Correlation of Microstructure and Transport Properties of Multilayered Graphene Spin Valves on SiO₂/Si

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Abstract. Multi-layered graphene based spin valves were deposited on SiO₂/Si substrates and the Co ferromagnetic and non-magnetic electrodes were patterned using electron-beam lithography. Aberration-corrected (scanning) transmission electron microscopy imaging and energy dispersive X-ray spectroscopy were employed to study the interfacial structure of the device components from thin cross-sectional lamellae obtained by focused ion beam microscopy. The robustness of the spin injection with a constant spin polarization under positive and negative bias voltage was attributed to the interface smoothness which leads to suppression of spin scattering at the interface between the ferromagnet and the multi-layered graphene.

1. Introduction
Multi-Layered Graphene (MLG) on SiO₂/Si substrates is a promising building block for spintronic devices [1]. Recently, MLG based spin valves with unprecedented robustness of spin polarisation have been demonstrated under positive and negative bias voltage [2, 3]. The room temperature magneto-resistance (MR) of these devices is constant with respect to the applied bias voltage, indicating that the spin injection is independent of the applied bias. This is a very desirable property that is lacking in metallic systems spin valves deposited on semiconductors and has been attributed to the high quality of the interface between graphene and ferromagnets. However, the quality of the interface was assessed by indirect methods only, namely through the comparison of bias-voltage dependence versus injection current in “local” and “non-local” schemes [2] but no micro-structural investigations were performed on the devices.

In this work we investigate the microstructure of these high performance MLG spin device structures by using aberration-corrected (scanning) transmission electron microscopy ((S)TEM) imaging and energy dispersive X-ray spectroscopy. This approach, by a direct correlation between the MLG spin valves’ magneto-transport properties and their structure, allows verification of the model of spin scattering suppression at the interface as described in [2].
2. Methods

2.1. Device deposition and magneto-transport studies
The devices were fabricated on SiO$_2$/Si substrates. MLG flakes were obtained by the peeling method using adhesive tape from highly oriented pyrolytic graphite (HOPG; NT-MDT Co.) and polyamide-oriented highly oriented graphite (Kaneka Co. super graphite) [4]. A MLG flake was deposited on the substrate before electron-beam lithography patterning of ferromagnetic (Co) and non-magnetic (Au/Cr) electrodes (Figure 1a). The MR effect in these devices was studied in the “non-local” geometry as described in [2,3].

2.2. Electron microscopy methods
A thin cross-sectional lamella was obtained by focused ion beam (FIB) microscopy from areas across four-terminal MLG spin device structures (across the black line as shown in Figure 1a). Electron microscopy analysis was done using a JEOL JEM-2200FS (scanning) transmission electron microscope (S)TEM equipped with CEOS probe and image aberration correctors. Analytical attachments include a high angle annular dark field (HAADF) detector and a Thermo scientific, Noran 7 energy dispersive X-ray spectroscopy system. Imaging conditions for HAADF STEM analysis were as following: convergence semi-angle of 24 mrad, HAADF inner and outer collection semi-angles were 110 mrad and 180 mrad respectively.

Figure 1. a) Light microscopy image of a MLG spin valve before deposition of Cr cap layer. The black line indicates the lamella removed by FIB; b) device cross-section STEM image showing an Au/Cr contact and Co electrodes (scale bar corresponds to 1 micron); c) EDX point analyses from Co1 electrode (filled squares), Cr cap (open circles), and Au1 electrode (open triangles). Inset the Cr-Kα peaks for Co electrode and the cap layer.
3. Results and discussion

From transport measurements on these devices, the spin polarization of the injected spin current was found to be constant up to +2.7V and -0.6V in positive and negative bias applications [2]. This remarkable property was attributed to the high degree of smoothness of the interface of the ferromagnets with the graphene multilayer [2].

