Report for ESRF Experiment 25-01 854

Coupling between Surface Plasmon Resonance and X-Ray Absorption in Co-Phthalocyanines/ Au bilayers

Introduction

Phthalocyanines (Pcs) represent an important type of semiconductor organic molecular solids that shows optical and electronic properties [1,2] with a wide range of applications, such as in solar cells [3], electrochromic devices, field effect transistors and light emitting diodes [4]. Pcs are thermally and chemically stable [5] and their versatility plays an important role in material science and technology [6]. However, an important obstacle of organic devices delays in the radiation damage [7,8]. Some studies can be found about the radiation damage on organic molecules, and concretely on Pcs. Cook *et al.* found that the irradiation with soft X-rays induces a shift in the Fermi level [8]. This modification on Pcs may be visible in their optical properties and moreover, the induced variations could depend on the Pc thickness and cristallinity [8, 9].

It is well known that the morphological properties of Pc thin films depend on the growth conditions among other parameters, controlling, thus, the degree of cristallinity, grain size and phase. In particular, the crystal structure of Pc films depends on the substrate temperature during deposition [10,11]. Usually, films deposited on amorphous substrates at room temperature (RT) produce the so-called α-phase while deposition temperatures above 150ºC lead to films with β-phase, which is characterized by elongated crystallites [10,12]. These phases exhibit different optical properties [13], therefore variations could be expect when Pc films are radiated.

We have recently developed a device for the measurement of Surface Plasmon Resonance (SPR) of metallic thin films at a synchrotron beamline [14]. The device follows the Kretschmann-Raether configuration and allows the simultaneous measurement of SPR and X-ray Absorption Spectroscopy (XAS). Hence, it permits the measurement of SPR *in situ* and real time while the system is being irradiated. SPR in metallic films is really sensitive to the features of the dielectric media (i. e., overlayers) [15]. Thus, measuring the SPR of metallic films while irradiating with X-rays allows studying changes in the real and imaginary parts of the refractive index of the layer deposited on the metallic film.

In this work we have prepared Au thin flms / Cobalt Pcs (CoPcs) onto silica glasses and used the above mentioned device to study *in situ* the effects of X-ray irradiation on the CoPcs , depending on CoPc film thickness and growth conditions.

Experimental setup

CoPc/Au samples were prepared in a Molecular Beam Epitaxy system with a base pressure of $1.5x10^{-10}$ Torr and a deposition pressure around $7x10^{-9}$ Torr . A 60 nm Au film was first deposited on silica glass substrate (1 mm thick) by electron beam evaporation. Then a CoPc thin film was thermally evaporated covering only half of the sample (Figure 1). Samples with CoPc films with nominal thicknesses of 2, 5 and 10 nm were prepared on substrates at RT and at 200 ^{o}C. Deposited Au and CoPc thicknesses were controlled by a quartz crystal microbalance which was calibrated using X-ray reflectometry performed on similar samples.

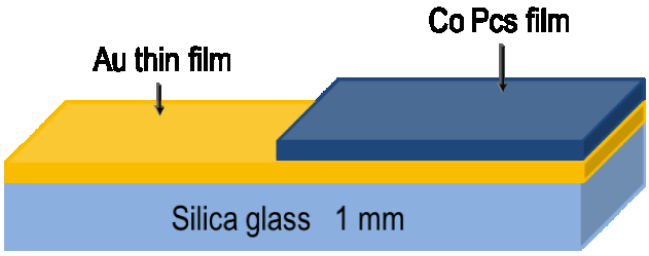


Figure 1. Scheme of the samples.

