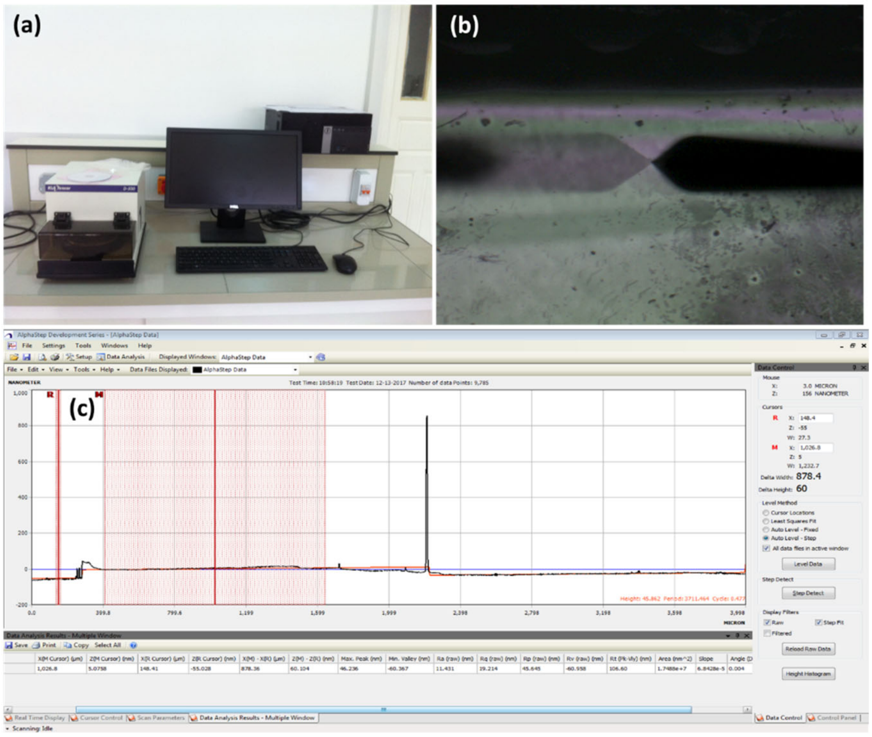
Chapter 3: Characterization methods of nanomaterials

There are many methods of characterization of nanomaterials to study the different properties, such as: X-ray diffraction for the structural properties, atomic force microscopy (AFM) and Field emission scanning electron microscopy (FESEM) for the morphological properties and UV-Visible and photoluminescence (PL) for the optical and electronic properties. The mechanical profilometer can be used for thickness measurements of thin films (2D).

I.1.1.1 Thickness measurement by Profilometer

The thickness measurements could be carried out using Stylus Profilometer (model: D 500) **(Figure 1.a)**. To perform the measurements, the sample is placed on a specimen holder and a stylus (diamond tip) is brought into contact with the sample surface **(Figure 1.b)**. After having determine the step between the substrate surface (the area where there is no deposit) and the deposit surface, we set a distance to be traveled by the stylus between the two surfaces, the scanning time (speed) and the stylus pressing force, the vertical displacement of the stylus is recorded as a function of its position on the sample **(Figure 1.c)**. Generally, to make thickness measurements by profilometer, the creation of a physical walk is mandatory. There are several methods to achieve this walk such as chemical attack. In our case, to create the step, we hid part of the substrate during the deposition of the thin layers.



Test Time: 10:58:19 Test Date: 12-13-2017 Number of data Points: 9,785

Height: 45.862 Period: 3711.464 Cycle: 0.477

X(M Cursor) (µm)	Z(M Cursor) (nm)	X(R Cursor) (µm)	Z(R Cursor) (nm)	X(M) - X(R) (µm)	Z(M) - Z(R) (nm)	Max. Peak (nm)	Min. Valley (nm)	Ra (raw) (nm)	Rq (raw) (nm)	Rp (raw) (nm)	Rv (raw) (nm)	Rt (Pk-Vly) (nm)	Area (nm^2)	Slope	Angle (D
1,026.8	5.0758	148.41	-55.028	878.36	60.104	46.236	-60.367	11.431	19.214	45.645	-60.958	106.60	1.7488e+7	6.8428e-5	0.004

Scanning: Idle

Mouse
X: 3.0 MICRON
Z: 156 NANOMETER

Cursors
R X: 148.4
Z: -55
W: 27.3
M X: 1,026.8
Z: 5
W: 1,232.7
Delta Width: 878.4
Delta Height: 60

Level Method
○ Cursor Locations
○ Least Squares Fit
○ Auto Level - Fixed
● Auto Level - Step
☑ All data files in active window

Step Detect

Display Filters
☑ Raw ☑ Step Fit
☐ Filtered

Figure 1. Thickness measurement; (a) Stylus Profilometer (model: D 500) (b) Contact of the stylus (diamond tip) on the sample surface and (c) Vertical displacement record of the stylus.

