

Chapter 2

Experimental Techniques

The fabrication of samples and the experimental techniques employed for their characterization are detailed in this chapter. Particular attention is paid to the experimental setup based on the Kretschmann-Raether configuration for measuring surface plasmons in thin films.



2.1 Introduction

This chapter describes in detail the preparation of samples and experimental techniques used to characterize them. Initially, the methods used for the fabrication of samples are explained. Their final properties depend on the growth parameters and conditions. Later, both structural and spectroscopic experimental techniques are described. A good understanding of these techniques allows a correct analysis of the samples and the results. Particularly, greater attention is paid to the designed and mounted system to measure surface plasmon resonance in metallic thin films under the Kretschmann-Raether configuration [1].

2.2 Sample Growth

In this work, thin films and bilayers were grown by thermal evaporation and some of the samples were treated thermally, in order to obtain different kinds of nanostructures. Next, the fabrication of the different samples is described in detail.

2.2.1 Thin Film Growth by Thermal Evaporation

The thermal evaporation is a technique of physical vapor deposition (PVD) [2], which consists of heating a material at high temperature to increase its vapor pressure. The material vapor finally condenses on the substrate surface forming a thin film [3, 4].

Usually, in this technique, low pressures below 10^{-4} torr are used to avoid reaction between the vapor material and chamber atmosphere. At these low pressures, the mean free path of vapor atoms is the of same order as the vacuum chamber dimensions, so these particles travel in straight lines from the evaporation source towards the substrate [3]. This can originate shadowing phenomena with 3D objects, especially in those regions not directly accessible from the evaporation source. Besides, in thermal evaporation techniques, the average kinetic energy of vapor atoms reaching the substrate surface is low (i.e., for Au, where the $T_{\text{evap}} = 1400^\circ\text{C}$, the average kinetic energy per atom is around 0.2 eV [3]) and thus, it is smaller than the binding energy of atoms in a material (of the order of 5–10 eV). It implies that the atoms reach the substrate surface with low energy, affecting the morphology of the films, and often obtaining low density films and with low adhesion on the substrate surface. When the binding energy is smaller than the average kinetic energy of vapor atoms, the formation of the thin films is more homogeneous [2, 3, 5].

The film growth is a complex process, where a number of steps occur at microscopic level: arrival of atoms onto the surface, adsorption and subsequent surface diffusion, nucleation, formation of new layers, etc. Each of these steps, shown in Fig. 2.1, depends on both the previous step and the parameters of deposition process: deposition rate, temperature, evaporated material, etc. All these steps determinate the growth and the morphology of evaporated films. Besides this, intrinsic parameters such as the interaction between the evaporated material and the substrate (i.e., interface energy) and the substrate cleaning, play an important role in the film morphology.

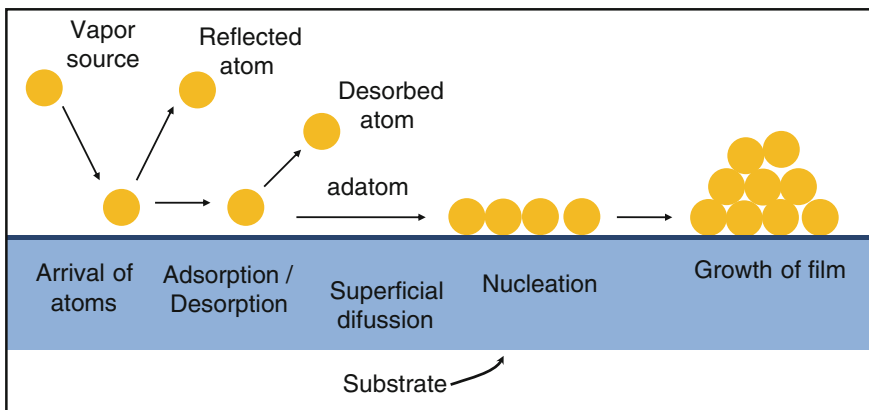
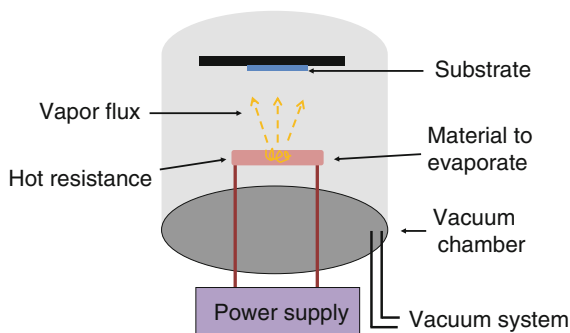


Fig. 2.1 Steps involved in the growth of thin films by PVD techniques

Fig. 2.2 Scheme of thermal evaporation by resistance heating



In thermal evaporation techniques, different methods can be applied to heat the source: by resistance heating or bombardment with a high energy electron beam (usually to several keV) from an electron beam gun [3]. In this work, all films were thermally evaporated by resistance heating, using a power supply of low voltage and high current to avoid the formation of electrical discharges between the contacts. Resistance heating is the process by which an electric current passes through a conductor, releasing heat (Joule effect, $Q \propto I^2 \cdot R$ being Q the amount of heat released, I the intensity and R the resistance). A simple scheme of thermal evaporation by resistance heating is shown in Fig. 2.2.

Different heating elements can be employed to evaporate by resistance heating. The most used is a spiral-shaped or “V”-shaped conductor filament (i.e., W, Mo), in order to generate deformed regions with a high concentration of defects, where the resistance increases (the heat increases) when the electric current passes through the filament. Usually the filament is used to evaporate material forming a wire and the electric current is increased, rising the temperature, until the wire is melted. For materials forming powders, metal boats or ceramic crucible surrounded by a filament are usually used. The powders are deposited in the boat or crucible and the electric current passes through the metal boat or filament, heating until the powder is evaporated. For materials that may react with the resistance or with a melting point close to that of the resistance, ceramic crucibles are used [3]. A scheme of different elements for evaporating by resistance heating is shown in Fig. 2.3. In this work,



Fig. 2.3 Scheme of different heating elements to evaporate by resistance heating: **a** tungsten filaments, **b** metal boat and **c** ceramic crucible

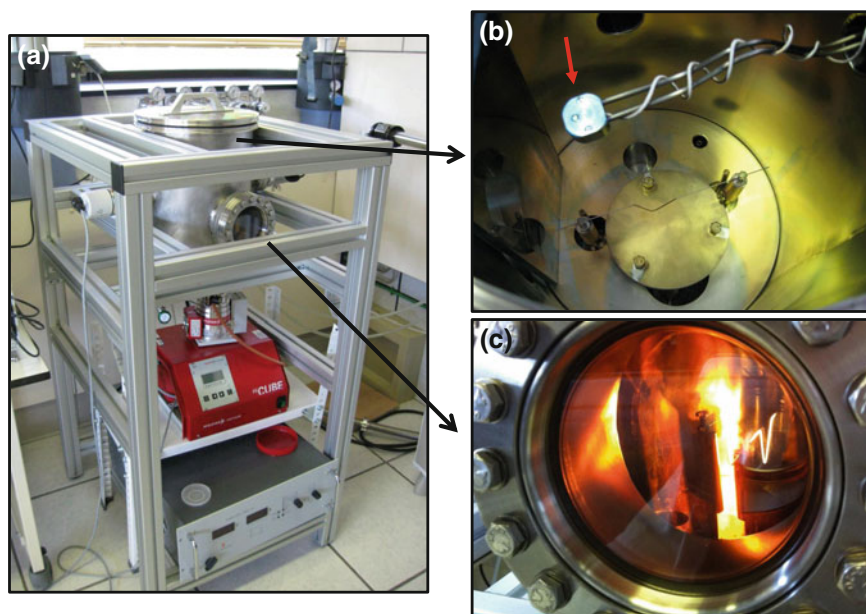


Fig. 2.4 Photographs of the home-made evaporation chamber mounted in the Departamento de Electrocerámica at the Instituto de Cerámica y Vidrio (CSIC) of Madrid: **a** front view, **b** view from top observing the chamber opened and **c** view from a glass window observing the deposition of a film

“V”-shaped tungsten filaments were used to grow metallic films from metal wires and a ceramic crucible was used to evaporate organic molecules.

