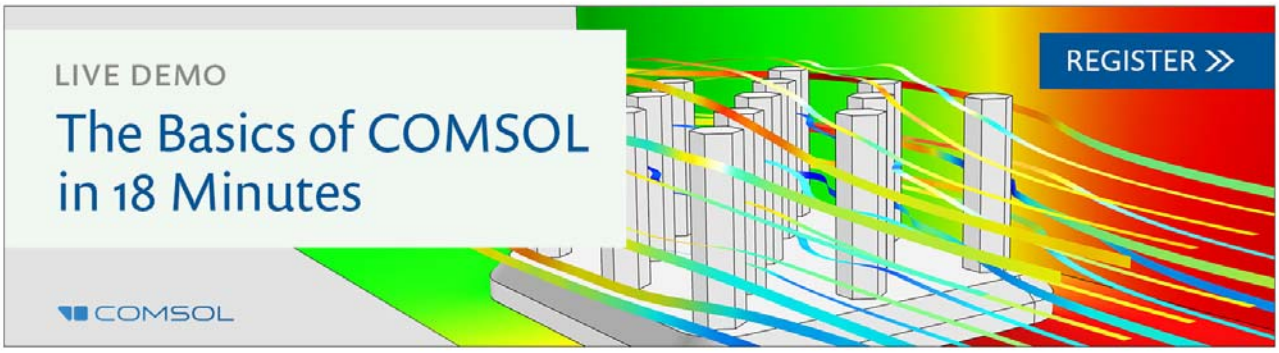
AIP | Applied Physics Letters

Protecting nickel with graphene spin-filtering membranes: A single layer is enough

M.-B. Martin, B. Dlubak, R. S. Weatherup, M. Piquemal-Banci, H. Yang, R. Blume, R. Schloegl, S. Collin, F. Petroff, S. Hofmann, J. Robertson, A. Anane, A. Fert, and P. Seneor

Citation: Applied Physics Letters **107**, 012408 (2015); doi: 10.1063/1.4923401
View online: http://dx.doi.org/10.1063/1.4923401
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/107/1?ver=pdfcov
Published by the AIP Publishing



Protecting nickel with graphene spin-filtering membranes: A single layer is enough

M.-B. Martin,[1] B. Dlubak,[1] R. S. Weatherup,[2] M. Piquemal-Banci,[1] H. Yang,[3,4] R. Blume,[5] R. Schloegl,[6] S. Collin,[1] F. Petroff,[1] S. Hofmann,[2] J. Robertson,[2] A. Anane,[1] A. Fert,[1] and P. Seneor[1]

[1]*Unité Mixte de Physique CNRS/Thales, 1 Avenue Augustin Fresnel, 91767 Palaiseau, France and Université Paris Sud, 91405 Orsay, France*
[2]*Department of Engineering, University of Cambridge, Cambridge CB21PZ, United Kingdom*
[3]*IBS Center for Integrated Nanostructure Physics (CINAP), Institute for Basic Science, Sungkyunkwan University, Suwon 440-746, South Korea*
[4]*Department of Energy Science, Sungkyunkwan University, Suwon 440-746, South Korea*
[5]*Helmholtz-Zentrum Berlin fur Materialien und Energie, 12489 Berlin, Germany*
[6]*Department of Inorganic Chemistry, Fritz Haber Institute of the Max Planck Society, Faradayweg 4-6, 14195 Berlin, Germany*

(Received 23 April 2015; accepted 21 June 2015; published online 10 July 2015)

We report on the demonstration of ferromagnetic spin injectors for spintronics which are protected against oxidation through passivation by a single layer of graphene. The graphene monolayer is directly grown by catalytic chemical vapor deposition on pre-patterned nickel electrodes. X-ray photoelectron spectroscopy reveals that even with its monoatomic thickness, monolayer graphene still efficiently protects spin sources against oxidation in ambient air. The resulting single layer passivated electrodes are integrated into spin valves and demonstrated to act as spin polarizers. Strikingly, the atom-thick graphene layer is shown to be sufficient to induce a characteristic spin filtering effect evidenced through the sign reversal of the measured magnetoresistance. [http://dx.doi.org/10.1063/1.4923401]

