REVIEW

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Van der Waals integration of artificial heterostructures and high-order superlattices

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Abstract: The recent blossom in 2D atomic crystals (2DACs) has ignited intense interest in a new type of bond-free van der Waals heterostructures (vdWHs), in which distinct material components are physically brought together within a vdW distance and held together by weak vdW interactions. Without direct chemical bonding between the constituent materials, the vdWHs negate the lattice matching requirements in typical epitaxially bonded heterostructures. Here we briefly summarize the key advances in the construction and fundamental investigation of versatile vdWHs from diverse 2DACs and beyond, and highlight a unique class of vdW superlattices (vdWSLs) consisting of alternating 2D atomic layers and/or self-assembled molecular layers, with tailored structural symmetry, electronic band modulation, interlayer coupling, and chirality. Lastly, we conclude with a brief outlook on the opportunities in exploring such artificial materials to unlock previously inaccessible physical limits and enable new device concepts beyond the reach of the existing materials.

Keywords: van der Waals, integration, heterostructures, high-order, superlattices

The construction of heterostructures and superlattices with spatially modulated chemical compositions and electronic structures is essential for tailoring and controlling the charge transport in solid-state materials and creating novel electronic and optoelectronic functions. The traditional heterostructures are often produced using high-temperature crystal growth and sequential epitaxial processes (e.g., molecular beam epitaxy (MBE), metal organic chemical vapor deposition (MOCVD)), with extensive bond breaking and structural reorganization to form the constituent materials and atom-to-atom covalent bonds to join them together. Thus, the achievable heterostructures are fundamentally dictated by thermodynamics [1] and generally limited to materials that meet strict lattice matching and processing compatibility requirements. A minute lattice mismatch could result in considerable interfacial defects and strain, which may propagate beyond the interface to form extensive dislocations, and in some cases, generate entirely disordered interfacial layers [2–5], thus fundamentally deviating from the designed heterostructure interfaces. As a result, high-quality epitaxial heterostructures or superlattices can only form between materials with nearly identical lattice structures and thus similar electronic properties. Materials with substantially different lattice structures can hardly be epitaxially grown together without generating too serious interfacial disorders to fundamentally alter/degrade their intrinsic electronic properties.

The recent blossom in 2D atomic crystals (2DACs) has ignited intense interest in a new type of bond-free van der Waals heterostructures (vdWHs), in which distinct material components are physically brought together within a vdW distance and held together by weak vdW interactions (Figure 1A) [6–21]. Without direct chemical bonding between the constituent materials, the vdWHs negate the lattice matching requirements in typical epitaxially bonded heterostructures. Additionally, the vdW integration process is typically conducted at or near room temperature without direct chemical processing on the existing materials, offering a low-energy approach for damage-free integration of highly distinct materials beyond thermodynamic limits in high temperature epitaxial growth. The weak vdW interactions largely preserve the pristine atomic structure and intrinsic electronic properties of the constituent materials after integration. It can thus enable a new generation of artificial heterojunctions with deterministic control of atomically clean and electronically sharp interfaces by design, unlocking previously inaccessible physical limits and enabling devices with superior performance or unprecedented functions.

The vdW integration process is particularly versatile for constructing diverse heterostructures from 2DACs. The 2DACs, as represented by graphene or MoS_2, consist of a large family of layered materials with covalently bonded atomic layers weakly held together by vdW interactions, and can be readily isolated into single- or few-atom thick membranes. Most notably, these atomic membranes feature a dangling bond free surface and thus few intrinsic surface traps, ensuring excellent electronic properties even at the ultimate single-atom thickness limit. Thus, a simple physical assembly of different atomic layers can lead to high-quality trapping free heterostructure interfaces that rival the highest-quality lattice-matched heterostructures obtained through sophisticated epitaxial growth processes. Without direct chemical bonding or chemical