In this work, samples were fabricated in different vacuum systems:

- A home-made evaporation chamber, which was designed and mounted in the Departamento de Electrocerámica at the Instituto de Cerámica y Vidrio (CSIC) of Madrid. Figure 2.4 displays some pictures of the vacuum system. This chamber contains, among other elements, of a large area where placing substrates of up to $20 \times 20 \text{ cm}^2$, a Q-microbalance (see Fig. 2.4b) in order to control the film thickness and a glass window to follow the deposition of the films on substrates (see Fig. 2.4c). The Q-microbalance is located close to the substrates in order to obtain thin films with similar thicknesses to those values detected by the microbalance, which is calibrated using X-ray reflectivity (see Sect. 2.6).
- Commercial Pfeiffer 306 auto coater located in the Departamento de Física de Materiales at the Universidad Complutense of Madrid. This chamber (see Fig. 2.5a) contains, among other elements, of a shutter to cover the substrates and to control parameters such as the time deposition or the homogeneity of the material vapor to deposit. The shutter is always open after a certain time, from which the possible impurities have been evaporated. Besides this, the system has a glass bell jar, which is very useful to follow the evaporation and see the deposition of the films

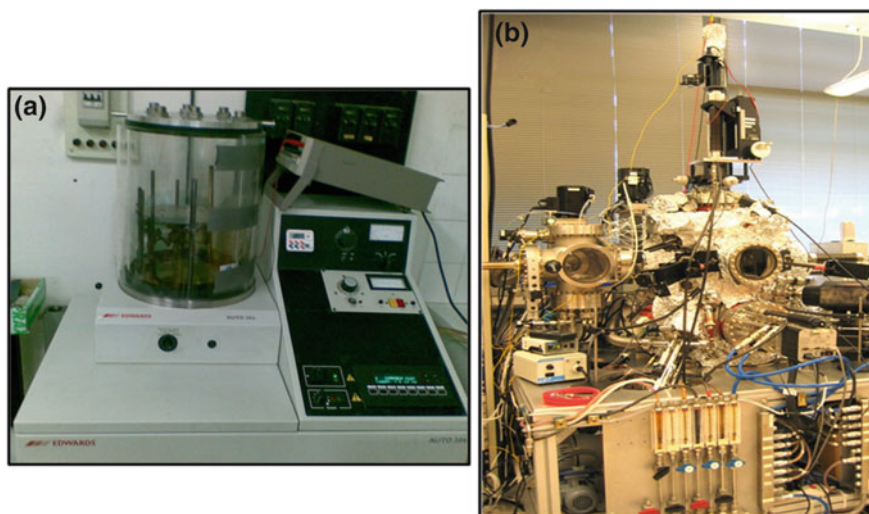


Fig. 2.5 Photographs of **a** commercial Pfeiffer 306 auto coater in the Departamento de Física de Materiales at the Universidad Complutense of Madrid and **b** the home-made evaporation chamber in the Schuller Nanoscience Group, at the University of California, San Diego

on substrates. With this chamber and the previous one, it is possible to grow metallic thin films (i.e., Au, Fe, Ag, Al films).

- A home-made evaporation chamber in the Schuller Nanoscience Group, at the University of California, San Diego. Figure 2.5b shows a picture of the vacuum system. This chamber consists of a Molecular Beam Epitaxy system and includes, among other elements, a Q-microbalance in order to control the thickness of the samples and a shutter to cover the substrates and to control the film deposition. Besides, with this chamber a homogeneous deposition can be achieved by a moderate rotation of substrate plate during the evaporation. With this chamber, it is possible to grow organic molecules in addition to metallic films.

Soda-lime and silica substrates were used in this work. Their features are the following:

- **Soda-lime:** commercial soda-lime glass substrates (Sigma-Aldrich) composed of SiO_2 73 %, Na_2O 14 %, CaO 7 %, MgO 4 %, Al_2O_3 2 %, with a thickness of 1 mm and a refractive index $n = 1.513$ ($\lambda = 645$ nm) [6].
- **Silica:** commercial silica glass substrates (UQG Optics) composed of SiO_2 99.9 % and Al_2O_3 , Fe_2O_3 , Na_2O , K_2O ppm, with a thickness of 1 mm and a refractive index $n = 1.457$ ($\lambda = 633$ nm) [7].

Prior to deposition of films, glass substrates were cleaned by a subsequent immersion in trichloroethylene, acetone, ethanol and distilled water and finally dried with N_2 flux or using soap and water and then dried with dry air flux. Later,

substrates were placed at a controlled distance from the evaporation source (see Fig. 2.2). Subsequently, Au films, Fe films, Fe/Au bilayers and Co-phthalocyanine (CoPc)/Au bilayers were thermally evaporated on the substrates, using resistance heating [3]. For thermal evaporation of Au and Fe films, Au or Fe wire (from Goodfellow) was placed onto a “V”-shaped tungsten filament in the vacuum chamber (see Fig. 2.2). The tungsten was chosen because presents a higher melting point ($T_{\text{evap}} = 3410\text{ }^{\circ}\text{C}$) than that of Au and Fe. The Au and Fe wires were initially melted to form a ball at the filament. Au films were grown using Au¹ wire of 99.99% purity and a 0.5 mm diameter. Au films were fabricated with the Commercial Pfeiffer 306 auto coater in the Departamento de Física de Materiales at the Universidad Complutense of Madrid. The thickness of the Au films was controlled with the deposition time and a shutter to cover the samples of the Au evaporation source. This was calculated using the optical absorption of films and integrating in the range between 400 and 700 nm (see Sect. 2.6). Fe films were grown using Fe² wire of 99.99% purity and a 0.5 mm diameter. Fe films and Fe/Au bilayers were grown using the home-made evaporation chamber in the Departamento de Electrocerámica at the Instituto de Cerámica y Vidrio (CSIC) of Madrid. The thickness of the Fe films and Fe/Au bilayers was controlled by the Q-microbalance. These depositions were performed at room temperature and under a 10^{-6} torr pressure, where the currents and deposition rates were varied depending on material and the type of deposition.

On the other hand, for the preparation of the CoPc/Au bilayers, CoPc films were evaporated from Cobalt(II) phthalocyanine ($\text{C}_{32}\text{H}_{16}\text{CoN}_8$) in powder, using a ceramic crucible. Before the CoPc evaporation, Au films were grown on substrates as indicated above. Prior to inserting the CoPcs into vacuum chamber to evaporate them, commercial CoPcs (from Sigma-Aldrich) were purified via sublimation in a vacuum furnace at 10^{-3} torr and $300\text{ }^{\circ}\text{C}$. The growth of CoPc thin films on Au films was carried out at $45\text{ }^{\circ}\text{C}$ in two steps: first, a degasification of Pcs to remove possible impurities while the Au films are covered by a shutter; second, the evaporation of CoPcs under a 10^{-9} torr pressure where the shutter is opened and the molecules are evaporated on the Au films. Homogeneous deposition was achieved by a moderate rotation of substrate plate. CoPc films were grown at room temperature (α -CoPcs) or at $200\text{ }^{\circ}\text{C}$ (β -CoPcs). For this work, CoPc/Au bilayers were fabricated by the home-made evaporation chamber in the Schuller Nanoscience Group, at the University of California, San Diego. The thickness of the CoPc/Au bilayers was controlled by the Q-microbalance and a shutter was used to cover the samples between the deposition of each layer (Au and CoPc layer).

¹Au shows a crystalline structure face-centered cubic (FCC) with a lattice constant of $4.080\text{ }\text{\AA}$.

²Commonly, Fe is found in its body-centered cubic (BCC) crystalline structure, with a lattice constant of $3.515\text{ }\text{\AA}$.

2.2.2 *Fabrication of Nanostructures by Annealing of Thin Films*

Metallic thin films grown on substrates with poor adhesion are known to exhibit substantial modifications when annealing in air or vacuum, including the formation of hillocks or strain-free extrusions, nucleation and growth of holes and agglomeration of islands leading to a discrete structure [8–13]. The difference in thermal expansion coefficient between the metal and the substrate can lead to the formation of hillocks due to the relaxation of the thermal stress during the course of the annealing process. The formation of hillocks triggers the dewetting process, which is given by the minimization of surface and interface energies: the surface energy of the film and the substrate, and that of the film/substrate interface [14, 15]. The hillock formation depends on the film thickness: when increasing the film thickness, the density of hillocks decreases and their average diameter increases. The decrease of the hillock density can be explained by the increase of the grain size in thicker films, since the process of the grain-boundary diffusion is a controlling mechanism for the hillock formation [16]. Higher annealing temperature favors the nucleation and growth of holes by surface diffusion. For larger temperatures, the holes percolate leading to the formation of islands, which can coalesce during the annealing changing and increasing the average island size in order to reduce the surface energy. This last stage of the process is known as recrystallization for individual particles and/or coalescence if multiples particles join together [17]. An example of the process is illustrated in Fig. 2.6 for a 45 nm Au film annealed at different temperatures.

