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	Experiment title:	Experiment number:
	Fe, Co and Ni impurities on graphene/SiC{0001}: graphene as a mediator for magnetic interactions	HE3417
Beamline: ID08	**Date of experiment**: from: 8.09.2010 to: 15.09.2010	**Date of report**: 14.03.2011
Shifts: 18	**Local contact(s)**: V. Sessi	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report

The aim of the experiment HE3417 was to study the magnetic properties of transition metal (TM) atoms deposited at low temperatures on graphene-like substrates. In particular, the value of the magnetic spin and orbital moment and the occurrence of long range magnetic interactions were under scrutiny. These measurements were intended as a test for recent theoretical calculations concerning a free-standing graphene layer which predict i) changes in the electronic configuration of adsorbed TM atoms [1-2], resulting in a significant reduction of the magnetic moments compared to the free atom case and ii) doping dependent, sizable RKKY interactions and magnetic screening effects ([3] and Refs. therein, [4]).

HE3417 suffered of several technical problems that did not allow us to use completely the 18 shifts. The main problem was the pressure in the magnet chamber, at the beginning of the experiment in the 10^{-9} mbar range which was too high for our purposes and required an additional bake-out.

However, we could study extensively one element, Co, for several experimental conditions. We have investigated (i) the effect of interaction with the substrate and (ii) time effects occurring after a few hours after the deposition.

These experiments have been extended during in-house beamtime by means of different TM elements and further investigation of the atomic impurity limit. The results are still under evaluation.

In this report we summarize only the measurements made during the experiment HE3417.

Experimental

The effect of hybridization of the Co *d* orbitals with the Carbon π band has been studied, by means of 4 substrates with different electronic properties: a few layers of graphene grown on the C-terminated surface of 6*H*-SiC(000-1) (FLG), a single layer of graphene grown on the Si-terminated surface of 6*H*-SiC(0001) (SL), Highly Oriented Pyrolitic Graphite (HOPG) and single layer graphene grown by Chemical Vapour Deposition (CVD) on Rh(111) (labelled as g/Rh(111)). Graphene-like substrates employed in the experiment have be grown ex-situ in the facilities of the Institut Néel in Grenoble as described in Refs. [5-6]. After air exposure the clean surface was recovered by annealing at 700°-900°C under UHV conditions. Sample cleanliness has been verified by Low Energy Electron Diffraction (LEED) and Scanning Tunneling Microscopy (STM). HOPG substrates have been instead cleaved directly before the measurements.

Deposition of 3*d* metal atoms has been performed at lowest temperatures available (~8K) in the magnet chamber, by means of electron bombardment evaporators. X-ray Absorption Spectroscopy (XAS) and X-ray Magnetic Circular Dichroism (XMCD) measurements have been performed at the Co $L_{3,2}$ absorption edges positioned at 778eV and 793eV, as a function of coverage, magnetic field and angle between magnetization and incident beam.
In the following, we report preliminary results about XAS, XMCD and magnetization versus magnetic field measurements for the same coverage of Co on the four substrates.

Results

For a Co coverage corresponding to **few percent of monolayer**, no large differences are found in the **XAS** spectra measured on the different samples. However, the XAS shape found in our experiments is different from what observed for other Co atoms on metals, for example Co on Pt(111). A shoulder exists at a few eV above the L_3, particularly pronounced for Co on the SiC{0001} samples that seem to be a carachteristic of this Co/Carbon systems.
We have observed a substrate dependent long range (t > 4h) **time effect** on the XAS spectra. We refer to measurements made right after deposition as time 't=0'. These measurements are summarized in Fig.1. Time effects are extremely pronounced for Co on the graphene/SiC{0001} substrates where they lead to multiplet splitting features that are not present right after deposition and to a decrease of the dichroic signal (Fig. 1 (a-b)). On HOPG instead a progressive broadening of the spectra are observed with time, and only a very slight multiplet splitting (Fig. 1 (c)). Finally for Co on g/Rh(111) no significant time effect was observed, neither in the XAS nor in the XMCD signal (Fig. 1 (d)).
In order to estimate the origin of the multiplet splitting in Co/SiC{0001} we performed a deposition at 30K on a FLG sample, to promote eventual atomic diffusion and occupation of preferential sites (the hole sites).

