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Synthesis of emerging 2D layered magnetic materials

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van der Waals atomically thin magnetic materials have been recently discovered. They have attracted enormous attention as they present unique magnetic properties, holding potential to tailor spin-based device properties and enable next generation data storage and communication devices. To fully understand the magnetism in two-dimensions, the synthesis of 2D materials over large areas with precise thickness control has to be accomplished. Here, we review the recent advancements in the synthesis of these materials spanning from metal halides, transition metal dichalcogenides, metal phosphosulphides, to ternary metal tellurides. We initially discuss the emerging device concepts based on magnetic van der Waals materials including what has been achieved with graphene. We then review the state of the art of the synthesis of these materials and we discuss the potential routes to achieve the synthesis of wafer-scale atomically thin magnetic materials. We discuss the synthetic achievements in relation to the structural characteristics of the materials and we scrutinise the physical properties of the precursors in relation to the synthesis conditions. We highlight the challenges related to the synthesis of 2D magnets and we provide a perspective for possible advancement of available synthesis methods to respond to the need for scalable production and high materials quality.

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Introduction

Magnetism and its application in spin electronics have been key to develop high-density data storage solutions. Phenomena such as GMR (giant magnetoresistance) and TMR (tunnel magnetoresistance) effects have been widely used in high efficiency hard drive read heads and have fueled the big data and cloud



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era revolution. With the development of fundamental mechanisms such as STT (spin transfer torque) and SOT (spin orbit torque), spintronics technologies have been moving to nonvolatile highly efficient and ultra-low power memory circuits such as MRAMs (magnetic random access memories) and are now progressively being integrated to CMOS-based devices for green technologies.²⁻⁵ Next generation spintronics is expected to provide opportunities to merge logic and memory functions in computing architectures under the unified spin variable, as well as in many disruptive approaches for post-CMOS computing such as stochastic, logic-in-memory architectures, neuromorphic, and quantum circuits.6-14

All these envisioned applicative exploitations of spin electronics fuel the development of innovative material platforms, which can bring novel functionalities and performance to devices. In particular, 2D materials have been expected to deliver many opportunities to tailor spin-based device properties and bring to light unseen possibilities. One of the first examples is the robust spin transport in graphene (the prototypical 2D material), which unveils the long sought possibility of a platform for spin transport and potential path for spin logics targeting beyond CMOS solutions. 15,16 More remarkably, the development and integration of 2D materials have also been impressive with respect to the basic building block of spintronics, the magnetic tunnel junction (MTJ) at the core of MRAM technology.¹⁷ Within only few years 2D materials have already been demonstrated to provide many outstanding novel properties for spintronics such as: interface protection and stabilisation, diffusion control, spin filtering, atomic control crafting of spinterfaces (ferromagnet/non-magnet interface), increase of perpendicular magnetic anisotropies, natural atom thick interfaces for spin-to-charge conversion and modulation of spin orbit torques. 18-33 Remarkably, while 2D materials already offer a strong materials platform for spin transport and manipulation towards spin information processing for beyond CMOS, their main potential remains to be unleashed: an unprecedented full control and tailoring of electronic and magnetic properties through gating.34,35 While the first explorations of 2D materials integration in MTJs concerned only the prototypical 2D materials graphene and h-BN, studies were soon extended to large families of 2D semiconductors such as transition metal dichalcogenides (TMDs). 36-39

Most of the initial studies exploring 2D materials properties for spintronics were based on atomically thin layers, which were mechanically exfoliated form bulk crystals. 40 This technique is known to enable the isolation of high quality atomically thin 2D materials in a relatively straightforward manner. However, this approach is not scalable and, additionally, is even detrimental for spintronics applications as the exfoliation is carried out in an oxidative environment. This has been a recurring limitation for the integration and study of 2D materials on typical ferromagnetic spin sourcing materials, such as Ni, Co, Fe, and their alloys. Indeed, the surface oxidation of these material quenches the spintronics properties, in turn leading to very limited spin extraction and transport performances in complete spin valve structures. In parallel to the exfoliation approach, the direct growth of 2D materials appears as a crucial to overcome both the issue of scalability and the integration with delicate spintronics materials. 17,19 This has been observed for graphene and h-BN with direct chemical vapour deposition (CVD) growth being central in the unlocking of their spintronics properties. 21,28

Among 2D materials, 2D ferromagnets (FM) are promising for spintronics as they could lead to a complete 2D MTJ. 41-44 Departure from usual spin sources would allow the exploitation of the 2D material characteristics (conformality, flexibility, atomic thickness control, etc.) for spin based circuits. In addition, 2D ferromagnets have been predicted to be half



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metallic (meaning only one spin direction is present at the Fermi level) materials, 45,46 i.e. the perfect fully polarised spin source. This would naturally offer infinite TMR for a 2D MTJ and has been a long-haul quest in spintronics. 47 Furthermore, magnetism at the 2D limit has barely been exploited in functional structures and promises to provide unseen properties for the control of spin functions. Indeed while ultimately achievable with conventional magnets, reducing thicknesses down to few atoms thick requires sophisticated engineering developments.⁴⁸ On the contrary this comes naturally to 2D materials with atomic precision and a wealth of gating opportunities of their magnetic/electronic properties. While the sole existence of spontaneous magnetisation in 2D materials has been questioned by the Mermin-Wagner-Hohenberg (MWH) theorem since the 60s,49 it is only very recently that intrinsic magnetic order was experimentally observed in ultrathin layers of 2D ferromagnets, such as CrI₃, CrGeTe₃, and Fe₃GeTe₂. ⁵⁰⁻⁵⁵ Compared to conventional ferromagnetic materials used in spintronics, those materials are extreme sensitive to external doping and electromagnetic fields. This gives for the first time the opportunity to play with their intrinsic magnetic and electronic properties, an asset unavailable before. In particular, the gating of 2D magnetic material could pave the way toward magnetic phase crafting at the atomic level and on-the-fly electrical control.

Concerning spintronics devices, the field is just blooming. Fully 2D MTJs based on 2D ferromagnets have been successfully demonstrated using metallic Fe₃GeTe₂ and h-BN barriers in Fe₃GeTe₂/h-BN/Fe₃GeTe₂ heterostructures. Remarkably, a clear TMR of 160% was observed at 4 K leading to a spin polarisation of 66% for the Fe₃GeTe₂/h-BN interface (Fig. 1(d-f)). Similarly, Fe₃GeTe₂ structures (using MoS₂ barriers or spacerfree homojunctions) presented more recently further confirm the interest in those 2D ferromagnets for spintronics. 44,57



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2012. Cecilia is a Fellow of the Royal Society of Chemistry and her research interest includes the precise synthesis of 2D materials with tailored characteristics and the investigation of their properties for energy conversion, energy storage, and nanoelectronics.

Here, beyond the remarkable observation of high spin polarisation for the Fe₃GeTe₂ electrode, one of the outstanding advantages remains to be unleashed and this is the tunability. The Curie temperature (T_c) of Fe₃GeTe₂ has been shown to be gate tunable and it could potentially reach room temperature.58 Such a material property holds very strong promise for future applications. For example, one could think of lowering T_c (or change the anisotropy), through gate control, to achieve ultralow power magnetisation switching and subsequently raise the temperature to obtain long term storage. In addition, most of these new 2D materials naturally offer perpendicular anisotropy, a property usually available only in ultrathin 3D ferromagnets which are inherently more difficult to grow.⁵⁹ The advantage of perpendicular magnetic anisotropy is that it withstands downscaling while maintaining thermal stability, which is a requirement for future ultrahigh density devices.² Along this way, their intrinsic 2D nature makes them also perfect candidates for hosting controllable topological protected skyrmions, 60 the ultimate spintronics memory element. 61

Also, in a very promising way, semiconducting CrI₃, the flagship of the chromium trihalides family, was reported as an efficient insulating spin-filtering barrier for 2D MTJs. Indeed, its strong spin filtering properties were evidenced for CrI3 sandwiched by two graphene electrodes in a Gr/CrI₃/Gr tunnel structure (Fig. 1(a-c)). 41,42,62 The MR in the device relied on the applied magnetic field switching the internal CrI3 interlayer magnetic configuration from antiferromagnetic (AFM) to ferromagnetic in a way mimicking the early GMR behavior. In the AFM state, every second layer of the CrI3 would filter out an opposite spin direction resulting in a large resistance for the tunnel barrier, while with an applied magnetic field all the layers would align. The latter would allow a preferential spin direction to pass through, and thus it would reduce the overall resistance. Very large TMR in the million percent range were found, thanks to the spin filtering high efficiency. Additionally voltage control was also demonstrated highlighting the potential of this type of 2D AFM/FM for future spintronics devices. 63,64 As such a new type of device could arise using 2D FMs to work as a gate-tunable tunneling barrier spin filter. It would rely on the property of tuning the interlayer coupling from ferromagnetic to antiferromagnetic through an external gate voltage, which would be unavailable using conventional FM.65