Experiments were carried out at the branch A of the BM25 SpLine beamline at the European Synchrotron Radiation Facility (ESRF) in Grenoble (France). This is a hard X-rays beamline arranged to perform X-ray Absorption Spectroscopy (XAS). The energy range of X-rays is between 5 and 45 keV and the flux is of the order of 10^{12} photons/s at 200 mA ring current [16]. In the experimental hutch, we have mounted the SPR device previously described [14]. Figure 2a shows a scheme of the system which follows the Kretschmann-Rather configuration [15]. Briefly, the sample is attached to a quartz prism (n=1.457 at λ= 633 nm) through the glass side using gel index matching. The sample is illuminated with a laser through the prism side in total reflection conditions. The evanescent field propagates across the Au film reaching the Au/air interface. For the proper incidence angle, the dispersion relation of the evanescent film matches that of the surface plasmons that are excited at the Au/air interface. The electromagnetic field propagates through the Au film towards the glass and interferes destructively with the incidence laser beam, reducing the intensity of the reflected beam. Recording the intensity of the reflected beam as a function of the incidence angle yields the SPR curve as that shown in figure 2b. The device

allows detecting a relative variation in the curve of the order of 10^{-3} -10^{-4} [14]. The proper performance of the device was tested comparing the SPR spectrum measured for a 60 nm Au film grown onto silica glass with a simulated spectrum, as shown also in figure 2b.

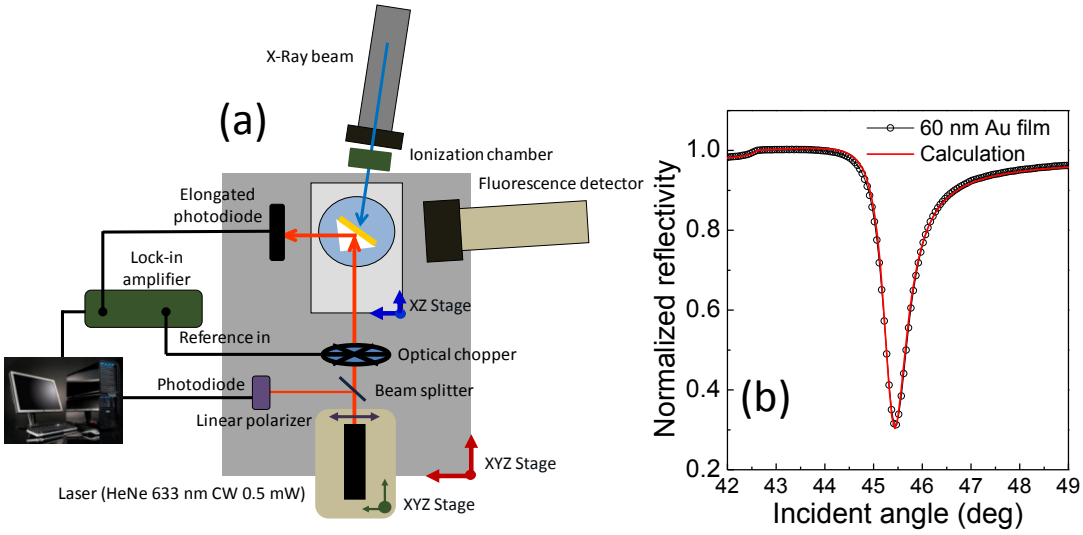


Figure 2. (a) Scheme of the device for simultaneous SPR and XAS measurements. (b) Experimental (black points) and calculated (red solid line) SPR curve of a 60 nm Au film on silica substrate without X-ray irradiation.

Experimental SPR spectra were measured before, during and after X-ray irradiation at 7.72 keV, that corresponds to the Co K edge. The X-ray irradiation of each sample was performed around 60 min.

Simulations of SPR spectra were performed with *Winspall*, a freeware software to simulate SPR spectra with great accuracy [17]. This code is based on the Fresnel equations for the system, including the correction of both reflection and refraction of the coupling prism.

Results and discussion

- SPR of Au thin films irradiated with X-ray

The quality of the Au film (in particular thickness and roughness) may cause variations in the SPR spectrum profile [18,19,20]. Thus, for the analysis of the CoPc/Au bilayers SPR spectra, it is required to characterize previously the spectra of the bare Au film. For this purpose, we measured SPR spectra in the region of the samples with the bare Au film with and without X-ray irradiation at 7.72 keV for 60 min. Figure 3 shows the results related to the bare Au film for 5 nm

CoPc grown at RT on Au film. A detail of the resonance region reveals that X-ray irradiation induces changes on SPR spectra, decreasing the reflected intensity around 0.003 and widening the resonance region about 0.01º. Moreover, we observed that these variations are mostly irreversible and after switching off the X-ray the effects remain.