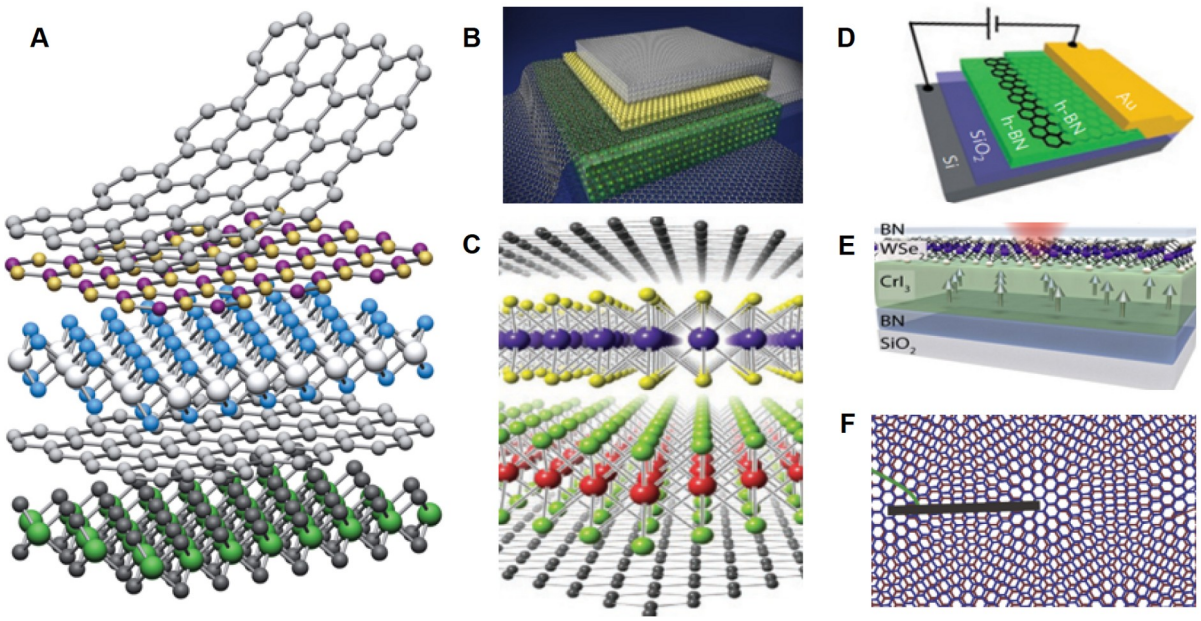

Figure 1 2D vdWHs. (A) Building vdWHs with various 2D materials. From top to bottom: graphene, hBN, MoS_2, WSe_2 and fluorographene. Adapted with permission from ref. [18]. (B) vdW complementary inverters. From top to bottom: Ti, MoS_2, graphene, $Bi_2Sr_2Co_2O_8$, graphene. Adapted with permission from ref. [17]. (C) Atomically thin vdW p-n junctions. From top to bottom: graphene, MoS_2, WSe_2 and graphene. Adapted with permission from ref. [23]. (D) vdW plasmonic device. Adapted with permission from ref. [25]. (E) vdW spintronic device. Adapted with permission from ref. [26]. (F) Twisted bilayer graphene with Moiré pattern. Adapted with permission from ref. [32].

processing on existing materials, this approach opens vast flexibility to arbitrarily combine highly distinct 2D atomic layers with radically different compositions or electronic structures, allowing to create a wide range of artificial heterostructures [18,19,21]. With this approach, a wide range of 2D atomic layers with distinct physical properties (e.g., metal, semiconductor, insulator, Weyl semimetal, topological insulator, superconductor, or ferromagnet) may be nearly arbitrarily mixed, paired and assembled together to form an essentially infinite combination of artificial heterostructures with designable electronic band offsets, providing an unprecedented playground for condensed matter physics and novel device concepts, including vertical tunneling transistors [16], vertical field-effect transistors [9] and logic integration (Figure 1B) [17], gate tunable photodiode [22], vertical p-n diodes (Figure 1C) [23,24], plasmonic devices (Figure 1D) [25], and 2D ferromagnet tunneling junctions (Figure 1E) [26–28]. Recently, other emerging vdW electronics were also developed, including sub-nm channel length field effect transistor [29], 2D/2D spin-orbit torque device [30], and magnetic Josephson junctions [31]. Additionally, the bond-free nature of the vdWHs also opens an additional twisting degree of freedom to further tailoring the interlayer electronic coupling and potential landscape, which creates a totally new material platform for exploring exotic quantum physics including unconventional superconductivity in magic angle graphene bilayers (Figure 1F) [32,33] and Moiré excitons in twisted (hetero-)bilayers of transition metal dichalcogenides [34–37].

Although the vdW heterostructures are mostly known and popularized within the 2D material community, the vdW interaction is a universal intermolecular force between any two objects when they are placed close enough. Thus, the vdW integration, in which prefabricated material/device components are physically laminated within a vdW distance, is in principle not limited to only 2D materials, but expandable to virtually all materials systems, including traditional 3D materials and particularly various nanoscale materials [11,13]. The ability to exploit vdW interactions to integrate traditional 3D materials with 2DACs and form atomically clean 2D/3D vdWHs is critical for capturing the merit of 2D materials in functional devices (Figure 2A and 2B) [10,20,38].

