

# Spectroscopy and Microscopy at DESY NanoLab

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September 5, 2018

By performing nano-characterization, nano-structuring and nano-synthesis techniques, the structure and properties of a wide range of materials are probed and measured, revealing characteristics such as their chemical composition and structural properties.

With this purpose, several experiments take place in DESY Nanolab, a facility for users and for in-house research at Deutsches Elektronen-Synchrotron (DESY), in Hamburg, Germany.

The aim of this document is to show the work and results accomplished during my eight-week internship at DESY Nanolab as a student of the 2018 Summer School Programme, under supervision of Dr. Heshmat Noei.

## Contents

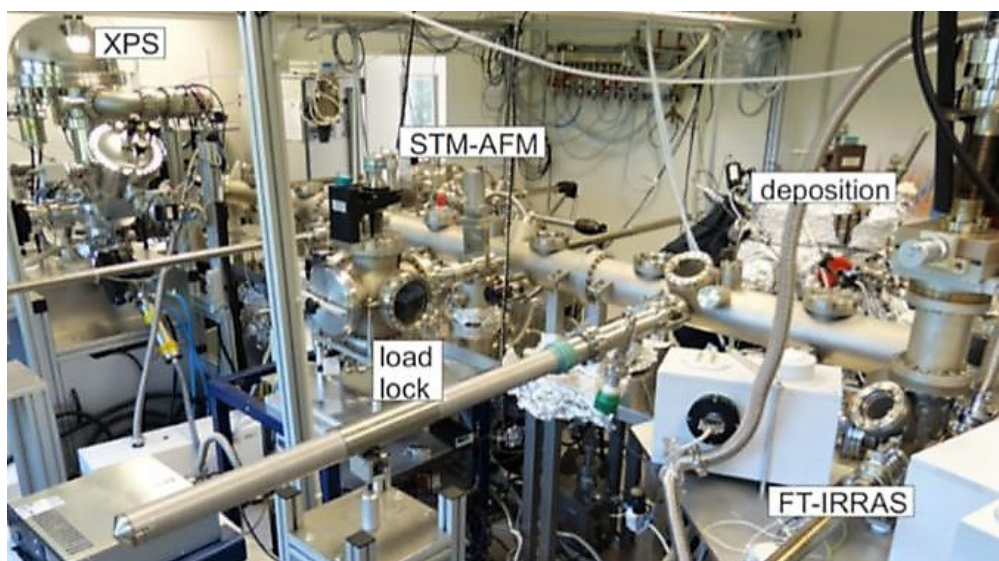
<b>1</b>	<b>Introduction</b>	<b>1</b>
	DESY Nanolab . . . . .	1
	Ultra-high vacuum . . . . .	2
<b>2</b>	<b>Experimental techniques</b>	<b>4</b>
	X-ray photoelectron spectroscopy (XPS) . . . . .	4
	Scanning electron microscopy (SEM) . . . . .	7
	Energy-dispersive X-ray spectroscopy (EDX) . . . . .	10
	Atomic force microscopy (AFM) . . . . .	13
<b>3</b>	<b>Experiments</b>	<b>14</b>
	Experiment I . . . . .	14
<b>4</b>	<b>Conclusions</b>	<b>16</b>

# 1 Introduction

## DESY Nanolab

The demanding experiments performed at synchrotron radiation facilities require deep pre- and post-experimental sample preparation and characterization with complementary techniques. The DESY Nanolaboratory (DESY NanoLab) is the facility responsible for those activities, providing external users, as well as in-house researchers, access to advanced nano-characterization, nano-structuring and nano-synthesis techniques, to compliment the advanced X-ray techniques available at DESY light sources.

The DESY NanoLab is being developed and operated by the DESY Research Group X-ray Physics and Nanoscience and consists several laboratories: Ultrahigh vacuum (UHV) and spectroscopy, X-ray diffraction (XRD) and microscopy labs. The UHV lab provides a variety of surface characterization techniques for surface preparation, growth of nanoparticles and films and sample characterization. The UHV lab features several surface analysis devices such as scanning tunneling and atomic force microscope (STM/AFM), X-ray photoemission spectrometer (XPS), Fourier transform infrared spectrometer (FTIRS) and two growth chambers. All these elements are connected via gate valves to the UHV tunnel, making it possible to transfer samples to different devices without exposing them to air. Samples are either brought into the vacuum by the fast entry load locks at the XPS and AFM/STM or through the main load chamber connected to one of the growth chambers.



**Figura 1: UHV and Spectroscopy lab at DESY NanoLab, [1].**

The X-ray diffraction laboratory allows specular reflectivity and grazing incidence X-ray diffraction measurements. In microscopy lab, a high resolution field emission scanning electron microscope (FE-SEM) is accessible, as well as a dual electron and focused ion beam

(FIB) for high precision sample structuring.

In conclusion, DESY NanoLab offers the instrumentation presented in the areas of surface spectroscopy, X-ray diffraction, high resolution microscopy and magnetic characterization; which makes it a perfect facility for a successful fabrication of a wide variety of structures, as well as sample preparation and sample surface characterization, before a precious synchrotron beamtime.

## Ultra-high vacuum

The UHV lab of Nanolab operates in ultra-high vacuum (UHV), which is the vacuum regime characterised by a rest gas pressure that allows the mean free path of a gas molecule to be 40 km, so the gas is in free molecular flow; see Table 1. This conditions are crucial for different techniques and experiments in scientific research, for example in surface science, cold atom gasses and particle accelerators.

