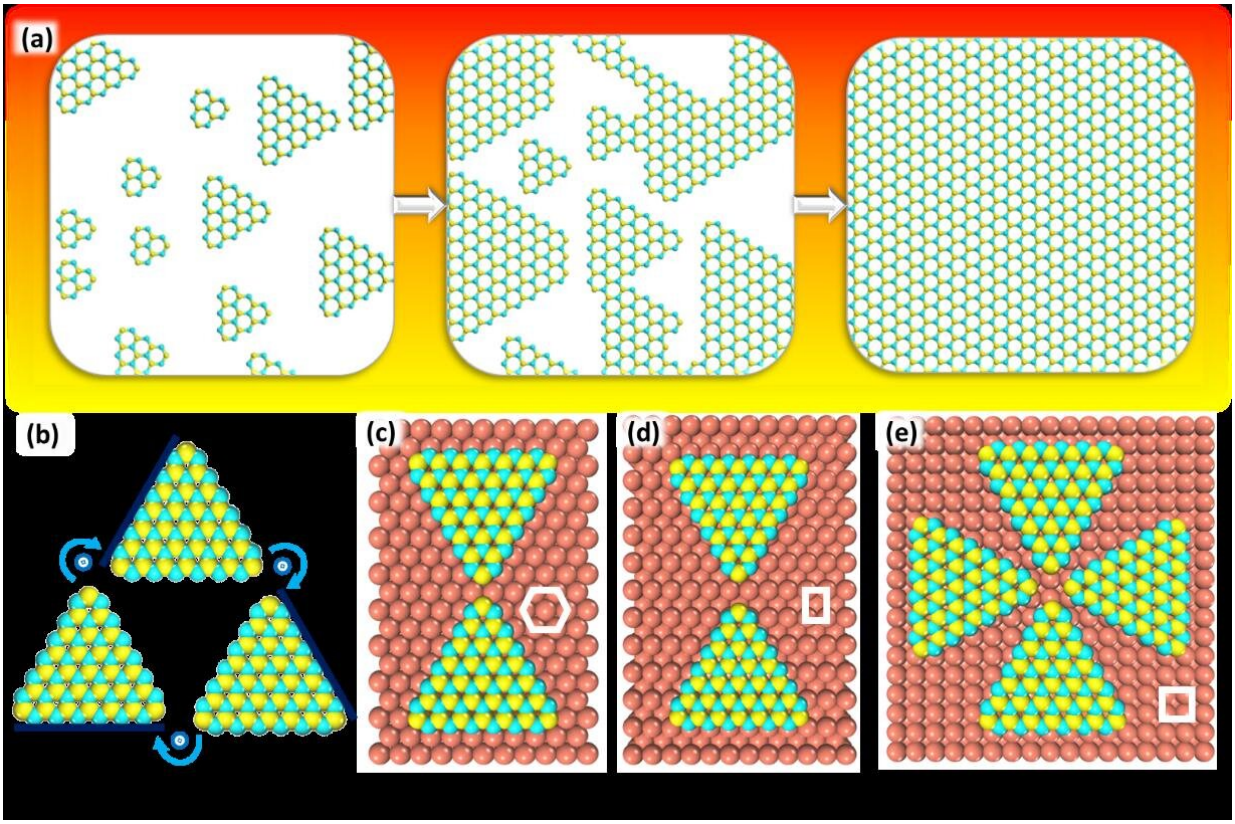
How to enlarge 2-D materials as single crystals