For example, 2D semiconductors have been widely speculated for continued transistor scaling for their superior electronic properties in the atomically thin body. However, conventional electronic manufacturing processes, including lithography, vacuum deposition, and plasma etching processes usually involve aggressive chemical processes and can induce undesired structural defects in the atomically thin 2D materials, seriously degrading their electronic properties [39–41]. To fully exploit the potential of the 2D atomic lattices in functional devices, it is essential to retain the pristine contact interfaces and dielectric interfaces with minimum interfacial trapping states. Indeed, even before 2D vdWHs became popular, the now widely adopted "transfer-and-lamination" process was used to directly integrate pre-synthesized 3D dielectric structures on graphene by exploiting weak vdW force [6–8,10–12,14]. This simple physical transfer process has enabled high-quality dielectric integration without damaging the delicate 2D crystals, thus achieving atomically clean interface without integration induced degradation to realize the highest mobility top-gated transistors (Figure 2C) [6]. This approach was further extended for the integration of the entire gate-stack (including gate dielectrics and gate electrodes) on graphene to produce the fastest graphene transistors with intrinsic cutoff frequency >400 GHz (Figure 2A) [10,15]. Similarly, this approach was also applied in damage-free gate integration on 2D semiconductors such as MoS_2 to enable nearly ideal transistor characteristics with a maximum oscillation frequency up to 50 GHz [42]. Further, vdW integration of a AgI superionic solids with 2D materials allows to use a superionic gate to induce programable ionic doping and a

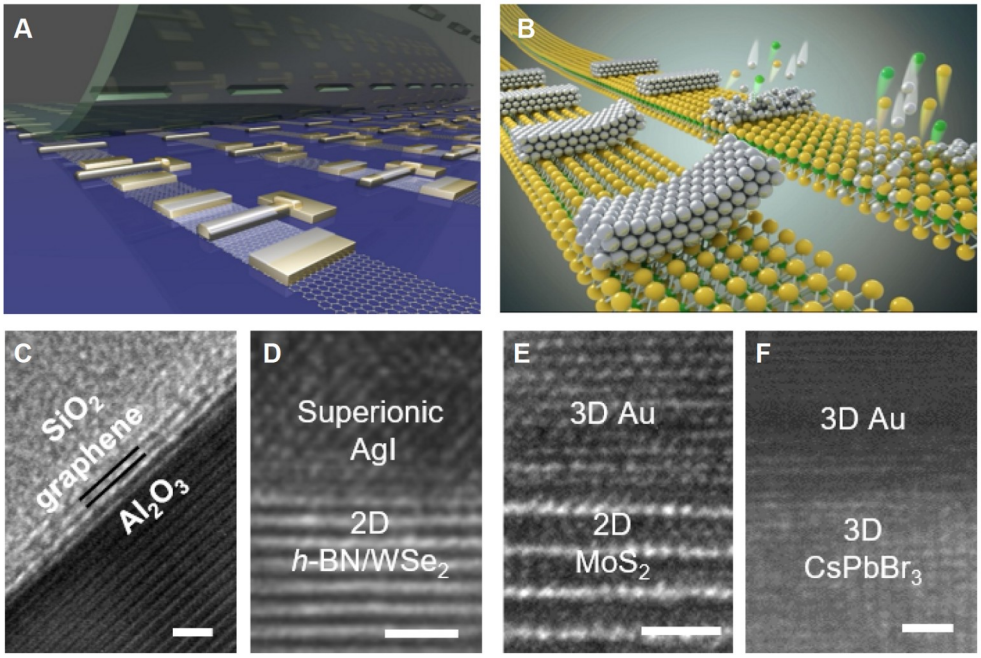

Figure 2 vdWHs beyond 2D materials. (A) Scalable fabrication of graphene high-speed transistor arrays with transferred gates. Adapted with permission from ref. [15]. (B) vdW metal contacts on 2D materials. Adapted with permission from ref. [20]. (C)–(F) Cross-sectional transmission electron microscopy images of the interfaces between bond-free van der Waals-integrated Al_2O_3/graphene ((C) adapted with permission from ref. [6]); AgI/h-BN/WSe_2 ((D) adapted with permission from ref. [43]); Au/MoS_2 ((E) adapted with permission from ref. [20]); Au/$CsPbBr_3$ ((F) adapted with permission from ref. [48]); Scale bars: 1 nm.

unique delible electronics for electronic security (Figure 2D) [43].

