Characterization of technological processes

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Introduction to material characterization

In this first chapter we will introduce some ideas, in order to show for a first time the most important elements that we need in order to study materials.

Every material we need to characterize, must be studied with electrical, optical or other types of tests; tests can be performed after the realization of the material, or during the growth process, with a real-time film width measure or something similar. The material is exposed to a beam of something: particles, photons or other type of radiations (electromagnetic radiations from the infrared over the visible range and ultraviolet, etc).

In order to characterize materials, there are three types of analysis:

- Microscopy: process aimed to magnify and show well the morphology of the sample, and have a direct idea of its structure;
- Diffraction: process aimed to the study of the interference between waves;
- Spectroscopy: technique which can establish the chemical composition of the material through the knowledge of the states of the electrons, their energy levels, energy gaps, and characterize the material in terms of quality, studying the density of impurities.

Generally, a characterization process is based on the following idea: from an energy source we hit the material, and it will answer our excitation with a set of particles or radiations; by collecting these elements we can use them to extrapolate informations about the object. The sources mainly used to characterize objects are three: **photons**, **electrons**, **ions**. Depending on what we use to excite the semiconductor, we will have, out of the material, or a response given by something of the same type of the excitation (photons and photons, ions and ions..), or something different (photons and electrons, electrons and ions..). There are two ways to see responses: outputs of the material can be classified as **emitted** or **reflected** by the material.

There are some parameters useful to know, in order to know our work:

- **Spatial resolution**: for spatial resolution we mean the minimum size of the structure which can be magnified; for example, with optical microscopy we can see up to 2000 times bigger of the original sample, so see clearly something in the order of width of the nanometer; optical microscopy in fact is limited by negative effects like optical diffraction, which gives problems, introducing errors;
- **Kinetic energy**: if we have a source of something (particles or photons), depending on their kinetic energy, they can go in depth or only in the surface of the material; both the informations can be good: maybe we only want to know informations about the material's surface, maybe we want to know something about the core, the bulk.
- **Spatial resolution**: it is dependent on the thickness of our beam: if our beam is narrow, we can characterize well our material, so have a high resolution.
- **Sensitivity**: for sensitivity we mean the minimum amount which can be detected. For *detected*, we mean *really detected*, not non-effective numbers or informations. As *detection limit* we mean the minimum element which can be detected.
- **Penetration depth profile**: this is the depth which can be reached from the characterization; it depends on kinetic energy, on the weight of the element we use: increasing kinetic energy, we can go more deep; if we have high masses we can have higher kinetic energy! This parameter depends also on which material we want to analyze: analyze a conductor with electrons is more easy respect to analyze an insulator, because insulators act as a shield respect to the energy of our radiation! Parameters which can act on this parameter are:
  - Density of the material;
  - Conductivity of the material;
  - Kinetic energy of our beam;
  - Type of source used for our beam.

The interaction between the probe and our material can be different: from an excitation, as already written, we can have many responses, many outputs, depending on the imprinting beam; by every output we will have different data (about surface, core...):

- Auger electrons: they provide informations about the surface;
- Secondary electrons: they are closer to the core, giving informations about few tens of nanometers respect to the surface;
- Backscattering electrons: more deep, about one or some micrometers respect to surface;
- X-ray photons: more deep.

By collecting and analyzing these informations, we can learn many informations about the material.

Capitolo 1

Optical microscopy

1.1 An introduction to geometrical optics

Optical microscopes are characterized by low resolution and low magnification; despite these characteristics, they are very useful, because optical analysis (generally) is not invasive; with optical microscopes we can analyze many kinds of materials, and their morphology.

The core of optical microscopes are **lenses**: namely, convergent lenses. As known from optical physics, a lens is a particular kind of glass, which has diffraction properties. We will use **convex** (also known as **convergent**) lenses: they are lenses with both convex curvatures. In these lenses, considering as origin of our reference system the lens, the focal point will be greater than 0, so near to the object that we want to magnify. There is an important parameter of a lens: the **focal point**; it is the point in which every ray passes, due to rifraction phaenomena. Another parameter is the **center** of a lens: it is the point for which there is no rifraction or reflection of the ray of light; it is the center of symmetry of the lens; this point, for a x-axis reference system, will be the origin (as said).

Let's consider the following image:

We can define the magnification M of our system simply as:

$$M = \frac{ab}{AB} = \frac{Oa}{OA} = \frac{q}{p}$$

As known from Physics, we can evaluate the focal point F_0 simply as:

$$\frac{1}{F_0} = \frac{1}{p} - \frac{1}{q}$$

By putting the object beyond the focal point we obtain nothing: the object must be put between the lens and the focal point F_0, in order to magnify the image. Studying the characteristics of the human eye, we can proof that the minimum image distance which can put in focus is 25 cm; we want so that the virtual image stays at least at 25 cm respect to the origin of the axis, in order to make the real image be visible: $\delta = 25$ cm. Using $q = \delta$, and considering the fact that the focal point is near to the object, we can say that:

$$M = \frac{q}{p} \sim \frac{\delta}{F_0}$$

This is the simplest idea we can use to realize a system which can magnify an image.

1.1.1 Compound microscope

Previously we wanted only to introduce the idea behind a lens; a microscope can not be realized with just one lens, because it can provide a very low magnification. A compound optical system must be composed of at least two lenses:

- Objective: this is a lens which must create real images; it must be put close to the sample we want to analyze: the sample must be put near the objective, but this time beyond it;
- Ocular: this is a lens which must create virtual images of our object; this must be put close to the eye, but at least in the minimum distance (25 cm).

We want that the real image of the objective goes into the focal plane of the ocular, in order to increase very much the magnitude of the image; the ocular will work as a magnification lens, so must be configured in order to have as virtual image an image visible at the minimum distance: 25 cm.

Using a system composed of many lenses, we can multiply the magnification coefficients, obtaining a much higher magnification.

In this case, we obtain a magnification equal to:

$$M = \frac{ab}{AB} = \frac{ab}{a'b'} \cdot \frac{a'b'}{AB} = M_{ac} \cdot M_{ab} = \frac{L\delta}{ff'}$$

1.1.2 Diffraction limits

The greatest problem of optical microscopy is diffraction: when we have to light an object through a little aperture, light can be stopped; what happens is that, out of the aperture, there is a behaviour of our light similar to a spherical one: in geometrical optics we assume all the times that our light has a plane wave behaviour; if the aperture stops light, out of it we will have a spherical wave behaviour, with hypothetical origin put in the aperture. This effect generates interference: we expect a plane wave behaviour, and obtain a different scattering of the light, so we will have issues. The amount of the diffraction effect depends on the angle of incidence, and on the wavelength of the optical beam: if we have many beams, and between they there is a great angle, the peaks of the two diffraction figures will not be overlapped, so we will not have too much problems: we will avoid interference.

If we have a circular slit instead of the simpler rectangular one, we can say (knowing better the theory) that diffraction pattern will be null for:

$$\sin(\vartheta) = 1,22\frac{\lambda}{D} \simeq 1,22\frac{\lambda}{D}, \quad \lambda \ll D$$

So using the Taylor's expansion stopped at first term. This theory can be applied to a compound optical microscope, obtaining:

$$AB = p \cdot \tan(\alpha) \simeq f \cdot \tan(\alpha) \sim f \cdot \alpha$$

Where:

$$\alpha \simeq \frac{\lambda}{D} = \frac{\lambda}{n}\frac{1}{2\tan(\beta)}$$

We can define another parameter which will be very important to our system: the numerical aperture. It is defined as:

$$\mathrm{NA} = n \cdot \sin(\beta)$$

β is the collection angle: increasing it, sine increases, and the size which permits to distinguish the image reduces. β can be chosen starting from the diameter of the lens and the focal length.

More complicated microscopes

In an actual microscope, there are many more lenses respect to the ideal microscopes we have shown; they are of three kinds:

- Objective lens: which imposes the diffraction pattern;
- Intermediate lenses: which introduces the most of the magnification;
- Ocular lens: which produces the last magnification, so the final image.

With these elements, the microscope will have a structure like the following one:

1.1.3 Structure of an optical microscope

There are at least two possibilities, in order to realize optical microscopes (supposing since now to use compound microscopes, so at least an objective, an ocular and a system of intermediate lenses);

- Microscope operating in transmission: it is a microscope in which light goes **through** the sample we want to analyze,
- Microscope operating in reflection: the difference respect to the previous one is the fact that light is coming from the high part of the microscope, not from the bottom; with a system of mirrors, light is reflected until it reaches the sample.

Considering that light becomes from the bottom of the system, down respect to the sample, we want to obtain high resolution; light can be deflected by diffusion, refraction of diffraction effects, and this is not good: we need, in order to have a high resolution (and focus on the sample well, obtaining clear images), to collect many light rays becoming from the sample. How many light comes from the sample depends on the numerical aperture parameter, but this is not enough: numerical aperture depends on the objective, but there are phaenomena which don't depend on the objective:

Our problem is the following one: from the sample to the objective there is **air**; this gives to us a trouble: a big discontinuity between sample and objective, in terms of n. In order to reduce this issue, we can introduce a liquid between the sample and the objective (maybe an oil, in order to prevent the formation of bubbles in the liquid, due to the high density of the chosen liquid).

The oil introduces more optical continuity, and we can take advantage of this, obtaining light to all the diameter of our objective, maximizing the numerical aperture.

1.1.4 Darkfield microscopes

Previously we studied brightfield microscopy. It can have problems: brightfield microscopy works well with coloured samples, or with samples with a well defined contour, but not so well with transparent objects, like cells in a physiological solution: from the light source through the sample to the objective comes too much light, so we don't see nothing, because the transparency of the object doesn't permit to identify any shape.