2D insulator/semiconductor ferromagnets could find their way in spin dynamics and more specifically, in the field of magnonics, ⁶⁶ targeting downscaled optics within magnetic materials through spin waves. In this emerging field, 2D insulator/semiconductor ferromagnets could lead to the demonstration of gate tunable magnonic channels. ⁶⁷ For example, long distance magnon transport was already demonstrated in 2D antiferromagnetic MnPS₃ connected by two Pt spin hall effect injector/detector (Fig. 1(g-i)). ⁶⁸ Their manipulation by STT and SOT has also been demonstrated in part. Indeed switching of the semiconducting van der Waals ferro-magnet CrGeTe₃ through SOT was demonstrated at the interface with Ta. ⁶⁹ Finally 2D insulator/semiconductor ferromagnets could also tackle the long quest for integrating magnetism into semi-

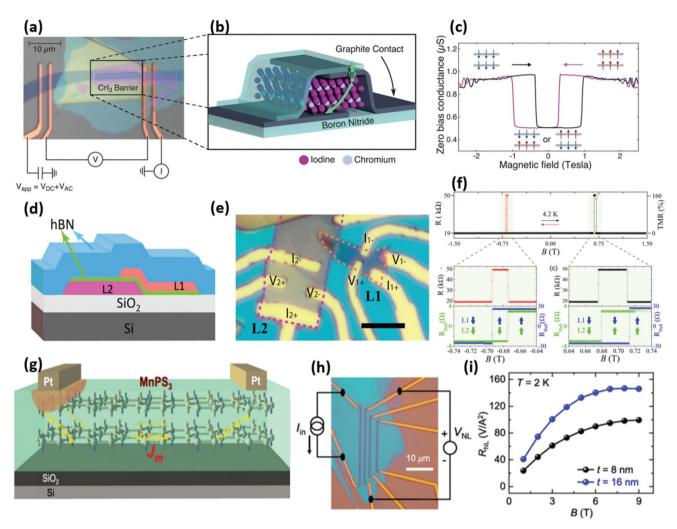


Fig. 1 2D magnet-based devices. (a–c) Optical image and schematic of a $Gr/CrI_3/Gr$ MTJ and measured magnetoconductance vs. applied magnetic field. Peproduced with permission from ref. 42. Copyright 2018 The American Association for the Advancement of Science. (d–f) Optical image and schematic of a tunnelling spin valve device based on a $Fe_3GeTe_2(L1)/h-BN/Fe_3GeTe_2(L2)$ heterostructure. The measured TMR reaches 160% at $B=\pm 0.7 \text{ T.}^{56}$ Scale bar is 5 μ m. Reproduced with permission from ref. 56. Copyright 2018 American Chemical Society. (g–i) Schematic and optical image of a magnonic transport-based device using a $MnPS_3$ bilayer as magnon transport medium from the Pt electrodes, acting as magnon source and detector. The graph shows the nonlocal magnon signal (R_{NL}) against the applied magnetic field B for devices of thicknesses 8 and 16 nm at 2 K. Reproduced with permission from ref. 68. Copyright 2019 American Physical Society.

conductors started by diluted magnetic semiconductors.⁷⁰ Providing high mobility could be found new 2D ferromagnet semiconductors (such as early highlighted CrSiTe₃ and CrGeTe₃ ^{54,71}), it might reboot the field in an unexpected way.

While pioneer works in this direction have been based on exfoliated material, ^{41–44} already unveiling a strong potential for spin performances and functionalities, large scale growth will not only allow the systematic study of their properties but also will enable the direct integration of these materials in heterostructures for the fabrication of functional devices. The integration of 2D magnets grown by CVD in functional spintronics heterostructures can be foreseen to serve to the emerging field of spintronics circuits.

In this article, we review the state of the art of the synthesis of the most investigated 2D materials with magnetic order.

Specifically, we discuss Fe_3GeTe_2 and other ternary tellurides, 72,73 CrX_3 (X=Cl, I, Br) and α -RuCl $_3$, $^{74-76}$ MPX $_3$ (M=metal, X=S, Se), 77,78 Cr and V dichalcogenides, $^{79-82}$ and metal doped TMDs. $^{83-85}$ The crystal structure, the electronic and the magnetic properties of these 2D magnets are reported in Table 1. In the first part of this review, we discuss the state of the art of synthesis of 2D magnets followed by a critical discussion of perspective synthetic solution to achieve a control over the materials characteristics. In the last section we discuss the application of metalorganic CVD (MOCVD) for the growth of 2D magnetic materials. Since MOCVD has been recently used for full-scale TMDs synthesis with thickness control, 86,87 we prospect that this technique may lead to similar results for 2D magnets. Moreover, ternary and quaternary alloys and compounds have already been achieved using MOCVD in thin

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Table 1 Crystal models, electronic and magnetic properties of the 2D magnets object of this review

Crystal	Side view	Top view	Space group	Electronic type	Magnetic type	Magnetic transition temperature (K)
CrS ₂ CrSe ₂ CrTe ₂ VS ₂ VSe ₂ VTe ₂	○ Cr, V ○ S, Se, Te		P3m1	Metallic	AFM AFM FM FM FM FM	219 ⁸⁸ >330 (f-L) ⁸⁹ 300 ⁹⁰
Fe ₃ GeTe ₂	● Fe ● Ge ● Te		P6 ₃ /mmc	Metallic	Ising-FM	130 91
CrCl ₃ CrI ₃ CrBr ₃	Cr Cl, I, Br	**	C2/m	Insulating	XY-FM Ising-FM Ising-FM	17 (f-L) ⁹² 45 ⁵¹ 34 ⁹³
FePS ₃ MnPS ₃ NiPS ₃	● Fe, Mn, Ni ● P ● S		C2/m	Insulating	Ising-AFM Heisenberg-AFM XY-AFM	110 ⁷⁸ 78 (5 L) ⁹⁴ <25 (155 bulk) ⁹⁵
FePSe ₃ MnPSe ₃ CrSiTe ₃ CrGeTe ₃	Fe, Mn, Cr P, Si, Ge Se, Te		R3	Insulating	Ising-AFM XY-AFM Ising-FM Heisenberg-FM	119 ⁹⁶ 74 ⁹⁶ 32 (bulk) ⁹⁷ 30 ⁵⁰
$MnBi_2Te_4$	Mn Bi Te		R3m	Insulating	Heisenberg-AFM	25 (bulk) ⁹⁸
α-RuCl ₃	Ru cl	**	P312	Semiconductive, direct bandgap 1.9 eV (ref. 99)	Kitaev-AFM	7 (bulk) ¹⁰⁰

films industry, and we envision possible pathways to synthesise phosphochalcogenides, binary and ternary tellurides and alloys using this method.

State of the art of magnetically active 2D crystal growth

Metal halides

One of the most studied classes 2D magnets are metal halides. These are chlorides, bromides, and iodides of transition metals such as Ti, V, Cr, Mn, Fe, Co and Cu. The majority of them have been predicted to be predominantly antiferromagnetic with two ferromagnetic exceptions, which are CrI₃, possessing a Curie temperature of 45 K as reported in Fig. 2(a), and CrBr₃.¹⁰¹ However, only a few of them have been obtained experimentally. Within this group, the Cr-based halides have been the most studied for their magnetic properties and control over their magnetic order has been achieved via gating, doping, pressure and stacking order. 51,74,102-105 Atomically thin flakes were obtained via mechanically exfoliation from chemical vapour transport (CVT) grown bulk crystals (Fig. 3(a)). 106 In this process, Cr powders were placed in an ampoule filled with halogen gas, which is inserted into a

furnace (set at 600-700 °C) while the other end is kept at room temperature. 92,107 Here the Cr powders are transported by the convective flux onto the colder end outside the furnace and after several days the slow reaction in the gas phase between Cr atoms with the halogen species yielded high quality bulk crystals. The synthesis of Cr halides alloys has been demonstrated by mixing precursors powders. 108 In specific, $CrCl_{3-x}Br_x$ and $CrBr_{3-x}I_x$ were obtained mixing $CrCl_3$ or $CrBr_3$ commercial powders with Br or I beads according to the desired final stoichiometry. By mixing Cr₂O₃ and CrCl₃ powders in a similar setup it is possible to obtain the vdW magnetic insulator CrOCl. 109

A different synthetic approach has been reported by Gamelin et al., who has demonstrated the colloidal synthesis of CrI₃, CrBr₃ and alloys. 110 Cr(OCMetBu₂)₃ and trimethylsilyl halide (C₃H₉SiX) have been used as precursors and the new phase of CrI₃ and CrBr₃ has been obtained via chemical reaction and precipitation occurring at 135-180 °C. The resulting crystals are nanoplatelets (Fig. 3(b)) as large as 26 nm and composed by 4-10 stacked layers. Magnetisation measuredemonstrated a similar behaviour to exfoliated ments crystals.