	Preassure (mbar)
Perfect vacuum	0
Ultra High Vacuum	$\sim 10^{-12}$
High Vacuum	$\sim 10^{-8}$
Medium Vacuum	$\sim 10^{-5}$
Low Vacuum	$\sim 10^{-3}$
Atmospheric preassure	$\sim 10^3$

**Table 1: Vacuum chart**

Achieving the UHV regime is not easy; it involves different stages of pumping the gas out of a UHV chamber with several devices. *Baking* the whole system is also required, which consists of increasing the temperature to a high level for many hours, in order to remove adsorbed water and other trace gases from the chamber walls; this restricts the use of some materials that can not withstand the heat. Also, it is not simple to transfer light, electricity and motion into an UHV system.

Moreover, an *interlock* is often used to maintain the integrity of the UHV volume; it has one valve facing the UHV side of the volume and another one against atmospheric pressure through which samples are initially introduced. After sample introduction and assuring that the door against atmosphere is closed, the interlock volume is typically pumped down to a medium-high vacuum; the gateway to the UHV chamber is then opened, the workpiece transferred to the UHV and the UHV valve re-closed. Although a little bit of gas is generally released into the UHV system when the valve to the interlock volume is opened, the UHV system pumps can generally remove this gas before it has time to adsorb onto the sample surface. The UHV system pumps mentioned consist of multiple vacuum pumps in series

and/or parallel, since there is no single vacuum pump that can operate all the way from atmospheric pressure to ultra-high vacuum.

Once the UHV regime is reached, relevant surface science experiments can be performed with techniques such as X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), etc. This is due to the fact that these kind of experiments require a chemically clean sample surface with the absence of any unwanted adsorbates and the UHV conditions are also suitable for the transmission of electron, ion or photon beams.

## 2 Experimental techniques

### X-ray photoelectron spectroscopy (XPS)

#### Theoretical background

X-ray photoelectron spectroscopy (XPS) is a surface-sensitive and quantitative spectroscopic technique which provides information about the elemental identity, chemical state and concentration of a selected sample. It is based on the photoelectric effect: on the emission of electrons from the sample, due to the excitation of core-level electrons by bombarding it with mono-energetic X-rays, see Figure 2.

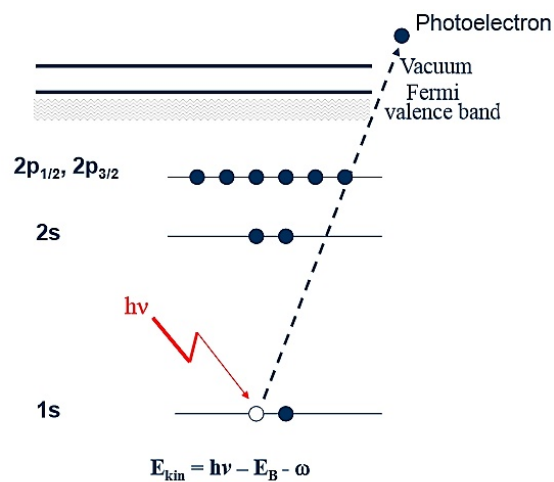
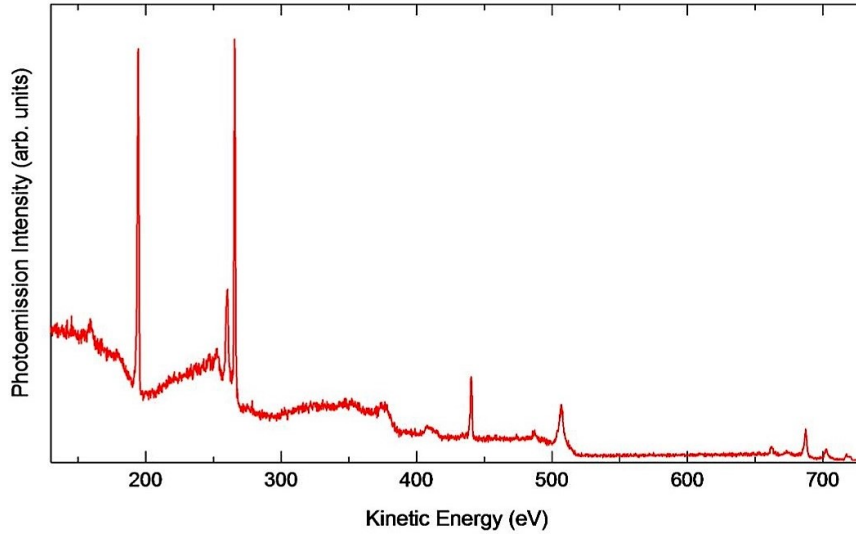


Figura 2: XPS event, [2].