There are two ideas in order to realize this:

- With transmission configuration, we put a diafram, in order to illuminate only a little part of the sample; in the objective will not come any one of the rays of the light source;
- With reflection coefficient, there is a mirroring system which introduced a marked obliquity respect to the useful part of the sample.

We are not illuminating the object, but only the space near it; this is useful, because light is scattered near to the sample, and what we collect with these microscopes is just the scattered light! This amplifies so the scattering near to the interface of the sample, showing better the contour of they.

Darkfield name derives by the fact that background is black, dark: we see, out of the ocular, the contrast of the object respect to the physiological solution. Signal will be less intensive, so it is more complicated to use respect to brightfield microscopes, but it can be very useful in critical situation like the previous one.

1.1.5 Confocal microscopy

In order to end this chapter about optical microscopes, we want to introduce a modern technique to realize microscopes, which has several advantages respect to the previous ones.

Let's consider the following block scheme:

The light source in this microscope is, in our considerations, a **polarized collimated laser**; at this condition, the microscopes which implement this idea are known as CLSM: Confocal Laser Scanning Microscopes. This name gives us an idea of the working mode of this microscope: it **scans** a sample, point by point, obtaining so out of it an association between position of the sample and its characteristics (in terms of shape or something else). This idea will be refreshed when we will talk about other types of microscopes, like SEM or others.

How does this microscope work? Well, probe is again light (it is optical!), but this time laser; we have to pay attention about it: with laser we have a big energy collimated in a little surface, so this type of analysis, in some types of materials, can be destructive. There is an impinging beam which goes to the sample, passing through a beam splitter; from the source to the sample, there will be no splitting. A system of lenses will collimate our beam, which be filtered by a pinhole; light will interact with the sample, put in the **focal point**, where are coming only the focus light rays (the others are blocked by the diafram with the pinhole). Pinhole is like a shield: the beam is collimated in a kind of sphere, of 2 μm or something similar; with this shrinking process we can analyze the region, imposing spatial resolution. Without the pinhole we obtain as output the convolution of the interaction of laser with many zones, obtaining interference terms. After the interaction, light goes back, passes through the pinhole, then comes to the beam splitter, which reflects to the objective only the useful light (not the source one!), and it goes to a detector (which can be a photoconverter, in order to obtain from light an electric signal, more simple to process). A piezoactuator changes the position from the objective of the microscope and the sample, but pinhole is fixed. By changing position, we can obtain something interesting: we can scan with very good resolution (respect to the other optical microscopes) the sample in surface but also in depth, obtaining the possibility to realize 3d scans with high resolution.

Capitolo 2

Electron microscopy

There are some types of electron microscopes; we will study at least two of these.

2.1 SEM : Scanning Electron Microscopes

The main difference respect to optical microscopy is the type of source: previously we used light as probe, now we will use electron beams. This is very interesting: the worst limit in optical microscopy was the diffraction limit, which imposed the resolution of the instruments; diffraction exists also here, but now we have something different respect to light: diffraction is a phaenomena which depends on λ, on the wavelengths of the light source: light has quite high wavelengths, so diffraction becomes an issue. With electrons, we can remember the famous De Broglie relations, which say that:

$$E = \frac{p^2}{2m} = \frac{\mathrm{h}^2}{\lambda^2 \cdot 2m_{electron}}$$

With this relations, we can imagine that we can choose λ by chosing the energy of the electron beam, but so we can reduce diffraction problems! Diffraction still exists, but now it is not very interesting: now we can avoid it, by choosing a good energy level.

These microscopes have many advantages also respect to confocal microscopes: with they we could only see clearly in a little region (the *sphere*), with a certain magnification, because we were collimating light in a small region; now we can see clearly all the volume, a very big volume, at the same time, clearly.

As we said, we have an electron beam; it is generated by an electron source, which is moved by electromagnetic lenses, which deflect the beam in different points of the sample surface. By the interaction of these electrons and the sample, we will have several radiations and particles, which must be collected in order to measure the amplitude/energy of each of them. All the system must be kept in vacuum: we have to enlarge the free path, in order to make electrons reach the sample and go back.

Let's analyze more in details the structure of this system.

2.1.1 Electron gun

Electron beam is generated by a device known as electron gun; studying the details, electrons are produced from thermionic or field emission process. There is a cylindrical grid which shrink the electron cloud emitted by one of the two mechanism until it becomes a point; we give energy to the point with a negative voltage, increasing E and choosing λ with the De Broglie relation; modern technologies can shrink the electron cloud to 1 nm or something less, obtaining a very high resolution: we don't have diffraction limits (or they are negligible respect to the beam size). Now, our limit is only technological!

We said that there are two types of methods, in order to generate electrons:

- Thermionic emission: applying a voltage to a filament of some material (the more used is tungsten), it will become heat, and will produce electrons out of it.

- Field emission: if we use a couple of electrodes which produce a very high electron field, for the electrons the working function is reduce, so for thermal energy it is more easy to make the electron skip from the covalent band to the conduction band, because we need less energy; this technique is very useful, because it permits to scan also insulating materials.

2.1.2 Electromagnetic lenses

In order to deflect the electron beam, we need to use lenses; these are not obviously optical lenses, because they can not deflect electrons! What we can do is use, as lenses, something which can move the electron beam:

- Magnetic lenses: using ferromagnetic material shaped in a cylindrical way, with coils inside it, the core will produce intensive magnetic fields which can deflect our particles, because of Lorentz's Force;

- Electric lenses: using couples of parallel plates connected to voltage generators, we can create an electric field which moves the charges;

- There are hybrid solutions which permit to use both electric and magnetic lenses, together.

2.1.3 Detectors and their use

After the deflection, our electron beam reaches the sample volume; there will be an interaction (or more interactions), which will product electrons or radiations; as previously done for confocal microscopes, we need to create a relation between position on the sample and characteristics in the position; because of the excitation of the electronic beam, we will have many different products for each point, so we will introduce, *for each point*, different detectors, in order to be able to catch the various outputs of the sample, detect and process, with analog and digital electronics. Out of each detector there will be a video amplifier, so an amplifier which will make our signal be treatable by a display, in order to show / store the results of our analysis.

2.1.4 Products of the electronic interactions

As we have already said, there are many products of the interaction of the electrons and the sample; we have to distinguish two kinds of electrons: backscattering electrons and secondary electrons. As *primary electrons* we will consider the electrons which realize the beam, and which are sent to the sample with very high energies, in order to obtain the interaction. The primary electron will be deflected, and, in order to obtain products, it can lose part of its energy. Once reached the sample, there are at least two possibilities:

- Primary electron hits one of the electrons of the sample, and it becomes free; primary electron will lose part of its energy, and the hit electron, from now called *secondary electron*, will go out (or try to go out) from the atom, and will be catched from one of the detectors;

- Another possibility for the primary electron is the following one: it reaches the sample, interacts with the core of the atom, but with no production of electrons or radiations: it is simply reflected, and so goes back, with the same energy of the impinging ray. These electrons are known as *backscattering electrons.*

If we put on a graph the energy of the electrons versus the number of electrons which reach this energy level, we can see that there are two peaks:

These two peaks are backscattering electrons (the one at high energy), and secondary electrons (at low energy). Energy of the secondary electrons is very lower respect to the primary/backscattering one, so we will distinguish the products in terms of energy; we can use different detectors, in order to obtain different informations on the material, distinguishing these types of electrons.

There is also possibility to produce X-ray photons: if a primary electron hits a secondary electron which is in low level, we create a vacancy; if an electron from an higher level goes to a lower level, in order to fill the octet, it will lose energy, and this will be emitted with an X-ray photon. When a low-level electron is hit, it goes out, as already said, with a low energy; in higher energy level it will probably interact with other electrons; if the electron's energy is high enough to get another electron out of its place, this electron can be catched, and it is known as *Auger electron*.

Without considering this last definition, which is the better choice, to obtain the highest resolution, in terms of electrons to study? Well, obviously, secondary electrons: they are characterized by much lower kinetic energy respect to the backscattering ones, so, due to the self-absorption effect already explained, most of the secondary electrons come from the surface of the sample: only these are easy to capture. By putting detectors near to the point where we expect to find electrons, we are sure, due to their little emission distance from surface, that comes from near, so that their information will be very important: electrons can not come from long distances, so they must bring informations useful, in terms of resolution. With backscattering electrons we have great energies, so they can come from any place, and their influence isn't useful: we cannot generate an effective function of position and energy, because they can come from everywhere!

Secondary electrons are mostly used for imaging, with high space resolution; backscattering electrons are now useless: they can be very useful in order to obtain the possibility to perform elemental composition mapping: depending on the density of the material, we will obtain electrons with higher or lower intensity, and starting from this data we will obtain this.

Each detector is composed by two sub-detectors, put with a particular symmetry:

By using these two detectors, we can do something clever: detectors are the same, but they catch electrons in a different way, *specular*; if we analyze the signal collected by the detector, we can see the change of intensity of the electrons; due to symmetry we can do something like this:

Very interesting: if we add the signals of the detectors we can appreciate better the elemental characteristic of the sample, and if we subtract the signals we can appreciate better the morphology of the surface, without knowing anything (almost anything) about the elemental composition.

Detectors for secondary electrons

In order to build detectors which can identify secondary electrons, we need to know the structure:

There are several parts: a photomultiplier, so a detector which can product a current proportional to a photon flux, an optical guide, in order to connect the photomultiplier to the last device, and the last device: the scintillator: it is a material which can catch electrons (which will are the secondary electrons, in this case), and turn they into photons; this is a system based on the photon processing, because of the following reason: we need to amplify very low signals, and it is hard to do electrically; with this system we can amplify over a million of times, and then convert into electron flux, which will be processed by electronic systems.