3.2- X-ray diffraction (XRD) analysis

The structural properties of samples (powders or thin films) could be obtained by X-ray diffraction (XRD). This technique allows to obtain a lot of information about the samples: crystallization, presence of parasitic phases, crystallographic parameters, orientation, grain size and the stresses.

The principle of this technique is based on Bragg's law, which is the law governing the diffraction of X-rays on a crystal. It was discovered by Sir William Henry Bragg and William Lawrence Bragg around 1915. This law establishes a link between the distance between the crystal atoms $d_{(hkl)}$ and the angles at which are the scattered X-rays hitting the crystal θ **(Figure 2.a)** [1].

$$2d_{hkl}\sin\theta_{hkl} = n\lambda \qquad (3.1)$$

Where:

d = Interreticular distance, ie distance between two crystallographic planes;

θ = X-rays angle incidence on the surface of the studied material;

n = order of reflection;

λ = X-rays wavelength.

Since Miller indices can be used to identify the crystallographic planes, we can index the diffraction peaks using these indices. For a given d_{hkl} value, and an incident X-ray with a fixed wavelength, the diffracted intensity can only be seen at 2 θ_{hkl} which represents a diffraction cone formed by the diffracted and incident rays. The phases present in a sample are identified by comparing its spectrum (positions and intensities of the diffracted lines) to known phase spectra [2].

In this study, The XRD analysis was carried out using the Philips "X'PERT PRO MPD" diffractometer in θ-θ mode (Bragg-Brentano configuration), equipped with a vertical goniometer with a 240 mm radius and fitted with a ray tube with copper anticathode. The interfaced detector is of the PIXcel-1D type.

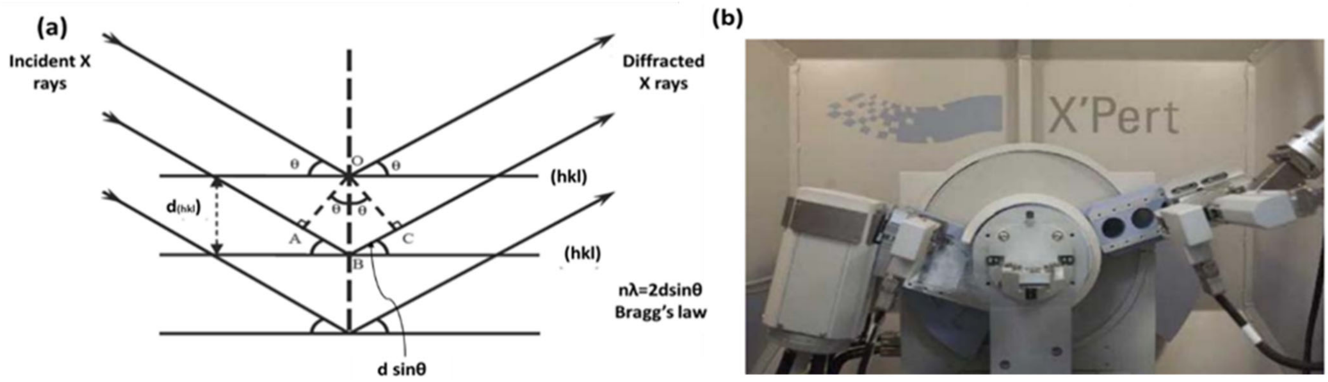


Figure 2. XRD analysis; (a) Principle of X-ray diffraction (b) X'Pert PRO MPD diffractometer.