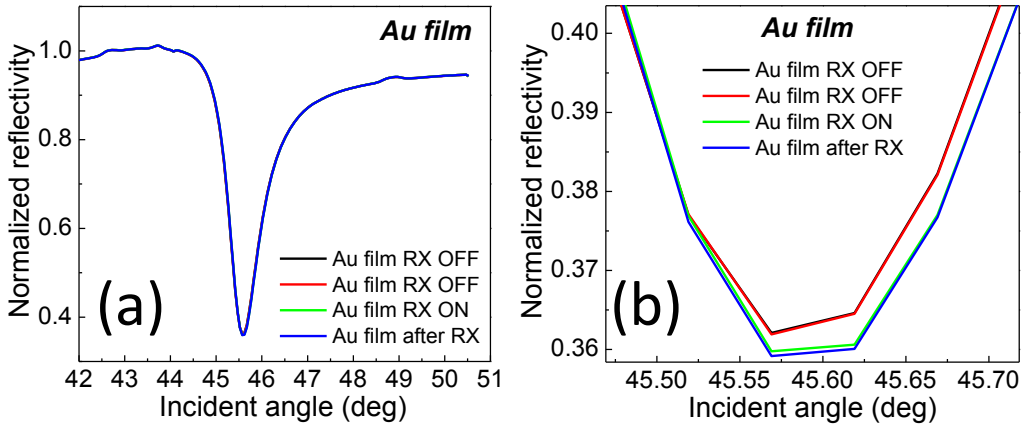


Figure 3. SPR curves for an Au film on silica glass before (black and red lines), during (green line) and after (blue line) irradiation with 7.720 keV X-rays. (a) Spectra normalized at the critical angle and (b) a detail of the resonance region.

- SPR of Co Pcs/ Au bilayers irradiated with X- ray

Figures 4, 5 and 6 show the results of experimental SPR spectra, with and without X-ray irradiation at 7.72 keV, related to CoPc films with thicknesses 2, 5 and 10 nm respectively, grown at RT and 200ºC on Au film. In all Co Pcs/Au bilayers, when they are irradiated with X-ray for 60 min, we observed modifications in the resonance region which depend on Co Pcs thickness and growth conditions. Moreover, we could see the effects related to X-ray are mostly permanents.

For 2 nm CoPcs grown at RT on Au film (see Figure 4a and 4b) we could observe that the resonance region is widening around 0.03º, is shifted toward larger angles about 0.01º and the intensity decreases 0.01, however when samples were grown at 200ºC (see Figure 4c and 4d) the resonance region is widening around 0.02º, is shifted toward lower angles about 0.02º and the intensity decreases 0.006. For 5 nm CoPcs grown at RT on Au film (see Figure 5a and 5b) we could observe that the resonance region is widening around 0.06º, the intensity decrease 0.01 and is shifted towards larger angles around 0.03º, however when samples were grown at 200ºC (see Figure 5c and 5d) the resonance region is widening around 0.03º, is shifted toward lower

angles about 0.04º and the intensity increases 0.004. For 10 nm Co Pcs grown at RT on Au film (see Figure 6a and 6b) we could observe that the resonance region is widening around 0.08º, the intensity decrease 0.003 and is shifted towards larger angles around 0.03º, however when samples were grown at 200ºC (see Figure 6c and 6d) the resonance region is widening around 0.06º, is shifted toward larger angles about 0.03º and the intensity increases 0.006. Therefore , as we can observe in Figures 4, 5 and 6 and table 1, modifications induced by X-Ray irradiation in SPR spectra of Co Pcs/Au bilayers are larger for the samples grown at RT than at 200ºC and they depend on Co Pcs thickness as well.