Depending on bias, we can choose which kinds of electrons we want:

- If we use negative bias, our detector will catch only backscattering electrons; in fact they have high kinetic energy, so they can go through the grid despite of the Coulomb interaction. Secondary electrons are repulsed, because of their low kinetic energy, so Coulomb's force becomes important;

- If we use positive bias, we can attract both backscattering and secondary electrons; backscattering electrons are not very important, because the amount of backscattering electrons which will come is almost equal to the amount of backscattering electrons which come with negative bias: kinetic energy is so high to make electrostatic energy negligible, respect to they. More important are secondary electrons: they will be very influenced by the electrostatic field, and attracted into the grid, so we will obtain a greater amount of secondary electrons respect to backscattering ones, because of their characteristic low kinetic energy.

Which is the structure of a photomultiplier? Well, something like this:

There is a bias voltage which is connected from cathode to anode; there are many resistances which are connected to plates, called **dynodes**; if we have a single photon impinging, due to its energy, it will be changed into one or more electrons; supposing that we have just one electron, it will be attracted from the first dynode, and, on it, it will give an energy higher respect to the extraction work (we are supposing that plates are in metal, so the only energy we need is the one necessary to get out an electron from the metal, without bands); depending on the energy, we will have many electrons out, and all these will go to the next dynode, will impinge into that, and get other electrons free; every time the number of electrons which go out increases, so we obtain an electron cascade, which is turned into a current by the R_L resistance. We talk about **quantum efficiency** η as a parameter which relates energy to the probability to get off electrons: if energy is too high or too small, we will have no electrons out of the metal.

Detectors for backscattering electrons

Like the other detectors, they are usually composed by several parts: there are different detectors disposed in different zones. By using a quite small distance respect to sample, we can obtain a greater angle, and so increase resolution, because we are collecting electrons from many places but all near to the impinging point.

Instead of the more complicated devices, now we are using a p-n junction, a photodiode, reversed biased: during the impinging a lot of electrons and vacancies are created, because light gives an energy which can get the electrons be promoted to the conductive band. With doping and other settings, we make the silicon have a current quite high, with just one electron hit.

2.1.5 Experimental parameters

Now we will study how we can change the characteristics of the scanning, with changing the experimental parameters. There are three fundamental parameters, which will be discussed soon.

Condenser strength and probe current

By increasing the condenser strength, we shrink the beam, making it narrower. This is interesting, because resolution becomes higher; in fact, with a narrow beam, we can observe narrower distances, so obtain electrons only from a little zone of the surface. If we increase the condenser strength, we decrease the probe current, so we obtain a good resolution, but obtain a less clear image, because only few electrons come: there will be more deflected electrons due to the increase of the field, so many electrons will not follow the beam, only few electrons will collide with the sample, and we will capture less secondary/backscattering electrons.

By increasing probe current and decreasing condenser strength, we lose resolution, but increase the clearness, the brightness of the image: we have more colliding electrons, so more data, with loss of resolution (because beam does not collide in a very narrow point).

Working distance

An important data is the focal length: with these microscopes in fact we can change the focal length of he lens; the magnetic objective lens is able to focus the beam, but we can change its bias point, obtaining different focus points; the sample must be moved, in order to be put in focus. We can vary the collection angle by changing the working distance, obtaining a different β (considering an analogy respect to the optical case); by increasing β, we increase its sine, so resolution!

We can think that the best idea is reduce the working distance, in order to increase the angle; this is not so good, because in this case we decrease the depth field, so the region which can be focused at the same time; this is very bad with 3d samples, because we cannot put in focus every zone.

Accelerating voltage

We can modulate the voltage from the cathode to the anode, so change the kinetic energy of the beam. If we increase the acceleration voltage we see a higher resolution image; we have a large amount of secondary electrons, but this is true only if our sample is conductive, like a metal, from an electrical point of view. If we are analyzing a piece of glass, or some other insulator, introducing a more powerful beam forms into the insulator a lot of localized charge, and this form an electrostatic shield for the other charges; this is known as **charge-up**. There is another side effect, related to charge-up: **edge effect**: if we have a rough region, and charge-up effect into it, we have a charge-up effect badly distributed, so near to the peaks we will have a behaviour, in plate zones another behaviour. In order to reduce charge-up effects there are at least three ways:

- Decrease electron intensity (so probe current);
- Decrease accelerating voltage; this is not so good, because if we decrease too much, we reduce the amount of electrons which will be produced by the sample, getting worse the image;
- The best idea is to cover with a conductive film the sample: if the film is very thin, we can increase conductivity and analyze the sample. This

process is good but destructive: we have to control the quality of the film during the process of growth; by metalizing the sample we change it, so it will change its characteristics; it becomes better for imaging, but not for other purposes.

2.1.6 X-ray analysis

What we can analyze from a scanning microscopy are not only electrons: after the primary beam excitation, we can observe that the decay of high level electrons caused by the formation of secondary electrons in low levels can generate photons, in the X-ray frequency range. These photons are characterized by an energy which depends on the element we are analyzing; studying the energy of the photon, so, we can identify the element. An element can have more then one only X-ray type: depending on the position of the electron we get out, we can have different levels; knowing 3 o 4 energy levels we are sure to identify the material.

There are so many peaks of excitations, in an X-ray analysis: each one is related to the presence of a particular element. There is also a noise: Bremsstrahlung radiation; it is the production of X-ray photons which depend on deceleration of primary electron beam.

There are at least two types of analysis based on X-ray; let's study they.

Energy Dispersive Spectroscopy

EDS is a spectroscopy based on this principle: when we excite some material (we are considering semiconductors), we give him energy, so we will generate electrons and vacancies; if we use a semiconductor detector, like a p-i-n junction, we can excite it with X-ray photons; photons become electrons/vacancies, so we obtain a series of charge pulses, which are converted in voltage pulses (in order to be well and easily processed), and put in an histogram:

Where I identifies the intensity of the current, of the pulse, and E the energy of the X-ray, related with λ, so with the element.

Wavelength Dispersive Spectroscopy

Another technology which can be integrated into the SEM is the WDS. It has larger resolution, in terms of energy, but has other issues.

As known from physics, every time we produce an X-ray, we can treat it as a ray of light (it is an electromagnetic radiation); what we can do is try to apply the Bragg's law, which say that:

$$n\lambda = 2d \sin \vartheta$$

What does it means? Well, given a particular λ, which is for us the wavelength of our X-ray, it is reflected with an angle ϑ, respect to the normal of the incidence point. So, given one λ, there is only one ϑ.

By introducing a diffraction crystal with λ similar to the distance of the atoms d, as Bragg's law asks, we it will reflect with the good angle just a monochromatic ray with the chosen λ, of ϑ.

Problem: this works only in one case: monochromatic signal! With polichromatic signals we have to change the detector's position (or the incidence angle) of the right position, in order to obtain reflection into the detector of the good signal; this needs many time, but products very good results!

As detector we can use a **gas proportional counter**: it is a device which has a low density atmosphere, with argon particles, and very high potential; if we impinge X-rays into the bulb they penetrate, interact with the argon and get out electron pairs, so current, which will be handled by electronic circuits; current is so proportional to the energy we give to the detector, with X-rays.

2.2 TEM : Transmission Electron Microscopes

With scanning electron microscopy we were interested in catching and studying secondary and backscattering electrons; now, we are interested in another idea: taking the electrons transmitted, from part to part of the material. If the sample is thick, at least few hundreds of nanometers, electrons can go through the material and reach the other part of the sample, becoming **transmitted**. There are two types of these electrons: the transmitted electrons, which are not deflected, and the **scattered** electrons, which are scattered due to the crystal shape.

First of all, we have to know something more about the material: we have to make the material be able to get crossed; this is done with this process:

1. We start with a mechanical abrasion process, with diamond wheels;
2. We glue to the sample a diafram, in order to select the region we want to analyze;
3. We end the abrasion process, beaming with argon ions which ablate the material.

The same process can be done also for cross section, simply by adding a plastic support which will be useful in order to keep a slice of the sample to analyze it.

2.2.1 Schematic

The schematic is quite similar to the SEM one: there is the electron gun, and a first system of deflection (in order to collimate the electron cloud in a beam); after the collimator we introduce the sample, which will be crossed with high energy (much more higher respect to SEM); after the sample we introduce the objective, and the projectors (some lenses: intermediate and last lens; this last one is similar to the optical ocular).

There are two ways to use these instruments:

- Basic configurations: brightfield, darkfield, or high resolution; these configurations are useful to magnify a sample;
- Electron diffraction configuration: this can be useful in microstructures, in order to characterize them, in terms of lattice.

The sample is on the top, and there are two ways for the electrons to propagate: some of the electrons will cross the sample, so they will interact with the crystal and go on, or be scattered by the crystal; depending on the symmetry of the crystal, they can be deflected in different ways.

The electrons with the same direction will converge in the same point, thanks to the focal plane; there are two types of points: the one generated by transmission beam, and the one generated by deflected beams. With crystals, we can observe that point are discretly separated by themselves: due to the symmetries present into the crystal, we see only deflected (and transmitted) beams in some points. In policrystals there is something similar: there is a perfect symmetry in a small region, but which is rotated, so to have many orientations of the same symmetry; this means to have circles. With amorphous elements there is no symmetry, so the projection given by the TEM gives no diffraction pattern: a continuous shadow.

There are three basic configurations for these microscopes, which will be analyzed now.