The analysis of the surface with this method is done by the study of the XPS spectrum, which gives direct information about the binding energy and intensity of the photoelectron peaks. In Figure 3 a typical XPS spectrum is shown: the number of electrons detected (sometimes per unit time) are plotted versus the binding energy of the electrons. Each element at the surface or subsurface produces a characteristic set of XPS peaks with a characteristic binding energy value of the measured sample. These characteristic spectral peaks correspond to the interaction of the X-ray beam with the electrons; their kinetic energy corresponds to

environment of each atom in the sample. The mathematical formula that shows the relation between the parameters mentioned is:

$$E_{kin} = h\nu - E_{Bind}$$



**Figure 3: Photoelectron spectrum  $TiO_2$**

Sometimes, the Auger peaks can be also observed in the XPS spectrum. As it is shown in Figure 4, if the incident photons have enough energy to ionize a core level of the atom, the vacancy will immediately be filled by another electron with higher energy ( $L_{23} \rightarrow K$  in Figure 4). The energy  $E_{L_{23}} - E_K$ , which is released by this transition, can be transferred to another electron called Auger electron with a specific kinetic energy independent of the incident photon energy, which can be estimated by the formula:

$$E_{kin} = (E_K - E_{L_1}) - E_{L_{23}}$$

This secondary process after photoemission always accompany XPS since the Auger electrons are emitted into the vacuum and detected, making the peaks of the spectrum broader and more complex in structure than just the photoemission peaks, due to the different valence levels involved.

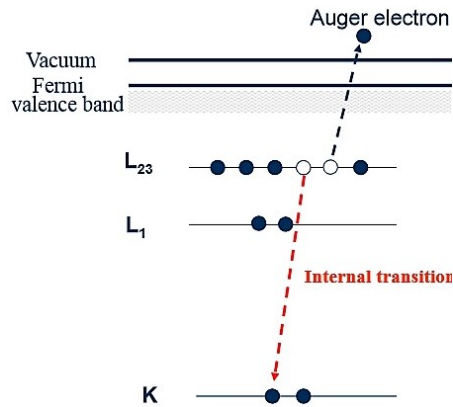


Figura 4: Auger effect, [2].

There is also a background contribution to the XPS signal as a result of the electrons from higher depth of the surface; these particles lose energy through inelastic scattering while they emerge from the sample, finally reaching the analyzer and detector with a reduced kinetic energy.

### Experimental display

Generally, a XPS setup consists of a X-ray source, measurement chamber, lenses, an electron analyzer and detector. The experiments require a monochromatic source of X-rays in a way that the initial energy of the beam is well defined; in this case, this is possible thanks to a lab based anode with an X-ray monochromator. The monochromator is based on a crystal and operates according to Bragg Law of X-ray diffraction: once the electron gun focuses high-energy electrons onto the anode causing X-rays to be emitted, the X-rays are intercepted by the crystals, so that only a narrow range of X-ray wavelengths are allowed to be diffracted and reach the sample. Additionally, the crystals are curved, focusing beam in order to produce a small spot at the sample, see Figure 5.

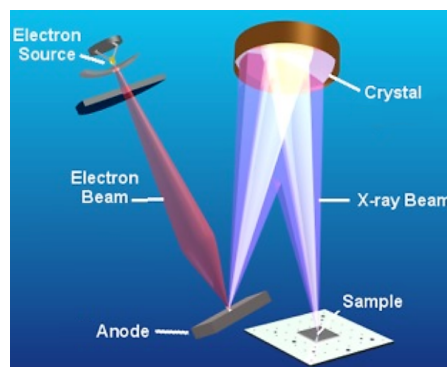


Figura 5: Monochromator, [3].

The sample chamber and the path that connects it to the electron detector require high vacuum or ultra-high vacuum conditions, to avoid the scattering of the resulting electrons with gases so that the error in the number of electrons acquired in the spectrum is minimal. The electron analyzer (Figure 6) has a hemispherical shape, it comprises two concentric hemispherical electrodes (inner and outer hemispheres) held at proper voltages. In this configuration, the electrons with the appropriate kinetic energy will do a circular trajectory from entrance slit to exit slit, where they are revealed by the detector; while the remaining particles will be dispersed along the path.

