ESRF	**Experiment title:** Oxidation of Graphite promoted by Co oxides as a method to obtain Graphene: a GIXRD study of the oxidized Graphite surface	**Experiment number**: 25-02- 816
Beamline: BM 25 B	**Date of experiment**: from: 11/09/2013 (08:00) – 14/09/2013 (08:00)	**Date of report**: 30/01/2015
Shifts: 9	**Local contact(s)**: **J. RUBIO ZUAZO**	*Received at ESRF:*

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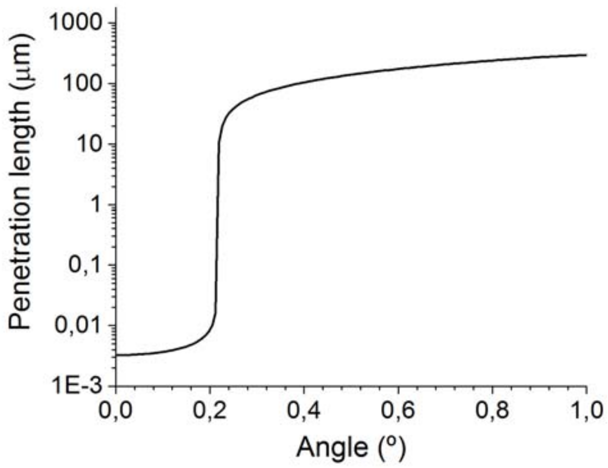
Report:

The main goal of this project was the in-depth study of the lattice parameter of graphite upon deposition of cobalt oxides layers which is expected to vary from the Graphite substrate upon oxidation. Grazing Incidence X-Ray Diffraction (GIXRD) is a suitable technique for this purpose. By exploring the difractograms obtained when varying the ℓ index the in depth information of the lattice parameter can be obtained. In previous works in this system using low energy X-Ray Absorption and photoemission Spectroscopies we have observed the oxidation of the HOPG graphite surface promoted by CoO [1].

To this end, we have measured different sets of samples grown in our Laboratory. All of them initially contained a CoO layer grown on HOPG at room temperature. Then, these samples with coverages ranging from 2 to 20 equivalent monolayers (Eq.ML) were submitted to reactive thermal annealing at different temperatures in the range 200º-400ºC, for different annealing times for 30 min to 120 min. As a way to measure the degree of oxidation of the HOPG substrate, i.e. the in-depth variation of the lattice parameter with respect to pure HOPG, GIXRD scans along the (1 0 ℓ) direction were performed at the B branch of the SpLine beamline at the ESRF for different sample-beam angles, ranging from 0 to 5°. A clean HOPG sample was also measured for reference purposes.

Figure 1 shows the penetration depth calculated for x-rays of hυ=15 keV as a function of the incidence angle (grazing incidence). It is seen a strong variation of the penetration depth for angles close to the total reflection angle (0.24º) and a slight variation for larger angles. The interplanar distances of the HOPG substrate as a function of the penetration depth are depicted in Figure 2. The results show almost no variation of the



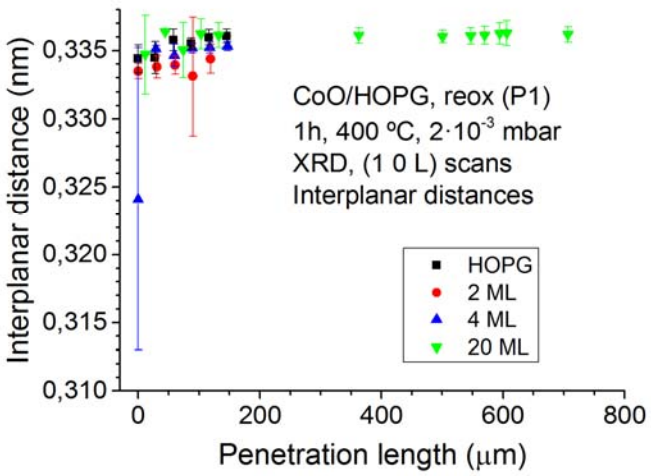
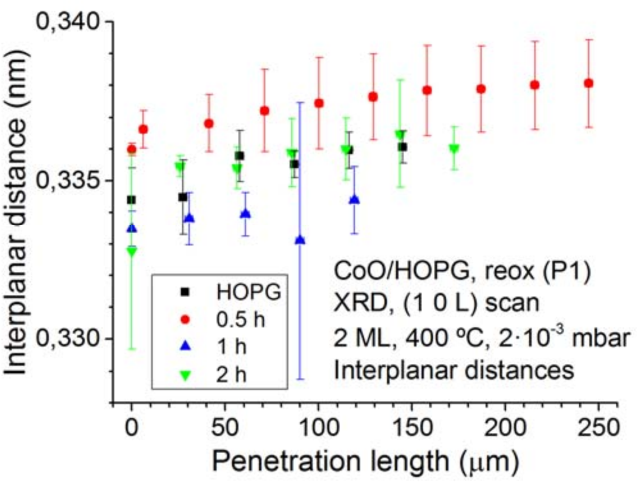


