

Phase transitions in 2D materials

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Abstract

The discovery and control of new phases of matter is a central endeavor in materials research. The emergence of atomically-thin 2D materials, such as transition-metal dichalcogenides and monochalcogenides, has allowed the study of diffusive, displacive and quantum phase transitions in 2D. In this Review, we discuss the thermodynamic and kinetic features of 2D phase transitions arising from dimensionality confinement, elasticity, electrostatics, defects and chemistry unique to 2D materials. We highlight polymorphic, ferroic and high-temperature diffusive phase changes, and examine the technological potential of controlled 2D phase transitions. Finally, we give an outlook on future opportunities in the study and applications of 2D phase transitions, and identify key challenges that remain to be addressed.

Web summary

Phase transformations in 2D materials have distinct kinetic and thermodynamic features, resulting from their reduced dimensionality and unique interactions. This Review discusses the properties of phase transitions and defects in 2D materials, and examines technological applications and challenges in the study of 2D phase transitions.

[H1] Introduction

Self-organization of a large number of nuclides and electrons leads to the emergence of different phases of matter. A phase represents a certain style of organization that can be spatially replicated ad infinitum, with properties that change continuously in response to external fields, that are distinct from the other phases. Therefore, certain system properties are altered as the material undergoes a phase transition. A general characteristic of a phase transition is that it either involves a discontinuity in an order parameter according to the Landau paradigm of phase transitions¹⁻³, or a change in a topological invariant^{4,5}.

The discovery, characterization and control of different phases of matter is a central task in condensed-matter physics and materials science. In particular, the study of phase transitions in 2D systems has played a crucial role in advancing our understanding of phase transitions (FIG.

1). 2D materials⁶⁻¹⁰ are matter that can infinitely replicate in two directions, but have thickness at atomic level in the third direction. For example, monolayer MoS₂ has a thickness of 6.7Å, and is typically μm in-plane in laboratory samples produced by mechanical exfoliation⁶, thus possessing an aspect ratio of $\sim 10^3$ or more. For comparison, a typical piece of A4-sized copy paper ($\sim 100 \mu\text{m} \times 29.7\text{cm} \times 21 \text{ cm}$) would have a similar aspect ratio of $\sim 10^3$. Although 2D \leftrightarrow 3D/1D phase transitions are certainly interesting subjects of discussion, here, we focus on 2D \rightarrow 2D transitions.

The earliest studies of 2D phase transitions were mostly theoretical; for example, the exact solution of the 2D Ising spin model¹¹, the proposition of the Hohenberg-Mermin-Wagner theorem^{12,13} and the discovery of the Kosterlitz-Thouless transition^{14,15} (FIG. 1). In the early 1980s, progress in semiconductor technology allowed the experimental study of 2D electron systems confined at semiconductor interfaces and under intense magnetic fields, which led to the ground-breaking discovery of the quantum Hall effect (QHE)¹⁶ and the fractional quantum Hall effect (FQHE)¹⁷. The invention of the scanning tunneling microscope (STM)¹⁸ and the atomic force microscope (AFM)¹⁹ in the 1980s enabled real-space imaging of surface reconstruction^{20,21} and of the phase transformation of Langmuir monolayers²². Techniques for isolating planar sheets of crystals from their bulk counterparts became only available in the early 2000s^{6,23}, paving the way for experimental studies of phase transitions in freestanding 2D materials. A wide range of phase transitions have been explored in 2D materials, including quantum electronic phase transitions, such as QHE²⁴, FQHE^{25,26}, metal-insulator transitions²⁷, superconductivity²⁸⁻³⁰, the quantum spin Hall (QSH) effect³¹⁻³⁵, the quantum anomalous Hall (QAH) effect³⁶⁻³⁸, magnetic phase transitions³⁹⁻⁴⁵ and classical phase transitions, such as polymorphic phase transitions⁴⁶⁻⁵⁴ and ferroic phase transitions⁵⁵⁻⁵⁹ (FIG. 1).

The reduction in dimensionality from 3D to 2D leads to peculiar statistical physics (for example, melting and critical point behaviors), quantum physics (for example, quantum confinement) and mechanics (for example, out-of-plane bending and buckling), and makes 2D systems more sensitive to the ambient chemical environment (for example, adsorption and corrosion), external fields and physical contacts. Indeed, investigating 2D materials could be regarded as the ultimate ‘surface science’, because all effects are happening on or near the surface. From an engineering perspective, this creates both opportunities and challenges for controlling and using phase change in 2D. For example, an optomechanical phase change^{59,60} is easier to induce in free-standing 2D materials owing to less elastic confinement and strong light-matter interactions in 2D compared to 3D bulk. However, air stability and chemical purity become bigger issues in 2D and influence the phase-change behavior.

Prior to the emergence of free-standing 2D materials, extended defects in 3D material host such as stacking faults, surfaces, grain boundaries and phase boundaries, have been considered 2D ‘phases’ in contact with 3D phase(s), on either or both sides of the 2D plane. Thermodynamic and kinetic features, such as interfacial segregation, pre-melting⁶¹ and glissile versus diffusive reconstruction, are analogous to phase transitions in free-standing 2D materials. Therefore, surface and interfacial science shares many features with 2D materials science, and aside from different long-range elastic and electrostatic energy expressions, many surface/interfacial phase transitions are similar to phase transitions in 2D materials.

In this Review, we outline unique features of phase transitions that emerge in 2D materials, and highlight recent key studies of 2D material phase transitions and technological implications of 2D phase changes. We will provide an outlook on future opportunities of phase transformations in 2D materials.

[H1] Unique features of 2D phase transitions

Dimensionality (D) reduction can strongly affect internal interactions and statistical physics, and thus the behavior of phase transitions. In 1968, Mermin showed that thermal fluctuations destroy the long-range diffraction order of infinite, free-standing 2D crystals⁶². Similarly, in 1D polymers, the preferred stress-free configuration at finite temperature is a ‘globule of yarn’ with an end-to-end distance of $\propto N^{1/2}$, where N is the contour length, caused by conformational entropy. A completely unconstrained 2D material cannot maintain its flatness in 3D space and would prefer to adopt the configuration of a ‘paper ball’. In contrast to 3D crystals or liquids, which can sustain static compression, free-standing 2D crystals cannot sustain static compression even at zero temperature owing to long-wavelength Euler buckling-like instability, that occurs at arbitrarily small compressive stress for infinite crystal. Thus, 1D and 2D crystals are more fragile than 3D crystals in the statistical physics sense, shown by the Hohenberg-Mermin-Wagner theorem^{12,13} for systems with sufficiently short-range interactions in $D \leq 2$. In reality, most 2D crystals are not completely free, and constrained either on the bottom by a substrate through adhesion and friction forces, or at the ends, preventing thermal fluctuations from destroying the flatness of the material. Nonetheless, out-of-plane flexural vulnerabilities are intrinsic to any 2D material, and when coupled with external stimuli locally or globally, they can give rise to a variety of interesting behaviors.

The effect of dimensionality can be understood in terms of short-range and long-range interactions. Short-range effects mainly occur in the form of coordination number and symmetry of chemical bonding, whereas long-range interactions can be much longer than the interatomic distance and include electrostatic, magnetostatic and elastic interactions. Both short- and long-range interactions can undergo substantial changes going from $D=3$ to $D=2$. In addition, the 2D nature of these materials facilitates coupling between the system and the environment, leading to higher susceptibility of phase stability to external stimuli.

[H2] Short-range interactions

Dimensionality reduction gives rise to the loss of coordination number, causing rehybridization of valence electrons (e.g. competition between sp^3 and sp^2 hybridization in carbonaceous materials) that can shift the energetic order of phases and cause the emergence of new symmetries. In 2D surfaces that we have argued to be analogous to 2D materials, cutting off one half of the bulk necessitates the breaking of strong bonding interactions, such as metallic, covalent or ionic bonds in the vertical direction, which can lead to the surface reconstruction of certain inorganic materials, such as the 7×7 reconstruction on the (111) surface of silicon²⁰. Indeed, surface reconstruction can be considered a 2D phase transition.

If a 2D material is exfoliated from the bulk through the removal of weak interactions, for example, in many-layered 3D crystals, in which interlayer interaction is predominantly of the van der Waals type, short-range coordination and symmetry can still be affected. In this case, electron-phonon interactions can change through confinement-induced modifications in the electronic structure^{63,64}, vibrational spectrum⁶⁵ or dielectric environment⁶⁶. Owing to the small

thickness of 2D materials, dielectric screening normal to the layer is limited; a 2D material in the out-of-plane direction resembles a molecule surrounded by vacuum. Therefore, the electrostatic potential generated by lattice vibrations in 2D materials is less screened than in 3D bulk materials, which increases the strength of electron–phonon interactions. Consequently, 2D materials are more susceptible to charge density wave (CDW) and Peierls distortions⁶⁷, lattice instabilities (FIG. 2a) that can significantly alter the short-range coordination and bonding symmetry.

[H2] Long-range interactions

Long-range interactions in 2D materials, such as electrostatic and elastic interactions, are also fundamentally different from their counterparts in 3D bulk materials (FIG. 2b). The dielectric property of a suspended, isolated 2D material is analogous to that of a layer of molecules owing to weak dielectric screening in the out-of-plane direction. In the in-plane directions, the Coulomb potential cannot be effectively screened at the long-wavelength limit either, given that most of the electric field lines associated with spatially separated charges would reside in the vacuum region and not pass through the 2D material⁶⁵. Therefore, the macroscopic dielectric screening in a 2D insulator is not characterized by a simple dielectric constant tensor as in the 3D crystal, but intrinsically dependent on the wavevector \mathbf{q} . At the long-wavelength limit, the in-plane dielectric function of an isotropic 2D dielectric can be written as $\epsilon(\mathbf{q}_{\parallel}) = 1 + 2\pi\alpha_{2D}|\mathbf{q}_{\parallel}|$, where \mathbf{q}_{\parallel} is the in-plane wavevector and α_{2D} is the polarizability of the 2D dielectric sheet⁶⁶. At the limit of \mathbf{q}_{\parallel} approaching zero, the value of the dielectric function reaches the vacuum value of unity, which means that the Coulomb potential becomes essentially unscreened.

The weakened dielectric screening in 2D materials has a range of consequences for phase transitions. In addition to the aforementioned CDW and Peierls instabilities, which can arise from enhanced electron–phonon interactions, because the thickness of 2D materials is typically smaller than the Debye screening length, 2D materials can be electrostatically doped. A high carrier density of up to $10^{14} \text{ e cm}^{-2}$ can be achieved by applying a gate voltage in the out-of-plane direction⁶⁸. Such electrostatic doping is not possible in 3D materials, because a net positive charge density $\rho [\text{e cm}^{-3}]$ in 3D bulk must lead to the divergence of the cohesive energy per atom, also called 3D Coulomb explosion. In contrast, electrostatic doping of a 2D sheet $[\text{e cm}^{-2}]$ in contact with 3D electrode is energetically feasible, and provides a versatile tool to control carrier density and phase transitions in 2D as long as there are compensating charges outside of the plane (electrical double layer). Indeed, electrostatic doping has been employed to study 2D phase transitions, including classical⁵¹ and quantum^{27,68,69} phase transitions. Remarkably, owing to restricted dielectric screening in the out-of-plane direction, 2D *metals*, such as few-layer WTe₂ and graphene, can also exhibit ferroelectricity^{70,71} or flexoelectricity⁷². Here, the out-of-plane polarity can be switched by an electric field (ferroelectricity) or generated by a strain gradient or a bending curvature⁷² (flexoelectricity). Such macroscopic polarization is not possible in a 3D metal, because electric polarization will be fully screened by free electrons.

Elastic interaction, which is an important long-range interaction in classical phase transition theory, is fundamentally altered when going from $D=3$ to $D=2$.⁷³ 2D materials, such as graphene and transition-metal dichalcogenides, exist in a 3D space and thus, can bend out-of-plane. In-plane compression will trigger buckling instability and therefore, only positive in-

plane stress (tension) can exist along any of the two principal axes of a homogenous stress field. In addition, owing to a lack of constraint in the z -direction, the elastic energy penalty along a phase transformation pathway is less significant than in 3D, in particular, if the membrane is slightly pre-compressed⁵⁹. It is known from physical metallurgy that long-range elastic energy often competes with short-range interfacial energy in determining the dominant length scale in microstructures, for example, the characteristic twin thickness of lath martensites in steel. The replacement of long-range elastic energy by shorter-range elastic bending energy⁷³ and van der Waals adhesion energy fundamentally alters the energy landscape of phase transitions in 2D crystals, as compared to bulk 3D crystals, leading to faster transitions^{59,60} with a lower nucleation energy barrier.

[H2] Spatial control

An important feature of 2D materials is that all atoms are either located on the surface or a few Ångströms away from the surface. Thus, the atoms in 2D materials are more exposed to the environment than in 3D materials. This, in conjunction with internal electronic structure properties, such as van Hove singularities in the electronic density of states⁷⁴, leads to enhanced coupling with external fields, such as electromagnetic waves of a certain frequency (FIG. 3c). Electric fields can penetrate through 2D semiconductors and insulators owing to their atomic thickness and restricted dielectric screening⁵². Based on this, electrostatic doping can uniformly or heterogeneously (“charge puddles”) control the carrier density of the material⁶⁸, and laser and focused electron beams can induce phase transitions at distinct locations⁵⁰. Moreover, adsorbates can cover the surface and induce phase transformations⁷⁵. The possibility of spatially controlled induction of phase transitions by external stimuli also allows atomic-level visualization of the phase transformation process by transmission electron microscopy (TEM)⁷⁶.

Optical or electrical readouts are often sensitive enough to locate 2D materials or detect monolayer-scale changes: consider, for example, Benjamin Franklin’s famed experiment at Clapham pond that described the swift spread of oil on water⁷⁷. Lord Rayleigh carried out a similar experiment about a century later and calculated, for the first time, the thickness of an oleic acid monolayer⁷⁸. Monolayer graphene can also be visually detected by naked eye because it absorbs 2.3% of light⁷⁹ - the physical basis of the Scotch-tape method of 2D sample preparation^{6,23}.

[H2] Thermodynamics

The free energy needed to drive a phase transition is a crucial factor for the application of phase-change materials. A first-order phase transition involves latent heat that originates from a discontinuity in entropy. The latent heat L is given by $L = T\Delta S$, where T is the transition temperature, and ΔS is the difference in entropy between higher- and lower-entropy phases. For a classical solid-to-solid diffusionless phase transition, the entropy difference ΔS mainly arises from a variation in the vibrational, electronic and/or magnetic entropy between two phases, whereas for a phase transition that involves a liquid or gas phase, a change in configurational entropy often dominates. Entropy is an extensive quantity and thus, the volume reduction associated with a dimensionality change from 3D to 2D can lead to a substantial decrease in latent heat. Therefore, in most cases, much less energy is required to induce a readable phase change in 2D materials compared to 3D materials.

Latent heat can be supplied either through contact with a heat bath or by dissipative processes, such as joule heating. In the general case that external work is also involved in driving a first-

order phase transition, the total external energy supply can be determined by the fundamental thermodynamic relation $dU = TdS + \sum_i Y_i dX_i$, where Y_i represents a generalized force and X_i represents the corresponding generalized displacement. For example, for a 2D structural phase transition induced by electrostatic gating⁸⁰, Y_i and X_i take the form of voltage V and total charge Q , respectively. Both X_i and S are extensive quantities and therefore, dimensionality reduction can result in a considerable reduction in the external energy input.