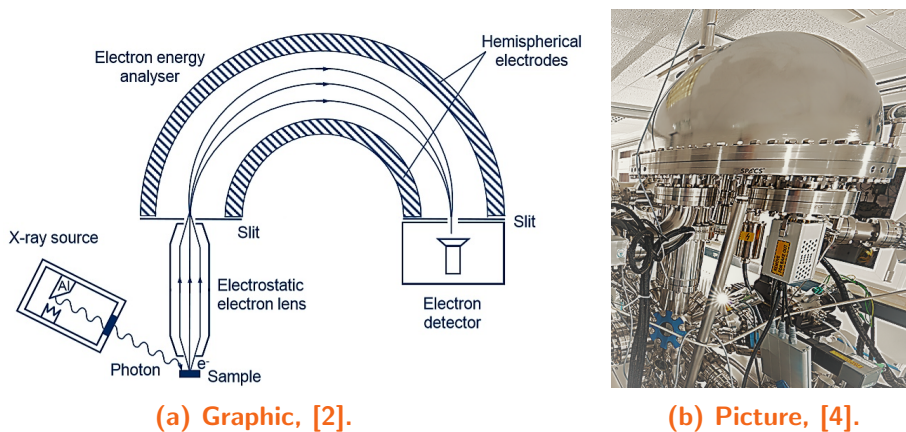


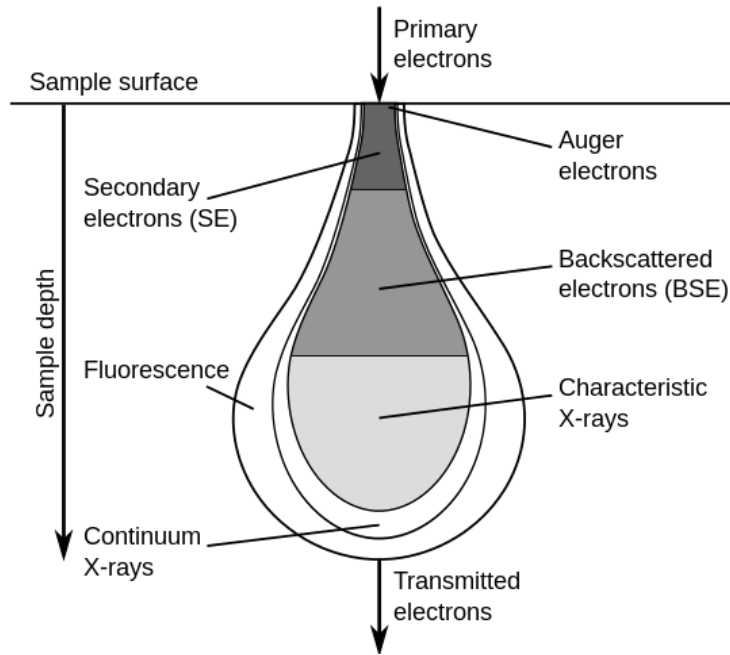
Figura 6: XPS analyzer.

## Scanning electron microscopy (SEM)

### Theoretical background

The scanning electron microscopy (SEM) is a type of electron microscopy technique that images the sample surface by scanning it with a fine beam of high-energy electrons. The electrons interact with the sample, producing different types of signals that contain information about the surface topography and its composition.

To interpret SEM images and to do a proper quantitative analysis, it is important to understand the concept of interaction depth: the region over which the incident accelerated beam electrons penetrate inside the sample and interact with it, both elastically and inelastically. The interaction volume has a distinct shape and increases with increasing incident beam energy and decreases with increasing average atomic number of the specimen. This characteristics determine the type of information obtained in SEM imaging, since they have an impact on the kind of signal that is measured. In particular, the signals come from backscattered electrons, secondary electrons, X-Rays, Auger electrons and cathodoluminescence, which permit to obtain complementary information from the sample surface. Figure 7 illustrates the signals generated by the electron beam after interaction with the sample in the scanning electron microscope and the regions in the interaction volume from which the signals can be detected.



**Figura 7: Interaction volume, [5].**

The signal coming from secondary and backscattered electrons is used to acquire a visual inspection of the surface of the sample under study; this kind of electrons are constantly being produced and they are a result of two separate types of interactions.

Secondary electrons are a result of the inelastic collision and scattering of incident electrons with the sample electrons; it is the most widely used signal produced in SEM. When the primary beam strikes the sample surface causing the ionization of specimen atoms, loosely bound electrons may be emitted and these are referred to as secondary electrons. As they have low energy, they can only escape from a region within a few nanometers of the material surface. So this kind of electrons accurately mark the position of the beam and help to resolve topographical contrast with a resolution of  $\sim 10$  nm or better. On the other hand, backscattered electrons are a result of an elastic collision and scattering event between incident electrons and the sample, which have escaped from the surface with an energy greater than 50 eV. They can be generated further from the surface of the material, so they carry information about deeper features and help to resolve topographical contrast and atomic number contrast with a resolution of  $< \mu\text{m}$ ; they also provide compositional information. As it was previously mentioned, there are other kinds of signals generated during the interaction between the sample and the electron beam. This is the case of the Auger electrons, cathodoluminescence and transmitted electrons. Auger electrons are produced following the ionization of an atom by the incident electron beam and the falling back of an outer shell electron to fill an inner shell vacancy. The excess energy released by this process may be carried away by an Auger electron. This electron has a characteristic energy and can therefore be used to provide chemical information. Because of their low energies, Auger



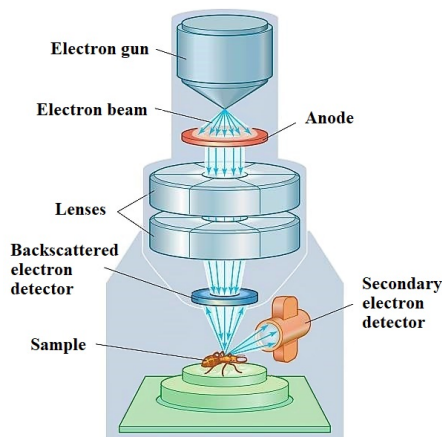
electrons are emitted only from near the top surface; they have escape depths of only a few nanometers and are principally used for surface analysis.

Cathodoluminescence is another mechanism for energy stabilization. Certain materials will release excess energy in the form of photons with infrared, visible, or ultraviolet wavelengths when electrons recombine to fill holes made by the collision of the primary beam with the specimen.

Finally, transmitted electrons is another method that can be used in the SEM to create an image if the specimen is thin enough for primary beam electrons to pass through (usually less than  $1\ \mu\text{m}$ ). This technique allows SEM to examine the internal ultrastructure of thin specimens. Coupled with x-ray microanalysis, transmitted electrons can be used to acquisition of elemental information and distribution. The integration of scanning electron beam with a transmission electron microscopy detector generates scanning transmission electron microscopy.

### Experimental display

A conventional scanning electron microscope tower is conformed by a few major components, as it is show in Figure 8a. The electron gun, which is on the top of the column, produces the electrons and accelerates them down the column to an energy level up to 30 keV. The electron beam goes through a series of lenses and apertures which control its diameter and they focus it on the selected sample; the focused electron beam scans across the surface of the material with the help of position, height and orientation controls, producing large numbers of signals. These can be detected and processed to produce an image or spectra by several systems, always in a high-vacuum environment, which allows electron travel without scattering by the air. The electronics controls provide real-time observation and image recording of the specimen surface.