This method to obtain nanostructures depends mainly on the high surface energy anisotropy [15] and the final nanostructure morphology can be modified and altered by different parameters, such as the film initial thickness, the morphology of substrate [17, 18] and annealing conditions. The formation process of nanostructures is more likely under presence of oxygen due to the relaxation of thermal stress by surface diffusion [10, 19]. This phenomenology was initially considered as a problem in the fabrication of microelectronic devices [16], but it has been recently used successfully to obtain noble metal nanoparticles [12, 20].

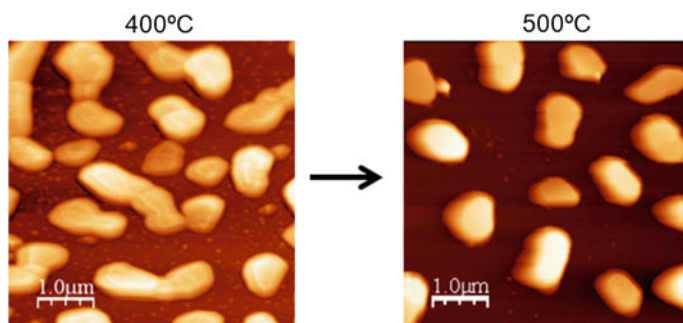


Fig. 2.6 Reshaping process for a 45 nm Au film annealed at 400 °C by recrystallization and coalescence when the sample is annealed at 500 °C

Table 2.1 Melting point and thermal expansion coefficient for different materials

Material	Melting point (°C)	Thermal expansion coefficient at 20 °C ($10^{-6}/\text{K}$)
Au	1063	14.2
Fe	1534	11.8
Soda-lime glass	700*	7.5
Silica glass	1600*	0.49

*Softening point

In this work, Au, FeO_x and Au/ FeO_x nanostructures were fabricated by annealing of thin films and bilayers grown by thermal evaporation. The fabrication process, initial parameters (i.e., film thickness, substrate) and the annealing conditions (i.e., annealing time, temperature, atmosphere) for each kind of nanostructures are described later, in Chaps. 3 and 4. Table 2.1 shows the melting points and the thermal expansion coefficients [11, 21] of the materials and substrates used, which were taken into account for the fabrication of the different nanostructures.

2.3 Reflected Light Optical Microscopy (RLOM)

The first optical microscope is usually associated with *Zacharias Janssen*, in Middleburg, Holland, around the year 1595 [22]. No doubt that the invention of the optical microscope (as the invention of the telescope by *Galileo*) has signified a revolution in human knowledge. The optical microscope, as called light microscope, is an instrument that uses visible light to produce a magnified image of an object (or specimen) that can be observed by the eye or by an imaging device. Nowadays, optical microscopes can be very simple. However, they usually present many complex designs aimed to improve sample resolution and contrast. Two microscope components are of critical importance for forming the image. The condenser lens, which focuses light from the illuminator onto a small area of the specimen, and the objective lens, which collects light reflected by the specimen and forms a magnified real image at the real intermediate image plane near the eyepieces [23, 24]. The microscope resolution is limited by the diffraction limit and is defined as [25]:

$$d = \frac{0.61\lambda}{NA} \quad (2.1)$$

where d is the minimum resolved distance, λ is the wavelength and NA is the numerical aperture of the objective lens.

In this work, reflected optical microscopy images were obtained by a polarized light Zeiss Axiophot microscope, using the digital camera AxioCam MRc5 for taking the micrographs. These measurements were carried out at the Instituto de Cerámica y Vidrio (CSIC).

2.4 Scanning Electron Microscopy (SEM)

The electron microscope was developed by *Max Knoll* and *Ernst Ruska* in 1931 [26]. The scanning electron microscopy (SEM) is a type of electron microscopy that uses a focused beam of electrons to generate a variety of signals at the surface of samples. The types of signals that derive from electron-sample interactions include secondary electrons, backscattered electrons, X-rays, cathodoluminescence, specimen current and transmitted electrons, which reveal information about the sample (morphology, chemical composition, crystalline structure and orientation) [27]. Most of the work done on a SEM is for obtaining topographical information, which is mainly provided by secondary electrons.

The main components of an electronic microscope are: a vacuum system (it is required when using an electron beam because electrons will quickly disperse or scatter due to collisions with other molecules); an electron beam generation system (usually, a tungsten filament) that provides the beam of electrons known as the primary electron beam; an electron beam manipulation system that consists of electromagnetic lenses and coils that control the size, shape and position of the electron beam that reaches the sample surface; and the beam-specimen interaction system that involves the interaction of the electron beam with the sample and the types of signals that can be detected [28].

In this work, samples were studied by a TM-1000 Tabletop Microscope using Hitachi at the Instituto de Cerámica y Vidrio (CSIC). This electron microscope permits to obtain images without a special sample preparation, working with an accelerating voltage of 15 kV.

2.5 Atomic Force Microscopy (AFM)

Atomic force microscopy (AFM) was developed in 1986 by *Binnig*, *Quate* and *Geber* [29]. AFM is a powerful tool that is used to study the morphology and structure of samples, allowing to characterize and manipulate a wide group of materials at the atomic level [30–32]. Easily, the AFM operation is based on measuring interactions between a tip and sample. Figure 2.7 shows the main interactions as a function of tip-sample distance.

The basic components of this system are a cantilever with a sharp tip (probe), a laser beam, a photodiode detector and a scanner, as illustrated in Fig. 2.8. The tip is attached to the free end of a cantilever and is approached very close to the surface of a sample. Attractive or repulsive forces, resulting from interactions between the tip and the surface, cause the bending of the cantilever. It is detected by means of a laser beam, which is reflected from the back side of the cantilever and collected in a photodiode. The variations on the topography of the sample will induce changes in the interactions between the tip and sample [30, 31], which will be detected by the bending of the cantilever. Figure 2.8 shows the basic concept of AFM, which can

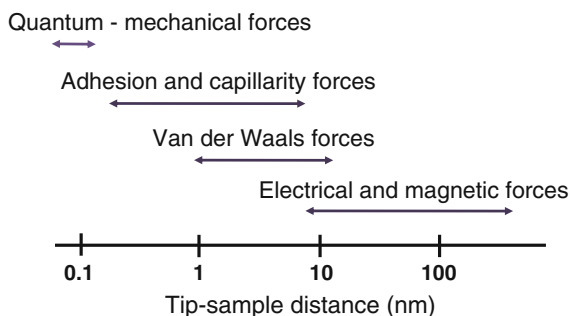


Fig. 2.7 Interaction forces between tip and sample in AFM

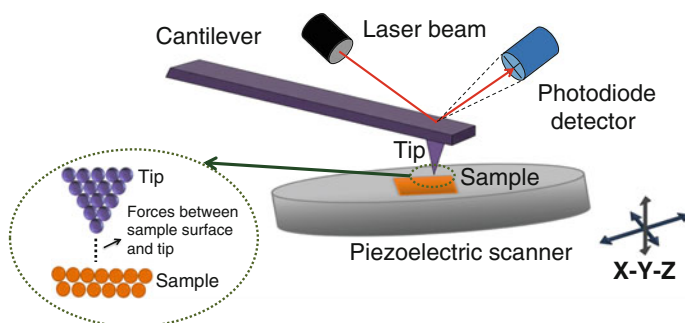


Fig. 2.8 Scheme of AFM

work in different modes of operation: contact mode, noncontact mode and tapping mode (intermittent contact mode).

The AFM can provide useful information through phase measurements, which collect the changes in the phase signal of the oscillating cantilever operating in noncontact or tapping mode of the microscope. Phase measurements are obtained simultaneously with the topography data and provide interesting information on localized tip-sample interactions on heterogeneous materials that present different surface properties, such as the composition, viscoelasticity or surface adhesion [33]. For materials with different properties, a shift in the phase signal between tip and sample is obtained, generating images with phase contrast [34], from which it is possible to distinguish the different local compositions.

In this work, topography and phase AFM images were taken with a Nanotec instrument of the Surface Science Group at the Universidad Complutense of Madrid. AFM measurements were performed in air, using silicon tips (with a resonant frequency of 200–300 kHz and an average tip radius ≤ 10 nm), in noncontact mode (the cantilever oscillates near its resonance frequency and the oscillation amplitude remains constant by a feedback system) and at room temperature. The images were analyzed using the *WSxM* software package from Nanotec [35].

2.6 Thickness Determination of the Films

The thickness of films was evaluated by different methods, depending on the vacuum chamber used to fabricate the samples:

- On the one hand, the thickness was determined using a quartz crystal microbalance, which was calibrated using X-ray reflectivity (XRR) performed on similar samples. The film thickness, in this case, is a nominal thickness. The chambers used in this way were: the home-made evaporation chamber in the Departamento de Electrocerámica at the Instituto de Cerámica y Vidrio of Madrid (CSIC) and the home-made evaporation chamber in the Schuller Nanoscience Group, at the University of California, San Diego.
- On the other hand, film thickness was evaluated using a linear relation obtained by the thickness (calculated using XRR) of similar films and their integrated absorbance in the range between 400 and 700 nm, obtained by the optical absorption spectra. Thicknesses calculated by this method correspond to Au films grown in the commercial Pfeiffer 306 auto coater, in the Departamento de Física de Materiales at the Universidad Complutense of Madrid.

