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Structural and quantum-state phase transitions in van der Waals layered materials

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Van der Waals layered transition metal dichalcogenides can exist in many different atomic and electronic phases. Such diverse polymorphisms not only provide a route for investigating novel topological states, such as quantum spin Hall insulators, superconductors and Weyl semimetals, but may also have applications in fields ranging from electronic and optical/quantum devices to electrochemical catalysis. And the methods for triggering robust phase transitions between polymorphs are evolving and diversifying—several growth processes, high-pressure/strain methods, and optical, electronic and chemical treatments have been developed. Here, we discuss recent progress on phase transitions and the related physics in layered materials, and demonstrate unique features compared with conventional solid-state materials.

Conventional phase transitions involve multiple phases (for example, liquid and solid) and their triggering factors, such as temperature and pressure. The corresponding phase diagrams provide extensive information on the phases and order parameters. The diverse interactions between the lattices, layers and strongly correlated electrons in two-dimensional (2D) van der Waals layered transition metal dichalcogenides (TMDs), however, lead to a much more complicated nature of phase transitions[1]. Two-dimensional TMDs with a transition metal layer sandwiched between two chalcogen atomic layers provide additional degrees of freedom in the structural transformation[2], in contrast to other representative monolayered 2D materials, such as graphene and hexagonal boron nitride (h-BN), which do not exhibit structural polymorphs or strongly correlated electrons. Furthermore, thickness-dependent lattice symmetry and electronic correlations in a 2D-confined geometry play crucial roles in the diverse structural and quantum phase transitions. All of these aspects allow multiple structural phases to be tailored and enable markedly different physical properties to be observed in a single substance[3–5]. The material breakthroughs associated with phase transitions, along with a wealth of related physics in 2D TMDs, are summarized in Fig. 1. And it is clear that abrupt changes in the electronic band structure[4] and the emergence of novel topological states such as the quantum spin Hall insulator[6–9] and various superconducting states are interrelated with structural phase transitions[10,11].

An appealing aspect of polymorphism in TMDs is the coexistence of multiple phases at certain temperatures and pressures[3–5]. From a physics point of view, a cohesive energy (or a total energy) is calculated for each structural phase, and the preferred structural phase is determined by comparing the cohesive energies of all polymorphs[4]; the preferred phase (polymorph) has the lowest cohesive energy. The coexistence of multiple phases can be understood on the basis of the small cohesive energy difference[4,5,12] between the multiple phases; this small energy difference also indicates that the more stable phase can be externally switched to the less stable phase by, for example, a charge injection. The presence of multiple phases has led to intriguing applications such as electronic and energy homojunction devices[5,13].

Novel topological states such as the quantum spin Hall insulator (2D topological insulator)[6–9] and the Weyl state in topological semimetals[14] have been observed in distorted octahedral and orthorhombic phases of group-6 TMDs. Whereas the electronic band structure of an experimentally well-defined and theoretically predicted crystal structure is critical for realizing these non-trivial topological phases, the physical properties of 2D group-6 TMDs are also largely influenced by the external electric field, the dielectric screening effect, and the sample dimensions of the materials[4].

Overall, the use of robust phase transitions to versatile 2D layered structures is a timely and challenging issue for science and technology. In this progress article, we present an overview of this topic and selected seminal achievements in this rapidly growing field.

Structures of single-layer TMDs and their transitions

Single-layer TMDs can adopt either a trigonal prismatic (1H or D_{3h}) or octahedral (1T or D_{3d}) coordination of atomic elements, as shown in Fig. 2a, but they are usually observed in one preferred phase that is thermodynamically favoured[4,5]. An intuitive way to understand the thermodynamic selectivity of the phase or the stability is to count the number of electrons in the d orbitals of the transition metals in the framework of crystal field theory. The oxidation degrees of the transition metals and the chalcogen atoms are +4 and −2, respectively; thus, the electron counts in the d orbitals of the metal atoms vary from 0 (d^0) for group-4 TMDs (Ti, Zr and Hf) up to +6 (d^6) for group-10 TMDs (Ni, Pd and Pt).