- In brightfield configuration, electrons are catched by absorption: denser material will be showed as darker regions. Now the image has only the unscattered beam, so we see all the image bright, except for the points of the pattern;

- In darkfield configuration, instead of the transmission beams we consider just the scattered beams;

2.3 Electron-Beam lithography

We can design a pattern into a mask, in order to destroy part of the material, and keep another part safe, realizing on a material the desired pattern. In order to do this thing, we must use photoresist, which can be classified in two cathegories:

- Positive photoresists: they are destroyed by light, so a part will become transparent and let light pass, destroying the material, and another part will protect part of the material, realizing the pattern;
- Negative photoresists: the idea is similar to the previous one, with a difference: now light makes the resist more resistive, and the remaining part becomes weak respect to photon beam, so will be destroyed by the beam.

Negative and positive photoresist increase or decrease the robustness, creating cross-links or scissing them, using the beam's energy.

This technique is very useful in order to obtain very precise patterns, for example in integrated circuits; in order to increase the precision, we want to increase the resolution of the instruments, so we need to decrease the wavelength: here diffraction effects are not very important, because we consider the fact that the shield (the surface where photons must collide in order to give their energy). We can shrink the wavelength or we can use *electrons*, in order to obtain very little wavelengths thanks to De Broglie relations: problem now is to have a very collimated electron beam, in order to do electron beam lithography: in this process photons are substituted by electrons, and we can confine the electrons, as already written in previous sections, to 1 nanometer of less. Depending on the material used as photoresist, we will design the desired pattern by destroying or creating the polymeric chains, obtaining the final shape.

This technique can be realized with something similar to scanning electron microscopy: we had, in SEM, to scan a rectangular area; now we must only scan a well defined pattern; what we can do is use a vectorial scanning: the domain can be confined in a rectangular area, so we can produce a well designed pattern simply by using or not using the electron brush; depending on the intensity of the beam and on the exposing time, we will obtain different behaviours.

Because we are using something similar to a raster scanning, we will have blanking times; there is something similar to a capacitor, which stops the beam to impinge the sample, during the blanking time.

There are many materials which can be used to realize resists:

Some materials can be used to realize positive resists, other to realize negative resists; we can see that PMMA is the best resist, in terms of resolution, so we can see that realize good positive resists is more easy (in terms of materials) respect to negative resists.

Like in SEM technology we can have crossings, but also scattering effects, due to the polymeric materials; we can so start with a very collimated beam, but obtain enlargements, which can be undesired; there are backscattering electrons, which are caused by the interaction with the nucleus of the material; despite the fact that beam is narrow, we can so have bad results; this issue can be mitigated with low density materials, like porous silicon. Depending on the kinetic energy used, we can reduce these effects; we can not decrease too much the energy, because if we do this, we will make electrons be absorbed by the material, reducing the scattering effects but also the clearness of the image/pattern.

An application of backscattering effect can be seen in the realization of planar waveguides for optical purposes: they must be realized by creating holes in the silicon, in order to create a path which can be crossed by light (photons).

When we are realizing these holes, we have to take account of the absorption of the material, of the backscattering effect, and of other issues: if we have backscattering, they can enlarge the holes in proximity of the other (this effect in fact is known as **proximity effect**); in order to realize precise waveguides, we have to maintain holes all equal to the others, so realize transparency or mirroring effects of the silicon respect to our light beam; by realizing a **dose modulation**, so a modulation of the intensity of the beam which takes account of the proximity effect, we can solve this issue and realize correctly our guide.

2.4 Focused Ion Beam (FIB) Microscopy

Until now we used an electron-based microscopy, so a microscopy based on using electrons as probe; now, we will introduce a system which can produce both imaging and micro/nano-machines from something different: ions. We will use a heavy element: gallium; why? Well, easy: if our element is heavy, we can use its weight to choose one from two different possibilities: the imaging one and the spatter one: we can choose the kinetic energy we want to impress to the ions, depending on the function. Imaging requires only some informations, without destroying the element, so our gallium ion must be excited with low energy (almost 5 keV); if we want to change the material, spattering it, we must use high kinetic energy (almost 50 or 100 keV).

Gallium is interesting for many reasons: it is quite stable, almost liquid at good temperatures, so easy to handle; the liquid gallium is inserted into a tungsten needle, which collimate it and ionize it; then, it is excited by the field, so goes to the sample impacting on it, and producing at least two types of particles: the well-known secondary electrons, and **secondary ions**, which can be used to see better interstices and other characteristics of the morphology, or in order to do corrosion studies (due to the relations between oxygen, revealing corrosions, and secondary ions), or something else: due to the low kinetic energy of the ions, we can evidence a lot of informations about the element composition.

We can take advantages from the channelling: depending on the incidence angle on the sample, we can obtain different pictures, different resolutions, evidencing the interstices:

By using a good angle, we can obtain more hits, so emphasize some characteristics of the morphology: with an axis parallel respect to the beam, only few of the ions will collide, so we will have less products; by using a rotation, we can see much more informations, because we are causing more collisions.

Micro machines permit to spatter material with high precision, so we can realize, with a focused ion beam, a litographic process; this is realized without masks, obtaining direct material modifications (like doping), without damaging the surface of the sample.

Capitolo 3

Scanning Probe Microscopy

3.1 Scanning Tunnel Microscopy (STM)

The basic principle which permits this technology is the well-known **tunnel effect**: with a very low distance between the probe (which will be a tip), and the sample, we will generate a current, due to the tunnel effect: if the potential barrier is very narrow, electrons can go through it instead of over it, as teaches quantum mechanics. What we can use, in order to realize a microscopy system, is the following idea: by correlating the intensity of the tunnelling current with the characteristics of the surface of the sample, we can realize an image which represents the material.

Tunnelling current comes from the atoms, but only the nearest ones produce a big current: more distance implies less current. We have to pay attention to a phenomena: if the surface of the material is too rough, the tunnelling current can came from a peak different from the one we are studying; this effect introduces misunderstandings, so risks to take wrong current contributes, or break the probe tip.

There are two ways to realize this type of microscopy:

- Constant height mode: the tip is all the times at the same height, and by measuring the current, as already said related to the distance from the tip to the sample, we can characterize the surface of the sample;
- Constant current mode: by maintaining the same current all the times less then a correction, we can use this idea: a control system connected to a piezoactuator changes the height of the tip, so, when we see that current is going to change, piezoactuator gives with a feedback signal the correction to the height, so we measure the position of the tip (and the corrections respect to the operating point).

This spectroscopy has a great drawback: in order to have tunnelling current, the sample surface has to be conductive, so this microscopes can be used only with conductive materials.

3.2 Atomic Force Microscopy

As already said, scanning tunnel microscopes have very high resolution, but a big issue: it works only with conductive materials. An alternative to tunnel effect is to use a mechanical probe as a nanotip, doesn't matter if metal, semiconductor or insulator; the effects we will consider now are atomic forces, related to the deflection of a cantilever, connected to the tip; the atomic force deflects the cantilever, so we can measure indirectly atomic forces, by measuring the deflection of the light. Depending on the intensity of the force we will have more intensive movements, from μN to nN. In case of physical contact, we will have obviously much intensive forces.

We can classify the operating modes of this system in two categories:

- Constant force mode: like constant current mode in tunnel microscopy, we maintain all the times the same force, and we change the height;
- Constant height mode: by maintaining all the times the same height, we can maintain constant the stored values of the force, sending a feedback signal to a piezotube in order to change height.

Depending on the apex angle we can collect, as information, the convolution of many contributes for many places; in order to increase resolution we want just the contributes of one point, so little apex angles are better. As drawback we have the fact that we have to take account of the fragility of a too narrow tip, and of the sample. In order to consider this, we are going to introduce another classification of the working modes of these microscopes:

- Contact mode: there is actuated a pressure of the tip on the sample, so there is contact; this means that resolution will be very high, comparable with the tunnelling microscopy (nanometers); the drawback depends on the material we have to study: we have high risks to destroy the sample or the tip: if sample is rough and fragile, we risk to damage it;
- In order to avoid risks like the previous ones, we must not have contacts; this means that we must use non-contact modes; there are atomic forces also without contact, but less intensive, so resolution will be worse; a

way to increase resolution is to make the tip oscillate with a certain frequency, in order to increase the interactions when the tip is close to the sample;

- Tapping mode: this is slightly different from the previous mode: there is no contact generally, but oscillation amplitudes can be high enough to realize contact for some short instants; oscillations have a frequency comparable with the resonance one, so we improve the previous method, increasing resolution.

3.3 Scanning Near-field optical microscopy

What we are going to introduce is a new type of optical microscopy: we have again an optical probe, which illuminates the sample, but this time **without diffraction limits**.

With standard optical microscopy we used lenses in order to focus; in the case of SNFOM we take account of the interaction with a very narrow spotlight of the sample: given an optical source, we confine the light through a cylinder, obtaining multiple reflection:

If we shrink the aperture of the cylinder, we make the light go out from a hole very smaller respect to the λ (wavelength) of the signal; out of this aperture we will have an evanescent field escaping: evanescent means that the amplitude of the field decreases very quickly by increasing the distance where we are taking it; this means that if we put a detector 1 μm far from the aperture, we will detect nothing.

We have to put in close vicinity respect to the apex the sample, in order to make our field impact against the sample; then, from the interaction with the evanescent field, we will produce a secondary field, which can be much more easily detected. In the former optical microscopy we used lenses to focus the field; now, we are using the aperture effect to shrink the collimation spot, increasing very much the resolution of the system.

Typically the cylinders are optical fibers: a core embedded in a cladding, with different reflective index, in order to have $n_{\text{core}} > n_{\text{cladding}}$.

Different morphologies give different optical responses, with few nanometers resolution.

Another possibility to use this microscopy is to realize a cantilevered optical fiber: we can actuate the optical lever, so control the local position measuring the local atomic force, measuring the secondary radiation escaping from the interactions.