May 22 2019



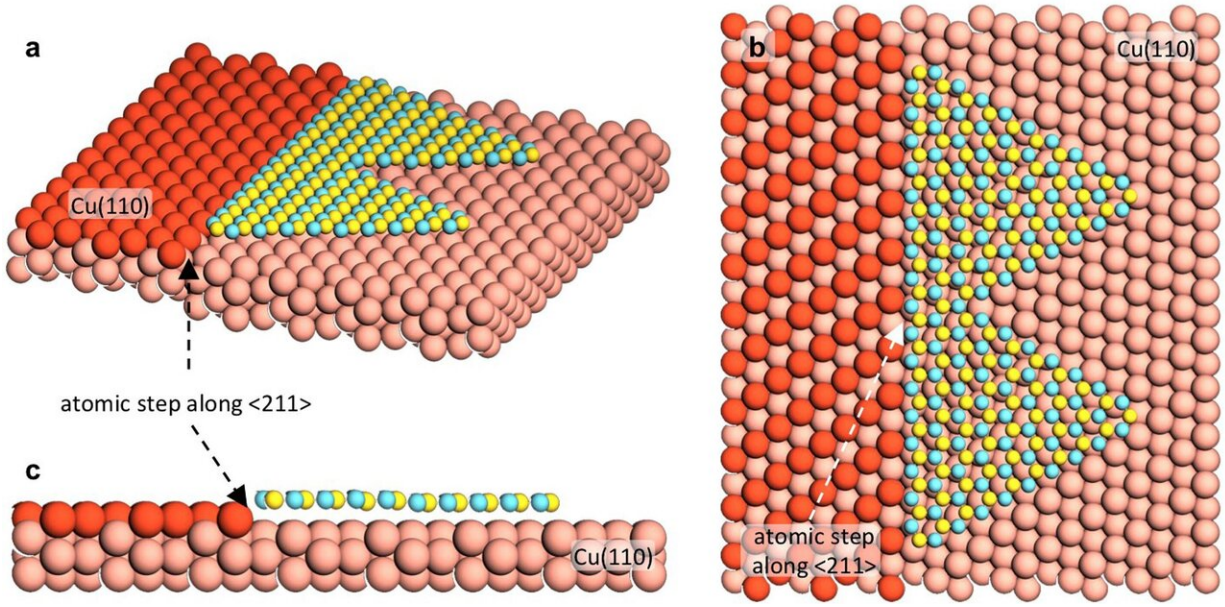
The hBN islands in (a) are unidirectional. In (b) the 3-fold symmetrical hBN shows 3 times of coincidences during the rotation form 0-360°. hBN has a 3-fold symmetry because the lattice of hBN will not be changed by rotating it by 360°/3 = 120°. (c-e) The equivalent alignments of hBN on copper surfaces (c-e), namely Cu(111), Cu(110) and Cu(100). The top layer atoms of (c),(d) and (e) show equivalent hBN alignments on substrates with 6-, 2-, 4-fold symmetries, respectively. The white shapes show the geometrical characteristic of the substrates, from which the symmetries of the substrates can be seen. Credit: IBS

What makes something a crystal? A transparent and glittery gemstone? Not necessarily, in the microscopic world. When all of its atoms are arranged in accordance with specific mathematical rules, we call the material a single crystal. As the natural world has its unique symmetry, e.g., snowflakes or honeycombs, the atomic world of crystals is designed by its own rules of structure and symmetry. This material structure has a profound effect on its physical properties as well. Specifically, single crystals play an important role in inducing a material's intrinsic properties to its full extent. Faced with the coming end of the miniaturization process that the silicon-based integrated circuit has allowed up to this point, major efforts have been dedicated to find a single crystalline replacement for silicon.

In the search for the transistor of the future, two-dimensional (2-D) materials, especially graphene, have been the subject of intense research around the world. Being thin and flexible as a result of being only a single layer of atoms, this 2-D version of carbon even features unprecedented electricity and heat conductivity. However, the last decade's efforts for graphene transistors have been held up by physical restraints—graphene allows no control over electricity flow due to the lack of band gap. So then, what about other 2-D materials? A number of interesting 2-D materials have been reported to have similar or even superior properties. Still, the lack of understanding in creating ideal experimental conditions for large-area 2-D materials has limited their maximum size to just a few millimeters.

Scientists at the Center for Multidimensional Carbon Material (CMCM) within the Institute for Basic Science (IBS) have presented a novel approach to synthesize on a large scale, silicon-wafer-size, single crystalline 2-D materials. Prof. Feng Ding and Ms. Leining Zhang in collaboration with their colleagues at Peking University, China and other

institutions have found a substrate with a lower order of symmetry than that of a 2-D material that facilitates the synthesis of single crystalline 2-D materials in a large area. "It was critical to find the right balance of rotational symmetries between a substrate and a 2-D material," notes Prof. Feng Ding, one of corresponding authors of this study. The researchers successfully synthesized hBN single crystals of 10 x 10 cm^2 by using a new substrate: a surface near Cu(110) that has a lower symmetry of (1) than hBN with (3).



