



Notice TPA

Microscopie à force atomique (AFM) *Scanning Probe Microscopy*

Résumé

SCANNING PROBE MICROSCOPY: Study of surfaces by 3-Dimensional images

I Introduction

Atomic Force Microscopy (AFM)

The Atomic force microscope (AFM) belongs to the new category of near field scanning probes such the Scanning Tunneling Microscope (STM), Scanning Near field Optical Microscope (SNOM), etc [1]. While optical or scanning electron microscopes give only information in two dimensions, AFM, STM and SNOM give 3-D topographic images of the scanned surfaces (see Fig. 1).

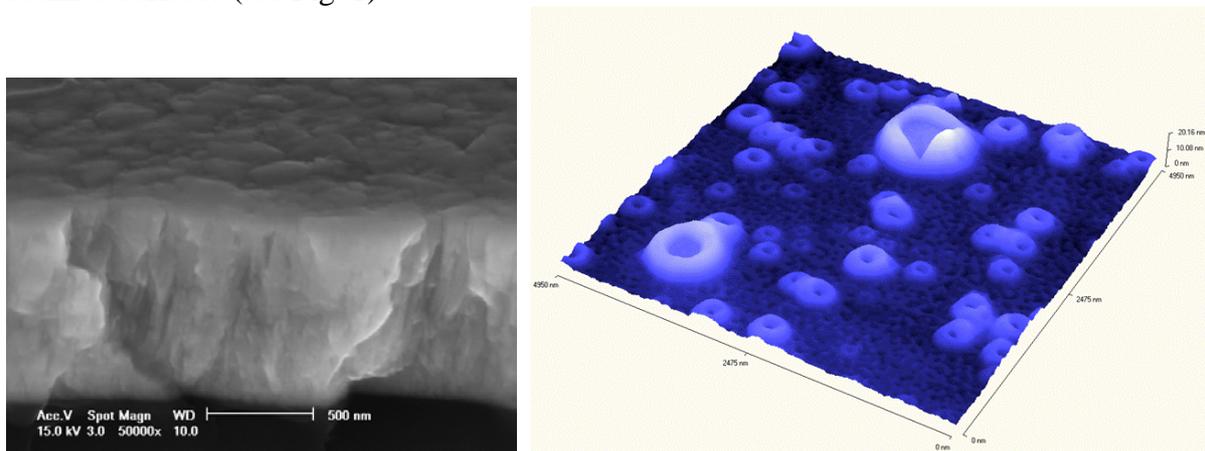


Fig.1 SEM (Scanning electron microscopy) image of a TiN thin film (left) and a 3 dimension AFM (Atomic force Microscopy) image of diblock copolymer on Si substrate.

AFM can then measure the topography of the surface, roughness, hardness, friction (using the lateral force mode). Fig. 2 shows a schematic of the physical principle and technical realisation of AFM.

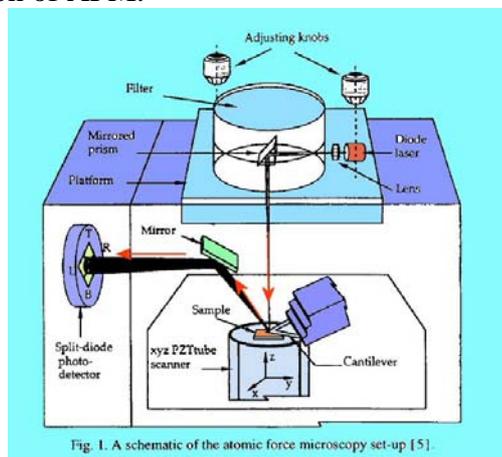


Fig. 1. A schematic of the atomic force microscopy set-up [5].

