Magnetic decoupling of ferromagnetic metals through a graphene spacer

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We study the magnetic coupling between different ferromagnetic metals (FMs) across a graphene (G) layer, and the role of graphene as a thin covalent spacer. Starting with G grown on a FM substrate (Ni or Co), we deposit on top at room temperature different FM metals (Fe, Ni, Co). By measuring the dichroic effect of $3p$ photoemission lines we detect the magnetization of the substrate and the sign of the exchange coupling in FM overlayer at room temperature. We show that the G layer magnetically decouples the FM metals.

I. INTRODUCTION

The electronic transport and the magnetic coupling between different magnetic species separated by a graphene layer (G) has recently triggered interest for spintronics applications [1-5]. Spin-dependent transport perpendicular to the graphene plane results in tunneling magnetoresistance. Concerning the behavior of different ferromagnetic metals (FMs) chemically separated by a G layer, it has been predicted that the coupling can be either ferromagnetic or antiferromagnetic, depending on the choice of the two species [6]. This behavior might provide the opportunity for tuning the coupling by varying the chemical composition of the FM/G/FM junction.

By recent X-ray magnetic circular dichroism (XMCD) measurements [7] on FM single atoms or islands deposited on G/Ni at T<5K, we observed a complex behavior of G in transmitting the exchange interactions through the perpendicular direction. Combined experimental and theoretical results have shown that the sign of the magnetic coupling depends on the adsorption sites for isolated atoms and varies in a complex way for dimers and larger aggregates. Accordingly, transitions between anti- and ferromagnetic coupling, depending on the geometrical arrangement of atoms at surface, have been observed. Those results prove a high sensitivity of the G-mediated exchange interaction to the local coordination of the adatoms.

Here, we examine the magnetic coupling between FM metals (Fe, Co, Ni), deposited at room temperature (RT) and measured in remanent magnetization conditions, on G/Co(0001) and G/Ni(111) substrates. We employ the linear dichroic effect in $3p$ photoemission lines to examine the magnetic coupling between FMs across a G layer. By measuring the line shape of $3p$ core levels as a function of the direction of magnetization and along different symmetry directions of the substrate, we are able to detect the magnetic coupling across the graphene layer or its absence. Our results show that for the selected FM/G/FM junctions, grown and measured at RT, no magnetic coupling is attained through the G layer. Therefore, the G inhibits the magnetic alignment that normally occurs when two FMs are put in contact.

II. METHODS

The experiments were performed at the VUV beamline of the Elettra synchrotron radiation laboratory (Trieste, Italy) using a Scienta R4000 electron energy analyzer at a base pressure of $5 \times 10^{-11}$ mbar. The W(110) crystal was prepared by repeated high temperature flash-annealing cycles in oxygen atmosphere until a sharp $1 \times 1$ low-energy electron diffraction (LEED) pattern and well-developed W 4f surface core level components were observed. The Co(0001) and Ni(111) films were grown on W(110) by evaporation of $10 \pm 25$ ML of Co (or Ni) at RT from an electron-bombed rod. The LEED showed a $1 \times 1$ hexagonal pattern for both Co and Ni films, with sharp diffraction spots upon annealing at about 420 K. The graphene layer was grown by CVD of ethylene at about 700 K, at the lower limit of temperature to avoid local breaking of the film [8]. Surface order and cleanliness were checked by LEED and core level measurements. The samples were magnetically saturated by applying a pulsed current to a coil wrapped around the sample holder, and always measured in remanence at RT. FMs (Fe, Co or Ni) were deposited on G/Co (or G/Ni) at RT. In this experimental conditions FMs tend to form 3D clusters without long-range order [9,13]. Starting from the submonolayer regime, the FM coverage was here estimated on the bare substrate by measuring the intensity ratio of $3p$ photoemission lines. Core levels photoemission spectra were collected using a photon energy of 150 eV. The scattering geometry of our experiments is reported as inset of Fig. 1a. Light with linear horizontal polarization was impinging the sample at 45° from the surface normal. Electrons were collected under normal emission with about 30° full acceptance along the scattering plane (xy). The Co or Ni easy magnetization axis is set to lie at different angles with respect to the scattering plane by means of azimuthal rotation of the
sample. If the easy magnetization axis is oriented along \( z \), namely perpendicularly to the scattering plane, core levels spectra exhibit a large dichroic signal when the magnetization is reversed from positive (\( M_{\text{up}} \)) to negative (\( M_{\text{down}} \)) \( z \) values. The Ni(111) and Co(0001) films were found to be in-plane magnetized along the [1\bar{1}0] and [\bar{1}100] symmetry directions, respectively. However, when the magnetic pulse was not applied in proximity of the easy axis, the largest dichroic signal was collected away from the perpendicular direction. For clarity, in these cases symmetry directions were not reported. In a typical Magnetic Linear Dichroism (MLD) experiment, the magnetization direction is simply reversed (e.g. by reversing the current through the coil) and this causes to first order to a change of the relative intensities of multiplet sublevels, due to dipole matrix element effects [14]. The dichroic signal is obtained by calculating the asymmetry, i.e. the difference between spectra acquired with different magnetization divided by their sum, \( A=(I_{\text{M up}}-I_{\text{M down}})/(I_{\text{M up}}+I_{\text{M down}}) \). This quantity is proportional to the surface magnetization, i.e. to the average orientation of magnetic moments at surface, thus defining an element-specific order parameter.