Beyond the passive dielectric interface where there is no charge injection across the interface, the vdW integration approach can also be used to create active metal/semiconductor junctions for efficient charge injection. Recently, this physical "transfer-and-lamination" approach was used to integrate lithographically defined metal thin film electrodes on 2D semiconductors to produce nearly ideal metal-semiconductor junctions with atomically clean vdW interfaces free of Fermi level pinning effects, allowing to experimentally achieve the Schottky-Mott limit that has been difficult to realize in conventional metal-semiconductor diodes due to unavoidable interfacial disordering and Fermi level pinning effect (Figure 2E) [20]. Taking a step further, such metal/2D vdW contacts were more recently used to construct high-performance photodiodes from 2D semiconductors with minimal contact interfacial disorder, minimizing the Shockley-Read-Hall recombination and achieving nearly ideal intrinsic excitonic photophysics dictated quantum efficiency [44]. Similar approaches have also been used to create metal/2D Schottky diode with designed barrier height for creating high performance metal-semiconductor field-effect transistors (MESFET) with ultralow subthreshold swing [45].

Besides 2D/3D vdW heterostructures, the assembly of 3D/3D vdWHs could also enable exciting opportunities. For example, the damage-free vdW contacts developed for 2D materials are also applicable for the delicate 3D materials, such as lead halide perovskites (LHPs). The LHPs have emerged as an exciting optoelectronic material, but are extremely delicate and can be easily degraded during the conventional lithography or metal deposition processes, resulting in excessive contact resistance that seriously plague the

intrinsic electrical transport studies [46,47] and compromise the relevant device functions. In this case, vdW integration of metal thin film contacts avoids any solvent treatment or direct metal deposition process on delicate LHPs, thus minimizing interfacial disordering to realize high-performance contacts (Figure 2F) [48,49], enabling a systematic study down to cryogenic temperature, and revealing a record-high carrier mobility exceeding 2000 $cm^2/(V\ s)$, an ultralow bimolecular recombination rate, a quantum interference-induced weak localization behavior, as well as key signatures of ferroelectric large polarons, which have been previously difficult to probe in LHPs due to the rapidly degrading contacts at cryogenic temperatures. The vdW contacts has been applied to the self-assembled molecular monolayers as well [50–52], which avoids deposition induced damages to delicate molecules and ensures intrinsic charge transport across the junction, and also serves as an encapsulation layer for the stable operation of the device. Examples of utilizing vdW integration on bulk materials can also be found in the Pt/β-Ga_2O_3 interface where a designed barrier height was used to ensure high performance rectifiers for MESFET [53], highlighting the generality of vdW contacts for creating artificial heterostructures with designable electronic interfaces. Additionally, recent experiment has shown one-step simultaneous vdW integration of both high-k dielectrics and contacts to enable high performance top-gated transistors on delicate emerging materials [54].

Taking a step further, the vdW interactions can also be used for creating vdW superlattices (vdWSLs) integrating radically different materials in high-order superstructures [55]. The bond-free vdW interactions between the neighboring constituent layers offer a natural mechanism for interfacial strain relaxation, allowing to retain nearly perfect crystalline structure within each layer regardless of the structure differences between layers. This is in stark contrast to conventional epitaxial superlattices, where a slight lattice mismatch could lead to extensive dislocations [5]. The flexibility to integrate radically different materials could enable a new generation of artificial materials with tailored electronic, magnetic or topological properties.

However, it is of considerable challenge to explore sequential "transfer-and-lamination" approach to construct high-order vdWSLs, due to the limited yield associated with each step. To efficiently produce high-order superstructure thus requires the development of new self-assembly strategies. To this end, a capillary-force-driven rolling-up process was recently used to delaminate synthetic 2D vdWHs from the growth substrate and produce roll-up structure with alternating monolayers, thus forming high-order vdWSLs (Figure 3A–3D) [56]. This strategy can be extended for creating diverse 2D/2D vdWSLs, more complex 2D/2D/2D vdWSLs (Figure 3E), and beyond-2D materials, including 3D thin-film materials and 1D nanowires, to generate mixed-dimensional vdWSLs.

Alternatively, an artificial vdW superlattice can also be prepared by intercalate selected molecular species into bulk layer crystals, creating a new class of hybrid superlattices consisting of alternating crystalline atomic layers and self-assembled molecular layers. For example, it has been shown that the electrochemical intercalation of black phosphorus (BP) generates a unique monolayer phosphorene molecular superlattices with atomic precise integration of highly distinct atomic crystals and molecular layers (Figure 3F and 3G) [57]. With the organic molecular layers sandwiched in between BP atomic layers, the BP layers are spatially separated and electronically decoupled with each other, thus producing a unique bulk monolayer material: a 3D material in bulk format but with monolayer physical characteristics. Such artificial vdWSLs can be expanded to a wide range of 2D host materials and designable intercalants with different electronic band offsets or structural symmetry [58–60], opening up vast possibilities for creating a rich library of artificial materials with widely variable chemical compositions, structural motifs and electronic functions. For ex-