Recently, a few studies on the synthesis of FeCl2 and α-RuCl₃ have been reported. Zhou et al. has demonstrated the

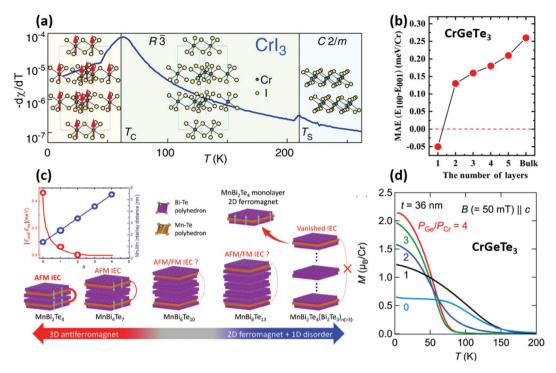


Fig. 2 The role of the structure and the composition of materials in determining the magnetic properties; (a) phase transition of bulk Crl₃. The crystal changes crystallography at 220 K and at 61 K (T_c) spins align and magnetisation arises.¹⁰⁷ Reproduced with permission from ref. 107. Copyright 2015 American Chemical Society. (b) Calculated magnetic anisotropy energy (MAE) vs. layer number in CrGeTe₃.¹¹¹ Reproduced with permission from ref. 111. Copyright 2019 AIP Publishing. (c) Evolution of the magnetic behaviour in MnBi₂Te₄(Bi₂Te₃)_n. The Bi₂Te₃ layers separate the ferromagnetic MnBi₂Te₄ sheets decreasing the magnetic interaction (upper left inset) and decoupling the antiferromagnetism present in bulk.¹¹² Reproduced with permission from ref. 112. Copyright 2020 John Wiley and Sons. (d) Magnetisation magnitude dependence on composition (controlled by P_{Ge}/P_{Cr}) in CrGeTe₃.¹¹³ Reproduced with permission from ref. 113. Copyright 2018 AIP Publishing.

synthesis of atomically thin ferromagnetic FeCl₂ on Au(111) and graphite *via* molecular beam epitaxy (MBE). ¹¹⁴ The grown material exhibited nanometric grain size and low substrate coverage, enabling only the fabrication of proof-of-concept devices.

Another synthetic strategy that has been utilised to grow 2D magnets is magnetron sputtering, by which thick films of FeCl₂ and FeCl₃ were grown. The technique enables to achieve high coverage in a short time, however, with poor control over the film thickness and ultimately leads to thick films with small grain size and irregular shape. $\alpha\text{-RuCl}_3$, which is a Kitaev antiferromagnet with a low magnetic transition temperature of 7 K in bulk, was synthesised using the vertical Bridgman method. Here RuCl₃ powders were slowly molten in a vertical furnace at 1100 °C and after 80 hours the crystals obtained were large and easy to exfoliate.

Many other members of these family have been predicted to be magnetically active, such as FeX₂ ⁴⁵ and MnX₃, ¹¹⁶ however the experimental demonstration of their synthesis is still missing (to the best of our knowledge). The physical vapour deposition (PVD) growth of NiI₂ has been recently reported by Liu *et al. via* low pressure sublimation of NiI₂ powders onto SiO₂ or h-BN as target substrate. ¹¹⁷ The growth temperature was set to 450 °C for both substrate materials, however h-BN required only one minute of growth time,

whereas SiO_2 needed 5–10 minutes. Monolayer and few layer flakes were selectively grown only on h-BN with lateral size up to 20 μ m, while on SiO_2 the deposited flakes were as thick as 40 nm. Interestingly, other magnetic vdW halides have been synthesised decades ago such as like $CoCl_2$, ¹¹⁸ GdI_2 , ^{119,120} and $FeBr_2$ ^{121,122} but no further attempts to grow these materials has been done recently.

Tellurides

Another important family of magnetic vdW crystals is the binary and ternary metal tellurides. Thus far, to the best of our knowledge, this consists of few materials which have been experimentally demonstrated: FeTe, Fe₃GeTe₂, CrXTe₃ (X = Ge or Si), MnBi₂Te₄, and GdTe₃. However many other tellurides have been recently predicted to show magnetic order, such as ferromagnetic VSnTe₃ and NiSiTe₃. 123 Fe₃GeTe₂ is a metallic ferromagnet in bulk with a Curie temperature of 220 K that drops to 130 K in monolayer form and it presents an Ising-type long range ordering. 91,124 The growth of this material has only been achieved via CVT where ultrapure Fe, Ge, and Te powders were mixed in the 3:1:2 ratio (Fig. 3(c)). The temperature gradient between the powders and the target zone was usually 700-750 °C along with I2 gas transport agent and the synthesis lasted for several days. 124

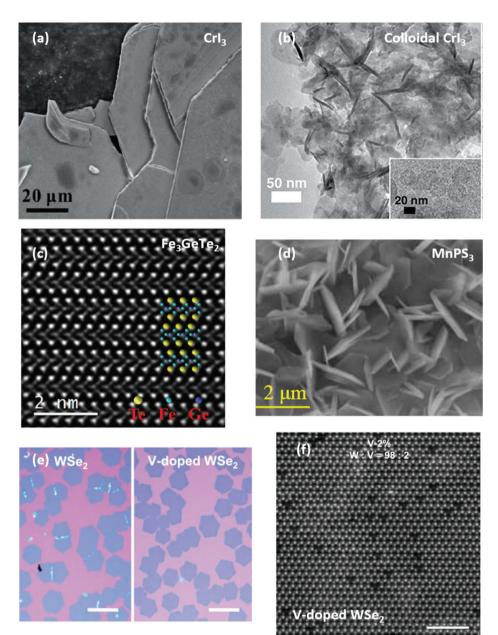


Fig. 3 Morphology of 2D magnetic crystals. (a) SEM image of a CVT grown Crl_3 single crystal. (a) Reproduced with permission from ref. 134. Copyright 2020 Elsevier. (b) Bright field transmission electron microscope (TEM) image of Crl_3 colloidal nanocrystals. (b) Reproduced with permission from ref. 110. Copyright 2020 American Chemical Society. (c) High-resolution (HR)TEM of the atomic structure of Fe_3GeTe_2 . (d) SEM image of CVD-grown Fe_3GeTe_2 . (e) Reproduced with permission from ref. 135. Copyright 2019 The American Association for the Advancement of Science. (d) SEM image of CVD-grown Fe_3GeTe_2 . (d) SEM image of CVD-grown Fe_3GeTe_2 . (e) Reproduced with permission from ref. 136. Copyright 2018 John Wiley and Sons. (e and f) Optical micrographs of CVD-grown undoped Fe_3GeTe_2 . (e) Fe_3GeTe_2 . (f) SEM image of CVD-grown undoped Fe_3Ge