2.6.1 X-Ray Reflectivity (XRR)

X-ray reflectivity (XRR) is a technique based on the X-ray diffraction phenomenon [36]. XRR provides information about the thickness, density and roughness of each layer of a thin film [37].

For the X-rays, the refractive index, n , of materials is slightly less than 1 and is given by [36, 37]:

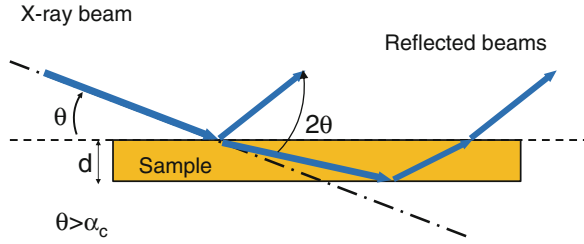
$$n = 1 - \delta + i\beta \quad (2.2)$$

where δ and β represent the dispersion and the absorption, respectively. For incident angles larger than the critical angle, the X-rays penetrate inside material (see Fig. 2.9). In this way, reflection occurs at the top and the bottom surface of the film. By measuring the total reflection intensity (reflectivity) from grazing incident X-ray beam as a function of the incident angle with respect to the thin film surface, a XRR profile can be obtained.

The XRR profile shows oscillations caused by the X-ray interference that occurs between the X-rays reflected from the sample surface and the sample/substrate interface.³ The oscillations of the XRR profile depend on the film thickness: the shorter period of the oscillations, the thicker films. From the reflectivity profile as a function of the incident angle, it is possible to determinate the film thickness using the following linear fit:

³For convectional $\theta-2\theta$ measurements, we obtain information from the lattice planes that are parallel to the sample surface.

Fig. 2.9 Reflection and refraction of X-rays at material surface with the incident angle $>$ total reflection critical angle



$$\alpha_m^2 = \alpha_c^2 + (m + \Delta m)^2 \frac{\lambda^2}{4d^2} \quad (2.3)$$

where m indicates the maximum or minimum order of the oscillations, Δm is 0 for minima or $\frac{1}{2}$ for maxima, λ is the wavelength of incident beam (in this work, $\lambda = 1.54 \text{ \AA}$ for Cu- K_α X-rays), α_m corresponds to the angle of the maximum or minimum, α_c corresponds to the critical angle and d is the film thickness.

2.6.2 Relation Between the Thickness of Films and Their Integrated Absorbance

In order to know the thickness of thin films using a fast and accessible route, a linear relation between the thickness of Au thin films (just Au thin films were grown in the commercial Pfeiffer 306 auto coater) and their integrated absorbance, in the range between 400 and 700 nm, was determined. First, the thickness of a set of samples was obtained using XRR (see Fig. 2.10a), according to Eq. 2.3. Table 2.2 shows the thicknesses obtained by XRR for four Au films. Later, the integrated absorbance, obtained by the optical absorption spectra, was calculated in the range between 400 and 700 nm (range marked with arrows in Fig. 2.10b).

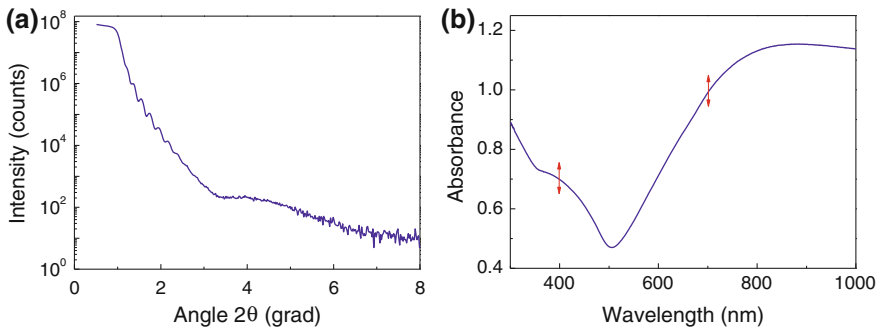
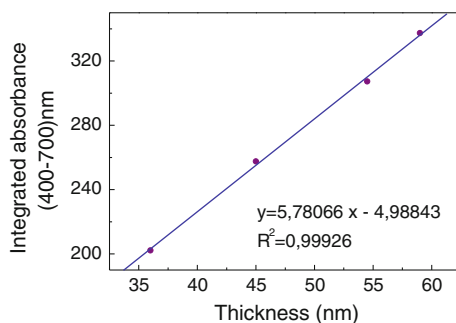


Fig. 2.10 **a** XRR curve and **b** optical absorption for a Au thin film with a width of $36 \pm 3 \text{ nm}$

Table 2.2 Thickness obtained by XRR, according to Eq. 2.3, for four Au thin films

Sample	Thickness (nm)
1	36 ± 3
2	45 ± 1
3	54 ± 1
4	59 ± 1

Fig. 2.11 Linear relation between the thickness and the integrated absorbance in the range between 400 and 700 nm



Finally, representing the integrated absorbance in the range between 400 and 700 nm as a function of the Au thin film thickness obtained by XRR (see Fig. 2.11), we obtain the following linear relationship:

$$d(\text{nm}) = \frac{I.A. + 4.988}{5.781} \quad (2.4)$$

where d and $I.A.$ represent the thickness and the integrated absorbance, respectively.

In this way, the thickness of the rest of the Au films was evaluated by Eq. 2.4, measuring the optical absorption spectrum and calculating its integrated absorbance in the range between 400 and 700 nm.

2.7 Raman Spectroscopy

Raman spectroscopy is a non-destructive technique that studies the vibrational, rotational and other low frequency transitions of molecules or crystal atoms. Raman effect was discovered by C.V. Raman in 1928 [38] and it is based on the inelastic scattering of monochromatic light, usually from a laser source. It depends on the polarizability of the molecules and it requires a change in the frequency of photons from monochromatic light upon interaction with a sample [3].

When a light source (laser) is focused on a material, most of this energy will be elastically scattered. In this case, the molecules of the substance are excited to a virtual electronic state and immediately fall back to their original state by releasing a photon. If the photon energy of this scattered light is equal to that of the incoming light, the

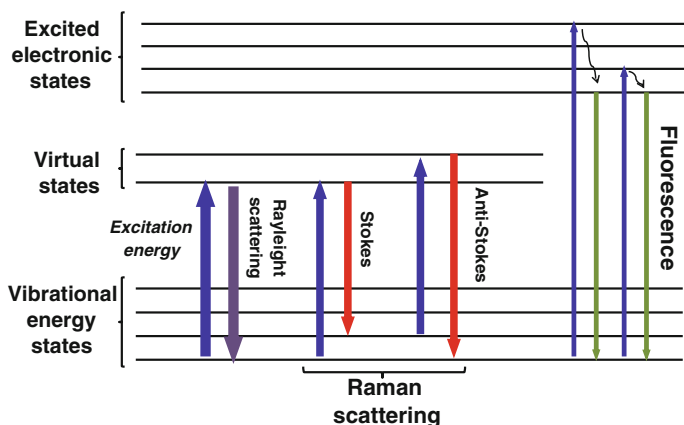


Fig. 2.12 Mechanisms of various light-scattering processes involved in Raman spectroscopy

process is called Rayleigh scattering. However, a molecule may also fall back from an excited electronic state to an energy state that is higher (Stokes type scattering, photon emission) or lower (anti-Stokes type scattering, photon absorption) than the original state (see Fig. 2.12). The difference of energy between the incoming and scattered photons (Raman shift) corresponds to the energy difference between vibrational energy levels of the molecule. The different vibrational modes of a molecule can, therefore, be identified by recognizing Raman shifts (or bands) in the inelastically scattered light spectrum [39].

Raman spectroscopy is extraordinarily sensitive to the chemical nature and the physical state of a sample. In the Raman spectra, the band position, intensity and bandwidth are closely related to the order, crystal size and defects in the samples [40]. The band position is sensitive to the presence of stresses or strains: a tensile stress will determine an increase in the lattice spacing and, hence, a decrease in the wavenumber of the vibrational mode. In the case of compressive strain, the decrease of the lattice parameter yields a corresponding increase of the vibrational frequency. The presence of crystalline disorder also produces changes in the frequency of the band, usually towards lower wavenumbers. These are related to the breaking of translational symmetry in the crystal, which can be due to structural defects, such as grain boundaries in nanocrystalline materials or dislocations. With respect to Raman bandwidth and bandshape, these are closely related to the crystalline order and the defect density. In principle, the bandwidth is related to the lifetime of the phonons. The presence of crystalline disorder produces a decrease of the phonon lifetime, generating an increase of the bandwidth. Other parameter very sensitive to the structure of crystals is the intensity of the Raman bands. The amount of material is directly related to the Raman intensity and a damage in the lattice leads to a decrease in the intensity of modes, related to the breaking of bonds and changes in atomic force displacements [40].

