

Two-dimensional ferroelectricity by design

A synthetic ferroelectric is made from a van der Waals assembly of boron nitride

By **Evgeny Y. Tsybal**

The discovery of ferroelectricity marks its 100th anniversary this year (1), and this phenomenon continues to enrich our understanding of many fields of physics and material science, as well as creating subfields on its own. All of the ferroelectrics discovered have been limited to those exhibiting a polar space group of the bulk crystal that supports two or more topologically equivalent variants with different orientations of electric polarization. On pages 1458 and 1462 of this issue, Yasuda *et al.* (2) and Vizner Stern *et al.* (3), respectively, show that ferroelectricity can be engineered by artificially stacking a nonpolar in bulk, two-dimensional (2D) mate-

rial, boron nitride (BN). A relatively weak van der Waals (vdW) coupling between the adjacent BN monolayers allows their parallel alignment in a metastable non-centrosymmetric coordination supporting 2D ferroelectricity with an out-of-plane electric polarization. These findings open opportunities to design 2D ferroelectrics out of parent nonpolar compounds.

Owing to the switchable electric polarization, ferroelectric materials are useful for various technological applications (4). A continuing quest for miniaturizing electronic devices inspires the search for appropriate materials exhibiting a reversible polarization at reduced dimensions. Although perovskite oxides have been widely used to explore ferroelectricity in

thin-film structures and, in certain cases, showed promising results, they suffer from several limitations (5). Among them is the strong sensitivity of thin-film ferroelectricity to boundary conditions, largely resulting from the dangling bonds inherited from the perovskite structure, and oxygen stoichiometry, which is often not easy to control.

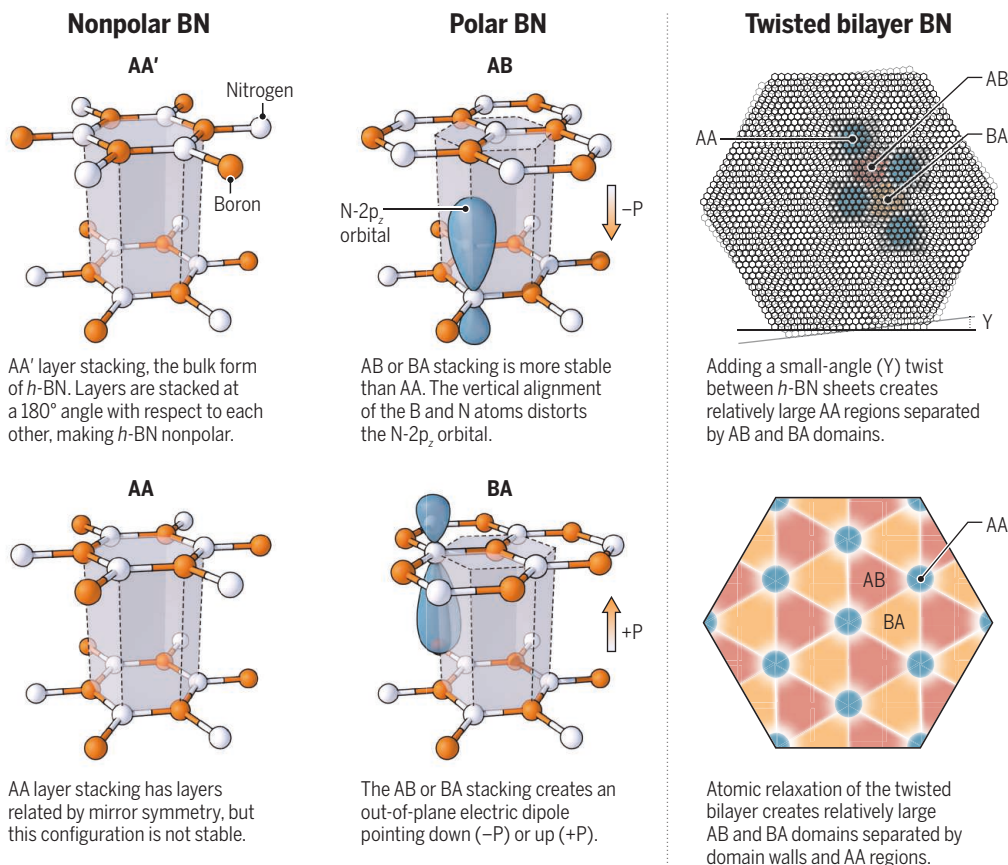
The rise of vdW materials (6) opened opportunities for materials science, including studies of collective phenomena such as 2D ferroelectricity (7). 2D vdW ferroelectrics are appealing because of their uniform atomic thickness, absence of dangling bonds, and the ability to be integrated with other vdW materials, which allows for useful functionalities. For example, in combination with high-mobility materials such as graphene,

