

Preface

In this work, surface plasmon resonance (SPR) spectroscopy has been employed as a probe for studying modifications in nanostructured systems based on Au. These modifications include: (a) structural and morphological changes induced by annealing and (b) electronic modifications upon X-ray irradiation. The use of SPR spectroscopy to follow the evolution of modifications in nanostructures (especially, in situ and in real time) has been scarcely explored and its study results interesting and relevant for the plasmonic technology. For this, different experiments have been planned and performed:

- Fabrication of nanostructures from Au films and Au/Fe bilayers annealed under different conditions. Study by SPR spectroscopy of samples in order to follow the morphological changes of the systems varying the sample features (i.e., initial thickness) and the annealing conditions.
- The design and development of a SPR system based on the Kretschmann-Raether configuration compatible with an X-ray absorption spectroscopy (XAS) beamline (SPR-XAS setup).
- Study, using the SPR-XAS device, of the effects of the X-rays on glasses and Co-phthalocyanines (CoPcs). For the study on glasses, two different types are analyzed: soda-lime and silica substrates, and for the case of the CoPcs, these are grown varying the film thickness and the growth conditions.

For the realization of this work, samples have been fabricated by thermal evaporation and the characterization has been carried out using diverse spectroscopies and microscopies. For the case of studying surface plasmons (SPs), optical absorption spectroscopy and an experimental setup in the Kretschmann-Raether configuration, designed and developed for this work, have been employed.

In the first set of experiments, we have used SPR spectroscopy to study structural modifications of Au films and Au/Fe bilayers annealed under different conditions. For the Au films, these have been deposited on soda-lime substrates, varying their thickness, and have been further annealed in air at different temperatures, from 300 up to 500 °C. Films without annealing exhibit extended surface plasmons (ESPs), which depend on the film thickness [1, 2]. When samples are

annealed, the thermal treatments promote modification of the continuous films toward Au isolated islands, which show morphological features that depend on the Au film initial thickness and the annealing temperature [3–5]. In this work, we follow the transition from ESPs in the initial films toward localized surface plasmons (LSPs) in the final Au nanostructures. Besides, features of SPR are correlated with the structural and morphological modifications induced in the films with the annealing. Specifically, for films with initial thickness below 30 nm, upon annealing, the Au NPs exhibit LSPs while thicker films lead to large islands (dimensions larger than visible light wavelength) that can exhibit ESPs [6].

On the other hand, for the case of Au/Fe bilayers, these are grown on silica substrates under various configurations and annealed in air or low vacuum at different conditions of the thermal treatments. Bilayer annealing represents a new method to fabricate large areas of complex nano and microparticles, which we present here for the first time. The morphological features of the complex particles depend on parameters such as layer initial thicknesses, the disposition of the layers, and the annealing conditions (i.e., temperature, atmosphere) [3, 7]. In this case, annealing also induces the Fe oxidation [8]. Thus, depending on the annealing atmosphere we obtain Au/ α -Fe₂O₃ or Au/ α -Fe₂O₃– γ -Fe₂O₃ nanostructures. In this way, we can promote the separation of Au and FeO_x nanostructures or the growth of complex dimers using the proper annealing conditions. SPR is modified depending on the different strategies carried out to fabricate the complex structures, since both Au and FeO_x particles exhibit different morphological features that affect the SPs.

In order to study changes induced by an external source in matter using SPs as probe thanks to their high sensitivity, we choose the XAS technique to combine it with the SPR, since it is well known that X-rays induce modifications in many kinds of materials [9–13]. The combination of both techniques, to our knowledge, has never been achieved. Thus, in this work, we have designed and developed a setup combining SPR and XAS: the SPR-XAS setup, which allows different types of measurements in situ and in real time, recording SPR or XAS signals while scanning other parameters such as time, energy, etc. This device is currently available for future experiments at the ESRF beamline BM25A-SpLine [14].

With this SPR-XAS setup, SPR spectroscopy has been used to study the changes in the refractive index induced by X-rays on glasses and CoPcs. For the case of glasses, Au films are grown on glass substrates using two types of glass substrates: soda-lime and silica substrates. In soda-lime glasses, X-ray irradiation induces color centers: HC1 and HC2 centers [15, 16]. Comparing the experimental results with simulated data, we observe that both the real and the imaginary parts of the refractive index of soda-lime glasses change upon irradiation in time intervals of a few minutes. After X-ray irradiation, the effects are partially reversible and the defects responsible for these modifications fade by recombination with electrons. The kinetics of the defect formation and fading process are also studied in situ and real time, obtaining a slow process with a characteristic time of the order of months and a fast process with a characteristic time of the order of minutes, which has not been previously reported [17]. This component has been measured thanks to the

device developed, which allows monitoring changes during and immediately after irradiation. For the case of silica glasses, defects that modify their refractive index have been identified, but they are not detected at the laser wavelength used in the device. However, slight variations, of the order of 0.01 %, are observed and attributed to changes where the Au thin film is involved.

With respect to the study of CoPcs irradiated with hard X-rays using SPR as a probe, CoPc/Au samples are grown on silica substrates varying the CoPc thickness (from 2 to 10 nm) and the growth temperature: room temperature (RT) and 200 °C [18]. X-ray irradiation generates modifications on SPR spectra depending on CoPc thickness and growth temperature. The changes in SPR reflectivity and the full width at half maximum (FWHM) are larger for samples grown at RT than for those grown at 200 °C and independently of the growth temperature, thicker CoPc films show larger FWHM modifications of SPR spectra. Monitoring the reflectivity as a function of time, in real time and in situ, we observe that the induced reflectivity changes on samples are accumulative with time and slowly recover. Comparing the experimental results of SPR spectra with simulated data, we observe that the refractive index of the CoPc layers changes around 1.5–5 % depending on their thickness and growth conditions. These modifications of the refractive index are not related to structural changes and they are associated with electronic modifications induced by the irradiation [13].

The main conclusions related to this work are:

- The annealing of Au films or Au/Fe bilayers grown on glass substrates provides a method to modulate the morphological properties of the samples and with that, a process to tune the plasmonic properties in a wide range of applications and over large areas not easily achievable by other methods. Specifically, annealing of Au/Fe bilayers allows fabricating complex nanostructures combining plasmonic properties with others as catalytic or magnetic ones.
- Development of an experimental setup to study the effect of X-rays in real time and in situ. Useful information about the refractive index is obtained comparing the experimental results of SPR with simulated spectra: about the formation and fading processes of color centers in glasses and about the electronic changes varying parameters such as the thickness or the growth temperature of CoPc layers.

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