Raman spectroscopy is employed to distinguish different materials and to determine the kinds of species in a same sample. Material as the metals (i.e., Au) can lead to optical emissions as the fluorescence phenomenon that can mask the Raman spectra of other materials. Many efforts have been carried out in the last years to avoid the fluorescence or to separate the Raman signal of a material from fluorescence emission [41]. However, useful information can be obtained by the fluorescence phenomenon, as we show in Chap. 4.

In this work, samples were investigated by a confocal Raman microscope [42] using the Witec Micro-Raman Confocal (ALPHA 300R). Measurements were carried out at room temperature with a Nd:YAG laser (532 nm) in p-polarization. The optical resolution of the confocal microscope in the lateral direction is of 200 and of 500 nm in the vertical direction. The spectral resolution of the system is 0.02 cm^{-1} , under the best measurement conditions. Raman spectra were recorded in the spectral range $0\text{--}3600 \text{ cm}^{-1}$. Samples were mounted in a piezo-driven scan platform with a positioning accuracy of 4 nm in lateral and 0.5 nm in vertical. In order to prevent any damage or oxidation in the samples, laser excitation power was fixed at 0.7 mW. Raman measurements were performed using a objective with a lens of numerical aperture, NA, of 0.9. Collected spectra were analyzed by using *Witec Control Plus* Software.

2.8 X-Ray Absorption Spectroscopy (XAS)

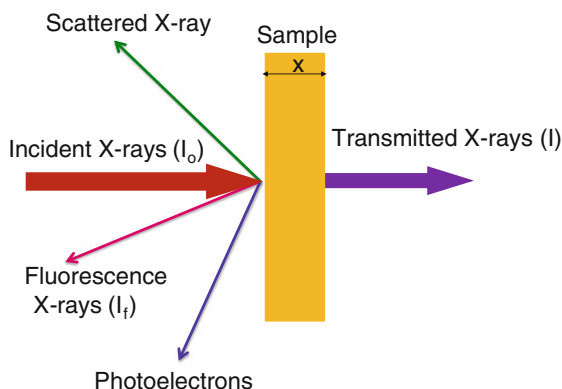
X-ray absorption spectroscopy (XAS) is a technique that provides element-specific information about the local geometric and/or electronic structure of a material. The experiments can be carried out at synchrotron radiation sources, which provide intense and tunable X-ray beams.

When the X-rays reach a material, the intensity of electromagnetic radiation is reduced by different processes of interaction, such as scattering or absorption (see Fig. 2.13). For X-ray photons, with energies ranging from 100 to 500 keV, the photoelectric effect is dominating, where an X-ray is absorbed and a core level electron is promoted out of the atom [43]. Hard X-rays are termed so when the energy is of the order of tens of keV, while those with lower energy are called soft X-rays [44]. With soft X-rays, excited levels are close to Fermi level and so they are more sensitive to electronic structure. However, hard X-rays are more sensitive to crystallographic structures, since the excited levels are more internal. When the monochromatic X-ray beam of intensity I_0 , passes through a sample of thickness x , the intensity is reduced according to the Lambert-Beer law:

$$I = I_0 e^{-\mu x} \quad (2.5)$$

where I is the transmitted intensity and μ represents the linear absorption coefficient, which depends on the types of atoms and the material density and the energy.

Fig. 2.13 X-ray absorption measurements: X-ray interaction with a sample

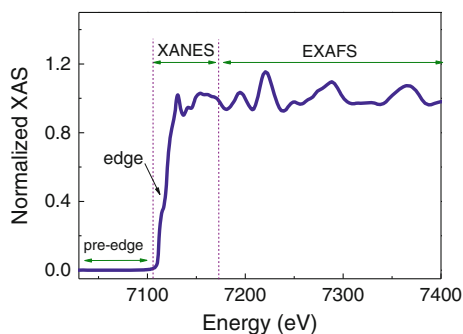


At certain energies, due to the discrete character of electronic levels, the absorption increases drastically and gives rise to an absorption edge. Such edge occurs when the energy of the incident photons, E , is just sufficient to cause excitation of a core electron of the absorbing atom to a continuum state, producing a photoelectron. In this process, the energies of the absorbed radiation at these edges correspond to the binding energies of electrons in the K, L, M, etc., shells of the absorbing elements.

An X-ray absorption spectrum (see Fig. 2.14) is generally divided into four sections [43, 45]:

- *Pre-edge*: where the $E < E_0$, being the E_0 the edge energy. The pre-edge together the post-edge are used for normalization of XAS spectra.
- *Absorption edge*: rapid increase of absorption at E_0 , which corresponds to the electron excitation energy from core levels to Fermi level. This region is very sensitive to the oxidation state of the materials, coordination number and it gives information about the electronic structure of the atom [43, 45]. The absorption edge is used for calibration of XAS spectra.
- *X-ray absorption near edge structure (XANES) region*: where the energy of the incident X-ray beam, E , is around 10 eV before and up to 50 eV above the edge.

Fig. 2.14 XAS spectrum at Fe K edge measured in transmission mode for an Fe foil, at branch A of the BM25 SpLine beamline at the ESRF



In the XANES region, transitions occur from core electrons to non-bound levels with energy close to Fermi energy. This region shows narrow and intense peaks because of the high probability of such transitions.

- *Extended X-ray absorption fine structure (EXAFS) region*, which is approximately from 50 eV above absorption edge and continues up to 1000 eV above the edge. This region shows soft oscillations of absorption coefficient due to the photo-electron scattering with the neighbor atoms. Studying EXAFS region, interatomic distances can be resolved as well as the identification of neighbor atoms.

In this work, XAS measurements were performed at the branch A of the CRG BM25-SpLine Beamline at the European Synchrotron Radiation Facility (ESRF) in Grenoble (France) [46, 47]. This beamline is split into two branches, A and B, each of them fully equipped with focusing optics and experimental stations that are independently operated.

Branch A enables the performance of XAS and high resolution powder diffraction measurements. This branch is located on the soft edge of the D25 bending magnet with a critical energy of 9.7 keV and energy resolution of $\Delta E/E = 1.5 \times 10^{-4}$. The X-ray energy ranges between 5 and 45 keV and the flux is of the order of 10^{12} photons/s at 200 mA ring current. The beam spot size can be varied for the whole energy range between $300 \times 100 \mu\text{m}^2$ and $40 \times 10 \text{mm}^2$ in the horizontal and vertical directions, respectively. The position and dimensions of the focused beam are kept constant during a ~ 1 keV energy scan, which represents standard conditions for EXAFS measurements. The XAS system is arranged onto an optical table for optimum placement and alignment of the environmental sample and the detection equipment components. The system is equipped with motors covering all degrees of freedom, three translation stages (X, Y, Z) and three rotation stages (θ , χ , φ) for centering the sample. The precision of such rocking cradle motors is 0.001° and they can tilt the sample stage within a range of $\pm 15^\circ$ along the directions parallel and perpendicular to the incident beam. While the beamline can operate in both transmission and fluorescence modes, only the later is used in this work for studying the samples. A gas ionization chamber (from Oken) working in the low-pressure range is placed for monitoring the incoming beam intensity. Fluorescence is detected with a nitrogen-cooled 13-element Si(Li) detector (from e2v Scientific Instruments). The low temperature of the Si(Li) and FET ensemble also diminishes leakage current and electronic noise. The Si(Li) fluorescence detector allows performing fluorescence measurements in a range between 3 and 30 keV. The energy resolution at 6 μs peaking time is around 140 eV in every crystal. The detector is also fully equipped with translation and rotation motors to optimize its position, reducing in this way the solid angle for elastic diffuse scattering contributions.

In this work, XAS measurements were performed at Au L edge ($E = 11.919$ keV), Fe K edge (7.112 keV) and Co K edge ($E = 7.720$ keV) at room temperature. Besides measuring XAS spectra, the X-rays were used to induce modifications on different samples [48]. The measurements were analyzed with *ATHENA* software [49].

2.9 Optical Absorption Spectroscopy

In a spectrophotometer of optical absorption, a monochromatic light source that is varied in a wide range of wavelengths passes through a material, promoting an electron from its fundamental state to a state of higher energy. In the process, electronic and vibrational transitions of material and their impurities, defects, etc., absorb light at a certain energy, showing zones in the absorption spectrum with high intensity, which are characteristics of each material [3]. Absorption bands corresponding to localized surface plasmons (LSPs) can be also determined by the optical absorption spectroscopy.