the 2D vdW ferroelectrics can be employed in ferroelectric field-effect transistors or can be used as ultrathin barriers in ferroelectric tunnel junctions (8).

Similar to perovskite oxides, however, the emergence of ferroelectricity in 2D vdW materials is limited by the requirement of the polar space group of the bulk crystal. In many-layered crystals, like hexagonal boron nitride (*h*-BN) and transition-metal dichalcogenides, the polarization is prohibited by a centrosymmetric vdW structure that has lower energy than other stacking configurations. Yasuda *et al.* and Vizner Stern *et al.* remedy this limitation by showing that an intrinsically centrosymmetric vdW material, *h*-BN, can be engineered on the atomic scale to become ferroelectric.

A bulk *h*-BN crystal has a layered structure where each BN monolayer displays a honeycomb coordination, similar to graphene, but with two interleaving sublattices composed of boron (B) and nitrogen (N). Bulk *h*-BN exhibits

Polarization in hexagonal boron nitride (*h*-BN)



AA' stacking (see the figure), where the top BN monolayer is 180° rotated with respect to the bottom so that the B (N) atoms are positioned atop the N (B) atoms, which makes the *h*-BN crystal centrosymmetric. A different BN coordination involves AA stacking, where two BN monolayers are stacked mirror symmetrically without rotation. This stacking is, however, unstable with respect to a B-N bond length displacement along the bond, which forms either AB or BA stacking configuration with half of the atoms lying atop each other and the other half facing empty centers of the hexagons (9). The AB and BA structures have broken inversion symmetry and exhibit an out-of-plane polarization, which can be qualitatively understood by the distortion of the 2p_z orbital of the N atoms sitting atop B atoms (10). The AB and BA stackings are related by mirror reflection and hence have opposite polarizations.

To realize AB (BA) stacked BN bilayers, an exfoliated BN monolayer was ripped off or few-monolayer *h*-BN flake were separated into two pieces, and then stamped them on top of each other with a precisely controlled twist angle. A zero-twist angle supports the AB (BA) stacking, whereas a small finite twist imposes interlayer translations forming a moiré pattern that consists of the three nearly commensurate stacking configurations AB, BA, and AA. Structural relaxation reconstructs this moiré pattern into large triangular domains of commensurate AB and BA stackings separated by abrupt incommensurate domain walls and topological AA defects that accommodate the global twist.

The staggered polarization of the twisted BN was demonstrated by using piezoelectric force microscopy (PFM) and Kelvin-probe force microscopy (KPFM). Both scanning probe methods revealed an array of triangular areas extending over several square micrometers and exhibiting an alternating contrast either in the piezoelectric response or in the electrostatic potential, thus indicating an opposite out-of-plane polarization of the AB and BA domains. The triangular contrast disappeared in a BN monolayer and AA' stacked regions, confirming that the polarization is driven by the AB (BA) interlayer stacking.

Notably, the authors showed that the spontaneous polarization can be switched by applied bias voltage. Yasuda *et al.* probed the polarization switching by measuring resistance of a graphene sheet deposited over a single AB (BA) domain to detect extra charge carriers induced by the BN-bilayer polarization. The forward and backward scans of the resistance versus gate voltage showed a pronounced hysteresis, indicat-

ing bistability driven by the polarization switching. In parallel, Vizner Stern *et al.* detected the polarization switching by scanning a biased tip above an individual AB (BA) domain. They observed redistribution of domain walls to orient the local polarization with the electric field under the biased tip. Scanning the same area with the tip of opposite polarity reversed the KPFM contrast, indicating that polarization switching was fully reversible.