Structural transitions in TMD single layers correlate with the number of electrons in the d orbitals. TMDs from group 4 (d^0) adopt the octahedral (1T) structure (Fig. 2c). However, according to crystal field theory, the energy level of the d_{z^2} orbital in the 1H phase is lower than that of the t_{2g} band of the 1T phase (Fig. 2a, bottom), thus indicating that it is possible to switch to the favoured phase by filling d orbitals with electrons. From transition metals in group 4 to those in group 5 or 6, the filling of d_{z^2} orbitals of 1H phase becomes more favourable. Indeed, group-5 TMDs (d^1) can be found in either the 1T or 1H phase, whereas group-6 TMDs (d^2) are typically in the 1H phase with a bandgap between the d_{z^2} and $d_{x^2-y^2,xy}$ orbitals. After the d_{z^2} orbitals are filled with two electrons (as in group-6 TMDs),

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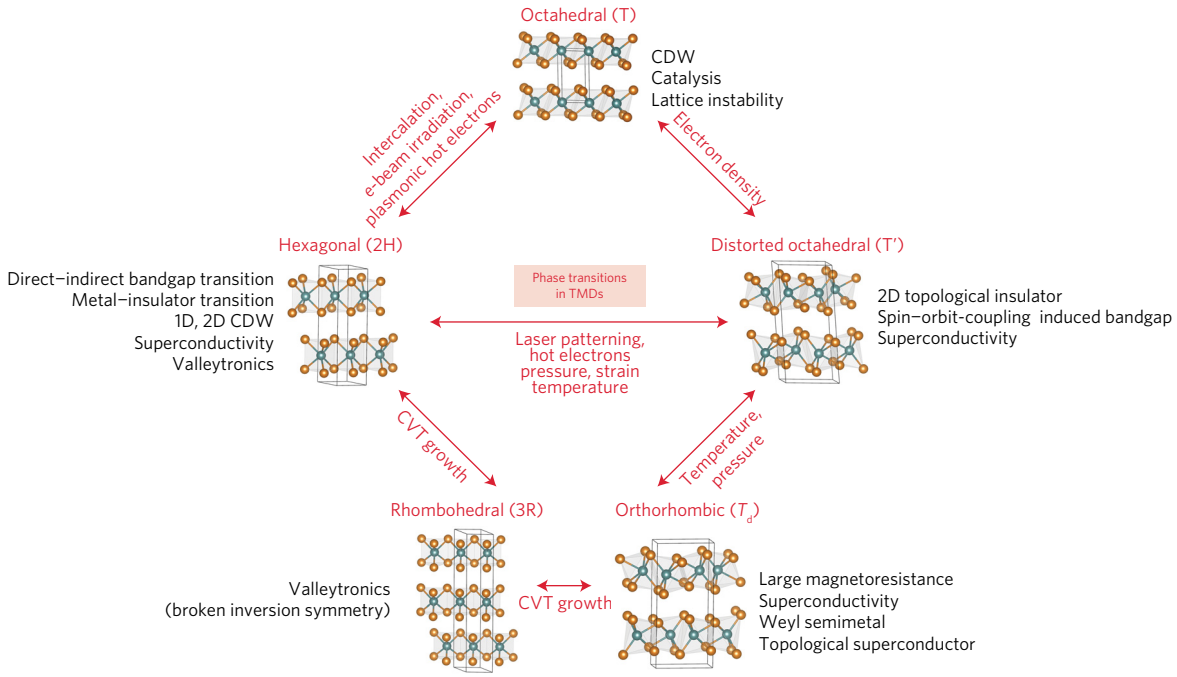

Figure 1 | Transition and correlation between phase and physics in TMDs.

adding more electrons destabilizes the 1H configuration, owing to the energy gap of ∼1 eV between the d_{z^2} and $d_{x^2-y^2,xy}$ orbitals, which again favours the 1T phase over the 1H phase. Group-7 (d^3) TMDs exhibit a distorted octahedral coordination characterized by clusterization or Peierls distortions of the metal atoms, and the regular octahedral coordination is observed for group-9 (d^5) and group-10 (d^6) TMDs.

Lattice distortion or superstructures of TMDs

Recently, intriguing quantum phenomena such as the quantum spin Hall insulator and Weyl semimetal have been predicted for the distorted octahedral structure (1T′, as shown in Fig. 2d) of group-6 TMDs[6,14]. The orientation of the lattice distortion could be controlled by strain, which opens a new field in phase transition; the mechanical control over the lattice directions, so called ferroelasticity, conceives shape memory applications with TMDs[15]. Such distortions, inducing topological quantum states and domain physics (ferroelasticity), naturally exist in the ground state of a group-6 TMD, WTe_2 (ref. 14). However, to obtain the structural and quantum phases, other group-6 TMDs must undergo a phase transition from their thermodynamically stable 1H phase to the 1T′ phase via chemical exfoliation or lithium intercalation[2].

The origin of the above distortions is attributed to electron transfer after lithiation between reducing agents (for example, *n*-butyl lithium) and TMD layers. The excess electron is carried by the *d* orbitals of group-6 transition metals; thus, the electron density of the *d* orbitals increases slightly from d^2 to d^{2+x}. Density functional theory (DFT) calculations demonstrate that the phase transition from the 1H phase to the 1T phase starts at a charge excess of $x = 0.2 - 0.4$ electrons per MX_2 (ref. 16); however, the slight increase in the *d*-orbital electron density cannot completely convert the 1H phase to an ideal 1T phase, so the lattice distortion or superstructure helps in the formation of 1T symmetry under a small increase in the number of *d*-orbital electrons.

