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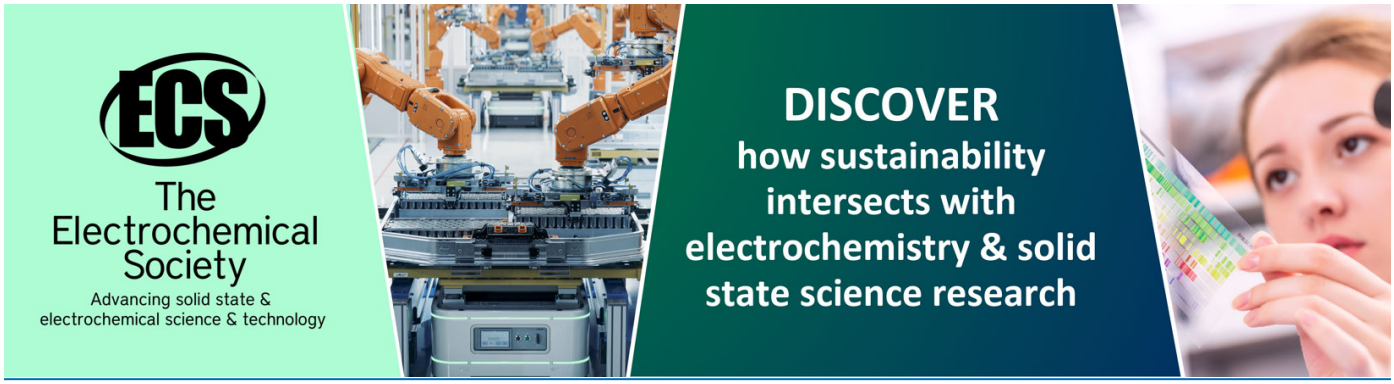

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Topical Review

2D-MTJs: introducing 2D materials in magnetic tunnel junctions

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Abstract

This review focuses on the recent experimental integration of 2D materials, mostly graphene but also h-BN and dichalochogenides, such as MoS_2 and WS_2, in magnetic tunnel junctions. The main remarkable characteristic of 2D materials is the ability to gain high homogeneous atomic control over their thickness, as this is barely achievable with the usual 3D materials deposited through conventional physical vapour deposition (PVD) growth techniques. This could become a critical asset for spintronics with regard to the fabrication of spin valves, where ultra-thin layers with extreme control are targeted, especially for spin-polarized electron tunnelling. A complete overview of the state of the art is presented, and the different integrative pathways of 2D materials with ferromagnets are addressed, including the exfoliation of 2D flakes from crystals, the wet transfer steps of large scale layers, and direct chemical vapour deposition (CVD) growths catalysed on ferromagnetic electrodes. Interestingly, these recent experiments have already highlighted some novel properties that emanate from 2D-based heterostructures, such as passivation against oxidation diffusion and augmented spin filtering at the interface. Many perspectives are thus being opened up in the exploration of the vast amount of 2D material families and their association in heterostructures, targeting specific spin device properties.

Keywords: 2D materials, graphene, spintronics, magnetic tunnel junctions, h-BN, TMDC, spin valve

(Some figures may appear in colour only in the online journal)

1. Introduction

Spintronics is a paradigm focusing on spin as the information vector. This is illustrated in fast and ultra-low-power non-volatile devices such as the new spin-transfer-torque magnetic random access memory (MRAM) [1]. Beyond its widely distributed applications in data storage [2], spintronics aims at providing more complex architectures and a powerful solution for beyond CMOS (see for instance the proposition of [3]). The recent discovery of graphene and other 2D materials (2DMs), such as hexagonal boron nitride (h-BN), has opened up novel exciting opportunities in terms of functionalities and performance of spintronics devices, as highlighted in this review. While to date graphene properties have been put

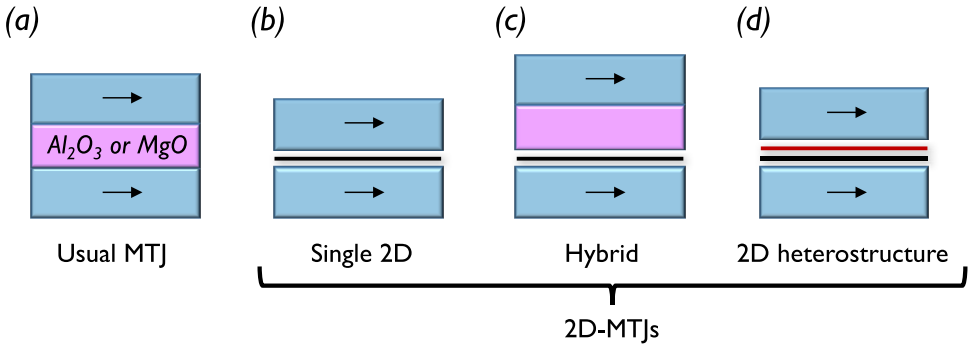

Figure 1. The MTJ structures under review: (a) the usual MTJ stack of spintronics, typically with an Al_2O_3 or MgO tunnel barrier interposed between two ferromagnets; (b) MTJs with 2D materials used as a spacer allowing atomic control of the thickness for tunnel barriers to be reached, beyond classical physical vapour deposition (PVD)-grown tunnel barriers; (c) MTJs encompassing 2D materials, inheriting specific functionality such as oxidation resistance to unlock new processes for MTJ fabrication, and enhanced spin filtering targeting large spin signals, etc; (d) ultimately, MTJs based on the heterostructures of 2D materials may allow the precise tailoring of spin properties.

forward mainly for efficient spin transport [4–6], we will detail here the results of another avenue for 2DMs in spintronics: their integration into the prototypical spintronics device, the magnetic tunnel junction (MTJ), as depicted in figure 1. Over the last years, MTJs have been the subject of intense development in the targeting of high TMR ratio, and more recently of switching performances. However, further improvement and downscaling has progressively unveiled issues relating to the control of the oxide barrier and the interfaces, the thermal stability, the annealing tolerance, and the robustness of the lifetime of the device. Two-dimensional materials may offer promising routes towards solving some of these issues, with layer-by-layer control of the thickness, sharp interfaces, the potential for a diffusion barrier (thermal stability), high perpendicular magnetic anisotropy, and even the possibility of new functionalities such as spin filtering. However, the integration of 2DMs is a challenge in itself. In this review, we provide an overview of the early steps of this nascent 2D-MTJ field and highlight the progress that has already been made.

An MTJ is a bi-stable device that can be used for sensors but also to store information, as exemplified in MRAMs. It consists of two ferromagnetic electrodes with a thin insulating barrier layer sandwiched between them. The latter is extremely thin, typically in the nm range, electrons can tunnel through it (perpendicularly to the stack) and current flows when a voltage is applied across the heterostructure. The most relevant property of an MTJ is that its resistance can be modulated by the change in relative orientation of the magnetization of the ferromagnetic (FM) electrodes. By (crude) analogy to optics, an FM electrode acts as a polarizer and an analyser of the spin information carried by the current. The normalized difference between the resistance obtained in these two configuration states is defined as tunnelling magnetoresistance (TMR) and is usually expressed in percentage form: $\mathrm{TMR} = \frac{R_{\mathrm{AP}} - R_{\mathrm{P}}}{R_{\mathrm{P}}}$, where R_{P} and R_{AP} correspond to the resistance across the stack when the magnetizations of the electrodes are parallel and antiparallel to each other, respectively. We note that while insignificant for a small TMR, the resistance variation is sometimes normalized preferentially by R_{AP} for large negative TMR cases in order to obtain values on the same scale as a positive TMR, and thus comparable in absolute terms (see [7]). A simple model proposed by Jullière in 1975 [8] gives an easy quantitative estimation of the TMR as a function of the spin polarization of both ferromagnetic electrodes, P_1 and P_2: $\mathrm{TMR} = \frac{2P_1P_2}{1 - P_1P_2}$. It is now well understood that tunnelling spin polarization is not an intrinsic property of the FM alone, but depends on the structural and electronic properties of the insulator and the FM/insulator interfaces (see for instance [7] and [9]). Still, in many non-fully crystalline cases, the formula remains a very useful tool, encompassing the key features of the underlying mechanisms when appropriately considering P_1 and P_2 as effective tunnelling current spin polarizations of the interfaces.

In terms of fabrication, the sensitivity of the TMR to the structural quality and the need for nm thin insulating barriers has proven to be particularly challenging. Indeed, if oxides are typically used as tunnel barriers in MTJs, the difficulty of growing extremely thin pinhole-free insulating layers, which can sustain annealing without degradation of the interface, diffusion in the barrier or oxidation of the FM, etc, has remained a key issue. The ultimately reduced thickness and natural sharp definition of the layers and interfaces of 2DMs are particularly impressive properties compared to what is routinely achieved with standard materials, such as Al_2O_3 or MgO, deposited by PVD techniques. However, we will show that their integration into MTJs has proved to be still delicate.

In sections 2 and 3, we will first review the approaches proposed early in the literature (soon after the first experimental isolation of graphene) to derive 2DMs on top of spin-polarized electrodes. These first experiments were mainly based on direct exfoliation from a thick crystal and on the wet transfer of larger scale 2D layers. These simple approaches enabled a great path for the fabrication of pioneering devices, and led to the first characterizations of FM/2DM systems. However, the observed spin signals remained desperately below expectations, probably limited by the degradation of the interfaces by these air/wet processes. In section 4, we will then focus on other methods proposed to integrate 2DMs in MTJs that circumvent the degradation issue, in particular direct chemical vapour deposition (CVD) on FM. This approach unlocked the exploration of the particular

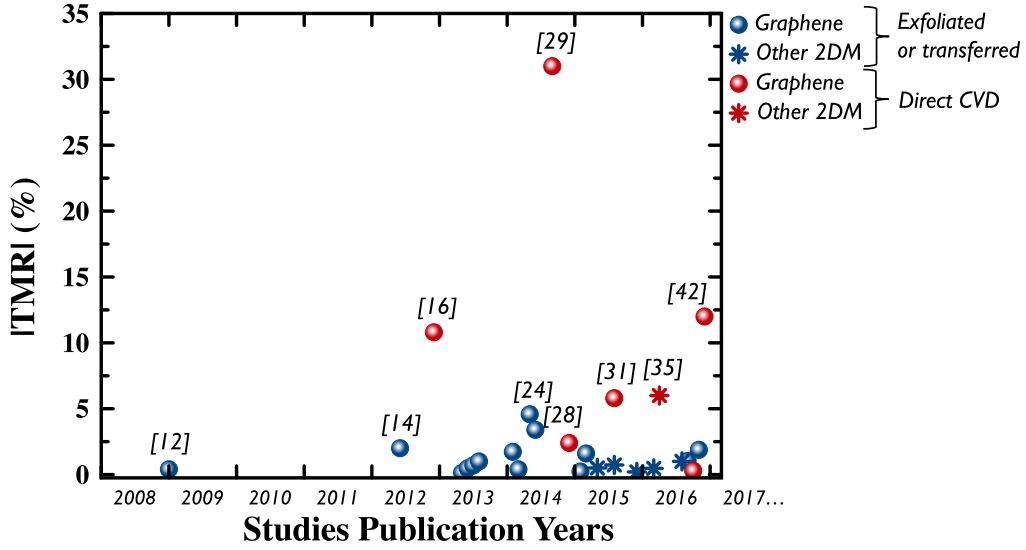

Figure 2. A timeline evolution of the absolute TMR in 2D-MTJs. Blue symbols: exfoliated or transferred 2DMs. Red symbols: direct CVD growth of the 2DM on ferromagnetic electrodes. Each of the 26 dots corresponds to a line of the 'maximum TMR spin signal' column of table 1. Overall, the direct CVD method is unveiled as particularly promising for 2DM integration in MTJs.

properties of FM/2DM systems such as passivation against oxidation diffusion and enhanced spin filtering. In section 5, we will then describe the expected properties of these systems as derived by computational means and compare them to the current experimental state of the art. Finally, in section 6 we will broaden the discussion beyond graphene to other 2DMs and their heterostructures and give a glimpse of awaiting opportunities.