The absorbance (A) of a material can be defined as the logarithm of the ratio between incident and absorbed light intensity [50]:

$$A = \log \frac{I_0}{I} = -\log T \quad (2.6)$$

where I_0 represents the incident intensity, I represents the transmitted intensity and T is the transmittance. The absorbance is adimensional [50].

In this work, the optical absorption bands of different samples were studied using two double-beam ultraviolet-visible spectrophotometers. A scheme of a double-beam spectrophotometer is shown in Fig. 2.15, where the beam from the light source is split in two: one beam illuminates the sample and the other one illuminates the reference (i.e., a substrate). Afterwards, the intensity of both beams is compared and the transmittance or absorbance of the sample can be obtained. Optical absorption spectra were recorded with:

- A Shimadzu UV-1603 double beam spectrophotometer in the Departamento de Física de Materiales at the Universidad Complutense of Madrid.
- A V-670 UV-visible double beam spectrophotometer in the Dipartimento di Chimica at the Università degli Studi di Firenze.

The optical absorption measurements were carried out in transmission mode and at room temperature. Baseline correction procedure (a spectrum in air was taken as baseline) was executed prior to each measurement session.

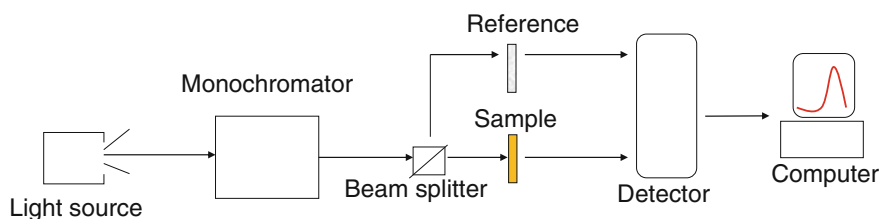


Fig. 2.15 Scheme of a double-beam ultraviolet-visible spectrophotometer

2.10 Surface Plasmon Resonance (SPR) in the Kretschmann-Raether Configuration

The Kretschmann-Raether configuration [1, 51, 52] is mostly employed for the excitation of surface plasmons (SPs) in thin films. Figure 2.16 displays a scheme of the home-made surface plasmon resonance (SPR) device designed and mounted in the Departamento de Electrocerámica at the Instituto de Cerámica y Vidrio (CSIC) of Madrid, showing the different elements of the experimental setup. Figure 2.17 shows a picture of the system.

In this geometry, SPs are excited in the attenuated total reflectance mode using a HeNe (632.8 nm) linearly polarized laser in a p-polarization geometry, with respect to the sample surface (the electric field in the plane of incident light). The laser is mounted on a cradle equipped with yaw and pitch movements for an accurate orientation of the beam on the sample. A linear polarizer is used to have a well-defined p-polarization. Subsequently, a beam splitter [53] deflects the laser intensity to a photodetector, in order to record fluctuations in laser intensity during the experiments. These fluctuations are of the order of 3 %, decreasing with time. Beyond the beam splitter, the laser beam is modulated with an optical chopper, working at 479 Hz. Finally, the laser light reaches the sample, which is coupled to a triangular quartz prism (semicircular prism can be also used). The sample consists of a thin metallic film (typically 50 nm of Au or Ag, using in this work Au films) grown on a glass substrate. Overlayers of dielectric materials can be grown. Sample is fixed to the prism through the substrate side using gel index matching for a good coupling. Both (sample and prism) are mounted on top of a rotating motor that allows varying the laser incidence angle (see Figs. 2.16 and 2.17). The sample stage has an independent XYZ translation stage for sample positioning. During the measurements, the laser beam reflected at the sample is collected by an elongated photodiode (to avoid moving the detector during the angle scan) as a function of the incident angle, by rotating

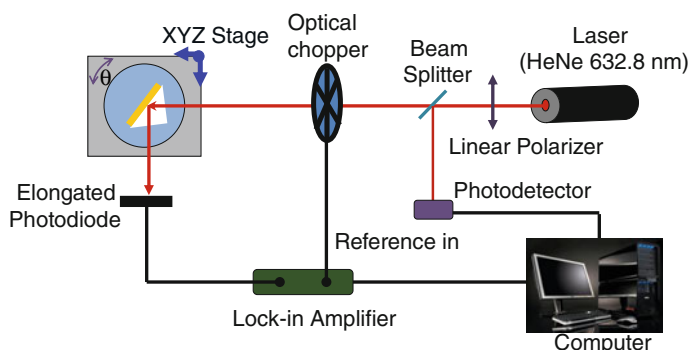


Fig. 2.16 A scheme of SPR setup in the Kretschmann-Raether configuration

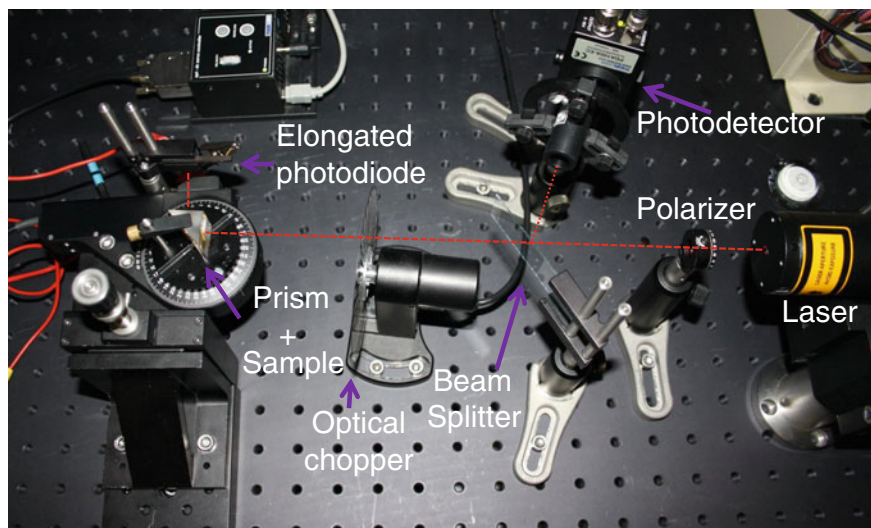


Fig. 2.17 Photograph of the mounted SPR device in the Departamento de Electrocerámica at the Instituto de Cerámica y Vidrio (CSIC) of Madrid, remarking the different elements

the sample [1]. The photodiode signal is registered with a lock-in amplifier, using the optical chopper frequency as reference frequency.

A detailed description of different elements employed in this experimental setup is enumerated below:

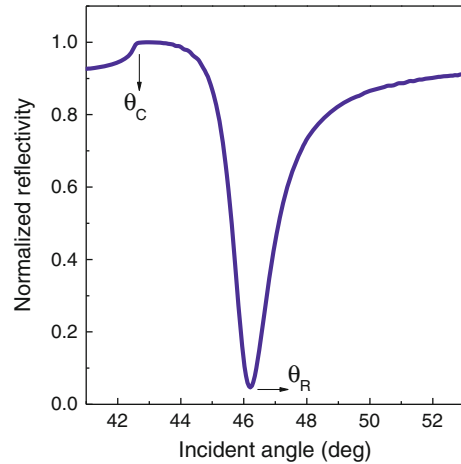
- HeNe laser, 632.8 nm: a Thorlabs linearly polarized laser (power 0.8 mW) in a p-polarization geometry with respect to the sample surface was used. The laser spot diameter is 0.48 mm, measured as the full width half maximum (FWHM) of Gaussian profile of the spot. The coherence length is around 30 cm.
- Beam splitter: a beam splitter optical device (microscope slide) was used to split the light beam in two. The beam splitter deflects about 5 % of the laser intensity.
- Linear polarizer: this is an optical filter that can convert a light beam of undefined or mixed polarization into a beam with well-defined polarization. In the experimental setup, in the Kretschmann-Raether configuration, the light was p-polarized with a Thorlabs linear polarizer, in order to excite the SPs [1].
- Optical chopper: the MC2000 optical chopper from Thorlabs was used to modulate the intensity of the light beam. Usually, it is a rotating slitted mechanical disc through which the laser source passes before reaching the sample. The laser beam was modulated at 479 Hz.
- Photodetector: a photodetector operates for converting the incident light to a voltage or current. In the experimental setup, a DET10A Thorlabs photodetector was used to record fluctuations of laser intensity when it is split by the beam splitter (laser intensity reference).