CrGeTe₃ and CrSiTe₃ are layered semiconductors and ferromagnetic insulators with Heisenberg and Ising spin order models, respectively.^{125,126} Similarly to the other 2D magnets these crystals are expected to present layer dependent magnetic properties, as shown in Fig. 2(b) where the magnetic anisotropy energy increases with the layer number.¹¹¹ Both crystals have been grown using a self-flux CVT process, in which Ge or Si and Te powders are loaded in large stoichiometric

excess (1:3:36 molar ration, for example) in an ampoule where they play the role of self-transport agents. $^{52,126-128}$ In this case the synthesis can last up to 20 days at temperatures higher than 1000 °C. MBE was used to tune the composition of the Cr–Ge–Te system from Cr_2Te_3 to CrGeTe_3 by varying the relative precursors supply. In this way, it has been possible to tune the magnetic response from a minimum, when Ge was absent, to a maximum where Ge supply was four

times larger than the Cr one, as reported in the plot in Fig. 2(d). 113

The antiferromagnetic topological insulator MnBi₂Te₄ has been also synthesised via self-flux CVT over a period of 7 days. 129 This technique has been implemented by mixing the elemental powders in the stoichiometric ratio under vacuum, heating the systems at 850 °C for 24 hours and subsequently at 595 °C for 150 hours. Interestingly, MnCl₂ can also be employed as transport agent, if the molar ratio of the three precursors is set at Mn:Bi:Te:MnCl₂ 1:1:1:0.3. This different molar ratio has resulted in higher Hall mobilities measured in a magnetoelectronic device. Not only elemental powders can be used, commercial Bi2Te3 and MnTe bulk powders were employed in the crystal growth and, in addition to this, a complete phase diagram was drawn with Bridgman vertical growth. This has highlighted a plethora of possible phases and stoichiometries. These MnBi_xTe_y (x = 2, 4, 6,...; y = 4, 7, 10, ...) phases have a peculiar structure, where Bi₂Te₃ are sandwiched in between two MnBi₂Te₄ layers. ¹¹² The separation of MnBi₂Te₄ layers has led to the isolation of single 2D ferromagnetic sheets, as represented in Fig. 2(c). Another antiferromagnetic layered material that has been recently reported is GdTe₃, which unlike MnBi₂Te₄ shows metallic characteristics. 132 The CVT synthesis used Te and Gd powder in a 97:3 ratio, where Te acts as the transport agent, heated at a temperature of 900 °C for 12 hours. Recently, platelets of the

2D ferromagnetic FeTe have been grown via ambient-pressure CVD using FeCl2 and Te powder as precursors on SiO2 substrates. 133 In this synthesis, it was possible to selectively grow the tetragonal phase at 530 °C, whereas increasing the growth temperature to 590 °C resulted in the growth of hexagonal crystals. The lateral size of these platelets ranged from 10 to 60 µm with thicknesses down to 2.8 nm.

Metal phosphochalcogenides

Metal phosphorus trichalcogenides are antiferromagnetic wide band gap semiconductors with general formula MPX3, where M is a metal, or a combination of metals matching the stoichiometry, and X is either S or Se. Specifically two metal atoms coordinate with $[P_2X_6]^{4-}$ ions within the individual layer and arrange into a hexagonal structure. The difference between sulphides and selenides are related to the stacking of the 2D layers in the bulk form, where the firsts are monoclinic (C2/m)space group) and the latter are rhombohedral (R3 space group).

Besides being magnetically active, these materials attracted research interest due to their catalytic properties and hence more efforts were made towards facile and scalable crystal growth methods. 138,139 CVT is the most used technique to synthesise these bulk crystals (Fig. 4(a)), which also enables to achieve mixed metals phosphochalcogenides such as CuCrP₂S₆, CuInP₂S₆, and alloys. 140,141 However, He et al.

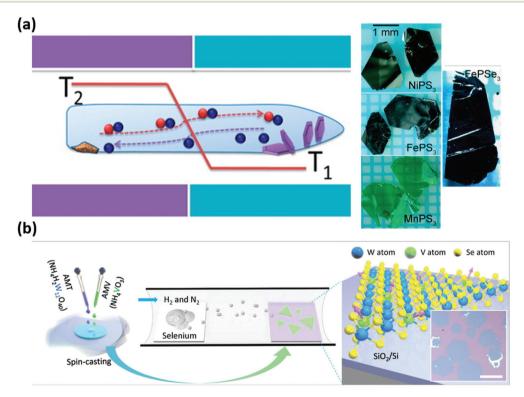


Fig. 4 Reported growth methods for 2D magnets: CVT and CVD. (a) CVT growth of metal phosphochalcogenides. The sketch depicts the reaction, where the halogen gas transports the elements from the hot to the cold side via convection. 146 Reproduced with permission from ref. 146. Copyright 2016 American Chemical Society. (b) CVD of V-doped WSe2. The mixed precursors react with Se on the SiO2 surface into ferromagnetic V-WSe₂. 147 Scale bar is 50 μm. Reproduced with permission from ref. 147. Copyright 2020 John Wiley and Sons.

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attempted and achieved a higher throughput protocol that involves the hydrothermal synthesis of metal oxides (NiO2 or MnO₂) and then a subsequent step in a CVD tubular furnace with stoichiometric quantities of S (Se) and P. 136,142,143 In order to avoid parasitic reactions (formation of metal sulphides), a single phosphosulphide precursor was prepared either by ball milling the powders together or by melting P and S in a pre-growth step. The result was a forest of multilayer MnPX₃ (Fig. 3(d)) or NiPS₃ with flakes of lateral size around 2-3 µm. While the morphology of such flowers is not suitable for planar device fabrication, this approach proved that it is possible to grow MPX₃ crystals via CVD. FePS₃ has been grown in a similar way, using FeS previously grown on carbon paper and then phosphorised and sulphurised in a tubular furnace at 550 °C. 144 The morphology and dimension of the FePS3 flakes are similar to what has been reported for Ni and Mn based phosphochalcogenides. Huang et al. reported analogous results using NaCl crystals as templates, which then are covered in solution with FeCl₃ and then placed in a CVD furnace at 500 °C along with P and S powders. 145

Transition metal dichalcogenides

Amongst the large family of TMDs the V (VS₂, VSe₂, VTe₂) and Cr (CrS2, CrSe2, CrTe2) compounds are magnetically active, intrinsically or they can become magnetic via doping with metal atoms.81,148-153 These TMDs are mainly antiferromagnetic (CrS2 and CrSe2 are ferromagnets), semimetallic and stable in the 1T trigonal phase (space group C2/m) with A-A stacking. CVD-based syntheses of these materials have been demonstrated. Shivayogimath et al. 154 have proposed a strategy to achieve a monolayer self-limited synthesis, which is based on the different solubilities of metals and chalcogens in gold recalling the self-limited synthesis of graphene on copper¹⁵⁵ and former growths of group VI TMDs. 156 A thin film of the metal precursor (20 nm) is deposited by PVD on a sapphire substrate and, subsequently, covered with a 500 nm thick gold foil. This composite film is then placed into a hot-wall tubular furnace at high temperature (850 °C) where it is exposed to chalcogen vapours for 10 to 15 minutes. The chalcogen solids are placed upstream and heated at 110 °C, 220 °C, and 420 °C for S, Se, and Te respectively. Since the metal chosen is soluble in gold and the chalcogens have good affinity (decreasing form S to Te) with it, the latter will tend to stick on the Au surface more easily compared to the normally used ceramic substrates (SiO₂, sapphire). This facilitates the formation of monolayers that can potentially cover the whole gold surface when adequate reaction time is provided. Using this method, it has been possible to grow flakes of CrS₂, CrSe₂, CrTe₂ and VS₂ in addition to many other non-magnetic TMDs. Large VX2 monolayer flakes on SiO₂ have been achieved by Liu et al. 157 using CVD by salt-assisted (KI) chalcogenisation of V₂O₅, a reaction commonly used for group 6 TMDs, 158 at temperatures between 680 to 750 °C in a hot-wall reactor at atmospheric pressure. A similar CVD configuration has been used for the synthesis of multilayered VTe2 nanoflakes by NH4Cl as evaporation assistant for V₂O₅ at temperatures ranging from 600 to 800 °C at

atmospheric pressure. ¹⁵¹ Whereas Chua *et al.* reported the CVD growth of VS₂ microflowers on carbon paper *via* sulphurisation of VCl₃ at just 500 °C at atmospheric pressure set by a mixture 95:5 of Ar/H₂. ¹⁵⁹ VCl₃ has also been used along with Te powder in the CVD growth of VTe₂ nanoplatelets at a growth temperature of 600 °C, resulting in triangular multilayer flakes up to 10 μ m in lateral size. ¹⁶⁰

Magnetism can be induced in other metallic and semiconductive TMDs, such as MoS₂, WSe₂, TaS₂ and NbS₂, via doping or alloying with a wide range of metal atoms. 84,161-165 However, only few reports have been published showing experimental characterisation of doped-TMDs obtained via CVT. Metallic TMDs, such as TaS2 and NbS2 can become magnetically active when layers of metal atoms are intercalated in between the TMDs sheets forming a new crystal structure (space group $P6_322$) with a new stoichiometry of $M_{1/3}$ Ta(Nb)S₂. In particular, Cr intercalation in Nb and Ta sulphides yields ferromagnets with T_c at 120 K and 110 K respectively, $^{166-168}$ whilst V_{1/3}NbS₂ and V_{1/3}TaS₂ are almost perfect XY antiferromagnets (spin is out-of-plane by 2°) with much lower Curie temperatures (50 K and 32 K respectively). 169 Fe can also be intercalated in NbS2 resulting in an Ising-nematic antiferromagnet.83