There are four operating ways:

- Transmission mode imaging. The sample is illuminated through the probe, and the light passing through the sample is collected and detected.
- Reflection mode imaging. The sample is illuminated through the probe, and the light reflected from the sample surface is collected and detected.
- Collection mode imaging. The sample is illuminated with a macroscopic light source from the top or bottom, and the probe is used to collect the light from the sample surface.
- Illumination/collection mode imaging. The probe is used for both the illumination of the sample and for the collection of the reflected signal.

3.3.1 SPM Lithography

With the technology studied, we can also perform litography; we are going to show the main principles:

- About tunnelling current, we can use it to melt the sample, with the possibility to perform atom modifications, so modifications at atomic resolutions;
- With atomic forces we can scratch **intentionally** the sample, realizing several types of patterns. What we can also do is the local atomic oxidation: the tip is modified in order to be conductive, so we introduce a bias, and humidity, causing oxidation in the sample; this can be useful for example with titanium or silicon integrated circuits.
- Hybrid: we can take advantages from the AFM, with a conductive tip, and apply a bias, exposing in the nanometric size the electron source, and controlling both local distance and flux of current. By using the AFM tip we can control the current of the electrons, which are crossing the tip out to the massive structure.

  We have an effect similar to a capacitance: we maintain fixed the current which is crossing by changing the voltage between the tip and the sample surface. Depending on what we must erase, we will have different responses (less or more voltage), so obtain precise surface profiles.
- With optical microscopy we can modify the structure with the same idea previously proposed: by using a light with frequency beyond the

threshold acceptable by the atom chains, we can break them and obtain the litography.

Capitolo 4

Optical spectroscopy

4.1 Reflectance and Transmittance spectroscopy

In order to start our study, we have to introduce a fundamental apparatus, which will be analysed as a black-box: the **dispersive spectrometer**. It is a block in which we introduce a polychromatic beam (so which contains several frequencies), collimated in the same spatial region; out of the block we will have a particular photon flux, with only a certain energy, and a certain wavelength. This means that this block can impinge in a particular area of the detector, in order to separate the various intensities at the various frequencies of the signal, wavelength by wavelength.

Basically, the dispersive monochromatic spectrometers can be used as optical filters or for optical analysis: this second application can be useful in order to do material analysis! A certain bulk can be more or less complex, like a thin film: when we excite it, can happen that there are some electron jumps from the bonding to antibonding states, and during the decay the system (composed by the atoms of the bulk) can produce different photon fluxes, maybe polychromatic; depending on the composition of the material, by analysing these fluxes, it is possible to distinguish the various contributes and characterize the material.

How to realize dispersive monochromators? The basis of these devices are **gratings**: they are a series of precisely ruled lines on a clear (transmissive) or reflecting (this is the type used in monochromators) base. Depending on operative wavelength we will have several diffraction patterns, which can be designed by choosing the way to realize the gratings: glasses or other growth materials. Due to Bragg's law, depending on the parameters of the designed grating and on the wavelengths, we will have many output fluxes.

Usually we maintain fixed the position of the input and the output device, in order to focus on the grating the polychromatic beam and obtain several fluxes, one for each angle; with a slit we can collect one or more beams per time and collect successive wavelengths, measuring the intensity of each beam. This is known as Czerny-Turner configuration.

The fundamental parameter which changes the diffraction rating is the density of the grows.

By rotating we can change the angles α and β, considering fixed the source and the output, rotating just the diffraction device.

An interesting parameter is the angular spreading versus the variation of the considered wavelength: if we start from the Bragg's law, we can obtain the relationship between the density of grows and the angular spreading: if we put the beam in a more dense material, the spreading can be much higher.

It is define the **resolving power**, as the ration between wavelength and what can be detected, d:

$$R = \frac{\lambda}{\mathrm{d}\lambda}$$

Where $\mathrm{d}\lambda$ is the minimum difference in wavelengths, between two spectral lines with the same intensity.

If our spreading permits us to distinguish the two components, we can obtain the difference as proportional to the area of the pulses.

There is a drawback in the use of high density materials: we have to pay attention on the brightness of the beam. Higher angular spreading mean higher resolving power, but also less intensity!

There is also another problem: the **grating efficiency**: depending on the considered wavelength, there is a different efficiency, as we can see from this:

Plots are not flat.

What happens is something like this:

We insulate just one chromatic component, by rotating the diffraction grating, maintaining constant each other flux but maintaining in the output just one of them.

4.1.1 Detectors

Photomultiplier-based

There are some ways to realize detectors; one is based on **photomultipliers**: by introducing a photomultiplier after the monochromator, in order to obtain a current proportional to the impinging flux. There is a characteristic like this one:

$$I_T = I_0 \mathrm{e}^{-\alpha d}$$

This formula says how many electrons are absorbed; by increasing the number of photons, we increase the number of lost electrons, of absorbed electrons, because we increase α; beyond a certain energy, all the electrons will be absorbed, preventing the possibility of photogeneration.

p-n junctions

The equation which model the p-n junction is the Shockley equation: if we apply a bias, we polarize the system, so obtain the well known exponential characteristic.

What happens if we impinge with a photon flux this system? Well, during the impinging process we create a lot of electrons and vacancies (if photon energy is high enough to promote electrons to the conductive band, so greater or equal to the energy gap).

What we can modulate is the saturation current: by measuring the current due to the photons we can obtain a parameter which says how many photons are colliding.

There are some configurations: the photovoltaic one, the short circuit configuration, or the reverse bias. We have to stay alert when we talk about voltages, because the characteristic, respect to voltage, is logarithmic, so studying as output a voltage value which static characteristic is logarithmic is critical, because we can not appreciate little variations. With short circuit we measure directly the photon current. With reverse bias configuration we put an external power supply which polarizes negatively the diode, in order to have more dark or light. With negative bias we can increase the depletion layers, decreasing the capacitance, so the response time of the diode.

In order to quantify the efficiency of these systems we have to take account also of the **quantum efficiency**: depending on the material we can have different possibilities to make, given a colliding photon, a creation of an electron-vacancy pair. The parameter which quantify this probability is the quantum efficiency.

Charge Coupled Device (CCD)

Last type of converter is this one: given for example a p-doped semiconductor, an insulator and a metal, we can realize a **metal-oxide-semiconductor** junction. Now: if we put positive potential, we can concentrate electrons at the close interface between semiconductor and insulator, in order to photogenerate charges. With null potential, photogenerated charge is collected at the same contact; what is possible to see is the movement of the charges, from one to another region.

So: we photogenerate charges in a particular region, and we move them. This device is useful in order to detect photon fluxes, and handle them.

In order to understand the working principle of this device can be useful to know its band diagram: at the thermodynamic equilibrium we know that E_F, the Fermi level, is constant; without pias so there is a boundary: local traps collect some of the negative charges; if we introduce a positive bias we increase the boundary, until we obtain the **inversion** status: a region with n-doped behaviour, close to the interface with the insulator. How can this be useful in order to detect photon fluxes? Well, we generate new charges when photons reach the semiconductor, accumulating charge close to a particular cell; if we put our photon flux which comes from a particular area, illuminating it, we can detect both presence and amount, intensity of the flux. What we can do is to put an opaque shield, in order to prevent a successive photon flux, synchronizing the movements; with something like a shift register we can move synchronously the charges from left to right, measuring the charge, building a map: we start selecting the chromatic component, so measuring with a photomultiplier or with a photodiode, introducing several cells which can detect different photon fluxes.

4.2 Interferometric Spectrometers

We will only introduce this type of spectrometry, and study it well another time. The idea is: we produce a beam, which goes to a mirror: one part is deflected, another reflected, by the beam splitter in E; by moving F we can change the optical path, changing the interference pattern; we collect light, split it into two branches, and modulate the optical path for the beams; finally, we collect the intensities to D: constructing and destructing interference.

4.2.1 Reflectance and Transmittance spectroscopy

What we can do is to use as a filter the monochromator, in order to make light impinge orthogonally in it, obtaining both transmitted and reflected light (transmitted can be computer as the complementary of the reflected).

Raman spectroscopy

We have to remember what phonons do: photons carry energy in discrete amounts; we can describe the band diagram in the same ways of the electrons, but using as y-axis the frequency of oscillation of the atom instead of the energy. If now energy is equal to the energy of the vibrations, phonons will be absorbed, put in oscillation the atom, in many types of oscillations:

What we can do is study energy by studying the energy of the photons absorbed by the material, so depending on the absorption reaction we can understand and study the characteristics of the material.

Capitolo 5

Characterization techniques

Now, we are going to expose some of the most important characterization techniques, for materials.

In order to classify them, we can introduce two groups, two classifications:

- Characterizations devoted to the surface of the materials;
- Characterizations devoted to the body of the materials.

The other characterization is the following one:

- Characterizations devoted to the study of the elemental composition;
- Characterizations devoted to the study of the structural composition.

5.1 Auger Electron Spectroscopy

Auger spectroscopy is a spectroscopy devoted to the investigation of the elemental composition of the surface of the material. A few words: it is important to distinguish, to separate surface and bulk, because the different reactions, interactions between the material and other elements is hidden into the surface of the material. As surface we will intend from 10 to 30 amstrong.

In the surface of the atoms there are few atomic layers: we must be able to separate the informations of the top of the material to the ones in the bottom.

Electrons and ions are very useful in the surface: they have a lot of collisions, so they use their energy quickly; AES is interested in the study of a particular class of electrons produced near to the surface of the material; let's remark that, less than the backscattering electrons, each electron has few energy, so only the electrons near to the surface can go out (and reach the detector); other electrons are useless: they have collisions with other atoms or other electrons, losing their energy, their *memory* (as *memory* we mean the energy, because their energy is very important in order to characterize the material).