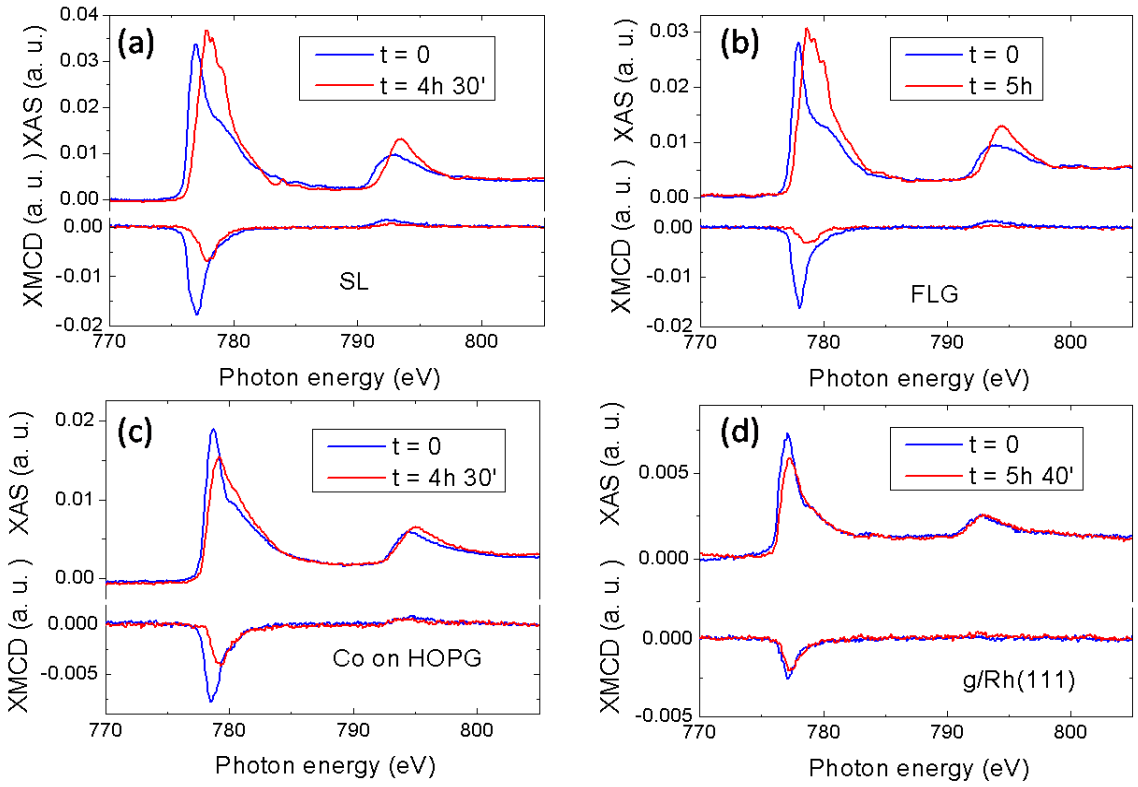

Figure 1: XAS and XMCD signals recorded with a 5T field perpendicular to the surface plane for Co deposited at 8K on the four different substrates indicated in the figures. The measurements are shown right after Co deposition (time t =0) and after several hours. Very strong time effect id observed for Co on the SiC {0001} samples, leading to multiplet splitting that was absent at time t = 0. For Co on HOPG we observe a broadening of the spectra and reduction of the dichrosim but no multiplet splitting. Finally for Co on g/Rh(111) we see no substantial variations after more than 5h.