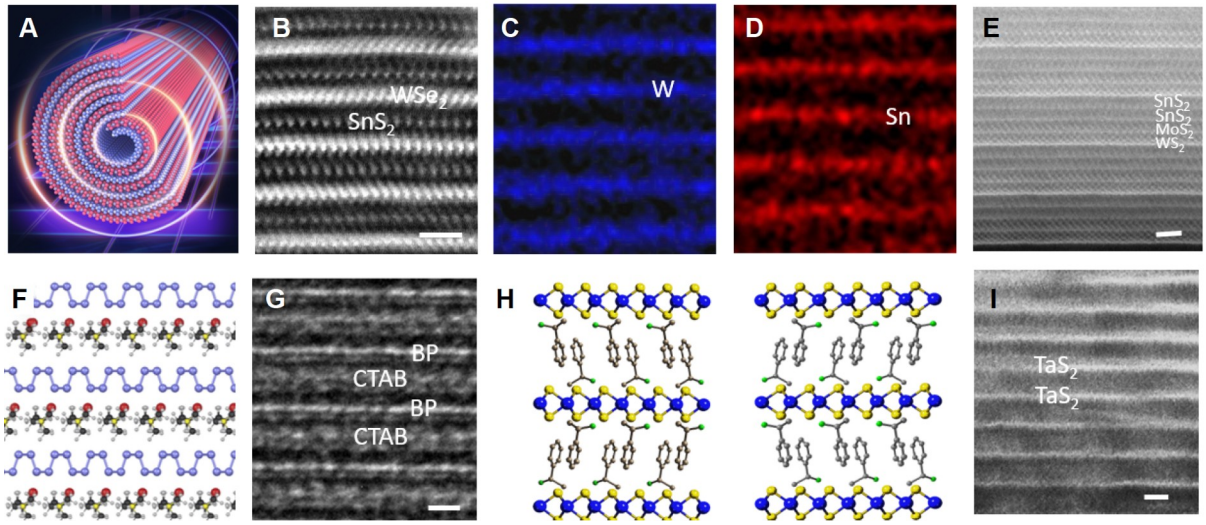

Figure 3 vdWSLs. (A) Schematic illustration of the roll-up vdWSLs. (B) Cross-sectional transmission electron microscopy image of the interfaces in SnS_2/WSe_2 superlattices. Corresponding EDS mapping images for W (C) and Sn (D). (E) Cross-sectional transmission electron microscopy image of the interfaces between $SnS_2/MoS_2/WS_2$. (B)–(E) Adapted with permission from ref. [56]. (F) Schematic illustration of higher-order organic/inorganic hybrid vdW superlattice created by electrochemical intercalation. (G) Cross-sectional transmission electron microscopy image of the interfaces between BP/CTAB. Adapted with permission from ref. [57]. (H) Schematic illustration of the chiral molecule intercalated vdW superlattices. (I) Cross-sectional transmission electron microscopy image of the chiral molecule intercalated TaS_2 superlattice. Adapted with permission from ref. [28]. Scale bars: 1 nm.

ample, the intercalation of chiral molecules into selected 2DACs has enabled a family of chiral molecular intercalation superlattices as the artificial chiral solids that show robust chiral-induced spin selectivity (Figure 3H and 3I) [28].

The vdWSLs provide an unprecedented flexibility for integrating distinct atomic layers without restrictions set by traditional chemical integrations, creating an entirely new generation of artificial superlattices with kinetic rather than thermodynamic stability. It could enable a new class of artificial quantum solids with elaborated modulation of chemical compositions, electronic band offsets, interlayer coupling, dimensionality, inversion or time-reversal symmetry, chirality, topology, spin degeneracies or valley degeneracies by design, with an atomic scale integration of distinct physical properties. The integration of the well-ordered atomic or molecular layers into the solid-state superlattices could open up the exciting opportunities to exploit highly versatile molecular design strategies to tailor solid-state materials and create a new platform of artificial quantum solids for exploring emergent physical phenomena.

Beyond the methods discussed above, chemical vapor deposition (CVD) has been widely explored for the scalable synthesis of vdWHs and vdWSLs [61,62]. However, the CVD growth typically requires high synthesis temperature, and thus with limited material and substrate choices (e.g., not readily applicable for hetero-integrating organic molecular layers and crystalline atomic layers). It is often difficult to achieve high-order superlattices since the requirement of repeated switch between different synthetic conditions could damage the delicate monolayer materials [63,64].