In addition to the volumetric effect, dimensional confinement can also decrease the entropy difference per volume. For a phase transition that involves substantial configurational entropy variation, for example, a melting transition or order-to-disorder solid-state transformation, such a reduction of entropy difference per volume occurs if the 2D material is confined in a heterostructure setup, spatially restricting out-of-plane atomic motion. Confined atomic movement reduces the phase space available for thermal excitation, causing entropy loss. Therefore, interfacial phase-change materials⁸¹, such as GeTe/Sb₂Te₃ superlattices, require considerably less switching energy than bulk Ge₂Sb₂Te₅ alloys, owing to melting-free switching in the confined GeTe layers, which occurs through the local atomic displacements of only the Ge atoms (FIG. 3d).

[H2] Transformation kinetics and defects

A first-order classical phase transition that entails a discontinuous change in the order parameter necessarily involves the nucleation and growth of a new phase. The kinetics of nucleation and growth are both substantially affected by D . For example, given that a first-order phase transition involves latent heat, the thermal conductivity of 2D materials, which depends on the dimensionality⁸², affects the growth kinetics. Whether the 2D material is on a 3D substrate or not can also matter. In addition, the atomic vibrational frequency, the reaction coordinate of unit processes and the energy barrier for atomic rearrangements control the transformation kinetics and depend on dimensionality. Phase boundaries and domain walls in 2D materials are quasi-1D objects, in contrast to the 2D nature of phase and domain boundaries in bulk materials. In particular, the great reduction of elastic energy constraints in 2D materials facilitates displacive phase transitions with glissile transformation interfaces. For example, an in situ TEM study of the phase transition between two structural polymorphs of monolayer MoS₂ showed that the transformation between the semiconducting (2H) and metallic (1T) phase involves the initial formation of an intermediate phase and subsequent gliding of atomic planes of sulfur and molybdenum within a single layer⁷⁶ (FIG. 3e) that would have very little elastic energy penalty, especially if the 2D membrane is slightly pre-compressed⁵⁹, i.e. given some “slack”.

Defects are the essential facilitators and by-products of phase transitions, and can also serve as preferred nucleation sites for new phases. In 2D materials, the physics and mechanics of defect nucleation and propagation are different than in 3D systems^{83,84}, leading to distinctly different defect population dynamics and inelastic relaxation mechanisms; namely, while the mechanical strength of large-volume 3D bulk materials are mainly controlled by the propagation of existing glissile defects like dislocations and cracks, the plastic flow or fracture strength of 2D materials are often controlled by defect nucleation. Consider, for example, that while there are glissile dislocations in 2D materials such as the pentagon-heptagon defect in graphene⁸⁵, there is no equivalence of the Frank-Read dislocation source in 3D materials. These factors enable 2D materials to withstand higher elastic strain before irreversible strain-energy relaxation processes occur, such as fracture and plasticity, as compared to 3D materials⁸⁴. For

example, experimentally confirmed tensile elastic strain limits of graphene and MoS₂ monolayers can be as high as 20% and 10%, respectively^{86,87}. In contrast, the elastic strain limit of many bulk inorganic materials is typically only ~0.2%, indicating that a substantially larger strain space becomes available for controlling the physical properties and phase transitions of 2D materials. Thus, elastic strain engineering⁸⁸ and inelastic strain engineering of 2D materials are experimentally more feasible than in 3D bulk materials owing to the higher tolerance of 2D materials to residual tensile and shear stresses before inelastic deformation such as plasticity, creep, or damage and fracture, occur. Large tensile strain-induced phase transitions have been theoretically⁴⁸ and experimentally^{89,90} demonstrated in 2D materials.

2D materials placed on curved surfaces of 3D materials also show defect mechanics distinct from 3D materials. For example, in 2D crystals self-assembled on the surface of liquid droplets, the spatial curvature of the droplets can lead to the free termination of grain boundaries in the crystal, resulting in a disclination monopole⁹¹. The disclination monopole is energetically too expensive to form in 3D bulk crystals, and therefore, grain boundaries in 3D bulk must terminate at triple junctions connected to other grain boundaries, which is not necessarily the case in 2D materials with 3D curvature.

[H2] Corrosion and passivation

Environmental stability is crucial for the practical usage of 2D materials. Chemical complexity and thermochemical stability issues are already well-known for grain boundaries and surfaces, as reflected by the Langmuir-McLean and Fowler-Guggenheim isotherms⁹². Generally speaking, if one regards surfaces and grain boundaries as 2D phases (embedded in a 3D phase), they have different equilibrium chemistries as exemplified by interfacial segregation and Gibbs adsorption isotherm, and also different thermochemical or electrochemical stability windows from the 3D host phase, meaning they can undergo phase transitions even when the 3D host does not, when an intensive thermodynamic variable (temperature T , stress σ , voltage U , etc.) is varied. Corrosion, which is the degradation of materials in a chemical environment, could be considered a phase transition.

Many 2D crystals corrode in air, and, with the exception of graphene, almost all metallic 2D materials have air stability problems⁹³ even at room temperature. For many 3D materials, the air stability problem is circumvented by the formation of a surface passivation layer; for example, a 2–5 nm stable layer of alumina is formed if aluminum is exposed to the air, that protects the material. Here, passivation layers would only make up a small fraction of the otherwise unreacted bulk material. By contrast, the thickness of 2D materials is comparable or even smaller than that of passivation layers, making their passivation challenging. The corrosion of materials depends on the availability of oxygen (O₂) and water (H₂O) or hydrogen (H₂). By changing the partial pressure of O₂ or H₂, the redox potential and chemical transformation can be controlled, illustrated in the Pourbaix diagram⁹⁴, which is a chemical or electrochemical phase diagram. A boundary line in the Pourbaix diagram corresponds to a chemical transformation induced by the environment and the redox potential. Most 2D materials cannot form a natural passivation layer from their own reaction products and therefore, strategies are required to restrict the contact of the material with O₂ and H₂O and to prevent the oxidation-dissolution cycle of corrosion. For example, environmentally fragile 2D materials can be covered with more robust materials, such as graphene or hexagonal boron nitride^{95,96}, or coated with water-repelling molecular monolayers such as linear alkylamines⁹⁷.

[H2] New phase engineering concepts

The unique features of 2D phase transitions have led to new concepts for engineering the phases and properties of 2D materials. For example, the possibility of precise spatial addressability (since 2D locating is much easier than 3D locating), strong coupling with light and the propensity for displacive phase transitions enable optomechanical switching. Here, a laser beam is used to induce ultrafast, diffusionless, order-to-order phase transitions in 2D materials with degenerate ground states⁵⁹. The large tensile elastic strain limit of 2D materials allows the imposition of a large elastic strain tensor for tuning the electrical⁹⁸, optical⁹⁹ and catalytic¹⁰⁰ properties of 2D materials, and for controlling their phase transitions⁸⁸. 2D materials cannot sustain compressive strain and they have less constraints for structural relaxation in the layer-normal direction, as compared to 3D materials. Therefore, compressive strain can lead to the formation of ripplocations⁷³ (FIG. 3f), which are line defects that play an important role in the deformation of layered materials. Furthermore, the atomic-level thickness of 2D materials and their weak environmental stability have led to the development of new protection strategies, such as coating with molecular layers on 2D materials⁹⁷ (FIG. 3g).

[H1] 2D phase transitions

A variety of 2D phase transitions have been investigated thus far. Here, we discuss notable examples, illustrating the richness of phase transformation behavior in 2D materials.

[H2] Polymorphic phase transitions

The most prominent examples of 2D materials discovered so far that exhibit polymorphic phase transitions in near-ambient conditions are derived from chalcogenides with layered structures^{10,101-106}. Compared to oxygen and most halogens (F, Cl, Br), chalcogen elements (S, Se, and Te) have a relatively small electronegativity and thus, in many chalcogenides, ionic and covalent bonding compete, which leads to the generation of structural polymorphs with different bonding configurations that are close in energy. Therefore, perturbations induced by weak external stimuli can drive polymorphic transitions in these materials. The most widely studied 2D materials exhibiting structural phase transitions are group 6 transition metal dichalcogenide monolayers with the chemical formula MX_2 , where M stands for Mo or W, and X stands for S, Se or Te. Monolayer MX_2 materials have three well-known structural polymorphs^{46,107}, that is, 2H, 1T and 1T' (FIG. 3a). The 2H phase has a trigonal prismatic coordination pattern, whereas the coordination patterns in the 1T and 1T' phases are octahedral and distorted octahedral, respectively. Monolayer MX_2 in the semiconducting 2H phase has an optical bandgap in the range of 1.0–2.5 eV¹⁰⁸. The 1T phase is metallic, but unstable in isolation and subject to Peierls distortion^{48,49}. The 1T phase spontaneously transforms into the 1T' phase through the distortion of octahedral coordination. The 1T' phase of monolayer MX_2 was first theoretically predicted³³, and then experimentally confirmed^{34,35,109} to be a quantum spin Hall insulator with a sizable bandgap on the order of 0.1 eV^{33,49,110}. The 1×2 Peierls reconstruction causes the metal-dominated d -band, which is typically the electron donor, to become *lower* in energy than the chalcogen-dominated p -band around the Γ -point, thus causing a topological band inversion and “tying a knot” in the electronic band structure in Brillouin zone. This gives a perfect edge conductance of $e^2/h=1/25.813\text{k}\Omega$ at $T<100\text{K}$ for 1T'-WTe₂ monolayer³⁵ with magnetic-field dependence, and combined with the fact that it is also a 2D superconductor at $T_c\approx 0.7\text{ K}$ ¹¹¹, gives rise to the prospect of using it for topological quantum computing.

Theoretical calculations based on density functional theory (DFT) indicate that the 2H phase is the ground-state phase of all monolayer MX_2 , except for WTe_2 , for which the 1T' phase has the lowest energy⁴⁸ (FIG. 3b). The energy differences between the 2H and 1T' phases decrease in the order of $\text{MS}_2 \rightarrow \text{MSe}_2 \rightarrow \text{MTe}_2$. For MoS_2 , the DFT-computed energy of the 1T' phase is ~ 0.5 eV per formula unit higher than that of the 2H phase, whereas for MoTe_2 , the DFT-computed energy is only 43 meV per formula unit higher. Thus, chemical processes are required for the transition between the 2H and 1T' phases of MoS_2 . By contrast, for MoTe_2 , the H-to-T' transition can be induced by non-chemical factors, including temperature^{49,112}, tensile strain^{48,89,90}, laser irradiation⁵⁰, electrostatic doping^{51,113} and electric fields⁵².

[H3] Chemically-induced transition

The transition of MoS_2 from the 2H phase to the 1T or 1T' phase occurs through the intercalation of alkali metals^{107,114,115} by charge transfer from the s orbitals of alkali metals to the d orbitals of the transition metal atoms. The increase in d -orbital filling causes the stability of the 1T or 1T' phase to be higher than that of the 2H phase beyond a certain doping threshold. This phenomenon can be understood in terms of crystal field theory^{10,101,116}. An incomplete doping-induced phase transition in monolayer MoS_2 can give rise to the coexistence of 2H, 1T, and 1T' phases with coherent phase boundaries⁴⁶. The 2H phase of MoS_2 is semiconducting, whereas the 1T phase is metallic, motivating the patterning of metallic and semiconducting regions on monolayer MoS_2 by area-selective phase transformation⁴⁷ (FIG. 3c). The metallic 1T region can serve as the low-resistance contact for MoS_2 transistors, leading to improved device performance that includes high drive currents, high electron mobility, low subthreshold swing values, and large on/off ratios⁴⁷.

[H3] Thermally-driven transition

Compared to MoS_2 , the 2H and 1T' phases of MoTe_2 have a smaller energy difference, enabling a wider range of external stimuli to induce the 2H-1T' phase transition. Temperature alone can drive the phase transition of MoTe_2 , from the 2H phase to the 1T' phase, owing to the higher vibrational and electronic entropy of the 1T' phase as compared to the 2H phase^{49,112}. The transition temperature in bulk MoTe_2 , which depends on the deficiency or excess of Te, is 500–820 °C, with Te deficiencies causing lower transition temperatures⁴⁹ (FIG. 3d). Theoretical calculations indicate that the transition temperature difference between bulk and monolayer MoTe_2 is modest ($<20\%$), owing to weak phonon dispersion along the out-of-plane direction¹¹². By alloying MoTe_2 with WTe_2 , the 2H-to-1T' phase transition temperature can be substantially decreased¹¹², because the 1T' phase is the stable phase of WTe_2 at ambient conditions.

[H3] Strain-driven transition

Tensile strain-induced transitions between the 2H and 1T' phases of MoTe_2 and other MX_2 monolayers have been theoretically⁴⁸ and experimentally investigated^{89,90}. The driving force for strain-induced phase transitions originates from the different unit-cell dimensions of the 2H and 1T' phases, allowing the system to minimize the thermodynamic potential by transforming into a phase that reduces the elastic strain energy. The critical strain value needed to drive the 2H-to-1T' phase transition is expected to depend on the mechanical boundary conditions⁴⁸. Experimentally, a phase transition in MoTe_2 thin films has been demonstrated at room temperature with a 0.2% in-plane biaxial strain⁸⁹. This level of strain can be generated by

mechanical deformation of a suspended 2D material using an AFM tip⁸⁹, or through the inverse piezoelectric effect of a ferroelectric, to which the 2D material is clamped⁹⁰ (FIG. 3e).

[H3] Laser-driven transition

Laser irradiation can cause the irreversible transition of a multilayer MoTe₂ in the 2H phase into the 1T' phase (FIG. 3f), owing to the generation of Te vacancies⁵⁰. DFT calculations showed that the formation of 3% Te vacancies alters the relative stability between the 2H and 1T' phases. This mechanism is consistent with the reduced 2H-to-1T' thermal phase transition temperature in MoTe₂ with a Te deficiency⁴⁹. Laser-induced phase transition enables the local patterning of metallic 1T'-regions in 2H-MoTe₂ multilayers, akin to phase patterning using chemical methods in MoS₂⁴⁷. The metallic 1T' phase forms an Ohmic homojunction with the semiconducting 2H phase, substantially increasing the carrier mobility of MoTe₂ transistors.

[H3] Electrostatic-doping-driven transition

Electrostatic doping through the application of a gate voltage can generate a carrier density of up to $10^{14} \text{ e cm}^{-2}$ in monolayer MX₂⁶⁸, corresponding to $\sim 0.1 \text{ e}$ per formula unit. This feature has motivated the study of electrostatic-doping-induced structural phase transitions in MX₂ monolayers. In an electrostatic gating device configuration, in which an appropriate dielectric is sandwiched between a MX₂ monolayer and a metal plate, a gate voltage of several volts can drive a 2H-to-1T' phase transition of monolayer MoTe₂, as shown by DFT-based theoretical analysis^{80,113}. Electrostatic doping-induced phase transition was further experimentally demonstrated in monolayer MoTe₂ using ionic liquid as the dielectric in a field-effect-transistor configuration⁵¹ (FIG. 3g); a gate voltage of $\sim 4 \text{ V}$ fully converted the 2H phase into the 1T' phase.

