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Magnetic Two-Dimensional Systems

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Abstract

Two-dimensional (2D) systems have considerably strengthened their position as one of the premier candidates to become the key material for the proposed spintronics technology, in which computational logic, communications, and information storage are all processed by the electron spin. In this article, some of most representative 2D materials including ferromagnetic metals (FMs) and diluted magnetic semiconductor (DMSs) in their thin film form, magnetic topological insulators (TIs), magnetic graphene and magnetic transition metal dichalcogenides (TMDs) are reviewed for their recent research progresses. FM thin films have spontaneous magnetization and usually high Curie temperature (T_c), though this can be strongly altered when bonded with semiconductors (SCs). DMS and magnetic TIs have the advantage of easy integration with the existing SC-based technologies, but less robust magnetism. Magnetic ordering in graphene and TMDs are even more fragile and limited to cryogenic temperatures so far, but they particularly interesting topics due to the desired long spin lifetime as well as the outstanding mechanical and optical properties of these materials.

1. Introduction

The possibility of providing ultimate logic bit by electron's spin rather than or in addition to its charge has claimed exciting new horizons in physics, material science and electronic engineering. For spin-electronics or *spintronics* purposes, the materials carrying out the mission must be spin polarized, such as magnetic metals with the broken symmetry between spin down and spin up states near the Fermi level (E_F). Historically the spin arrangement has long been investigated within the context of conventional FM and their alloys, while the study of spin generation, relaxation, and spin-orbit coupling in non-magnetic materials has taken off rather recently with the advent of spintronics and it is here that many novel 2D materials and systems can find their greatest potential in both science and technology.

The earliest studies of 2D magnetic phenomena can be tracked back to discussions of the interfacial magnetism of FM/SC heterojunctions.[1-18] In this regard, a large portion of the research work over the last two decades was stimulated by the idea of creating a spin field effect transistor (SFET),[19] in which the transport of the electron spins is confined in a high mobility 2D electron gas (2DEG) channel and can be manipulated by the application of a gate voltage. An ideal spin-injected SC would demonstrate high spin polarization, operate at room temperature (RT) and be both robust and easily fabricated for potential high throughput needs. Various FM/SC heterostructure have been hotly investigated since it was demonstrated that substantial spin accumulation and diffusion occurs at the FM/SC interface.[20] The generation of high-spin-polarization current is essential for the SFET concept and therefore the half metallic materials (such as Heusler alloys, Fe_3O_4, and CrO_2) have also been integrated into the hybrid systems.[21-23] Although an all electrical all semiconductor spin field effect transistor has recently been demonstrated, all be it at 300 mK and requiring quantum ballistic point contacts;[24] hybrid systems with ferromagnetic source and sink of spin and an easily gate tuned channel through a high mobility 2D material may offer a route to the spin field effect transistor at room temperature.

Van der Waals materials such as graphene, layered TMDs, copper oxides, and iron pnictides with properties dominated by their 2D structural units have become the new focus of 2D magnetism research for the recent few years. The success of single-layer graphene has shown that it is not only possible to exfoliate stable, single-atom or single-polyhedral-thick 2D materials from bulk van der Waals solids, but also that these materials can exhibit fascinating and technologically useful properties. In graphene's band structure, the linear dispersion at the *k* point gives rise to novel physical phenomena, such as the anomalous quantum Hall effect (AQHE) at room temperature, and has opened up a new category of

"Dirac" physics. Stimulated by the rise of graphene, other 2D crystals including layered hexagonal-boron nitride (h-BN) and TMDs were subsequently demonstrated. The more recently discovered TIs, featured with an insulating bulk gap and gapless Dirac-like band dispersion surface states, are new members of the 2D family. Unlike that of graphene, the electron states of TIs surface are strongly spin–orbit coupled and immune to time-reversal-invariant disorders. Magnetism is not common for the elements consisting Van der Waals 2D materials; however, spin polarization in these materials can still be induced by defects, edge states, magnetic dopants and/or via the proximity to an adjunct magnetic source *etc*.. Compared to FM, they generally have less robust magnetism, but significantly longer spin lifetime or spin coherence length, which are eagerly desired in spintronics. Furthermore, their capacity of integration with FM offers a promising direction toward the development of hybrid devices that can perform logic, communications, and storage within the same material technology.

In the reminder of this article, a selection of magnetic 2D systems will be introduced, following their historical path of emergence. This includes FM and DMS in their thin film form, magnetic TIs, magnetic graphene and magnetic TMDs, as illustrated in Figure 1. The very recent advances of the study of these materials will be reviewed. This article does in no way try to give a complete overview of the emerging 2D systems, as many of them are still under fast developing till this day; neither is it intended to give deep theoretical descriptions of why the many fascinating phenomena occur in them. The purpose of this article is, instead, to present some of the most important findings of these material systems and to highlight a few hotly debated topics of the contemporary magnetic 2D systems research.

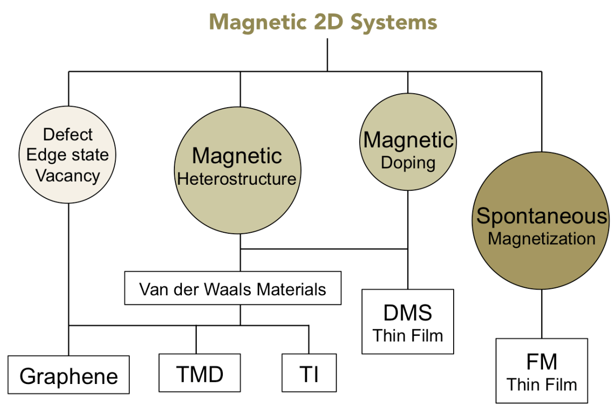

Figure 1. Schematic illustration of the magnetic 2D systems included in this review.

2. Ferromagnetic Metal Thin Films

As the simplest form of magnetic 2D system, transition metal thin films and their alloys have been most thoroughly exploited in the history, as they are relatively easy to grow epitaxially on III-V semiconductors (SCs) such as GaAs, InAs and InGaAs *etc*.. [1-18] In a FM/SC heterojunction, the best opportunity for spin transport could only be achieved in the absence of a magnetic dead layer at the interface. The atomic-scale interfacial magnetization of the FM/SC is, in turn, closely linked with two general questions, namely (*i*) how the magnetic ordering changes with reduced dimensionality and (*ii*) how the magnetic ordering changes due to electronic bonding at the interface with the SC substrate.

In general, three factors are predominately responsible for the suppressed magnetization of the FM/SC interfaces. One rises from the stacking of FM when epitaxially deposited on SC. Bulk-like Co has its stable and metastable phase as hexagonal close packed (hcp) and face center cubic (fcc), but can form into a body center cubic (bcc) stacking by epitaxial growth on GaAs. The bcc Co/GaAs was firstly demonstrated by Prinz[2, 4, 25] in 1985 and since then many experiments on Co/GaAs were reported with inconsistency, making this issue rather complex.[1-6] Using high-resolution transmission electron microscopy (TEM), Gu *et al*.[1] demonstrated hcp-structured epi-Co on GaAs and Mangan *et al*.[2] observed the coexistence of bcc and hcp phases. Idzerda *et al*.[3] confirmed the bcc structure of Co on GaAs(110) using extended x-ray absorption fine structure and theory suggests that bcc Co is not a metastable phase but a forced structure originating from imperfections.[4, 5] Calculations suggest bulk bcc Co can have a magnetic moment as large as 1.7 μ_B/atom.[6] The tendency to form into bcc stacking, which doesn't exist in nature, has also been found in epitaxial Ni thin films on GaAs. This was firstly demonstrated by Tang *et al*.[7] as early as 1986 by growing Ni on GaAs(001) at RT and the presence of bcc phase was observed up to 2.5 nm. This study was late on reproduced by X. M. Jiang *et al.*,[8] who alternatively did the growth at 170 K and obtained a thicker bcc Ni, i.e. 3.5 nm. The bcc Ni/GaAs(100) as having a Curie temperature (T_c) of 456 K and a magnetic moment of 0.52 μ_B/atom, reveals a remarkably different electronic structure to that of fcc Ni and crucially a positive cubic anisotropy of $+4.0\times10^5$ ergs/cm^3, as opposed to -5.7×10^4 ergs/cm^3 for the naturally occurring fcc Ni.