3.3- Atomic force microscopy (AFM)

Atomic force microscopy (AFM) is one of the most common technique for surface analysis. This technique developed in 1986 by researchers Gerd Binning, Calvin Quate, and Cristoph Gerber in collaboration with IBM and Stanford University. The AFM allows extreme magnifications in the x-, y-, and z-directions, which facilitates atomic scale imaging with high resolution. So, this method led to see the shape of a surface in three-dimensional (3D) detail down to the nanometer scale. AFM can image all type of materials and do not require any special sample preparation [3].

This technique is essentially based on the scanning and measurement of interatomic forces between an ultra - sharp tip (radius less than 10 nm), which is attached to flexible cantilevers, and the sample surface at very short distance (0.2–10 nm tip-sample separation) (Figure III.10). These interaction forces, which could be Van der Waals forces, electrostatic forces, magnetic forces or even ionic repulsion forces, can be described using Hooke's law: $F = - k x$. where F is the tip-sample force, k is the spring constant of the cantilever, and x is the extent of cantilever deflection [3]. This cantilever deflections resulting from variations in force between the tip and the sample during scanning are most often measured by optical detection. A laser beam is focused on the back of the cantilever, which can move in all x, y, z directions, then reflected in a photodiode constituting the detector. The direction changes result a difference in light intensity and therefore a voltage difference. Thus, they are recorded and transmitted to the computer system to allow an analysis and a three-dimensional representation of the surface [4].

The flexible cantilever can move in all x, y, z directions using a piezoelectric scanner. The x, y scan can range from a few nanometers to a few hundred micrometers. The z-sensitivity is on the order of a fraction of nanometer, and the z-shift can be up to a few micrometers. The sample is fixed on a device composed of piezoelectric ceramics allowing movement in the three directions of XYZ space with an accuracy of the order of a tenth of an angstrom.

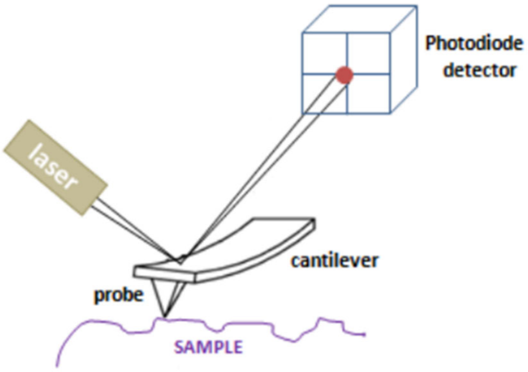


Figure 3. Concept of AFM and the optical lever

The AFM can operate in several modes which can be grouped in two categories: contact mode (static) and tapping mode (dynamic) (**Figure 4)** [5].

Contact mode: in this mode, the cantilever with the tip presses on the sample. A repulsive force between the surface and the tip is created because of repulsion of electrons from the sample and the tip. In this case, the weak interaction between the sample and the tip is kept constant by changing the height of the sample. The variation in height gives the height of the surface at the studied location (**Figure 4. a**).

Tapping mode or intermittent contact: this is the most commonly used mode. In this mode, the cantilever oscillates at a given frequency of about 100 kHz and at a fixed amplitude. In this case, the sample exerts a short-range (van der Waals-type) attractive force on the cantilever and the tip. The amplitude of the oscillation changes. It is kept constant by moving the height z of the sample (**Figure 4.b**).

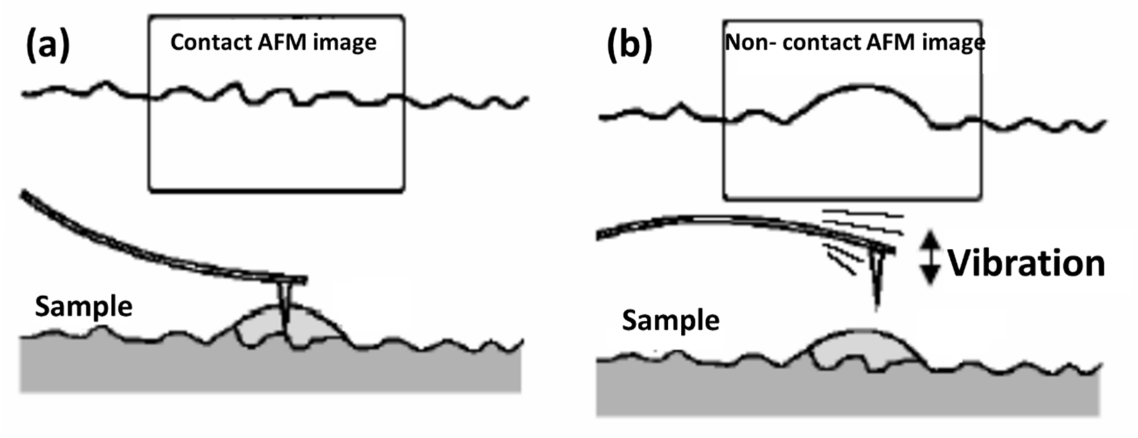


Figure 4. AFM modes; (a) contact mode and (b) tapping mode.