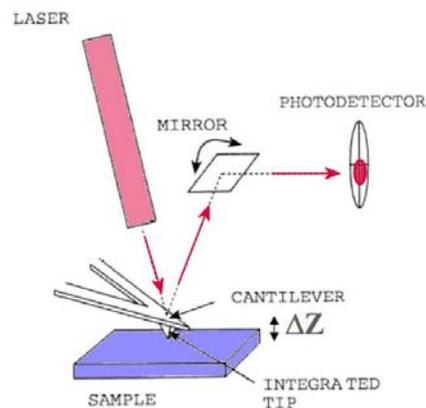


Fig. 2 A schematic of the atomic force microscopy

The AFM scanner is a PZT tube that moves the sample (or the probe tip) in x - y - z directions. To generate a scan in the x - y plane the system uses an electronic raster signal while in the z direction the deflection of the cantilever (with the integrated tip probe) is detected by a 4-Q photodetector (see the notice in the labs). In contrast to STM which needs electrically conducting samples, AFM can be used with metallic or insulating samples. AFM works in two modes: a) in **contact mode** with a useful option mode namely **lateral force** and b) in **non-contact mode** (tapping mode or force modulation mode). The choice of the working mode depends on the nature of the information that the researcher is looking for and/or to overcome the limitation of the contact mode such as the tip-surface interaction modifications of the sample. The non-contact modes are suitable in case of soft materials like polymers, biomaterials and organic materials.

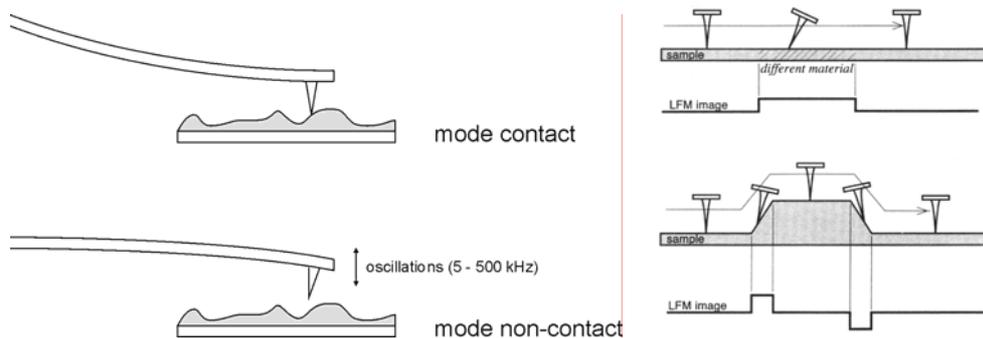


Fig. 3 Contact and non-contact modes. The lateral force mode allows identifying soft and hard regions.

AFM Applications.

Among surface topography characterizations, nowadays AFM constitutes a powerful tool for viewing and manipulating single biological molecules, imaging proteins and biological membranes, measuring non-specific forces (such as Van der Waals forces, electrostatic forces, cell elasticity), functionalizing biological surfaces, etc.

Aim: The purpose of the present TP is to introduce to student to the AFM technique, to get qualitative and quantitative information including topographic mapping, particle and pore size, size distribution and modification due to thermal atomic diffusion.

II SOLIDIFICATION/CONDENSATION and CRYSTALLIZATION

In gas or liquid states, atoms of a metal are free to move in a random manner. In a solid state the atoms occupy specific sites in a specific geometric arrangement namely crystal lattice owing to their atomic bonding nature. There are fourteen basic lattices; most common metal like Ti, Co, Au, Ag, Cu, Cr, Fe crystallize in the form of close-packed hexagonal (CPH), phase-centered cubic (FCC) or body-centered cubic (BCC) crystal lattices (see Fig. 4). When metal atoms are frozen from the gas or liquid state by lowering the higher temperatures below a certain critical temperature (condensation/solidification temperature) they crystallize, then the freezing process leading to the solidification of a gas or liquid is termed **crystallization**.