Many TMDs from group 5 (with the exception of NbS_2) and group 7 exhibit dimension-dependent charge-density waves (CDWs), breaking the symmetry of their 1T phase[17]. Recent studies have shown that there is a large increase in the CDW transition temperature with decreasing thickness from 33 K in bulk up to 145 K near the single-layer regime[17], thus revealing a promising engineering application for CDW states in 2D systems.

Superconducting and topological phase transitions

Strong spin–orbit coupling and low dimensionality involving lattice distortion in polymorphs of 2D layered TMDs have appeared as physical origins for novel superconducting (Fig. 3a,b) and non-trivial topological states (Fig. 3c–e). Ising superconductivity has been experimentally realized[10,11], whereas the quantum spin Hall effect (2D topological insulator) and Weyl semimetal primarily remain theoretical in 2D TMD systems[14]. Here, we discuss the progress in novel thickness- and phase-dependent superconductivities (Fig. 3b) and topological states in group-6 TMDs related to phase engineering and polymorphisms.

Thickness has been regarded as a critical factor for various electronic band structure changes in TMDs. For instance, a variety of optical properties have been extensively studied in terms of direct and indirect bandgap transitions according to the number of TMD layers[18]. Regarding the quantum physics in hexagonal semiconducting TMDs, the number of layers determines the symmetry of the materials: in-plane inversion symmetry (bulk) and its breaking (monolayer)[10,11]. Together with the strong spin–orbit coupling and effective Zeeman fields in 2D TMDs, the breaking of in-plane inversion symmetry produces an out-of-plane spin polarization that depends on the valley (K or −K point) in momentum space (Fig. 3a). The unique spin polarization has been demonstrated by using a large anisotropic critical magnetic field to quench the superconducting state in 2H-MoS_2, which has also been interpreted as 2D Ising superconductivity. Currently, topological superconductivity in TMDs is of great interest; a superconducting state has been observed in monoclinic and 1T′ $MoTe_2$, wherein 2D topological insulator and Weyl semimetal states are expected[6,14,19].

The lattice distortion in the distorted octahedral phase in group-6 TMDs drives an intrinsic band inversion near the Fermi level with chalcogenide-*p* and metal-*d* bands (Fig. 3c,d). These topologically protected non-trivial (surface or edge) electron bands have led to two important issues in solid-state physics: the quantum spin Hall effect and the Weyl state. Two major polymorphs are involved in the quantum states: distorted octahedral (T′) and orthorhombic

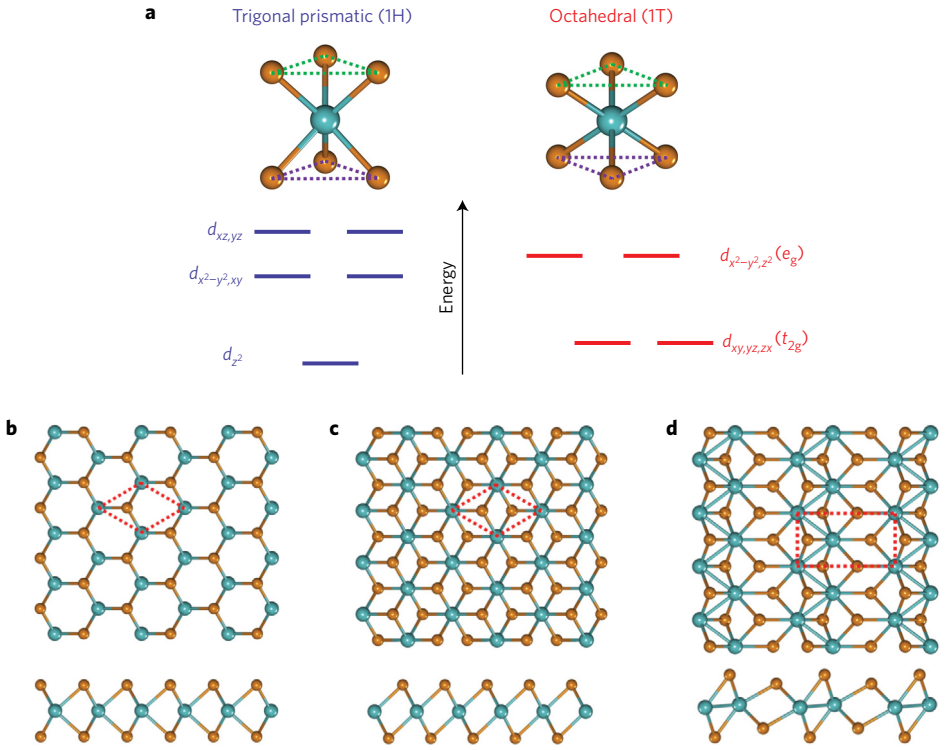

Figure 2 | Structures of single-layer TMDs. a, Schematic images of 1H and 1T lattice symmetries and energy levels of *d*-orbital electrons induced by the crystal field. **b**–**d**, Top and side structures of 1H (**b**), 1T (**c**) and distorted 1T or 1T′ (**d**). Blue spheres represent transition metals, and orange spheres denote chalcogen elements.