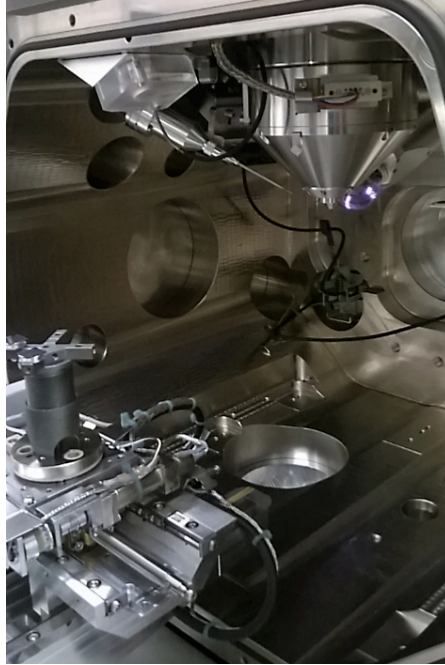
(a) Graphic, [5].



(b) Picture, [6].

Figura 8: SEM Instrument.

Besides the different kind of detectors used to collect the diverse signals, there is a platinum gas injection needle, observable in Figure 9, which is use for focused ion beam technique (FIB). This method has diverse applications such as transmission electron microscope (TEM) sample preparation, since it requires very thin samples (typically  $\sim 10 - 100$  nm).



**Figura 9: Chamber view, [6].**

Since the SEM is operated under high vacuum the specimens that can be studied must be compatible with that regime. This means that liquids and materials containing water and other volatile components cannot be studied directly and fine powder samples need to be fixed firmly to a specimen holder substrate so that they will not contaminate the SEM sample chamber. Moreover, non-conductive materials need to be attached to a conductive specimen holder and be coated with a thin conductive film by sputtering or evaporation.

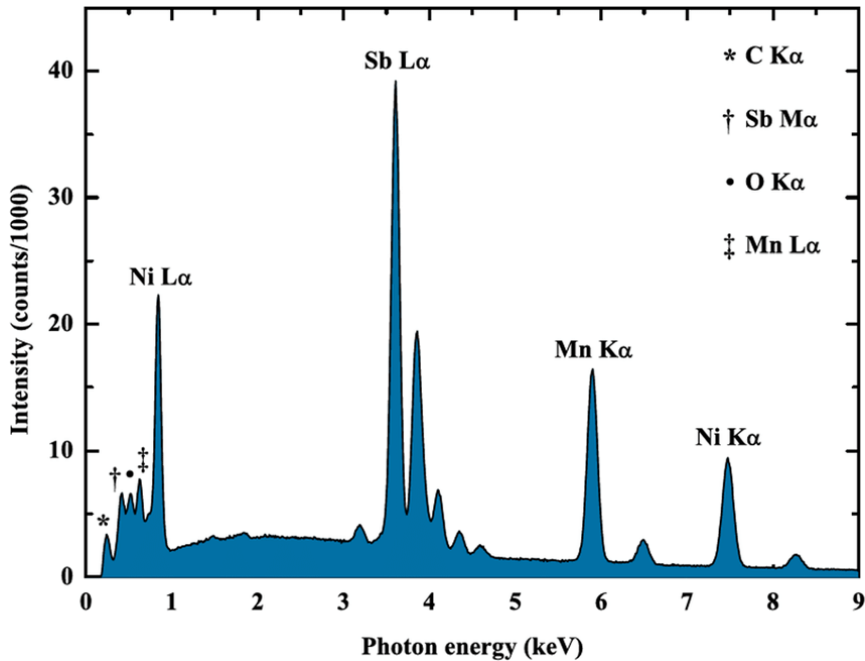
## **Energy-dispersive X-ray spectroscopy (EDX)**

### **Theoretical background**

Energy-dispersive X-ray spectroscopy (EDX or EDS) is a technique used for the elemental analysis or chemical characterization of a sample; it relies on the interaction of that sample and some source of X-ray excitation. Its characterization capabilities are mostly due to the fundamental principle that each element has a unique atomic structure, allowing a unique set of peaks on its electromagnetic emission spectrum.

To stimulate the emission of characteristic X-rays from a specimen, a high-energy beam