Substitutional doping of TMDs has been reported a few times but is yet to be established, and rarely it has been achieved during the CVD growth by adding a third precursor. 170-172 Interestingly, Lee et al. have synthesised ferromagnetic monolayer V-doped WSe2 with lateral dimensions of approximately 100 μm onto SiO₂ via a two-step process. ^{137,173} Firstly, tungsten and vanadium precursors (NH₄H₂W₁₂O₄ and NH₄VO₃) are dissolved in deionized water in amount proportionate to the target doping level, then the solution is spincoated onto a silicon substrate along with NaOH acting as growth promoter. Then, at 750 °C in presence of H₂ the metal precursors decompose in metal oxides and react with selenium to form atomically thin V-doped WSe₂ monolayers (Fig. 4(b)) extended over tens of microns (Fig. 3(e and f)). A similar synthesis protocol has also been recently used by Pham et al. to obtain 10 µm-sized V-doped WSe2 monolayer flakes where larger saturation magnetisations were measured for higher V doping levels up to 8 at%, point in which the distance between the dopant atoms becomes too small to allow ferromagnetism. 174

Pathways towards wafer scale synthesis of 2D magnets

CVD is a manufacturing technique which can be upscaled and due to its success in 2D materials synthesis it can be regarded as a promising route for the synthesis of atomically thin 2D magnets over wafer-size areas. Therefore, in this section we will outline the possible pathway towards establishing the (MO)CVD growth of these materials, describing the fundamental physics, possible precursors, process parameters and substrate effects.

Fundamentals of CVD and MOCVD

After describing the state-of-the-art of 2D magnetic crystals growth, the next step is to identify pathways for the wafer-scale production of these materials and subsequent integration into devices. Looking at the modern electronics industry, most of the materials used for the fabrication of commercial devices require uniform high-quality films with precisely controlled composition to achieve the desired specifications. A technique that conjugates throughput, scalability and precise process control is CVD. Furthermore, CVD can be applied to a wide variety of materials, given the large library of compounds currently employed as precursors for the growth of oxides, semiconductors, nitrides, and metal thin films. The CVD reactor design, related physics, reaction kinetics, and substrate contribution have been extensively investigated for the growth of 2D materials.

After a few years since the isolation of graphene, the CVD synthesis of self-limited monolayer films on a cm² scale were achieved via H2-aided reduction of methane on metal films. 155,175 These results paved the way for the growth atomically thin h-BN and TMDs and similar processing strategies to the ones identified for the graphene synthesis, yielded high quality crystals. 176-178 Up until now, powder precursors have been the nearly the only suitable precursors for the growth of high quality atomically thin TMDs due to their reactivity at high temperature and their relative low cost. 179 However, powder-based CVD lacks of a precise control over precursors supply and the growth time is determined by the powder amount, which ultimately limits the coverage and the thickness control. Thus, MOCVD, where the precursors are high vapor pressure solids, liquids, or gases and are individually controlled, has been proposed as a possible solution to these limitations. MOCVD enables control on the precursor flowrates with the possibility to extend the growth time up to several hours. This technique enabled the growth of MoS₂, MoSe₂, WS2, and WSe2 over more than 2-inch wafers with performances approaching the ones of materials grown using powders.86,87,180-182

As we mentioned in the previous section, other bottom-up techniques are used for the growth of 2D materials. We described how MBE can cover a wide range of compositions with high resolution in the Cr-Ge-Te system. Analogous results have also been reported for TMDs, 183,184 where the high degree of process control provided by MBE enabled fundamental studies of nucleation and growth of monolayer WSe₂. 185 However, despite the extremely high crystal quality that is achieved, MBE currently leads only to sub micrometric flake sizes with slow deposition rate. Additionally, the technique itself requires extremely pure elemental precursors, high temperatures and ultra-high vacuum in the reaction chamber. Atomic layer deposition (ALD) is less demanding in terms of cost and it can produce large films with controllable thickness. 186 The polycrystalline films with domains normally (within 1-2 µm) much smaller than CVD-grown materials, 187,188 (several microns in lateral size) currently represent the main limitation in using ALD to grow TMDs and it is possibly due to the low deposition temperatures, which are usually around 500 $^{\circ}$ C.

The physics of the MOCVD reactors

CVD is a multiscale process, as it involves both macroscopic and microscopic phenomena. The former are: precursor evaporation, reactor fluid dynamics, and heat transport. 189,190 While the latter are: precursors reaction, diffusion, and nucleation and growth. 189 Analogously to liquids flowing in pipes, the physics in a CVD reactor is governed by the Reynolds number Re, which determines whether the flow is turbulent or laminar and consequently the fluid dynamics and the precursors distribution. 189 Conventional CVD parameters nearly always result in low Re and therefore the process can be modelled using the well-known Navier-Stokes equations, which model the conservation of momentum and mass, and the conservation of heat and chemical species. 191 Solving these equations for the reactor geometry, given specific boundary conditions, results in the temperature, velocity, and concentration profiles across the tube, which are essential information for the process parameter optimisation. To distinguish the individual concentration profiles of all the chemical species, the direct and the inverse reaction rates must be considered, which are usually Arrhenius-like power laws. The solutions of the mass, heat and momentum balance can be included into mesoscale simulations (Kinetic Monte Carlo and phase-field models) as boundary conditions to predict morphology, distribution and size of 2D materials. 192,193 Another key phenomenon to be considered is the formation of the boundary layer where the flow meets the substrate. Within the boundary layer the viscous component of the forces dominate and the gas velocity acquires a component normal to the substrate, inducing a concentration gradient through the layer, as described in Fig. 5(a). 194 Additionally, the boundary layer thickness increases along the substrate by the square root of the x coordinate in a horizontal reactor and this causes a drop in the growth rate, ultimately leading to an inhomogeneous film. 195 This is generally mitigated tilting or rotating the substrate to level off the boundary layer contribution, 196,197 however this configuration is rarely present in research labs while it is normally use at industrial level. Therefore, a solution to this issue has been found in using vertical reactors; where the gas flow is normal to the substrate and hence the boundary layer thickness is homogeneous. This ultimately results in a uniform distribution of products (Fig. 5(b)). 198 This configuration proved to be particularly advantageous for MOCVD of TMDs, since J. Robinson, J. Redwing and coworkers have been able to reduce the growth time from the 26 hours, reported for horizontal MOCVD synthesis, 87 to just one hour in a vertical reactor. 199 Moreover, the use of a coldwall reactor where the substrate is placed onto a graphite susceptor heated by an induction system, which prevents parasitic reactions in the gas phase and minimises the vapour transport led to the synthesis of epitaxial WSe2 monolayer films over large sapphire and h-BN substrates. 199-202

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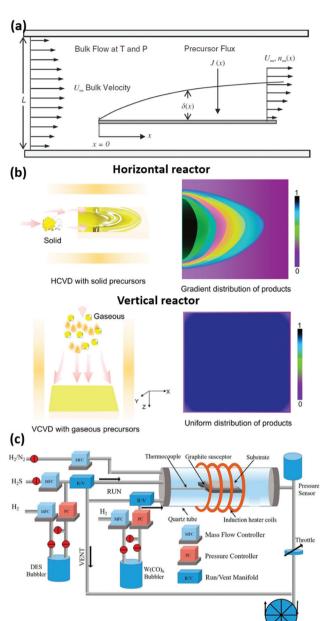


Fig. 5 Fundamentals of CVD physics and equipment. (a) Sketch of the boundary layer arising in a horizontal furnace. The precursor flux towards the substrate J(x) is a function of the layer thickness $\delta(x)$ and the precursor concentration n(x), both dependent on the horizontal coordinate. (a) Reproduced with permission from ref. 189. Copyright 2008 The Royal Society of Chemistry. (b) Comparison between a conventional horizontal reactor and a vertical reactor. The boundary layer presence results in an inhomogeneous product distribution. (a) Reproduced with permission from ref. 198. Copyright 2020 American Chemical Society. (c) Schematic of a cold-wall CVD reactor for the growth of WS2 from solid (W(CO)6), liquid (diethyl sulphide, DES) or gaseous (H2S) precursors. (203 Reproduced with permission from ref. 203. Copyright 2018 American Chemical Society.