In AES we send electrons to the surface of the material, in order to excite it, collecting then other electrons. We have an electron beam, focused into a point, composed by **primary electrons**; primary electrons will interact with the electrons of the surface, obtaining Auger electrons; we collect them, and analyse their energy spectrum, obtaining informations about the composition of the surface.

What happens, in details? Primary electron collision produces a secondary electron; a rearrangement of the atom will produce Auger electrons, and this will be detected: when we have the vacancy, an electron from higher levels will fill the hole; this process releases some energy, which can be emitter with an X-ray photon, or with an electron, in order to make it go out of the material: this is the Auger electron.

A remark: the energy of the Auger electron depends on the filling process, but **not** on the primary electron energy: if we change the energy of the electron beam, we do not change the energy of the Auger electrons out. Let's remember that X-ray and Auger electron emissions are **competitive** processes: we can have one or the other one, but not both, with different probabilities.

The experts of the spectrometries (and of the characterization of materials) use a particular convention for indexing the names of the different energy levels: instead of the well-known s, sp, p... , we have K, L_1, L_2, L_3, M_1, and so on: they are a different convention which is normally used to talk about states. The effect previously explained is known as **Auger effect**, and it is written with the names of the three energy levels included in the process: the first one is the place where we create the vacancy, the hole; the second one is the donor level, which gives an electron to fill the vacancy; the third one is the level which donates the Auger electron.

An Auger electron can be emitted also from valence band, so we can identify this level with V: these electrons are not useful for our actual purposes, because in this case Auger comes not from a single atom, but from each atom in the valence band.

This technique is more sensitive with lighter elements: depending on the atomic number of the element we will have different responses, obtaining more X-rays or more Auger electrons:

The release process can be modelized with quantum mechanics applied to Coloumb's interaction; this, obviously, does not work with photon production!

Only very thin materials can generate Auger electrons, because in wider materials we have more collisions, so electrons will scatter, losing their energy.

5.1.1 Equipment

The equipment needed to perform this spectroscopy is an electron gun, an electron energy analyzer, and a data acquisition system.

What we have to do is to filter electrons emitted by the surface, in order to collect only the Auger ones and count them; we can use the following idea:

The inner cylinder has a potential positive respect to the outer one: by changing the voltage we can change the electrons we want to take, depending on their energy! The output electron flux will go into an electron multiplier (very similar to a photomultiplier), so the output signal will be proportional to the number of electrons with this energy. Obviously, this technique must be applied in ultra-vacuum chambers, so it is expensive.

The main problem is the following one: we have also secondary electrons, which are more than the others, and, due to the scattering effects, have random energies out of the atom; what we can do is introducing the derivative mode of the device, obtaining something similar to the derivative of the spectrum, so of the derivative of the number of electrons collected as function of energy. We have to add a small alternate voltage to the energy, like:

$$E = E(v) = V_{DC} + V_0 \sin \omega t$$

By applying the derivative operator, we can only see the dynamic contribute, because V_{DC} is constant, static:

$$I_{lock-in} \propto \frac{\mathrm{d}}{\mathrm{d}E} I$$

Where I is the energy spectrum, and $I_{lock-in}$ is the product of a lock amplifier, which can take only the variable part of the signal.

In the device we must add a little change: when we get the values of the minimum, there is a little difference: maximums and minimums are close to the point we expect, but slightly shifted.

A final information: we know how to analyse thin films, thin materials; and if we want to analyse not the surface, but the bulk? Well, the only way is to sputter the material, destroying it, until reaching the desired zone, and then applying what was previously said.

5.2 Xray Photoemission Spectroscopy (XPS)

Also this is a surface elemental composition characterization, like the previous one; like previously done, we collect electrons; just one difference: now, instead of electrons, in order to excite the material we use **photons**. They have some advantages: they can penetrate deeper, without having the scattering problems of the electron beams. The great advantage is the fact that X-ray photons (we usually have as frequencies the X-ray or the UV ones) can irradiate greater volumes, and excite them all together.

The physical basis of this technique is the **photoelectric effect**: by irradiating material with photons with high energy, they will ionize atoms, and energy can be used to produce electrons; we will so collect these electrons, that we will call **photoelectrons**, and analyze them. This technique has advantages, like a better lateral resolution, making it more suitable in order to realize maps of the surface. Photoelectric effect can be explained with the following steps:

- Excitation: a photon is absorbed by the material, generating something similar to what was previously done for Auger electrons: they come out of the material. The analogy is not total: the energy E of the electron will be:

  $$E = \hbar\omega - E_B$$

  Where E_B is the unknown. This mean that the final energy of the electron depends on the energy the the photons, due to the De Broglie relations between waves and particles; in Auger spectroscopy we had nothing like this: previously the energy of the beam was not important at all, now it is very important. E_B permits to characterize the atom: it is the bonding energy, so the energy needed to break the bond, and determining it we can determine the elemental composition of the atom; UV photons can excite electrons from valence band, so they are not useful for our actual purposes.

- Propagation: the electron is not instantly out of the solid, because it must go through it, crossing it. We can have two kinds of scattering effects: electrons-photons interactions, and electrons-phonons interactions; these effects are bad, because they change the energy of the electron (E), making the previous relation not true, making us lose informations about E_B. The probability of going out of the material depends on the mean free path of it: this depends on electron energy and on the direction of the motion respect to the crystal oscillation.

- Emission: after the propagation we have the emission step, so the step in which electron goes out of the material. There are conservation rules, about the parallel component of the electron wave-vector.

5.2.1 XPS equipment

Fundamental is a light source, so an X-ray tube or a synchrotron; an electron detector, which can be different respect to the previous one: now we have more spatial resolution, so it is possible to use hemispherical analysers, in order to take account also of the direction of emission of the electron; like usually, we need to perform ultra-vacuum conditions, in order to prevent contamination effects.

It is very important to have X-ray sources with narrow bandwidth, in order to have precise wavelengths, so precise energies; this can be critical. With X-ray tubes we have a bombardment on an anode with electrons; it produces a too large bandwidth, but we can use a filter which gives, by diffraction, like with a crystal, the quasi-monochromatic beam.

Like before, we need to acquire electrons, after a filtering process; when we collect electrons which come from the surface, the final kinetic energy of electrons depends on the beam energy, so on photon energy, and on material's working function. What we obtain is something like this:

Each position of each peak is related to an element; in order to take account of the different sensitivities, at different energies, we consider $N(E)/E$.

We can also get Auger lines: in fact it is possible to have an Auger process if we excite a core level.

The final observation regards a particular phenomena: the **chemical shift**. The chemical shift is the fact that the same element can have different peak positions; this happens because atoms can be bonded with different other atoms, so we will have small modifications of the bounding energies, obtaining this effect.

5.3 Secondary Ion Mass spectroscopy (SIMS)

This is the last spectroscopy which is suited for the elemental analysis of the surface of our sample; obviously, like the previous ones, it can work also on bulk, by removing (with sputtering processes) many layers of the sample, in order to reach quickly the bulk.

Now, we have an **ion beam**. There are two ways to use this spectroscopy:

- Static mode: we want to analyze just the surface;

- Dynamic mode: we want to analyze the composition.

We will come back soon; some machines are able to do both the analysis together. Let's remember that this technique is destructive!

How does it work? Well, given our device, we impinge on it a flux of ions, called **primary ions**; out of the sample we will have many products: atoms, electrons, **secondary ions**: we are interested in the last ones. Once detected a certain number of ions, we will study the mass spectrum of the secondary ions, in order to characterize the material, so we will plot a $N(m)$ graph, where N is the number of particles detected with mass m.

5.3.1 Sputtering process

The interaction between primary ions and surface removes some material from the surface; we have so a transfer of kinetic energy, with cascade effect: the primary ion accelerated give energy to some of the atoms in the surface, which will be accelerated, collide with other atoms, obtaining a cascade effect.

Let's remark that we are able to detect just charged atoms, so **ions**: primary ions energy must exceed the bonding energy, in order to destroy the bond and let some particle go out from the surface of the sample. There are many modes for these techniques:

- Use an energy E less than 1 keV : this can be useful in order to remove a single atom from the surface: we use a little energy and we have few products.
- Use an energy E in this range:

  $$1\text{keV} < E < 1\text{MeV}$$

  With this, energy can be so high to give enough energy to make interactions with also other atoms, obtaining more than 1 atom emitted;
- With $E >$ 1MeV, we can have strong damages, because we have very high energy; this can be useful in order to have sputtering processes.

Like for each other techniques, there are some parameters which can be useful in order to study the quality of the characterization: let's define the sputtering yield Y as:

$$Y \triangleq \frac{\text{number of particles extracted}}{\text{number of impinging ions}}$$

So, we can define the primary ion current density:

$$J_{PI} = ev$$

Where v is the ion flux density.

Given the surface density $n(t)$ at the time t, considering the starting value n_0 (before the sputtering process), we can say that the coverage of the adsorbate layer is:

$$\vartheta(t) = \frac{n(t)}{n_0}$$

Due to sputtering, some atoms will be removed, so we can say that $n_0 \geq n(t)$. The number of ions colliding in a single time are:

$$\mathrm{d}N_{\text{ions}} = vA\mathrm{d}t$$

So, we can quantify how many atoms are removed from the collision area A:

$$\mathrm{d}N = -\vartheta(t)Y\mathrm{d}N_{\text{ions}} = -\frac{n(t)}{n_0}YvA\mathrm{d}t =$$
$$= \frac{N(t)Yv}{n_0}\mathrm{d}t$$

By solving this differential equation, we can obtain that the number of atoms removed from the surface is:

$$N(t) = N_0 \exp\left(-\frac{Yv}{n_0}t\right)$$

So, we have an initial value, and an exponential decrease. We can define a τ parameter, which gives an indication about the characteristics of the technique applied:

- if $\tau \sim 9$ hours, we have a static characterization;
- if $\tau \sim 3$ seconds, we have something quicker, dynamic.