[H3] Electric-field-driven transition

In vertical devices based on MoTe₂ and Mo_{1-x}W_xTe₂ thin films, an electric field applied across the film thickness direction can induce the transition of MX₂ from the 2H phase into a distorted transient structure, 2H_d, in which the monolayer structure is distinct from the three known phases of MX₂ (FIG. 3h)⁵². The exact atomic configuration of monolayers in the 2H_d phase has not yet been fully resolved; however, experimental evidence⁵² suggests that 2H_d monolayers have a transitional structure, between 2H and 1T'. As a side remark, a strong enough vertical electric field can also cause topological-insulator to normal-insulator transition within the same structural polymorph³³, an extremely rapid (femtosecond level) transition in the quantum Z₂ invariant for electronic structure.

[H2] Ferroic phase transitions

Ferroics possess two or more orientation states (domain variants), which are degenerate in free energy and can be switched by an external field¹¹⁷. Ferroics can be categorized into four types, based on the properties associated with the orientation states, that is, ferroelectrics, ferromagnets, ferroelastics, and ferrotoroidics. Ferroics have been extensively studied in bulk form. Ferroelectrics show spontaneous electric polarization, which can be switched by an electric field; ferromagnets show spontaneous magnetization, which is switchable by a magnetic field; ferroelastics possess domain variants with spontaneous stress-free strain, which can be switched by applying stress; and ferrotoroidics possess internal chiral order. Ferroic materials are typically formed through ferroic phase transitions characterized by the loss of

point-group symmetry operations, for example, by spatial inversion in the case of ferroelectricity, rotational symmetry in the case of ferroelasticity, or time-reversal symmetry in the case of ferromagnetism¹¹⁷. A material is multiferroic if more than one ferroic order is present.

[H3] Ferroelastic transition

The high elastic strain limit and the abundance of structures with low symmetry render 2D materials promising candidates for distinct mechanical response related to ferroelasticity. In group 6 transition metal dichalcogenide monolayers, the 1T-to-1T' phase transition was theoretically predicted to be a ferroelastic phase transition accompanied by spontaneous hydrostatic and shear strains⁵⁷, which has been supported experimentally¹¹⁸. The three symmetry-equivalent directions of structural distortion lead to three orientation variants with distinct unit-cell dimensions. Thus, transformation strains (also called stress-free strains) of a variant can couple to the energetics of the system, causing the transformation from one orientation variant to another. DFT calculations suggested that a tensile strain of a few percent is sufficient to switch monolayer 1T'-WTe₂ from one orientation domain to another. Strain energy minimization can also lead to the coexistence of different domains and the stable formation of domain or phase boundaries (FIG. 4a). Monolayer 1T'-MX₂ are quantum spin Hall insulators³³ and therefore, their phase boundaries possess distinct electronic transport properties due to the bulk-edge correspondence (BEC) in topologically nontrivial systems^{119,120}.

First-principles calculations have also shown that α -SnO becomes ferroelastic if the thickness of the material is at the monolayer level¹²¹. The low-temperature ferroelastic phase of α -SnO has an orthorhombic symmetry with two equivalent orientation states. The degenerate structural ground states can be energetically biased when illuminated with a linearly polarized laser pulse⁵⁹. For example, when the system is subjected to an alternating electric field with a particular polarization direction, the anisotropic dielectric response of the low-symmetry ferroelastic phase will lead to non-degenerate free energy landscape along the reaction coordinate of the phase transformation, which is similar to optical tweezing of dielectric microbeads, but along the generalized reaction coordinate of the phase transformation instead of x - y position of a bead. Phase-change materials have been proposed to operate on the basis of such optomechanically driven 2D martensitic transitions^{59,60}, which have multiple advantages compared to traditional thermally-driven phase-change systems (such as Ge-Sb-Te alloys), including faster transformation kinetics, reduced energy dissipation, and more robust resistance against functional fatigue.

[H3] Ferroelectric transition

Ferroelectricity in thin-film perovskite materials has been intensively studied¹²²; however, in ferroelectrics with out-of-plane polarization, the ferroelectric order disappears if the film thickness is below a critical value, owing to the effects of the depolarization field and surface reconstruction^{122,123}. By contrast, in-plane polarization is less susceptible to the thickness-dependent depolarization effect, and thus, ferroelectric order may remain stable in 2D. Indeed, robust in-plane ferroelectricity has been experimentally realized in atomic-thick SnTe, with a ferroelectric transition temperature of 270 K⁵⁵ (FIG. 4b). Ferroic phase transitions have also been theoretically investigated in group-IV monochalcogenide MX (M=Ge, Sn; X=S, Se),

which are closely related to SnTe ^{58,124-128}. MX monolayers can further be ferroelectric and ferroelastic at the same time, making them multiferroic.^{58,124}

Ferroelectricity has also been experimentally demonstrated in other 2D systems, including In_2Se_3 ^{56,129-132}, CuInP_2S_6 ^{133,134}, monolayer MoTe_2 with distorted 1T phase^{135,136}, as well as bilayers and trilayers of WTe_2 ⁷⁰. In particular, out-of-plane ferroelectricity can be present in 2D semimetals, for example, in few-layer WTe_2 , because dielectric screening in the layer-normal direction is suppressed in a 2D system. Remarkably, ultrafast symmetry switching behavior was observed in 3D bulk WTe_2 ⁵³, a type-II Weyl semimetal¹³⁷. In contrast to monolayer 1T' WTe_2 , which is centrosymmetric, multilayer and bulk WTe_2 have an orthorhombic structure with distorted octahedral coordination and broken inversion symmetry (the T_d phase, space group $Pmn2_1$)¹³⁸. Upon electric gating along the layer-normal direction, multilayer WTe_2 shows ferroelectric switching with a butterfly-shaped conductance curve^{54,70}. Different from local atomic-movement-induced ferroelectric transition¹³⁹ (for example, through breaking and switching of local W-W bonds, or by local distortion and rotation of W-Te bonds), low-energy interlayer gliding is likely responsible for the switching behavior in multilayer and bulk WTe_2 ^{71,140}.

[H3] Ferromagnetic transition

A consequence of the Hohenberg-Mermin-Wagner theorem^{12,13} is that long-range ferromagnetism cannot exist at finite temperature in 2D, if the spin Hamiltonian has a continuous symmetry with sufficient short-range interactions¹³, as ample gapless spin waves will destroy the ferromagnetic state. However, ferromagnetism can be stabilized at finite temperature if magnetic anisotropy is present in the system¹⁴¹⁻¹⁴³. Furthermore, finite size effects can stabilize phase transitions in 2D, including a ferromagnetic transition, because the divergence of fluctuations in 2D is only logarithmic with sample size and thus, a slow divergence⁶². Ferromagnetism has been experimentally observed in a range of 2D materials⁴¹⁻⁴⁵, including semiconducting $\text{Cr}_2\text{Ge}_2\text{Te}_6$ ⁴⁰, CrI_3 ³⁹, CrXBr ($\text{X}=\text{S}, \text{Se}$)¹⁴⁴⁻¹⁴⁷ and metallic Fe_3GeTe_2 ^{70,148,149} (FIG. 4c,d).

[H2] High-temperature diffusive phase changes

In diffusive transformations, changes in labelled atomic registries are non-deterministic, and the macroscopic order parameters of the new phase or domain do not reveal detailed atom-to-atom correspondences between the old and new phase, because changes in the registry are caused by multiple randomized atomic hops. By contrast, in an ideal displacive transformation, the nearest-neighbour relation of an atom either remains unchanged or changes in a deterministic way within a domain variant. Displacive transformations are often driven by a strong enough directional field, for example, stress, an electric field or a magnetic field. Most ferroelastic and ferroelectric transitions, which involve the loss of rotational symmetry or spatial inversion symmetry, are displacive transformations. The kinetics of displacive transformations are characterized by a threshold-type behavior of the domain-growth speed v with respect to the thermodynamic driving force F ; the nonlinear $v(F)$ is nearly zero below a certain threshold, but dramatically increases above a threshold F_{thresh} , and then saturates at the phonon group velocity. The growth speed of a displacive phase-change domain thus has to be fitted by a highly nonlinear function $v \propto (F/F_{\text{thresh}})^n$ where n can be as large as 20. In comparison, diffusive transformations have a more linear-response type growth velocity law $v(F)$ where n is 1 or close to 1, but is often much more temperature sensitive.

Diffusive motion is usually thermally activated and therefore more prevalent at high temperatures, at which atomic defects have higher concentration and also become more labile, allowing the system to fully sample the configurational space (entropy), which results in an optimal organization (phase) and thus, approaching the equilibrium phase diagram. By changing the chemical precursors during chemical vapor deposition, 2D [Mo,W]S₂ forms either a two-phase MoS₂/WS₂ heterostructure with sharp phase boundaries at 650°C, or a single-phase random solid solution Mo_xW_{1-x}S₂ at $\geq 680^\circ\text{C}$ ¹⁵⁰ (FIG. 5a). Compared to lattice diffusion in 3D crystals, diffusion in 2D crystals is easier because surface diffusivity is commonly acknowledged to be much faster than bulk diffusivity. The phase-separated MoS₂/WS₂ heterostructure can be applied in optoelectronics, and the solid-solution Mo_xW_{1-x}S₂ alloy phase can be used to tune the relative phase stabilities of different polymorphs (2H, 1T, and 1T') by changing the Mo/W ratio. Generally speaking, at high temperatures, it is important to probe and precisely navigate the equilibrium temperature-composition phase diagram.

The size, morphology and defect content of 2D materials not only depend on the composition, but also on the growth conditions (FIG. 5b). For example, large-area growth of 2D metal chalcogenides can be achieved by using molten salt as a growth medium,¹⁵¹ which reduces the melting point of metal-ion-bearing precursors and allows passivation of different growth edges¹⁵². Moreover, under out-of-thermal-equilibrium conditions, for example, under external irradiation (photons, electrons), electrical current or plasma treatment, phase changes can occur in a manner that does not abide by the equilibrium phase diagram¹⁵³. In addition, conditions can be designed to directly grow thermodynamically metastable phases^{105,154,155} (FIG. 5c).

2D and 2D-templated diffusive phase transformations have played a key role in the development of phase-change memory (PCM) materials. PCM provided the basis for information storage in CDs and DVDs as well as for the newest generation of non-volatile solid-state drives. For example, sub-nanosecond writing has been achieved with Sc_{0.2}Sb₂Te₃ as the active crystalline-to-amorphous phase change material¹⁵⁶. However, several challenges remain to be addressed, including high temperature-induced volatility and resistance-level drifting¹⁵⁷, which will require a thorough understanding and fine control of the ionic motion during device operation. Owing to their atomic thickness, 2D active materials have distinct thermal conduction characteristics and phase transformation kinetics, featuring less elastic energy constraints, facile diffusion kinetics and sensitive coupling to external conditions, as compared to 3D bulk materials. These characteristics can be exploited to improve the temperature-driven read, write and storage performance of PCM devices, increasing speed, reducing energy consumption and increasing storage density. For example, in a PCM device constructed from a 2D Sb₂Te₃-GeTe superlattice, the diffusion of Ge and Te atoms within a 5Å-thick GeTe 2D crystal layers can be modulated by the immobile and strained Sb₂Te₃ 2D crystal layer¹⁵⁸. The strained Sb₂Te₃ layer affects the quenching-to-amorphous and crystallization kinetics of the GeTe layer in the van der Waals heterostructure, leading to increased atomic diffusivity in the active layer and higher energy efficiency of the device. Similarly, 2D TiTe₂/3D Sb₂Te₃ phase-change heterostructures also show ultralow noise and drift¹⁵⁹. The 2D TiTe₂ layers in the heterostructure suppress damage in the 3D Sb₂Te₃ structure by blocking the electrical-field-assisted transport of charged species (FIG. 5d).

[H1] Technological applications

The possibility to change material properties by 2D phase transitions, which can be coupled to external stimuli, enables a broad range of potential devices applications. For example, the 2H-to-1T or 2H-to-1T' phase change of transition metal dichalcogenides can be induced by alkali metal intercalation, which can be exploited to improve the electrocatalytical performance of these materials for electrochemical hydrogen gas evolution¹⁰⁰, or to fabricate lateral heterostructures of semiconducting and metallic phases for 2D electronic devices with low contact resistance^{47,101}. Such ohmic lateral heterophase junctions formed between the semiconducting 2H and metallic 1T' phases of MoTe₂ can also be fabricated by laser-induced phase transition, which causes the 2H-to-1T' transition of MoTe₂ as a result of the creation of Te vacancies⁵⁰.

The electrical and/or optical property changes associated with 2D phase transitions are particularly interesting for the fabrication of non-volatile memories and transport devices. For example, resistive random access memories and ferroelectric phase change transistors have been designed based on electric-field-induced⁵² and strain-induced⁹⁰ 2H-to-1T' phase transitions of transition metal dichalcogenides, respectively. Since the 1T' phase of group-6 monolayer transition metal dichalcogenides is a quantum spin Hall insulator³³, controlling their topological electronic properties based on the above phase transition can potentially enable the design of new quantum electronic devices.

2D materials with ferroic phase transitions and properties enable the design of a range of ultrathin and flexible smart materials and functional devices, with potential usages in micro/nano systems and conformal devices; for example, 2D ferroelastics can be used for nanoscale actuators and shape-memory materials⁵⁷; 2D ferroelectrics can be applied for memory devices⁵⁵ and ferroelectric tunnel junctions¹⁶⁰; and 2D ferromagnets can be used for spintronics^{42,44}. Certain 2D multiferroics, such as group IV monochalcogenides, can exhibit strong coupling between ferroelectric and ferroelastic orders as well as strong and anisotropic excitonic absorption¹⁶¹, making them attractive for the development of 2D ferroelectric memory, 2D ferroelastic memory, 2D nonvolatile photonic memory and 2D ferroelectric excitonic photovoltaics⁵⁸.

Several novel device prototypes that take advantage of phase transitions in 2D materials have been experimentally demonstrated. For example, excellent memristive behavior can be achieved by exploiting the reversible 2H-to-1T' phase transition of layered MoS₂ films, driven by electric-field induced Li⁺ ion redistribution, for example, for the implementation of artificial neural networks in neuromorphic computing¹⁶² (FIG. 6a). Metallic-semiconducting (1T/1T'-to-2H) phase heterojunctions of MoS₂ layers have been used to fabricate atomically thin and flexible lateral Schottky diodes with ultralow junction capacitance and low series resistance. These Schottky diodes enable the design of flexible and ultrafast rectifiers, which can convert A.C. electrical signals waves into D.C. electricity at a frequency of up to 10 GHz. Such flexible rectennas can harvest wireless radio-frequency energy at the WiFi band¹⁶³ (FIG. 6b,c).

In addition, ferroelectricity-driven nonlinear photocurrent switching and a ferroelectric nonlinear anomalous Hall effect have been theoretically predicted^{140,164} and experimentally demonstrated⁵⁴ in time-reversal invariant few-layer WTe₂. Upon ferroelectric transition in few-layer WTe₂, nonlinear anomalous Hall voltage switches the sign in odd-layer WTe₂ (except

monolayer 1T' WTe₂), but remains invariant in even-layer WTe₂ (FIG. 6d,e). This oscillation originates from the absence and presence of Berry curvature dipole reversal and shift dipole reversal owing to distinct ferroelectric transformations in even- and odd-layered WTe₂¹⁴⁰. These theoretical predictions and experimental demonstrations establish Berry curvature and shift dipole as nonlinear order parameters, opening a route toward unconventional memory devices, such as a Berry curvature memory based on nonlinear susceptibility. Weak interlayer gliding in WTe₂ also offers a strategy to engineering and controlling 2D ferroelectric patterns by electric gating and optical switching, enabling high speed and low activation energy for electromechanical, optomechanical and neuromorphic applications.