The FESEM images could be analyzed by the WSxM 5.0 software program (Nanotec Electronica S.L.) [6].

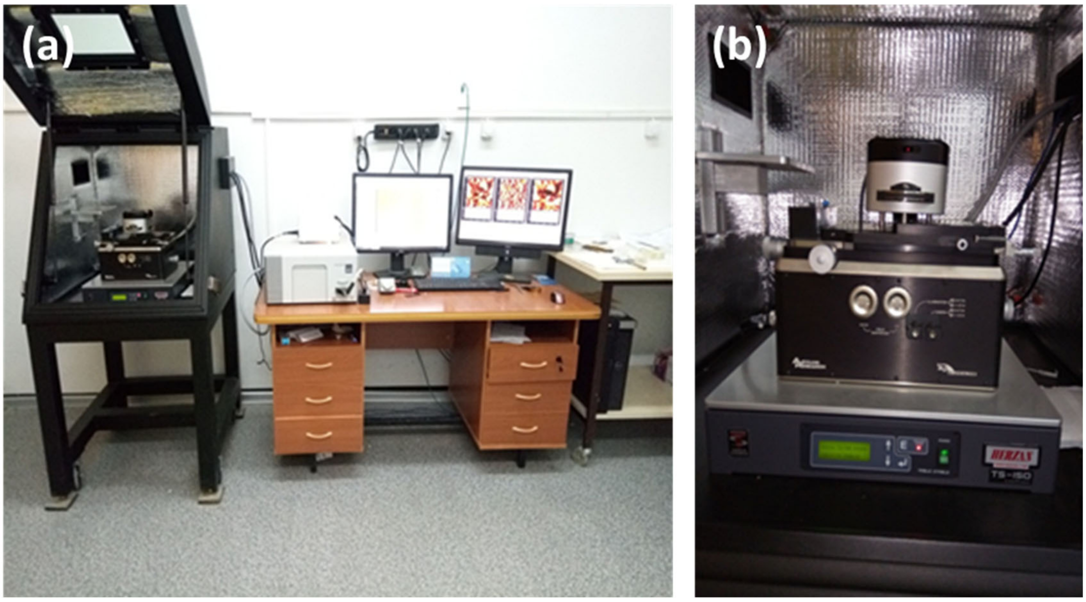


Figure 5. Atomic Force microscopy; (a) Image of the used microscope Asylum Research, MFP-3D Classic model and (b) Sample holder.

3.4- **Scanning electron microscope**

Scanning electron microscopy SEM is one of the most used instruments in research areas and semiconductor industries due to its large depth of field which allows a large amount of the sample to be in focus at one time and produces an image that is a good representation of the surface topography and due to its high resolution, which makes possible the examination of features at high magnification. It is also a non-destructive technique that provides information on the morphology of the sample, its mode of crystallization, sometimes to estimate the crystallites sizes and the thickness of the sample from cross sectional view [7].

SEM is based on the electron-matter interaction. Its principle consists of sweeping, point by point, the surface of the analyzed sample, which is placed in a maintained column under a secondary vacuum, by an energetic electron beam of some ten kilovolts. The electrons are generated by a thermionic emission or field emission gun. These so-called "primary" electrons are focused on the surface of the sample by a system made up of a set of electromagnetic lenses. The interaction of the electron beam with the sample leads to the emission of different particles and radiations such as: secondary electrons, backscattered electrons, Auger electrons and X-rays. This emission occurs in a volume having the shape of a pear, of which the size is on the order of cubic micron (**Figure 6.a**). A detector collects a mixture of the various types of radiation emerging from this volume and the resulting signal is amplified and displayed on a cathode ray tube (CRT) or television screen scanning synchronous with the scan on the specimen. The signals carry topological, compositional and crystallographic information about the sample and in particular secondary electrons give information about morphology and topography whereas backscattered ones provide compositional contrast (**Figure 6.**b) [7, 8].