Another possibility is associated with the detrimental interdiffusion between the FM and the SC atoms. Theoretical calculations suggest a bulk bcc Co can carry a magnetic moment as large as 1.7 μ_B/atom,[6, 9] while experimental reports are always below this value. By careful analyses of the RHEED patterns, Monchesky *et al.*[10] demonstrated a ferromagnetically dead layer associated with the formation of interfacial Co_2GaAs for Co thickness less than 3.4 monolayers (MLs) and an abrupt in-plane spin-reorientation transition reorients the magnetization along the [001] direction at 7 ML. It should be noted that all these boundaries discussed above are not absolute values but strongly depend on the specific sample deposition conditions, such as the substrate configuration and the temperature *etc*.. For example, passivating layers such as S and Sb have been used to reduce the chemical interaction at the Co/GaAs interface and the latter gives a factor of 2.3 enhancement of the magnetic moment compared to the film deposited on bare GaAs(110) substrate.[3] Characterized by x-ray photoelectron spectroscopy (XPS), the presence of the As peak in the 6-nm Ni film reveals the occurrence of As diffusion into the Ni layer destroying the magnetic properties of the fcc Ni film and leading to a 20% reduction of the magnetization compared to the bulk value.[11] In the study of the evolution of interface properties of the electrodeposited Ni film upon annealing, a significant increase of As out-diffusion has been observed for annealing temperatures up to 623 K accompanying a rise in the Schottky barrier height, which has been attributed to the Ni-Ga-As compound formation.[12]

The third reason is the reduced thickness. It is well known that FM materials follow the so-called island growth geometry at low coverage. In other words, FM atoms at low thicknesses, typically less than a few MLs, may be too diffused for them to intensively interact with one another. For example, many researchers have reported on high quality epitaxial growth of Fe on GaAs, among which there exist the long lasting debate over the presence of magnetic dead layer at the Fe/GaAs interface.[13] This detrimental effect used to be attributed to the formation of antiferromagnetic Fe_2As[14] and half-magnetized $Fe_3Ga_{2x}As_x$ in the vicinity of the interface, until Xu *et al.*[15] demonstrated the evolution of the magnetic phase of Fe/GaAs corresponding to the growth morphology. This result was further confirmed with unambiguous x-ray magnetic circularly dichroism (XMCD) measurement of the Fe/GaAs(100) interface.[16]

Direct experimental demonstration of the magnetic state of epitaxial FM/SC interface down to the atomic scale remains a nontrivial task, even up to this day, partially due to the inaccessibility of the buried layer (referred to as FM_2 hereafter) between the upper layers (referred to as FM_1 hereafter) and the substrate. One classical method of resolving this problem is to engineer the $FM_1/FM_2/SC$ superstructure, as shown in Figure 2.[16-18] Here, the FM_2 layers, usually with one monolayer thickness, are epitaxially deposited on the SC and then capped with a thick layer of FM_1 ($\neq FM_2$), which serves as the stabilizing layer. The thick FM_1 is chemically distinguishable but magnetically akin to the FM_2, providing it with a source of exchange interaction. Combined with the unique element selectivity of XMCD, this structure allows direct observation of the interfacial behavior of the bulk FM_2 on the SC. Applying this approach to two model FM/SC systems, namely Co/GaAs and Ni/GaAs, Liu *et al.*[18] observed a robust room temperature magnetization of the interfacial Co, whilst that of the interfacial Ni was strongly diminished down to 5 K due to hybridization of the Ni $d(e_g)$ and GaAs sp^3 states. The validity of the selected method was confirmed by *first-principles* calculations, showing only small deviations (<0.02 and <0.07 μ_B/atom for Co/GaAs and Ni/GaAs, respectively) compared to the real FM/SC interfaces. Their work also proved that the electronic structure and magnetic ground state of the interfacial FM_2 is not altered when the topmost FM_2 is replaced by FM_1 and that this model is applicable for probing both magnetically active and dead layers.

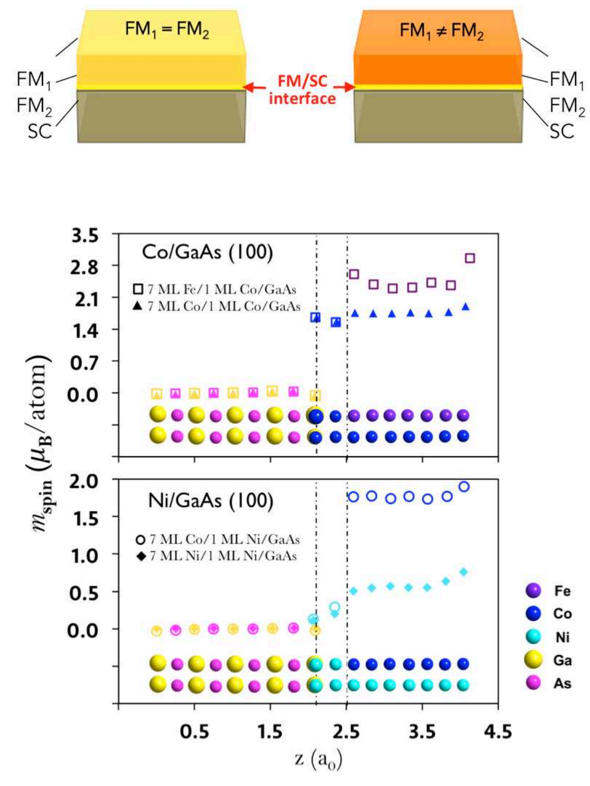

Figure 2. Demonstrate of the $FM_1/FM_2/SC$ superstructure model. Upper row: Illustration of the $FM_1/FM_2/SC$ structure (right) retrieving the FM_2/SC structure (left). Lower row: the magnetic moment of Co/GaAs and Ni/GaAs interfaces versus distance along the (100) direction. The dashed lines indicate the interfacial or the FM_2 region, where the magnetic ground state of the interfacial FM_2 is not altered when the topmost FM_2 is replaced by FM_1.[18]

3. Diluted Magnetic Semiconductor Thin Films

One of the most useful aspects of SCs resides in their capacity to be doped with impurities, by which the electrical properties of the SC can be tuned. This approach has been developed to introduce magnetic ions into non-magnetic SCs to make them magnetic, known as DMSs.[26] The concept behind it is that to transfer spin between similar materials would be a simpler task than over a metal-SC interface due to the retained control over band-gap engineering. The long established presence of spin filtering effects in these SCs[27] and more recently observed properties for spontaneous[28, 29] or field controlled[30, 31] magnetic ordering add to their viability in this field. The early experimental efforts on the demonstration of DMSs started from II-VI (such as CdTe and ZnSe) in which the transition metal ions (such as Mn) are easy to be doped to high concentrations.[32] The fabrication of III–V DMSs, on the other hand, was limited mostly to (In,Mn)As,[28] (Ga,Mn)Sb,[33] and (Ga,As)Mn,[29, 34, 35] in which demonstrably carrier-mediated ferromagnetism already persists.