The HAADF image in Figure 1b) shows an overview of the first Au/Cr electrode \textit{Au1}, and the two Co ferromagnetic electrodes labelled as \textit{Co1} and \textit{Co2}. EDX point analyses (Figure 1c) confirm the composition of the device components: the spectrum from Au1 electrode (open triangles) shows a marked Au-M\alpha peak at 2.12 keV as well as the Cr-K\alpha peak at 5.41 keV, the spectrum from Cr cap layer (open circles) shows the Cr-K\alpha peak. Finally a strong Co-L\alpha peak at 0.68 keV is shown in spectrum from the Co1 electrode (filled squares). Due to the presence of the FIB protective layer, the W-M\alpha peak at 1.77 keV is present in all the three spectra. An overview of the layered structure at the terminal Co/MLG is shown in Figures 2a) and 2b). A 285nm silicon dioxide layer can be seen on top of the Si doped substrate. The thickness of the MLG is 50 nm, corresponding to about 150 monolayers of graphite. On top of the MLG a 0.7 micron wide and 60 nm thick Co electrode is shown with a good uniformity and parallel surfaces. Above the electrode, a 60nm thick Cr capping layer is shown, the material further on top corresponds to tungsten, residue of the protection mask deposited in the FIB in order to preserve the structure during the ion milling.

![Figure 2](image-url)

**Figure 2.** a) High angle annular dark and b) bright field STEM images of the multilayered structure of the device at the Co/MLG terminal; c) interface Cr capping layer to Co ferromagnet. Dotted lines highlight the multigranular structure of the electrode.

The most important area of the sample for the spin current injection consists of the two ferromagnets, the Co electrodes [2,3]. We found that the Co electrodes consist of coalesced grains with an average width of about 10 nm, as shown in Figure 2c). Metallic Co is known to have two major crystallographic structures: hexagonal close-packed (hcp) structure (P6\text{3}/mmc) with lattice parameters \(a=0.2170\), \(c=0.2045\) and face centred cubic (fcc) structure (F m-3m) with lattice parameter \(a=0.3544\) [5].

Fast Fourier Transform (FFT) analysis was applied to HRSTEM images from several grains finding areas along [001] zone axis with lattice spacing of \((0.177\pm0.002)\)nm corresponding to the (002) planes of the cobalt cubic structure at the top surface of the Co. However, the presence of the hcp structure of the cobalt cannot be completely ruled out. In fact, in Figure 3a), two adjacent grains labelled G1 and G2 are imaged at the interface with the MLG. The stacking planes of the MLG are parallel to lattice planes visible in the off-axis grain G1. Their distance was measured to be \((0.205\pm0.002)\)nm which is compatible with both the (0002) planes of the hcp structure \((0.2045\) nm) or the (1-11) planes of the fcc structure \((0.2046\) nm). Grain G2 shows a large variation of lattice arrangement at the nanometre scale due to the presence a high density of crystal defects in addition to
surface amorphisation due to the FIB sample preparation. The FFT from the G2 area shows a cubic symmetry of the Bragg spot pattern, but the presence of multiple spots make it difficult to ascertain the crystal structure of the grain. However, a set of planes of Bragg reflections (highlighted by white circles in the FFT in Figure 3c) are clearly aligned with respect to the MLG stacking planes showing a good quality of the interface.

Figure 3. a) BF-STEM image of the interface Co-MLG showing two grains in the Co with different epitaxial relationships with respect to the MLG; b) FFT of interface G1 and G2 showing the stacking of Co planes parallel to the MLG (0001). c) FFT of Grain 2 white circles highlight the Co planes aligned parallel to the MLG stacking planes.

4. Conclusions
Aberration corrected (S)TEM analytical and imaging techniques were applied to study the microstructure of MLG-based spin valves devices, showing high robustness of spin polarisation under positive and negative bias. The smoothness of the interface between the multilayered graphene and the ferromagnetic (Co) electrode was confirmed by bright field STEM imaging. Our results support the theory that the robustness of the spin injection can be attributed to the suppression of spin scattering at the interface between the ferromagnet and the graphene.

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