(T_d) phases (Fig. 1). DFT calculations demonstrate that all group-6 TMDs in the distorted octahedral phase have such band inversion, thus resulting in the quantum spin Hall effect[6,7]. In addition to the role of thickness in the superconducting state through inversion-symmetry breaking, the number of layers affects the bandgap amplitude of the TMDs, and this is critical in realizing a dissipationless spin transfer by the quantum spin Hall effect; achieving a large bulk bandgap was a key objective of that study[20,21]. As a promising application of this concept, it has been theoretically verified that the external electric field can turn the topological state on and off, thus suggesting that this system is a topological field-effect transistor (FET)[6] (Fig. 3e).

The inversion-symmetry breaking in orthorhombic T_d-WTe_2 and T_d-$MoTe_2$, in contrast to their T′ phases, has been shown to induce the Weyl semimetallic state[14]. The orthorhombic lattice of the T_d phase can be obtained through a phase transition by controlling defects, cooling the T′ crystal below 240 K or applying high pressure to the T′ phase[19]. The limitations in crystallographic and spectroscopic characterizations under such extreme physical conditions (pressure and temperature) should be further resolved to deploy topological states for next-generation devices.

Electrical-, optical- and strain-driven phase transitions

Stable lattice structures of 2D TMDs have been found by varying external parameters such as the carrier concentration[4] and mechanical strain[22]. This diverse phase transition occurs among different group-6 TMDs, thus highlighting the subtle physics of the structural change depending on the atomic species.

The atomic phase transition between the 1H and 1T phases in MoS_2 has been verified by transmission electron microscopy, which is capable of simultaneous lattice imaging[23]. A metastable transient phase and multiple atomic structures of phase boundaries have been observed, thus revealing the gliding of Mo and S atomic planes in the phase transition. Similarly to using chemical Li-intercalation for a phase transition, it has been demonstrated that direct electron injection in a transmission electron microscope can allow for *in situ* patterning of the T phase with atomic resolution[23], thus revealing an electron-induced structural phase transition at atomic scale.

Large-scale and practical methods based on laser illumination have further demonstrated the physical mechanism of phase transitions. Here, we discuss three different mechanisms for such transitions and related perspectives. Local heating and the resulting chalcogenide defects have been found to trigger an irreversible phase transition from the hexagonal to monoclinic phase in $MoTe_2$ (ref. 5). Similarly, a phase transition from the monoclinic to hexagonal phase in MoS_2 by laser irradiation has been reported, with an estimated activation energy of ∼400 meV for the transition[24]. In both cases, the undesired oxidation is not involved in the optical processes, but minimum-energy pathways or feasible transient polymorphs remain a challenging issue. Second, plasmonic hot electrons can be manipulated to induce a phase transition in MoS_2 from its hexagonal to monoclinic phase[25]. In the presence of hot electrons injected into molybdenum's 4*d* bands (Fig. 2a), crystal field theory indicates that the monoclinic phase is more stable than the hexagonal phase, and thus, a phase transition occurs. Third, a route of ultrafast local and selective band structure control in monolayer TMDs via optical electronic excitation has been theoretically demonstrated[26].

Controlling one of the phase triggering factors affects the other factors for the phase transition, thus representing an intriguing feature of 2D layered materials that may have numerous applications. For example, infrared-light detection using a sufficiently low phase-transition temperature (near room temperature) could be conceived through engineering the mechanical strain of a 2D TMD[22].

2D homojunction for device and energy applications

Phase transitions and polymorphisms of 2D TMDs under ambient conditions have led to a breakthrough for electrical