Despite the exciting opportunities vdW integration offer, there are considerable challenges. For example, for the “transfer-and-lamination” approach, although it is most popular among 2D/2D systems and has also been recently successfully expanded to many 3D/2D structures for scientific research, examples of utilizing it

on traditional 3D semiconductors (e.g., GaAs, Ge and Si) are still quite limited. Further exploiting its applicability on traditional 3D material system could greatly expand its technological potential. For high-order vdWSLs, although the out-of-plane modulation has been well characterized and features highly ordered structures (e.g., sharp peak in the XRD patterns), the in-plane structures are less studied. For example, in the hybrid superlattice, the in-plane molecular structure, ordering and its exact coupling with 2D host lattice is largely unexplored at this moment. Due to the presence of wrinkle, air bubble, molecular domains, etc., in-plane structures may be less ordered. Therefore, more studies on the in-plane geometry and their impact on the fundamental physical properties of the hybrid superlattices are required for further development of vdWSLs to couple the in-plane functions among distinct layers.

Together, the bond-free vdW integration offers vast flexibility for damage-free integration of highly distinct materials beyond the thermodynamic limits of traditional epitaxial growth. It can enable a new generation of artificial heterostructures and superlattices with essentially arbitrary modulation of chemical compositions and electronic structures by design. Such unprecedented flexibility defines a rich library of artificial materials and provides a versatile material platform for exploring intricate electronic and spin interactions across the highly tunable heterostructure interfaces, for controlling the generation, confinement, and modulation of charge, exciton, and spin states at the limit of single-atom thickness and across the alternating layers, and for tailoring the electronic structure, ferroelectricity, ferromagnetism, and superconductivity at such atomic interfaces. It could seed transformative advances across diverse areas ranging from traditional electronics, optoelectronics to the emerging areas of spintronics and quantum information science. Considering the rich electronic functions generated from a few limited semiconductor heterostructures and superlattices in today's semiconductor industry, the opportunities that may be brought by such highly versatile vdWHs and vdWSLs with nearly infinite variations seem boundless. It could open a new field of artificial solids for exploring emerging physical phenomena, new device concepts and unprecedented technological opportunities.

Author contributions

X.D. conceived the concept. Q.Q., Z.W. and X.D. wrote the manuscript.

Conflict of interest

The authors declare no conflict of interest.

References

1 Arthur JR. Molecular beam epitaxy of compound semiconductors. *Surf Sci* 1994; **299-300**: 818–823.

2 Matthews JW, Blakeslee AE. Defects in epitaxial multilayers. *J Cryst Growth* 1974, **27**: 118-125.

3 Vallet M, Claveau Y, Warot-Fonrose B, *et al.* Highly strained AlAs-type interfaces in InAs/AlSb heterostructures. *Appl Phys Lett* 2016; **108**: 211908.

4 Niehle M, Rodriguez JB, Cerutti L, *et al.* On the origin of threading dislocations during epitaxial growth of III-Sb on Si (001): A comprehensive transmission electron tomography and microscopy study. *Acta Mater* 2018; **143**: 121–129.

5 Ni Y, Zhou D, Chen Z, *et al.* Influence of the carbon-doping location on the material and electrical properties of a AlGaN/GaN heterostructure on Si substrate. *Semicond Sci Technol* 2015; **30**: 105037.

6 Liao L, Bai J, Qu Y, *et al.* High-κ oxide nanoribbons as gate dielectrics for high mobility top-gated graphene transistors.

Proc Natl Acad Sci USA 2010; **107**: 6711–6715.

7 Liao L, Bai J, Lin YC, *et al.* High-performance top-gated graphene-nanoribbon transistors using zirconium oxide nanowires as high-dielectric-constant gate dielectrics. *Adv Mater* 2010; **22**: 1941–1945.

8 Liao L, Bai J, Cheng R, *et al.* Top-gated graphene nanoribbon transistors with ultrathin high-*k* dielectrics. *Nano Lett* 2010; **10**: 1917–1921.

9 Dean CR, Young AF, Meric I, *et al.* Boron nitride substrates for high-quality graphene electronics. *Nat Nanotech* 2010; **5**: 722–726.

10 Liao L, Lin YC, Bao M, *et al.* High-speed graphene transistors with a self-aligned nanowire gate. *Nature* 2010; **467**: 305–308.

11 Liao L, Bai J, Cheng R, *et al.* Sub-100 nm channel length graphene transistors. *Nano Lett* 2010; **10**: 3952–3956.

12 Liao L, Duan X. Graphene-dielectric integration for graphene transistors. *Mater Sci Eng-R-Rep* 2010; **70**: 354–370.

13 Liu Y, Cheng R, Liao L, *et al.* Plasmon resonance enhanced multicolour photodetection by graphene. *Nat Commun* 2011; **2**: 579.

14 Liao L, Bai J, Cheng R, *et al.* Scalable fabrication of self-aligned graphene transistors and circuits on glass. *Nano Lett* 2012; **12**: 2653–2657.

15 Cheng R, Bai J, Liao L, *et al.* High-frequency self-aligned graphene transistors with transferred gate stacks. *Proc Natl Acad Sci USA* 2012; **109**: 11588–11592.