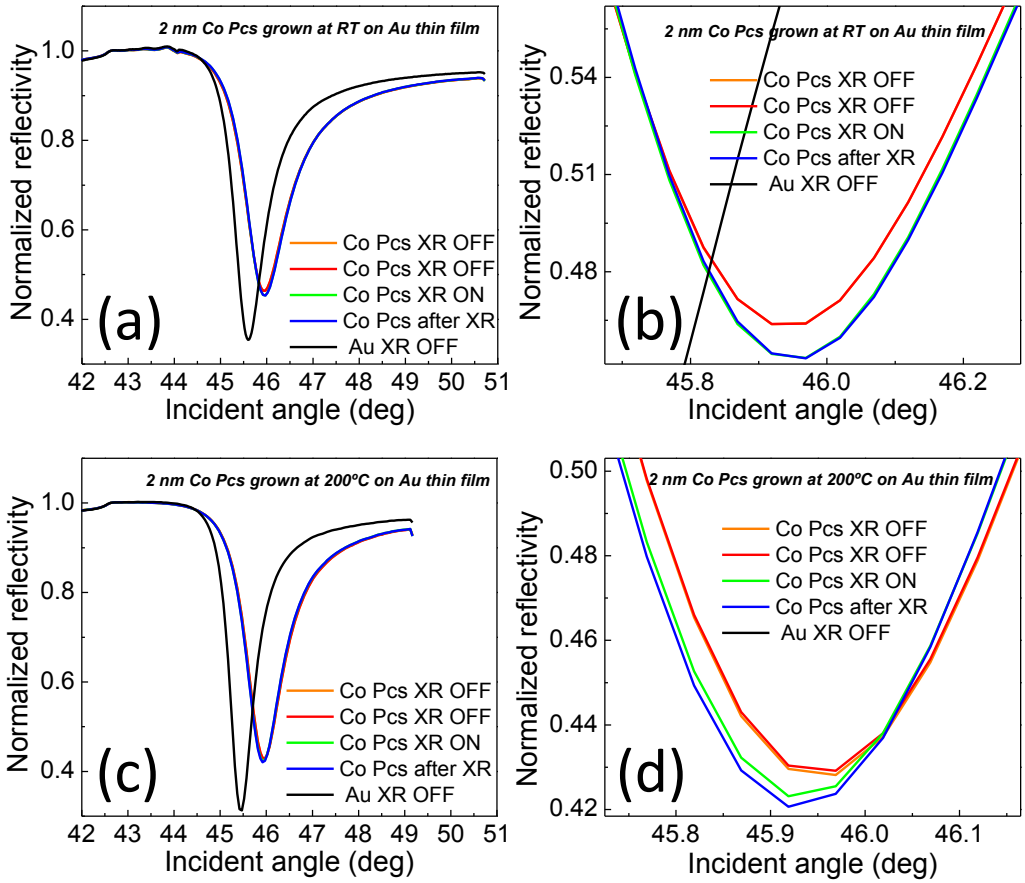


Figure 4. SPR curves for a 2 nm CoPcs/ Au bilayer on silica glass before (black and red lines), during (green line) and after (blue line) irradiation with X-rays at 7.72 keV. (a) Spectra normalized at the critical angle and (b) a detail of the resonance region for CoPcs grown at RT and (c) Spectra normalized at the critical angle and (d) a detail of the resonance region for CoPcs grown at 200ºC.