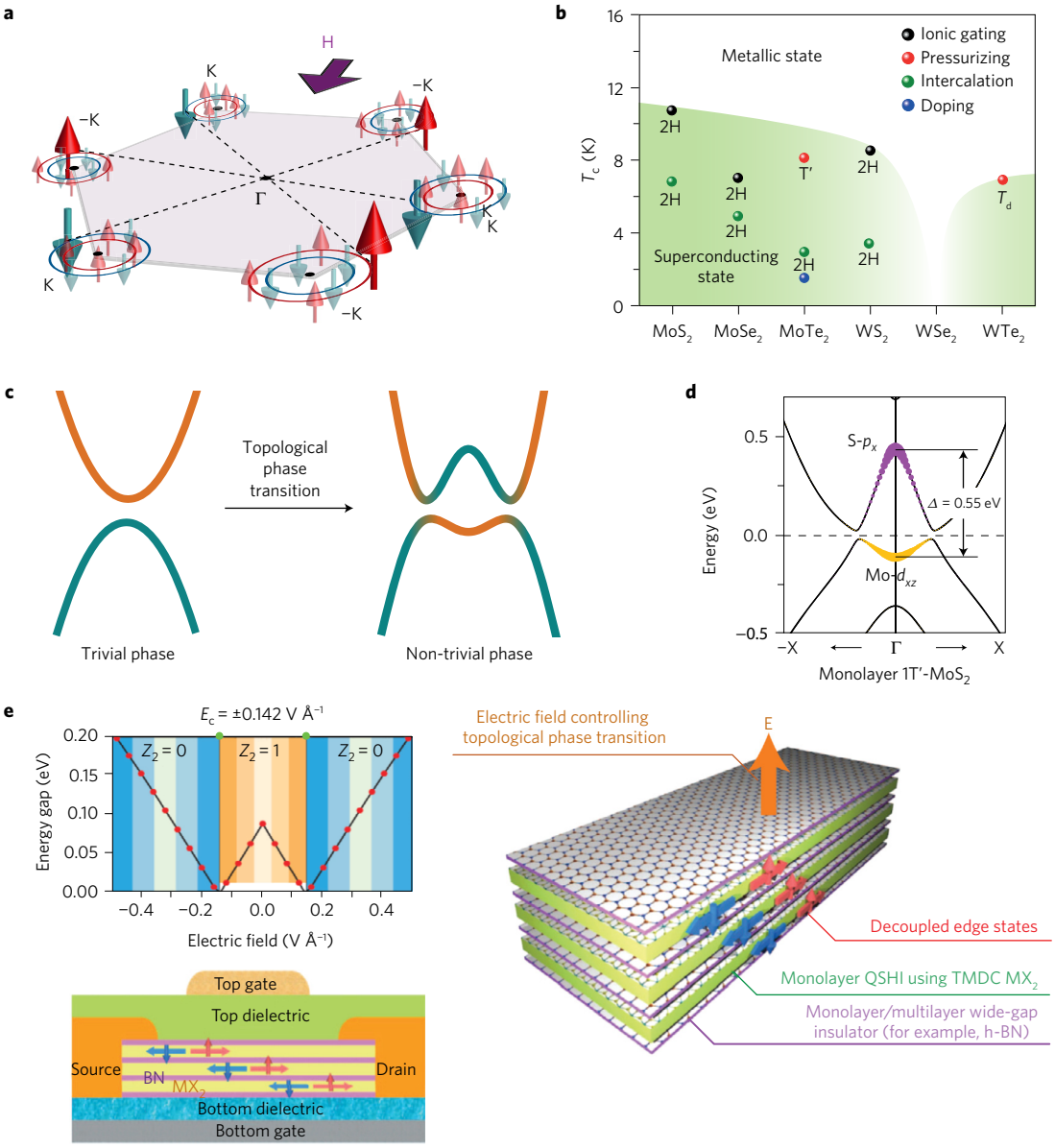

Figure 3 | Superconductivity and topological phase transitions in TMDs. a, Schematic image of out-of-plane polarized spins in the T′ phase of TMDs under an in-plane magnetic field. **b**, Superconducting polymorphism in TMDs. The superconducting transition temperatures are plotted as a function of composition and phase. **c**, Schematic image of a topological phase transition. A band inversion due to lattice distortion is shown. **d**, Calculated band structure of monolayer T′-MoS_2 near the Γ point, showing the band inversion[7]. **e**, Proposed structure of a topological FET. Reproduced from ref. 10, Macmillan Publishers Ltd (**a**); ref. 7, APS (**c**,**d**); and ref. 6, AAAS (**e**).

and energy devices. Whereas the contact resistance between 2D semiconducting channels and metal electrodes remains a critical issue, the fabrication of atomically clean ohmic homojunctions without use of the 'manual-transfer method' has been achieved with semiconducting group-6 TMDs such as MoS_2 and $MoTe_2$ (refs 3,5,27). We note that vertical heterostructures fabricated by the 'manual-transfer method' could conceptually be replaced by atomically clean homojunctions; this concept has led to novel scientific insights into 2D devices and energy applications.

A local phase transition from the semiconducting 2H phase to the metallic 1T phase in MoS_2 was used to decrease the contact resistance in MoS_2 FETs[3]. Figure 4a,b shows a spatial distribution of 2H and 1T phases in which metal source–drain electrodes are located only in the 1T phase area. The role of the 1T phase area is to create an ohmic junction with the metal electrode, connecting the 2H semiconducting channel. Moreover, laser-driven phase engineering approaches without Li intercalants have been developed in $MoTe_2$ FETs[5], which have demonstrated 50 times higher mobility through the use of homojunction fabrication (Fig. 4c,d).