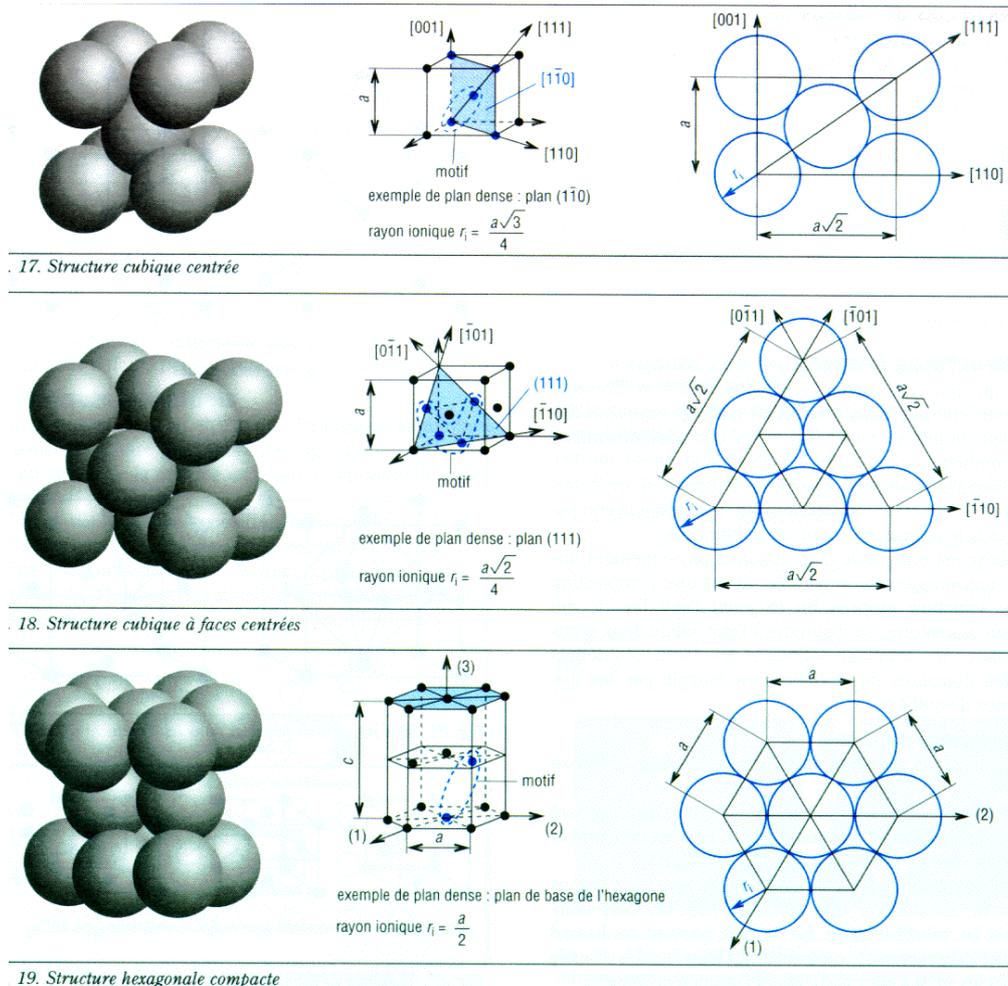


Fig. 4 Crystalline nature of metals and geometry of lattices. Most of common metals and alloys exist in the form of FCC, BCC and HCP lattices.

II.1 Crystallization mechanism

Crystallization occurs in two stages: the **nucleation** and the **crystallite growth**. In the first stage a nucleus is established, i.e. one atom is fixed on a favorable site on which the crystal can be developed. In the second step, from the nucleation site a small crystal (often called crystallite or grain) grows until it meets another neighboring crystallite (see Fig. 5). Therefore, solid metals are composed of small crystallites exhibiting HCP, FCC, or BCC crystal lattices (the solid is called **polycrystalline** material) [2].