2. Early expectations and results

The expectations for graphene-based MTJs were first set by calculations published in 2007. Indeed, in their seminal paper, Karpan *et al* [10] explored the potential of graphene layers for vertical magnetic tunnel junctions in terms of spin polarizations by computational means. They presented a theoretical study of the spin polarization expected for FM/graphene interfaces, and the resulting TMR spin signal expected for FM/graphene/FM systems. This study put forward the matching of the band structure of graphene with that of nickel, highlighting that at the Dirac point, only minority spins are available in nickel. They predicted extremely large spin polarizations close to 100%, with the resulting TMR well in excess of hundreds of %. We will discuss these results more specifically in section 5 of this review. A first experimental hint was published in this direction in 2008, when Dedkov and co-workers [11] presented the spin- and angle-resolved photoemission spectroscopy of a graphene-covered Ni surface. They discussed the spin polarization of the surface, and suggested that graphene's band structure was hybridized with that of Ni. The same year, Mohiuddin *et al* [12] demonstrated the first transport results with the fabrication of a complete MTJ encompassing a graphene layer. This study confirmed that a spin current could be preserved, with transport occurring perpendicular to the graphene layer. However, the spin polarization was limited (Mohiuddin *et al* [12] reported an MR spin signal of 0.4% in FM/graphene/FM devices, see below) and there was still no sign of the spin filtering effect.

The initial theoretical results triggered a strong interest in graphene (and more recently other 2DMs) for vertical magnetic tunnel junctions, with the hope of harnessing this envisioned spin filtering effect to achieve large spin signals. But already, the experimental studies had highlighted the potential of these systems as well as the difficulties associated with them: many parameters have an impact on the spin properties, and the integration of 2DMs between oxidation-prone metallic ferromagnets is far from trivial.

Thus, the heart of early developments exposed in the present review concerns the exploration of the integration pathways for 2DMs with spin-polarized ferromagnetic electrodes, toward the exploitation of the high-performance 2D-MTJs anticipated by theory.

3. Working with exfoliated and transferred graphene

Figure 2 and table 1 summarize the state of the art prior to 2017. Here, we discuss the maximum achieved TMR spin signal reported in these studies, usually obtained at lower temperatures (the TMR varies by about a factor of two from room to cryogenic temperatures when studied [20]). As expected during the first years, the literature focused mainly on graphene for the magnetic tunnel junctions, and different strategies have been devised to combine 2D layers with ferromagnets. In the following, we will first describe the earliest studies, which took advantage of the ease of graphene exfoliation (and later of transferred CVD graphene), in order to exploit high-quality 2D crystals. We will highlight the advantages and limitations of this approach as well as the workarounds which have been proposed.

In 2008, relatively shortly after the first demonstration of the graphene monolayer isolation in 2004 [43], a pioneering study using graphene as a spacer in an MTJ was published

Table 1. State of the art of studies demonstrating the vertical magnetic tunnel junctions making use of 2D materials. Blue: studies mainly focusing on graphene, green: studies mainly focusing on TMDC, red: studies mainly focusing on h-BN.

Publication year	Reference	Structure	Maximum TMR spin signal	Spin polarization $P_{FM/2DM}$	Fabrication process for 2D material integration
2008	Mohiuddin *et al* [12]	NiFe/**SLG**/NiFe	0.4%	4.5%[a]	Exfoliation
2010	Banerjee *et al* [13]	NiFe/Au/**FLG**/Au/Co	—	—	Exfoliation
2012	Cobas *et al* [14, 15]	NiFe/**SLG**/Co	2%	10%	Wet transfer
2012	Dlubak *et al* [16]	Ni/**FLG**/Al_2O_3/Co	−10.8%	−16%	Direct few layer CVD on FM [17, 18], sputtered spin analyser [19]
2013	Iqbal *et al* [20]	NiFe/**SLG**/NiFe NiFe/**BLG**/NiFe	0.14% 0.48%	2.6%[a] 4.9%[a]	Wet transfer
2013	Chen *et al* [21] and Meng *et al* [22]	Co/**SLG**/Co Co/**BLG**/Co	0.7% 1%	6% 7.1%	Wet transfer
2014	Singh *et al* [23]	Ni/Al_2O_3/**SLG**/Co	−0.4%	−4%[a]	Wet transfer
2014	Park *et al* [24]	NiFe/**FLG**/NiFe	4.58%	15%[a]	Exfoliation, two-step process
2014	Li *et al* [25]	LSMO/**SLG**/Co	−1.73%	−9.3%[a]	Wet transfer
2014	Godel *et al* [26]	Ni/**FLG**/TiO_2/MgO/Co	−2.4 %	−11%[a]	Direct few layer CVD on FM, MBE grown spin analyser [27]
2014	Li *et al* [28]	NiFe/**SLG**/Co	3.4%	12.8%[a]	Wet transfer, *in situ* process
2014	Martin *et al* [29]	Ni/**FLG**/ Al_2O_3/Co	−31%	−42%	Direct few layer CVD on FM [17, 18], ALD grown spin analyser
2015	Dankert *et al* [30]	NiFe/**h-BN**/Co	0.5%	0.25%	Wet transfer
2015	Martin *et al* [31]	Ni/**SLG**/Al_2O_3/Co	−5.8%	−9.8%	Direct monolayer CVD on FM [17, 18], ALD grown spin analyser [29]
2015	Iqbal *et al* [32]	NiFe/**SLG**/Co NiFe/Al_2O_3/**SLG**/Co	0.23% −1.6%	3.4%[a] [b]	Wet transfer
2015	Wang *et al* [33]	NiFe/Au/**MoS_2**/NiFe	0.73%	[b]	Wet transfer
2015	Wu *et al* [34]	Fe_3O_4/**MoS_2**/Fe_3O_4	0.2%	3.2%[a]	Sulfurized Mo
2016	Piquemal-Banci *et al* [35]	Fe/**h-BN**/Co	6%	17%	Direct monolayer CVD on FM [36, 37]
2016	Iqbal *et al* [38]	NiFe/**WS_2**/Co	0.47%	4.8%	Exfoliation
2016	Asshoff *et al* [39]	NiFe/**h-BN**/Co NiFe/**SLG**/Co	1% 1.03%	7.1%[a]	Exfoliation, *in situ* process
2016	Entani *et al* [40]	NiFe/**SLG**/NiFe	0.29%	3.9%[a]	Direct CVD on FM
2016	Iqbal *et al* [41]	NiFe/**SLG/h-BN**/Co	−1.88%	[b]	Double wet transfer
2016	Cobas *et al* [42]	NiFe/**FLG**/Fe	−12%	−25%[a]	Direct CVD on FM. Spin polarization predicted to reach >80%. No hysteretic behaviour.

[a]Spin polarization deduced from magnetoresistance signals through the Jullière model [8] when not calculated by authors.
[b]Spin polarization could not be deduced with the available data. SLG: single layer graphene, BLG: bilayer graphene, FLG: few layer graphene.

by Mohiuddin *et al* [12] (see figure 3). In this initial study, the authors pre-patterned a SiO_2(100 nm)/Si substrate with a dense matrix of magnetic 1 μm × 20 μm permalloy (NiFe) lines. They then proceeded to exfoliate graphene using the recently discovered scotch tape method [43] on the patterned silicon substrate. The SiO_2 thickness was chosen in order to provide enough optical contrast to be able to spot micron-sized graphene flakes on the surface [44]. After inspection of the resulting surface, they identified a flake of several layers of graphene covering one of the magnetic elements. The authors contacted this flake using a top magnetic contact, which specifically targeted the monolayer area. This was done through an electronic lithography step, in which the lithography mask was carefully crafted to connect the selected flake while avoiding short-circuits with the surrounding NiFe electrodes and other exfoliated graphene layers. This led to the fabrication of the first reported NiFe/graphene/NiFe MTJ. By sweeping the magnetic field and switching the magnetizations of the two NiFe electrodes independently, the authors investigated the spin-dependent transport across the graphene interlayer and reported a magnetoresistance of 0.4%.

In this work, the authors pointed out for the first time the difficulty of integrating graphene into magnetic heterostructures without oxidizing them. The bottom magnetic electrode

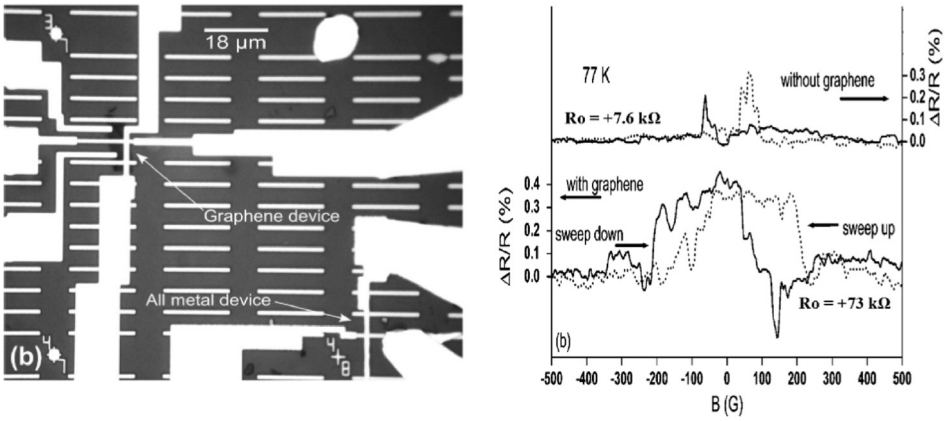

Figure 3. (Left) NiFe/graphene/NiFe MTJ fabricated by exfoliating a micron-sized graphene flake on top of NiFe electrodes in air. (Right) Measured TMR of about a 0.4% spin signal for this device. Reprinted with permission from [12]. Copyright (2008) IEEE.

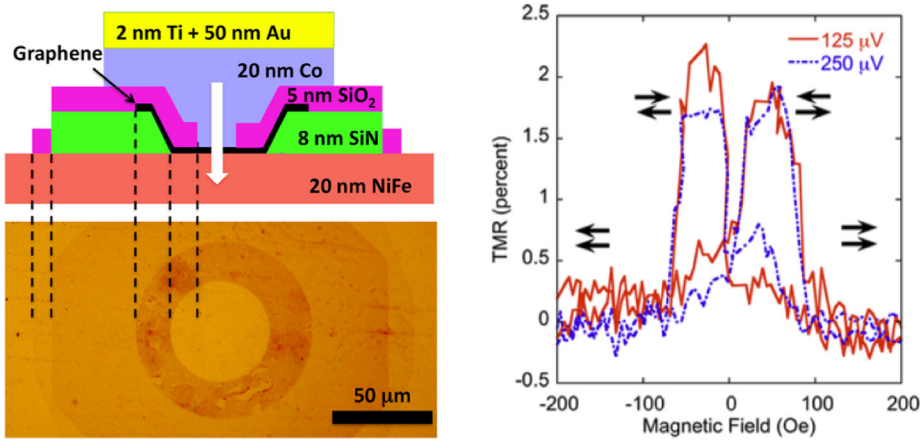

Figure 4. (Left) A NiFe/graphene/Co MTJ fabricated by the wet-transfer of CVD graphene in air initially grown on Cu. (Right) A spin signal measured in this type of device reaching a TMR of about 2%. Reprinted with permission from [14]. Copyright (2012) American Chemical Society.

was patterned following standard ambient lithographic steps, and further exposed to air during exfoliation and the final definition of the top contact. In comparison, standard spintronics fabrication processes relied on high vacuum deposition conditions in order to guarantee the preserved spin properties of the interfaces, and in turn provide large spin signals.