These considerations regarding the flow are of concern of both CVD and MOCVD alike, however the higher degree of precursors flow control in MOCVD makes this technique particu-

larly promising for the growth of 2D materials. In fact, the precursors supply in powder-based CVD cannot be efficiently control as its evaporation rate depends on many factors such as temperature, carrier gas velocity, powder heap height and geometry.²⁰⁴ Additionally, the precursors amount is limited and therefore does not allow prolonged growth times needed for full coverage on wafer scale. Several strategies to control the precursor flowrates have been proposed, such as using low volatile oxides, to limit the metal precursor evaporation, 205 or mapping the evaporation rate via calorimetric analysis, 157 which has improved the crystal quality. On the contrary, in MOCVD the precursors are placed outside the furnace in stainless steel cylindrical bubblers where the carrier gas flows into the cylinders and transport the precursor's vapour in the reactor. The precursor flowrate F is given by $F = \frac{p(T)}{P - p(T)} F_{\text{in}}$, where $F_{\rm in}$ is the flowrate of the carrier gas, p(T) is the precursor's vapour pressure at the bubbler temperature T and P is the bubbler pressure. Hence, for a robust control of the precursor flowrate a bubbler necessitates to be linked to an upstream mass flow controller (MFC), a pressure controller (PC) downstream and to be placed into a water bath, which controls the temperature and consequently the vapour pressure. If the precursors are compressed gases (i.e. hydrides) only a single MFC is required. Such bubblers can be placed in parallel for multielement compounds, alloying and doping enabling a wide range of compositions in the final product. Alongside the conventional CVD equipment, the precursors used in MOCVD are usually pyrophoric, flammable, or toxic and therefore additional equipment for the effluent treatment is often needed and hazards must be carefully assessed. A good example of a custom-built MOCVD system used for the growth of TMDs is schematically reported in Fig. 5(c).

Potential precursors for the MOCVD growth of 2D magnets

The general requirements of MOCVD precursors are: high volatility, high reactivity, stability under atmosphere and possibly low toxicity. However, we can refine these specifications looking at the current state-of-the-art MOCVD growth of TMDs for key parameters and precursors. A key precursor requirement is a low carbon content since it has been shown that organic precursors lead to the deposition of carbonaceous species on the final product. 203,206 This has been partially solved for WSe2 utilising H2Se, which has massively decreased the contamination from carbon and other elements.86 In addition to this, 2D materials growth needs low precursors flowrates (0.01 sccm for metals and 0.4–5 sccm for chalcogens) unlike classic MOCVD of coatings and thin films where the flowrates are orders of magnitude larger. Thus, it is possible to opt for less volatile precursors when advantageous in terms of safety, availability, and ease of handling.

Looking at the classes of 2D magnets we described earlier, they are formed by: metals (Cr, V, Fe, Mn, Bi, Ni, Ta and Nb), chalcogens (S, Se and Te), halogens (Cl, Br and I), Si, Ge and P. For all these elements there are precursors which are used in CVD industry or research that can be employed for the

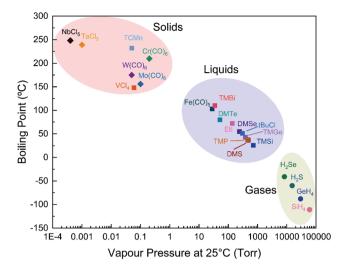


Fig. 6 Physical properties of the proposed precursors for the (MO)CVD growth of 2D magnets. On the upper-left corner the precursors are in the powder form (VCl₄ and TCMn are liquids), in the middle the precursors are liquid and on the lower-right the hydride gases.

growth of 2D magnets. Fig. 6 and Table 2 summarise the physical properties of the proposed precursors.

Cr-Precursors. Cr(CO)₆ is highly volatile and even more than the currently used molybdenum and tungsten carbonyls (vapour pressures at 25 °C in torr: 0.2 Cr(CO)₆, 0.1 Mo(CO)₆ and 0.05 W(CO)₆)²⁰⁷ that have been extensively used for MOCVD of MoX2 and WX2. Furthermore, Cr carbonyl has a high pyrolysis rate at temperatures lower than 500 °C enabling the possibility to grow on temperature sensitive substrates.²⁰⁸ Comparing Cr carbonyl with other Cr-containing commercial MOCVD precursors, it outperforms more complex organochromium molecules in the growth of Cr₂O₃ at 500 °C achieving the highest growth rate with negligible carbon contamination left.209

V-Precursors. In the MOCVD growth of VO2 coatings, a wide range of vanadium precursors has been reported, 210 however the most successful compound in terms of phase selectivity and product purity is vanadyl acetylacetonate (VO(acac)₂), whose volatility matches the requirements for MOCVD and leaves negligible carbon contamination. 211,212 Another molecule that can potentially be used is VCl4 that has the same vapour pressure of tungsten carbonyl at room temperature. This would be advantageous as V is already in the +4 oxidation state and it does not leave carbon contaminations. 210 However HCl would evolve from the reaction with the chalcogen precursors and hence precautions must be taken.

Mn-Precursors. Several organomanganese compounds have been used as dopant source for II-VI semiconductors and in principle can be proposed for the growth of MnBiTe4 and MnPX₃. 213 The most widely used is methylcyclopentadienylmanganese tricarbonyl ((CO)3CH3C5H4Mn, TCMn) despite having the highest cracking temperature of all the class and low volatility. 214,215 As it possesses a vapour pressure comparable to the one of W(CO)₆ (0.05 torr at 25 °C)²¹⁴ at room temperature it may be volatile enough to sustain the growth of atomically-thin materials. Other MOCVD compatible compounds are (C₅H₅)₂Mn, (MeC₅H₄)₂Mn, Me(CO)₅Mn and Et (CO)5Mn, which might be more advantageous than TCMn having lower carbon atoms.

Fe-Precursors. Another element to cover is iron for the synthesis of FePS₃, FePSe₃, and Fe₃GeTe₂. Iron pentacarbonyl (Fe (CO)₅) and ferrocene (FeC₁₀H₁₀) are low in carbon content and they have been established in the MOCVD growth of Fe, FeS2 and Fe₂O₃. ²¹⁶⁻²¹⁸ Iron pentacarbonyl could be better suitable since it has lower carbon content and a lower cracking temperature of 300 °C than ferrocene. 219,220

Ni-Precursors. Similarly, Ni(CO)₄ can potentially be used as Ni-precursor since it has been employed for the growth of Ni thin films at low temperature (175-400 °C), due to its extremely high volatility and low cracking temperature of ~200 °C.221 However, it presents acute toxicity and hence, alternative nickelorganic precursors have also been reported. 222 Nickel pentacene (Ni(C5H5)2) and Ni(dmg)2 (nickel bis(dimethylglyoximate)) proved to be efficient to yield Ni films of high quality with a negligible amount of impurities. 223-225

Bi-Precursors. The perfect example of a Bi-based material to look at is Bi₂Te₃, as it is a vdW crystal and it is widely produced via MOCVD. The typical MOCVD growth is based on the reaction between trimethyl bismuth (TMBi) and an organotelluride that can be diethyl telluride (DETe) or di-isopropyl telluride (DiPTe) at the moderate temperature of ~450 °C. 226-228 Most of the Bi₂Te₃ produced is in the form of films of hundreds of nm in thickness using precursors flowrate several order of magnitudes larger than values reported for TMDs. Bi₂Te₃ in the monolayer or few-layered form has not been reported yet.