Another important parameter is: how much of the particles sputtered are ionized: the ionization degree α. We can say that:

$$Y\alpha = \frac{N(\text{secondary ions})}{N(primaryions)}$$

These parameters are empirically evaluated, because the maths are quite complicated.

5.3.2 Equipment

The core of the system is the **ion source**: it is more complicated respect to the more simple electron source. After that we need a mass filter, which use magnetic and electric fields in order to separate different elements with different masses, so an electrostatic mirror reflects the filtered particle until it reaches the detector which is an electron multiplier, and so on.

Mass spectroscopy is based on the use of four rods, which make ions to pass: they are disposed on a direction parallel respect to the motion one, and they are biased using the superposition of a static and a dynamic voltage. Ions with different masses have different inertias, so different accelerations; by changing the dynamic potential, we can choose which mass we want to catch and analyze.

Given the following bias equations:

$$V(t) = U_0 + V_0 \cos \omega t$$

Where $\omega \sim 1$ Mrad/s, we must know and remember that:

$$\frac{U_0}{V_0} = 6$$

If this condition is satisfied, we have, out of the spectrometer, just one mass value. We can change one of the two values, but we **must** change also the other, in order to maintain the ratio constant to 6.

There are two situations:

- If we have high mass, it will follow the x-axis force, but not the y-axis one: from the x point of view we will se the contribute of the mass, from the y point of view just some oscillation, because this mass can be caught by the constant contribute of the bias point;
- If we have low masses, we have the opposite effect: a contribute on y-axis, and some oscillation in x-axis, for the same previous reason.

If spectrum is static, it remains the same; dynamic spectrum changes with the time.

There is a **detector limit**, so a minimum number of atoms we are able to detect. It depends on the mode we are using:

- Dynamic mode: we need higher current density, because dynamic mode has less resolution, so by increasing the current we increase the primary ions number, increasing resolution.
- Static mode: does not need to increase resolution, because it is already very good.

5.4 Rutherford BackScattering and Elastic Recoil Detection Analysis

These two techniques are suited for the analysis of the elemental composition, but this time mainly in the bulk, not in the surface. Knowing which elements are inside the material can be very useful, for many reasons.

Now the main word will be **scattering**: by impinging light ions with the Coloumb's field, we will not sputter the material, but penetrate into it, and, after a reflection which happens inside the material, re-catch the ions, backscattered, and study their changes. Now, as already said, we are using **light** ions, because we need to have few interactions with the sample; another difference respect to the previous idea is what we want to measure: now, we will plot an **energy spectrum** graph.

The physical process is known as Rutherford scattering: our impinging beam, known as **projectile**, goes into the atom, until it reaches a particular atom of the crystal lattice, which is called **target**, so it will scattered; there is a very low energy transfer from the projectile to the lattice, due to the difference of the masses between the two elements; we are considering the fact that energy transfer is just caused, in this type of analysis, by the scattering process.

There are two types of scattering:

- Elastic scattering: the total energy of the system is conserved: after the scattering, the target moves (a little) with the energy which is given by the primary flux, but there is no emission of anything;
- Inelastic scattering: part of the energy is transferred and emitted in some way, with photons for example.

We will consider just **elastic cases**. Given b the **impact parameter**, so the distance from the moving curve and the atom level, and d the distance of closest approach, we can say that:

$$d = \frac{Z^p Z^t e^2}{4\pi\epsilon_0 E_1^p}$$

Usually, most of the collisions are elastic, and can be modelized with the previous equation. With elastic scattering we have something like this:

θ is the scattering angle, ϕ is the recoil angle: scattering happens due to the change of movement of the impact with the atom, the recoil for the same reason.

We can use the conservation law, considering the fact that kinetic energy and momentum remains the same; by using the basic physic laws, we can evaluate the θ angle, so put a detector in the right point, in order to catch the backscattering ions and studying its mass. There is a very useful formula which says that:

$$K(m_p, m_t, \theta) = \frac{E_{p2}}{E_{p1}} = \sqrt{\frac{\sqrt{m_t^2 - m_p^2 \sin^2(\theta)} + m_p \cos(\theta)}{m_p + m_t}}$$

By knowing the energy change of the ion from the primary one to the backscattering one, we can evaluate the mass of the target, identifying its characteristics! Depending on the mass of the target, in fact, the primary ion flux will give it a different energy.

Another important parameter is the differential scattering cross-section, σ:

$$\sigma = \frac{1}{\phi}\frac{\mathrm{d}N}{\mathrm{d}\Omega} = \frac{\text{number of scattered particles}}{\text{(particle flux)(differential of solid angle)}}$$

Remember that all this theory works, with an important hypothesis: that the target receives an energy too low to have motions; the error, respect to this approximation, is:

$$\varepsilon_{\text{approximation}} \sim 2\left(\frac{m_p}{m_t}\right)^2$$

5.4.1 Channelling

Depending on which path we are using, ions well go deep toward the core or remain close to the surface; if we change the impinging angle of the projectile respect to the surface, we change the quantity of useful signal which is backscattered out of the sample.

This idea can be very useful in order to analyze the epitexiality of the material: if the material is epitaxial rays can go deep, with the right angle; if material is non-epitaxial, rays will stop at the interface, and there is no way to choose an angle to make they go deeper.

5.4.2 Elastic recoil detection

The RBS technique has an issue: it is very insensitive respect to light ions: we are using light ions as probe, so they will hardly be useful in order to catch other informations. What we can do now is similar to SIMS: if we use again a projectile, but with greater mass respect to the target, we will remove part of the target, so by catching the product and analyzing it we will produce a plot of the energy spectrum of the target. For example, in order to analyze deuterium (which is an isotope of hydrogen), we can use helium, which is heavier respect to deuterium. Let's remark that ERDA can damage seriously the material, and that, respect to the previous idea, requests an ion source more accelerated, in order to obtain higher kinetic energy.

We need a filter which selects in RBS the projectile, and in ERDA the product, excluding the backscattered projectile.

This is an example of ERDA spectrum:

With constant energy we will have out of the material projectiles with different energies, depending on the material we are analyzing.

5.5 X-ray diffraction

Now we will introduce another diffractive technique, based on the diffraction of particles or photons inside of the material.

5.5.1 Introduction

If we have a crystal irradiated by a monochromatic radiation, we have as result the absorption process of the X-ray photons, so emission; we are going to use an important approximation: we consider that we have emission of the same wavelength, so the **kinematic approximation**. Radiation is produced by spherical waves, so by waves which have spherical wave fronts. When these waves interfere at long distances, respect to the distance from emission samplers, we have an interference effect between emitted radiation and atomic radiations.

So: we impinge the radiation, which is diffracted by the atoms of the crystal; by catching with a detector the diffracted signal/particle flux we can do analysis.

5.5.2 X-ray absorption and diffraction

When we impinge with the photon beam the sample, it reacts, relaxing its atoms; our supposition, as already written, is the **kinematic approximation**, so the fact that the wavelength of the signal which has been impinged and the diffracted one, the one re-emitted by one of the atoms of the lattice, is conserved. We want to create interference effects between the spherical waves of the X-ray diffraction, at long distance; long distance means that we can approximate the spherical waves with plane waves, more easy to study and with more useful properties; we need to impinge X-rays because we need to generate a diffraction pattern, and this is possible only if the wavelength of the signal is comparable to the inter-atomic distance.

In order to be sure to have **constructive interference**, we can study a fundamental conditions which guarantees the presence of this type of phenomena: the **Laue condition**. Considering the reciprocal lattice instead of the direct one, given $\vec{k}$ the incidence vector in the sample, and $\vec{k'}$ the scattered vector, if $\vec{G}$, the vector defined as difference of the previous two, is a vector of the reciprocal lattice, we can guarantee that there is constructive interference. We can see this rule by showing this plot:

Given the two vectors of the reciprocal lattice, if their difference is a vector which passes through particles of the lattice, Laue condition guarantees what we want.

There is a dual condition, applied to the direct lattice: the **Bragg condition**. Given the direct lattice, we can apply something similar to the Bragg's law: the fact that $\vartheta_{inc} = \vartheta refl$ guarantees that interference is constructive. The condition, given by Bragg's law, is:

$$2d \sin \vartheta = n\lambda$$

Where α is the angle of the X-ray impinging radiation respect to the surface plane of the sample, and ϑ the angle of incidence of X-rays respect to the crystal plane (which **can be different** to the surface plane of the sample). Bragg's law says us also another thing: we know the ϑ angle, so we now where we must locate the detector, in order to get the maximum intensity of re-emitted X-rays!

There exists a notation which permits to determine, in some type of crystal, the crystal plane: the **Miller index** notation.

There are many types of lattices, of crystal types:

- monocrystalline : the whole material is a single crystal (although some defects will always be present);
- polycrystalline: the material contains crystal grains of micrometric dimensions, that can differ for the crystal type and/or for the orientation respect to the surface;
- micro/nanocrystalline: the material contains crystal grains of dimensions ranging from the nanoscale to the microscale, often immersed in an amorphous matrix;
- amorphous: the material does not show a long range order.

All our theory is based on the absorption of X-rays in the crystal: absorption depends on how many atoms are in the lattice, so on the atomic density; this parameter will put conditions on the μ parameter of the following law:

$$I(x) = I_0 \exp(-\mu x)$$

Where μ is the absorption coefficient. It has a strongly dependence on the atomic number of the material, Z.