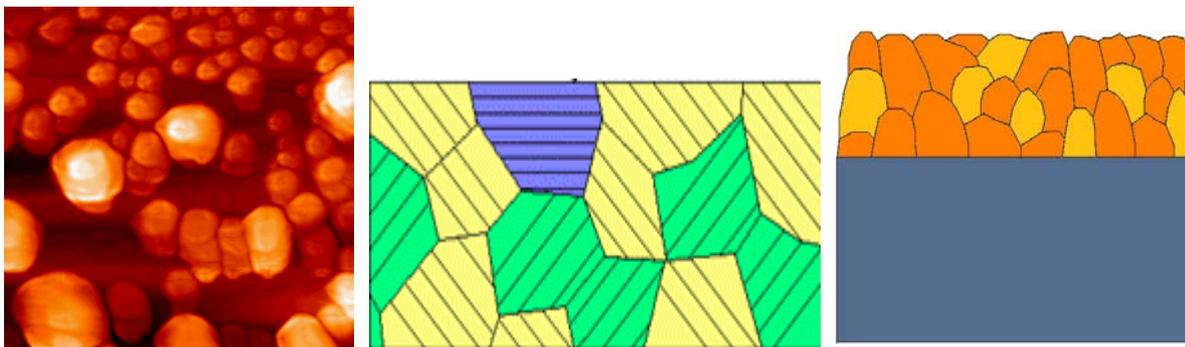


Fig.5 From the left to the right: STM image in plan view of Cu nanocrystallites deposited on Si substrate, schematic plan view and cross section view of polycrystalline thin film

During the crystallization process the frozen atoms stack preferentially on less-dense crystallographic planes. For example, in the hexagonal lattice the {0001} plan is the dense, close-packed plane while in the FCC lattice it is the {111} plane. Atoms attempting to freeze on these dense planes need to fit exactly into their right place. On the contrary the others planes such as the {100} plane have more place to fit new atoms and are the preferred freezing planes. Thus, the crystal lattice systems have preferred direction in which the growth usually takes place (see Fig. 6). In the hexagonal lattice the directions perpendicular to the prism faces are preferred directions while in cubic lattice it is the {100} direction or the direction perpendicular to the cube faces.

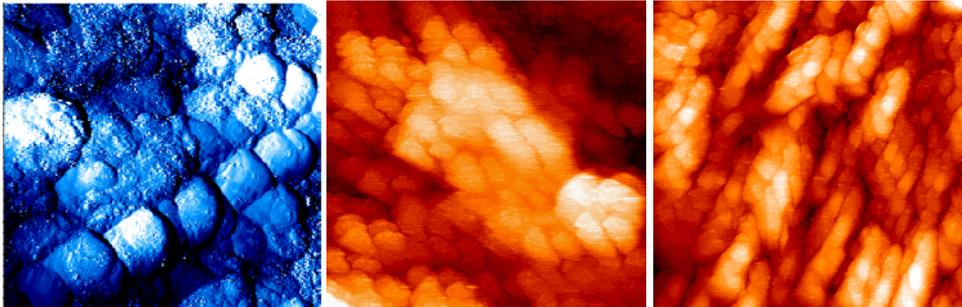


Fig.6 STM images of CrN thin films exhibiting preferential crystallite orientation (from the left to the right: fcc-(200) CrN, fcc-(111)CrN and hex-(111)Cr₂N

II.2 Crystallite size (grain size) and grain boundaries

In the case of solidification, the size of crystallite depends on the number of nucleation sites available in the molten liquid. In the case of condensation from vapor phase the **crystallite size** depends on the nature of the substrate surface and the interaction of it with the impinging atoms or molecules. In general, the more nucleating sites there are, the more grains will be generated and smaller the resulting grains will be. If the nucleation sites are scarce, large sized crystallite will be developed.

Grain boundaries are regions where the atom lattice of one grain does not match with the lattice of its neighbors (see Fig. 7). The **grain boundary** region can be considered as areas containing atomic discontinuities and those with irregular non-crystalline structure (amorphous like region).