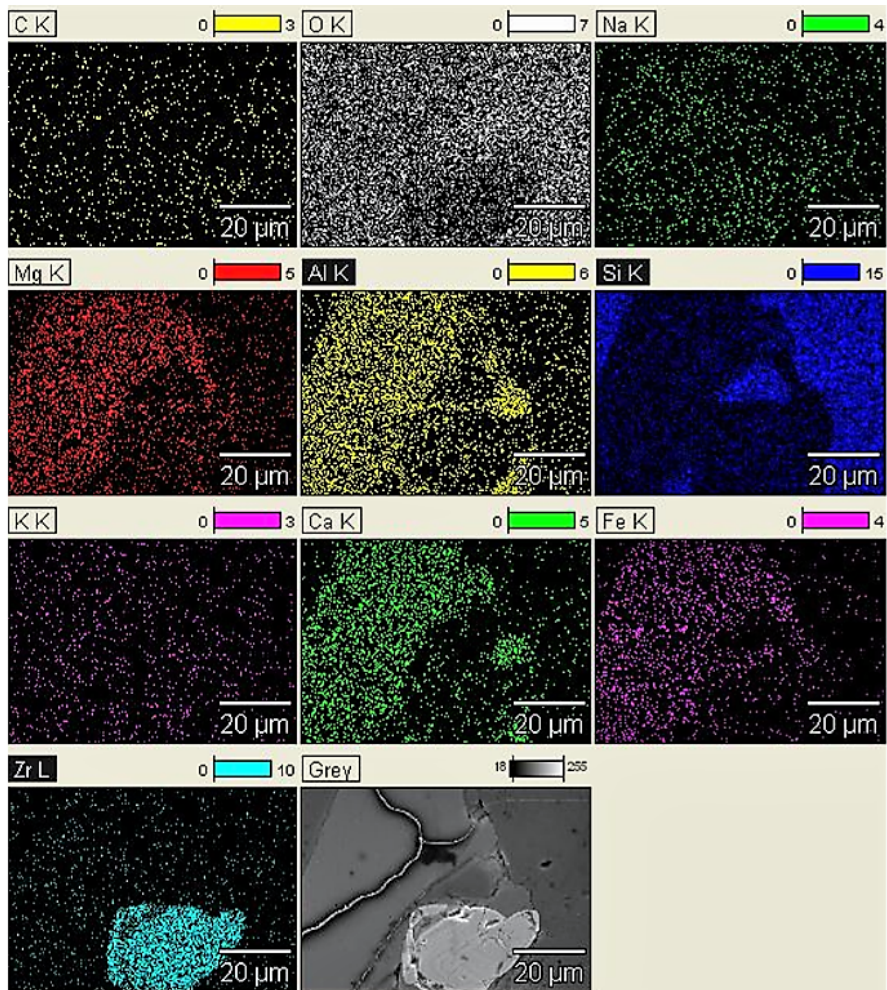
of electrons is focused into the sample being studied. At rest, an atom within the sample contains ground state electrons in discrete energy levels or electron shells bound to the nucleus. The incident beam may excite an electron in an inner shell, ejecting it from the shell while creating an electron hole where the electron was. An electron from an outer, higher-energy shell then fills the hole, and the difference in energy between the higher-energy shell and the lower energy shell may be released in the form of an X-ray.



**Figura 10: EDX Spectrum**

As shown in Figure 10, the data generated by EDX analysis consist of spectra showing peaks corresponding to the elements making up the true composition of the analyzed sample. The identification of the lines in the spectrum and is fairly straightforward due to the simplicity of X-ray spectra, information available in the form of computer database.

Moreover, EDX can also provide spatial distribution of elements through mapping; an example of this powerful approach is shown in 11, where it is possible to see the distribution and relative proportion (intensity) of previously defined elements over a scanned area.



**Figura 11: EDX mapping, [7].**

### Experimental display

In DESY Nanolab, the energy-dispersive X-ray spectroscopy measurements are made with the same setup as the scanning electron microscopy, since it provides the high-energy focused electron beam that stimulates the emission of characteristic X-rays.

A detector is used to convert X-ray energy into voltage signals; this information is sent to a pulse processor, which measures the signals and passes them onto an analyzer for data display and analysis.

Although the accuracy of the sample composition acquired with the analysis of the EDX spectrum is affected by various factors, such as the overlap of various X-ray emission peaks from different elements ( $Ti K_{\beta}$  and  $V K_{\alpha}$ ,...) and the nature of the sample, the EDX is an X-ray technique powerful in many scientific fields.

## Atomic force microscopy (AFM)

### Theoretical background

Atomic force microscopy (AFM) is a very-high-resolution type of scanning probe microscopy (SPM), atomic resolution as well as chemical sensitivity can be obtained. One of the major areas of application of the AFM technique is to image the topography of conducting and insulating surfaces. It is a mechanical microscope, which means that there are no optics focusing radiation on the sample; the imaging is based purely on an image synthesis of the surface topography by scanning with a fine tip the sample surface. This gives certain limits to the technique, but also a range of advantages. The AFM images are a result of a multitude of atomic forces interacting between the tip and the sample and by carefully controlling these forces, very high image resolution can be achieved.

In order to examine this sample-tip behaviour in detail, in Figure 12 the force-distance curve is shown. At the right side of the curve the atoms (tip and surface atoms) are separated by a large distance. As the atoms are gradually brought together, they first weakly attract each other. This attraction increases until the atoms are so close together that their electron clouds begin to repel each other electrostatically. This electrostatic repulsion progressively weakens the attractive force as the inter-atomic separation continues to decrease. The force goes to zero when the distance between the atoms reaches a couple of angstroms, which is about the length of a chemical bond. The attractive forces for larger distances are mainly due to Van der Waals forces. At a distance of about the scale of atomic bonds the repelling Coulomb interaction dominates.