This first study had already highlighted a paradox: while very high quality graphene was readily available by the exfoliation technique, its integration was going to be challenging—all the more so if large-scale fabrication was targeted. The authors of [12] proposed a solution to the oxidation problem by covering the bottom NiFe electrode with a 2 nm thick Au layer, leading to the fabrication of an asymmetric NiFe/Au/graphene/NiFe device. This led to the measurement of improved magnetoresistances of about 5%; however, the use of Au was known to be detrimental to the spin polarization of the electrodes (similar to the native oxides of ferromagnets such as NiFe, etc).

Moving in the same direction were Banerjee *et al* [13], who fabricated heterostructures encompassing graphene by first depositing a thin NiFe magnetic layer, protected by an Au capping layer on a conductive Si substrate. They then took out the sample from the deposition chamber to proceed to the *ex situ* exfoliation of multilayer graphene flakes. The NiFe being capped by Au, it was supposed to be protected against oxidation. Finally, a top Au/Co/Au layer was deposited. They contacted the device by placing an STM tip on top of the structure and measuring the current going through it as a function of the magnetic field. The authors were able to measure a spin signal for NiFe/Au/graphite/Au/Co and compare it to a graphene-free NiFe/Au/Co (however, the impact of the Au layer was not discussed). The spin current appeared to be unaffected by transport through graphite in the case of the 17 nm thick flake they studied. The authors derived a minimal spin diffusion length >100 nm from these measurements for spin transport perpendicular to graphite planes.

In both the cases of Mohiuddin *et al* [12] and Banerjee *et al* [13], an Au layer had to be inserted between the graphene/graphite layer and the NiFe electrode to avoid its potential oxidation during the exfoliation process. While protecting the NiFe, this otherwise unwanted additional layer (see for instance [45]) was expected to have a strong impact on the MTJ. Again, the difficulty of integrating graphene with ferromagnets is thus highlighted. Hence, these pioneering works called for the study of alternative integration pathways.

In 2012, another fabrication process was proposed by Cobas *et al* [14, 15] (see figure 4). Instead of exfoliating thin

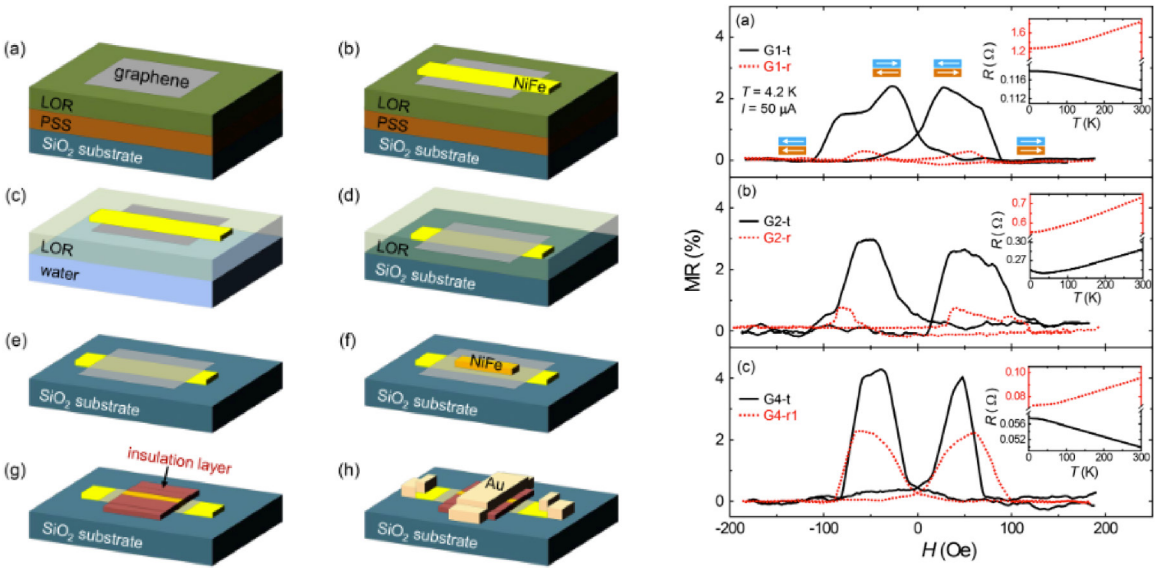

Figure 5. (Left) A NiFe/graphene/NiFe MTJ fabrication process developed to reduce the exposure of ferromagnets to air; NiFe is deposited on exfoliated graphene. The stack is flipped and a second NiFe electrode is deposited on the other side of the graphene layer. (Right) The TMR reaches 4% with this improved fabrication process. Reprinted with permission from [24]. Copyright (2014) by the American Physical Society.

graphene flakes, they transferred a large scale graphene layer grown by CVD on Cu on the top of ferromagnetic structures. In a similar way to previous studies, they first patterned a bottom ferromagnetic NiFe electrode. To control the junction area and provide a homogeneous contact (by avoiding edge states for instance), the authors used two insulation layers with a well-defined hole. The first one (8 nm of SiN) was deposited directly on top of NiFe with a large opening. Then the graphene layer was wet transferred on the NiFe using a PMMA support after etching a Cu growth catalyser with a wet ammonium persulfate etchant. The PMMA was removed in acetone. The second insulating layer (evaporated SiO_2) was deposited, defining openings with diameters of tens of microns. The top ferromagnetic Co/Ti/Au electrode was finally evaporated on the graphene layer. This approach had the benefit of displaying more systematic fabrication as the transferred graphene layer covers the whole wafer dice. However, as underlined by the authors, the issue of oxidation remained a limitation—especially due to the wet transfer steps. Interestingly, while the authors did not use an Au passivation layer on the NiFe, they still observed a spin signal of up to 2%.

Following with this study, many groups fabricated and characterized similar systems by transferring CVD-grown graphene through a wet process, with the resulting measured spin signals in the 1% range. In 2013, Iqbal *et al* [20] presented a work similar to Cobas *et al* [14]. The authors fabricated structures in which single or double layer graphene were transferred onto patterned NiFe electrodes, and further contacted the stack with a top ferromagnetic NiFe electrode. Spin-dependent transport revealed MR spin signals up to 0.14% for single layer graphene and 0.48% for double layer graphene structures. While this MR remained quite low compared to expectations and previous reports, interestingly, the authors provided data for a set of about 10 samples, which confirmed this trend. In 2013, a study by Meng *et al* and Cheng *et al*, detailed in two papers [21, 22], presented the data for Co/graphene/Co vertical structures with a similar conclusion: MTJs based on monolayer CVD graphene showed an MR of 0.7%, whilst those based on bilayer graphene showed an MR of up to 1%. After 2014, these different works were further developed in follow-up papers, where the graphene layer is still transferred by wet chemistry, but with slight changes to the device structure in order to extract complementary information [23, 32, 41]. In particular, in 2015, by introducing a tunnelling interface to decouple the graphene from the top ferromagnetic electrode (as per Dlubak *et al* [16], see section 4), Iqbal *et al* [32] were able to better characterize the spin polarizations of the graphene-covered FM in these systems.

These different studies represented a turning point in graphene integration, as they allowed large-scale fabrication thanks to CVD-grown layers. They strengthened the conclusions of Cobas *et al* [14], demonstrating that graphene already showed some promise for MTJs. However, the devices constantly displayed measured magnetoresistances below 2%. This limitation of the spin signal is certainly linked to the degradation and contamination of the interfacial spin properties during the harsh step of graphene transfer.

Thus, to alleviate this limitation, alternative integration pathways were suggested by other studies. This eventually led to higher spin polarizations. In 2014, Park *et al* [24] showed the process of graphene integration in MTJ for which the exposition of NiFe electrodes was more strictly controlled (see figure 5). In the 'flip-transfer' method they described, graphene was first exfoliated on an LOR resist that had been spin-coated on top of a water-soluble PSS resist. The first NiFe electrode was subsequently deposited on top of it. By dissolving the water-soluble resist, a transfer step allowed the stack on the SiO_2/Si substrate to be reversed, thus defining the bottom NiFe/graphene electrode without exposing the NiFe

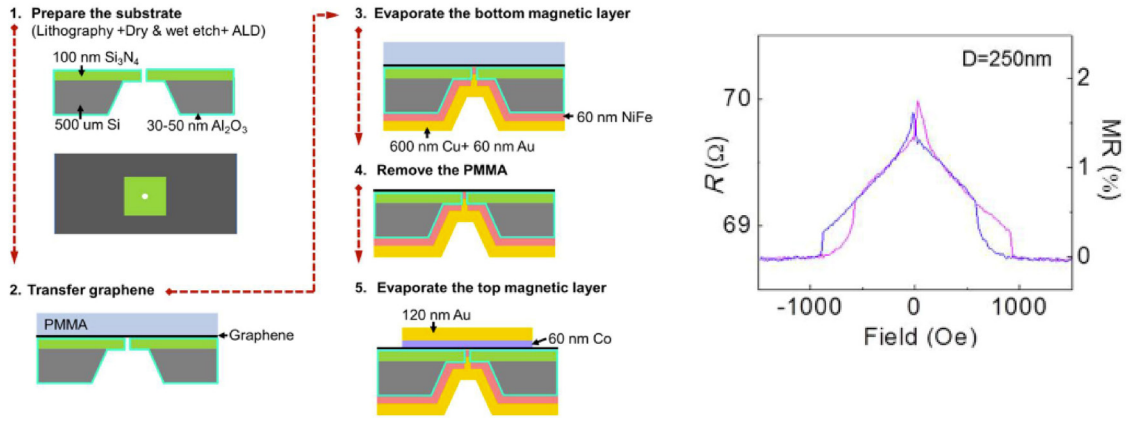

Figure 6. (Left) The NiFe/graphene/Co MTJ fabrication process based on a perforated membrane. This technique allows ferromagnets to be deposited on both sides of the graphene layer in a vacuum, i.e. without exposing the interfaces to air. (Right) A TMR spin signal up to 3.4% is reported in such systems. Reprinted with permission from [28]. Copyright (2014) by the American Physical Society.

directly to air. Finally, a second NiFe electrode was deposited on top of the reversed stack. The authors reported spin transport across different graphene layer thicknesses (one, two, three and four layers) with a large range of MR for each thickness (from below 0.5% to a few %). The largest signal was obtained for one of the devices with four graphene layers, measuring an MR of 4.58%. While the improved transfer process may still have been impacted by contamination, better control of the oxidation issue led to enhanced spin properties and an MR which was more than twice as large as that following simple exfoliation or transfer steps, as in Mohiuddin *et al* [12] or Cobas *et al* [14]. The authors suggested that an antiferromagnetic coupling between the FM electrodes could be reducing the spin polarization and ascribed the lack of spin filtering to the possible absence of lattice matching between the graphene layer and the electrodes. Still, analysed in light of the standard Jullière model [8], this result led to an average spin polarization of $P = 15\%$, which was already significant. Very interestingly, it is also worth noting that the absence of oxidation of the electrodes led to a much reduced resistance $\times$ area ($R \times A$) product of around 0.2 $\Omega \cdot \mu m^2$ for these MTJs compared to the 40–100 000 $\Omega \cdot \mu m^2$ frequently reported for previous MTJs comprising FM electrodes exposed to air (and hence covered with native oxide).