While DMSs may offer opportunities of easy integration with conventional SC-based devices, it is however a great challenge to improve the quality of DMS and in particular to enhance their magnetism.[35-43] With the thickness down to nanometer scale, these issues become even more sophisticated. For example, (Ga,As)Mn is a technological important material due to its potential use in short-range optical communications, however, whose highest T_c up to now is no more than 200 K even after combining efforts of heavy Mn doping, nano-patterning, optimizing the growth conditions, and post-growth annealing.[34, 35, 37, 44] RT ferromagnetism has been predicted and demonstrated in magnetic oxide SCs such as Co- and Mn-doped ZnO, though debates exist on whether the ferromagnetism obtained in DMS oxides is intrinsic or not.[38, 39]

In a magnetic bilayer system, the exchange coupling from a ferromagnetic layer can induce a spin polarization in the nonmagnetic layer or enhance the T_C in the other magnetic layer with low ordering temperatures through the proximity effect. By such approach, substantial increase of T_C from 40 to 70 K due to the presence of a few monolayers of Fe atop (Ga,Mn)As was obtained by Song *et al.* in a lateral spin injection device.[40] The magnetic proximity effect persists to room temperature at Fe/(Ga,Mn)As interfaces was reported by Maccherozzi *et al.*,[41, 42] who observed a significant induced magnetic order in the (Ga,Mn)As layer that extends over more than 2 nm, as shown in Figure 33. An antiparallel magnetic coupling between Fe and Mn, with ferromagnetic order in the (Ga,Mn)As layer was observed and high exchange bias up to 240 Oe was revealed in this system by Olejnik *et al.*.[43] Altering the Fe induction layer with the high T_c half metallic Heusler alloy Co_2FeAl, Nie *et al.* demonstrate that a 1.36 nm thick (Ga,Mn)As thin film remains ferromagnetically order up to 400 K. Unlike the antiferromagnetic coupling in Fe/(Ga,Mn)As system, these authors observed a parallel alignment between the Fe, Co and the Mn in the Co_2FeAl/(Ga,Mn)As system.

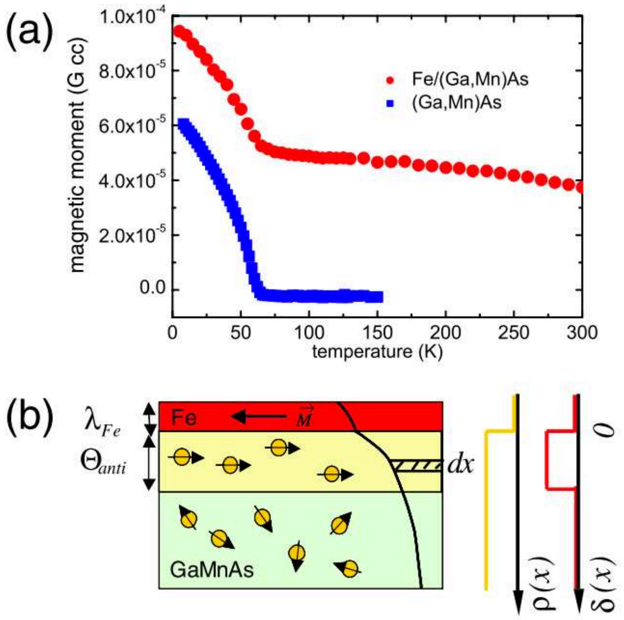

Figure 3. Demonstration of the enhanced magnetism of (Ga, Mn)As via proximity effect with Fe. (a) Spontaneous M(T) curves of Mn from a Fe/(Ga, Mn)As and a pure (Ga, Mn)As. (b) Sketch of the model for the Mn distribution ρ(x) and the fraction of ferromagnetic Mn δ(x) at RT. [41]**Error! Bookmark not defined.**

4. Magnetic Topological Insulators

As a class of matter with newly discovered eccentric electronic phase, the spin-orbit induced TIs have a rather short history but fast growing family.[45-47] Since they were first theorized in 2005[48] and experimentally produced in 2006,[49] TIs, with their ability to insulate on the inside and conduct on the outside, have presented new possibilities for the future spintronics applications. Three-dimensional (3D) TIs feature novel phases of quantum matter characterized by sharp changes in electronic structure at their very surfaces, i.e. with insulating bulk band gap and gapless Dirac-like band dispersion surface state (SS). Unlike the different electronic properties of the surface and the bulk universally existing in all solids owing to the inevitable termination of periodic lattice structure when approaching the edges, TIs present a new class of nontrivial SS arising from the intrinsic strong spin-orbital coupling (SOC) and characterized by a Rashba spin texture.[50-52] These low-dimensional conducting states are immune to localization as long as the disorder potential is time-reversal-invariant and therefore have strong implications for the emerging technologies such as dissipationless spin transport and quantum computing.[53, 54] Breaking time-reversal-invariance by introducing magnetic perturbation, on the other hand, reveals a complex phenomenology associated with an excitation gap of the surface spectrum, resembling that of a massive Dirac fermion.[55, 56] Such a system with a tunable gap promises rich exotic topological phenomena and would allow purely electric control of the surface transport and magnetization.[45, 57, 58]

Two categories of route for introducing ferromagnetic order or breaking time-reverse symmetry (TRS) in TIs have been developed. One route is to dope the TI host with specific elements, by which ferromagnetism has been observed in Cr- and Mn-doped single crystals of Sb_2Te_3,[59-61] Fe-, and Mn-doped single crystals of Bi_2Te_3, [62, 63] and Mn- and Cr-doped thin films of Bi_2Se_3.[64, 65] However, for the electronic and magnetic ground state of the magnetically doped TIs, evidence from the experimental observations including magneto-transport measurements,[60] global magnetometry,[55] and core-level spectroscopies[66-68] are so far inconclusive. Magnetic studies on epitaxial, Cr-doped Bi_2Se_3 using superconducting quantum interference device - vibrating sample magnetometer magnetometry (SQUID-VSM)[64] and polarized neutron reflectometry (PNR)[68] universally reported a magnetic moment of no more than ~2 μ_B/atom, remarkably lower than the Hund's rule of 3 μ_B/atom of substitutional Cr^{3+} on Bi sites. According to the pioneering work by Haazen *et al.*,[64] the magnetic moment of $Bi_{2-x}Cr_xSe_3$ decreases with increasing doping concentration and sharply drops beyond ~10%. This is well resembled by Liu *et al.*[69] using a combined approach of XMCD and density function theory (DFT) calculation, as summarized in Figure 44. These authors found a remarkable fraction of the $(Cr_{Bi}\text{-}Cr_I)^{3+}$ antiferromagnetic dimers in the $Bi_{2-x}Cr_xSe_3$ for $0.02 < x < 0.40$, which was neglected in previous studies. Significant mismatch also exists in Mn- and Fe-doped Bi_2Se_3, who typically show global magnetic moments of ~1.5 μ_B/atom and ~3μ_B/atom, while their Hund's rule prediction is 5 μ_B/atom. It has been proposed that in magnetic TIs, ferromagnetic moments can be developed not only through the *s-d* exchange interaction such as in diluted magnetic semiconductors (DMSs),[34, 70-73] but also through the van Vleck mechanism, by which magnetic ions are directly coupled through the local valance elecrons.[47] Both types of mechanism have been observed independently in Mn-doped $Bi_2(TeSe)_3$[74] and Cr-doped $(BiSb)_2Te_3$[75] thin films. Delicate technique like time-resolved angular-resolved photoemission spectroscopy (TR-

ARPES) has been performed to distinguish bulk and surface electron-phonon coupling of the bare TI.[76] In the regard of magnetic TI, β-nuclear magnetic resonance (β-NMR) was very recently used to depth-profile the electronic wavefunctions at topological surfaces.[77]