5.5.3 Equipment

There are not many things to write about the equipment: we need an X-ray emission tube, so an X-ray source, a monochromator, which produces a more pure beam, and an X-ray detector, which can catch the re-emitted X-rays in order to study and analyse they. We have a configuration similar to the following one:

The detector is moving, in order to have all the times an angle equal to the double of the impinging one respect to the crystal plane.

5.5.4 Configurations

There are two configurations for this technique:

- Bragg-Brentano (BB) configuration: we keep incidence and detection angle equal **all the times**; this technique is useful in a particular (but important) case: when crystal planes are parallel to the surface; if the crystal plane is not parallel to the surface, BB does not work;

- Thin-film configuration (TF): if we use a very low incidence angle respect to the surface, ϑ will be greater than α all the times; now we can not detect peaks related to crystal planes parallel to the surface of the sample, but we can detect all the other planes! The *thin-film* name derives from the main use of this configuration: the study of polycrystalline thin films.

5.5.5 XRD spectra

The spectrum represents the intensity of the X-ray radiation detected as a function of the detection angle; by studying the crystal plane we can determine the ϑ angle of the Bragg's rule, which is a good reference.

This technique is useful in order to determine structural characteristics: diffraction is useful because the scattering process depends on the lattice of the crystal, so from the analysis of the diffraction pattern we can determine the shape of the sample. The width of the diffraction peaks can be related to the average size of the crystals: if crystals are big, peaks are sharp. The diffraction pattern can contain informations about the crystallinity of the material so the portion of crystals versus the amorphous zones.

The combination of BB and TF configurations can be useful, for example, for distinguish epitaxial and non-epitaxial configurations: epitaxial configuration has a highest signal in BB configuration, and lowest in TF; for non-epitaxial films, we have the opposite result, because from non-epitaxial films we get more informations from the film than from the substract.

5.6 LEED/RHEED

Low Energy Electron Diffraction (LEED) and Reflection High Energy Electron Diffraction (RHEED) are techniques used for the structural analysis of the surface of a material. The probe used for these types of analysis are electrons, instead of X-rays photons. We will study again elastic scattering, but now of **electrons**.

This technique can be useful in order to analyse materials with freshly prepared thin films (like epitaxial ones), or the analysis of the growth process in certain deposition techniques. These techniques are **not** suited for elemental analysis: we obtain information on the way atoms are disposed on the surface, not on their identity!

Like before, we study interference patterns, which are generated not by X-ray diffraction, but by electron scattering! Considering that one electron impinge with a vector $\vec{k}$, it is scattered by a vector $\vec{k}'$, maintaining its kinetic energy; it is quite similar to the XRS, but with some differences: now we must separate the contribution of normal and parallel components, respect to the surface of the sample. In order to define something similar to the previous Laue's condition, we introduce the idea of **surface unit cell**:

It is defined by the previous plot, identifying a base of two vectors which close the surface unit. As said, there is something similar to the Laue's condition, but now it must be applied not on the entire wave vector like we've done before, but only on the **projection** on the surface of the wave vectors:

If the two projections of the vectors are joined by a vector which lies on the plane, we can guarantee that interference is constructive, and will provide some useful informations.

Ideally, we want to study just the surface, so just the first atomic layer; this is possible only in an ideal world and in an ideal surface: we will see also contributes of some secondary layers, obtaining some distorsions respect to the ideal reciprocal lattice image.

Let's analyse more in details LEED and RHEED.

5.6.1 LEED

In LEED, given the sample and the electron beam, impinging with a direction normal respect to the surface plane, we will acquire the signal given by the elastic scattering in the surface; inelastically scattered electrons can be simply filtered: inelastical scattering introduces a loss of energy, so by filtering with some electromagnetic lens we can choose only the **good** ones: the ones which are scattered without losing energy.

There are some issues: surfaces are not ideal, so they can provide, as already written, different lattices from the ideal reciprocal one; re-construct the direct lattice so can be difficult. Kinematic approximation is no longer valid: a strong interaction can cause multiple scattering events, changing so the wavelengths in game.

5.6.2 RHEED

In this case we send electrons with an angle very low respect to the surface, but with high energy; high energy electrons can penetrate deeper in the material, but surface sensitivity is obtained due to the low angle of incidence. By putting a detecting screen we can catch the products of the interaction with the surface, in order to perform the characterization process.

Energy is higher, so, if we want (like done with XRS) to analyse the characteristics of the technique with the Ewald's sphere, due to high energies, we will have a very great radius, respect to the spacing rows of the reciprocal lattice.

Obviously, the intensity of the output depends on the surface coverage, and on the flatness of the surface: if a surface is flat, so if it has'nt many 3d features, signal will be high, because there is less constructive interference.

5.6.3 Equipment

The goal of this technique is to collect elastically scattered electrons and reject inelastically scattered electrons; we must use something similar to the XFS equipment, using electron probes and detectors instead of X-rays; as said, we need also some filter: the **selecting grid**. They can be retarding grids, which filter inelastically scattered electrons, and accelerating grids, which increase the energy of the electrons which are not filtered, exciting in a better way the fluorescence in the screen.

This equipment is useful in both LEED and RHEED; there are some little differences: RHEED uses more powerful electron guns in order to give more energy to the electrons; we must use electromagnetic accelerators in order to accelerate electrons. Grids are not useful, because elastically and inelastically scattered electrons have a great difference.

5.7 EXAFS/SEXAFS

These last techniques are useful to analyse the structure **without diffraction**: this is great, because they can work also in materials where does not exist a diffraction pattern related to the structure, so amorphous materials!

In order to perform these techniques, we need a wide emission range, of X-rays: a synchrotron (which is not easy to have).

5.7.1 EXAFS

Previously we studied interference effects caused by diffraction effects in the crystal; now we are interested in some other phenomena: the reactions to the absorption of X-rays. When a material absorbs an X-ray, which as enough energy (so a quite high frequency), the atom will produce an electron, called **photoelectron** (because its emission is caused by the excitation of the photon)

What EXAFS measures is the ratio of the intensity of the material's radiation respect to the emitted one; depending on how many photoelectrons we will measure, we will know how many photons are absorbed, so the characteristics of the material.

The peaks of the figure are the absorption edges of the photons.

As known from quantum mechanics, an electron can be characterized by knowing its wave function; the presence of neighbour atoms respect to the interacting one changes the wave function of the electron, so its behaviour; considering averages, we can say that the energy of the electron, E, is equal to:

$$E = h\nu - E_{bond}$$

Where E_{bond} is the energy which must be provided in order to get out the electron from the atom. If the energy of the electron is low, the interference effects will be higher, on its wave function. With low energy electrons, the neighbours effects will become great, and they will act as scattering centers. There are two possibilities for our photoelectron:

- being scattered;
- being unscattered.

Can so be defined a transition probability, starting from the final and initial state representation of the electron, as superposition of the scattered and unscattered electron wave functions (the wave functions which take or take not account of the scattering event). The oscillatory behaviour depends to these backscattering events, caused by the neighbours of the ionized atom.

Absorption coefficient is a function of the transition probability; this is obvious: to an absorption event corresponds a photoelectron emission; if the electron is not emitted, we can say that we will not observe an absorption event. So:

1. We send photons to an atom; photon energy will change the energy of the photoelectron;
2. Depending on the photoelectron energy we will have more probable backscattering effects, with the neighbour atoms;
3. Depending on the scattering processes, we will have changes of the energy of the photoelectron, so of its equivalent wavelength;
4. Depending on the wavelength, there will be a different transition probability;
5. Depending on the transition probability the photoelectron can be or can not be emitted, so the absorption coefficient increase or not inrease.

Absorption coefficient is usually expressed as:

$$\mu = \mu_{0K}\left(1 + \chi(k)\right) + \mu_0$$

χ provides the oscillatory component of the absorption spectrum, which provides many informations on the structure of the material, of the sample. Considering a single-scattering event approximation, we can approximate $\chi(k)$ as:

$$\chi(k) \sim \sum_i A_i \sin\left[2kR_i + \rho_i(j)\right]$$

Where R_i is the distance from the ionized atom, A_i is proportional to the backscattering amplitude and ρ_i takes account of the absorbing and backscattering potentials on the wave function.

What we do in order to carry on the analysis/measure, is:

- Measure the initial intensity I_0 of the X-ray beam;
- Measure the intensity I_T transmitted through the sample;
- Invert the exponential law and estimate μ; given the sample distance d:

$$\mu = \frac{1}{d} \ln \left(\frac{I_0}{I_T} \right)$$

5.7.2 SEXAFS

The previous analysis can be done in order to collect informations from the bulk of the material; it involved in fact the level K, and some higher energy levels. SEXAFS uses again X-rays, but only in order to obtain surface contributes!

The basis phenomena we will use in order to perform this analysis is the Auger process: Auger electrons can be emitted not onlt due to absorbed electrons, but also to absorbed photons! Absorption of X-ray photons can cause a relaxation of the electrons, so Auger electrons can be emitted; by catching and counting the Auger electrons we can determine the probability of the absorption of photons!

Like in the previous technique, our goal is to plot a graph which relates wavelength of the X-ray sent and number of absorbed radiations; what we can do is so select just an energy of Auger electrons, treating only it, filtering all the others.

5.7.3 Equipment / spectra

Just a few words about the equipment which must be used in this characterization process: in order to perform the analysis we need a synchrotron as probe, and a way to measure the intensity before and after the absorption process; by studing the position and the intensity of the peaks (in wavelengths) we can determine the structure of the atom.

An example of the spectrum of this characterization is the following one:

Each peak provides informations about the distance of the neighbour atoms: depending on the wavelengths of the peaks, we will understand where atoms are respect to the main one (ionized).