The homojunction provides an opportunity to study the physical origin of the poor performance of the hydrogen-evolution reaction (HER) at the MoS_2 basal plane, compared with the MoS_2 edge[13]. By manipulating the contact resistance between the metal electrode and electrochemical catalysts, as shown in Fig. 4e, we find that the edge itself does exhibit a catalytic performance similar to that of the basal plane in MoS_2 (Fig. 4f). In contrast to previous knowledge, the geometry of the catalytic active sites[28] is not the dominating factor in HER; instead, the contact resistance is the key factor.

Metal–insulator transition in a single structural phase

Two-dimensional semiconducting TMDs have provided a unique platform for fundamental studies of metal–insulator transition (MIT), owing to their susceptibility to external control parameters

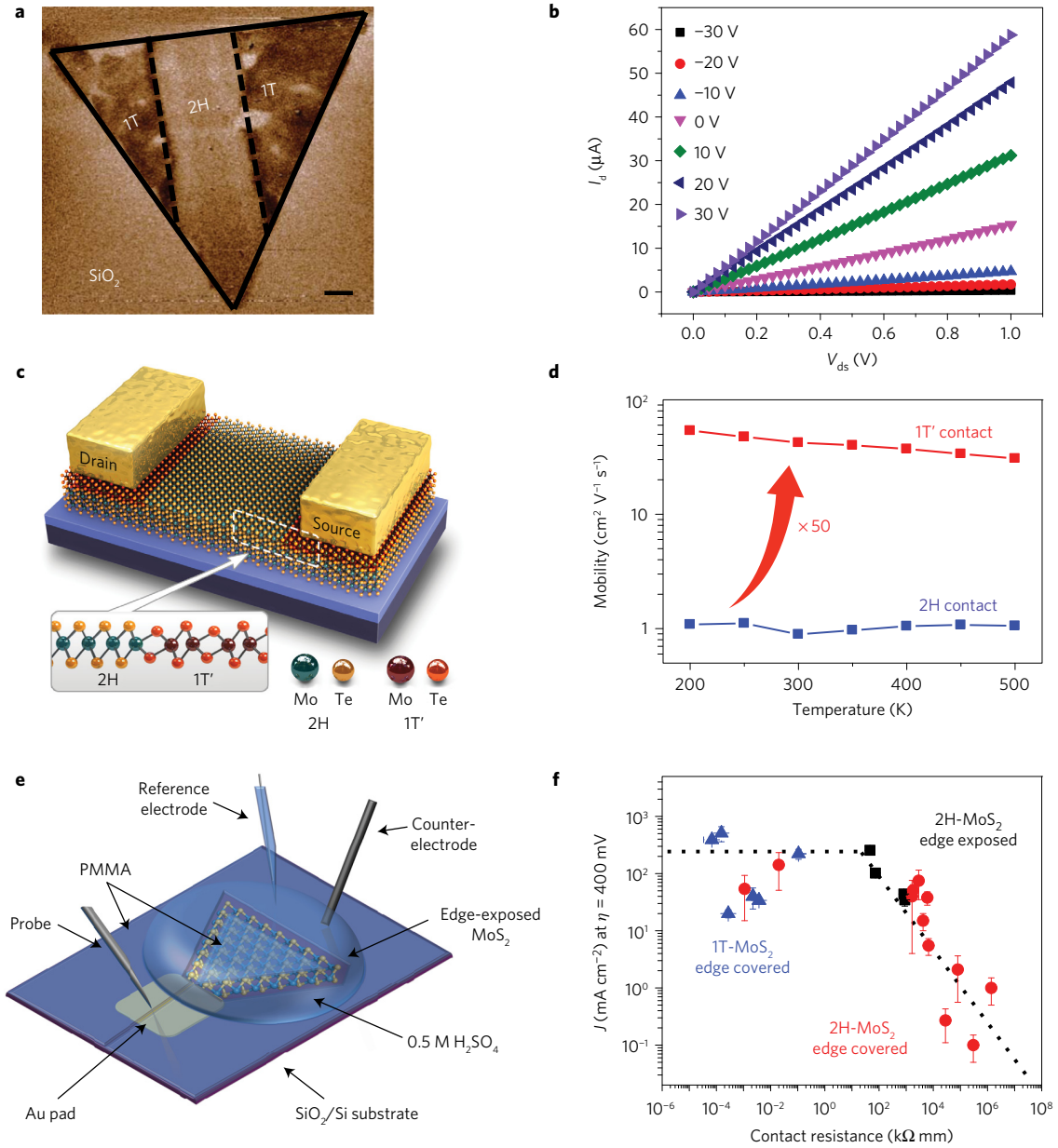

Figure 4 | Homojunction for transistors and hydrogen-production applications. a, Electrostatic-force microscopy phase image of a homojunction in MoS_2. **b**, Current–voltage characteristics of the homojunction device in **a**. **c**,**d**, $MoTe_2$ homojunction FET produced by laser phase patterning and the mobility improvement achieved by contact treatment. **e**, Schematic image of the experimental set-up for HER. **f**, HER as a function of contact resistance. The edges and basal planes showed similar performances. Reproduced from ref. 3, Macmillan Publishers Ltd (**a**,**b**); ref. 5, AAAS (**c**,**d**); and ref. 13, Macmillan Publishers Ltd (**e**,**f**).

such as doping by electrical gating in the 2D geometry[29]. An example of a MIT is shown in Fig. 5a, in which a crossover in the temperature-dependent conductivity occurs in MoS_2 as the carrier density increases.

Two primary theoretical models have been proposed to explain this phenomenon: percolation[30]; and quantum phase transition[31] (QPT). In percolation, the conductance (σ) can be fitted by a power law $\sigma = A(n - n_c)^{\delta}$, where n is the carrier density and δ is 4/3 for an ideal 2D system[29] (Fig. 5b). In previous studies, however, the percolation density n_c from the fitting is 10 times smaller than the experimental value. This discrepancy is ascribed to the disorders and degraded mobility in the 2D system, susceptible to environmental conditions.

The QPT model is based on non-thermal physical parameters such as pressure and electric and magnetic fields to induce a spatially homogeneous MIT. In QPT, short-range disorders are dominant; Anderson localization or a weak localization effect by quantum interference is often claimed to be the origin of the insulating state[32], whereas the metallic phase is believed to be driven by carrier–carrier interactions. Figure 5c–e shows two branches of metallic and insulating phases collapsed by temperature scaling, with a scaling temperature T_0.

Despite the satisfactory conductivity scaling, a key issue is that the two seemingly contradictory phenomena (percolation and QPT) are observed simultaneously in the same device. Such a non-trivial interplay of two phenomena cannot be simply explained and perhaps strong carrier interactions and disorder effects may play a novel role to confirm the true nature of MITs in 2D systems.

Conclusion and outlook

Various structural and electronic phases in van der Waals layered TMDs have given rise to a new research field, which often involves