Oxidation has always been a key issue for spintronics. Indeed, any undesired surface oxidation of typical metallic ferromagnets (nickel, cobalt, iron, and their alloys) quenches their delicate spin polarization properties rendering them useless for spintronics. Hence, the fabrication of functional spin-valves, the basic building block of mainstream data-storage technologies,[1] has up to now mainly relied on high vacuum physical deposition setups. However, recent developments in spintronics have highlighted the need to find new ways to circumvent this issue. Indeed, the integration of ambient/oxidative fabrication steps such as atomic layer deposition (ALD) of high quality dielectrics[2,3] and liquid phase deposition of organic materials[4] (e.g., self assembled monolayers of molecules[5] and tunable conducting polymers[6]) would reduce costs and open up new opportunities (e.g., ultimate downscaling with single molecule magnets[7] and chemically engineered functionalities with spinterfaces[8,9]). The identification of spin sources tolerant to oxidative fabrication conditions is thus central to the development of these novel applications of spintronics.

Graphene has shown a strong potential as a membrane preventing atomic diffusion. Bunch *et al.*[10] demonstrated the impermeability even to helium of exfoliated pristine monolayer graphene flakes. Interestingly, since then, several studies have discussed the possibility of passivating metals with chemical vapor deposition (CVD) of graphene layers over large areas, however, with contrasting conclusions.[11–17] For spintronics and in the case of multilayer CVD graphene on nickel, functional spin valves devices based on multilayer graphene protected ferromagnetic electrodes (GPFE) have demonstrated the feasibility of this approach.[13] However, a controversy exists in the case of copper, where studies[15,16] report on failure to passivate the metallic surface and even on the enhanced degradation of the Cu surface by the graphene layer in contrast to the previous studies.[11] This failure of the passivation has been attributed by Prasai *et al.*[14] to the defects of the CVD graphene sp^2 structure while Kidambi *et al.*[17] ascribed it to the weakly coupled graphene/copper interface which in turn allows further diffusion and accumulation of oxidative species. The sharp differences between these experiments question the possibility of passivating ferromagnetic electrodes with a single layer of graphene in spin-valve devices.

Here, we show that a single layer of graphene, derived by a direct CVD step with low enough temperatures (450 °C) to be compatible with complementary metal-oxide-semiconductor (CMOS) processes,[18,19] is sufficient to protect the surface of a nickel electrode against oxidation and maintain a spin polarization. The downscaling of the graphene coating to an ultimate single atom thickness (Figure 1) still ensures that the metallic nature of the nickel electrode surface is preserved after ambient air exposure (Figure 2). The resulting ferromagnetic electrodes protected by a single layer graphene sheet are then shown to maintain a spin polarization through their integration in functional spin valves (Figure 3).

Figure 1 shows the graphene/nickel electrodes considered herein. While nickel can easily promote the growth of multilayers by CVD, an experimental process has been carefully developed here, with theoretical support, to limit the growth to monolayer graphene.[18–20] The graphene monolayer is directly