A solution to prevent the oxidation issue has been to use ferromagnetic oxides, such as the half-metal $LaSrMnO_3$ (LSMO), instead of metallic Co or Ni electrodes. In 2014, in their study, Li *et al* [25] defined LSMO electrodes by pulsed laser deposition growth through a shadow mask, on top of which they wet-transferred a CVD graphene layer. A Co top electrode was then deposited through another shadow mask to define 500 μm^2 MTJs. While this approach allowed the oxidation issue to be mitigated, the obtained low of MR $= -1.73\%$ indicated integration issues (e.g. degradation of the LSMO interface induced by transfer resist and chemicals). Indeed, LSMO usually presents a very high spin polarization of up to 95%, which seems to have been strongly quenched here during the wet transfer process. Integration of graphene thus still appears problematic, even with electrodes that are more chemically robust.

Another original approach has been developed to integrate graphene in MTJs by two different teams [28, 39]. The main idea was to deposit the graphene layer over a perforated membrane and to grow ferromagnets on both sides by flipping the sample. This approach was designed to strongly limit the oxidation of interfaces in the resulting junctions. Li *et al* [28] presented a work where PMMA-covered monolayer CVD graphene was deposited on an $Al_2O_3/Si_3N_4/Si$ membrane with holes ranging from 250 nm to a few μm in diameter (see figure 6). NiFe was then evaporated through the holes on the back side of the graphene layer. The carrier PMMA film on top of the structure was then washed in acetone and replaced by an evaporated Co film. The authors reported on the spin-dependent transport characterization of this NiFe/graphene/Co structure with an MR of up to 3.4%. This is the largest reported value for wet-transferred CVD graphene, thus demonstrating the importance of preserving the quality of the interfaces. Similarly, in 2016 Asshoff *et al* [39] reported on the exfoliation and transfer of graphene on membranes with holes with a measured MR of about 1%. While the improvement in measured spin signals demonstrated in these studies points to the importance of preserving high-quality FM/2DM interfaces, the signal quality remained far from what was expected. Furthermore, integration of these processes on a large scale is certainly problematic.

4. Direct integration of graphene in MTJ by CVD

In parallel to exfoliation and transfer, a new approach was introduced in 2012 in order to derive graphene layers on spin-polarized electrodes using a direct CVD step. Instead of relying on *ex situ* processes (exfoliation, transfer, etc), here the CVD step makes direct use of the metallic ferromagnetic electrode as a catalyst to grow the graphene layer. This suppresses the need to stack the graphene layer on the ferromagnetic electrode, leading to its oxidation (see figure 7). However, the growth of graphene by catalytic CVD processes requires an in-depth investigation of the parameter space for each FM growth substrate. Whereas 2D materials grown by CVD on ferromagnets had already been envisaged (see for instance [46] in 1995), its in depth investigation had only recently

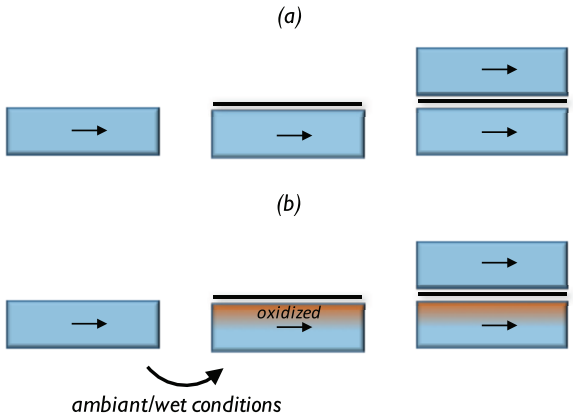

Figure 7. (a) In the case of a direct CVD on top of the bottom ferromagnet, the graphene layer is grown on a metallic surface. Its strong resistance to diffusion, in particular regarding oxygen, prevents oxidation. The resulting MTJs thus possess two preserved ferromagnetic interfaces. (b) In the case of a simple exfoliation or transfer process, the bottom ferromagnetic electrode is exposed to air and to wet chemistry. The graphene layer thus traps an already oxidized interface. This leads to the fabrication of MTJs with a degraded interface that strongly quenches the performance of the device.

begun [17, 47, 48]. In these studies, ferromagnetic catalysts were exposed to carbon-based molecules such as C_2H_2 or C_2H_4, at conditions of temperature and pressure under which they dissociate on the surface. Then, by keeping the right carbon balance at the surface, the nucleation and growth of graphene layers was observed. Typically, the CVD processes on Ni or Co were known to give rise to multilayers being grown. The parameter space of these processes has only recently been investigated by *in situ* x-ray photoelectron spectroscopy (XPS) measurements during CVD growth, allowing careful understanding of the mechanisms at play [18, 49]. Usually, growth is enabled at temperatures >600 °C, but a fine tuning of the processes allowed the growth to be limited to a monolayer and the temperature to be lowered down to 450 °C and below (thus compatible with the usual CMOS processing) [18, 50]. This highlights the effort required to achieve high-quality FM/graphene interfaces. In this regard, recently demonstrated FM intercalation could prove to have high potential, opening an easy path for the tailoring of the FM/graphene interface [51].

Based on these studies of direct graphene CVD on FM [17, 18], Dlubak *et al* [16] showed a simple CVD process for graphene integration in MTJs (see figure 8 left-hand panel). This process led to the growth of multilayer graphene on top of a nickel electrode. No oxidative step was required here to derive the graphene layer, with the targeted goal of preventing the surface oxidation of the ferromagnet. In order to highlight this point, an XPS study was presented, comparing the chemical surface state of the Ni samples exposed to air with and without a CVD graphene overlayer. This showed (see figure 8 right-hand panel) the clear passivation effect of the graphene multilayer, even after the sample had been left for seven days in air (ambient conditions). The result unambiguously highlighted the effectiveness and robustness of the graphene-passivated ferromagnetic electrode (GPFE). A follow-up paper further demonstrated this property after 18 months of ambient exposure for both nickel and cobalt covered with graphene layers [52]. Graphene thus appeared to be a very appealing material for unlocking the use of oxidative processing on top of the usual ferromagnets, and more generally for blocking diffusion processes on the surface and inside heterostructures.

Transport measurements revealed the presence of a ~120 mV dip around zero-voltage in the dI/dV curves, which was emphasized as a clear indication of tunnelling into graphene. The dip related to the distinct signature of electrons tunnelling vertically into graphene layers had previously been reported in a study using scanning tunnelling spectroscopy [53]. The appearance of a ~120 mV gap-like feature was ascribed to the low probability of elastic tunnelling in graphene due to a k vector mismatch between the vertical tunnelling electrons and in-plane states of the graphene layer. When a threshold bias voltage corresponding to the energy of the out-of-plane acoustic phonon mode of graphene was reached, inelastic conduction paths were opened and the conductivity was enhanced [53, 54].

The relevant spintronics demonstration is an extraction of the spin-polarized current in a real device. This was further achieved in [16], as this novel GPFE electrode was integrated in a complete spin device to evaluate its spintronics properties. The authors made use of the well-known Al_2O_3/Co tunnel stack to analyse the spin (positive spin polarization $P = +32\%$) [19, 55] of the current that had been extracted from the GPFE electrode. A strong spin signal on the order of MR $= -10\%$ was measured. This not only further demonstrated that the graphene was efficiently able to protect the nickel surface from oxidation during the fabrication steps, but also that it would preserve the spin polarization for this ferromagnetic electrode. Interestingly, beyond its large amplitude, the sign of the measured MR in these devices was found to be negative, leading to the first observation of negative spin polarization (P estimated at -16%), pointing to a spin filtering effect arising at the graphene/nickel interface (and the reversal of the spin polarization) as further detailed below.

Later, Godel *et al* [26] also integrated multilayer-graphene-covered nickel electrodes in spintronics devices. The authors developed an MBE growth process to fabricate a MgO/Co tunnel spin analyser on top of graphene [27]. They analysed the sign variations of the TMR using the MgO/Co stack and measured the reversal of the spin polarizations of the GPFE as a function of the applied voltage ascribed to the specific electronic structure of the Ni/graphene interface. This work confirmed the observation of a spin filtering effect at this interface, and discussed the underlying physical mechanisms based on experimental observations.

In another study [29], using the same multilayer GPFE as in [16], the authors substituted the more usual Al_2O_3-sputtered tunnel barrier [19, 55] with an atomic-layer- deposited (ALD) one (see figure 9). The GPFE was thus used to demonstrate the possible integration of well-known oxidative processes (such as ALD) in spintronics devices based on metallic spin

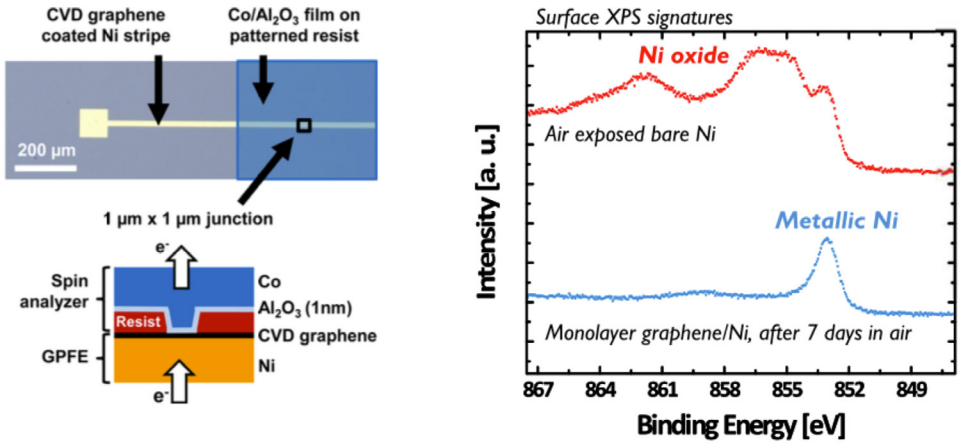

Figure 8. (Left) The Ni/graphene/Al_2O_3/Co MTJ fabrication process based on a direct CVD step on top of the Ni electrode. The graphene layer is thus grown on a metallic ferromagnetic electrode. A standard Al_2O_3/Co tunnel spin analyser is deposited on top to extract the spin properties of the Ni/graphene electrode. Reprinted with permission from [16]. Copyright (2012) American Chemical Society. (Right) The XPS spectra revealing the chemical state of the electrode's surface. If the electrode is not covered by graphene it immediately oxidizes in air, and NiO_x signatures appear in the XPS spectra. In contrast, a Ni electrode covered with graphene remains metallic even if it is left in air for extended periods. This demonstrates the stability of graphene-passivated ferromagnetic electrodes (GPFE) and their suitability for spintronics devices. Reproduced from [31]; CC BY 3.0.

sources. While the ALD of Al_2O_3 is known to be an oxidative process—usually dubbed as incompatible with spintronic devices [56, 57]—here the graphene was used as protection, to avoid the oxidation of the FM surface. This in turn protected the spintronics properties of the device, as demonstrated by the measurement of the large spin signals. In particular, this study underlined that the Ni/graphene interface was able to provide a strong spin filtering effect with a spin polarization of $P = -42\%$ in this case of multilayer graphene. A process was specifically designed to allow high homogeneous wetting of graphene during ALD cycles (which has been shown to be challenging, see for example [58]), and this process was achieved in particular by using an ozone-based approach. Interestingly, the particular conformal layer-by-layer growth mode of ALD allows ultra-thin films to be grown below the nm scale. Reference [29] demonstrated Al_2O_3 tunnel barriers with thicknesses down to 0.6 nm, to be contrasted with the issues of PVD techniques concerning the correct film closure (defects, pinholes) when reaching for such thin films. The efficient graphene passivation layer has allowed ALD to be ultimately beneficial for MTJ fabrication. Interestingly, ALD is a process which was otherwise already being widely used in the fabrication of microelectronic components (gate oxides in current microprocessor transistors nodes [59], DRAM capacitors [60], etc).