Nb-Ta-precursors. Several organometallic compounds are widely used for the growth of Nb and Ta nitrides and oxides, (such Ta(NCMe₃)(NEtMe)₃ or $Nb(N^{t}Bu)(NMe_{2})\{C$ (NⁱPr)₂(NMe₂)₂) however these are large molecules with a high number of carbon atoms and functional groups. 229-233 Therefore, precursors more suitable for the growth of 2D NbX₂ and TaX2 could be carbon-free molecules such as NbCl5 and TaCl₅. These two precursors both possess high vapour pressures234 and have already been used for the growth of atomically-thin sulphides by reaction with sulphur powder at high temperature. 235-237 Additionally, a solid example of the use of NbCl₅ in MOCVD has been reported by Kozhakhmetov et al. where few layered 3R-NbS2 was obtained using gaseous H2S and H2 as carrier gas.182

S, Se, Te-precursors. Chalcogen precursors for 2D materials have been extensively explored in MOCVD of group VI sulphides and selenides. The most used one are organochalcogens, which are formed by two alkyl tails of length ranging from one to three carbon atoms bonded with a chalcogen atom. In particular diethyl sulphide (DES) has been used in almost all of the MOCVD reports of MoS2 and WS2 achieving full coverage of monolayers on both sapphire and amorphous silica, showing good optical and electronic transport properties despite the submicrometric grain size. 87,238 It is poss-

Table 2 Vapour pressure laws, melting and boiling point of potential precursors

Precursor	Melting point (°C)	Boiling point (°C)	$Log(P_{vapour}, torr)$
Group V			
VCl_4	-25	148	0.06 at 298 K (ref. 265)
NbCl ₅	205	248	$17.263-4732/T - 0.7912\ln(T) - 29263/T^2$ (ref. 234)
TaCl ₅	216	239	$21.199-4831/T - 1.399\ln(T) - 7648/T^2$ (ref. 234)
Group VI			
$Cr(CO)_6$	90	210	$11.475 - 3622.9/T^{207}$
$Mo(CO)_6$	150	156	$11.7274 - 3788.3/T^{207}$
$W(CO)_6$	170	175	$10.947 - 3640.4/T^{207}$
Group VII			
TCMn	-1	232	0.05 at 298 K (ref. 266)
Group VIII			,
Fe(CO) ₅	-21	103	$8.073-1960.869/(T-0.228)^{267}$
$Fe(C_5H_5)_2$	173	249	,
Group X			
Ni(CO) ₄	-17	43	$7.512-1409.037/(T-11.637)^{267}$
$Ni(C_5H_5)_2$	171		$7.512-1409.037/(T-11.637)^{267} $ $2.124-3651.114/T^{268}$
Group XIV			
SiH ₄	-185	-112	$7.097 - 703.987/(T + 5.352)^{267}$
TMSi	-99	26	$6.852 - 1047.272/(T - 36.057)^{269}$
SiCl ₄	-69	58	$7.704-1616.546/(T+5.305)^{270}$
GeH ₄	-165	-88	$6.981-736.692/(T-4.665)^{267}$
TMGe	-88	43	$6.986-1166.492/(T-33.005)^{267}$
GeCl ₄	-50	87	$6.557 - 1080.101/(T - 63.588)^{267}$
Group XV	30	07	0.557 1000.101/(1 05.500)
P (red)		590 (sublimates)	$7.917 - 2819.239/(T + 6.399)^{267}$
PH ₃	-133	-88	$6.9-702.651/(T-11.065)^{267}$
TMP	-86	38	$7.7329-1512/T^{257}$
TEP	-80	127	$7.86 - 2000/T^{257}$
TMBi	-86	110	$6.984-1388.9/(T-42.374)^{271}$
Group XVI	-80	110	$0.904 \ 1300.9/(1-42.574)$
S S	115	445	$91.489 - 8170/T - 12.61 \ln(T) + 0.0035 T^{272}$
H_2S	-82	-60	$7.403-958.587/(T-0.539)^{267}$
DMS	-98	36	$7.403 - 338.387/(1 - 0.339)$ $7.162 - 1201.134/(T - 29.906)^{273}$
DES	-98 -104	92	$7.102 - 1201.134/(1 - 29.900)$ $7.541 - 1560.523/(T - 26.557)^{267}$
Se	221	685	$8.0886-4989/T^{274}$
H ₂ Se	-66 07	-41	$6.492 - 596.484(T - 66.353)^{267}$
DMSe	-87	55	$7.696-1665.9/T^{275}$
DMSe ₂	450	156	$13.585 - 3912.8/T^{275}$
Te	450	988	$7.5999-5906.2/T^{274}$
DMTe	-10	82	$7.97 - 1865/T^{257}$
DETe		137	$7.99-2093/T^{257}$
DiPTe		49	$8.288-2309/T^{276}$
Group XVII	9.5		7 400 4004 040//W - :>267
tBuCl	-26	51	$7.129 - 1281.242/(T - 21.795)^{267}$
nHexCl	-94	133	$6.769-1304.968/(T-73.092)^{277}$
EtI	-111	72	$6.96-1247.135/(T-39.612)^{267}$

ible to use dimethyl sulfide to reduce the carbon incorporation as shown by Shinde et al. however its extremely high volatility may reduce the flowrate control. 180 Di-tert-butyl sulphide has also been reported as precursor for MoS2, however the high number of carbon atoms resulted in carbon contamination specifically at high pressure and temperature. 239,240 Analogously, dimethyl selenide (DMSe) proved to be a suitable precursor for MoSe₂ and WSe₂ owing to its lower volatility compared to DMS and therefore easier to control.241,242 In order to prevent the carbon contamination, it is possible to switch to hydrides (H₂S and H₂Se), however these compounds are extremely toxic and it might be challenging their use in university research laboratories, posing also concerns over the scalability of the synthesis. 203,206 As no atomically-thin telluride has been reported via MOCVD yet, therefore to propose a suitable precursor for future synthesis of binary and ternary

magnetic telluride we have to look at the production of nonlayered semiconductors. The perfect example is the epitaxial growth of HgCdTe, a small band gap semiconductor used for infra-red detection. This material is the result of a solid solution between HgTe and CdTe, whose bandgap can be tuned by varying the Hg/Cd ratio during growth.243 Such a fine tuning has been achieved via MOCVD adjusting the flowrates of mercury vapours and dimethyl cadmium (DMCd) using GaAs, Si or sapphire as epitaxial substrates.²⁴⁴ The metal precursors react with dimethyl telluride (DMTe) and hydrogen to form Hg_xCd_{1-x} Te at a temperature of 400 °C, which is much lower than the temperatures used for liquid phase growth techniques.²⁴⁵ Similarly, CdZnTe can be grown using similar precursors and temperature starting from diethylzinc (DEZn).246 Interestingly, the low growth temperature allows to control the rate limiting step of the process, since at T < 430 °C the reac-

tion is kinetically-driven and the activation energy determines the final composition whereas for higher temperature the limiting step is the mass transport and the diffusivity of each element.247

Si-Ge precursors. Similarly to chalcogens, silicon and germanium hydrides are established gaseous carbon-free precursors. In fact, SiH4 and GeH4 are both used for epitaxial growth of Si and Ge films and Si-doping of GaAs and they possess moderate cracking temperature in presence of H2 as carrier gas (~600 °C for GeH₄). ^{248–252} However, they are both pyrophoric and extremely toxic. Both tetramethyl silane and germane have been reported as suitable MOCVD precursors being highly volatile and much less toxic than hydrides. 253-255 Furthermore, SiCl₄ and GeCl₄ have low toxicity and they are C-free precursors often used in epitaxial growth of Ge, GeO₂ and SiO₂ growth. 255,256

P-Precursors. For the growth of metal phosphochalcogenides, we listed the potential precursors for metals, sulphur and selenium, therefore we discuss possible precursors for P, proposing alternatives to the extremely toxic phosphine gas (PH₃). Trimethyl and triethyl phosphine ((CH₃)₃P TMP, (CH₃CH₂)₃P TEP), are highly volatile at room temperature (VP: 493 torr for TMP, 15 torr for TEP) and their toxicity level is lower than the phosphine one, thus they could be available option.²⁵⁷ Their use has already been tested in the MOCVD growth of InP and as P-dopants sources in n-type diamond, without any difference in quality compared to the use of PH₃. ²⁵⁸⁻²⁶¹

Halogen precursors. Very few precursors are reported in the literature since most of the metal halides are synthesized via CVT where gaseous chlorine, iodine and bromine are used. Potential Cl precursors were tested by Barrioz et al. in the MOCVD growth of CdCl2 on CdTe films, tert-butyl chloride (tBuCl) and n-hexyil chloride (n-HexCl) reacted with DMCd at temperatures ranging from 350 to 450 °C.262 The best result was achieved with tBuCl at 400 °C since n-HexCl did not efficiently crack at the explored temperatures. Similarly, the only iodine MOCVD precursor reported in the literature is iodoethane (CH3CH2I, ethyl iodide), which has a vapour pressure of 100 torr at room temperature and it has been employed as I-dopant source for ZnS and Cu films. 263,264 Unfortunately, bromine is yet to be reported as element in a CVD process, therefore, in analogy with the I-precursor, we propose bromoethane as potential precursor. Alternatively, it may be possible to use halogen gases directly in the MOCVD process analogously to oxygen and hydrogen, widely used as reagents or reducing/oxidant agents.