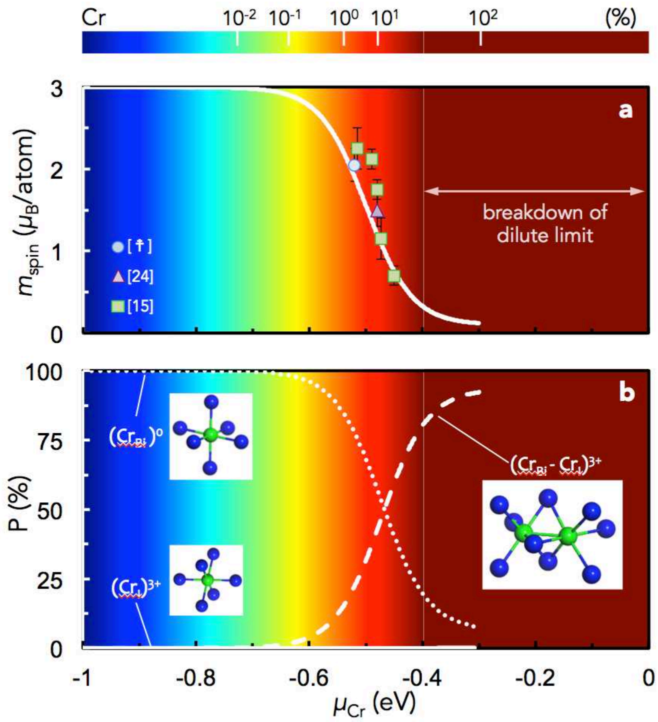

Figure 4. A summary of the experimentally measured and the DFT-calculated dependence of (a) magnetic moment and (b) the fraction of the three predominant defects Cr_I^{3+}, Cr_{Bi}^{0}, and $(Cr_{Bi}-Cr_I)^{3+}$, as a function of the chemical potential of Cr (μ_{Cr}) in $Bi_{2-x}Cr_xSe_3$.[69]

The other routine of making TIs magnetic is to engineer layered heterostructures, where the SS of TIs experience the exchange interaction from an adjacent ferro- or ferri-magnetic material. This route subsequently can be divided into two ways in terms of ferro- or FM and ferro- or ferri- magnetic insulator (FMI) induction. Pioneering theoretical work[78-80] suggests that suitable FMIs have the potential to achieve a strong and uniform exchange coupling in contact with TIs without significant spin-dependent random scattering of helical carriers on magnetic atoms. Progresses are made experimentally in FMI/TI heterostructures including GdN/Bi_2Se_3 by Kandala *et al.*,[81] EuS/Bi_2Se_3 by Yang *et al.*,[82] and Wei *et al.*,[83] respectively, although the effect observed is limited to low temperature (< 22 K) due to the low T_C of EuS. The interface magnetism of (anti-) FM/TI heterostructures, such as Fe/Bi_2Se_3,[56, 84, 85] Co/Bi_2Se_3,[85] and Cr/Bi_2Se_3,[86] has also been investigated. Remarkably, Vobornik *et al.*[87] demonstrated that long-range ferromagnetism up to RT can be induced in $Bi_{2-x}Mn_xTe_3$ by a deposited Fe overlayer, as shown in Figure 5. However, in the presence of a metallic layer, the nontrivial surface states of the TI can be significantly altered due to their hybridization with the bulk states of the (anti-) FM in contact. Besides, the metallic layer naturally short circuits the TI layer and therefore fundamentally restrict the device design. Using high-T_c ferrimagnetic insulator, [88] Liu *et al.*[89] demonstrated the magnetic proximity effect of $Bi_{2-x}Cr_xSe_3/Y_3Fe_5O_{12}$ and obtained a large (6.6 nm at 30 K) but fast decreasing penetration depth compared to that of ordinary DMSs. This could indicate a novel mechanism for the interaction between the ferromagnetic insulator and the nontrivial TIs surface and has strong implications for the TI-based dissipationless electronic devices, as it no longer limits the "proximity" to short range.

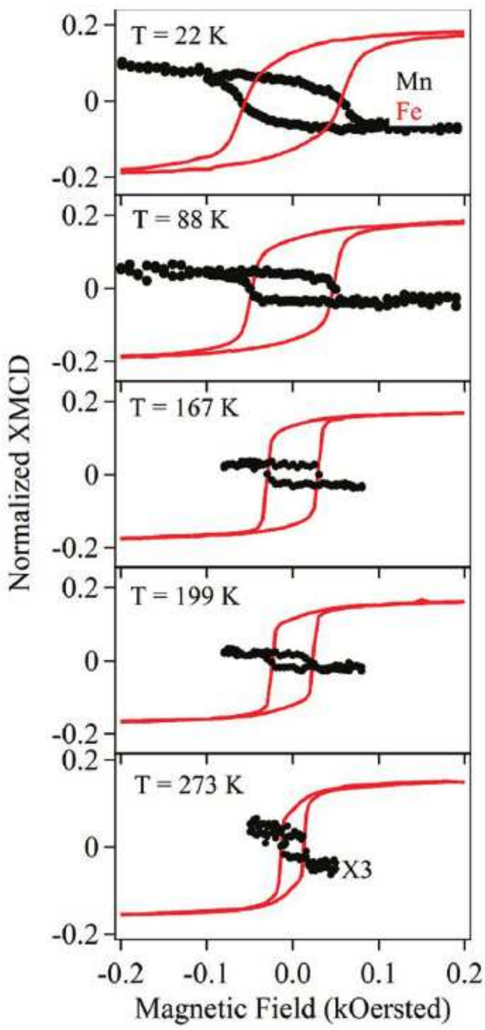

Figure 5. The antiferromagnetically coupled hysteresis loops of Mn and Fe, respectively, from the Fe/ $Bi_{2-x}Mn_xTe_3$ bilayer from 22 K to 273 K.[87]

5. Magnetic Graphene and Transition Metal Dichalcogenides

Since its successful synthesis by mechanical exfoliation from graphite in 2004, graphene has attracted enormous attention in the community of physics, chemistry and materials science.[90] As a prototypical two-dimensional quantum system, graphene displays a combination of exceptional properties including large charge carrier mobility, high thermal conductivity, strong mechanical strength, excellent optical characteristics, electrically tuneable band gap, as well as the recently discovered long spin coherence length.[91-93]

The revolutionary nature of graphene makes it a prime candidate to become a key material for the proposed spin transistors, in which the generation and tuning of spin-polarized currents are prerequisites.[94-96] In pristine state, graphene exhibits no signs of conventional spin-polarization and so far no experimental signature shows a ferromagnetic phase of graphene. This gap is now filling up by combined efforts in multi-disciplinary research. While ideal graphene is non-magnetic, many of its related materials and nanostructures, either realized in practice or considered theoretically, have shown various scenarios of magnetism. Pioneering works reveal that spin origin in graphene are defect, vacancy, and edge state where topological frustration of the p-bonds occurs. This was first discussed by Son, Cohen and Louie, who showed that external electric fields can induce half-metallicity – the coexistence of a metallic state for electrons with one spin orientation and an insulating state for electrons with the opposite spin orientation, in the zigzag graphene nano-ribbon (ZGNR), as shown in Figure 66.[97] Enoki *et al.* observed localized spins in nano-graphite domains of activated carbon fibers and attributed the origin to the zigzag edges.[98]

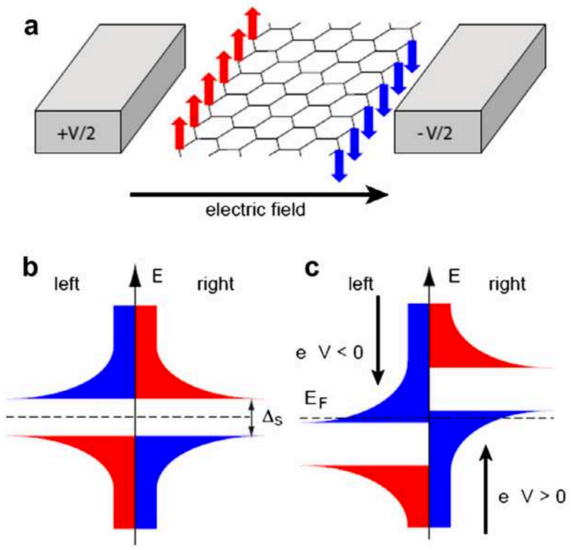

Figure 6. Scheme of electric-field-induced half-metallicity in ZGNR. (a) Electric field is applied

across the nanoribbon, from left edge (spin-up, red arrows) to right edge (spin- down, blue arrows). (b) Schematic representation of the spin-resolved local density of states for the opposite edges at zero applied field. (c) Applied electric field breaks the symmetry for different spin types.[99]**Error! Bookmark not defined.**