However, no difference has been found in the XAS shape compared to deposition at 8K. This suggests that the observed time effect is not due to thermally activated diffusion of atoms on the surface.
The latter might instead be due to adsorption of O_2 molecules in the proximity of the Co nanostructures, for example on top of Co. An eventual crystal field, present on the SiC samples but not on the HOPG, might then lead to the observed line shapes for Co on FLG and SL substrates. These ideas need to be verified by theoretical simulations.
Since the time constant of the time effect was of several hours, we could always take a snapshot at $t = 0$ that was considered as the virgin system state. Results are reported in Fig.2 (a). Co on SiC{0001} substrates shows large values of the **XMCD** over **XAS** peak ratio at the L_3 absorption edge and pronounced magnetic anisotropy. On the HOPG samples the XMCD/XAS ratio is smaller and there is no magnetic anisotropy. Finally, on the monolayer graphene on Rh(111) the XMCD/XAS ratio is even smaller than on the HOPG. S-shape **magnetization** versus magnetic field loops, with almost saturated magnetization at 5T are found with the exception of the g/Rh(111) where the saturation occurs at much higher magnetic fields (Figs. 2(b-e)). It is reasonable to attribute these differences to the different nature and strenght of the chemical bond between Co nanostructures and substrate but a more quantitative analysis is needed. For this coverage, **no remanent magnetization at zero magnetic field was found for all the four samples.**

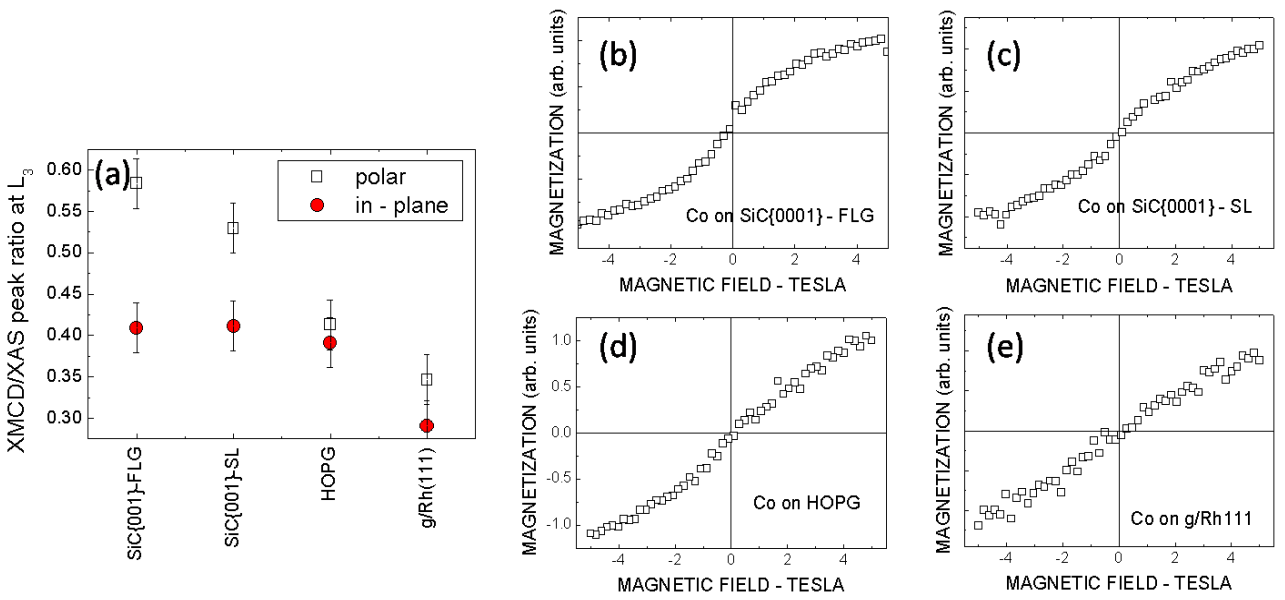

Figure 2: Measurements at *t*=0*:* (a) Ratio between the peak height at the Co L_3 absorption edge of the XMCD and XAS signals with the magnetic field parallel (in-plane) or perpendicular (polar) to the surface for Co on the four substrates investigated. This signal is proportional to the average Co magnetization along the applied magnetic filed. From this plot evidences a pronounced anisotropy of the magnetization for Co on the SiC{0001} substrates but not for Co on HOPG or Co on g/Rh(111). (b-e) Magnetization versus magnetic field curves for Co on the four substrates. In this case, the value of the TEY at the Co absorption edge normalized by the value at the pre-edge are recorded versus magnetic field, for a given polarization. In these plots we recognize that the magnetization at 5T is saturated for Co on FLG, almost saturated for Co on SL and not saturated for Co on HOPG and Co on g/Rh(111).

References

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