In 2015, a further study focused on monolayer graphene GPFE [31]. By deeper control of the growth conditions, a process was developed to limit the growth of graphene to a single layer on nickel. An XPS study confirmed that even when reduced to a monolayer, graphene still protects the Ni electrode against oxidation. This in turn allows the spin properties of the monolayer graphene/nickel interface to be probed. In order to be able to compare this to the multilayer case, the exact same structure as in [29] was fabricated, but with a graphene thickness limited to one monolayer. In particular, dI/dV spectroscopy and MR measurement characterizations

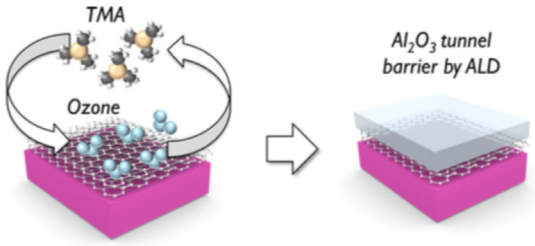

Figure 9. An illustration of the ALD process on top of a graphene-passivated ferromagnetic electrode (GPFE). TMA and ozone cycles are carried on top of the electrode, leading to its homogeneous coverage by Al_2O_3 ultra-thin films. The graphene layer protects the ferromagnet against oxidation during this ozone-based process. Reprinted with permission from [29]. Copyright (2014) the American Chemical Society.

were carried out. In a similar way to the multilayer case, the dI/dV showed a clear dip in the −60 mV to 60 mV region, indicative of electron tunnelling to the graphene monolayer, as described in previous studies [53]. The MR measurements showed a negative spin signal, which was a significant result demonstrating that even when reduced to a monolayer, graphene still had a very strong effect on the spin polarization of the nickel electrode—even being able to reverse its sign. The use of a well-known spin analyser (Co/Al_2O_3) as one of the interfaces in this set of studies provides us a first glimpse of the dependence of the spin polarization of GPFE and its increase with the number of graphene layers, as expected from theory [10] (see figure 10). More recently, Entani *et al* [40] and Cobas *et al* [42] presented magneto-dependent FM/graphene/FM MTJ transport structures using similar direct CVD processes on FM. Interestingly, [42] showed negative magnetoresistance signals ascribed to spin filtering at one of the two interfaces reaching up to MR of −12%. This corresponds to a mean spin polarization of $P = 25\%$ in absolute terms for the two interfaces, when one interprets the result

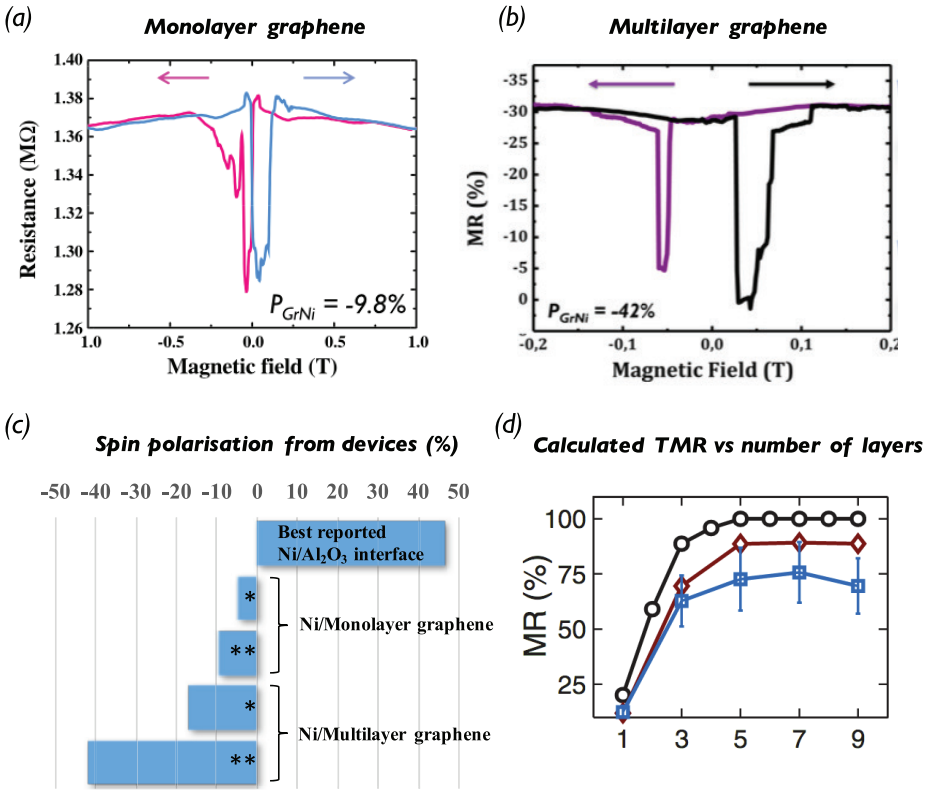

Figure 10. (Top) The TMR spin signals measured in Ni/graphene/Al_2O_3/Co MTJs making use of a direct CVD process to derive the graphene layers. Two different CVD processes have been used giving rise to either monolayer graphene or multilayer graphene (about five layers). The measured TMR spin signals reach −42% in the multilayer case. Reprinted with permission from [29]. Copyright (2014) American Chemical Society. Reproduced from [31]; CC BY 3.0. (Bottom left) A comparison of the extracted spin polarization of a graphene-covered Ni electrode to state-of-the-art Ni spin sources without graphene. Ni/Al_2O_3 electrodes have been reported to give a polarization of +46% at best [61]. With graphene multilayers, the strong spin filtering effect is able to fully reverse this spin polarization. ∗Sputtered Al_2O_3/Co spin analyser on top. ∗∗ALD-grown Al_2O_3/Co spin analyser on top. (Bottom right) The calculated TMR spin signals for Ni/graphene/Ni MTJs as a function of the number of graphene layers. This theoretical result anticipated a strong increase in the TMR in the multilayer case. Reprinted with permission from [10]. Copyright (2010) by the American Physical Society.

through the standard Jullière model [8]. The authors also further predicted spin polarization up to 98% for one of the two interfaces through a two-channel analysis of the system. This would then in turn mean a possible MR $= 2P^2/(1 - P^2)$, which would be well in excess of few hundred % if both interfaces were able to provide such high spin polarizations through the envisioned strong spin filtering effect of GPFE.

5. Spin filtering at the FM/graphene interface

Similarly to graphene that had its band structure described way before its first experimental investigation, graphene MTJs were first described from a theoretical point of view. Based on the idea that 2D materials could lead to perfectly structured interfaces and hence solve the longstanding issue of robust spin injection, Karpan *et al* [10] proposed that graphene could be embedded as a barrier in an MTJ. In their work, they proposed that graphene acting as a tunnel barrier between two ferromagnetic layers could play the role of a quasi-perfect spin filter of minority spin and lead to a very high MR. To identify this spin filtering effect, they calculated the electronic band structure of (1 1 1) fcc or (0 0 0 1) hcp Ni or Co. Here, fcc Ni and hcp Co have the same hexagonal first Brillouin zone as graphene (they present a low lattice mismatch of only 1.3% with graphene). The authors showed for both the Ni(1 1 1) and Co(0 0 0 1) orientations that only minority spin states were available at the Fermi level on the K and Γ points, while majority ones were only present at the M point (figure 11). This was compared to the band structure of graphene, where the only available states were at the Dirac K points, highlighting the matching of available minority spins of the FM with the conduction states of graphene. Further calculations of the transmission by simple first principles tight-binding let Karpan *et al* [10] predict the appearance of a strong spin filtering effect at the graphene/FM interface: minority spins were predicted to be matched to a conduction path through the graphene layers, while majority spins were predicted to be exponentially filtered out (figure 12). They predicted extremely large spin polarizations of close to 100%, with the resulting TMR well in excess of hundreds of %. In a follow-up paper [62], the authors highlighted the potential role of the interface quality and hybridization on the resulting efficiency to emphasize the robustness of the effect.

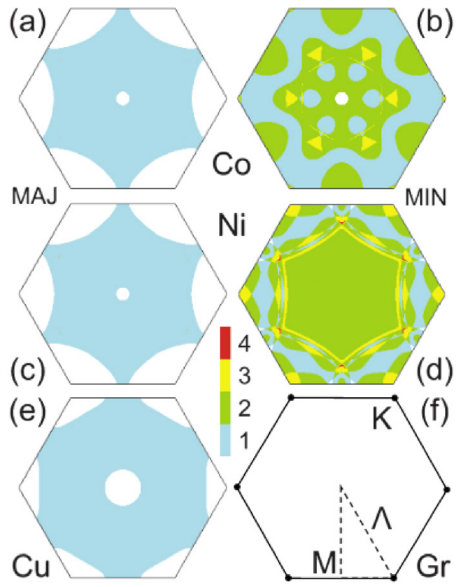

Figure 11. (a)–(e) The calculated Fermi surfaces for Ni and Co: yellow and red indicate the highest state densities. In particular, in the case of Ni, the minority spins appear to match (f) the graphene Dirac points. Reprinted with permission from [10]. Copyright (2010) by the American Physical Society.

However, as seen in section 3, the experimental implementation revealed itself to be a challenge. Neither of the two predictions of (i) minority spin filtering or (ii) high MR were observed at first. The first issue was that for a symmetric FM/Gr/FM heterostructure, evidence of the main prediction of negative spin polarization could not be possibly provided through a negative TMR, as it would give rise to a positive TMR (see figure 10, bottom right), expected for any symmetric structure. Indeed, as the TMR is proportional to the product of the spin polarizations $P_1 \times P_2$, two positive or two negative spin polarizations would give the same TMR sign. Another striking issue concerned the out-of-plane electrical conduction in devices encompassing only a graphene layer between the two ferromagnetic electrodes, with still no experimental consensus yet on the role of the graphene spacer. Some of the earlier mentioned studies reported on graphene acting mainly as a metallic spacer [20, 21, 24, 32, 39], whilst other studies reported on it acting as a tunnel barrier [14, 24, 28]. One study [25] even reported that its role varied with temperature. Park *et al* [24] explained the variability in their own results by suggesting that their most resistive junctions (with the $R \times A$ product $>1\ \Omega\ \mu m^2$) had a metallic contribution from the contact (which is responsible for the linearity of the *I–V* curves), dominating the less resistive non-linear contribution from the intrinsic out-of-plane resistivity of graphene. Meng *et al* [22] ascribed the ohmic property of their graphene barriers to the differences of the work functions of both interfaces (the bottom FM-graphene and the graphene-FM on top). However, the particularities of each reported system and the limitations in the presented fabrication processes (ferromagnets at the interfaces being exposed to air or to a resist during the fabrication process) certainly also contributed. Thus, a conclusive statement remains elusive.

