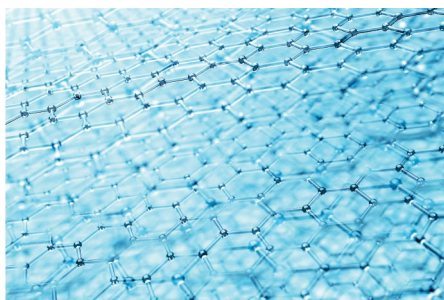


# Ferroelectricity and multiferroicity down to the atomic thickness



**Ultrathin ferroelectric materials, including perovskites, hafnium oxides, and van der Waals stacks are of increasing interest because they exhibit properties that are hard to achieve in bulk and because of their suitability for low-power miniaturized devices.**



**F**erroelectric materials – which, despite their name, do not necessarily need to contain iron – display spontaneous electric polarization that is switchable by an external electric field. Some materials, known as multiferroics, exhibit more than one primary ferroic ordering, such as ferromagnetism, ferroelectricity, ferroelasticity or ferrotoroidicity, in a single phase. Traditional bulk ferroelectric and multiferroic materials are typically incompatible with the requirements of current microelectronics technology fabrication processes. However, the discovery of ultrathin ferroelectric and multiferroic materials has aroused broad interest; particularly after the recent observation of room-temperature ferroelectricity in perovskite oxides, hafnium oxide, and van der Waals materials.

Normally, the thinner the perovskite material, the weaker the ferroelectricity. This size effect is evident in perovskite  $\text{PbTiO}_3$  films, where the ferroelectric phase is stable only up to the critical thicknesses of 1.2 nm (three unit cell), implying that no thickness limit is imposed on miniaturized devices<sup>1</sup>. Moreover, switchable out-of-plane spontaneous polarization in one-unit-cell-thick  $\text{BiFeO}_3$  – a lead-free multiferroic material – can be used as ferroelectric tunnel junctions in miniaturized devices<sup>2</sup>.

While there are severe challenges on the integration of perovskite oxides with modern semiconductor processes, hafnium oxides are promising for applications in polarization-driven memories and ferroelectric-based transistors due to their compatibility with complementary-metal-oxide-semiconductor technology. Inversion symmetry breaking and switchable

polarization have been reported in  $\text{Hf}_{0.8}\text{Zr}_{0.2}\text{O}_2$  with thickness of 1 nm (ref. 3), showing no ferroelectricity critical thickness. Unlike perovskites, hafnium oxides show increased polar distortion with reduced film thickness; a useful effect for polarization-driven low-power memories. Moreover, structures with such binary oxides are simpler than those of  $\text{ABO}_3$  perovskite oxides.

The ferroelectric properties of van der Waals ferroelectrics are obviously different from those of bulk ferroelectrics, due to their size and stacking effects. Only a few examples of out-of-plane two-dimensional (2D) ferroelectrics, including  $\text{CuInP}_2\text{S}_6$ ,  $\text{In}_2\text{Se}_3$  and  $\text{MoTe}_2$ , have been reported, while pure in-plane ferroelectricity was discovered in 2D  $\text{SnS}$  (ref. 4). Besides these inherent 2D ferroelectric materials, 2D sliding ferroelectrics based on the vertical stacking mismatch between two or more van der Waals layers has been proposed and experimentally observed in multilayer  $\text{WTe}_2$  (the monolayer of  $\text{WTe}_2$  is non-polar, but its bilayer or trilayer shows spontaneous out-of-plane electric polarization due to the stacking mismatch)<sup>5</sup>.

Because the electronic band structure and the crystal symmetry of van der Waals materials depend on the stacking arrangement of constituent layers, it is possible to engineer a ferroelectric stack even though the material is non-ferroelectric in bulk. A robust ferroelectric order emerges in twisted boron nitride sheets in a metastable non-centrosymmetric parallel orientation, which changes the dynamics of switching due to the formation of moiré ferroelectricity with staggered polarization<sup>6,7</sup>. By stacking two identical monolayer

transition metal dichalcogenides, namely  $\text{WSe}_2$ ,  $\text{MoSe}_2$ ,  $\text{WS}_2$  or  $\text{MoS}_2$ , room-temperature ferroelectric hysteresis was also observed<sup>8</sup>. A different strategy to obtain out-of-plane ferroelectric properties would be to stack alternating layers of  $\text{MoS}_2$  and  $\text{WS}_2$ , which breaks symmetry without requiring twisting<sup>9</sup>.

Two-dimensional multiferroic materials have attracted wide interest for magnetoelectric applications, owing to the coexistence of and coupling between ferromagnetic and ferroelectric orders. For example, a few-layer  $\text{CuCrP}_2\text{S}_6$  – a type-II multiferroic material – shows an inversion-symmetry-breaking magnetic order inducing ferroelectric polarization and polarization–magnetization coupling<sup>10</sup>. Multiferroic state was also optically detected in a single atomic layer of the van der Waals material  $\text{NiI}_2$ , although direct magnetic and electric measurements would be needed to confirm its multiferroic properties<sup>11</sup>.

Due to their high versatility, van der Waals crystals are ideal systems to enlarge the landscape of multiferroic materials. It is usually difficult to achieve simultaneous multiple ferroic orders in a single-phase material, as ferroelectricity normally requires empty  $d$  orbitals occupation of metal ions, while ferromagnetism often comes from partially filled  $d$  orbitals. Yet, heterogeneous stacking of 2D magnet and 2D ferroelectric materials can display the necessary coupling between ferroelectric and magnetic order to achieve multiferroicity. For example, a strong interlayer magnetoelectric effect has been predicted in a bilayer heterostructure of ferromagnetic  $\text{Cr}_2\text{Ge}_2\text{Te}_6$  and ferroelectric  $\text{In}_2\text{Se}_3$  monolayers<sup>12</sup>, with several other ferromagnetic/ferroelectric heterobilayer<sup>13</sup> and antiferromagnetic/ferroelectric structures proposed<sup>14</sup>.

Compared to bulk ferroelectric oxides, many chalcogenide-based or halide-based 2D van der Waals ferroelectric materials are unstable under ambient conditions, owing to their reactivity with oxygen and water. Frontier research lies on developing encapsulation techniques to prevent degradation of the van der Waals film without compromising ferroelectric properties.

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