot\text{m}$  [2]. Moreover, the conductivity in graphite is highly anisotropic, caused by the different bonding nature of atoms in the same plane from that of atoms in different layers.

It is thus clear that the crystalline structure is one of the most important physical characteristics of a material, and an alteration of this property leads to a change of other physical variables. Such a typical structure alteration is present in every real crystal and is given by the surface, being formed by atoms with a reduced coordination number and allocated in a structure of reduced symmetry. Hence, at the surface of a solid, many novel and interesting physical properties are present [3]. For example, in a heteropolar semiconductor compound like GaAs the choice of a surface along a particular symmetry direction corresponds to the choice of having a surface terminated with either only one or both chemical species, i.e. the surface is either polar or non-polar. This difference is reflected in the geometrical ordering at the surface. In fact, the (110) surface with both Ga and As atoms does not change the overall translational symmetry, although bond lengths angles at the surface are modified, while the surfaces with Ga- or As-termination exhibit changes in the symmetry of the unit cell. This leads to a so-called *surface reconstruction*, with consequences on the electronic structure and other physical and chemical behaviour, such as, for example, adsorption processes.

Atoms and molecules adsorbed on a surface may grow in thin films in various ways, via island formation, or epitaxially in a 2D mode, depending on many physical and chemical variables, like the temperature of the substrate, or the chemical environment in which the evaporation is performed, the reactivity of both the substrate and the adsorbed species, or the presence of defects on the surface, etc. In a new sub-field of surface science, i.e. nanotechnology, various aspects of thin film growth and of molecular adsorption on surfaces are investigated in order to find new and promising features. In particular, the case of semiconductor substrates is very interesting, where a further complication is caused by surface reconstructions. Hence, a detailed knowledge of these systems can be obtained only by a

complete characterization of the surface reconstruction. This consideration stresses the importance of studying semiconductor surface reconstructions, and shows how intrinsically complex systems can be analyzed starting from simpler basic steps. In these terms we have studied the reconstruction of the semiconductor **6H – silicon carbide** cleaved along the  $\langle 0001 \rangle$  direction. The technique, used for obtaining the clean surface, leads to a reconstruction never observed up to now on this compound, and makes a comparison possible with similar elemental semiconductors such as Si, C and Ge [4].

Interfaces between solids or solids and molecules are of fundamental importance in many aspects, in semiconductor lasers, for example, formed by semiconductor heterostructures, or in field effect transistors (FET), made of semiconductor interfaces with either metal, semiconductor or oxide counterparts. Here, abrupt and lattice-matched interfaces are required and the operation characteristics of these devices is determined by the charge distribution in the spatial region next to the interface, the space-charge layer [5]. Electronic properties of such interfaces are widely studied because they are responsible for the correct operation of novel nanotechnology devices based on 2D-superstructures. The way the substrate-adlayer interface is formed is of extreme importance and may lead to different properties of the system. Reactive systems present a smooth interface, obtained by interdiffusion of the different species present at the interface. This is the case for the **Mn/Si(111)** system presented in this thesis: transition metals show a strong reactivity which results, upon adsorption on a silicon substrate, in the formation of a silicide. This silicide forms already at very low coverage, through the incorporation of manganese atoms into the silicon substrate, and continues until flat silicide films are formed. The way the Mn-Si silicide forms, and its electronic properties, are studied here by means of photoemission, and its structure is analyzed using the scanning tunneling microscope.

The reactivity of certain systems may be reduced by decreasing the temperature at which the interface is formed. This limits the diffusion of the adlayer atoms and can result in an abrupt interface. It has been demonstrated that reactive systems like Mg/Si and Al/Si obtained by deposition at low temperature have a very low reactivity [6]. The nearly free electrons of the metal adlayer are then confined between the vacuum and the interface, and show discretization of the electronic dispersion in close similarity with the “particle in a box” model. Thin metallic films thus provide a labora-

tory for basic quantum mechanical concepts and 2D systems. In addition, fine tuning of the microscopic sample structure can result in macroscopic effects, as in the case of the “electronic growth”, where the electronic contribution to the film energy plays a decisive role to determine film stability [7]. Here the study of quantum well states has been extended to thin films of **Al – Mg/Si(111)** alloys.

In this thesis, for each system studied, both the electronic and structural properties are investigated. The results obtained are the following: in SiC, the cleaved polar (0001) surface, with the two terminations, has in both cases a  $2\times 1$  reconstruction. Similarities with and differences between the  $2\times 1$  reconstruction observed in cleaved (111) surfaces of Si, C and Ge are discussed on the basis of photoemission data, and two distinct reconstruction models are proposed for the two respective surface terminations. In particular, for the Si-terminated surface, the buckling model seems to be adequate to explain the observed surface core level shifts. On the other hand, the C-terminated surface cannot be explained by the same model and more accurate calculations are required.

Silicide formation in manganese films on Si(111) was directly observed by means of STM and photoemission techniques. For  $< 1\text{ML}$  deposition, manganese atoms form small clusters on step edges and terraces. Consequently, the substrate order is destroyed by the inclusion of Si atoms in the clusters, in order to form the silicide. The composition of this phase is thought to be  $\text{MnSi}_{1.7}$  and shows semiconducting character.

For  $> 1\text{ML}$  deposition, a  $(\sqrt{3} \times \sqrt{3})R30^\circ$  LEED pattern is observed. STM images show flat layers on a large part of the surface, but also strain relief represented by deep holes and Moiré patterns. Contrary to the submonolayer deposition, the surface has a metallic character and is thought to be formed of MnSi silicide. Using core level spectroscopy, core level shifts from  $\text{MnSi}_{1.7}$ , in the submonolayer, and from MnSi, in the monolayer range, are detected. Si surface-related components are detected as well. A detailed analysis led us to the conclusion that the silicide films are terminated with a layer of Si atoms.

Finally, alloys of Al and Mg were grown on Si(111). Alloys in a wide range of composition were epitaxially grown, and were studied by means of angle resolved photoemission. For some compositions, the system Al-Mg/Si shows electronic confinement in the thin film, with the observation of quantum

well states and of a surface state in the photoemission spectra. For other compositions, only the surface state was observed. The binding energies of both quantum-well (when present) and surface states show a dependence on the alloy composition; the shifts are related to the electronic density of the system in a jellium-model approach. A deviation from this relation is explained by the formation of phases with different composition. Finally, the occurrence of collective electron excitations was investigated by means of photoemission used in the constant initial state mode, and the dependence of the bulk-like and multipole plasmon on both the alloy composition and the film thickness was observed.