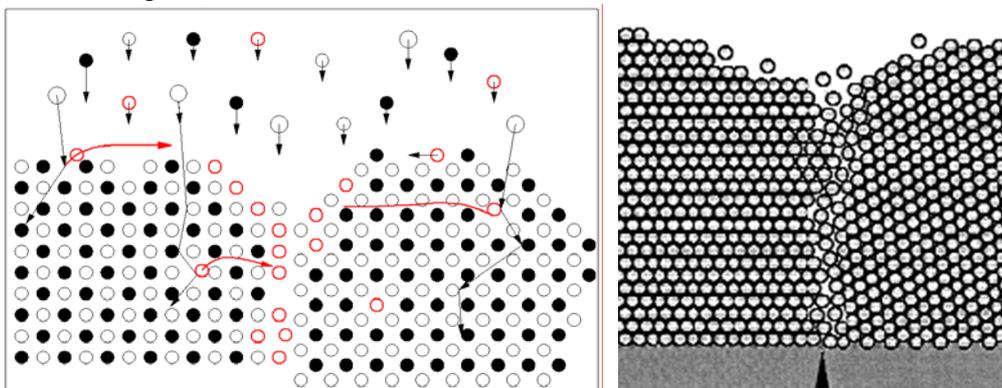


Fig. 7 Schematic presentations of crystallite growth and grain boundary formation during the condensation of atoms.

III ANNEALING or THERMAL TREATMENT

As a polycrystalline metal is heated at enough high temperature it can enter in the re-crystallization stage. During the solidification or condensation, a fast freezing process can lead to quenching of atoms out of the normal lattice positions deforming the lattice and generating stresses namely residual stresses. Recrystallization suggests then the reforming or reorganization of atoms into its perfect crystal lattice without stresses. If the temperature is raised above that required for recrystallization, the metal enters the stage called crystallite-growth stage (or grain-growth stage). Depending on the temperature and holding time, in this stage the crystallites become larger, consequently the number of crystallite and the grain boundaries decrease. The reduction of the energy contained in the grain boundaries seems to be the forces that drive the growth of the crystallites. In grain growth regime the larger grains expand and move into and absorb the adjacent smaller grains

IV OBJECTIVE

The subjects of investigation by using the AFM technique [1] depend on the imagination of students and on the ability of preparing "clean" sample surfaces. AFM is very sensitive to surface impurities and surface contamination. Below you will find some suggestions:

- A) Investigation of the re-crystallization process in Au, Ag and/or Ag/Au thin films deposited by thermal evaporation on Si or graphite substrates.
- B) Investigation of the re-crystallization of Cu after cold-working.
- C) Investigation of the atomic diffusion of Cr in the interface Cr/Au.
- D) Study of the growth mode of organic compounds and structural modifications after thermal treatment on Si and Au substrates.

Review Questions

- 1) What is the main difference between AFM and SEM?
- 2) What is the low limit of the spatial resolution of AFM?
- 3) Describe briefly the two operating modes of the AFM: contact and non-contact?
- 4) Do you know the field of applications of the AFM?
- 5) What does it mean for a metal "recrystallization" and "sintering"?
- 6) Is the atomic bulk diffusion energy similar to that of the atomic surface diffusion? Give some values of activation energies typically found for metals and alloys.
- 7) Is the atomic diffusion a thermal activated process?
- 8) Explain how grain growth occurs and what effect it has on a metal's properties.
- 9) Give some characteristic values of crystallization temperature of Au, Ag, Cu, Sn.
- 10) Are there preferred crystallographic directions during the crystallization?

For further studies

- [1] "Les Nanosciences: Nanotechnologies et nanophysique", Eds. M. Lahmani, C. Dupas, Ph. Houdy; Collection Echelles, Edition Berlin 2004. [AFM, Chapitre 4](#)
- [2] "The Technology of metallurgy", by W. K. Dalton; Macmillan Publishing Company, NY, 1993.