16 Britnell L, Gorbachev RV, Jalil R, *et al.* Field-effect tunneling transistor based on vertical graphene heterostructures. *Science* 2012; **335**: 947–950.

17 Yu WJ, Li Z, Zhou H, *et al.* Vertically stacked multi-heterostructures of layered materials for logic transistors and complementary inverters. *Nat Mater* 2013; **12**: 246–252.

18 Geim AK, Grigorieva IV. Van der Waals heterostructures. *Nature* 2013; **499**: 419–425.

19 Liu Y, Weiss NO, Duan X, *et al.* Van der Waals heterostructures and devices. *Nat Rev Mater* 2016; **1**: 16042.

20 Liu Y, Guo J, Zhu E, *et al.* Approaching the Schottky-Mott limit in van der Waals metal-semiconductor junctions. *Nature* 2018; **557**: 696–700.

21 Liu Y, Huang Y, Duan X. Van der Waals integration before and beyond two-dimensional materials. *Nature* 2019; **567**: 323–333.

22 Yu WJ, Liu Y, Zhou H, *et al.* Highly efficient gate-tunable photocurrent generation in vertical heterostructures of layered materials. *Nat Nanotech* 2013; **8**: 952–958.

23 Lee CH, Lee GH, van der Zande AM, *et al.* Atomically thin p-n junctions with van der Waals heterointerfaces. *Nat Nanotech* 2014; **9**: 676–681.

24 Cheng R, Li D, Zhou H, *et al.* Electroluminescence and photocurrent generation from atomically sharp WSe_2/MoS_2 heterojunction p-n diodes. *Nano Lett* 2014; **14**: 5590–5597.

25 Woessner A, Lundeberg MB, Gao Y, *et al.* Highly confined low-loss plasmons in graphene-boron nitride heterostructures. *Nat Mater* 2015; **14**: 421–425.

26 Zhong D, Seyler KL, Linpeng X, *et al.* Van der Waals engineering of ferromagnetic semiconductor heterostructures for spin and valleytronics. *Sci Adv* 2017; **3**: 1603113.

27 Huang B, Clark G, Navarro-Moratalla E, *et al.* Layer-dependent ferromagnetism in a van der Waals crystal down to the monolayer limit. *Nature* 2017; **546**: 270–273.

28 Qian Q, Ren H, Zhou J, *et al.* Chiral molecular intercalation superlattices. *Nature* 2022; **606**: 902–908.

29 Liu L, Kong L, Li Q, *et al.* Transferred van der Waals metal electrodes for sub-1-nm MoS_2 vertical transistors. *Nat Electron* 2021; **4**: 342–347.

30 Shin I, Cho WJ, An ES, *et al.* Spin-orbit torque switching in an all-van der Waals heterostructure. *Adv Mater* 2022; **34**: 2101730.

31 Ai L, Zhang E, Yang J, *et al.* Van der Waals ferromagnetic Josephson junctions. *Nat Commun* 2021; **12**: 6580.

32 Cao Y, Fatemi V, Demir A, *et al.* Correlated insulator behaviour at half-filling in magic-angle graphene superlattices.

Nature 2018; **556**: 80–84.

33 Cao Y, Fatemi V, Fang S, *et al.* Unconventional superconductivity in magic-angle graphene superlattices. *Nature* 2018; **556**: 43–50.

34 Tran K, Moody G, Wu F, *et al.* Evidence for Moiré excitons in van der Waals heterostructures. *Nature* 2019; **567**: 71–75.

35 Seyler KL, Rivera P, Yu H, *et al.* Signatures of Moiré-trapped valley excitons in $MoSe_2/WSe_2$ heterobilayers. *Nature* 2019; **567**: 66–70.

36 Alexeev EM, Ruiz-Tijerina DA, Danovich M, *et al.* Resonantly hybridized excitons in Moiré superlattices in van der Waals heterostructures. *Nature* 2019; **567**: 81–86.

37 Jin C, Regan EC, Yan A, *et al.* Observation of Moiré excitons in WSe_2/WS_2 heterostructure superlattices. *Nature* 2019; **567**: 76–80.

38 Liu Y, Duan X, Shin HJ, *et al.* Promises and prospects of two-dimensional transistors. *Nature* 2021; **591**: 43–53.

39 Amick JA, Schnable GL, Vossen JL. Deposition techniques for dielectric films on semiconductor devices. *J Vacuum Sci Tech* 1977; **14**: 1053–1063.

40 Park JH, Movva HCP, Chagarov E, *et al. In situ* observation of initial stage in dielectric growth and deposition of ultrahigh nucleation density dielectric on two-dimensional surfaces. *Nano Lett* 2015; **15**: 6626–6633.