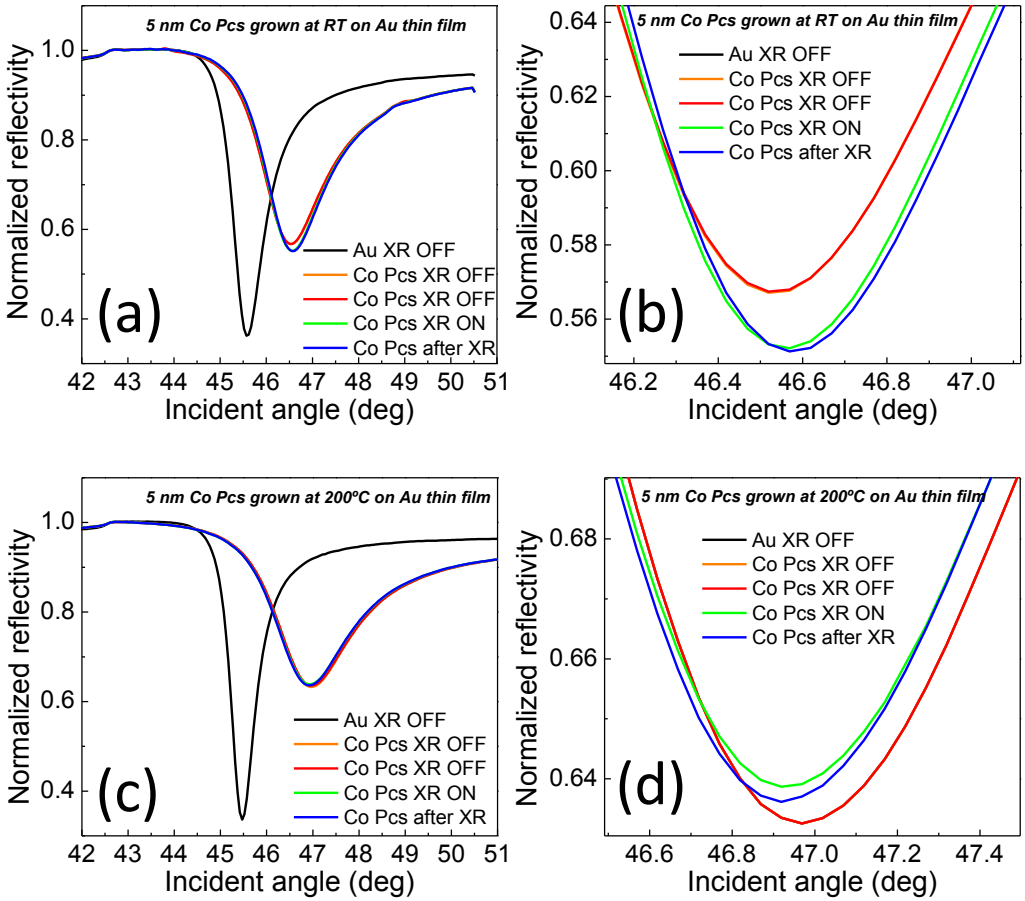
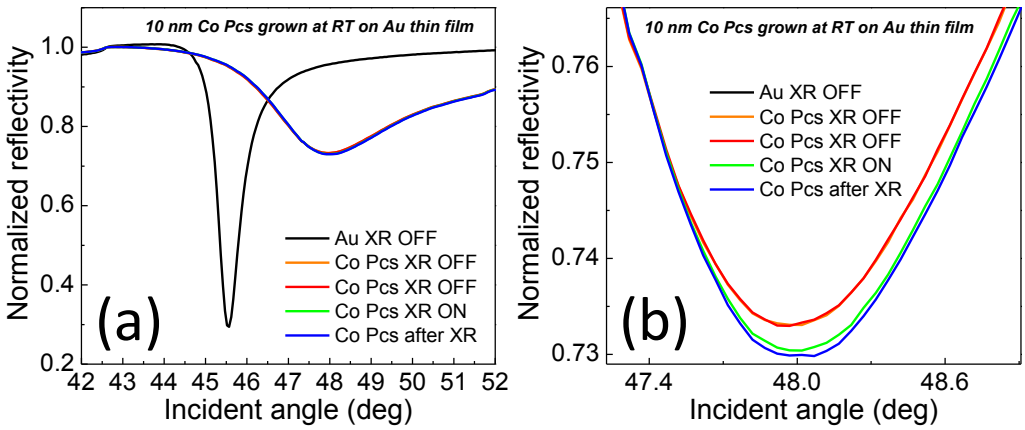


Figure 5. SPR curves for a 5 nm CoPcs/ Au bilayer on silica glass before (black and red lines), during (green line) and after (blue line) irradiation with X-rays at 7.72 keV. (a) Spectra normalized at the critical angle and (b) a detail of the resonance region for CoPcs grown at RT and (c) Spectra normalized at the critical angle and (d) a detail of the resonance region for CoPcs grown at 200ºC.