The use of a positive spin-polarized interface acting as an analyser helped to isolate the spin polarization of the graphene-FM electrode and solve this issue. Hence, the first experimental evidence in [16] of the theoretical prediction of minority spin filtering at the FM/graphene interface was achieved with devices for which a well-known Al_2O_3/Co spin analyser was used. Following the scheme of [7], these devices allowed a single and clean Ni/graphene interface to be probed independently, unambiguously demonstrating the spin filtering effect through inverse magnetoresistance measurements (see figure 9). A sizeable negative spin polarization of $P = -16\%$ was reported for the Ni/graphene/Al_2O_3 interface [16]—a value which should be compared to the positive $P \geqslant 30\%$ usually reported for Ni/Al_2O_3 interfaces [61]. This result thus revealed a strong spin filtering effect.

The spin polarization sign in MTJs has been a subject of debate for a long time in spintronics. At first, the spin polarization in tunnelling experiments was expected to be directly related to the electrode density of states (DOS). This led to a longstanding discrepancy between the theory and experiments, i.e. the negative sign expected from the DOS of the 3*d* bands at the Fermi level in Ni and Co and the observed positive sign for Ni or Co at the Al_2O_3 interfaces in the early spin-polarized tunnelling Meservey–Tedrow experiments [64]. An important step was achieved in the late 90s, explaining the discrepancy between the demonstration of the role of the interface in band and spin selection [7]. This was quickly followed by the first predictions of spin filtering using the symmetry of Bloch states in the electrodes and of evanescent states in crystalline barrier layer MgO [65, 66]. This leads to the observation of very large TMR in the MgO structures as we know them today.

However, the mechanism at play in the GPFE structures appears to differ from the ones previously reported. In MgO-based structures, spin selectivity was achieved through competition between the exponentially decaying states, which are high symmetry $\Delta 1$ states (having an *sp* character) that are only present for one spin direction, and that have a much slower decay rate compared to the $\Delta 5$, $\Delta 2$ and $\Delta 2'$ ones [65, 66]. Here, the two spin channels are expected to follow different mechanisms. While the majority carriers are forced to tunnel through the graphene stack and are hence expected to be exponentially attenuated as in MgO MTJs, the minority ones are coherently transmitted through the graphene layers with metallic-like behaviour. From a simple model of metallic conduction for minority spins and tunnelling for majority spins, one would then expect the spin filtering effect to increase exponentially with the number of graphene layers. This led to the prediction by Karpan *et al* [10] of the enhancement of the spin filtering effect with an increasing number of graphene layers in such Ni/graphene/Ni spin valves. They predicted that the conductivity of the minority carrier would remain almost constant with the number of graphene layers, while in contrast, the conductivity of the majority carrier would dramatically decrease, exponentially. Beyond nine graphene layers, the majority spin conductivity was predicted to be about eight orders of magnitude lower than that of the minority carriers.

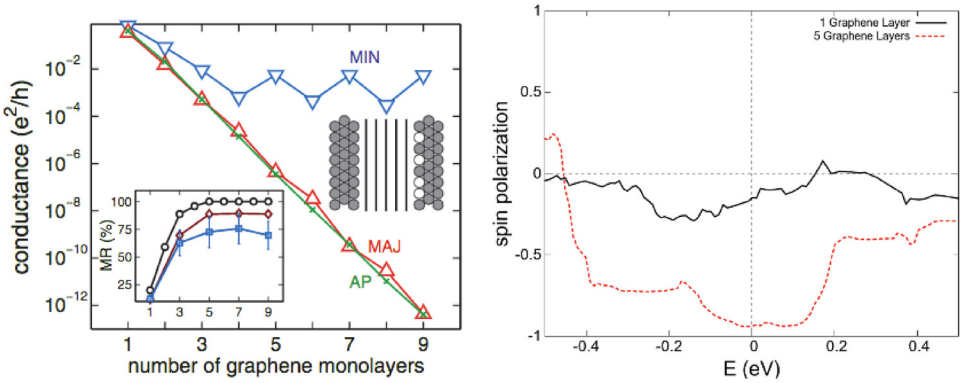

Figure 12. (Left) The calculated dependence of majority and minority spin conduction through the graphene layers at the Ni/graphene interface (the inset shows the calculated resulting TMR signal). Reprinted with permission from [10]. Copyright (2007) by the American Physical Society. (Right) The calculated spin polarization for one and five graphene layers. Reprinted with permission from [63]. Copyright (2014) by the American Physical Society.

Evidence of this prediction was only very recently experimentally provided [29, 31]. Indeed, going from a monolayer with $P = -9.8\%$ in [31] to multilayers with $P = -42\%$ in [29], a clear trend appears: the spin filtering effect increases with the number of layers. This experimental observation matches the expectations set by the theoretical analyses quite nicely (see figures 9 and 11). Strikingly, the very strong spin filtering observed for a GPFE of $P = -42\%$ corresponds to an almost full reversal when compared to the best reported Ni/Al_2O_3 spin sources of $P = +46\%$ [61].

Still, a question remains regarding the influence of ferromagnet coupling to the first layer of graphene. Remarkably, while it is clear that the π states of the first graphene layer are strongly hybridized with the nickel surface, Karpan *et al* [10, 62] considered this to be potentially detrimental. They tried to emphasize the robustness of the spin filtering effect, highlighting that it would not depend on details of how the graphite was bonded to the ferromagnetic leads (as long as translational symmetry was preserved), but mainly on the thickness of graphite [10]. It is hence outstanding that a negative spin polarization of -9.8% could be observed for a single layer of graphene [31] known to be hybridized with the surface [52]. Hybridization with a ferromagnetic surface had already been shown to lead to a reversal of the spin polarization [67]. A step in this direction was made by Lazic *et al* [63] in an effort to highlight the impact of Ni/graphene hybridization on graphene. The authors presented in-depth calculations demonstrating the proximity effect of graphene/Ni(1 1 1), and showed that strong and negative proximity-induced spin polarization could occur for the graphene/Ni(1 1 1) interface, thereby potentially explaining the single layer observation. However, this could not fully account for the increase from -9.8% to -42% with the increase in the thickness of the graphene layer.

We can hence explain the observed experimental dataset using two convoluted contributions, each giving rise, in the case of Ni/graphene, to negative spin polarization: one arising from band structure modification through the proximity effect and another one exponentially rising from spin filtering through the graphene's band structure. While a deeper understanding remains to be achieved, this highlights the convergence of experiments and theory towards the very high potential of direct CVD growth on FM for 2DM integration into MTJs.

6. Other 2D materials beyond graphene in magnetic tunnel junctions

While graphene is the first 2DM to have been envisioned and implemented in magnetic tunnel junctions, the 2DM family is extremely extensive, with materials demonstrating a wide range of available properties [68–71]. Very recently, a few other 2DMs have been studied, and two main classes of materials have been more thoroughly explored: hexagonal boron nitride (h-BN), which is an insulating isomorph of graphene, and TMDCs (MoS_2, WS_2, etc), which is semiconducting family of layered materials. The problems at play here are similar to those discussed with graphene. In particular, the studies have been limited by the availability of large-scale processes for integration which are compatible with oxidation-prone ferromagnets.

A pioneering study by Dankert *et al* [30] made use of an h-BN layer which had been wet-transferred on top of ferromagnetic NiFe and Co electrodes. The h-BN layer was grown on the Cu by CVD (as received from the Graphene Supermarket) and transferred to the ferromagnet using a standard PMMA-assisted transfer step. The authors then characterized the spin transport in NiFe/h-BN/Co and Co/h-BN/Co MTJs. The magnetoresistance measurements revealed a spin signal of up to TMR $= 0.5\%$ corresponding to spin polarizations of $P = 0.25\%$ extracted from the FM/h-BN interfaces. The expected degradation of the spin properties of the interfaces by oxidation led to the limitation of the spin signals, as was the case with the initial studies presented above using transferred graphene in MTJs. Illustratively, the authors of [72] showed that once the FM electrode had been oxidized, transferring the h-BN layer to the top could marginally slow down any further oxidation of the electrode. Similarly to graphene, the oxidation induced by wet transfer steps in air remained a strong limitation for the fabrication of such systems.

In parallel, following the path developed in section 4, the mechanisms of the CVD growth of large-scale h-BN layers

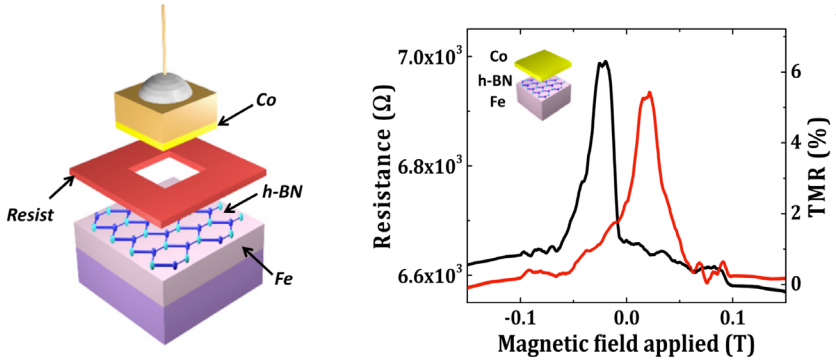

Figure 13. (Left) Fe/h-BN/Co MTJ fabricated by a direct CVD step on the top of Fe in order to grow the monolayer h-BN sheet. (Right) A spin signal of TMR = 6% is measured in these devices. Reprinted from [35]. CC BY 3.0.

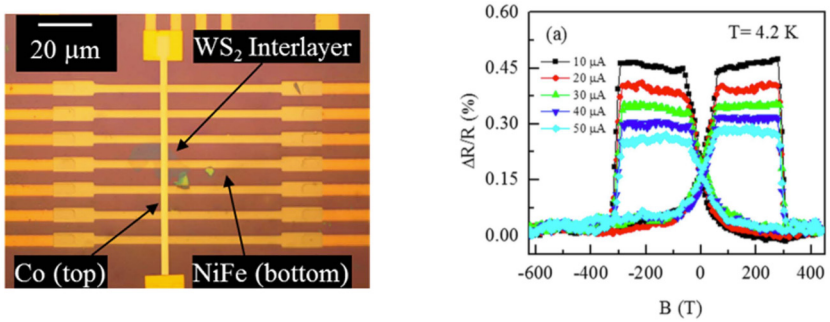

Figure 14. (Left) An optical picture of a NiFe/WS_2/Co MTJ device based on a WS_2 flake exfoliated in air on top of a prepatterned NiFe electrode. (Right) The reported TMR spin signal reached about 0.5%. Reprinted from [38]. CC BY 4.0.

directly onto the FM have been studied, in particular in the case of the Fe catalyst [36, 37]. Monolayer h-BN films of high quality (grains of hundreds of microns) were grown by the catalysed decomposition of borazine on the Fe surface. This achievement required an understanding of the careful balance of B and N feeding the catalyst for optimal growth [36, 37]. Owing to the knowledge gained through these studies, the integration of h-BN as an ultimately thin tunnel barrier in efficient spin valves has been enabled (see figure 13). In 2016, Piquemal-Banci *et al* [35] reported on the fabrication of Fe electrodes covered with h-BN and further contacted by Co through the patterning of lithographic junctions. The resulting Fe/h-BN/Co junctions based on this h-BN direct CVD growth on FM exhibited large spin signals for a purely 2D tunnel barrier. The authors reported a TMR = 6% and estimated the spin polarization for their FM/h-BN interfaces to be of $P = 17\%$, which is two orders of magnitude larger than the previous result with the transferred h-BN [30]. This study highlighted the use of high quality h-BN/Fe spin injectors for spintronics. In particular, it demonstrated the possibility of controlling the resistance of the tunnel barrier with the number of h-BN sheets deposited layer-by-layer through a conductive-tip atomic force microscopy (AFM) study, extracting a barrier height of $\phi = 0.85$ eV. As alternatives to the CVD method, other promising h-BN integration pathways have been suggested, such as the MBE growth of h-BN on Co [73] or the *in situ* growth of FMs over both the faces of h-BN flakes suspended on etched membranes [39]. These methods also allowed the metallic state of the interfaces to be preserved. Reference [39] used a similar process for exfoliated graphene and h-BN MTJs using perforated membranes: the fabricated Co/h-BN/NiFe devices exhibited an MR of 1%.