Engineering FM/graphene heterojunction is one of the most promising avenues to realise efficient spin injection into graphene and this was first achieved by Ohishi *et al.* into ZGNRs at room temperature.[100] Fascinating properties of spin transport phenomena have been presented in the Co/graphene system,[100, 101] though theoretical calculations show that the atomic magnetic moment of Co can be reduced by more than 50% when absorbed on graphene surface.[102] The magnetic moment of monolayer Fe is reduced but still sizable when epitaxially deposited on graphene, and this in turn induces a spin polarization in the carbon atoms.[103] The graphene-based FET has been demonstrated in back gated devices on highly doped Si,[104] and the conductance of the top surface of such structure can be modulated via gas exposure and top-back dual gates.[102] The spin valve effect was also successfully demonstrated in NiFe/graphene/NiFe vertical structures and the signal is enhanced when the number of graphene layers is doubled.[105] An inserted graphene sheet can drastically improve the spin-injection efficiency from a ferromagnet into silicon.[106] All these demonstrations indicate that the interaction of graphene with FM surface plays a fundamental role in the related technological process, which has renewed the interest of FM/SC heterojunctions, although the binding mechanism of the FM/graphene interface is still far from a complete understanding.

Beyond graphene, the unique electronic and optical properties of TMDs are establishing them as the next hotspot in 2D materials research. Despite the plethora of reports on the electronic structure of the single layer TMDs it was only recently that their magnetic features have been investigated. So far VS_2 and VSe_2 are the only 2D materials with their magnetism confirmed in the pristine state.[99] For metal intercalated TMDs, Fe_xNbSe_2 and Cu_xNbSe_2 were proved to be magnetic.[107] In the case of MoS_2 the presence of magnetism was believed to be related to the defects (including structural defects and/or adatoms and/or impurities).[108] The substitution of a S atom by atoms of complete d band (Pd and Au) was found not to lead to magnetic polarization except for a slight modification of the density of states near E_F.[109] On the other hand, substitution of a S atom by atoms with incomplete d band atoms (Fe, Mn and V) was found to induce spin polarization and significant modification of the states near the band edges.[110] The adsorption of several adatoms on 2D MoS_2 can also incur magnetism.[109, 111]

Very recently the effect on TMD's magnetism upon cation substitution with magnetic impurities has became a key subject of interest. Mishra *et al.*[112] investigated the long-range ferromagnetic ordering in fairly diluted Mn doped (less than 5%) MoS_2, $MoSe_2$, $MoTe_2$, and WS_2 within the density functional theory–spin polarized generalized gradient approximation and Hubbard- U (SGGA+U) parametrization. Cheng *et al.* [113] studied the magnetism of the MoS_2 monolayer doped with Mn, Fe, Co, Zn, Cd, and Hg and found that the Fe and Co doping lead to antiferromagnetic ground states, while the doping with Mn, Zn, Cd, and Hg lead to ferromagnetic ground states. Ramasubramaniam and Naveh[114] compared the results for the exchange coupling coefficient among Mn dopants in MoS_2. They found noticeable differences only at the nearest neighbor dopant distances and that ferromagnetic coupling between Mn dopants and antiferromagnetic spin polarization between the Mn dopants and their fist nearest neighbor S anions. The very first successful experimental demonstration of in situ doping of monolayer TMD is the Mn-doped MoS_2 included in Figure 7, reported by Zhang *et al.*[115] with the assistance of a graphene buffer layer on sapphire. Unlike the theoretical studies which have focused on doping of freestanding 2D materials, these authors show that the capacity of the incorporation of magnetic dopants in TMD is highly dependent on the choice of the substrate.

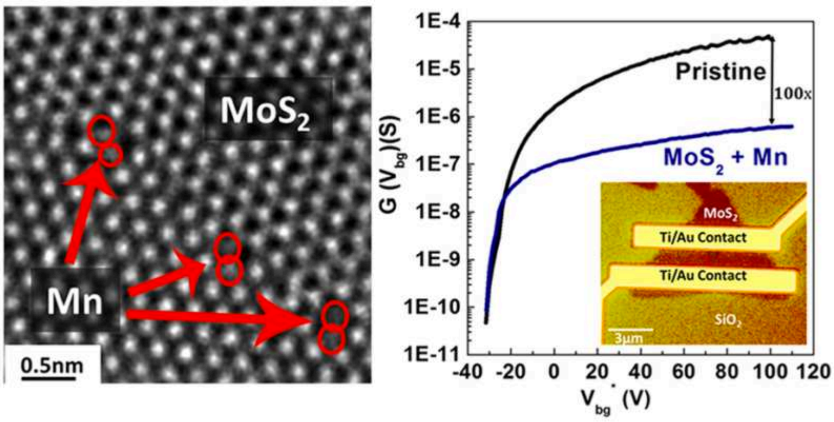

Figure 7. Experimental demonstration of Mn-doped MoS_2. Left: TEM image of Mn-doped MoS_2. Right: Two-terminal conductance versus back gate voltage measurements indicating that Mn-doping leads to an increase in the density of states in the bandgap of the MoS_2 and thus lower saturation conductance.[115]

6. Summary and Outlook

2D systems have become one of the most exciting new classes of materials due to the wealth of exceptional physical properties that occur when charge, spin and heat transport are confined to a plane. Their unique 2DEG-like behaviours not only enrich the world of low-dimensional physics, but also provide a platform for transformative technical innovations. In the pursuit for such goals, the intrinsic material properties (*e.g.* mobility, anisotropy, conductivity *etc*.) are important indicators and the artificially synthetized hybrid systems (*e.g.* multilayers, hybrid systems, and nano-structures *etc*.) are valuable models for studying spin-dependent phenomena and could potentially be used as actual components for an eventual spintronic device.

Among the four representative 2D systems reviewed in this article, FM thin films have the topmost advantages of spontaneous magnetization and usually high T_c. Their electronic and magnetic ground states have been intensively studied in the history, though dramatic alterations occur when it comes to the FM/SC interface. Using FM as spin filters also bring problems such as the well-known conductivity mismatch, based on the fact that a FM metal has a conductivity typically several orders of magnitude larger than that of a SC, which has limited the efficiency of spin injection. Interface engineering by means of improved epitaxial deposition, interface doping, and buffer layer insertion *etc*. may eliminate the undesired effects and further enhance the operation temperature of the FM/SC-based spintronic devices. By contrast, DMS thin films naturally avoid the difficulties of integration with conventional SC-based technologies; however great challenges remain to improve their crystallinity and in particular their T_c. Magnetic proximity effect is a promising pathway in this regard. Not only many DMS thin films, but also the newly discovered TIs have shown their pronounced capacities with several high T_c magnetic materials via proximity. The later even reveals an increasing penetration depth, which are expected to free the proximity effect from short-range limit. Future work to explore the tuning of the magnetization of TIs and its dependence on the band filling will be of both great fundamental interest and practical merits.

2D materials like graphene and TMDs carry the desired long spin lifetime as well as the outstanding mechanical and optical properties that FM, DMSs and TIs don't have. It is rather unconventional to seek for magnetism from these Van der Waals materials, which were believed nonmagnetic. Nevertheless research into magnetic graphene and magnetic TMDs has rapidly taken off, though their magnetic signatures are so far fragile and limited to cryogenic temperatures. This is because the origin of spin polarization of these materials are usually defects, vacancies, edge states, impurities and/or via the proximity to an adjunct magnetic source *etc*.. Direct magnetic doping to high concentration and forming long-range magnetic ordering persisting up to RT are still major obstacles for magnetic graphene and TMDs. Investigations into the interplay between imbalanced spin states and the Dirac-like band dispersions will lead to find experimental approaches to enhance the magnetism in 2D materials and can give rise to novel physical phenomena such as AQHE at RT.