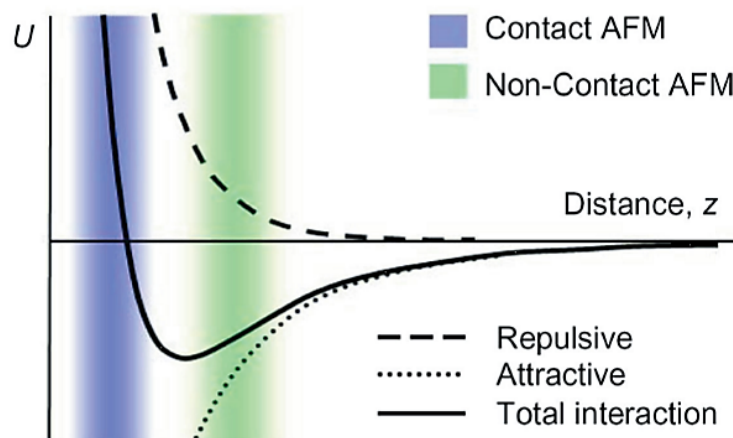


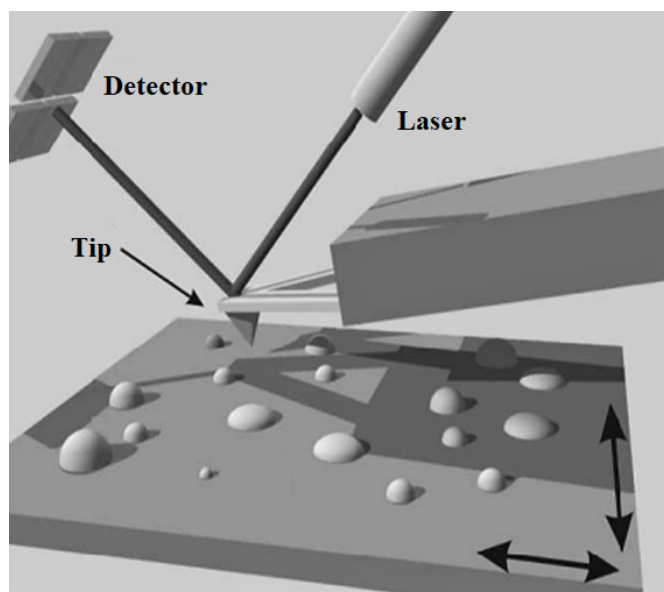
Figure 12: STM force-distance curve, [8].

### Experimental display

In AFM, the surface under investigation is scanned with a sharp tip in the same way that an electron beam scans the surface in an SEM, but in a much slower pace. As it was mentioned, the imaging process is impacted by the forces between the tip and the sample,

so the undergone forces have to be measured.

Considering that the tip used in AFM is attached to the end of a cantilever with a low spring constant, as the scanner gently traces the tip across the sample, the contact force causes the cantilever to bend due to repulsive or attractive forces. These forces are not measured directly, but are calculated by measuring the deflection of the lever. This movement is measured using a focused laser beam that is focused on its tip; the reflected light from the tip is detected on a quadrant detector that can determine both lateral and vertical movement of the tip corresponding to bending and torsion, respectively. In Figure 13 it is shown a sketch of this arrangement.



**Figura 13: STM sketch, [8].**

In this way, AFM can detect molecular layers over comparatively large areas; the technique is applied to problems in a wide range of disciplines of the natural sciences, including solid-state physics, semiconductor science and technology, molecular engineering, polymer chemistry and physics, surface chemistry, molecular biology, cell biology, and medicine.

### **3 Experiments**

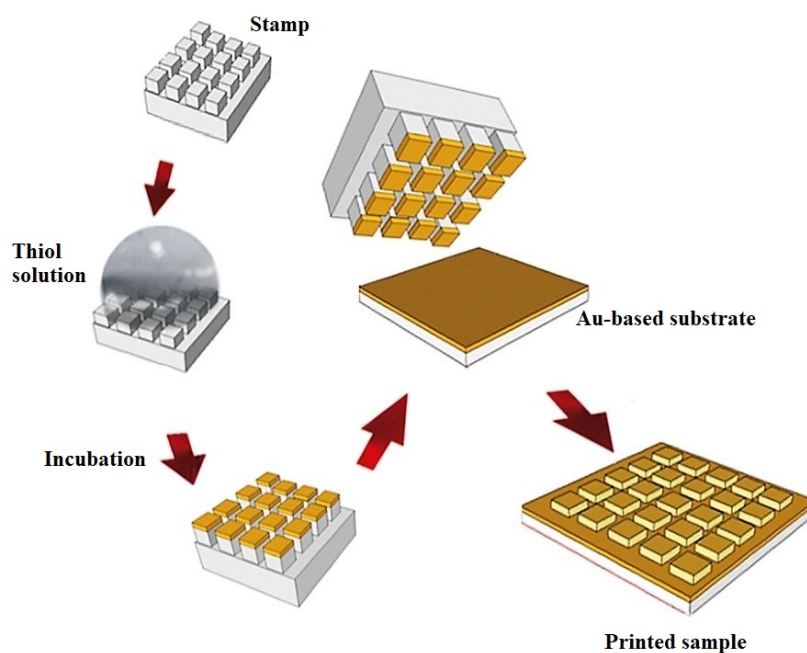
#### **Experiment I**

Despite many studies on macroscopic corrosion and its inhibition effects in the presence of organic molecules and thiols, the initial stages of corrosion and corrosion inhibition at the subnanometer or molecular scale are poorly understood.

Understanding this early stage of corrosion and its possible corrosion protection at that level is the main purpose of the studies performed by Shova Neupane as an external user at DESY

Nanolab. Her work focuses on the dealloying of a noble metal alloys (Au-based) in the presence of inhibitor thiol molecules, disposed in a self-assembled monolayer.

In Figure 14, it is shown an schematic picture of the followed multistep printing process of the organic self-assembled thiol monolayer on the Au-based substrate used in the experiment. As it is presented, a stamp composed of an array of micrometer-sized squares with micrometer-sized separations among them are exposed to the thiol solution for  $\sim 30$  s and dried gently. The thiol-containing stamp was then placed onto Au-based substrate without any external pressure for another  $\sim 30$  s and immediately peeled off, creating the appropriate molecular assembly.