Finally, optomechanical devices could benefit from the strong coupling between 2D phase change materials and light, as well as from the extraordinary mechanical properties of 2D materials. For instance, a linearly polarized laser pulse can drive an ultrafast diffusion-less martensitic phase transition of 2D ferroelastic materials, for example, of monolayer SnO and SnSe⁵⁹. Memory devices based on such optomechanical martensitic transitions require an order of magnitude lower energy input than traditional Ge-Sb-Te alloys⁵⁹ (FIG. 6f). In bilayer hexagonal boron nitride, a laser with selected frequency can modify the energetics of different (meta)-stable stacking patterns, and reversibly and controllably switch the stacking patterns without barriers, making this material attractive for data storage and optical phase masks⁶⁰ (FIG. 6g).

[H1] Outlook

To enable the industrial applications of 2D materials, the realization of large-area growth of high-quality materials, facile and robust materials processing, high-performance devices and systems, as well as long service lifetimes all need to be achieved. The phase behavior of 2D materials is important in all these growth-processing-service steps. Furthermore, phase transitions have long been explored to improve or enable distinct material functionalities. In particular, 2D phase transitions have a variety of unique features, which can be exploited for electronic, optical, magnetic, electromechanical¹⁶⁵, optomechanical⁵⁹ and magnetomechanical¹⁶⁶ systems. However, important challenges remain to be addressed in the field of 2D phase transitions.

[H2] Discovery and characterization of new 2D phase-change materials

Most known 2D phase-change materials are derived from chalcogenides that have a layered bulk structure. Expanding the portfolio of 2D phase-change materials will open new application spaces. In principle, 2D phase-change materials could exist in a range of materials systems, either in a freestanding or substrate-supported form, for example, oxides, pnictides and halides. First-principles calculations can play a key role in the discovery of new phase-change materials; for example, crystal structure prediction tools¹⁶⁷ and machine learning¹⁶⁸⁻¹⁷⁰ could be applied to explore the free energy landscape and discover new 2D phase-change materials, which may not even have a bulk counterpart. Importantly, certain phase-change 2D materials could be entropically stabilized at elevated temperatures, as a result of large configurational entropy (compositional complexity)¹⁷¹ or vibrational entropy (due to the presence of soft phonon modes or strong lattice anharmonicity)¹⁷², and remain stable or metastable at room temperature. These materials may not be accessible in traditional structural prediction algorithms¹⁶⁷ or from the mining of existing crystallographic databases¹⁷³⁻¹⁷⁷, as at present these approaches typically do not consider the entropy contribution to phase stabilization.

[H2] Understanding the kinetics and controlling 2D phase transitions

The thermodynamics of 2D phase transitions have been extensively studied; however, the kinetics of 2D phase transitions remain less explored. In 2D materials, the transformation interfaces and pathways are expected to be substantially different than in bulk materials. Understanding kinetics is required to precisely control 2D phase transitions. In situ structural studies during phase transitions may be performed in real space (for example, by in situ TEM¹⁷⁸) or in reciprocal space (for example, by in situ X-ray diffraction¹⁷⁹ or ultrafast electron diffraction¹⁸⁰). In parallel with structural evolution, the accompanying changes in electronic structure, vibrational spectra, or symmetry properties can be probed by time-resolved angle-resolved photo-emission spectroscopy (tr-ARPES)¹⁸¹, time-resolved infrared and Raman spectroscopy, or time-resolved second-harmonic generation (SHG) spectroscopy¹⁸², respectively. Recent advances in ultrafast dark-field electron microscopy further allow the real-space imaging of order-parameter dynamics during structural phase transitions in transition metal dichalcogenides with nanometer spatial and femtosecond temporal resolution¹⁸³. Combining in situ TEM experiments, aberration-corrected TEM imaging of atomic-level structural evolution⁷⁶, and dark-field TEM imaging of order-parameter and microstructural dynamics^{183,184}, a multiscale view of the kinetics of 2D structural phase transitions driven by a variety of stimuli can be obtained.

[H2] Flexural engineering of 2D phase transitions

The flexural mode^{73,185} in 2D materials offers the possibility to control and configure 2D phase transitions, which is difficult to achieve in bulk materials; for example, giant pseudomagnetic fields⁹⁸ and exciton funneling⁹⁹ in inhomogeneously strained 2D materials. Flexo-electric, flexo-magnetic and flexo-optic couplings likely affect 2D phase transitions, which may allow precise control of phase changes at a desired temperature and spatial location, by configuring specific structural patterns (for example, ripples). Such periodic patterns could be achieved by stacking 2D materials on a soft substrate, followed by mechanical deformation (for example, tension and compression) or temperature change (for example, by using substrates with different thermal expansion coefficient), to construct periodically patterned ripples and wrinkles. Here, the combination of out-of-plane interfacial energy and in-plane patterns may affect the phase transition. In addition, in 2D materials stacked on a substrate with a large lattice mismatch or finite twisting angle, spatial inhomogeneity in the interlayer interaction and separation is naturally induced, which leads to the creation of tunable periodic structures with a strain gradient and flexoelectricity, as observed in Moiré superlattices¹⁸⁶. The flexoelectricity could be exploited to control local deformation and thus, phase transitions by external electric field.

[H2] Phase transitions in stacked 2D materials and van der Waals heterostructures

Monolayer 2D materials have ultrathin thickness and cover a wide variety of electronic-structural types (metals, semiconductors, insulators, topological insulators and topological metals³³). Their absence of surface dangling bonds and the weak van der Waals interactions between layers enable the construction of stacked layers and van der Waals heterostructures with infinite possibilities⁹³. In such stacked materials, there is a hierarchy in the bonding energy scales between intralayer and interlayer interactions (covalent versus mostly van der Waals, with the former being much stronger^{71,187}) in stacked layers, yet the interlayer electronic interactions can still be strong and have a significant influence on the properties of the resulting

materials. The emergence of flat bands and strong-correlation physics from stacked bilayer graphene with a twisting angle including superconductivity transitions^{27,30,188,189}, as well as the transition of monolayer MoS₂ from a direct-bandgap semiconductor to an indirect-bandgap semiconductor in bilayers⁶⁴ are eminent examples.

Phase transitions of 2D materials become richer in stacked 2D materials and van der Waals heterostructures, as in addition to monolayer structural degrees of freedoms (polymorphs, domain variants, and ripples), additional stacking degrees of freedom (stacking materials and stacking order, including the relative shifts and orientation angles between layers¹⁹⁰) also come into play. These stacking degrees of freedom are often easier to manipulate as the energy barriers between stacking orders are usually smaller than the monolayer structural degrees of freedom, owing to weak interlayer bonding interaction, thus facilitating their control by external stimuli. The interplay between multiple external fields (electrical, optical, magnetic, thermal, mechanical, or chemical), monolayer phase transitions, and stacking phase transitions can result in rich materials responses by altering band structures and topologies⁵³, electron-phonon interactions, and electron-electron correlations^{27,30}, to name a few, leading to new fundamental discoveries and device concepts. As an example of phase transition driven by a change in layer stacking geometry, electrically driven interlayer sliding in few-layer WTe₂ accompanied by ferroelectricity and the ferroelectric nonlinear anomalous Hall effect based on Berry curvature dipoles open up avenues for the development of 2D semimetal-based memory devices⁵⁴. This concept can be expanded to ferroelectric few-layer 2D semiconductors (for example, monolayer GeSe and SnTe)¹⁶⁴ and topological quantum materials (e.g. MnBi₂Te₄ that shows quantum anomalous Hall effect)¹⁹¹. For instance, a ferroelectric transition could be induced in odd-layer GeSe or SnTe and the corresponding shift current response could be measured. Demonstration of shift current switching would provide the experimental foundation for realizing shift-dipole-based nonlinear memory¹⁶⁴. Furthermore, optomechanics could play a key role in the phase engineering of stacked 2D materials by shifting interlayer stacking configurations through altering the energy landscape by a light field with a selected frequency⁶⁰, or through the excitement of coherent phonons by terahertz light¹⁹², driving the system into a metastable or more stable phase. This kind of strongly nonlinear light-matter interactions, driving phonon-polaritons to the nonlinear regime and even beyond the convex part of the phonon energy landscape, could lead to a variety of nonlinear optical and stimulated emission effects that are quantum mechanical in nature. Optomechanics could also result in the change of the twist angles of stacked 2D materials, either through the direct change of orientation degrees of freedom accompanying of a light-induced ferroeleastic transition⁵⁹, or by the mechanical coupling to the strain induced by optomechanical phase transitions, thus contributing a useful set of tools in the emerging field of twistronics^{189,193-195}.

In closing, we note that the rapid progress in semiconductor technology has given us the Moore's law. Commercial transistors can now be produced with a feature size of 5 nm, which may soon be reduced to 3 nm and below¹⁹⁶. Applying 2D materials exhibiting phase transitions could address the challenge of further miniaturization, resulting in more energy-efficient and faster memory^{54,80}, computing³³, sensing and actuating^{57,59} devices. Therefore, research in this area will not only produce fundamental new knowledge but will also play a crucial role in the development of new devices and technologies in the coming decades.

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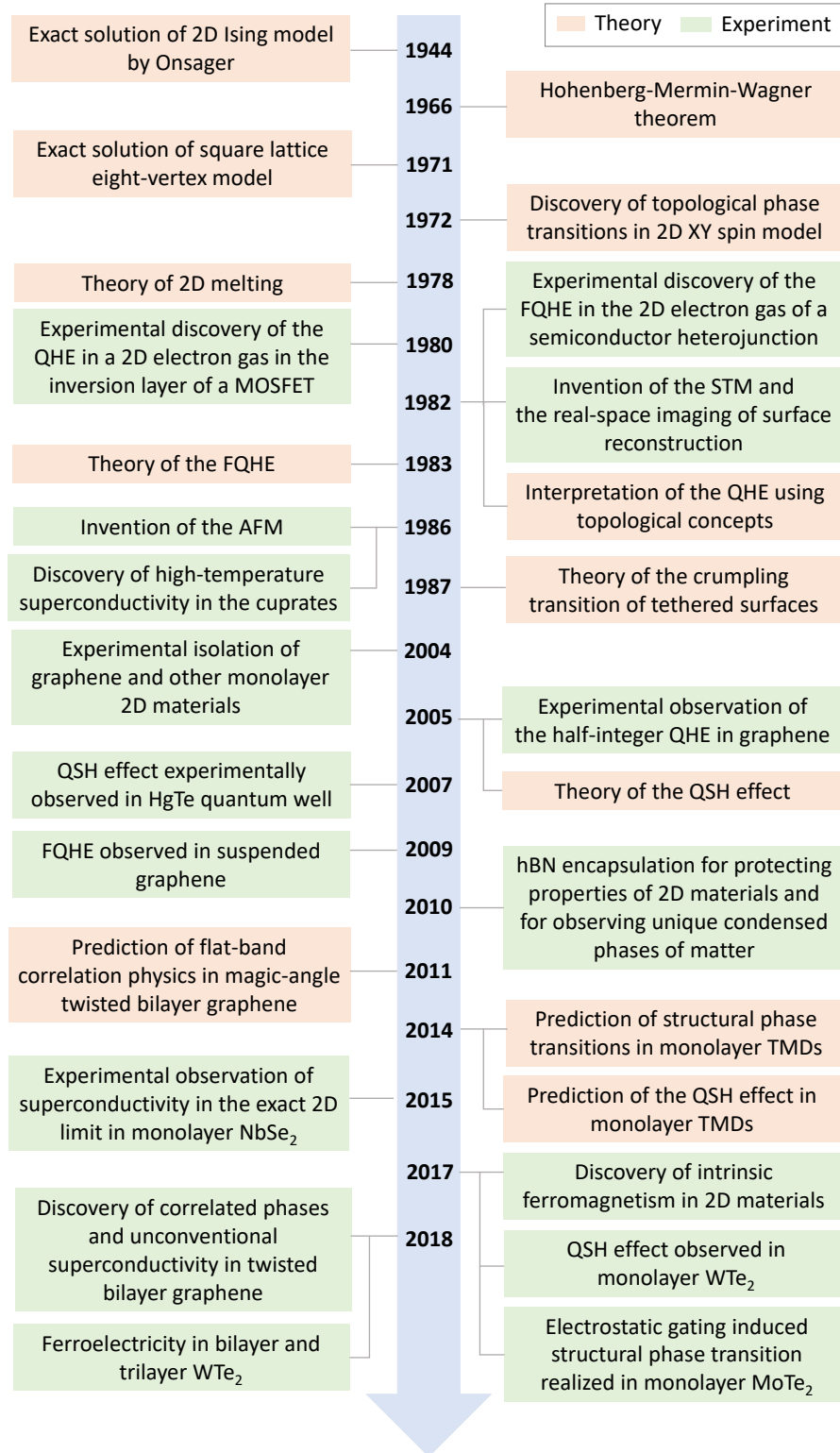


Figure 1 | **Timeline of key developments in the study of 2D phase transitions.** QHE, quantum Hall effect; MOSFET, metal oxide semiconductor field effect transistor; FQHE, fractional quantum Hall effect; STM, scanning tunneling microscope; AFM, atomic force microscope; QSH, quantum spin Hall; hBN, hexagonal boron nitride; TMD, transition metal dichalcogenide.

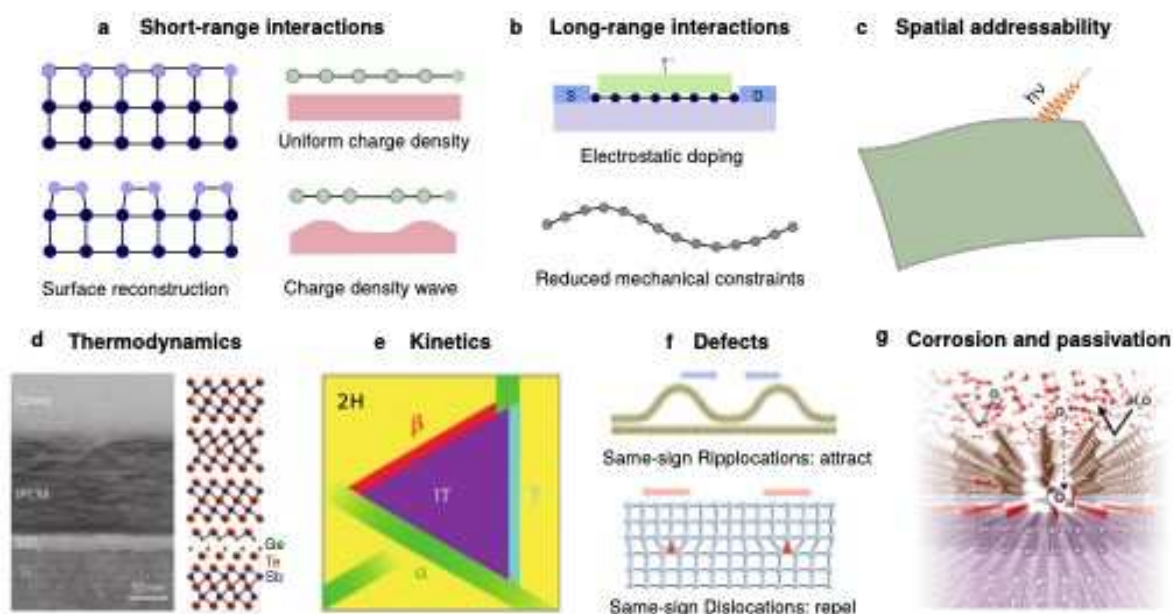


Figure 2 | Distinct features of phase transitions in 2D materials. **a|** Short-range interactions. Dimensionality reduction causes the breaking of chemical bonds, which can lead to 2D structural transformations, such as surface reconstruction of inorganic materials. Dimensionality confinement can also cause an increase in charge density wave instability and Peierls distortion, which are short-range lattice instabilities owing to electron–phonon interactions. **b|** Long-range interactions. Weak dielectric screening in the out-of-plane direction enables electrostatic doping of 2D materials to achieve high carrier densities. In addition, mechanical constraints are reduced in 2D materials owing to the volumetric nature of the strain energy and the low energy cost of forming ripples. **c|** Spatial addressability allows coupling with external stimuli and the precise local control of phase transitions. **d|** The thermodynamics of 2D phase transitions are illustrated in interfacial phase change materials. A transmission electron micrograph and atomistic model of $(\text{GeTe})_2(\text{Sb}_2\text{Te}_3)_4$ are shown⁸¹. Confined atomic motion results in low volume and small entropy loss per volume, and thus, low switching energy. **e|** Phase transformation kinetics are illustrated by the 2H-to-1T phase transition of monolayer MoS_2 ⁷⁶. Intermediate phases (α , β and γ) are formed prior to the transformation from the 2H to 1T phase. **f|** Defects, such as ripplocations, can form in 2D materials during phase transition⁷³, which attract each other when close in distance; by contrast, same-sign dislocations in 3D repel each other. **g|** The atomic thickness and poor environmental stability of 2D materials require new passivation strategies against corrosion, for example, coating with waterproof monolayers to prevent the oxidation-dissolution cycle in corrosion. Panel **d** and **e** are adapted with permission from REF.⁸¹ and REF.⁷⁶, respectively, Springer Nature Limited. Panel **f** is adapted with permission from REF.⁷³, ACS. Panel **g** is adapted from REF.⁹⁷, National Academy of Sciences of the USA.