References

[1] Gu E, Gester M, Hicken R, Daboo C, Tselepi M, Gray S, et al. Fourfold anisotropy and structural behavior of epitaxial hcp Co/GaAs (001) thin films. Physical Review B. 1995;52:14704.

[2] Mangan M, Spanos G, Ambrose T, Prinz G. Transmission electron microscopy investigation of Co thin films on GaAs (001). Applied physics letters. 1999;75:346-8.

[3] Idzerda Y, Elam W, Jonker B, Prinz G. Structure determination of metastable cobalt films. Physical review letters. 1989;62:2480.

[4] Subramanian S, Liu X, Stamps R, Sooryakumar R, Prinz G. Magnetic anisotropies in body-centered-cubic cobalt films. Physical Review B. 1995;52:10194.

[5] Izquierdo M, Dávila M, Avila J, Ascolani H, Teodorescu C, Martin M, et al. Epitaxy and magnetic properties of surfactant-mediated growth of bcc cobalt. Physical review letters. 2005;94:187601.

[6] Bagayoko D, Ziegler A, Callaway J. Band structure of bcc cobalt. Physical Review B. 1983;27:7046.

[7] Moruzzi V, Marcus P, Schwarz K, Mohn P. Total energy surfaces in the MV plane for bcc and fcc cobalt. Journal of magnetism and magnetic materials. 1986;54:955-6.

[8] Tian C, Qian D, Wu D, He R, Wu Y, Tang W, et al. Body-centered-cubic Ni and its magnetic properties. Physical review letters. 2005;94:137210.

[9] Bland J, Bateson R, Riedi P, Graham R, Lauter H, Penfold J, et al. Magnetic properties of bcc Co films. Journal of Applied Physics. 1991;69:4989-91.

[10] Monchesky T, Unguris J. Magnetic properties of Co⁄ GaAs (110). Physical Review B. 2006;74:241301.

[11] Chen C, Idzerda Y, Lin H-J, Smith N, Meigs G, Chaban E, et al. Experimental confirmation of the X-ray magnetic circular dichroism sum rules for iron and cobalt. Physical review letters. 1995;75:152.

[12] Scheck C, Evans P, Zangari G, Schad R. Sharp ferromagnet/semiconductor interfaces by electrodeposition of Ni thin films onto n-GaAs (001) substrates. Applied physics letters. 2003;82:2853-5.

[13] Filipe A, Schuhl A, Galtier P. Structure and magnetism of the Fe/GaAs interface. Applied physics letters. 1997;70:129-31.

[14] Prinz G, Rado G, Krebs J. Magnetic properties of single‐crystal {110} iron films grown on GaAs by molecular beam epitaxy. Journal of Applied Physics. 1982;53:2087-91.

[15] Xu Y, Kernohan E, Freeland D, Ercole A, Tselepi M, Bland J. Evolution of the ferromagnetic phase of ultrathin Fe films grown on GaAs (100)-4× 6. Physical Review B. 1998;58:890.

[16] Claydon J, Xu Y, Tselepi M, Bland J, Van der Laan G. Direct Observation of a Bulklike Spin Moment at the F e/G a A s (100)− 4× 6 Interface. Physical review letters. 2004;93:037206.

[17] Giovanelli L, Panaccione G, Rossi G, Fabrizioli M, Tian C-S, Gastelois P, et al. Layer-selective spectroscopy of Fe∕Ga As (001): Influence of the interface on the magnetic properties. Physical Review B. 2005;72:045221.

[18] Liu W Q, Zhou Q H, Chen Q, Niu D X, Zhou Y, Xu Y B, Zhang R, Wang J L, and van der Laan G. Probing the Buried Magnetic Interfaces. ACS App Mater Inter. 2015;00 11438p.

[19] Datta S, Das B. Electronic analog of the electro‐optic modulator. Applied Physics Letters. 1990;56:665-7.

[20] Lou X, Adelmann C, Furis M, Crooker S, Palmstrøm C, Crowell P. Electrical detection of spin accumulation at a ferromagnet-semiconductor interface. Physical review letters. 2006;96:176603.

[21] Nie S, Chin Y, Liu W, Tung J, Lu J, Lin H, et al. Ferromagnetic interfacial interaction and the proximity effect in a Co_2FeAl/(Ga, Mn) As bilayer. Physical review letters. 2013;111:027203.

[22] Liu W, Xu Y, Wong P, Maltby N, Li S, Wang X, et al. Spin and orbital moments of nanoscale Fe_3O_4 epitaxial thin film on MgO/GaAs (100). Applied Physics Letters. 2014;104:142407.

[23] Liu W, Song M, Maltby N, Li S, Lin J, Samant M, et al. X-ray magnetic circular dichroism study of epitaxial magnetite ultrathin film on MgO (100). Journal of Applied Physics. 2015;117:17E121.

[24] Hu Y, Zeng L, Minnich AJ, Dresselhaus MS, Chen G. Spectral mapping of thermal conductivity through nanoscale ballistic transport. Nature nanotechnology. 2015;10:701-6.

[25] Prinz G. Stabilization of bcc Co via epitaxial growth on GaAs. Physical Review Letters. 1985;54:1051.

[26] Ohno H. Making nonmagnetic semiconductors ferromagnetic. Science. 1998;281:951-6.

[27] Esaki L, Stiles P, Von Molnar S. Magnetointernal field emission in junctions of magnetic insulators. Physical Review Letters. 1967;19:852.

[28] Munekata H, Ohno H, Von Molnar S, Segmüller A, Chang L, Esaki L. Diluted magnetic III-V semiconductors. Physical Review Letters. 1989;63:1849.

[29] Ohno H, Shen A, Matsukura F, Oiwa A, Endo A, Katsumoto S, et al. (Ga, Mn) As: a new diluted magnetic semiconductor based on GaAs. Applied Physics Letters. 1996;69:363-5.

[30] Ohno H, Chiba D, Matsukura F, Omiya T, Abe E, Dietl T, et al. Electric-field control of ferromagnetism. Nature. 2000;408:944-6.

[31] Matsukura F, Chiba D, Omiya T, Abe E, Dietl T, Ohno Y, et al. Control of ferromagnetism in field-effect transistor of a magnetic semiconductor. Physica E: Low-dimensional Systems and Nanostructures. 2002;12:351-5.

[32] Hovel HJ. Semiconductor and semimetals, Vol. 11. Solar cells. 1975:24.

[33] Adhikari T, Basu S. Electrical properties of gallium manganese antimonide: a new diluted magnetic semiconductor. Japanese journal of applied physics. 1994;33:4581.

[34] Edmonds K, van der Laan G, Farley N, Campion R, Gallagher B, Foxon C, et al. Magnetic linear dichroism in the angular dependence of core-level photoemission from (Ga, Mn) As using hard X rays. Physical review letters. 2011;107:197601.

[35] Wang M, Campion R, Rushforth A, Edmonds K, Foxon C, Gallagher B. Achieving high curie temperature in (Ga, Mn)As. Applied Physics Letters. 2008;93:132103.

[36] Edmonds K, Wang K, Campion R, Neumann A, Farley N, Gallagher B, et al. High Curie temperature GaMnAs obtained by resistance-monitored annealing. applied Physics Letters. 2002;81:4991.

[37] MacDonald A, Schiffer P, Samarth N. Ferromagnetic semiconductors: moving beyond (Ga, Mn)As. Nature materials. 2005;4:195-202.

[38] Coey J. Dilute magnetic oxides. Current Opinion in Solid State and Materials Science. 2006;10:83-92.

[39] Dietl T. A ten-year perspective on dilute magnetic semiconductors and oxides. Nature materials. 2010;9:965-74.

[40] Song C, Sperl M, Utz M, Ciorga M, Woltersdorf G, Schuh D, et al. Proximity induced enhancement of the Curie temperature in hybrid spin injection devices. Physical review letters. 2011;107:056601.