### III. RESULTS AND DISCUSSION

In Fig. 1, MLD measurements taken on the Ni/G/Co system are reported. The sample was prepared by depositing 0.2 ML of Ni on the G/Co substrate remanently magnetized (Fig. 1a). The line shape of Co 3p and Ni 3p photoemission peaks is monitored along different azimuthal directions, and pair spectra were obtained by reversing the magnetization. The dichroic signal is present for the Co 3p photoemission peak, while is not observed for the Ni 3p peak, as confirmed by the asymmetry curve reported in Fig. 1c. The dichroism measured at the Co 3p peak consists in a plus/minus feature about 1.5 eV wide, and a maximum peak-to-peak asymmetry of about 9%, in agreement with previous results [15]. Extrema (minimum and maximum) correspond to sublevels of the Co 3p multiplet [10]. Our MLD results show that while the Co substrate is magnetized, no magnetic coupling is transmitted to the Ni clusters. The capability of the clusters to align their magnetic moments was checked by applying a magnetic pulse to the Ni/G/Co system and measuring the core levels (Fig. 1b). As shown in Fig. 1d, a detectable asymmetry of Ni 3p is extracted (1.3%) and the similarity between dichroic signals, with a prominent minus feature, indicates that Ni and Co moments are parallelly aligned.

Similar experiments were performed with Fe clusters deposited on top of G/Co (Fig. 2a) and G/Ni (Fig. 2b).
substrates. With respect to the Ni 3p photoemission peak, the Fe 3p one exhibits a strong dichroic behavior [17], allowing to detect also faint line shape variation induced by the substrate. Similarly to the experiment of Fig. 1a, we show in Fig. 2 that while the Co and Ni substrates exhibit the expected magnetization, with the easy magnetization axis along [1T00] and [1T0], respectively, no dichroic effect is seen for the Fe 3p photoemission peak.

In order to investigate further the effect of graphene in FM/G/FM junctions, we compare previous results with those obtained for a partially covered FM substrate. As a starting point, we show in Fig. 3a the dichroic behavior of Fe clusters (0.2 ML) deposited on a pristine Co film. As expected, Co atoms and Fe overlayer produce a significant ferromagnetic coupling (Fig. 3b). Further, we show a partially covered G/Co surface (Fig. 3c), achieved by means of exposures to ethylene below the saturation condition. The uncovered Co surface was es-

FIG. 2: (Color online) Core level measurements taken on (a) 0.4 ML Fe/G/Co, (b) 0.3 ML Fe/G/Ni, showing 3p photoemission peaks acquired along selected azimuthal directions and for different magnetizations (M up and M down).

FIG. 3: (Color online) Core level measurements taken on (a) 0.2 ML Fe/Co, (c) partially covered 0.2 ML Fe/0.9 ML G/Co, showing Fe3p and Co3p photoemission peaks acquired along selected azimuthal directions and for different magnetizations; (b-d) asymmetry curves extracted from data taken +0° of panels (a) and (c), respectively.
timated to be below 10% by evaluating the ratio of C 1s/Co 3p photoemission peaks, taken at about 700 eV of photon energy (data not shown), with respect to the ratio obtained at the saturation coverage. Comparing corresponding MLD measurements with those obtained for a fully covered substrate (Fig. 2a), it is deduced that the Fe-Co ferromagnetic coupling seen in Fig. 3d is due to a direct contact of the two metals in the reduced uncovered regions. Therefore, we conclude that the presence of G in our junctions weakens the exchange interactions between FMs, leading to a decoupling of their magnetic moments.

The electronic and magnetic properties of G/Ni(111) and G/Co(0001) have been widely characterized \[18, 19\]. The Dirac cone of G is split in several parts above and below the Fermi level due to the interaction between C 2p \(_z\) and d state of the metallic substrate. These interface states with a notably contribution of graphene \(\pi\) orbitals acquire a partial spin polarization by the magnetic substrates, due to hybridization with distinct majority and minority Co (or Ni) d bands. As consequence, in a defect-free G/Ni system the net magnetic moment of carbon was evaluated to be of about 0.01 \(\mu_\text{B}\) per atom \[20, 21\], taking into account that in the two different absorption sites on Ni(111) carbon atoms acquire opposite polarization with respect to the substrate. The magnetic interactions through graphene is based on direct exchange, and has a direct contact of the two metals in the reduced uncov-

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