Concerning the TMDC layers, the relevant pioneering studies are also extremely recent. Two studies have managed to derive large MoS_2 layers on ferromagnetic spin sources [33, 34]. In 2015, Wang *et al* [33] described the introduction of MoS_2 layers in MTJs. The authors developed a process for MoS_2 growth which required a wet transfer step for integration with ferromagnets, leading to the same issues already encountered with graphene (as shown in section 3). The authors grew the MoS_2 layers by CVD on SiO_2 and identified triangular islands ~10 microns wide to be monolayer MoS_2 using photoluminescence and Raman spectroscopy techniques. The authors had to introduce particular electrodes which sustained the process with minimum oxidation issues: they used a Au-protected NiFe electrode in order to avoid oxidation during the MoS_2 transfer. They then further contacted the stack on top with another NiFe electrode. The MR was shown to increase from 0.4% to 0.73% by the introduction of the Au protection layer. While this study underlined the problem of MoS_2 integration, the Au layer still led to the limitation of the spin properties of the device. The same year Wu *et al* [34] made use of ferromagnetic oxide Fe_3O_4 in MoS_2-based MTJs. In this case, the authors developed a technique of sulfurization of the MBE-grown Mo layers to derive the MoS_2 sheets on Fe_3O_4. The devices were contacted on the top by a second Fe_3O_4 electrode, and the junctions were defined by electron beam lithography. While this process did not seem affected by oxidation issues, the spin signal remained limited to an MR of 0.2%, which was far from expectations. More recently, in 2016 an

attempt was made to demonstrate an MTJ with micron-sized exfoliated WS_2 flakes [38] (see figure 14). The authors exfoliated WS_2 in air on patterned NiFe electrodes and contacted them on the top with Co. The resulting NiFe/WS_2/Co MTJs led to measurements of MR = 0.47%, which were certainly still limited by the oxidation of the bottom ferromagnetic electrode.

While h-BN has already given promising results, the use of TMDCs in MTJs is still in its initial stage and much improvement can be foreseen if the multiple fabrication parameters are optimized, as they have been for graphene. For now, an unexplored route for TMDCs (but successfully demonstrated for graphene and h-BN) is the use of a direct CVD process on the ferromagnets. This kind of process for TMDCs on an FM remains to be demonstrated and studied, with the promise of good opportunities for spintronics.

7. Conclusion and perspectives

Graphene has come a long way since the first attempt at its introduction into MTJs. While the studies presented in this review are just the first of a very emergent field, they have already shown its potential. Up to now, two main properties have been identified:

(i) Graphene, as an impermeable interfacial material, has been shown to unlock wet/ambient processes for spintronics. Illustratively, a low-cost high-quality conformal ALD process has been demonstrated for tunnel barrier growths in functional MTJs, thanks to graphene protected FM electrodes. The use of such an oxidative process, without quenching the properties of a metallic FM, is unprecedented. Hence, graphene allows an integrative pathway for wet processes in spintronics, with further perspectives for robust and simplified spin-polarized contact to nano-objects [74] and organic/molecular materials [75–77].

(ii) Graphene-based MTJs have shown a promising spin filtering effect, which match the amplitude of the best Ni/Al_2O_3 interfaces, with indications of experimental control, in particular regarding the number of stacked 2D layers. This spin filtering effect for graphene-covered nickel GPFE has already shown a full reversal of the spin polarization [29] compared to the best Ni/Al_2O_3 [61]. Convergence between the theory and experiments (see figure 10) is very encouraging, and will enable further understanding of the underlying mechanisms, eventually leading to the precise engineering of structures with very large spin signals.

The presented studies are very encouraging, as they demonstrate the successful integration of different 2D materials, each possessing very specific transport properties, in MTJ spin valve structures. While many perspectives remain to be explored in terms of functionality and performance (for example it was shown that FM/graphene interfaces could lead to strongly enhanced perpendicular magnetization [51, 78], etc), new unique interesting properties have been unveiled in these 2DM-based MTJs in addition to their reduced thickness down to the atomic level. As of now, the most promising road appears to be direct CVD on FM (see the state of the art in figure 2), which has provided the largest spin polarizations to date with graphene [29] ($P = -42\%$) and h-BN [35] ($P = 17\%$), and also unveiled the potential for perpendicular magnetization.

Further integration engineering, especially the continued understanding of 2D growth processes on FM, will certainly lead to improved device performance. It will also allow the particular properties of each 2DM to be captured more successfully. In this regard, the presented studies are certainly just a start; indeed, many integration parameters are still not clearly understood. Each 2DM can been grown in very different ways. Potentially, parameters such as the FM crystallinity, the FM surface chemical state (in a particular dissolved species), the 2DM quality, the FM/2DM interaction, the FM/2DM relative crystallographic orientation, the 2DM thickness or functionalization, and intercalation of FM at 2DM interfaces, etc, will prove to have a fundamental impact on the interfacial spin properties. Furthermore, many properties remain to be explored in addition to the high TMR ratio, such as thermal stability, mechanical stress, switching current, annealing tolerance, device lifetime (see for instance [79]). The very high stability of 2DMs, such as graphene and h-BN (strong in-plane bonds), and their resistance to diffusion processes will certainly prove to be a major asset in this regard. It is also fascinating to realize that while the literature has mainly focused on graphene so far, with a few other pioneering studies concerning h-BN and TMDCs, many other 2DMs are yet to be explored, and their association in heterostructures is virtually endless. This holds the promise of the introduction of new concepts for layered spin valves with atomic level control of their transport properties, tailored toward the specific processing of the spin information flow.

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References

[1] Khvalkovskiy A V *et al* 2013 Basic principles of STT-MRAM cell operation in memory arrays *J. Phys. D: Appl. Phys.* **46** 74001
[2] Chappert C, Fert A and Van Dau F N 2007 The emergence of spin electronics in data storage *Nat. Mater.* **6** 813–23
[3] Behin-Aein B, Datta D, Salahuddin S and Datta S 2010 Proposal for an all-spin logic device with built-in memory *Nat. Nanotechnol.* **5** 266–70
[4] Seneor P, Dlubak B, Martin M-B, Anane A, Jaffres H and Fert A 2012 Spintronics with graphene *MRS Bull.* **37** 1245–54
[5] Han W, Kawakami R K, Gmitra M and Fabian J 2014 Graphene spintronics *Nat. Nanotechnol.* **9** 794–807
[6] Roche S *et al* 2015 Graphene spintronics: the European flagship perspective *2D Mater.* **2** 30202
[7] De Teresa J M, Barthélémy A, Fert A, Contour J P, Montaigne F and Seneor P 1999 Role of metal-oxide