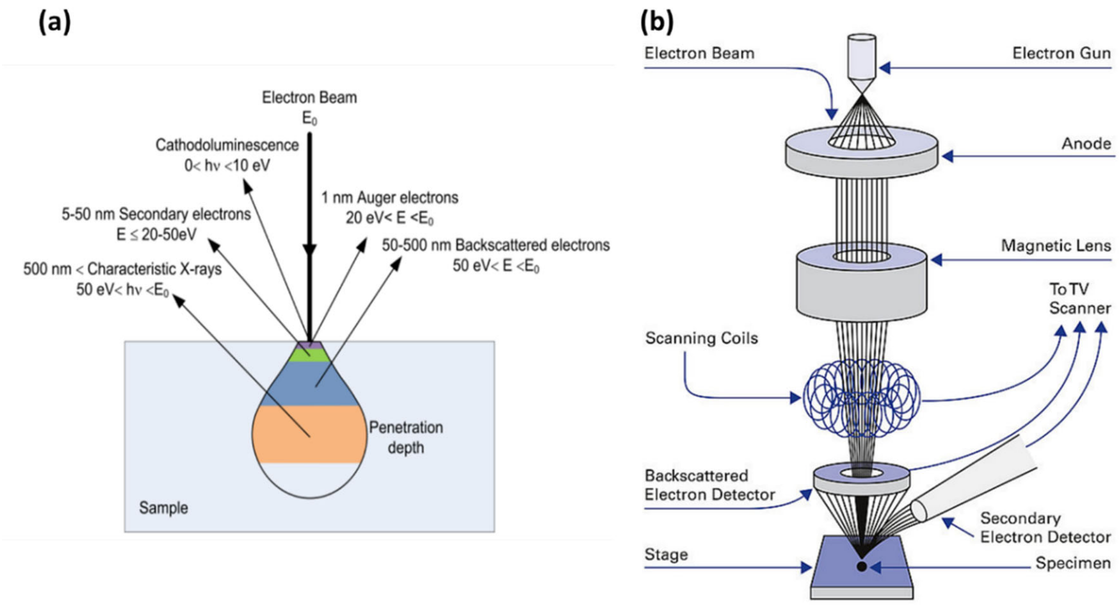


Figure 6. Scanning electron microscopy; (a) Effects produced by electron bombardment of a specimen [7] and (b) Principal design of a scanning electron microscope [9].

The scanning electron microscope in the (**Figure 7**), is of type (FESEM; Zeiss Supra 35 VP) Scanning microscope.

Figure 7. Image of the used scanning electron microscopy Zeiss Supra 35 VP.

4.5- UV-visible spectroscopy

UV-Visible spectrophotometry is an optical characterization method used to study the optical properties of a material such as the transparency, the refractive index, extinction coefficient, energy gap, etc., from the detection of the transmitted (T), absorbed (A) or reflected (R) radiation. These are the three possible radiation when an incident beam of intensity strikes a sample. According to the frequency of the incident radiation, the radiation-matter interaction involves various types of energy levels of matter. The involved energies have the same magnitude order as molecule binding energies, and this radiation can also cause bond breaks. More generally, they cause electronic transitions between the different energy levels of molecules. The type of obtained information will depend on the sensitivity apparatus and the nature of the sample.

The UV-vis absorption spectroscopy provides information of absorption light as a function of wavelength, which describes the electronic transitions occurring in the measured samples. The UV-vis spectrophotometer detects the light intensity passing through a sample and compares the detected intensity to incident light intensity (light before passes through the sample).

The light transmission in materials is an essential element in physics. The general transmission principle which is given by the Beer-Lambert law, expresses the light intensity variation as a function of the thickness d of the traversed object by the light and the absorption coefficient α of the used material [10].

$$I = I_0 \exp(-\alpha d) \qquad (3.2)$$

I: the light beam intensity exiting the sample. I_0: the light beam intensity entering the sample. The light intensity I decreases exponentially with the increases of the thickness d of the absorbent medium. The transmission measurement principle is to measure the transmitted light in two samples, one of them is the reference sample and the other is the sample to be analyzed. The following formula gives the relationship between transmission and intensities.

$$T\% = \frac{I}{I_0}\,100 \tag{3.3}$$

The optical transmission measurements within the framework of this study were obtained by a UV-Visible UV 3101 PC spectrophotometer type Shimadzu (**Figure 8.a**). The light source, the sample holder with the reference, and the measurement system are the three main components of this UV-visible spectrophotometer (**Figure 8.b**).