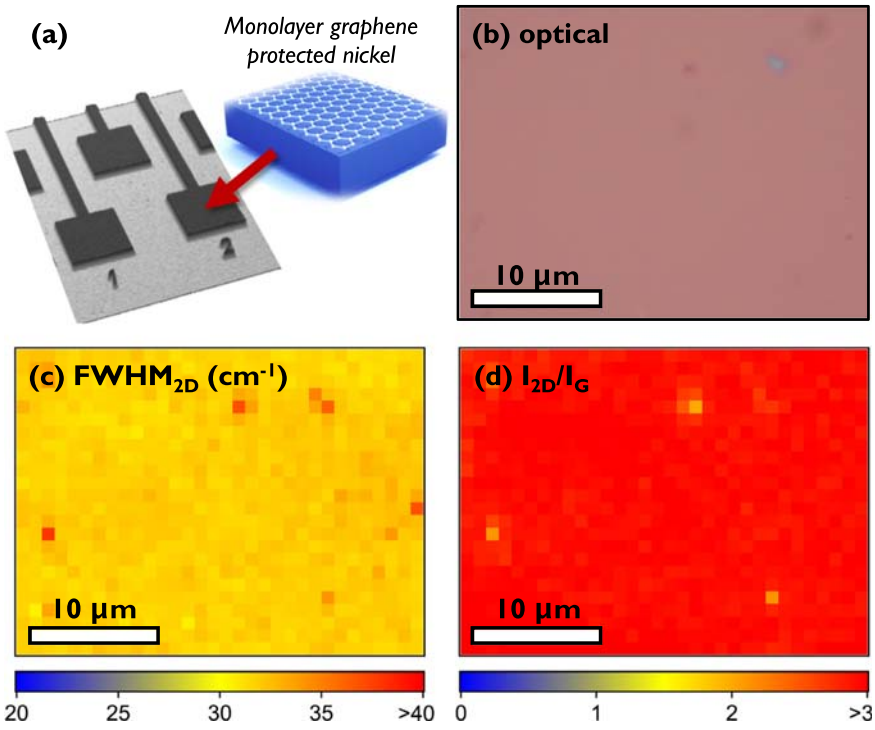


FIG. 1. (a) Optical profilometer image of monolayer graphene passivated ferromagnetic electrodes (monolayer GPFE). In our growth conditions, the graphene layer on nickel is homogeneously monolayer as shown by (b) optical images of the transferred sheet on SiO_2, (c) the mapping of full width at half maximum of the Raman 2D peak, and (d) the mapping of the intensity ratio of the Raman 2D/G peaks.

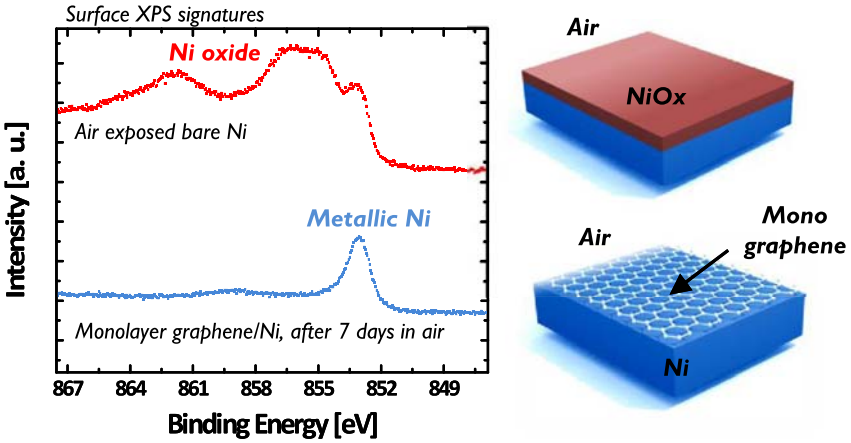


FIG. 2. XPS measurements of the surface state of nickel (BESSY II synchrotron at the ISISS end station of the FHI-MPG). Top: bare nickel exposed to air (i.e., ambient atmosphere) has oxidized. Bottom: nickel protected by a monolayer graphene membrane after 7 days in air has resisted oxidation and remains metallic.