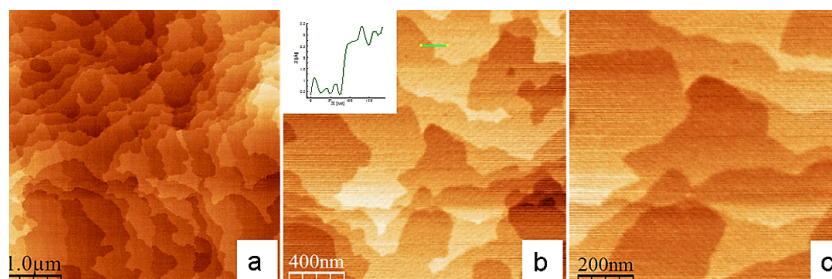
**Figura 14: Multistep printing process, [9].**

In particular, the work carried out in Nanolab was the Au-based film preparation and characterization, prior to further studies of dealloying on the atomic scale. The sample preparation is a significant step, which main aim is to achieve clean and atomically flat surfaces.

The whole procedure involves several cycles of sputtering and annealing in ultra high vacuum, as well as an electrochemical cleaning process. Once the samples are transferred into the UHV chamber, they were sputtered by  $Ar^+$  and annealed for several hours with a very low heating rate to a maximum temperature of 800K. This process of sputtering and annealing normally leads to clean surfaces, where surface contamination by C or other impurities are eliminated, and atomically flat surfaces can be produced. After repeating twice this kind of cycles, a clean and atomically flat surface may not be completely achieved; therefore, electrochemical cleaning treatments are used, which helps to get rid of surface defects, such

as microscopic lines or scratches due to mechanical grinding. Afterwards, another preparation cycle is carried out, which ensures the achievement of an impurities-depleted and atomically flat sample surface.

After the complete preparation process, the surface cleanliness and ordering is verified with XPS and AFM characterization; from which it can be concluded that it led to a clean, smooth and microscopically flat Au-based surface; an excellent testing ground for nanoscale phenomena such as corrosion initiation and inhibition. Figure 15 shows an example of AFM images of the film surface after the different cycles of the UHV preparation, where the improvement of the sample is observable.



**Figure 15: AFM images after the different steps of the UHV preparation, [9].**

## 4 Conclusions

Throughout this document, some of the several experimental techniques that are available in DESY NanoLab are explained; their theoretical background and general experimental displayed has been introduced.

It is important to remind that the X-ray photoelectron spectroscopy (XPS) is a surface-sensitive and quantitative spectroscopic technique which provides information about the elemental identity, chemical state and concentration of a selected sample. The scanning electron microscope (SEM) is one of the most versatile instruments available for the examination and analysis of the microstructure morphology and chemical composition characterizations. Energy-dispersive X-ray spectroscopy (EDX) is an x-ray technique used to identify the elemental composition of materials and can be used to estimate their relative abundance. And finally, atomic force microscopy (AFM) provides a three dimensional profile of the surface on a nanoscale, by measuring forces.

In summary, the DESY NanoLab provides a versatile platform for DESY photon science users for in depth sample nano-characterization by spectroscopy, microscopy, magnetism and X-ray diffraction, complimenting the advanced X-ray techniques available at DESY light sources. Moreover, the facility will be highly beneficial in the next future when the fourth generation of synchrotron radiation sources is operational.



## Acknowledgements

I am very grateful to the organizers of the 2018 DESY Summer School Programme for making the wonderful experience of working in a scientific research institute become true. I want to give a special thank to my supervisor during the internship, Dr. Heshmat Noei, and all the members of the X-ray Physics and Nanoscience research group for all the help given.

## References

- [1] H. NOEI, V. VONK, T. F. KELLER, *DESY NanoLab*. Journal of large-scale research facilities, 2, A76 (2016)
- [2] SPYROS DIPLAS, *X-ray photoelectron spectroscopy - An introduction*. Universitetet i Oslo, (2013).
- [3] ANALYSIS FEATURES, *X-Ray Generation*.  
[https://xpssimplified.com/xray\\_generation.php](https://xpssimplified.com/xray_generation.php)
- [4] DESY FACILITIES, *DESY NanoLab*.  
[http://photon-science.desy.de/facilities/desy\\_nanolab/index\\_eng.html](http://photon-science.desy.de/facilities/desy_nanolab/index_eng.html)
- [5] WEILIE ZHOU, ROBERT P. APKARIAN, ZHONG LIN WANG and DAVID JOY, *Fundamentals of Scanning Electron Microscopy*.
- [6] THOMAS F. KELLER , *Scanning Electron Microscopy at DESY NanoLab*.
- [7] B. HAFNER, *Energy Dispersive Spectroscopy on the SEM: A Primer*. Characterization Facility, University of Minnesota.
- [8] G. N. ANKAH, *Fundamental Investigations of the Selective Dissolution of Cu<sub>3</sub>Au(111)*. Dissertation zur Erlangung des Grades Doktor-Ingenieur der Fakultät für Maschinenbau der Ruhr-Universität Bochum (2011).
- [9] S. NEUPANE, P. LOSADA-PEREZ, S. VIVEGNIS, Z. MEKHALIF, J. DELHALLE, A. BASHIR and F. U. RENNER, *Two-Step Nanoscale Approach for Well-Defined Complex Alkanethiol Films on Au Surfaces*. Langmuir 2018 34 (1), 66-72.