- **Elongated Photodiode [54]:** the most common used photodetector is the photodiode. In this device, the S2387-130R Hamamatsu Si photodiode was used working in photoconductive mode (there are two modes of operating: photovoltaic and photoconductive modes) with a load resistance of 10 k Ω and applying a voltage of 8 V. In this mode, the photodiode is reverse biased, obtaining a current proportional to the light intensity. In the SPR measurements, the photodiode signal depends on both the light intensity and the incidence angle, and therefore the photodiode sensitivity changes along the SPR curve. Consequently, the measured SPR spectrum can be distorted, affecting the fits and numerical analysis of SPR curves [55]. To avoid this, SPR measurements were carried out under the same conditions, with the photodiode placed in the same position, parallel to the laser beam.
- **Lock-in amplifier [56]:** the lock-in amplifier or phase-sensitive detector, SRS Model SR830, was used to collect the photodiode signal. Usually, a lock-in amplifier is employed to improve the signal-to-noise ratio. These devices are able to isolate the signal of a specific frequency (i.e., reference frequency of chopper), so that noise signals at different frequencies than that of reference are rejected and they do not affect the measurement.

In the Kretschmann-Raether configuration, using triangular prisms, only the points along the rotation axis remain at the same position when the sample rotates. If the laser spot does not impinge at the sample on this rotation axis, its position will change during the angle scan. This is not critical when samples are homogeneous. To avoid misalignments, semicircular prisms are preferable since for triangular prisms the refraction at the prism surface will induce a certain horizontal deviation of the laser beam, which is dependent on the incident angle. For instance, for 1 cm side triangular quartz ($n = 1.457$ at $\lambda = 633$ nm [7]) prism, when scanning the incidence angle in a range of 10° , the spot will move about 0.6 mm. However, the cross-section of a semicircular prism is not completely semicircular and this must be reduced by the thickness of the glass substrate, using glass substrates with a specific thickness. Such limitation on the thickness of glass substrate does not exit with triangular prism [57]. Besides this, using semicircular prisms with a small width comparable with the spot size of the laser, focalization problems can be obtained due to the wavefront is no plane. For this reason, in this work, triangular quartz prisms are used and measurements were carried out with the laser spot impinges at the sample on this rotation axis.

As previously discussed in Chap. 1, in the Kretschmann-Raether configuration, the glass/metal interface is illuminated with the laser beam in total reflection conditions. In these conditions, the evanescent field of the incident light propagates through the metallic film looking for the metallic/dielectric interface. For a certain incidence angle, the dispersion relationship is coincident with that of the SPs and these are excited. In this way, the reflectivity versus incident angle can be measured, obtaining the SPR spectrum. Figure 2.18 shows a SPR spectrum for a 50 nm Au film. In the SPR spectrum, we can distinguish the resonance angle (θ_R), which corresponds to

Fig. 2.18 SPR spectrum for a 50 nm Au film grown on a silica substrate



the incident angle for which the reflected intensity shows a minimum and the critical angle (θ_C) that is the incident angle above which the total internal reflection occurs [1] (see Fig. 2.18). The resonance angle and the whole SPR spectrum depend on different parameters, such as dielectric constants and the thickness of both the metallic thin film and its surrounding media (substrate and possible overlayers). However, the critical angle depends just on the refractive index of the quartz prism and the air. The total reflection takes place at the substrate/Au interface. When the laser passes from the prism to the substrate, according to Snell's law, the refraction keeps the component of the light wavevector parallel to the surface in both media constant. As the substrate/Au interface is illuminated in total reflection conditions, there is an evanescent field propagating through the second medium that does not suffer refraction but keeps the wavevector of the incident medium. The main limitation and advantage of the evanescent field is that it decays exponentially in the perpendicular direction to the interface, so its effects are limited to a few nanometers (see Fig. 1.14 in Chap. 1).

As the critical angle depends just on the refractive index of the quartz prism and the air, and these remain fixed in this work, we use this angle as parameter to adjust and normalize the SPR spectra. A slight drift of the rotating motor, on which sample and prism are mounted, was observed. In our measurements, this drift is corrected by adjusting the θ_C of the SPR spectra to a same value: using a quart prism with a refractive index of 1.457 for $\lambda = 633$ nm and assuming the air refractive index as 1, θ_C is 42.61° , taking into account the prism refractions.

In this work, this home-made device was used to measure and analyze the extended surface plasmon resonance (ESPR) in Au thin films, in order to study the characteristics of both the metallic film and the surrounding media.

2.10.1 Software to Measure SPR Spectra

Data of the laser beam reflected as a function of the incident angle were collected with a computer using a home-made VISUAL BASIC code. This software allows observing the SPR spectra while the measurements are performed (see Fig. 2.19). Besides this, it is possible to measure the laser intensity deflected by the beam splitter to a photodetector during the experiments. Therefore, we can examine both the SPR reflectivity and the same normalized by the laser intensity deflected (reference) as a function of the incident angle. The software allows the modification of measurement parameters such as the step per point, the integrating time in each measurement and the range of incident angle. This software generates files in the ASCII code for the data processing.

2.10.2 Reproducibility of SPR Spectra

Figure 2.20a shows five consecutive SPR spectra for a 52 nm Au film grown onto a glass substrate, which have been collected in the same conditions. The relative

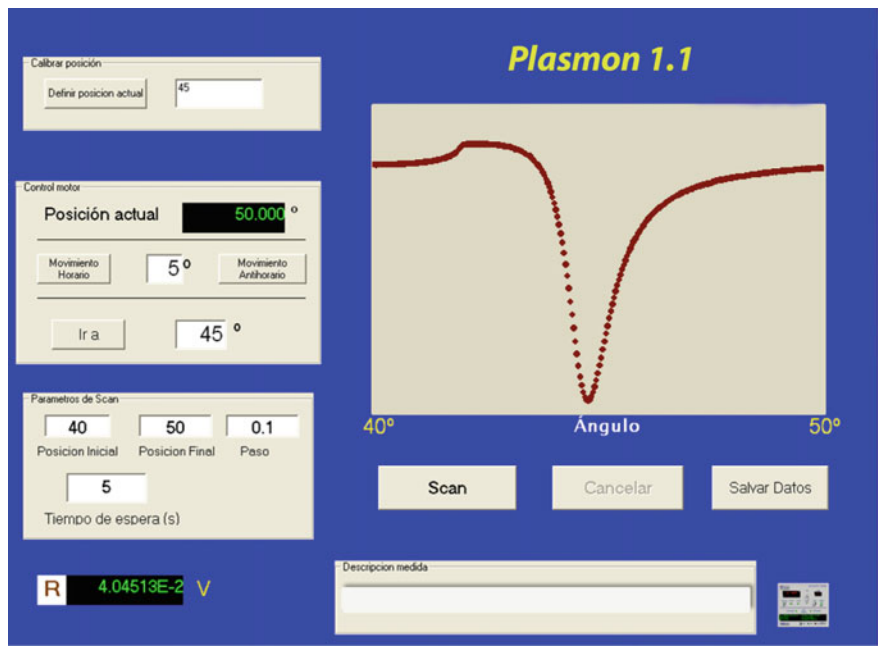


Fig. 2.19 SPR measurement with the home-made VISUAL BASIC code

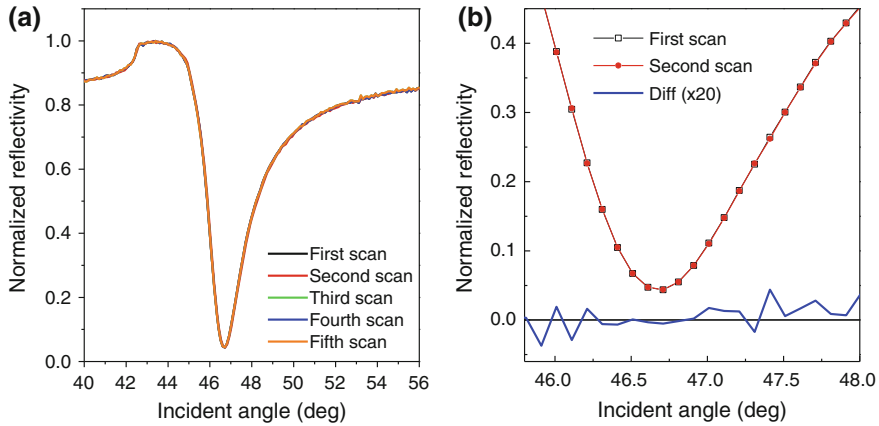


Fig. 2.20 **a** Consecutive spectra for a 52 nm Au film grown onto a glass substrate obtained with the SPR device shown in Fig. 2.16 and **b** a detail of the resonance region between the first and second scans and the difference in the scans (multiplied $\times 20$)

difference between the first and second spectra (see Fig. 2.20b) is of the order of $\Delta R/R = 10^{-2}$ for the whole region of the spectrum. Therefore, with this equipment, one can clearly detect relative differences below 1 % with single scans. The resolution of the measurement can be improved upon accumulation of scans (scans in Fig. 2.20 take 20 min each one). A drift of the SPR spectra was found due to the rotating motor, which was corrected adjusting the SPR spectra at the θ_C , as previously explained.

