Ferroelectricity in 2D Elemental Materials

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Ferroelectric materials are typically made up of various elements. By introducing atomic displacements,[1] such as octahedral tilts/rotations[2,3] or interlayer sliding,[4–7] the positive and negative charge centers can be separated, resulting in spontaneous polarization. Due to their homogeneity, it is difficult to achieve ferroelectricity in elemental materials where opposite charge centers must be generated. However, electron degeneracy between identical elements may be a crucial factor for achieving ferroelectricity in such materials.

Theoretical Prediction. The first elementary ferroelectrics were proposed for group V elements (As, Sb, Bi) in monolayer black phosphorous structures using first-principles calculations. Charge transfer between sublattices induces a lone pair in the p_z orbitals, stabilizing the ferroelectric buckled structure and producing in-plane polarization comparable to that of monolayer SnTe.[8] This prediction has inspired further attempts to explore ferroelectricity in non-centrosymmetric elemental structures. In group VI, tellurium (Te) is non-centrosymmetric in bulk materials and can be grown epitaxially in two-dimensional form.[9] Interlayer interaction-induced ferroelectricity was predicted in multilayer Te. However, the repulsion between lone pairs in monolayer Te makes it a centrosymmetric structure. In bilayer Te, the interlayer lone-pair interaction can be weakened through in-plane polar distortions, resulting in in-plane polarization of 1.02×10^{-10} C/m.[10] The presence of ferroelectricity in bulk elemental materials is extremely rare due to their high symmetry. In contrast, surfaces are considered to have low symmetry, where non-centrosymmetric structures often occur. For example, asymmetric dimer reconstruction was reported in Si(001) and Ge(001) surfaces due to Peierls instability.[11] Theoretical work has shown that in asymmetric dimer reconstruction in Si(001), in-plane local polarization of 0.45×10^{-10} C/m is induced due to the dehybridization of p_z orbitals. With compressive strain, the interdimer interactions can be enhanced, and the ferroelectricity can be sustained up to room temperature.[12]

Experimental Investigation. Ferroelectricity is typically verified experimentally through phase hysteretic and butterfly loops in piezoresponse force microscopy (PFM). PFM has confirmed piezoelectricity with spontaneous polarization and ferroelectric-like hysteresis behavior in 2D Te devices.[13] However, for materials with small bandgaps such as black-phosphorous-like bismuth[14] or semimetal WTe_2,[15] it can be challenging to perform PFM at domain walls due to large leakage current. Recently, ferroelectricity was confirmed in 2D black-phosphorous-like bismuth by combining various characterization techniques. Atomic-resolved noncontact atomic force microscopy (AFM) measurements first confirmed the buckled structure with a height difference of 40 pm between sublattices. The dI/dV spectra obtained by scanning tunneling spectroscopy (STM) showed the shark peak in the gap, indicating non-split p_z orbitals at the domain wall that move to a higher binding energy at normal positions. In addition, the potential difference between sublattices was illustrated by dI/dV mapping and local contact potential difference, further confirming charge transfer between sublattices in Bi monolayer. By combining the above experimental evidences, spontaneous polarization was confirmed in monolayer bismuth, consistent with the theoretical predictions.

Furthermore, in order for a material to exhibit ferroelectricity, its spontaneous polarization should be able to be reversed by an external electric field. This can be achieved by applying a sweeping voltage at a 180° head-to-head domain using a conductive STM/AFM tip, as evidenced by the asymmetric dI/dV spectrum and AFM images that show movement of the domain wall and reversal of polarization. Interestingly, anomalous phenomena were also observed in the conjugated 180° tail-to-tail domain walls, which had a wider width of 56 Å and identical band bending direction as the head-to-head walls (15 Å). According to the Landau–Ginzburg–Devonshire theory, when the screened Coulomb interaction is taken into account, the width of the tail-to-tail walls becomes larger, matching with the experimental observations. Furthermore, by considering the variation in electronic structure correlated with the height of the buckle, the anomalous electric potential measurements can be reproduced.[16]

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Theoretical predictions and experimental measurements of single-element ferroelectricity have broadened our understanding of the mechanisms of ferroelectrics. Elementary ferroelectric materials may now be promising candidates for 2D ferroelectric devices.

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