interface in determining the spin polarization of magnetic tunnel junctions *Science* **286** 507
[8] Julliere M 1975 Tunneling between ferromagnetic films *Phys. Lett.* A **54** 225–6
[9] Tsymbal E Y, Mryasov O N and LeClair P R 2003 Spin-dependent tunnelling in magnetic tunnel junctions *J. Phys.: Condens. Matter* **15** R109–42
[10] Karpan V, Giovannetti G, Khomyakov P, Talanana M, Starikov A, Zwierzycki M, van den Brink J, Brocks G and Kelly P 2007 Graphite and graphene as perfect spin filters *Phys. Rev. Lett.* **99** 176602
[11] Dedkov Y S, Fonin M and Laubschat C 2008 A possible source of spin-polarized electrons: the inert graphene/Ni(1 1 1) system *Appl. Phys. Lett.* **92** 52506
[12] Mohiuddin T M G, Hill E, Elias D, Zhukov A, Novoselov K and Geim A 2008 Graphene in multilayered CPP spin valves *IEEE Trans. Magn.* **44** 2624–7
[13] Banerjee T, van der Wiel W G and Jansen R 2010 Spin injection and perpendicular spin transport in graphite nanostructures *Phys. Rev.* B **81** 214409
[14] Cobas E, Friedman A L, van't Erve O M J, Robinson J T and Jonker B T 2012 Graphene as a tunnel barrier: graphene-based magnetic tunnel junctions *Nano Lett.* **12** 3000–4
[15] Cobas E, Friedman A L, van't Erve O M J, Robinson J T and Jonker B T 2013 Graphene-based magnetic tunnel junctions *IEEE Trans. Magn.* **49** 4343–6
[16] Dlubak B *et al* 2012 Graphene-passivated nickel as an oxidation-resistant electrode for spintronics *ACS Nano* **6** 10930–4
[17] Weatherup R S, Bayer B C, Blume R, Ducati C, Baehtz C, Schlögl R and Hofmann S 2011 *In situ* characterization of alloy catalysts for low-temperature graphene growth *Nano Lett.* **11** 4154–60
[18] Weatherup R S, Dlubak B and Hofmann S 2012 Kinetic control of catalytic CVD for high-quality graphene at low temperatures *ACS Nano* **6** 9996–10003
[19] Dlubak B, Martin M-B, Deranlot C, Bouzehouane K, Fusil S, Mattana R, Petroff F, Anane A, Seneor P and Fert A 2012 Homogeneous pinhole free 1 nm Al_2O_3 tunnel barriers on graphene *Appl. Phys. Lett.* **101** 203104
[20] Iqbal M Z, Iqbal M W, Lee J H, Kim Y S, Chun S-H and Eom J 2013 Spin valve effect of NiFe/graphene/NiFe junctions *Nano Res.* **6** 373–80
[21] Chen J-J, Meng J, Zhou Y-B, Wu H-C, Bie Y-Q, Liao Z-M and Yu D-P 2013 Layer-by-layer assembly of vertically conducting graphene devices *Nat. Commun.* **4** 1921
[22] Meng J, Chen J-J, Yan Y, Yu D-P and Liao Z-M 2013 Vertical graphene spin valve with Ohmic contacts *Nanoscale* **5** 8894
[23] Singh A K and Eom J 2014 Negative magnetoresistance in a vertical single-layer graphene spin valve at room temperature *ACS Appl. Mater. Interfaces* **6** 2493–6
[24] Park J-H and Lee H-J 2014 Out-of-plane magnetoresistance in ferromagnet/graphene/ferromagnet spin-valve junctions *Phys. Rev.* B **89** 165417
[25] Li F, Li T and Guo X 2014 Vertical graphene spin valves based on $La_{2/3}Sr_{1/3}MnO_3$ electrodes *ACS Appl. Mater. Interfaces* **6** 1187–92
[26] Godel F, Venkata Kamalakar M, Doudin B, Henry Y, Halley D and Dayen J-F 2014 Voltage-controlled inversion of tunnel magnetoresistance in epitaxial nickel/graphene/MgO/cobalt junctions *Appl. Phys. Lett.* **105** 152407
[27] Godel F, Pichonat E, Vignaud D, Majjad H, Metten D, Henry Y, Berciaud S, Dayen J-F and Halley D 2013 Epitaxy of MgO magnetic tunnel barriers on epitaxial graphene *Nanotechnology* **24** 475708
[28] Li W, Xue L, Abruña H D and Ralph D C 2014 Magnetic tunnel junctions with single-layer-graphene tunnel barriers *Phys. Rev.* B **89** 184418
[29] Martin M-B *et al* 2014 Sub-nanometer atomic layer deposition for spintronics in magnetic tunnel junctions based on graphene spin-filtering membranes *ACS Nano* **8** 7890–5
[30] Dankert A, Venkata Kamalakar M, Wajid A, Patel R S and Dash S P 2015 Tunnel magnetoresistance with atomically thin two-dimensional hexagonal boron nitride barriers *Nano Res.* **8** 1357–64
[31] Martin M-B *et al* 2015 Protecting nickel with graphene spin-filtering membranes: a single layer is enough *Appl. Phys. Lett.* **107** 12408
[32] Iqbal M Z, Iqbal M W, Jin X, Hwang C and Eom J 2015 Interlayer dependent polarity of magnetoresistance in graphene spin valves *J. Mater. Chem.* C **3** 298–302
[33] Wang W *et al* 2015 Spin-valve effect in NiFe/MoS_2/NiFe junctions *Nano Lett.* **15** 5261–7
[34] Wu H-C *et al* 2015 Spin-dependent transport properties of Fe_3O_4/MoS_2/Fe_3O_4 junctions *Sci. Rep.* **5** 15984
[35] Piquemal-Banci M *et al* 2016 Magnetic tunnel junctions with monolayer hexagonal boron nitride tunnel barriers *Appl. Phys. Lett.* **108** 102404
[36] Caneva S *et al* 2015 Nucleation control for large, single crystalline domains of monolayer hexagonal boron nitride via Si-doped Fe catalysts *Nano Lett.* **15** 1867–75
[37] Caneva S *et al* 2016 Controlling catalyst bulk reservoir effects for monolayer hexagonal boron nitride CVD *Nano Lett.* **16** 1250–61
[38] Iqbal M Z, Iqbal M W, Siddique S, Khan M F and Ramay S M 2016 Room temperature spin valve effect in NiFe/WS_2/Co junctions *Sci. Rep.* **6** 21038
[39] Asshoff P U, Sambricio J L, Mishchenko A, Rooney A P, Hill E W, Haigh S J, Geim A K, Fal'ko V I, Vera-Marun I J and Grigorieva I V 2016 Magnetoresistance of vertical Co-graphene-NiFe junctions controlled by charge transfer and proximity-induced spin splitting in graphene (arXiv: 1607.00983)
[40] Entani S, Seki T, Sakuraba Y, Yamamoto T, Takahashi S, Naramoto H, Takanashi K and Sakai S 2016 Magnetoresistance effect in $Fe_{20}Ni_{80}$/graphene/$Fe_{20}Ni_{80}$ vertical spin valves *Appl. Phys. Lett.* **109** 82406
[41] Iqbal M Z, Siddique S, Hussain G and Iqbal M W 2016 Room temperature spin valve effect in the NiFe/Gr–hBN/Co magnetic tunnel junction *J. Mater. Chem.* C **4** 8711–5
[42] Cobas E D, van 't Erve O M J, Cheng S-F, Culbertson J C, Jernigan G G, Bussman K and Jonker B T 2016 Room-temperature spin filtering in metallic ferromagnet-multilayer graphene-ferromagnet junctions *ACS Nano* **10** 10357–65
[43] Novoselov K S, Geim A K, Morozov S V, Jiang D, Zhang Y, Dubonos S V, Grigorieva I V and Firsov A A 2004 Electric Field Effect in Atomically Thin Carbon Films *Science* **306** 666–9
[44] Blake P, Hill E W, Castro Neto A H, Novoselov K S, Jiang D, Yang R, Booth T J and Geim A K 2007 Making graphene visible *Appl. Phys. Lett.* **91** 63124
[45] LeClair P, Swagten H J M, Kohlhepp J T, van de Veerdonk R J M and de Jonge W J M 2000 Apparent spin polarization decay in Cu-dusted Co/Al_2O_3/Co tunnel junctions *Phys. Rev. Lett.* **84** 2933–6
[46] Nagashima A, Tejima N, Gamou Y, Kawai T and Oshima C 1995 Electronic dispersion relations of monolayer hexagonal boron nitride formed on the Ni(1 1 1) surface *Phys. Rev.* B **51** 4606–13
[47] Reina A, Jia X, Ho J, Nezich D, Son H, Bulovic V, Dresselhaus M S and Kong J 2009 Large area, few-layer graphene films on arbitrary substrates by chemical vapor deposition *Nano Lett.* **9** 30–5

[48] Dahal A and Batzill M 2014 Graphene–nickel interfaces: a review *Nanoscale* **6** 2548

[49] Weatherup R S *et al* 2014 Interdependency of subsurface carbon distribution and graphene–catalyst interaction *J. Am. Chem. Soc.* **136** 13698–708

[50] Weatherup R S, Bayer B C, Blume R, Baehtz C, Kidambi P R, Fouquet M, Wirth C T, Schlögl R and Hofmann S 2012 On the mechanisms of Ni-catalysed graphene chemical vapour deposition *ChemPhysChem* **13** 2544–9

[51] Rougemaille N, N'Diaye A T, Coraux J, Vo-Van C, Fruchart O and Schmid A K 2012 Perpendicular magnetic anisotropy of cobalt films intercalated under graphene *Appl. Phys. Lett.* **101** 142403

[52] Weatherup R S, D'Arsié L, Cabrero-Vilatela A, Caneva S, Blume R, Robertson J, Schloegl R and Hofmann S 2015 Long-term passivation of strongly interacting metals with single-layer graphene *J. Am. Chem. Soc.* **137** 14358–66

[53] Zhang Y, Brar V W, Wang F, Girit C, Yayon Y, Panlasigui M, Zettl A and Crommie M F 2008 Giant phonon-induced conductance in scanning tunnelling spectroscopy of gate-tunable graphene *Nat. Phys.* **4** 627–30

[54] Wehling T, Grigorenko I, Lichtenstein A and Balatsky A 2008 Phonon-mediated tunneling into graphene *Phys. Rev. Lett.* **101** 216803

[55] Barraud C, Deranlot C, Seneor P, Mattana R, Dlubak B, Fusil S, Bouzehouane K, Deneuve D, Petroff F and Fert A 2010 Magnetoresistance in magnetic tunnel junctions grown on flexible organic substrates *Appl. Phys. Lett.* **96** 72502

[56] Bubber R, Mao M, Schneider T, Hegde H, Sin K, Funada S and Shi S 2002 ALCVD AlO_x barrier layers for magnetic tunnel junction applications *IEEE Int. Digest of Technical Papers on Magnetics Conf.* vol 38

[57] Mao M, Bubber R and Schneider T 2006 ALD for data storage applications *ECS Trans.* **1** 37–47

[58] Dlubak B, Kidambi P R, Weatherup R S, Hofmann S and Robertson J 2012 Substrate-assisted nucleation of ultra-thin dielectric layers on graphene by atomic layer deposition *Appl. Phys. Lett.* **100** 173113

[59] Mistry K *et al* 2007 A 45 nm Logic technology with high-k + metal gate transistors, strained silicon, 9 Cu interconnect Layers, 193 nm dry patterning, and 100% Pb-free packaging *2007 IEEE Int. Electronics and Devices Meeting* pp 247–50

[60] Kim S K, Choi G-J, Lee S Y, Seo M, Lee S W, Han J H, Ahn H-S, Han S and Hwang C S 2008 Al-doped TiO_2 films with ultralow leakage currents for next generation DRAM capacitors *Adv. Mater.* **20** 1429–35

[61] Kim T H and Moodera J S 2004 Large spin polarization in epitaxial and polycrystalline Ni films *Phys. Rev.* B **69** 020403

[62] Karpan V M, Khomyakov P A, Starikov A A, Giovannetti G, Zwierzycki M, Talanana M, Brocks G, van den Brink J and Kelly P J 2008 Theoretical prediction of perfect spin filtering at interfaces between close-packed surfaces of Ni or Co and graphite or graphene *Phys. Rev.* B **78** 195419

[63] Lazić P, Sipahi G M, Kawakami R K and Žutić I 2014 Graphene spintronics: Spin injection and proximity effects from first principles *Phys. Rev.* B **90** 85429

[64] Meservey R and Tedrow P M 1994 Spin-polarized electron tunneling *Phys. Rep.* **238** 173–243

[65] Butler W H, Zhang X-G, Schulthess T C and MacLaren J M 2001 Spin-dependent tunneling conductance of Fe|MgO|Fe sandwiches *Phys. Rev.* B **63** 54416

[66] Mathon J and Umerski A 2001 Theory of tunneling magnetoresistance of an epitaxial Fe/MgO/Fe(0 0 1) junction *Phys. Rev.* B **63** 220403

[67] Barraud C *et al* 2010 Unravelling the role of the interface for spin injection into organic semiconductors *Nat. Phys.* **6** 615–20

[68] Butler S Z *et al* 2013 Progress, challenges, and opportunities in two-dimensional materials beyond graphene *ACS Nano* **7** 2898–926

[69] Bhimanapati G R *et al* 2015 Recent advances in two-dimensional materials beyond graphene *ACS Nano* **9** 11509

[70] Wang Q H, Kalantar-Zadeh K, Kis A, Coleman J N and Strano M S 2012 Electronics and optoelectronics of two-dimensional transition metal dichalcogenides *Nature Nano* **7** 699

[71] Zhang Y, Rubio A and Le Lay G 2017 Emergent elemental two-dimensional materials beyond graphene *J. Phys. D: Appl. Phys.* **50** 053004

[72] Zihlmann S, Makk P, Vaz C A F and Schönenberger C 2016 Role of hexagonal boron nitride in protecting ferromagnetic nanostructures from oxidation *2D Mater.* **3** 11008

[73] Tonkikh A A, Voloshina E N, Werner P, Blumtritt H, Senkovskiy B, Güntherodt G, Parkin S S P and Dedkov Y S 2016 Structural and electronic properties of epitaxial multilayer h-BN on Ni(1 1 1) for spintronics applications *Sci. Rep.* **6** 23547

[74] Godel F, Mouafo L D N, Froehlicher G, Doudin B, Berciaud S, Henry Y, Dayen J-F and Halley D 2017 Conductance oscillations in a graphene/nanocluster hybrid material: toward large-area single-electron devices *Adv. Mater.* **29** 1604837

[75] de Oliveira T V A G, Gobbi M, Porro J M, Hueso L E and Bittner A M 2013 Charge and spin transport in PEDOT:PSS nanoscale lateral devices *Nanotechnology* **24** 475201

[76] Corso M, Auwärter W, Muntwiler M, Tamai A, Greber T and Osterwalder J 2004 Boron Nitride Nanomesh *Science* **303** 217

[77] Zhang H G *et al* 2011 Assembly of iron phthalocyanine and pentacene molecules on a graphene monolayer grown on Ru(0 0 0 1) *Phys. Rev.* B **84** 245436

[78] Yang H, Vu A D, Hallal A, Rougemaille N, Coraux J, Chen G, Schmid A K and Chshiev M 2016 Anatomy and giant enhancement of the perpendicular magnetic anisotropy of cobalt–graphene heterostructures *Nano Lett.* **16** 145–51

[79] Tyagi P and Hinds B J 2010 Mechanism of ultrathin tunnel barrier failure due to mechanical-stress-induced nanosized hillocks and voids *J. Vac. Sci. Technol.* B **28** 517