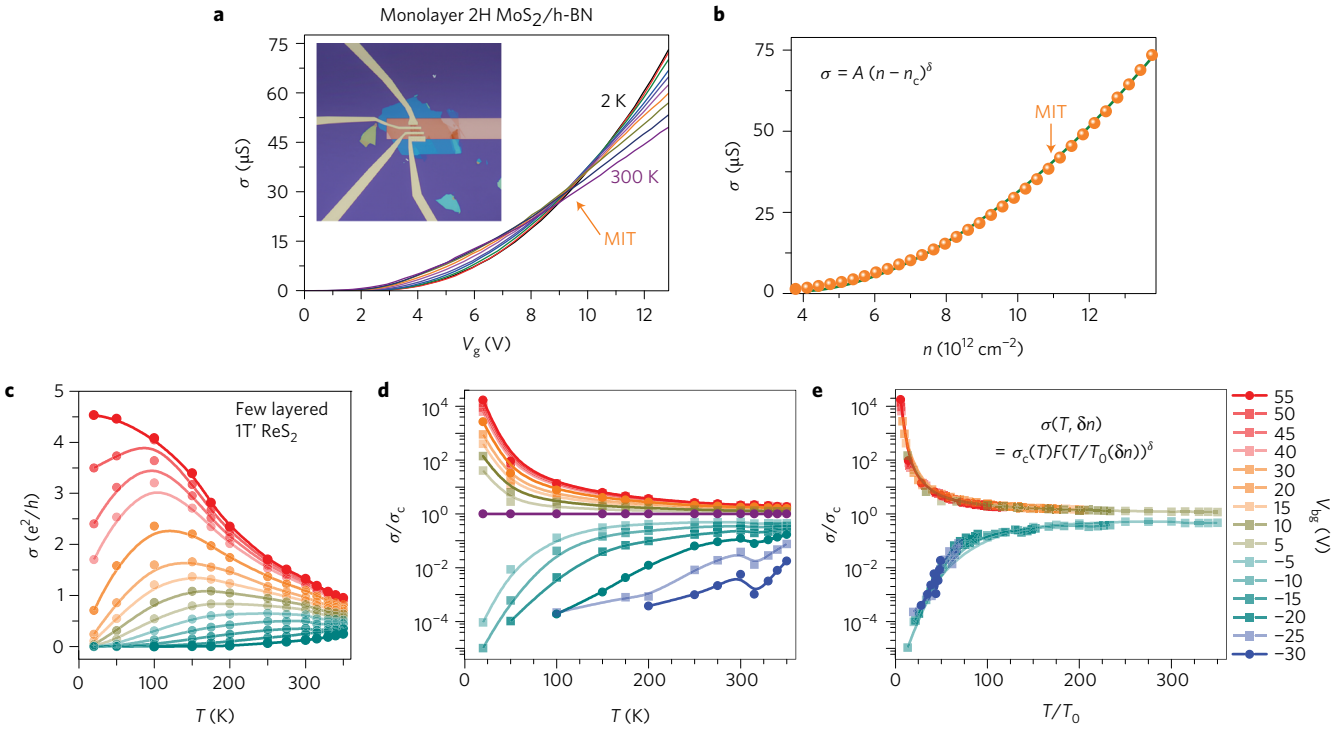

Figure 5 | MIT in 2D TMDs. a, MIT in a monolayer MoS_2/h-BN vertical heterostructure on the basis of the temperature (T) dependence of σ measurements as a function of back-gate bias. **b**, Fitting for the power law of carrier-density (n) dependence, $\sigma = A(n - n_c)^{\delta}$ (green line). **c**, T dependence of σ in few-layered 1T′ ReS_2 for several back-gate bias voltages. **d**, Various σ curves normalized by σ_c, where σ_c denotes the critical conductivity corresponding to the MIT. **e**, Rescaled conductivity σ/σ_c as a function of T/T_0 and $\delta n = (n_H - n_c)/n_c$, where T_0 is the crossover temperature and n_H is the carrier density extracted from a Hall effect measurement. Reproduced from ref. 29, Macmillan Publishers Ltd (**a**,**b**); and ref. 32, ACS (**c**–**e**).

emerging quantum states such as quantum spin Hall insulators, topological insulators, Weyl semimetals, 2D superconductivity and quantum critical metallic states. Even more intriguing is the interweaving of quantum phenomena with structural phases that are strongly material-dependent. The disorder-related structural phase is more complicated and may also influence novel quantum phenomena. Although such phenomena have been observed in some materials such as $MoTe_2$ (ref. 5), the exploration of additional layered TMD materials is certainly required to fully understand the physical origins of these complex quantum phenomena.

The structural phase transitions and engineering of the resulting electronic/quantum phases in van der Waals 2D materials may be more robust than those in 3D materials. Furthermore, whether the origin of 2D phase transitions is similar to that of 3D phase transitions and the influence of van der Waals interactions on structural and electronic phase transitions remain to be explored. Although previous techniques such as phase-change memory have introduced a phase change (between amorphous and crystalline phases) for certain applications[33], the new approaches using 2D TMDs and their phase transitions involve versatile phase-control factors (such as temperature, pressure, strain, light, carrier density, atomic defects) for subtle structural changes among diverse polymorphs. With these new platforms, polymorphic TMDs may initially appear to have industrial potential (for example, catalysis), because of their promising electrical and optical properties, but the resulting phases have also provided opportunities to explore novel 2D physics.