41 Leonhardt A, Chiappe D, Afanas'ev VV, *et al.* Material-selective doping of 2D TMDC through Al_xO_y encapsulation. *ACS Appl Mater Interfaces* 2019; **11**: 42697–42707.

42 Cheng R, Jiang S, Chen Y, *et al.* Few-layer molybdenum disulfide transistors and circuits for high-speed flexible electronics. *Nat Commun* 2014; **5**: 5143.

43 Lee SJ, Lin Z, Huang J, *et al.* Programmable devices based on reversible solid-state doping of two-dimensional semiconductors with superionic silver iodide. *Nat Electron* 2020; **3**: 630–637.

44 Chen P, Atallah TL, Lin Z, *et al.* Approaching the intrinsic exciton physics limit in two-dimensional semiconductor diodes. *Nature* 2021; **599**: 404–410.

45 Wang J, Cai L, Chen J, *et al.* Transferred metal gate to 2D semiconductors for sub-1 V operation and near ideal subthreshold slope. *Sci Adv* 2021; **7**: eabf8744.

46 Haick H, Ambrico M, Ghabboun J, *et al.* Contacting organic molecules by metal evaporation. *Phys Chem Chem Phys* 2004; **6**: 4538–4541.

47 Spicer WE, Chye PW, Garner CM, *et al.* The surface electronic structure of 3–5 compounds and the mechanism of Fermi level pinning by oxygen (passivation) and metals (Schottky barriers). *Surf Sci* 1979; **86**: 763–788.

48 Wang Y, Wan Z, Qian Q, *et al.* Probing photoelectrical transport in lead halide perovskites with van der Waals contacts. *Nat Nanotechnol* 2020; **15**: 768–775.

49 Qian Q, Wan Z, Takenaka H, *et al.* Photocarrier induced persistent structural polarization in soft-lattice lead halide perovskites. *Nat Nanotechnol* 2022; https://doi/org/10.1038/s41565-022-01306-x.

50 Jia C, Famili M, Carlotti M, *et al.* Quantum interference mediated vertical molecular tunneling transistors. *Sci Adv* 2018; **4**: eaat8237.

51 Famili M, Jia C, Liu X, *et al.* Self-assembled molecular-electronic films controlled by room temperature quantum interference. *Chem* 2019; **5**: 474–484.

52 Jia C, Grace IM, Wang P, *et al.* Redox control of charge transport in vertical ferrocene molecular tunnel junctions. *Chem* 2020; **6**: 1172–1182.

53 Liu Y, Wang P, Wang Y, *et al.* Van der Waals integrated devices based on nanomembranes of 3D materials. *Nano Lett* 2020; **20**: 1410–1416.

54 Wang L, Wang P, Huang J, *et al.* A general one-step plug-and-probe approach to top-gated transistors for rapidly probing delicate electronic materials. *Nat Nanotechnol* 2020; **17**: 1206–1213.

55 Ren H, Wan Z, Duan X. Van der Waals superlattices. *Natl Sci Rev* 2022; **9**: 2021–2023.

56 Zhao B, Wan Z, Liu Y, *et al.* High-order superlattices by rolling up van der Waals heterostructures. *Nature* 2021; **591**: 385–390.

57 Wang C, He Q, Halim U, *et al.* Monolayer atomic crystal molecular superlattices. *Nature* 2018; **555**: 231–236.

58 Lin Z, Liu Y, Halim U, *et al.* Solution-processable 2D semiconductors for high-performance large-area electronics. *Nature* 2018; **562**: 254–258.

59 Qian Q, Wan Z, Duan X. Boosting superconductivity in organic-inorganic superlattices. *Sci Bull* 2020; **65**: 177–178.

60 Lin Z, Wan Z, Song F, *et al.* High-yield exfoliation of 2D semiconductor monolayers and reassembly of organic/inorganic artificial superlattices. *Chem* 2021; **7**: 1887–1902.

61 Zhao Y, Zhang C, Kohler DD, *et al.* Supertwisted spirals of layered materials enabled by growth on non-Euclidean surfaces. *Science* 2020; **370**: 442–445.

62 Li J, Yang X, Liu Y, *et al.* General synthesis of two-dimensional van der Waals heterostructure arrays. *Nature* 2020; **579**: 368–374.

63 Zhang Z, Chen P, Duan X, *et al.* Robust epitaxial growth of two-dimensional heterostructures, multiheterostructures, and superlattices. *Science* 2017; **357**: 788–792.

64 Zhang Z, Huang Z, Li J, *et al.* Endoepitaxial growth of monolayer mosaic heterostructures. *Nat Nanotechnol* 2022; **17**: 493–499.