The light source contains two lamps, one to cover the ultraviolet range (190- 400nm) and the other for the visible and near infrared range from 350 to 900nm wavelength range. The light sources are switched automatically in conjunction with wavelength scanning.

To record the spectra, the UV-Vis spectrophotometer is connected to a microcomputer, which allows the data to be processed by software. The principle of measurement consists of two main steps: putting a reference substrate on one of the device's slits and leaving the other slit empty which is crossed by the light, resulting a spectrum of the substrate. The obtained spectrum is saved as a base spectrum. The purpose of this step is to remove the effects of the substrate. The sample is then placed on the second slit, while the reference substrate stays on the first slit. The recorded spectra only reflect the transmission or absorption of thin films.

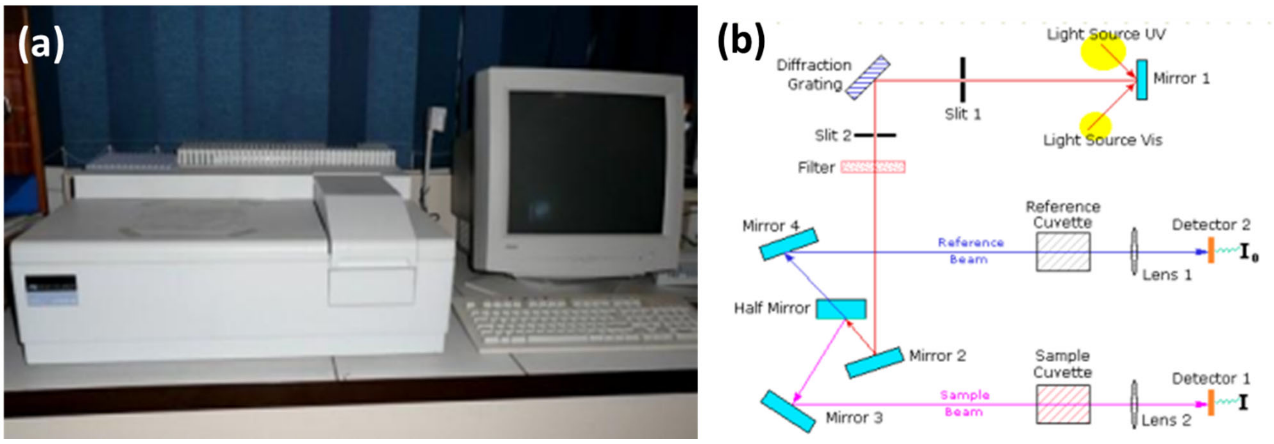


Figure 8. UV-Visible spectroscopy; (a) UV 3101 PC spectrophotometer type Shimadzu and (b) Schematic diagram of the UV spectrophotometer setup [11].

3.5- Photoluminescence spectroscopy PL

Luminescence is described as the emission of any visible, ultraviolet or infrared electromagnetic radiation, that is not strictly thermal in origin. It can be caused in a variety of ways, including by exposing the material to photons (photoluminescence), X-rays (X luminescence), accelerated electrons (cathodoluminescence), (α, β) particles (radioluminescence), or even an electric field (electroluminescence).

The phenomenon of luminescence is often divided into two phases: the excitation of the substance's electronic system, and its de-excitation during which light is emitted. Excitation and emission can be separated by intermediate phases, resulting in the distinction of two forms of light emission: fluorescence, which occurs almost immediately after excitation (t of the order of 10^{-8} s), and phosphorescence, which occurs after a longer period of time (t can range from a fraction of a second to several days).

