Discovery of Ferroelectricity in An Elementary Substance

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National University of Singapore (NUS) physicists have discovered a novel form of ferroelectricity in a single-element bismuth monolayer that can produce regular and reversible dipole moments for future applications of non-volatile memories and electronic sensors.

Ferroelectricity refers to the phenomenon of certain materials exhibiting a spontaneous electric polarisation that can be reversed by applying an external electric field. Ferroelectric materials are characterised by a crystal structure that lacks a centre of symmetry.

Due to the potential applications for data storage, ferroelectric materials have attracted widespread research attention. Besides, their piezoelectric, thermoelectric and nonlinear optical properties have been extensively studied in research areas such as renewable energy, micro-electro-mechanical systems and optical devices. In recent years, two-dimensional (2D) ferroelectric materials have emerged as a new contender in the field of neuromorphic synapse devices, displaying the advantage of low dimensionality. However, the development of 2D ferroelectric materials is still limited due to the small number of available materials.

Ferroelectricity commonly occurs in compounds composed of multiple constituent elements, where the gain and loss of electrons between the constituents promotes the formation of positive and negative ions in the crystal. Regular atom distortion or charge ordering between sublattices leads to the breaking of the central symmetry, thus promoting the formation of ferroelectric polarisation.

Recently, a research team led by Professor Andrew WEE from the Department of Physics, NUS, made a breakthrough discovery of the single-element ferroelectric state in 2D black phosphorus-like bismuth (BP-Bi), overturning the traditional understanding of ferroelectricity

mentioned above. By using optimised scanning tunnelling microscopy (STM) and non-contact atomic force microscopy (nc-AFM) techniques, the researchers did a detailed observation of the centrosymmetry-breaking on the atomic structure and charge transfer between sublattices in BP-Bi. For the first time, the single-element ionicity, single-element in-plane polarisation and single-element ferroelectricity were all demonstrated in the bismuth monolayer experimentally. This discovery changes the concept that ionic polarisation only exists in compounds with cations and anions, and expands the scope of ferroelectricity development in the future. This work is undertaken in collaboration with Professor Lan CHEN from the Institute of Physics, Chinese Academy of Sciences and Professor Yunhao LU from the School of Physics, Zhejiang University. The findings were published in Nature.

Figure (A) shows the ball-and-stick model of black phosphorus-like bismuth (BP-Bi) with top view (top panel) and side view (bottom panel). Different from black phosphorous, BP-Bi has a nonzero buckling Dh. Figure (B) and (C) show the typical non-contact atomic force microscopy (nc-AFM) image and Kelvin probe microscopy (KPFM) map of the same location respectively. Figure (D) represents the domain wall movement detected by nc-AFM when performing the polarisation switching. The top and bottom halves are the images acquired after forward and backward bias sweeping respectively. Figure (E) is the tip-height dependence of the current during the bias sweep.

The researchers prepared the high-quality BP-Bi on the Van der Waals graphite surface so that the monolayer BP-Bi is intact and flat enough for the measurements. Taking advantage of the high spatial resolution of nc-AFM, the buckling atomic configuration ($Dh \neq 0$) of BP-Bi, as well as the charge redistribution between the two sublattices were determined by AFM imaging and Kelvin probe microscopy (KPFM) measurements. Thereafter, a regular in-plane dipole arrangement is confirmed in the BP-Bi monolayer. In comparison, single layer phosphorous (phosphorene) has no buckling in each sub-layer – therefore it is centrosymmetric and nonpolarised. Then, polarisation switching of BP-Bi is realised by using the in-plane electric field produced by the STM tip, which is the basis for writing on the non-volatile memory devices.

Ferroelectricity relative to magnetism is advantageous for its manipulation by only the

electric field. This makes it more suitable to be contained in integrated circuit devices. Many studies found that it is possible to manipulate other material attributes by coupling ferroelectricity with these properties. In BP-Bi, the buckling degree of atomic structure determines the ferroelectric polarisation and, at the same time, controls the basic band structure. This results in an interlock between the electronic structure and ferroelectric polarisation. This new type of ferroelectricity offers a promising way to modulate the electronic structure of materials by an external electric field through ferroelectric distortion.

Dr Jian GOU, the lead author for the research paper, said, “Other research has also shown that BP-Bi exhibits topologically nontrivial states at a specific buckling height, suggesting a potential opportunity for tuning topological states through an electric field.”

In fact, the polarisation characteristics have a critical impact on the basic optical and electrical properties of materials. The discovery of single-element ferroelectric polarisation adds a new viewpoint to the study of the basic physical properties of elementary substances.

Prof Wee said, “In addition to overturning the common-sense idea that ionic polarisation only exists in compounds, we believe that single-element ferroelectricity in BP-Bi would introduce a new perspective to the study and design of novel ferroelectric materials, and inspire new physics of elemental materials in the future.”

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