The role of the growth substrate

The substrate choice is a fundamental parameter in the CVD process since crystal structure, morphology and high temperature stability of the substrate material directly influence the growth kinetics. These aspects have been extensively discussed in recent reviews. 179,278,279 For 2D materials in particular, the interactions between film and substrate determine not only

the morphology of the grown layer but also nuclei density, optical properties, strain and crystal phase. We can divide the substrates into chemically inert versus chemically reactive. The most prominent example of this second category is Cu for the growth of graphene that acts as a catalyst for methane cracking reaction combined with the poor C solubility. 280 Similarly, h-BN growth is catalysed by iron that additionally acts as nitrogen reservoir when preannealed with ammonia, enabling in this way full coverage. 281,282 Au foil plays a similar role for TMDs where the limited solubility of chalcogens confines the growth to the first layer resulting in large area monolayers. 283-285

Regarding chemically inert substrates, the most used one is SiO₂/Si as it is inexpensive and technologically relevant for electronic devices and it enables a stark optical contrast between the flakes and the substrate. Numerous examples of large isolated TMDs flakes have been reported in the literature using powder CVD, 290,291 whereas full coverage has been achieved via MOCVD.87,180 However, the roughness of the silica combined with the difference in thermal expansion coefficient compared with TMDs induces in the flake a consistent strain, which is detrimental for the optical properties of the grown material. 292,293 Moreover, the orientation of the flakes is completely random and therefore when coalescing the film presents a high concentration of grain boundaries, which is detrimental for the charge carrier mobilities. Substituting amorphous SiO2 with crystalline substrates, such as sapphire, h-BN (Fig. 7(a)) or SrTiO₃, it is possible to govern the domain orientation and minimise the antiphase boundaries. 202,294,295 Additionally the vdW surface of 2D materials prevents the bonding between the film and the substrate avoiding possible lattice mismatches and therefore the presence of strain. It is also possible to engineer the nucleation via spincoating organic compounds (perylene-3,4,9,10-tetracarboxylic acid tetrapotassium salt, PTAS the most common)287 that lower the nucleation energy barrier and act as nucleation promoters, as reported in Fig. 7(c and d). In this way, it has been demonstrated the possibility of CVD of MoS₂ over large area at a lower temperature ~650 °C compared to conventional powder CVD. 296 The substrate crystal lattice can also be used to select the phase of 2D materials in case of polymorphism. A notable example is the lattice restructuring of orthorhombic SnS into 1T-SnS2 onto monolayer WS2 that act as templating substrate and that has the advantage of a dangling bond-free and clean interface as represented in Fig. 7(b) ²⁸⁶ Similarly, 2D γ-InSe can be grown selectively from other layered stoichiometries and phases by vapor transport starting from InSe powder.²⁹⁷ Applying a moderate temperature gradient (500-600 °C) on the template substrate, which is mechanically exfoliated ε-GaSe, the separation of the desired γ-InSe in the coldest zone and the In₂Se₃ polytypes in the hottest one is achieved. Another notable example is the growth of the non-vdW ferromagnetic Cr₂S₃, because Cr exists also in +3 oxidation state and it forms rhombohedral Cr₂S₃ as well as 1T-CrS₂.^{298,299} In particular, the former was achieved by using atomically smooth fluorophlogopite mica since SiO2 yielded mixed phases and an irregular morphology. 300,301

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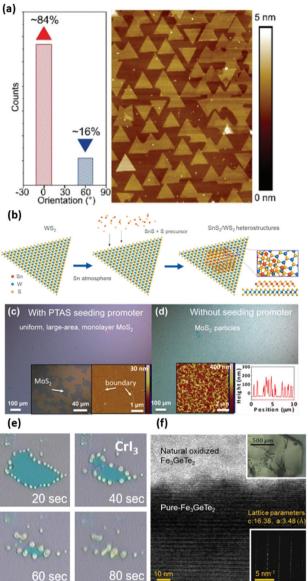


Fig. 7 Substrate and environment influence on 2D materials. (a) Atomic force microscopy (AFM) map of highly-oriented WSe2 grown via MOCVD on h-BN and relative orientation count.²⁰² Reproduced with permission from ref. 202. Copyright 2019 American Chemical Society. (b) Schematic that shows a WS2 flake that templates the growth of layered SnS₂ from SnS and S precursors. ²⁸⁶ Reproduced with permission from ref. 286. Copyright 2019 American Chemical Society. (c and d) Optical images and AFM maps of MoS₂ crystals grown with and without the nucleation promoter PTAS.²⁸⁷ Reproduced with permission from ref. 287. Copyright 2014 American Chemical Society. (e) Extremely fast degradation of fewlayered CrI₃ under atmosphere and focused light.²⁸⁸ Reproduced with permission from ref. 288. Copyright 2018 American Chemical Society. (f) HRTEM micrograph that reports the visibly thick oxide layer on multilayer Fe₃GeTe₂. ²⁸⁹ Reproduced with permission from ref. 289. Copyright 2019 IOP Publishing.

Encapsulation of 2D magnetic materials

A shared issue for the whole 2D materials is the degradation under atmosphere via reaction with oxygen and moisture.302

Oxidation in atomically thin crystals has been demonstrated to be extremely detrimental for optical and electronic properties and poses an additional challenge for the future device integration. 303-305 2D tellurides (MoTe₂ and WTe₂) are particularly sensitive to the environmental conditions where Te converts into Te oxides after few hours after the synthesis. 306-308 Similar phenomena has also been observed in 2D magnetically active tellurides CrSi(Ge)Te3 309 and Fe3GeTe2, whose oxidation led to poorer magnetic properties in a multilayer sample (Fig. 7(f)).²⁸⁹ CrI₃ undergoes an even more severe degradation process, which is catalysed by ambient light and dissolves exfoliated crystals in a few minutes as seen in Fig. 7(e). 288 Several possible strategies to overcome this important limitations have been proposed, such as coating with polymers or encapsulating with air-stable thin films. 310 The encapsulation with h-BN layers has proved to be a successful strategy for protecting 2D materials, which also enables to improve charge carrier mobilities³¹¹ and light emission properties in MoS₂.^{312,313} Regarding the synthesis of h-BN, several MOCVD papers have reported the large-scale growth of mono- and fewlayers over different metallic and inert substrates. 314-317 Therefore, after the first growth of the desired 2D magnet it may be possible to directly deposit a protective layer of h-BN by switching precursors and parameters in the same reactor. Additionally, the use of glove boxes connected with the MOCVD chamber would enable to preserve air and moisture sensitive material and to deposit protective capping layer of different nature using different deposition techniques.

Conclusions and outlook

van der Waals materials with magnetic ordering holds tremendous interest for fundamental physics investigation and novel device fabrication. Progress has been made in the understanding of their fundamental properties and device demonstration is at the early stages. We have described how pioneering work have been based on exfoliated materials to understand magnetism and spin dynamics in 2D. We have emphasised how materials grown in mono and few-layered form extended over large areas will not only allow the systematic study of their properties but will also enable the direct integration in van der Waals heterostructures for the fabrication of functional devices. The integration of 2D magnets grown by CVD in functional spintronics heterostructures can be foreseen to serve to the emerging field of spintronics circuits. As the use of CVD synthesis has revolutionised the investigation of graphene, similarly MOCVD is enabling the advancement of 2D TMDs devices. We envision that the wide range of 2D magnets can also see a similar progress once MOCVD enables the achievement of large area atomically thin films. Here we have reviewed the state of the art of the synthesis of metal halides, binary and ternary metal tellurides, doped TMDs, and metal phosphochalcogenides. We have highlighted that CVT is the predominant available synthesis route, which leads to the formation of high-quality bulk crystals that then require to be microme-

chanically exfoliated to be studied in the atomically thin form. The only 2D magnetic materials that have been CVD grown in the atomically thin form are V and Cr-based TMDs as well as doped-TMDs. We have then identified potential precursors for the main classes of 2D magnetic materials, and we have critically discussed their suitability for the MOCVD synthesis on the bases of their physical properties, research and industrial usage and safety. In specific, the precursor volatility is critical as highly volatile compounds enable an efficient supply with robust control. More efforts in this synthesis technique will be required to see the field moving towards the construction of different device architecture and materials assembly to explore the potential of spintronic circuits. We believe that the establishment of a new platform for vdW atomically thin and magnetically ordered materials synthesis will provide exciting opportunities for future data storage and communication devices.

Conflicts of interest

The authors declare no conflicts of interest.

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