Chapter 1

Introduction

Photoelectron spectroscopy (PES) is a very valuable tool for the characterization of surfaces [1]. It is intrinsically surface sensitive and it can be quantitatively used for the determination of the surface composition and chemical state. However, it does not suffice for the understanding of many large scales applications, such as heterogeneous catalysis. The main reason is the high complexity of such catalysts which may comprise clusters of various composition and size. Our knowledge of the physical and chemical properties of these systems relies on the development of instruments capable of adding the lateral resolution to the classical surface science techniques, that can commonly deliver chemical and structural information. Thereafter, macroscopic observations such as reactivity can be correlated to the microscopic properties of the particles. Due to the dimensions of the active sites, edges and terraces, the instrumental lateral resolution has to be in the nanometer range. For similar reasons, the energy resolution has to be below 0.5 eV.

We briefly review the main surface science methods which have (i) surface sensitivity, (ii) lateral and (iii) energy resolution. Due to (i-ii) all techniques which image photons can be excluded. This is because the focusing of x-rays is rather challenging and surface sensitivity can be achieved only for grazing-angle geometries. It becomes clear that electrons are the most suited particles for the imaging. The surface sensitivity of electrons is high at low energies, high resolution spectrometers are available and electromagnetic optical elements are relatively simple. Other probes such as ions, atoms or molecules do not fulfill the above conditions.

The instruments can be divided in two main categories: micro-spectroscopes and spectro-microscopes.

The first group is based on the a scanning method. For example, an incident x-ray beam can be focused on a very small surface area and the emitted electrons measured by an analyzer. This method, known as scanning photoemission microscopy, can achieve a lateral resolution that is limited by the focusing of the x-rays. A common lateral resolution with Fresnel micro-zone plates is approx. 100–200 nm, and in optimum conditions 15 nm [2]. The energy resolution depends on the electron analyzer and is typically below 100 meV. Alternatively the sample can be homogeneously illuminated on a larger area and the analyzer focused on a small sample area. The obtainable lateral resolution is $\sim$ 100–150 nm. In all the above mentioned methods, the imaging is achieved by scanning the sample position. In scanning electron microscopes an electron beam is focused and scanned on the surface and the secondary emission is monitored. Such instruments have a good lateral resolution ($<$ 1 nm), but no quantitative chemical information. However, these systems can be equipped with other detectors which can provide for some chemical sensitivity by measuring, e.g., the energy of the emitted photons (for a detailed review on the method, see [3]).

In the second group, spectro-microscopy, the photoemission or reflection of electrons from a homogeneously illuminated region is magnified and projected on a screen. Both methods can be integrated in one instrument having a so-called beamsplitter. Many imaging modes are available [4]: PEEM, XPEEM, UV-PEEM, LEEM, VPEEM, MEM, XAS-PEEM, LEED, PED, XPS. A list of acronyms is shown in the appendix. The substantial differences among these methods lie in the excitation source used. While with photons the surface chemical composition can be imaged, with electrons the structural differences are enhanced. The experimental lateral resolution limit of such instruments is under optimum conditions below 10 nm for LEEM and $\sim$ 20 nm for x-ray PEEM (XPEEM).

From this brief, and incomplete, list of available instruments a selection of the most appropriate tool capable of bridging (i) chemical and (ii) structural information with (iii) lateral resolution, has to be made. Scanning techniques cannot convey any structural information, meant as long range order or $\vec{k}$. Transmission methods have already been excluded due to the reduced surface sensitivity. Only spectro-microscopy

can achieve such prerequisites and is thus suited for comprehensive characterizations of complex surfaces.

However, the lateral and energy resolution of commercial instruments is too low for the observation of processes on the nanometer scale. In 1992 *H. Rose* proposed an aberration corrected LEEM/PEEM with energy filter aiming at a lateral resolution of 2 nm and an energy resolution below 100 meV [5]. The layout of the complete finished instrument was completed by *D. Preikszas* [6]. Soon after, started a broad cooperation (BMBF: 05 KS4 WWB/4) between universities, institutes and companies, for the development of the ***S**pectro-**M**icroscope for **A**ll **R**elevant **T**echniques* (SMART). The team was composed by: Uni. Würzburg, TU Clausthal and TH Darmstadt, the Fritz-Haber-Institut der Max-Planck-Gesellschaft, BESSY and LEO Elektronenmikroskopie GmbH.

The part of this work is devoted to the implementation of the aberration corrector. Since this is the first corrector that uses a mirror, considerable efforts have been devoted to the testing of the new component. The magnetic analyzer is a second-order aberration corrected energy filter. During this work, the resolution of the analyzer has been improved and is now at reach of the theoretically expected value of 100 meV. Chapters 2 and 4 present the spectro-microscope and its capabilities.

The preliminary testing of the instrument had to be done on a model system that would at the same time offer relatively large scales of structures and crystallites, in the μm-range, and relatively easy handling of the experimental conditions. Owing to a strong cooperation and the extensive experience of *Würzburg* group, we opted for the investigations of the growth dynamics of organic thin films on nobel metal surfaces. This research project deals with *in-situ* investigations of the organic molecular beam deposition of 3,4,9,10-perylene-tetracarboxylic acid dianhydride on the Ag(1 1 1) and the Au(1 1 1) surfaces. Chapter 3 briefly describes the most well known properties of this system.

The later chapters cover a wide range of aspects of the organic thin film growth. Since these are the first measurements done on large aromatic organic molecules on metal surfaces, we begin in chapter 5 with the introduction of the imaging properties of this specific system. First with a mercury short-arc lamp (often referred to as UV-PEEM) we observe that the intensity not only is strongly dependent on the work

function, but also on the PTCDA layer thickness. The inelastic mean free path (IMFP) has been evaluated with both UV-PEEM and laterally-resolved NEXAFS. The imaging with reflected electrons reveals rotational domains that extend over single steps and for areas of approx. 4–6 μm.

PTCDA molecular solids with metallic interfaces have attracted a great deal of interest in the field of organic LEDs or transistors. However, the electrical and optical properties of organic films strongly depend on their structural and morphological properties. Ideal epitaxial growth resulting in perfect, nearly defect-free films requires optimum conditions [7]. This is particularly difficult in the heteroepitaxy of very different materials like, e.g., organic-inorganic heterostructures [8, 9]. The problem with the preparation of such systems lies in the nature of the involved substances. Whereas the structural periodicity in inorganic compounds is on the scale of few Ångström, the dimensions of organic unit cells are usually in the range of nanometers. In addition, the anisotropic shape and intermolecular interaction, the very different thermal expansion coefficients, and the (partly excited) internal degrees of freedom, e.g. the soft vibrational and phonon modes of condensed molecules may result in different structural modifications (polymorphoism) in the condensed phase and in unexpected growth behavior. Thus, imperfections at the interface which may extend into the growing film are discussed. First chapter 6 discusses the effects of the substrate morphology on the growth kinetics, then in chapter 7 the details of the growth dynamics, with metastable layers and three-dimensional islands, is discussed. A theoretical model is suggested for the description of metastable layer growth.

In the concluding chapter, the spectroscopic properties of organic thin films are exploited. The *in-situ* PES experiments presented exclude, within experimental resolution, the presence of chemically metastable phases. The laterally-resolved near edge x-ray absorption fine structure (NEXAFS) experiments determine the molecular orientation (linear dichroism). Unexpectedly, the excitation with circularly polarized light reveals crystallites which exhibit x-ray natural circular dichroism (XNCD).