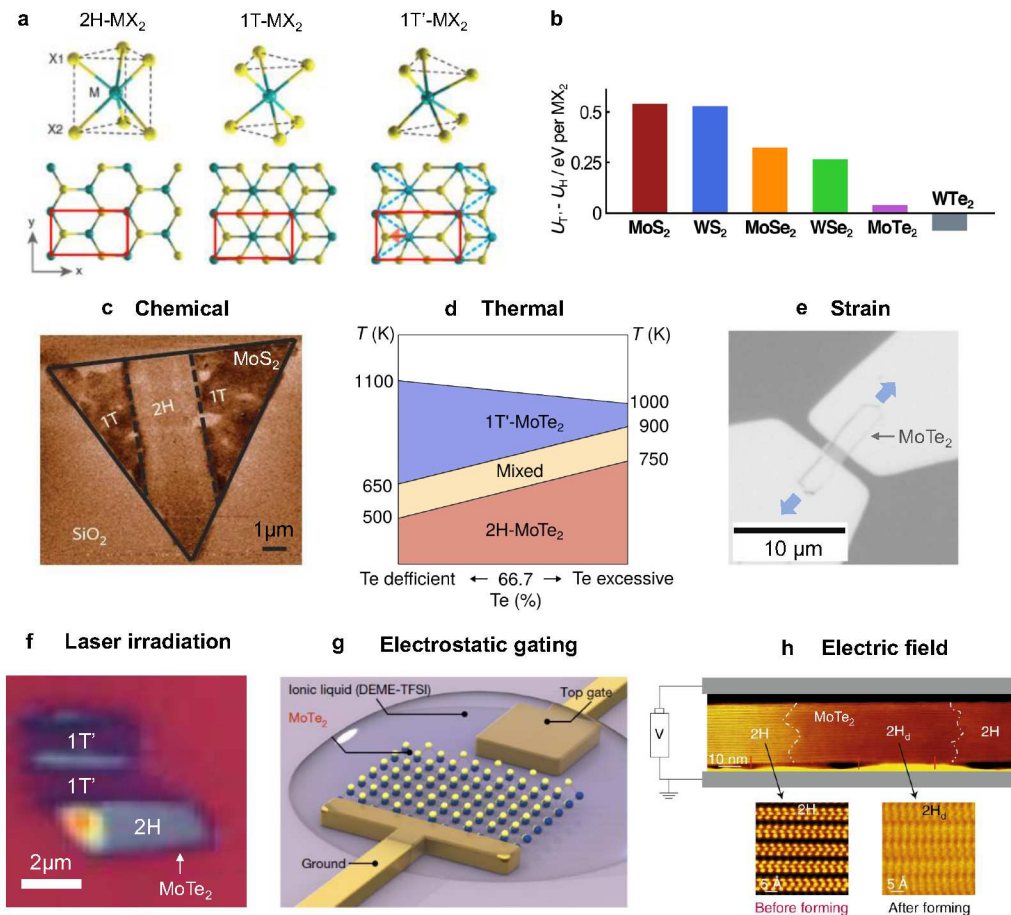


Figure 3 | Polymorphic transitions in 2D transition-metal dichalcogenides. **a** Atomistic structures of MX₂ monolayers. M represents (Mo, W) and X represents (S, Se, Te). Three structural polymorphs, that is, 2H, 1T and 1T' phases, are shown. The red rectangles outline the unit cells. **b** Energy differences (eV per MX₂) between the 1T' and 2H phase ($U_T - U_H$) are shown for different MX₂ monolayers, computed by density functional theory. **c** Chemically-driven polymorphic transition of MoS₂. The electrostatic force microscopy phase image shows the local conversion of a MoS₂ nanosheet from the 2H phase into the 1T phase through chemical patterning using organolithium. **d** Thermally-driven polymorphic transition of MoTe₂. Tellurium deficiency decreases the thermal transition temperature of MoTe₂ from the 2H to the 1T phase. **e** Strain-driven transition of MoTe₂. The optical micrograph shows a MoTe₂ flake on a ferroelectric substrate, which can impose electric-field-induced strain on MoTe₂ flakes owing to the inverse piezoelectric effect. **f** Laser-induced patterning of MoTe₂ few-layers from the 2H into the 1T' phase. **g** Schematic of an ionic liquid field-effect transistor, showing the electrostatic-doping-driven phase transition of a 2H MoTe₂ monolayer to the 1T' phase. DEME-TFSI refers to Diethylmethyl(2-methoxyethyl)ammonium bis(trifluoromethylsulfonyl)imide. **h** Vertical electric field-induced formation of a conducting filament with 2H_d phase in 2H-MoTe₂. Panel **a** is adapted with permission from REF.³³, AAAS. Panel **b** is reproduced with permission from REF.¹¹², ACS. Panel **c** is adapted from REF.⁴⁷, Springer Nature Limited. Panel **d** is adapted from REF.⁴⁹, Springer Nature Limited. Panel **e** is adapted from REF.⁹⁰, Springer Nature Limited. Panel **f** is adapted with permission from REF.⁵⁰, AAAS. Panel **g** is adapted from REF.⁵¹, Springer Nature Limited. Panel **h** is reproduced from REFS.^{52,197}, Springer Nature Limited.

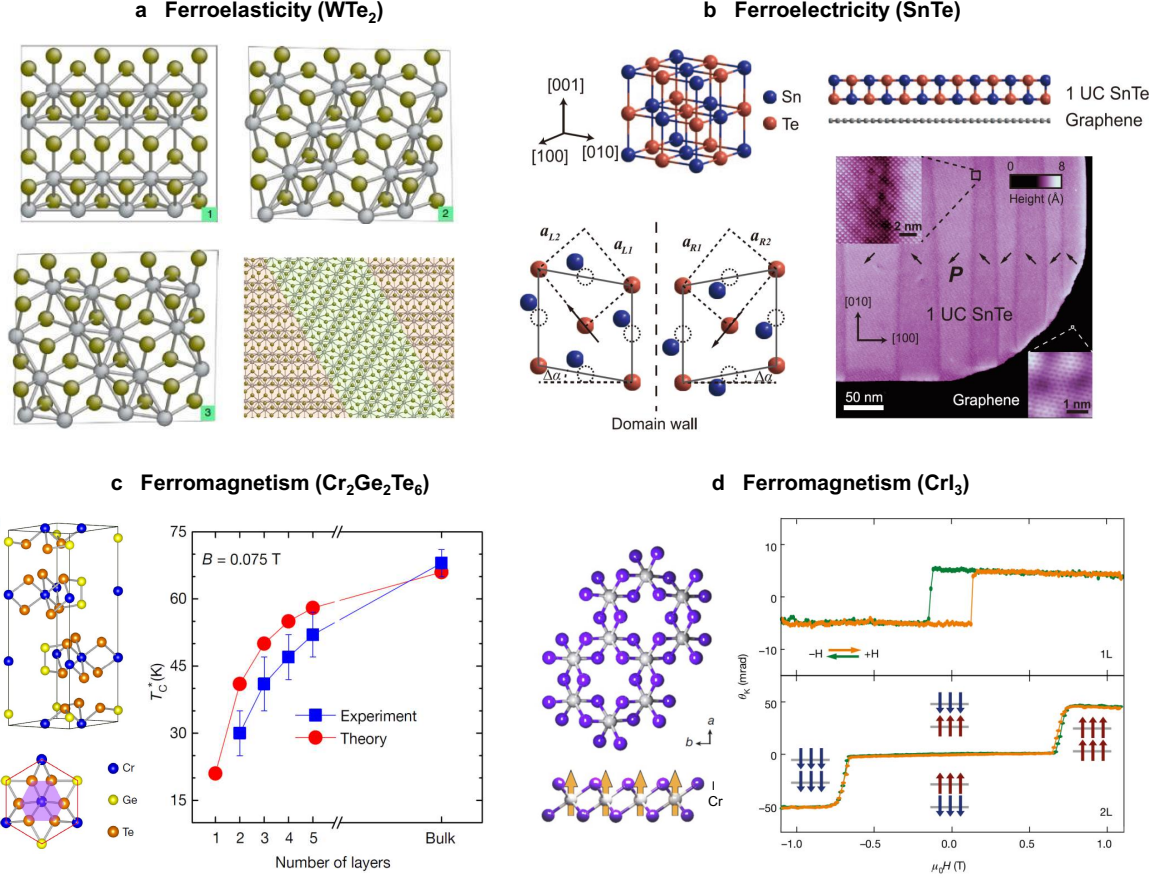


Figure 4 | Ferroic phase transitions in 2D materials. **a** | Symmetry-equivalent orientation states and ferroelasticity in monolayer $1\text{T}'\text{-WTe}_2$. The three orientation variants have slightly different spontaneous strains with respect to the parental 1T phase, which allows strain-induced switching from one orientation to another. The atomistic model shows domain boundaries formed between two orientation variants. **b** | Ferroelectricity in atomically-thin SnTe . Schematic of the crystal structure of SnTe and SnTe thin films is shown with a thickness of one unit-cell (UC). Lattice distortion and atomic displacements are illustrated in the ferroelectric phase. Two symmetry-equivalent distortion directions lead to two variants of ferroelectric domains separated by domain walls, as shown in the STM image of atomically-thin SnTe colored in purple. **c** | Ferromagnetism in $\text{Cr}_2\text{Ge}_2\text{Te}_6$ atomic layers. The crystal structure of $\text{Cr}_2\text{Ge}_2\text{Te}_6$ and the layer-dependent ferromagnetic transition temperature under a perpendicular magnetic field of 0.075 T are shown, obtained from experimental measurements (blue squares) and theoretical calculations (red circles). **d** | Ferromagnetism in atomically thin CrI_3 . The crystal structure of a monolayer CrI_3 and the Kerr rotation angles (θ_K) of monolayer (1L) and bilayer (2L) CrI_3 as a function of the perpendicular magnetic field ($\mu_0 H$) are shown, providing evidence of magnetic ordering. Insets schematically show the magnetic ground states of the systems under different field strengths. Panel **a** is adapted with permission from REF.⁵⁷, Springer Nature Limited. Panel **b** is adapted with permission from REF.⁵⁵, AAAS. Panel **c** is adapted with permission from REF.⁴⁰, Springer Nature Limited. Panel **d** is adapted with permission from REF.³⁹, AAAS.

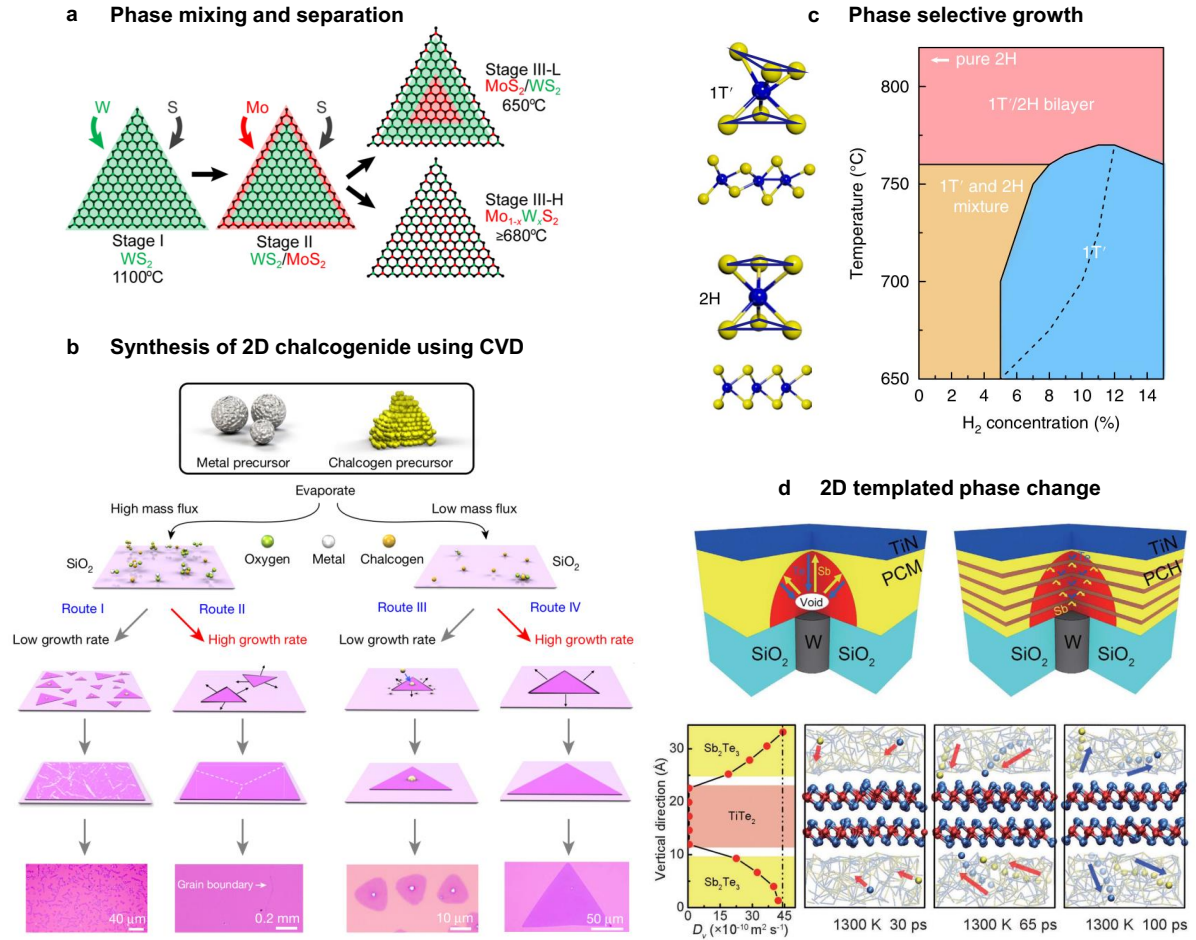


Figure 5 | 2D or 2D-templated diffusive phase transitions. **a**| Chemical vapor deposition growth of a phase-separated MoS_2/WS_2 heterostructure and solid-solution $Mo_xW_{1-x}S_2$ alloy. Compositional mixing and segregation are favored at high and low growth temperatures, respectively. **b**| Synthesis of 2D transition metal chalcogenides by chemical vapor deposition. The morphology and defect content of 2D transition metal chalcogenides depend on the growth kinetics, including mass flux of metal precursors and growth rate. **c**| Phase diagram for the growth of the 1T'- and 2H-phase of a MoS_2 monolayer using K_2MoS_4 as the growth precursor. Controlled growth of 1T' and 2H phases can be realized by varying the growth temperature and H_2 concentration. **d**| 2D-templated diffusive phase transition in a $TiTe_2/Sb_2Te_3$ phase-change heterostructure. The 2D $TiTe_2$ layers, which have a lower diffusion coefficient (D_v) than the Sb_2Te_3 layers, block the electrical-field-assistant transport of charged species in the Sb_2Te_3 diffusive switching layers, leading to less noise and drift for memory operation than traditional phase change materials (PCMs). Panel **a** is reproduced from REF.¹⁵⁰, ACS. Panel **b** is adapted with permission from REF.¹⁵¹, Springer Nature Limited. Panel **c** is adapted with permission from REF.¹⁵⁵, Springer Nature Limited. Panel **d** is adapted with permission from REF.¹⁵⁹, AAAS.