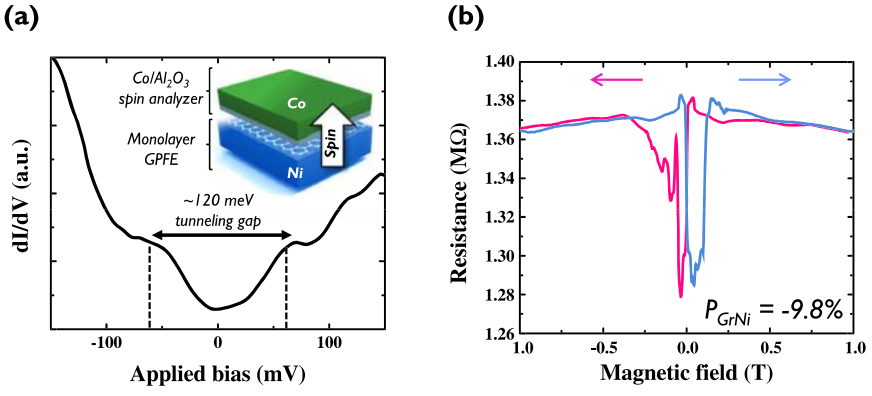


FIG. 3. (a) dI/dV spectroscopy of the complete monolayer GPFE/Al_2O_3/Co functional spin valve revealing the gap-like feature characteristic of electron injection in graphene. (b) Magneto-transport characterization of the monolayer graphene coated Ni/Al_2O_3/Co spin valve. A reverse spin signal is measured, arising from the spin filtering of the monolayer graphene/nickel interface.

grown on nickel ferromagnetic electrodes by CVD. First, a 150 nm-thick nickel layer is deposited onto the SiO_2(300 nm)/Si substrate by thermal evaporation. The sample is loaded into a custom-built cold-wall reactor with a 10^{-6} mbar base pressure and heated in H_2 (1 mbar) to 450 °C for 30 min to fully reduce the catalyst. C_2H_2 (5×10^{-6} mbar) is then introduced for 15 min to catalytically grow monolayer graphene. We note that a small amount of gold (1%–2%) is added to the nickel layer in order to achieve an increased domain size and graphitic quality whilst suppressing the uncontrolled nucleation of graphene multilayers. This process conveniently avoids any transfer of the graphene layer by readily making use of the nickel (also used as catalyst) as the spin source of our devices. Characterization of the resulting monolayer is presented in Figures 1(b)–1(d), and further details can be found in Refs. 18 and 19.

To characterize the chemical state of the nickel surface protected by monolayer graphene, X-ray photoelectron spectroscopy (XPS) measurements are performed (Figure 2). After the growth of monolayer graphene on nickel, the sample is removed from the CVD setup and left in air for an extended period of time (ambient atmosphere for 7 days). Strikingly, XPS measurements after this air exposure reveal that the surface of nickel under the graphene sheet remains metallic, as it was when measured after reduction during pregrowth annealing. As a reference, a nickel layer that has been reduced but had no graphene overlayer formed on top is also exposed to air. In this case, the measured XPS spectra show the characteristic peaks of oxidized nickel. This demonstrates that a single layer of CVD-grown graphene is enough to effectively protect our ferromagnetic electrode against oxidation. The GPFE thus appears a promising candidate as an oxidation resistant electrode in spin devices even when only a single graphene monolayer is present.

We probe the monolayer GPFE spin injector properties by integrating it in a functional spin valve Ni-Gr/Al_2O_3(1 nm)/Co(15 nm). Here, the Al_2O_3/Co stack acts as a spin analyzer. The Al_2O_3 layer is grown by ALD, a process previously highlighted as particularly adapted to grow ultra-thin high quality tunnel barriers on graphene.[3] We measure the electrical properties of the Ni-Gr/Al_2O_3/Co junction at 1.4 K. The junction resistance is in the MΩ range, as expected for high quality 1 nm Al_2O_3 tunnel barriers. In Figure 3(a), the resulting dI/dV spectroscopy of the junction is presented. A characteristic tunneling phonon dip of ~120 mV is observed revealing the presence of graphene in the junction as previously ascribed in STM experiments and multilayer graphene spin valves.[3,21,22] Still, we note that this dip is expected to be weakened compared to the situation with multilayer graphene due to potential direct tunneling to the underlying nickel electrode.