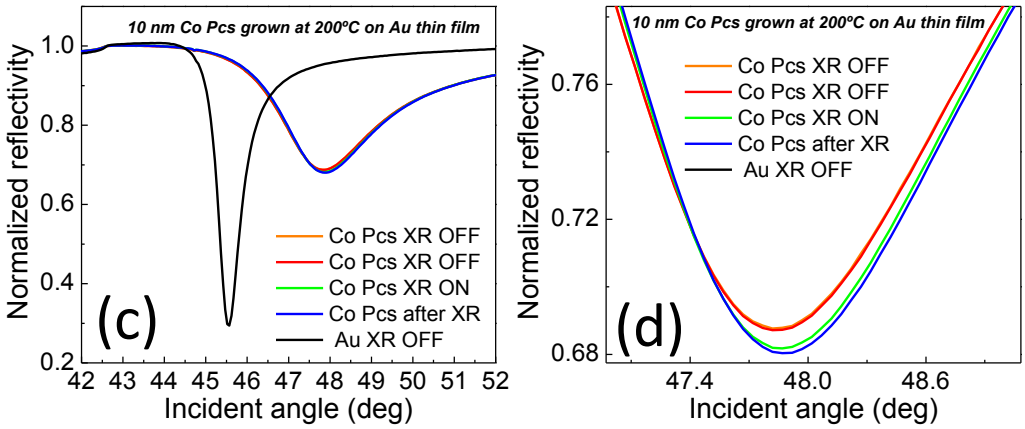


Figure 6. SPR curves for a 10 nm CoPcs/ Au bilayer on silica glass before (black and red lines), during (green line) and after (blue line) irradiation with X-rays at 7.72 keV. (a) Spectra normalized at the critical angle and (b) a detail of the resonance region for CoPcs grown at RT and (c) Spectra normalized at the critical angle and (d) a detail of the resonance region for CoPcs grown at 200ºC.

X-ray effects	Bare Au	Au/2nmCoPc RT	Au/2nmCoPc 200ºC	Au/5nmCoPc RT	Au/5nmCoPc 200ºC	Au/10nmCoPc RT	Au/10nmCoPc 200ºC
Widening (º)	0.01	0.03	0.02	0.06	0.03	0.08	0.06
Shift (º)		+ 0.01	-0.02	+ 0.03	-0.04	+ 0.03	+ 0.03
Intensity	+0.003	+ 0.01	+ 0.006	+ 0.01	-0.004	+ 0.03	+ 0.006

Table 1. Modifications in the resonance region after X-ray irradiation at 7.72 keV, for 60min. (The + / - symbol represents SPR changes due to the irradiation towards larger/slower values with respect to the SPR spectrum of samples without irradiating).

In order to analyze the changes induced on the dielectric constants when Co Pcs/Au bilayers on silica substrates are irradiated with X-ray, we have performed the SPR simulations varying the refractive index of the modified layer (CoPc film), in our five-media system, in order to reproduce the experimental results presented in Figure 7 for the 2 nm CoPc grown at 200ºC on Au thin film. The refractive index of Co Pcs film upon X-ray irradiation is determined by fitting the experimental SPR curve. In this fit, the refractive index of the Co Pcs layer is the only free parameter, while the rest of parameters remain fixed with the same value as those prior to X-ray irradiation. We can obtain a very good agreement with the experimental results assuming that the refractive index of

the modified layer upon irradiation changes from n_{layer} =1.93 + 0.37i (non-irradiated value) to n_{layer} =1.87 + 0.33 i, (see Figure 7), around 10 %.