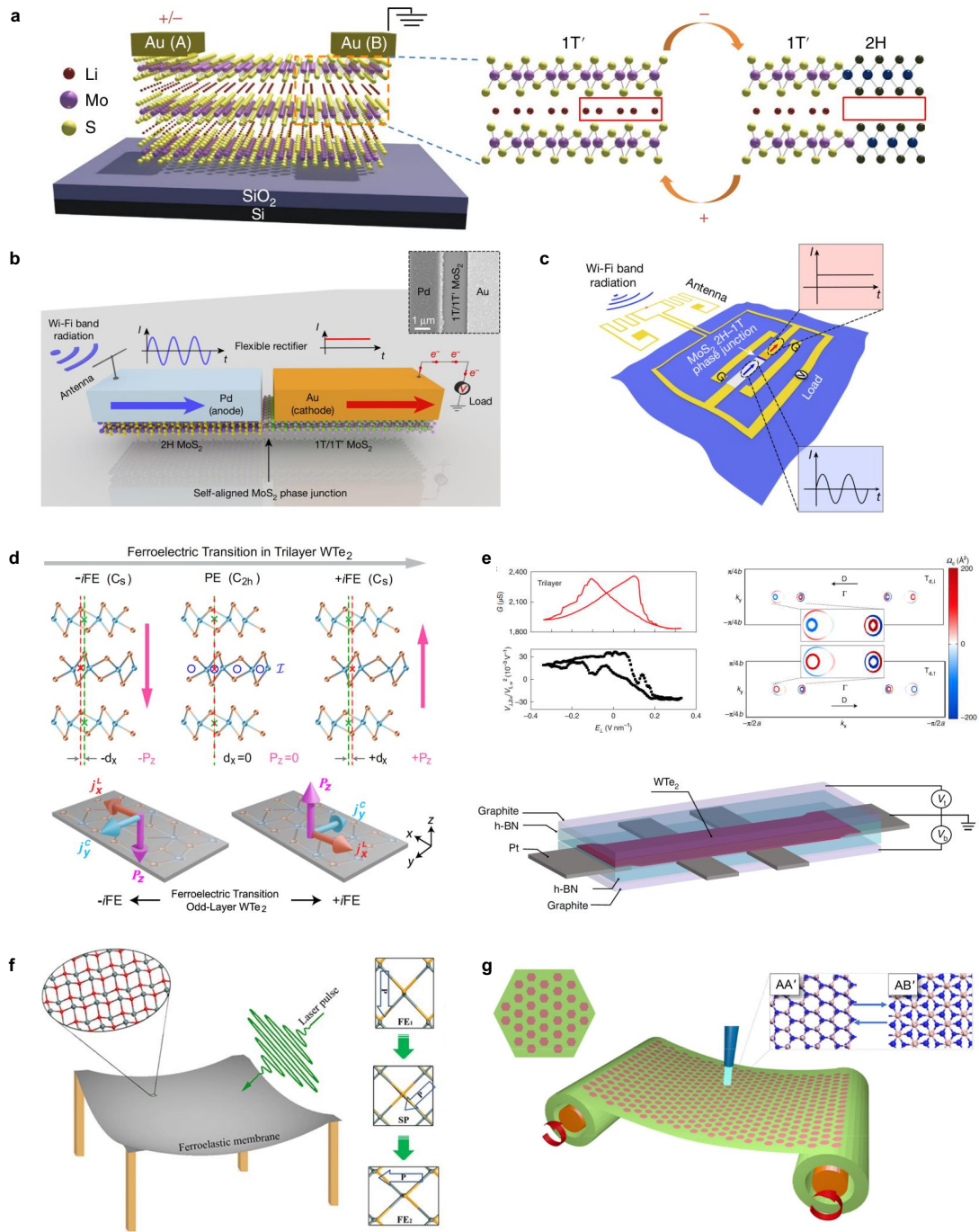


Figure 6 | Novel device applications of 2D phase-change materials. **a** | Schematic of the reversible 2H–1T' phase transition of Li_xMoS_2 films through electric-field controlled migration of Li^+ ions. An increase in Li^+ ion concentration causes the transformation of the 2H phase into the 1T' phase, and vice versa. Such reversible local phase transitions impart electronic devices with excellent memristive properties¹⁶². **b** | Schematic of a MoS_2 lateral Schottky diode, with the core component including a MoS_2 semiconducting–metallic (2H–1T/1T') phase junction. The resulting low resistance and ultralow junction capacitance allow fabrication of a flexible and ultrafast rectifier that can generate D.C. electricity from A.C. signals at a frequency up to 10 GHz. **c** | Combining the high-speed rectifier with a flexible antenna results in a flexible rectenna that can harvest wireless radio-frequency energy at the Wi-Fi-band. **d** | The ferroelectric nonlinear anomalous Hall effect in time-reversal invariant systems provides the

theoretical basis for nonlinear memory. Nonlinear anomalous Hall current switches in odd-layer WTe₂, but remains invariant in even-layer WTe₂ upon ferroelectric transition. P_z stands for electric polarization along z direction, and d_x indicates the offset of the inversion centers between the middle and top/bottom layer along x direction. Two ferroelectric states are related to each other by inversion operator, thus denoted as $+i\text{FE}$ and $-i\text{FE}$, respectively. Upon the ferroelectric transition, nonlinear anomalous Hall current j_x^L due to linear photogalvanic effect switches between $-x$ and $+x$ direction under external field with in-plane linear polarization, while nonlinear anomalous Hall current j_y^C due to circular photogalvanic effect switches between $-y$ and $+y$ direction under circularly polarized light with normal incidence. **e|** Experimental demonstration of the ferroelectric nonlinear anomalous Hall effect and Berry curvature memory in trilayer WTe₂. Nonlinear Hall voltage can be easily detected, and its sign informs the memory state directly. $V_{\perp,2\omega}$ and $V_{\parallel,\omega}$ stand for nonlinear transverse voltage at frequency 2ω and nonlinear longitudinal voltage at frequency ω , respectively. The ratio of $V_{\perp,2\omega}/(V_{\parallel,\omega})^2$ is proportional to Berry curvature dipole D . As electric field E_{\perp} switches, the longitudinal conductance G shows a butterfly-shape hysteresis, while $V_{\perp,2\omega}/(V_{\parallel,\omega})^2$ switches the sign, indicating the flipping of Berry curvature dipole D . This is reflected in the Berry curvature Ω_c distribution in the two-dimensional k_x - k_y Brillouin zone. **f|** Optomechanical martensitic transition induced by a linearly polarized laser pulse in ferroelastic monolayer SnO (left) and SnSe (right). SnSe is multiferroic, showing both ferroelastic and ferroelectric order. Displacive domain switching associated with the optomechanical martensitic transition is accompanied by the switching of polarization directions (FE₁ and FE₂). SP is the saddle point of ferroelastic and ferroelectric switching. **g|** Scrollable optical disk drive based on the optomechanically-driven transition in bilayer hexagonal boron nitride. Upon illumination by a laser pulse, the layer stacking pattern of each bilayer hexagonal boron nitride domain can switch from AA' to AB'. The size of each domain is comparable to the spot size of the laser. The optical disk drive contains a lattice of domains, which can be scrolled to increase data density. Panel **a** is reproduced from REF.¹⁶², Springer Nature Limited. Panel **b** and **c** are reproduced from REF.¹⁶³, Springer Nature Limited. Panel **d** is reproduced from REF.¹⁴⁰, Springer Nature Limited. Panel **e** is reproduced from REF.⁵⁴, Springer Nature Limited. Panel **f** is reproduced from REF.⁵⁹, ACS. Panel **g** is reproduced from REF.⁶⁰, Springer Nature Limited.

References

- 1 Ma, S. *Modern theory of critical phenomena*. (W. A. Benjamin, Advanced Book Program, 1976).
- 2 Goldenfeld, N. *Lectures on phase transitions and the renormalization group*. (Addison-Wesley, Advanced Book Program, 1992).
- 3 Christian, J. W. *The theory of transformations in metals and alloys*. 3rd edn, (Pergamon, 2002).
- 4 Sachdev, S. *Quantum phase transitions*. 2nd edn, (Cambridge University Press, 2011).
- 5 Fradkin, E. *Field theories of condensed matter physics*. 2nd edn, (Cambridge University Press, 2013).
- 6 Novoselov, K. S. *et al.* Two-dimensional atomic crystals. *Proceedings of the National Academy of Sciences* **102**, 10451-10453 (2005).
- 7 Wang, Q. H., Kalantar-Zadeh, K., Kis, A., Coleman, J. N. & Strano, M. S. Electronics and optoelectronics of two-dimensional transition metal dichalcogenides. *Nature Nanotechnology* **7**, 699-712 (2012).
- 8 Novoselov, K. S., Mishchenko, A., Carvalho, A. & Castro Neto, A. H. 2D materials and van der Waals heterostructures. *Science* **353**, aac9439 (2016).
- 9 Manzeli, S., Ovchinnikov, D., Pasquier, D., Yazyev, O. V. & Kis, A. 2D transition metal dichalcogenides. *Nat Rev Mater* **2**, 17033 (2017).
- 10 Yang, H., Kim, S. W., Chhowalla, M. & Lee, Y. H. Structural and quantum-state phase transitions in van der Waals layered materials. *Nature Physics* **13**, 931-937 (2017).
- 11 Onsager, L. Crystal Statistics. I. A Two-Dimensional Model with an Order-Disorder Transition. *Physical Review* **65**, 117-149 (1944).
- 12 Hohenberg, P. C. Existence of Long-Range Order in One and Two Dimensions. *Physical Review* **158**, 383-386 (1967).
- 13 Mermin, N. D. & Wagner, H. Absence of Ferromagnetism or Antiferromagnetism in One- or Two-Dimensional Isotropic Heisenberg Models. *Physical Review Letters* **17**, 1133-1136 (1966).
- 14 Kosterlitz, J. M. & Thouless, D. J. Long range order and metastability in two dimensional solids and superfluids. (Application of dislocation theory). *Journal of Physics C: Solid State Physics* **5**, L124-L126 (1972).
- 15 Kosterlitz, J. M. & Thouless, D. J. Ordering, metastability and phase transitions in two-dimensional systems. *Journal of Physics C: Solid State Physics* **6**, 1181-1203 (1973).
- 16 Klitzing, K. v., Dorda, G. & Pepper, M. New Method for High-Accuracy Determination of the Fine-Structure Constant Based on Quantized Hall Resistance. *Physical Review Letters* **45**, 494-497 (1980).
- 17 Tsui, D. C., Stormer, H. L. & Gossard, A. C. Two-Dimensional Magnetotransport in the Extreme Quantum Limit. *Physical Review Letters* **48**, 1559-1562 (1982).
- 18 Binnig, G., Rohrer, H., Gerber, C. & Weibel, E. Surface Studies by Scanning Tunneling Microscopy. *Physical Review Letters* **49**, 57-61 (1982).
- 19 Binnig, G., Quate, C. F. & Gerber, C. Atomic Force Microscope. *Physical Review Letters* **56**, 930-933 (1986).
- 20 Binnig, G., Rohrer, H., Gerber, C. & Weibel, E. 7×7 Reconstruction on Si(111) Resolved in Real Space. *Physical Review Letters* **50**, 120-123 (1983).
- 21 Zhang, J., Liu, J., Huang, J. L., Kim, P. & Lieber, C. M. Creation of Nanocrystals Through a Solid-Solid Phase Transition Induced by an STM Tip. *Science* **274**, 757-760 (1996).
- 22 Kaganer, V. M., Möhwald, H. & Dutta, P. Structure and phase transitions in Langmuir monolayers. *Reviews of Modern Physics* **71**, 779-819 (1999).
- 23 Novoselov, K. S. *et al.* Electric Field Effect in Atomically Thin Carbon Films. *Science* **306**, 666-669 (2004).
- 24 Zhang, Y. B., Tan, Y. W., Stormer, H. L. & Kim, P. Experimental observation of the quantum Hall effect and Berry's phase in graphene. *Nature* **438**, 201-204 (2005).