Figure 3(b) shows the spin dependent transport characterization. The observed magneto-resistance (MR) signal reveals that the monolayer graphene protected nickel is spin polarized. The measured MR signal is negative, meaning that the monolayer GPFE acts as a spin filter. While we already measured this spin-filtering phenomenon in multilayer graphene (2–5 layers) GPFE-based functional spin valves,[3,13] this study further shows that a single layer of graphene is enough to invert the spin polarization. We extract the spin polarization using a classical interpretation of the magnetoresistance signal following Julliere model.[23] Comparatively, the spin polarization obtained here with monolayer graphene ($P = -9.8\%$) is about 4× lower in amplitude than our previous results with multilayers ($P = -42\%$).[3] While its exact origin is still under study,[24] the increase of spin polarization with the number of layer is in agreement with the reported predictions of Karpan *et al.*[25] and more recently Laczic *et al.*[26] We note that the observed negative sign of the magneto-resistance and its amplitude has been observed reproducibly.

In conclusion, it is shown here that the one atom thick single layer of graphene is enough to efficiently protect nickel spin sources against deleterious oxidation. We also show that this single layer is enough to trigger a spin filtering effect at the nickel/graphene interface, and additionally that the dependence of this effect on graphene thickness follows theoretical predictions.[25,26] Interestingly, this work is based on a readily scalable, CMOS-compatible (450 °C), single-step CVD process for the direct growth and integration of monolayer graphene in spin devices. Overall, this highlights the potential of 2D materials for spin devices beyond the more usual lateral spin transport.[27,28] While the manipulation of the spin information by the ferromagnet/graphene proximity has direct implications for lateral spin transport in monolayer graphene, we more particularly show here effective passivation using graphene which offers new opportunities, for example, in the integration of organic materials in spin valve devices.[4–9]

We acknowledge the Helmholtz-Zentrum-Berlin Electron storage ring BESSY II for provision of synchrotron radiation at the ISISS beamline and we thank the BESSY staff for continuous support of our experiments. R.S.W. acknowledges a Research Fellowship from St. John's College, Cambridge. S.H. acknowledges funding from ERC grant InsituNANO (No. 279342) and EPSRC grant GRAPHTED (EP/K016636/1). P.S. acknowledges the Institut Universitaire de France for a junior fellowship. This research was partially supported by the EU FP7 Work Programme under Grant GRAFOL (No. 285275) and Graphene Flagship (No. 604391).

[1]C. Chappert, A. Fert, and F. N. Van Dau, Nat. Mater. **6**, 813 (2007).
[2]M. Mao, R. Bubber, and T. Schneider, ECS Trans. **1**, 37 (2006).
[3]M.-B. Martin, B. Dlubak, R. S. Weatherup, H. Yang, C. Deranlot, K. Bouzehouane, F. Petroff, A. Anane, S. Hofmann, J. Robertson, A. Fert, and P. Seneor, ACS Nano **8**, 7890 (2014).
[4]S. Sanvito and A. R. Rocha, "Molecular-Spintronics: The Art of Driving Spin Through Molecules," J. Comput. Theor. Nanosci. **3**(5), 624 (2006).
[5]M. Galbiati, C. Barraud, S. Tatay, K. Bouzehouane, C. Deranlot, E. Jacquet, A. Fert, P. Seneor, R. Mattana, and F. Petroff, Adv. Mater. **24**, 6429 (2012).
[6]T. V. de Oliveira, M. Gobbi, J. M. Porro, L. E. Hueso, and A. M. Bittner, Nanotechnology **24**, 475201 (2013).
[7]L. Bogani and W. Wernsdorfer, Nat. Mater. **7**, 179 (2008).
[8]C. Barraud, P. Seneor, R. Mattana, S. Fusil, K. Bouzehouane, C. Deranlot, P. Graziosi, L. Hueso, I. Bergenti, V. Dediu, F. Petroff, and A. Fert, Nat. Phys. **6**, 615 (2010).
[9]M. Galbiati, S. Taty, C. Barraud, A. V. Dediu, F. Petroff, R. Mattana, and P. Seneor, MRS Bull. **39**, 602 (2014).
[10]J. S. Bunch, S. S. Verbridge, J. S. Alden, A. M. van der Zande, J. M. Parpia, H. G. Craighead, and P. L. McEuen, Nano Lett. **8**, 2458 (2008).