[41] Maccherozzi F, Sperl M, Panaccione G, Minár J, Polesya S, Ebert H, et al. Evidence for a magnetic proximity effect up to room temperature at Fe/(Ga, Mn) As interfaces. Physical review letters. 2008;101:267201.

[42] Sperl M, Maccherozzi F, Borgatti F, Verna A, Rossi G, Soda M, et al. Identifying the character of ferromagnetic Mn in epitaxial Fe/(Ga, Mn) As heterostructures. Physical Review B. 2010;81:035211.

[43] Olejnik K, Wadley P, Haigh J, Edmonds K, Campion R, Rushforth A, et al. Exchange bias in a ferromagnetic semiconductor induced by a ferromagnetic metal: Fe/(Ga, Mn) As bilayer films studied by XMCD measurements and SQUID magnetometry. Physical Review B. 2010;81:104402.

[44] Edmonds K, Wang K, Campion R, Neumann A, Farley N, Gallagher B, et al. High Curie temperature GaMnAs obtained by resistance-monitored annealing. arXiv preprint cond-mat/0209554. 2002.

[45] Chang C-Z, Zhang J, Feng X, Shen J, Zhang Z, Guo M, et al. Experimental observation of the quantum anomalous Hall effect in a magnetic topological insulator. Science. 2013;340:167-70.

[46] Liu C-X, Qi X-L, Dai X, Fang Z, Zhang S-C. Quantum anomalous Hall effect in $Hg_{1-y}Mn_yTe$ quantum wells. Physical review letters. 2008;101:146802.

[47] Yu R, Zhang W, Zhang H-J, Zhang S-C, Dai X, Fang Z. Quantized anomalous Hall effect in magnetic topological insulators. Science. 2010;329:61-4.

[48] Kane CL, Mele EJ. Z 2 topological order and the quantum spin Hall effect. Physical review letters. 2005;95:146802.

[49] Bernevig BA, Hughes TL, Zhang S-C. Quantum spin Hall effect and topological phase transition in HgTe quantum wells. Science. 2006;314:1757-61.

[50] Hasan MZ, Kane CL. Colloquium: topological insulators. Reviews of Modern Physics. 2010;82:3045.

[51] Moore JE. The birth of topological insulators. Nature. 2010;464:194-8.

[52] Hsieh D, Xia Y, Qian D, Wray L, Dil J, Meier F, et al. A tunable topological insulator in the spin helical Dirac transport regime. Nature. 2009;460:1101-5.

[53] Roushan P, Seo J, Parker CV, Hor Y, Hsieh D, Qian D, et al. Topological surface states protected from backscattering by chiral spin texture. Nature. 2009;460:1106-9.

[54] Fu L, Kane CL, Mele EJ. Topological insulators in three dimensions. Physical Review Letters. 2007;98:106803.

[55] Chen Y, Chu J-H, Analytis J, Liu Z, Igarashi K, Kuo H-H, et al. Massive Dirac fermion on the surface of a magnetically doped topological insulator. Science. 2010;329:659-62.

[56] Wray LA, Xu S-Y, Xia Y, Hsieh D, Fedorov AV, San Hor Y, et al. A topological insulator surface under strong Coulomb, magnetic and disorder perturbations. Nature Physics. 2011;7:32-7.

[57] Garate I, Franz M. Inverse spin-galvanic effect in the interface between a topological insulator and a ferromagnet. Physical review letters. 2010;104:146802.

[58] Yokoyama T, Tanaka Y, Nagaosa N. Anomalous magnetoresistance of a two-dimensional ferromagnet/ferromagnet junction on the surface of a topological insulator. Physical Review B. 2010;81:121401.

[59] Dyck J, Drašar Č, Lošt'ák P, Uher C. Low-temperature ferromagnetic properties of the diluted magnetic semiconductor $Sb_{2-x}Cr_xTe_3$. Physical Review B. 2005;71:115214.

[60] Kou X, He L, Lang M, Fan Y, Wong K, Jiang Y, et al. Manipulating surface-related ferromagnetism in modulation-doped topological insulators. Nano letters. 2013;13:4587-93.

[61] Dyck JS, Hájek P, Lošt'ák P, Uher C. Diluted magnetic semiconductors based on $Sb_{2-x}V_xTe_3$(0.01<~ x<~ 0. 0 3). Physical Review B. 2002;65:115212.

[62] Hor Y, Roushan P, Beidenkopf H, Seo J, Qu D, Checkelsky J, et al. Development of ferromagnetism in the doped topological insulator $Bi_{2-x}Mn_xTe_3$. Physical Review B. 2010;81:195203.

[63] Kulbachinskii V, Kaminskii AY, Kindo K, Narumi Y, Suga K, Lostak P, et al. Ferromagnetism in new diluted magnetic semiconductor $Bi_{2-x}Fe_xTe_3$. Physica B: Condensed Matter. 2002;311:292-7.

[64] Haazen P, Laloë J-B, Nummy T, Swagten H, Jarillo-Herrero P, Heiman D, et al. Ferromagnetism in thin-film Cr-doped topological insulator Bi_2Se_3. Applied Physics Letters. 2012;100:082404.

[65] Kou X, Lang M, Fan Y, Jiang Y, Nie T, Zhang J, et al. Interplay between different magnetisms in Cr-doped topological insulators. ACS nano. 2013;7:9205-12.

[66] Figueroa A, van der Laan G, Collins-McIntyre L, Zhang S-L, Baker A, Harrison S, et al. Magnetic Cr doping of Bi_2Se_3: Evidence for divalent Cr from x-ray spectroscopy. Physical Review B. 2014;90:134402.

[67] Collins-McIntyre L, Watson M, Baker A, Zhang S, Coldea A, Harrison S, et al. X-ray magnetic spectroscopy of MBE-grown Mn-doped Bi_2Se_3 thin films. AIP Advances. 2014;4:127136.

[68] Watson M, Collins-McIntyre L, Shelford L, Prabhakaran D, Speller S, Mousavi T, et al. Study of the structural, electric and magnetic properties of Mn-doped Bi_2Te_3 single crystals. New Journal of Physics. 2013;15:103016.

[69] Liu W, West D, He L, Xu Y, Liu J, Wang K, et al. Atomic-Scale Magnetism of Cr-Doped Bi_2Se_3 Thin Film Topological Insulators. ACS nano. 2015;9:10237-43.

[70] Ruderman MA, Kittel C. Indirect exchange coupling of nuclear magnetic moments by conduction electrons. Physical Review. 1954;96:99.

[71] Yosida K. Magnetic properties of Cu-Mn alloys. Physical Review. 1957;106:893.

[72] Jungwirth T, Sinova J, Mašek J, Kučera J, MacDonald A. Theory of ferromagnetic (III, Mn) V semiconductors. Reviews of Modern Physics. 2006;78:809.

[73] Hong NH, Sakai J, Poirot N, Brizé V. Room-temperature ferromagnetism observed in undoped semiconducting and insulating oxide thin films. Physical Review B. 2006;73:132404.

[74] Checkelsky JG, Ye J, Onose Y, Iwasa Y, Tokura Y. Dirac-fermion-mediated ferromagnetism in a topological insulator. Nature Physics. 2012;8:729-33.

[75] Chang CZ, Zhang J, Liu M, Zhang Z, Feng X, Li K, et al. Thin Films of Magnetically Doped Topological Insulator with Carrier‐Independent Long‐Range Ferromagnetic Order. Advanced materials. 2013;25:1065-70.

[76] Sobota JA, Yang S-L, Leuenberger D, Kemper AF, Analytis JG, Fisher IR, et al. Distinguishing bulk and surface electron-phonon coupling in the topological insulator Bi_2Se_3 using time-resolved photoemission spectroscopy. Physical review letters. 2014;113:157401.

[77] Koumoulis D, Morris GD, He L, Kou X, King D, Wang D, et al. Nanoscale β-nuclear magnetic resonance depth imaging of topological insulators. Proceedings of the National Academy of Sciences. 2015;112:E3645-E50.