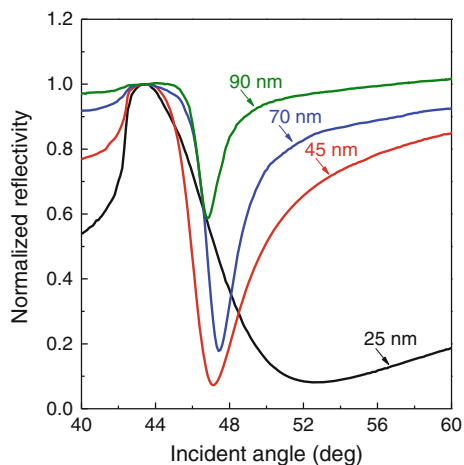
2.10.3 Capabilities of the Experimental Setup

By means of the SPR device, different kinds of samples can be measured. Some examples are presented here, in order to illustrate the information that can be extracted from SPR spectra.

Figure 2.21 shows the SPR spectra for Au films with different thicknesses. We can observe the dependence on the SPR spectra with the Au film thickness. For films thicker than 80 nm, the transmission of the evanescent field of the incident light decreases exponentially across the metallic film leading to a weak electromagnetic field at the metal/dielectric interface, while films that are too thin (25 nm Au film) exhibit reduced resonance due to SPR damping and there is no chance to excite them effectively.

The SPR setup can also be used to study organic and inorganic dielectric layers grown on top of the metallic film, since SPR spectroscopy is extremely sensitive to the features of the dielectric medium over the metallic film [1, 58, 59]. Figure 2.22a shows the SPR spectra for a 2 and 5 nm Co-phthalocyanine (CoPc) layer grown at RT on a 50 nm Au film deposited onto a soda-lime substrate. We can observe the

Fig. 2.21 SPR spectra for Au films with different thickness: 25, 45, 70 and 90 nm



changes of the SPR spectrum depending on the CoPc layer thickness: the larger the CoPc thickness, the larger the decrease of the intensity and the larger is the shift of the θ_R towards larger angles. Figure 2.22b shows the SPR spectra for a 5 nm CoPc layer grown at RT and 200 °C on a 50 nm Au film deposited onto a soda-lime substrate. The sample grown at 200 °C shows a shift towards smaller angles and a reduction in the reflectivity at the resonance, with respect to the sample grown at RT with the same thickness. Literature reports that the growth temperature changes the morphology and grain size of CoPc layers [60], modifying their dielectric permittivity. These modifications of SPR curves can be studied to determinate the changes in both real and imaginary parts of the refractive index of CoPc layers with great accuracy [61].

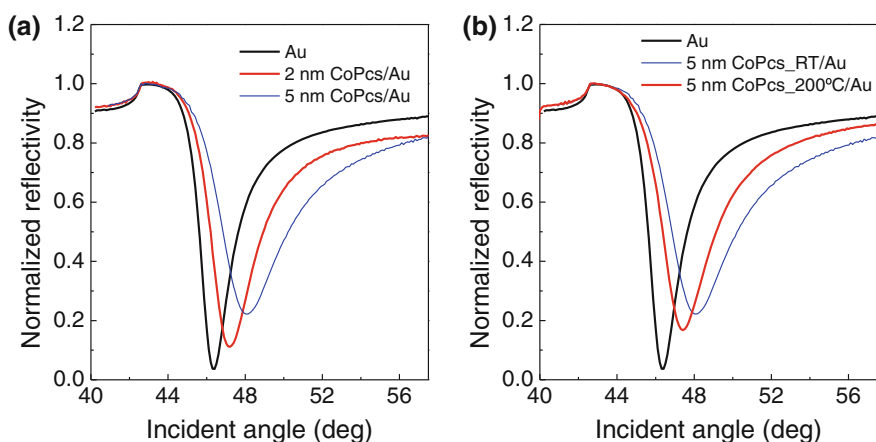


Fig. 2.22 SPR curves of **a** CoPc layers of 2 (red line) and 5 nm (blue line) nominal thicknesses grown at RT on a 50 nm Au film/soda-lime system and **b** CoPc layers of 5 nm nominal thickness grown at RT (blue line) and 200 °C (red line) on 50 nm Au film/soda-lime system

2.10.4 Software to Simulate SPR Spectra

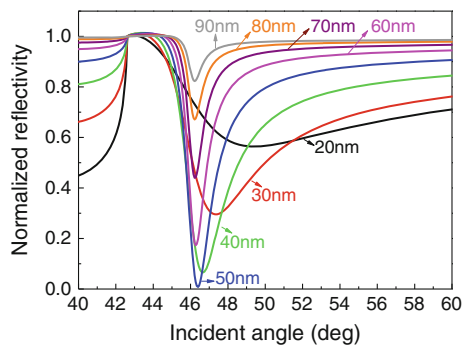
Simulations of SPR spectra were performed with the software Winspall [62] version 3.02, a freeware software to calculate and simulate SPR spectra with great accuracy. This code is based on the Fresnel equations, including the correction of both reflection and refraction of the coupling prism. The software allows taking into consideration parameters such as the kind of prism (i.e., triangular, semicircular), the excitation light polarization or wavelength, the spectral range and the number of points.

Given a system, the calculation of SPR curves can be performed knowing the parameters (thickness and dielectric constants) of each layer. The layers are the different media of one system. For the case of a Au film grown on a silica substrate, we have a four-media system: prism, silica substrate, Au film and air. If a dielectric overlayer is grown on the metallic film, then a five-media system should be considered. On the other hand, simulations of SPR spectra can be carried out for different systems. For that, we can fix the known parameters and leave free the unknown ones. Manual and iterative simulations can be achieved. A manual simulation is considered good by visual inspection while the iterative one shows a divergence, which represents the deviation between the simulated and measured spectra.

Figure 2.23 illustrates the calculated SPR spectra for Au films with different thickness [62], showing the dependence of the resonance curve with the Au film thickness. Parameters such as the resonance angle, reflected intensity and the bandwidth depend on the film thickness. That can be observed in Fig. 2.24a, which shows the variation of the reflectivity at θ_R as a function of θ_R for Au films with different thicknesses, from calculated SPR curves. We find that the reflectivity at θ_R decreases when the film thickness increases up to a certain thickness, around 50 nm, where the reflected intensity increases. Figure 2.24b illustrates the decrease of the θ_R when the Au film thickness increases up to a thickness of around 50 nm, from which the θ_R remains almost constant.

In this work, the software Winspall is employed to calculate SPR spectra for different systems knowing the parameters of each layer (dielectric constants and thickness of each media). Simulations of measured SPR spectra are carried out for

Fig. 2.23 Calculated SPR spectra for Au films ($\varepsilon_1 = -11.74$ and $\varepsilon_2 = 1.25$, according to Johnson and Christy [63]) with different thickness onto silica glass ($n = 1.457$ at $\lambda = 633$ nm)



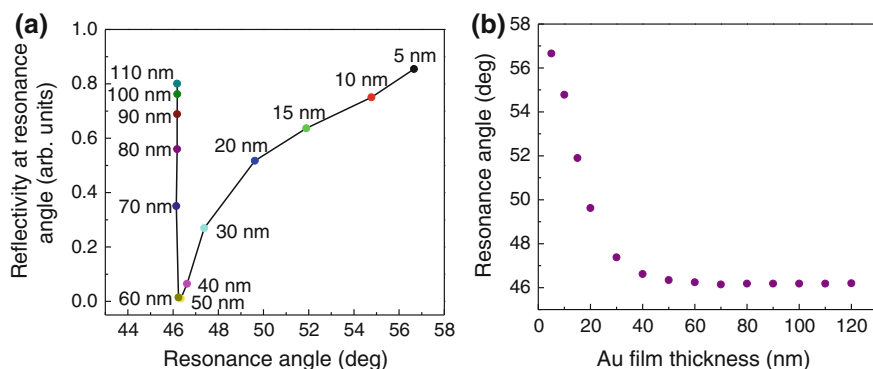


Fig. 2.24 **a** SP reflectivity as a function of the θ_R and **b** θ_R as a function of the thickness for Au films with different thicknesses. Data obtained from calculated SPR spectra

systems that show variations, in order to determine the modified layer and the new parameters [64] after modification. For each analyzed system, we show the kind of simulation, the free and fixed parameters, the values of the dielectric constants and the thickness of each layer.

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