- 25 Bolotin, K. I., Ghahari, F., Shulman, M. D., Stormer, H. L. & Kim, P. Observation of the fractional quantum Hall effect in graphene. *Nature* **462**, 196-199 (2009).
- 26 Du, X., Skachko, I., Duerr, F., Luican, A. & Andrei, E. Y. Fractional quantum Hall effect and insulating phase of Dirac electrons in graphene. *Nature* **462**, 192-195 (2009).
- 27 Cao, Y. *et al.* Correlated insulator behaviour at half-filling in magic-angle graphene superlattices. *Nature* **556**, 80-84 (2018).
- 28 Xi, X. X. *et al.* Ising pairing in superconducting NbSe₂ atomic layers. *Nature Physics* **12**, 139-143 (2016).
- 29 Saito, Y., Nojima, T. & Iwasa, Y. Highly crystalline 2D superconductors. *Nat Rev Mater* **2**, 16094 (2017).
- 30 Cao, Y. *et al.* Unconventional superconductivity in magic-angle graphene superlattices. *Nature* **556**, 43-50 (2018).
- 31 Kane, C. L. & Mele, E. J. Quantum spin Hall effect in graphene. *Physical Review Letters* **95**, 226801 (2005).
- 32 König, M. *et al.* Quantum spin hall insulator state in HgTe quantum wells. *Science* **318**, 766-770 (2007).
- 33 Qian, X. F., Liu, J. W., Fu, L. & Li, J. Quantum spin Hall effect in two-dimensional transition metal dichalcogenides. *Science* **346**, 1344-1347 (2014).
- This paper predicts that several group 6 transition-metal dichalcogenide monolayers in 1T' phase are quantum spin Hall insulators competing with the trivial semiconducting 1H phase and metallic 1T phase.**
- 34 Tang, S. J. *et al.* Quantum spin Hall state in monolayer 1T'-WTe₂. *Nature Physics* **13**, 683-687 (2017).
- 35 Wu, S. F. *et al.* Observation of the quantum spin Hall effect up to 100 kelvin in a monolayer crystal. *Science* **359**, 76-79 (2018).
- 36 Chen, G. *et al.* Tunable correlated Chern insulator and ferromagnetism in a moiré superlattice. *Nature* **579**, 56-61 (2020).
- 37 Serlin, M. *et al.* Intrinsic quantized anomalous Hall effect in a moiré heterostructure. *Science* **367**, 900-903 (2020).
- 38 Polshyn, H. *et al.* Electrical switching of magnetic order in an orbital Chern insulator. *Nature* (2020).
- 39 Huang, B. *et al.* Layer-dependent ferromagnetism in a van der Waals crystal down to the monolayer limit. *Nature* **546**, 270-273 (2017).
- The first demonstration that intrinsic ferromagnetism can be present in monolayer CrI₃.**
- 40 Gong, C. *et al.* Discovery of intrinsic ferromagnetism in two-dimensional van der Waals crystals. *Nature* **546**, 265-269 (2017).
- The first demonstration of layer-dependent ferromagnetic transition in 2D Cr₂Ge₂Te₆.**
- 41 Burch, K. S., Mandrus, D. & Park, J. G. Magnetism in two-dimensional van der Waals materials. *Nature* **563**, 47-52 (2018).
- 42 Gong, C. & Zhang, X. Two-dimensional magnetic crystals and emergent heterostructure devices. *Science* **363**, eaav4450 (2019).
- 43 Gibertini, M., Koperski, M., Morpurgo, A. F. & Novoselov, K. S. Magnetic 2D materials and heterostructures. *Nature Nanotechnology* **14**, 408-419 (2019).
- 44 Mak, K. F., Shan, J. & Ralph, D. C. Probing and controlling magnetic states in 2D layered magnetic materials. *Nature Reviews Physics* **1**, 646-661 (2019).
- 45 Huang, B. *et al.* Emergent phenomena and proximity effects in two-dimensional magnets and heterostructures. *Nature Materials* **19**, 1276-1289 (2020).
- 46 Eda, G. *et al.* Coherent Atomic and Electronic Heterostructures of Single-Layer MoS₂. *ACS Nano* **6**, 7311-7317 (2012).
- 47 Kappera, R. *et al.* Phase-engineered low-resistance contacts for ultrathin MoS₂ transistors. *Nature Materials* **13**, 1128-1134 (2014).

- 48 Duerloo, K.-A. N., Li, Y. & Reed, E. J. Structural phase transitions in two-dimensional Mo- and W-dichalcogenide monolayers. *Nature Communications* **5**, 4214 (2014).
This paper is the first comprehensive theoretical study of structural phase transitions in monolayer transition-metal dichalcogenides.
- 49 Keum, D. H. *et al.* Bandgap opening in few-layered monoclinic MoTe₂. *Nature Physics* **11**, 482-486 (2015).
- 50 Cho, S. *et al.* Phase patterning for ohmic homojunction contact in MoTe₂. *Science* **349**, 625-628 (2015).
- 51 Wang, Y. *et al.* Structural phase transition in monolayer MoTe₂ driven by electrostatic doping. *Nature* **550**, 487-491 (2017).
- 52 Zhang, F. *et al.* Electric-field induced structural transition in vertical MoTe₂- and Mo_{1-x}W_xTe₂-based resistive memories. *Nature Materials* **18**, 55-61 (2019).
- 53 Sie, E. J. *et al.* An ultrafast symmetry switch in a Weyl semimetal. *Nature* **565**, 61-66 (2019).
- 54 Xiao, J. *et al.* Berry curvature memory through electrically driven stacking transitions. *Nature Physics* **16**, 1028–1034 (2020).
The first experimental demonstration of the theoretically predicted ferroelectric nonlinear Hall effect and Berry curvature memory in 2D semimetals.
- 55 Chang, K. *et al.* Discovery of robust in-plane ferroelectricity in atomic-thick SnTe. *Science* **353**, 274-278 (2016).
The first experimental report of in-plane ferroelectricity in an atomically thin material.
- 56 Ding, W. *et al.* Prediction of intrinsic two-dimensional ferroelectrics in In₂Se₃ and other III₂-VI₃ van der Waals materials. *Nature Communications* **8**, 14956 (2017).
The first theoretical prediction of simultaneous out-of-plane and in-plane ferroelectricity in monolayer α -In₂Se₃.
- 57 Li, W. B. & Li, J. Ferroelasticity and domain physics in two-dimensional transition metal dichalcogenide monolayers. *Nature Communications* **7**, 10843 (2016).
One of the earliest studies of ferroelasticity and ferroelastic transitions in 2D materials.
- 58 Wang, H. & Qian, X. Two-dimensional multiferroics in monolayer group IV monochalcogenides. *2D Materials* **4**, 015042 (2017).
- 59 Zhou, J., Xu, H. W., Li, Y. F., Jaramillo, R. & Li, J. Opto-mechanics driven fast martensitic transition in two-dimensional materials. *Nano Letters* **18**, 7794-7800 (2018).
- 60 Xu, H., Zhou, J., Li, Y., Jaramillo, R. & Li, J. Optomechanical control of stacking patterns of h-BN bilayer. *Nano Research* **12**, 2634-2639 (2019).
- 61 Mishin, Y., Asta, M. & Li, J. Atomistic modeling of interfaces and their impact on microstructure and properties. *Acta Materialia* **58**, 1117-1151 (2010).
- 62 Mermin, N. D. Crystalline Order in Two Dimensions. *Physical Review* **176**, 250-254 (1968).
- 63 Splendiani, A. *et al.* Emerging Photoluminescence in Monolayer MoS₂. *Nano Letters* **10**, 1271-1275 (2010).
- 64 Mak, K. F., Lee, C., Hone, J., Shan, J. & Heinz, T. F. Atomically Thin MoS₂: A New Direct-Gap Semiconductor. *Physical Review Letters* **105**, 136805 (2010).
- 65 Sohler, T., Gibertini, M., Calandra, M., Mauri, F. & Marzari, N. Breakdown of Optical Phonons' Splitting in Two-Dimensional Materials. *Nano Letters* **17**, 3758-3763 (2017).
- 66 Cudazzo, P., Tokatly, I. V. & Rubio, A. Dielectric screening in two-dimensional insulators: Implications for excitonic and impurity states in graphane. *Physical Review B* **84**, 085406 (2011).
- 67 Xi, X. X. *et al.* Strongly enhanced charge-density-wave order in monolayer NbSe₂. *Nature Nanotechnology* **10**, 765-769 (2015).
- 68 Ye, J. T. *et al.* Superconducting Dome in a Gate-Tuned Band Insulator. *Science* **338**, 1193-1196 (2012).

- 69 Li, L. J. *et al.* Controlling many-body states by the electric-field effect in a two-dimensional material. *Nature* **529**, 185-U129 (2016).
- 70 Fei, Z. Y. *et al.* Ferroelectric switching of a two-dimensional metal. *Nature* **560**, 336-339 (2018).
- 71 Yang, Q., Wu, M. & Li, J. Origin of two-dimensional vertical ferroelectricity in wte₂ bilayer and multilayer. *J Phys Chem Lett* **9**, 7160-7164 (2018).
- 72 Feng, J., Qi, L., Huang, J. Y. & Li, J. Geometric and electronic structure of graphene bilayer edges. *Physical Review B* **80**, 165407 (2009).
- 73 Kushima, A., Qian, X. F., Zhao, P., Zhang, S. L. & Li, J. Ripplations in van der Waals Layers. *Nano Letters* **15**, 1302-1308 (2015).
- 74 Britnell, L. *et al.* Strong Light-Matter Interactions in Heterostructures of Atomically Thin Films. *Science* **340**, 1311-1314 (2013).
- 75 Elias, D. C. *et al.* Control of Graphene's Properties by Reversible Hydrogenation: Evidence for Graphane. *Science* **323**, 610-613 (2009).
- 76 Lin, Y. C., Dumcencon, D. O., Huang, Y. S. & Suenaga, K. Atomic mechanism of the semiconducting-to-metallic phase transition in single-layered MoS₂. *Nature Nanotechnology* **9**, 391-396 (2014).
- 77 Franklin, B. Of the stilling of waves by means of oil. *Philosophical Transactions of the Royal Society of London* **64**, 445-460 (1774).
- 78 Lord Rayleigh. Measurements of the Amount of Oil Necessary in Order to Check the Motions of Camphor upon Water. *Proceedings of the Royal Society of London* **47**, 364-367 (1890).
- 79 Nair, R. R. *et al.* Fine Structure Constant Defines Visual Transparency of Graphene. *Science* **320**, 1308-1308 (2008).
- 80 Rehn, D. A., Li, Y., Pop, E. & Reed, E. J. Theoretical potential for low energy consumption phase change memory utilizing electrostatically-induced structural phase transitions in 2D materials. *npj Computational Materials* **4**, 2 (2018).
- 81 Simpson, R. E. *et al.* Interfacial phase-change memory. *Nature Nanotechnology* **6**, 501-505 (2011).
- 82 Gu, X. K., Wei, Y. J., Yin, X. B., Li, B. W. & Yang, R. G. Colloquium: Phononic thermal properties of two-dimensional materials. *Reviews of modern physics* **90**, 041002 (2018).
- 83 Li, J. The mechanics and physics of defect nucleation. *Mrs Bull* **32**, 151-159 (2007).
- 84 Zhu, T. & Li, J. Ultra-strength materials. *Progress in Materials Science* **55**, 710-757 (2010).
- 85 Yakobson, B. I. Mechanical relaxation and "intramolecular plasticity" in carbon nanotubes. *Applied Physics Letters* **72**, 918-920 (1998).
- 86 Lee, C., Wei, X., Kysar, J. W. & Hone, J. Measurement of the Elastic Properties and Intrinsic Strength of Monolayer Graphene. *Science* **321**, 385-388 (2008).
- 87 Bertolazzi, S., Brivio, J. & Kis, A. Stretching and Breaking of Ultrathin MoS₂. *ACS Nano* **5**, 9703-9709 (2011).
- 88 Li, J., Shan, Z. W. & Ma, E. Elastic strain engineering for unprecedented materials properties. *Mrs Bull* **39**, 108-117 (2014).
- 89 Song, S. *et al.* Room Temperature Semiconductor–Metal Transition of MoTe₂ Thin Films Engineered by Strain. *Nano Letters* **16**, 188-193 (2015).
- 90 Hou, W. *et al.* Strain-based room-temperature non-volatile MoTe₂ ferroelectric phase change transistor. *Nature Nanotechnology* **14**, 668-673 (2019).
- 91 Bausch, A. R. *et al.* Grain boundary scars and spherical crystallography. *Science* **299**, 1716-1718 (2003).
- 92 Masel, R. I. *Principles of adsorption and reaction on solid surfaces*. (Wiley, 1996).
- 93 Geim, A. K. & Grigorieva, I. V. Van der Waals heterostructures. *Nature* **499**, 419-425 (2013).
- 94 Jones, D. A. *Principles and prevention of corrosion*. 2nd edn, (Prentice Hall, 1996).
- 95 Dean, C. R. *et al.* Boron nitride substrates for high-quality graphene electronics. *Nature Nanotechnology* **5**, 722-726 (2010).

This work shows that hexagonal boron nitride is an excellent material for protecting the properties of 2D materials.

- 96 Nine, M. J., Cole, M. A., Tran, D. N. H. & Losic, D. Graphene: a multipurpose material for protective coatings. *J Mater Chem A* **3**, 12580-12602 (2015).
- 97 Su, C. *et al.* Waterproof molecular monolayers stabilize 2D materials. *P Natl Acad Sci USA* **116**, 20844-20849 (2019).
- 98 Levy, N. *et al.* Strain-Induced Pseudo-Magnetic Fields Greater Than 300 Tesla in Graphene Nanobubbles. *Science* **329**, 544-547 (2010).
- 99 Feng, J., Qian, X. F., Huang, C. W. & Li, J. Strain-engineered artificial atom as a broad-spectrum solar energy funnel. *Nature Photonics* **6**, 865-871 (2012).
- 100 Voiry, D. *et al.* Enhanced catalytic activity in strained chemically exfoliated WS₂ nanosheets for hydrogen evolution. *Nature Materials* **12**, 850-855 (2013).
- 101 Voiry, D., Mohite, A. & Chhowalla, M. Phase engineering of transition metal dichalcogenides. *Chemical Society Reviews* **44**, 2702-2712 (2015).
- 102 Wang, J., Wei, Y., Li, H., Huang, X. & Zhang, H. Crystal phase control in two-dimensional materials. *Science China Chemistry* **61**, 1227-1242 (2018).
- 103 Xiao, Y., Zhou, M., Liu, J., Xu, J. & Fu, L. Phase engineering of two-dimensional transition metal dichalcogenides. *Science China Materials* **62**, 759-775 (2019).
- 104 Wang, X. *et al.* Potential 2D Materials with Phase Transitions: Structure, Synthesis, and Device Applications. *Advanced Materials* **31** (2019).
- 105 Sokolikova, M. S. & Mattevi, C. Direct synthesis of metastable phases of 2D transition metal dichalcogenides. *Chemical Society Reviews* (2020).
- 106 Bergeron, H., Lebedev, D. & Hersam, M. C. Polymorphism in Post-Dichalcogenide Two-Dimensional Materials. *Chemical Reviews* **Article ASAP**, DOI: 10.1021/acs.chemrev.1020c00933 (2021).
- 107 Wilson, J. A. & Yoffe, A. D. The transition metal dichalcogenides discussion and interpretation of the observed optical, electrical and structural properties. *Advances in Physics* **18**, 193-335 (1969).
- 108 Xia, F., Wang, H., Xiao, D., Dubey, M. & Ramasubramaniam, A. Two-dimensional material nanophotonics. *Nature Photonics* **8**, 899-907 (2014).
- 109 Fei, Z. *et al.* Edge conduction in monolayer WTe₂. *Nature Physics* **13**, 677-682 (2017).
- 110 Zheng, F. *et al.* On the Quantum Spin Hall Gap of Monolayer 1T' -WTe₂. *Adv. Mater.* **28**, 4845-4851 (2016).
- 111 Sajadi, E. *et al.* Gate-induced superconductivity in a monolayer topological insulator. *Science* **362**, 922-925 (2018).
- 112 Duerloo, K.-A. N. & Reed, E. J. Structural Phase Transitions by Design in Monolayer Alloys. *ACS Nano* **10**, 289-297 (2015).
- 113 Li, Y., Duerloo, K.-A. N., Wauson, K. & Reed, E. J. Structural semiconductor-to-semimetal phase transition in two-dimensional materials induced by electrostatic gating. *Nature Communications* **7**, 10671 (2016).
- 114 Py, M. A. & Haering, R. R. Structural destabilization induced by lithium intercalation in MoS₂ and related compounds. *Canadian Journal of Physics* **61**, 76-84 (1983).
- 115 Gordon, R. A., Yang, D., Crozier, E. D., Jiang, D. T. & Frindt, R. F. Structures of exfoliated single layers of WS₂, MoS₂, and MoSe₂ in aqueous suspension. *Physical Review B* **65**, 125407 (2002).
- 116 Chhowalla, M. *et al.* The chemistry of two-dimensional layered transition metal dichalcogenide nanosheets. *Nature Chemistry* **5**, 263-275 (2013).
- 117 Wadhawan, V. K. *Introduction to ferroic materials*. (Gordon & Breach, 2000).
- 118 Wang, G.-Y. *et al.* Formation mechanism of twin domain boundary in 2D materials: The case for WTe₂. *Nano Research* **12**, 569-573 (2019).
- 119 Pedramrazi, Z. *et al.* Manipulating Topological Domain Boundaries in the Single-Layer Quantum Spin Hall Insulator 1T' - WSe₂. *Nano Letters* **19**, 5634-5639 (2019).