Several scientific and engineering challenges remain in the use of TMD polymorphisms. As experienced in graphene research over the past decade, large-area (wafer-scale) and high-quality growth of the materials is the first task that must be addressed. Chemical-vapour deposition has been developed for this purpose, but the coverage and homogeneity of the structural phase achieved by this method should be further improved to industrial levels[34,35]. Second, controllable doping of TMDs for applications (for example, logic devices) remains elusive. Non-adjustable charge–carrier doping and Fermi level pinning in MoS_2 have triggered extensive studies, but practical electronic heterojunctions of TMDs are still limited to certain cases. Control over the defect density and the susceptibility to oxidation in TMDs are also important and challenging issues. Many groups have used glove-box systems to avoid oxidation problems, and it has been found that the performances of TMD devices vary greatly depending on the fabrication method[36]. Proper passivation and inspection methodologies for oxide and defect formation are required. Finally, we underline the complexities of structural phases and their physical properties correlated with local (for example, defects or doping) and global (for example, pressure or temperature) phase-control factors. Transient phases[23] and subtle bandgap opening[4] or quantum states[7] have been introduced through these complexities and require further systematic investigations.

In conclusion, the diversity of theoretical and experimental physics for phase transitions in van der Waals 2D TMDs represents a novel breakthrough for future 2D material-based science and technology. The progress of this rapidly growing field and the remaining issues require interdisciplinary approaches to advance the use of 2D materials in applications that can benefit society.

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Competing financial interests

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Erratum: Structural and quantum-state phase transitions in van der Waals layered materials

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In the version of this Progress Article originally published, the title contained a typographical error and should have read 'Structural and quantum-state phase transitions in van der Waals layered materials'.