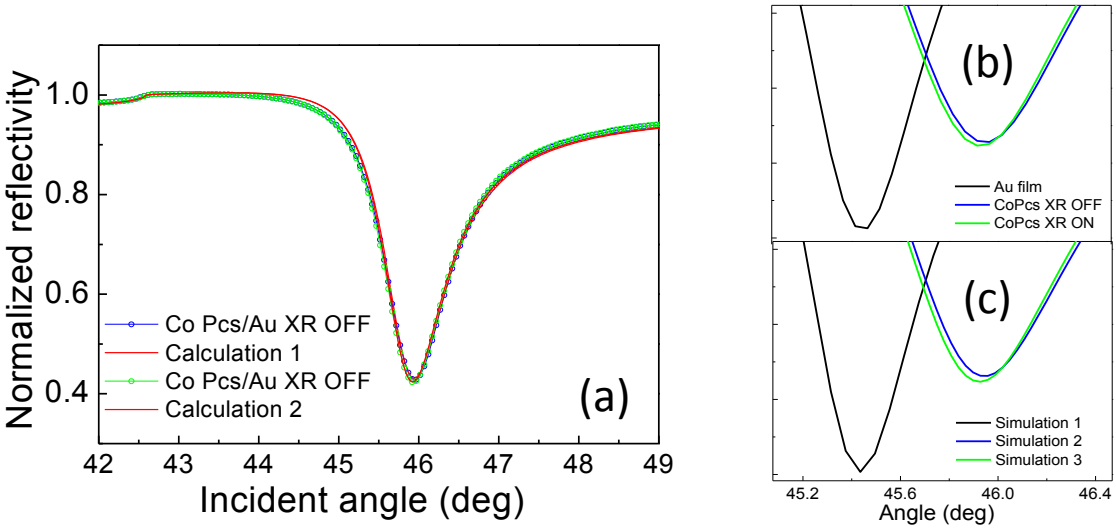


Figure 7. (a) Calculated and experimental SPR curves for a 2 nm CoPcs/ Au bilayer on silica glass before and after irradiation with 7.72 keV X-rays, (b) a detail of resonance region of experimental spectra and (c) a detail of resonance region of calculated spectra.

Using the same SPR device, we have measured the reflectivity for a fixed incident angle close to the resonance (45.6º) when switching on and off the X-rays irradiation. These measurements could, in principle, have been carried out without the Au thin film or in transmission mode using the same setup, but measuring in this configuration we could obtain information of changes on refractive indexes of samples by SPR curves. Figure 8 shows the effect of X-rays irradiation on a 2 nm Co Pcs film grown at RT, at 7.75 keV, above the Co K edge. The results confirm that the reflectivity decreases upon irradiation with X-ray and after irradiating the reflectivity is partially recovered, remaining mostly stable.

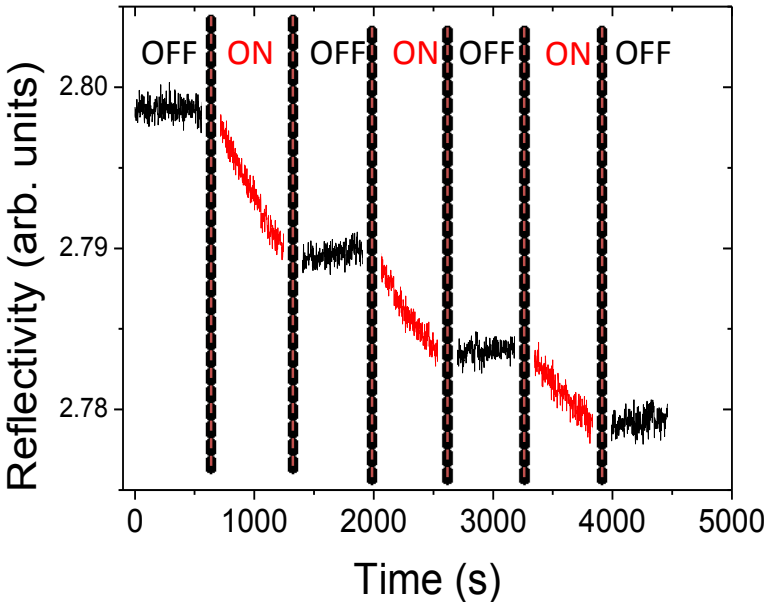


Figure 8. The time dependence of the reflectivity when switching on and off the X-rays at 7.75 keV, *in situ* and in real time.

Therefore, we can say that CoPc/Au samples irradiated with X-ray show SPR spectra modified with respect to samples without irradiating. Studying bare Au thin films in the same conditions that CoPcs/Au bilayers we could discard the effects induced by X-ray on samples are due to modifications on Au films / silica substrate system. Therefore, X-ray irradiation induces changes on CoPc films modifying their refractive index around 10%, depending on the CoPc film thickness and growth conditions. As it is well known, the physical properties of Co Pcs depend on the film thickness due to charge transfer processes. Moreover the substrate temperature during deposition of Co Pcs films controls the formation of crystals with distinct molecular arrangements [21,22]. Therefore, the different modifications of CoPc SPR spectra observed after X-ray could be due to the different properties of the molecules depending on the thickness and growth conditions.