[11]S. Chen, L. Brown, M. Levendorf, W. Cai, S. Y. Ju, J. Edgeworth, X. Li, C. W. Magnuson, A. Velamakanni, R. D. Piner, J. Kang, J. Park, and R. S. Ruoff, ACS Nano **5**, 1321 (2011).
[12]Y. S. Dedkov, M. Fonin, and C. Laubschat, Appl. Phys. Lett. **92**, 052506 (2008).
[13]B. Dlubak, M.-B. Martin, R. S. Weatherup, H. Yang, C. Deranlot, R. Blume, R. Schloegl, A. Fert, A. Anane, S. Hofmann, P. Seneor, and J. Robertson, ACS Nano **6**, 10930 (2012).
[14]D. Prasai, J. C. Tuberquia, R. R. Harl, G. K. Jennings, and K. I. Bolotin, ACS Nano **6**, 1102 (2012).
[15]M. Schriver, W. Regan, W. J. Gannett, A. M. Zaniewski, M. F. Crommie, and A. Zettl, ACS Nano **7**, 5763 (2013).
[16]F. Zhou, Z. Li, G. J. Shenoy, L. Li, and H. Liu, ACS Nano **7**, 6939 (2013).
[17]P. R. Kidambi, B. C. Bayer, R. Blume, Z. J. Wang, C. Baehtz, R. S. Weatherup, M.-G. Willinger, R. Schloegl, and S. Hofmann, Nano Lett. **13**, 4769 (2013).
[18]R. S. Weatherup, B. C. Bayer, R. Blume, C. Ducati, C. Baehtz, R. Schloügl, and S. Hofmann, Nano Lett. **11**, 4154 (2011).
[19]R. S. Weatherup, B. Dlubak, and S. Hofmann, ACS Nano **6**, 9996 (2012).
[20]R. S. Weatherup, C. Baehtz, B. Dlubak, B. C. Bayer, P. R. Kidambi, R. Blume, R. Schloegl, and S. Hofmann, Nano Lett. **13**, 4624 (2013).
[21]Y. Zhang, V. W. Brar, F. Wang, C. Girit, Y. Yayon, M. Panlasigui, A. Zettl, and M. F. Crommie, Nat. Phys. **4**, 627 (2008).
[22]E. Sutter, D. P. Acharya, J. T. Sadowski, and P. Sutter, Appl. Phys. Lett. **94**, 133101 (2009).
[23]M. Julliere, Phys. Lett. A **54**, 225 (1975).
[24]F. Godel, V. Venkata Kamalakar, B. Doudin, Y. Henry, D. Halley, and J.-F. Dayen, Appl. Phys. Lett. **105**, 152407 (2014).
[25]V. M. Karpan, G. Giovannetti, P. A. Khomyakov, M. Talanana, A. A. Starikov, M. Zwierzycki, J. van den Brink, and P. J. Kelly, Phys. Rev. Lett. **99**, 176602 (2007).
[26]P. Lazic, G. M. Sipahi, R. K. Kawakami, and I. Zutic, Phys. Rev. B. **90**, 085429 (2014).
[27]O. M. J. Van't Erve, A. L. Friedman, E. Cobas, C. H. Li, J. T. Robinson, and B. T. Jonker, Nat. Nanotechnol. **7**, 737 (2012).
[28]P. Seneor, B. Dlubak, M.-B. Martin, A. Anane, H. Jaffres, and A. Fert, MRS Bull. **37**, 1245 (2012).