Figure 1: penetration depth calculated for x-rays of hυ=15 keV as a function of the incidence angle (grazing incidence)

Figure 2: Interplanar distance in HOPG as a function of the penetration depth for sample of 2, 4 and 20 Eq.-ML.

interplanar distances with depth. The thickest sample (20 ML) could be measured for a larger range of incident angle. The results, in general, does not show an increase of the interplanar distances at the surface as expected in the outer planes of oxidized HOPG.



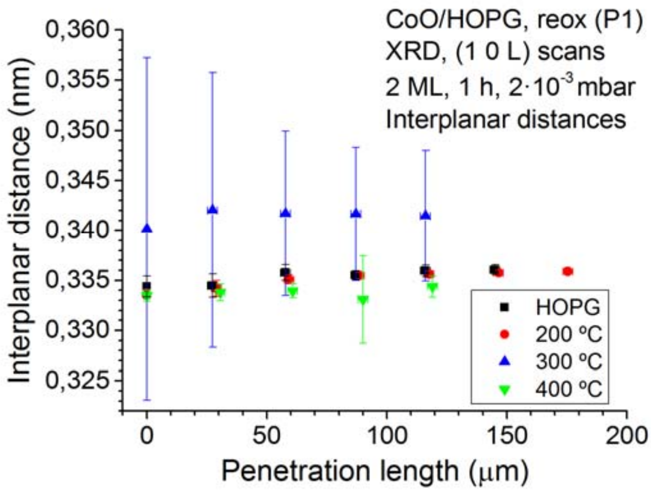


Figure 3: Interplanar distance in HOPG as a function of the penetration depth for samples with coverages of 2 ML and submitted to annealing at 400ºC for 0.5, 1 and 2 h.

Figure 4: Interplanar distance in HOPG as a function of the penetration depth for samples with coverages of 2 ML and submitted to annealing for 1h at: 200º, 300º and 400ºC.

Figure 3 shows the interplanar distances in HOPG as a function of the penetration depth for samples with coverages of 2 ML and submitted to annealing at 400ºC for 0.5, 1 and 2 h. As in the previous case, these results do not show tsuch increase of the interplanar distances of the outer HPG planes, however it shows a samll variation of this parameter as a function of the annealing duration. On the other hand, Figure 4 shows Interplanar distance in HOPG as a function of the penetration depth for samples with coverages of 2 ML and submitted to annealing for 1h at: 200º, 300º and 400ºC. In this case, also no variation of the interplanar distances with depth is observed.

As conclusions, we can say that the experiments have not been successful enough to observe the expected variation of the interplanar distances. The reason for this fail is probably the lack of in depth resolution (in the range of μm) of this method to analyzed this system whose dimensions are of the order of a few nm.

References:

[1] D. Díaz-Fernández, J. Méndez, A. del Campo, R.J.O. Mossanek, M. Abbate, M.A. Rodríguez, G. Domínguez-Cañizares, O. Bomatí-Miguel, A. Gutiérrez, L. Soriano, "Nanopatterning on highly oriented pyrolytic graphite surfaces promoted by cobalt oxides". Carbon 85, 89 –98, 2015.