The experiments were performed by SPR system in the beamline hutch, in the air. In order to discard that the observed effects on SPR spectra are due to an instable conductivity in Co Pcs and/or the adsorption, induced by irradiation, of molecular or atomic species or impurities on the surface of CoPc layer, such as atomic oxygen when the surface is eventually exposed to the ozone produced by synchrotron radiation, it requires the experiments under Ar or He atmosphere to avoid possible adsorption on the Co Pcs surface and the conductivity of them is stable.

Conclusions

We have studied the effect of hard X-ray (7.72 keV) irradiation on CoPcs layers grown at RT and 200ºC onto Au film/silica substrate system. For this aim, we have used a developed experimental setup, capable of simultaneously measuring XAS and SPR at a synchrotron beamline. Using SPR spectroscopy as a probe we could monitor that the induced changes of the refractive index in the CoPc layers are around 10%, depending on the layer thickness and growth conditions. Monitoring, in real time and *in situ*, the reflectivity as a function of time, we have determined that the induced effects on Co Pcs layer are accumulatived with the time and mostly irreversible.

References

[1] Georgi L. Pakhomov, Solid State Communications 134, 491–495 (2005)

[2] Phthalocyanines: Properties and Applications, ed. C. C. Leznoff and A. B. P. Lever, VCH, Weinheim, 1989, 1993, 1996, vols. 1–4

[3] J. G. Xue, B. P. Rand, S. Ushida, S. R. Forrest, *Adv. Mater. 17,* 66 (2005).

[4] R. F. Service, *Science*, *310*, 1762 (2005)

[5] Gema de la Torre et al., Chem. Commun., 2000–2015 (2007).

[6] Sandrine Heutz et al. , Adv. Mater., 19, 3618–3622 (2007).

[7] G. Cabailh et al., Applied Surface Science 234 144-148 (2004).

[8] Peter L. Cook et al., The journal of Chemical Physics 131, 214702 (2009).

[9] Benny Joseph and C. S. Menon,, E-Journal of Chemistry, Vol. 5, No. 1, pp. 86-92 (2008).

[10] C. W. Miller, A. Sharoni, G. Liu, C. N. Colesniuc, B. Fruhberger, I. K. Schuller, Phys. Rev. B 72, 104113 (2005).

[11] K. P. Gentry, T. Gredig, I. K. Schuller, Phys. Rev. B 80, 174118 (2009).

[12] S Ikeda Ikeda, H. Yamakawa, M. Kiguchi, M. Nakayama, K. Saiki, T. Shimada, T. Miyadera, K. Tsutsui and Y. Wada Mol. Crys Liq. Cryst. 455, 347 (2006).

[13] Study of Co-Phthalocyanine films by Surface Plasmon Resonance spectroscopy, J. Appl. Phys., 113, 113104 (2013)

[14] A. Serrano, O. Rodríguez de la Fuente, V. Collado, J. Rubio-Zuazo, C. Monton, G. R. Castro and M. A. García; Rev. Sci. Inst., 83, 083101 (2012)

[15] H. Raether, *Surface Plasmons on smooth and rouge surfaces and on gratings*. ed. Springer-Verlag (1988)

[16] G.R. Castro, J. Synchrotron Rad. 5, 657 (1998).

[17] We simulated the spectra with the *Winspall* freeware code: http://www.mpip-mainz.mpg.de/knoll/soft/

[18] A. Kolomensky et al., Appl. Opt. 48, 5683 (2009).

[19] Braundmeier et al., J. Phys. Chem Solids 35, 517 (1971).

[20] S. Zhang, L. Berguiga, J. Elezgaray, T. Roland, C. Faivre-Moskalenkoa, F. Argoul, Surf. Sci. 601, 5445 (2007).

[21] C. Schünemann, C. Elschner, A.A. Levin, M. Levichkova, K. Leo, M. Riede, Thin Solid Films, 519 3939 (2011).

[22] Yuh-Lang Lee, Wen-Ching Tsai, Jer-Ru Maa, Appl. Surf. Sci. 2173 352 (2001).