The polarization switching was found to occur through the domain nucleation and growth mechanism reminiscent of that known to occur in perovskites oxides. However, whereas in perovskites the two polarization states are distinguished by the minute displacements of tightly bonded atoms, in the AB (BA) stacked BN, they differ by a double B-N bond length translation along a weakly coupled interface. As a result, the polarization reversal could be regarded as a lateral sliding of one BN monolayer with respect to the other occurring through domain-wall motion.

Yasuda *et al.* and Vizner Stern *et al.*, along with recent work by Woods *et al.* (11) and Zheng *et al.* (12), identify synthetic ferroelectricity as an emergent field of research. These findings provide new opportunities for the fundamental studies of 2D ferroelectricity, as well as paving the way for innovative device applications. The proposed engineering of 2D ferroelectrics can be extended beyond BN to other vdW materials, such as transition metal dichalcogenides. The synthetic 2D ferroelectrics can be combined with other vdW materials to functionalize their electronic, spintronic, and optical responses. Overall, there are no doubts that this emergent field is rich in opportunities, and exciting new developments are to come. ■

REFERENCES AND NOTES

1. J. Valasek, *Phys. Rev.* **17**, 475 (1921).
2. K. Yasuda, X. Wang, K. Watanabe, T. Taniguchi, P. Jarillo-Herrero, *Science* **372**, 1458 (2021).
3. M. Vizner Stern *et al.*, *Science* **372**, 1462 (2021).
4. J. F. Scott, *Science* **315**, 954 (2007).
5. L. W. Martin, A. M. Rappe, *Nat. Rev. Mater.* **2**, 16087 (2016).
6. A. K. Geim, I. V. Grigorieva, *Nature* **499**, 419 (2013).
7. C. Cui, F. Xue, W.-J. Hu, L.-J. Li, *npj 2D Mater. Appl.* **2**, 18 (2018).
8. E. Y. Tsymlal, H. Kohlstedt, *Science* **313**, 181 (2006).
9. G. Constantinescu, A. Kuc, T. Heine, *Phys. Rev. Lett.* **111**, 036104 (2013).
10. L. Li, M. Wu, *ACS Nano* **11**, 6382 (2017).
11. C. R. Woods *et al.*, *Nat. Commun.* **12**, 347 (2021).
12. Z. Zheng *et al.*, *Nature* **588**, 71 (2020).

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GENE EXPRESSION

Repeat after Me(CEP2)!

A motif of dinucleotide repeats in the genome may be associated with Rett syndrome

By Jian Zhou^{1,2} and Huda Zoghbi^{1,2,3,4}

Rett syndrome (RTT) is a devastating neurodevelopmental disease caused primarily by loss-of-function mutations in *methyl-CpG-binding protein 2* (*MECP2*) (1). MeCP2 is a DNA binding protein (2) that controls gene expression, but the precise molecular mechanism by which MeCP2 loss drives RTT pathology remains unclear, partially because a distinct DNA motif that specifies MeCP2-DNA interactions is lacking. On page 1411 of this issue, Ibrahim *et al.* (3) demonstrate that MeCP2 binds modified cytosine in cytosine-adenine (CA) dinucleotide repeats, providing a new signature DNA motif for MeCP2 binding. MeCP2 protects CA repeats from high nucleosome occupancy, raising questions about the consequence of this binding on maintaining chromatin structure in neurons.

MeCP2 was first characterized as binding to methylated cytosine residues in the context of cytosine-guanine (CG) dinucleotides. Many mutations in the methyl-CpG binding domain (MBD) of MeCP2 cause the most severe RTT phenotypes in patients and mouse models of the condition, indicating that DNA binding is essential to MeCP2 function (4–6). Later studies revealed that MeCP2 also binds methylated CH [mCH, where H is adenine (A), cytosine (C), or thymine (T)], hydroxymethylated CA (hmCA), and methylated or hydroxymethylated CAC (7–9). Unlike canonical transcription factors, the characterization of MeCP2 binding sites did not identify a signature motif. Because of this featureless binding pattern and high abundance of the protein—MeCP2 broadly coats the genome (10)—it has been challenging to associate MeCP2 DNA binding with specific gene expression changes. Identifying the DNA sequences and modifications that

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