- 120 Kim, H. W. *et al.* Symmetry Dictated Grain Boundary State in a Two-Dimensional Topological Insulator. *Nano Letters* **20**, 5837-5843 (2020).
- 121 Seixas, L., Rodin, A. S., Carvalho, A. & Castro Neto, A. H. Multiferroic Two-Dimensional Materials. *Physical Review Letters* **116**, 206803 (2016).
- 122 Dawber, M., Rabe, K. M. & Scott, J. F. Physics of thin-film ferroelectric oxides. *Reviews of Modern Physics* **77**, 1083-1130 (2005).
- 123 Ahn, C. H., Rabe, K. M. & Triscone, J.-M. Ferroelectricity at the Nanoscale: Local Polarization in Oxide Thin Films and Heterostructures. *Science* **303**, 488-491 (2004).
- 124 Wu, M. & Zeng, X. C. Intrinsic Ferroelasticity and/or Multiferroicity in Two-Dimensional Phosphorene and Phosphorene Analogues. *Nano Letters* **16**, 3236-3241 (2016).
- 125 Fei, R., Kang, W. & Yang, L. Ferroelectricity and Phase Transitions in Monolayer Group-IV Monochalcogenides. *Physical Review Letters* **117**, 097601 (2016).
- 126 Hanakata, P. Z., Carvalho, A., Campbell, D. K. & Park, H. S. Polarization and valley switching in monolayer group-IV monochalcogenides. *Physical Review B* **94**, 035304 (2016).
- 127 Mehboudi, M. *et al.* Structural phase transition and material properties of few-layer monochalcogenides. *Physical Review Letters* **117**, 246802 (2016).
- 128 Mehboudi, M. *et al.* Two-dimensional disorder in black phosphorus and monochalcogenide monolayers. *Nano Letters* **16**, 1704-1712 (2016).
- 129 Zhou, Y. *et al.* Out-of-plane piezoelectricity and ferroelectricity in layered α - In_2Se_3 nanoflakes. *Nano Letters* **17**, 5508-5513 (2017).
- 130 Cui, C. *et al.* Intercorrelated in-plane and out-of-plane ferroelectricity in ultrathin two-dimensional layered semiconductor In_2Se_3 . *Nano Letters* **18**, 1253-1258 (2018).
- 131 Xiao, J. *et al.* Intrinsic two-dimensional ferroelectricity with dipole locking. *Physical Review Letters* **120**, 227601 (2018).
- 132 Zheng, C. *et al.* Room temperature in-plane ferroelectricity in van der Waals In_2Se_3 . *Science Advances* **4**, eaar7720 (2018).
- 133 Belianinov, A. *et al.* CuInP_2S_6 room temperature layered ferroelectric. *Nano Letters* **15**, 3808-3814 (2015).
- 134 Liu, F. *et al.* Room-temperature ferroelectricity in CuInP_2S_6 ultrathin flakes. *Nature Communications* **7**, 12357 (2016).
- 135 Yuan, S. *et al.* Room-temperature ferroelectricity in MoTe_2 down to the atomic monolayer limit. *Nature Communications* **10**, 1775 (2019).
- 136 Shirodkar, S. N. & Waghmare, U. V. Emergence of Ferroelectricity at a Metal-Semiconductor Transition in a 1T Monolayer of MoS_2 . *Physical Review Letters* **112**, 157601 (2014).
- 137 Soluyanov, A. A. *et al.* Type-II Weyl semimetals. *Nature* **527**, 495-498 (2015).
- 138 Brown, B. E. The crystal structures of WTe_2 and high-temperature MoTe_2 . *Acta Crystallographica* **20**, 268-274 (1966).
- 139 Cochran, W. Crystal stability and the theory of ferroelectricity. *Advances in Physics* **9**, 387-423 (1960).
- 140 Wang, H. & Qian, X. Ferroelectric nonlinear anomalous Hall effect in few-layer WTe_2 . *npj Computational Materials* **5**, 119 (2019).
- 141 Herring, C. & Kittel, C. On the theory of spin waves in ferromagnetic media. *Physical Review* **81**, 869-880 (1951).
- 142 Fröhlich, J. & Lieb, E. H. Existence of phase transitions for anisotropic Heisenberg models. *Physical Review Letters* **38**, 440-442 (1977).
- 143 Li, W. *et al.* High temperature ferromagnetism in π -conjugated two-dimensional metal-organic frameworks. *Chemical Science* **8**, 2859-2867 (2017).
- 144 Wang, H., Qi, J. & Qian, X. Electrically tunable high Curie temperature two-dimensional ferromagnetism in van der Waals layered crystals. *Applied Physics Letters* **117**, 083102 (2020).

- 145 Jiang, Z., Wang, P., Xing, J., Jiang, X. & Zhao, J. Screening and Design of Novel 2D Ferromagnetic Materials with High Curie Temperature above Room Temperature. *ACS Applied Materials & Interfaces* **10**, 39032-39039 (2018).
- 146 Telford, E. J. *et al.* Layered Antiferromagnetism Induces Large Negative Magnetoresistance in the van der Waals Semiconductor CrSBr. *Advanced Materials* **32**, 2003240 (2020).
- 147 Lee, K. *et al.* Magnetic Order and Symmetry in the 2D Semiconductor CrSBr. *arXiv preprint, arXiv:2007.10715* (2020).
- 148 Zhuang, H. L., Kent, P. R. C. & Hennig, R. G. Strong anisotropy and magnetostriction in the two-dimensional Stoner ferromagnet Fe₃GeTe₂. *Phys Rev B* **93**, 134407 (2016).
- 149 Deng, Y. *et al.* Gate-tunable room-temperature ferromagnetism in two-dimensional Fe₃GeTe₂. *Nature* **563**, 94-99 (2018).
- 150 Bogaert, K. *et al.* Diffusion-Mediated Synthesis of MoS₂/WS₂ Lateral Heterostructures. *Nano Letters* **16**, 5129-5134 (2016).
- 151 Zhou, J. *et al.* A library of atomically thin metal chalcogenides. *Nature* **556**, 355-359 (2018).
- 152 Li, X. *et al.* Surfactant-Mediated Growth and Patterning of Atomically Thin Transition Metal Dichalcogenides. *ACS Nano*, 6570–6581 (2020).
- 153 Zhu, J. *et al.* Argon plasma induced phase transition in monolayer MoS₂. *J. Am. Chem. Soc.* **139**, 10216-10219 (2017).
- 154 Zhou, L. *et al.* Large-area synthesis of high-quality uniform few-layer MoTe₂. *Journal of the American Chemical Society* **137**, 11892-11895 (2015).
- 155 Liu, L. N. *et al.* Phase-selective synthesis of 1T' MoS₂ monolayers and heterophase bilayers. *Nature Materials* **17**, 1108-1114 (2018).
- 156 Rao, F. *et al.* Reducing the stochasticity of crystal nucleation to enable subnanosecond memory writing. *Science* **358**, 1423-1426 (2017).
- 157 Zhang, W., Mazzarello, R., Wuttig, M. & Ma, E. Designing crystallization in phase-change materials for universal memory and neuro-inspired computing. *Nat Rev Mater* **4**, 150-168 (2019).
- 158 Kalikka, J. *et al.* Strain-engineered diffusive atomic switching in two-dimensional crystals. *Nature Communications* **7**, 11983 (2016).
- 159 Ding, K. *et al.* Phase-change heterostructure enables ultralow noise and drift for memory operation. *Science* **366**, 210 (2019).
- 160 Wu, J. *et al.* High tunnelling electroresistance in a ferroelectric van der Waals heterojunction via giant barrier height modulation. *Nature Electronics* **3**, 466-472 (2020).
- 161 Shi, G. & Kioupakis, E. Anisotropic Spin Transport and Strong Visible-Light Absorbance in Few-Layer SnSe and GeSe. *Nano Lett* **15**, 6926-6931 (2015).
- 162 Zhu, X. J., Li, D., Liang, X. G. & Lu, W. D. Ionic modulation and ionic coupling effects in MoS₂ devices for neuromorphic computing. *Nature Materials* **18**, 141-148 (2019).
- 163 Zhang, X. *et al.* Two-dimensional MoS₂-enabled flexible rectenna for Wi-Fi-band wireless energy harvesting. *Nature* **566**, 368-372 (2019).
- 164 Wang, H. & Qian, X. Ferroicity-driven nonlinear photocurrent switching in time-reversal invariant ferroic materials. *Science Advances* **5**, eaav9743 (2019).
- 165 Peng, B. *et al.* Phase transition enhanced superior elasticity in freestanding single-crystalline multiferroic BiFeO₃ membranes. *Science Advances* **6**, eaba5847 (2020).
- 166 Jiang, S., Xie, H., Shan, J. & Mak, K. F. Exchange magnetostriction in two-dimensional antiferromagnets. *Nature Materials* **19**, 1295-1299 (2020).
- 167 Oganov, A. R., Pickard, C. J., Zhu, Q. & Needs, R. J. Structure prediction drives materials discovery. *Nat Rev Mater* **4**, 331-348 (2019).
- 168 Butler, K. T., Davies, D. W., Cartwright, H., Isayev, O. & Walsh, A. Machine learning for molecular and materials science. *Nature* **559**, 547-555 (2018).
- 169 Schmidt, J., Marques, M. R. G., Botti, S. & Marques, M. A. L. Recent advances and applications of machine learning in solid-state materials science. *npj Computational Materials* **5**, 83 (2019).

- 170 Cheon, G. *et al.* Revealing the Spectrum of Unknown Layered Materials with Superhuman
Predictive Abilities. *The Journal of Physical Chemistry Letters* **9**, 6967-6972 (2018).
- 171 Oses, C., Toher, C. & Curtarolo, S. High-entropy ceramics. *Nat Rev Mater* **5**, 295-309 (2020).
- 172 Souvatzis, P., Eriksson, O., Katsnelson, M. I. & Rudin, S. P. Entropy Driven Stabilization of
Energetically Unstable Crystal Structures Explained from First Principles Theory. *Physical
Review Letters* **100**, 095901 (2008).
- 173 Lebègue, S., Björkman, T., Klintenberg, M., Nieminen, R. M. & Eriksson, O. Two-Dimensional
Materials from Data Filtering and Ab Initio Calculations. *Physical Review X* **3** (2013).
- 174 Ashton, M., Paul, J., Sinnott, S. B. & Hennig, R. G. Topology-Scaling Identification of Layered
Solids and Stable Exfoliated 2D Materials. *Physical Review Letters* **118** (2017).
- 175 Cheon, G. *et al.* Data Mining for New Two- and One-Dimensional Weakly Bonded Solids and
Lattice-Commensurate Heterostructures. *Nano Letters* **17**, 1915-1923 (2017).
- 176 Mounet, N. *et al.* Two-dimensional materials from high-throughput computational exfoliation
of experimentally known compounds. *Nature Nanotechnology* **13**, 246-252 (2018).
- 177 Hastrup, S. *et al.* The Computational 2D Materials Database: high-throughput modeling and
discovery of atomically thin crystals. *2D Materials* **5**, 042002 (2018).
- 178 Taheri, M. L. *et al.* Current status and future directions for in situ transmission electron
microscopy. *Ultramicroscopy* **170**, 86-95 (2016).
- 179 Lindenberg, A. M., Johnson, S. L. & Reis, D. A. Visualization of Atomic-Scale Motions in
Materials via Femtosecond X-Ray Scattering Techniques. *Annual Review of Materials Research*
47, 425-449 (2017).
- 180 Sciaini, G. & Miller, R. J. D. Femtosecond electron diffraction: heralding the era of atomically
resolved dynamics. *Reports on Progress in Physics* **74**, 096101 (2011).
- 181 Bovensiepen, U. & Kirchmann, P. S. Elementary relaxation processes investigated by
femtosecond photoelectron spectroscopy of two-dimensional materials. *Laser & Photonics
Reviews* **6**, 589-606 (2012).
- 182 Raschke, M. B. & Shen, Y. R. Nonlinear optical spectroscopy of solid interfaces. *Current Opinion
in Solid State and Materials Science* **8**, 343-352 (2004).
- 183 Danz, T., Domröse, T. & Ropers, C. Ultrafast nanoimaging of the order parameter in a
structural phase transition. *Science* **371**, 371-374 (2021).
- 184 Huang, P. Y. *et al.* Grains and grain boundaries in single-layer graphene atomic patchwork
quilts. *Nature* **469**, 389-392 (2011).
- 185 Fasolino, A., Los, J. H. & Katsnelson, M. I. Intrinsic ripples in graphene. *Nature Materials* **6**,
858-861 (2007).
- 186 McGilly, L. J. *et al.* Visualization of moire superlattices. *Nature Nanotechnology* **15**, 580-584
(2020).
- 187 Kim, H.-J., Kang, S.-H., Hamada, I. & Son, Y.-W. Origins of the structural phase transitions in
MoTe₂ and WTe₂. *Physical Review B* **95**, 180101(R) (2017).
- 188 Bistritzer, R. & MacDonald, A. H. Moire bands in twisted double-layer graphene. *Proceedings
of the National Academy of Sciences* **108**, 12233-12237 (2011).
- This paper predicts the existence of strong-correlation physics in magic-angle twisted
bilayer graphene.**
- 189 Balents, L., Dean, C. R., Efetov, D. K. & Young, A. F. Superconductivity and strong correlations
in moiré flat bands. *Nature Physics* **16**, 725-733 (2020).
- 190 Qian, X., Wang, Y., Li, W., Lu, J. & Li, J. Modelling of stacked 2D materials and devices. *2D
Materials* **2** (2015).
- 191 Wang, H. & Qian, X. Electrically and magnetically switchable nonlinear photocurrent in PT-
symmetric magnetic topological quantum materials. *npj Computational Materials* **6**, 199
(2020).
- 192 Salén, P. *et al.* Matter manipulation with extreme terahertz light: Progress in the enabling THz
technology. *Physics Reports* **836-837**, 1-74 (2019).

- 193 Carr, S., Fang, S. & Kaxiras, E. Electronic-structure methods for twisted moiré layers. *Nat Rev Mater* **5**, 748-763 (2020).
- 194 Andrei, E. Y. & MacDonald, A. H. Graphene bilayers with a twist. *Nature Materials* **19**, 1265-1275 (2020).
- 195 Kennes, D. M. *et al.* Moiré heterostructures as a condensed-matter quantum simulator. *Nature Physics* **17**, 155-163 (2021).
- 196 *The International Roadmap For Devices And Systems: 2020*. (IEEE, 2020).
- 197 Rehn, D. A. & Reed, E. J. Memristors with distorted structures. *Nature Materials* **18**, 8-9 (2019).