Photoluminescence (PL) is an optical technique for characterizing semiconductors and insulating materials. Its principle is based on the excitation of electrons in the sample to be studied by a monochromatic laser-type radiative source with a short wavelength. When the sample is exposed to radiation with a higher energy than the gap, the electrons in the valence band absorb it and cross the gap to the conduction band. Radiative or non-radiative transition mechanisms would then de-excite these electrons, allowing them to return to their original state. In the non-radiative transition mechanism, the electrons de-excite by giving up some of their energy to the crystal lattice in the form of acoustic vibrations called phonons. While in the radiative transition, electrons de-excite by emitting photons whose energy approaches that of the gap. The optical diagram of the device is shown in (**Figure 9.**a) [12].

The presence of impurities in the crystal lattice causes low energy electronic transitions to appear. The nature and proportion of these impurities can have a big impact on physical properties like electrical conductivity, which is why photoluminescence measurements are so significant.

A Perkin Elmer LS 50 luminescence spectrometer was used for photoluminescence measurements (**Figure 9.**b). The light source is a 150 W xenon lamp. The lamp's light beam is focused on the entrance slit of an excitation monochromator, which determines the sample's excitation wavelength. The excitation wavelength used is 325 nm. A semi-transparent blade (Beam splitter) divides the outgoing beam, with a part reflecting to a control detector (reference photodiode) and the other part interacting with the sample. The luminescence radiation produced by the latter is directed towards the monochromator and the corresponding intensity value is measured by the photomultiplier. A computer system served for data collection and visualization.

Parameters such as the opening of the two monochromators' slits, the spectrum sweep speed, and the response time of the apparatus are all calibrated before the measurements are taken. The spectral resolution depends on the slit’s width. It increases when the slit width decreases. However, for very narrow slits, a small amount of energy reaches the photomultiplier, and noise can affect spectral quality.

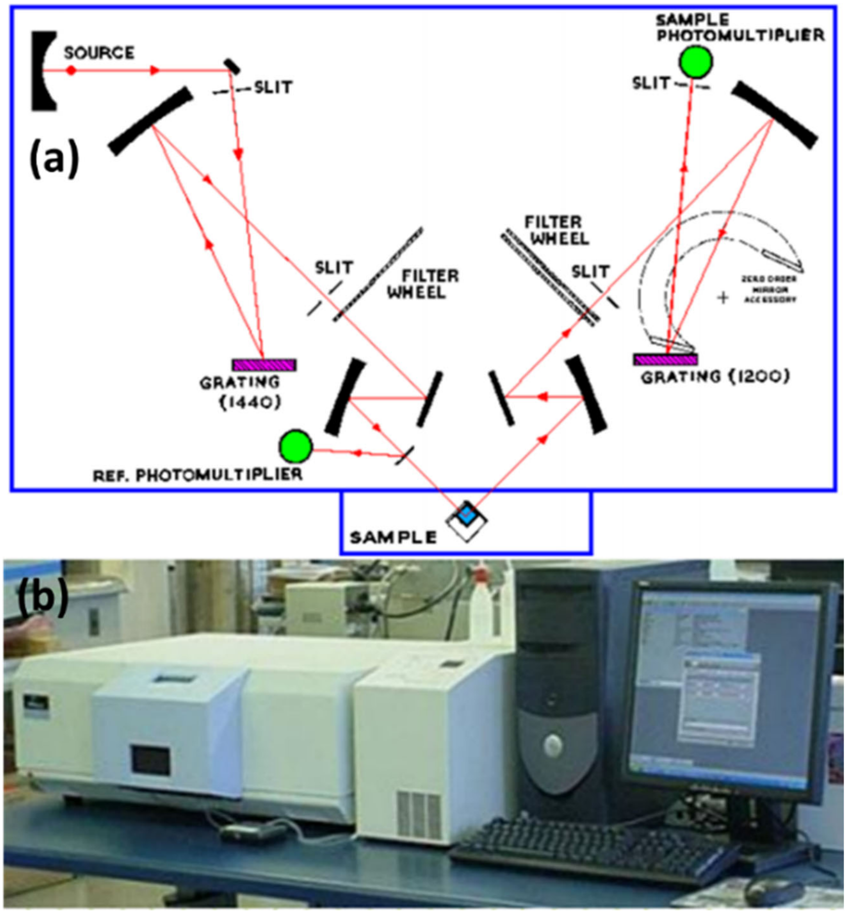


Figure 9. Photoluminescence spectroscopy PL; (a) Schematic diagram of the photoluminescence setup [13] (b) Perkin Elmer LS 50B luminescence spectrometer.

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