[78] Luo W, Qi X-L. Massive Dirac surface states in topological insulator/magnetic insulator heterostructures. Physical Review B. 2013;87:085431.

[79] Eremeev S, Men'shov V, Tugushev V, Echenique PM, Chulkov EV. Magnetic proximity effect at the three-dimensional topological insulator/magnetic insulator interface. Physical Review B. 2013;88:144430.

[80] Men'shov V, Tugushev V, Eremeev S, Echenique PM, Chulkov EV. Magnetic proximity effect in the three-dimensional topological insulator/ferromagnetic insulator heterostructure. Physical Review B. 2013;88:224401.

[81] Kandala A, Richardella A, Rench D, Zhang D, Flanagan T, Samarth N. Growth and characterization of hybrid insulating ferromagnet-topological insulator heterostructure devices. Applied Physics Letters. 2013;103:202409.

[82] Yang QI, Dolev M, Zhang L, Zhao J, Fried AD, Schemm E, et al. Emerging weak localization effects on a topological insulator–insulating ferromagnet (Bi_2Se_3-EuS) interface. Physical Review B. 2013;88:081407.

[83] Wei P, Katmis F, Assaf BA, Steinberg H, Jarillo-Herrero P, Heiman D, et al. Exchange-coupling-induced symmetry breaking in topological insulators. Physical review letters. 2013;110:186807.

[84] Li J, Wang Z, Tan A, Glans P-A, Arenholz E, Hwang C, et al. Magnetic dead layer at the interface between a Co film and the topological insulator Bi_2Se_3. Physical Review B. 2012;86:054430.

[85] West D, Sun Y, Zhang S, Zhang T, Ma X, Cheng P, et al. Identification of magnetic dopants on the surfaces of topological insulators: Experiment and theory for Fe on Bi_2Te_3 (111). Physical Review B. 2012;85:081305.

[86] Zhao X, Dai X-Q, Zhao B, Wang N, Ji Y-Y. Cr adsorption induced magnetism in Bi_2Se_3 film by proximity effects. Physica E: Low-dimensional Systems and Nanostructures. 2014;55:9-12.

[87] Vobornik I, Panaccione G, Fujii J, Zhu Z-H, Offi F, Salles BR, et al. Observation of Distinct Bulk and Surface Chemical Environments in a Topological Insulator under Magnetic Doping. The Journal of Physical Chemistry C. 2014;118:12333-9.

[88] Lang M, Montazeri M, Onbasli MC, Kou X, Fan Y, Upadhyaya P, et al. Proximity induced high-temperature magnetic order in topological insulator-ferrimagnetic insulator heterostructure. Nano letters. 2014;14:3459-65.

[89] Liu W, He L, Xu Y, Murata K, Onbasli MC, Lang M, et al. Enhancing magnetic ordering in Cr-doped Bi_2Se_3 using high-TC ferrimagnetic insulator. Nano letters. 2014;15:764-9.

[90] Geim AK, Novoselov KS. The rise of graphene. Nature materials. 2007;6:183-91.

[91] Min H, Hill J, Sinitsyn NA, Sahu B, Kleinman L, MacDonald AH. Intrinsic and Rashba spin-orbit interactions in graphene sheets. Physical Review B. 2006;74:165310.

[92] Tombros N, Jozsa C, Popinciuc M, Jonkman HT, Van Wees BJ. Electronic spin transport and spin precession in single graphene layers at room temperature. Nature. 2007;448:571-4.

[93] Schwierz F. Graphene transistors. Nature nanotechnology. 2010;5:487-96.

[94] Li X, Wang X, Zhang L, Lee S, Dai H. Chemically derived, ultrasmooth graphene nanoribbon semiconductors. Science. 2008;319:1229-32.

[95] Wang X, Ouyang Y, Li X, Wang H, Guo J, Dai H. Room-temperature all-semiconducting sub-10-nm graphene nanoribbon field-effect transistors. Physical review letters. 2008;100:206803.

[96] Prinz GA. Magnetoelectronics. Science. 1998;282:1660-3.

[97] Huang B, Yan Q-m, Li Z-y, Duan W-h. Towards graphene nanoribbon-based electronics. Frontiers of Physics in China. 2009;4:269-79.

[98] Shibayama Y, Sato H, Enoki T, Endo M. Disordered magnetism at the metal-insulator threshold in nano-graphite-based carbon materials. Physical review letters. 2000;84:1744.

[99] Ma Y, Dai Y, Guo M, Niu C, Zhu Y, Huang B. Evidence of the existence of magnetism in pristine VX_2 monolayers (X= S, Se) and their strain-induced tunable magnetic properties. ACS nano. 2012;6:1695-701.

[100] Ohishi M, Shiraishi M, Nouchi R, Nozaki T, Shinjo T, Suzuki Y. Spin injection into a graphene thin film at room temperature. Japanese Journal of Applied Physics. 2007;46:L605.

[101] Han W, Kawakami RK. Spin relaxation in single-layer and bilayer graphene. Physical review letters. 2011;107:047207.

[102] Ando K, Saitoh E. Inverse spin-Hall effect in palladium at room temperature. Journal of Applied Physics. 2010;108:113925.

[103] Liu W, Wang W, Wang J, Wang F, Lu C, Jin F, et al. Atomic-Scale Interfacial Magnetism in Fe/Graphene Heterojunction. Scientific reports. 2015;5.

[104] Novoselov KS, Geim AK, Morozov S, Jiang D, Zhang Y, Dubonos Sa, et al. Electric field effect in atomically thin carbon films. Science. 2004;306:666-9.

[105] Iqbal MZ, Iqbal MW, Lee JH, Kim YS, Chun S-H, Eom J. Spin valve effect of NiFe/graphene/NiFe junctions. Nano Research. 2013;6:373-80.

[106] Van't Erve O, Friedman A, Cobas E, Li C, Robinson J, Jonker B. Low-resistance spin injection into silicon using graphene tunnel barriers. Nature nanotechnology. 2012;7:737-42.

[107] Koh Y, Cho S, Lee J, Yang L-X, Zhang Y, He C, et al. Growth and Electronic Structure Studies of Metal Intercalated Transition Metal Dichalcogenides M_xNbSe_2 (M: Fe and Cu). Japanese Journal of Applied Physics. 2013;52:10MC5.

[108] Ataca C, Ciraci S. Functionalization of single-layer MoS_2 honeycomb structures. The Journal of Physical Chemistry C. 2011;115:13303-11.

[109] Fuhr JD, Saúl A, Sofo JO. Scanning Tunneling Microscopy Chemical Signature of Point Defects on the MoS_2 (0001) Surface. Physical review letters. 2004;92:026802.

[110] Andriotis AN, Menon M. Tunable magnetic properties of transition metal doped MoS_2. Physical Review B. 2014;90:125304.

[111] He J, Wu K, Sa R, Li Q, Wei Y. Magnetic properties of nonmetal atoms absorbed MoS_2 monolayers. Applied Physics Letters. 2010;96:082504.

[112] Mishra R, Zhou W, Pennycook SJ, Pantelides ST, Idrobo J-C. Long-range ferromagnetic ordering in manganese-doped two-dimensional dichalcogenides. Physical Review B. 2013;88:144409.

[113] Cheng Y, Zhu Z, Mi W, Guo Z, Schwingenschlögl U. Prediction of two-dimensional diluted magnetic semiconductors: doped monolayer MoS_2 systems. Physical Review B. 2013;87:100401.

[114] Ramasubramaniam A, Naveh D. Mn-doped monolayer MoS_2: an atomically thin dilute magnetic semiconductor. Physical Review B. 2013;87:195201.

[115] Zhang K, Feng S, Wang J, Azcatl A, Lu N, Addou R, et al. Manganese doping of monolayer MoS_2: the substrate is critical. Nano letters. 2015;15:6586-91.