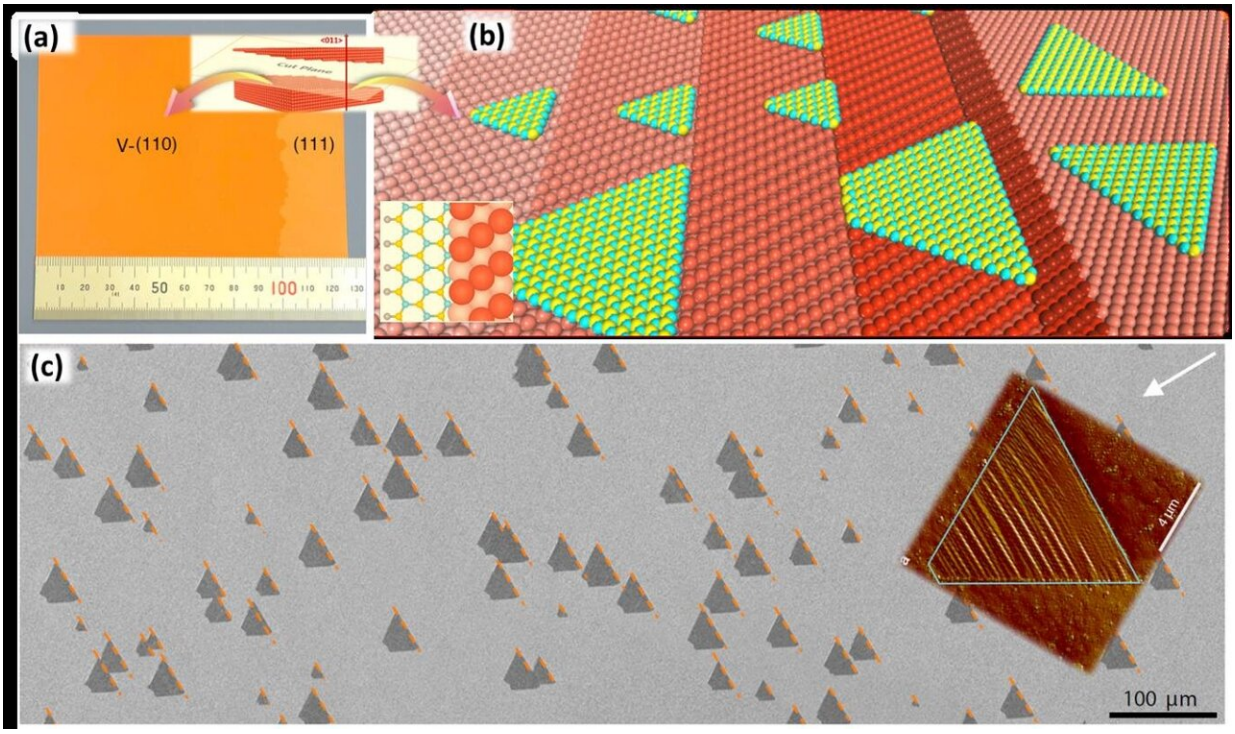
(a-c), schematic of edge-coupling-guided hBN growth on a Cu (110) vicinal surface with atomic step edges along the direction. (b) shows the top view and (c) shows a side view. Credit: IBS

Why does symmetry matters? Symmetry, in particular rotational symmetry, describes how many times a certain shape fits on to itself during a full rotation of 360 degrees. The most efficient method to synthesize large-area and single crystals of 2-D materials is to arrange

layers over layers of small single crystals and grow them upon a substrate. In this epitaxial growth, it is quite challenging to ensure all of the single crystals are aligned in a single direction. Orientation of the crystals is often affected by the underlying substrate. By theoretical analysis, the IBS scientists found that an hBN island (or a group of hBN atoms forming a single triangle shape) has two equivalent alignments on the Cu(111) surface that has a very high symmetry of (6). "It was a common view that a substrate with high symmetry may lead to the growth of materials with a high symmetry. It seemed to make sense intuitively, but this study found it is incorrect," says Ms. Leining Zhang, the first author of the study.

Previously, various substrates such as Cu(111) have been used to synthesize single crystalline hBN in a large area, but none of them were successful. Every effort ended with hBN islands aligning in several different directions on the surfaces. Convinced by the fact that the key to achieve unidirectional alignment is to reduce the symmetry of the substrate, the researchers made tremendous efforts to obtain vicinal surfaces of a Cu(110) orientation; a surface obtained by cutting a Cu(110) with a small tilt angle. It is like forming physical steps on Cu. As an hBN island tends to position in parallel to the edge of each step, it gets only one preferred alignment. The small tilt angle lowers the symmetry of the surface as well.

The researchers eventually found that a class of vicinal surfaces of Cu (110) can be used to support the growth of hBN with perfect alignment. On a carefully selected substrate with the lowest symmetry (or the surface will repeat itself only after a 360 degree rotation), hBN has only one preferred direction of alignment. The research team of Prof. Kaihui Liu at Peking University has developed a unique method to anneal a large Cu foil, up to 10 x 10 cm^2, into a single crystal with the vicinal Cu (110) surface, and with it, they have achieved the synthesis of hBN single crystals of the same size.



(a) large area single-crystal copper foil with a low symmetric surface, a vicinal surface of Cu(110) orientation, namely V-(110). (b) the growth of large number of unidirectional aligned hBN islands on the vicinal Cu(110) surface. (c) SEM and AFM images of hBN islands on vicinal Cu (110). Credit: IBS

Besides flexibility and ultrathin thickness, emerging 2-D materials can present extraordinary properties when they are enlarged as single crystals . "This study provides a general guideline for the experimental synthesis of various 2-D materials. Besides the hBN, many other 2-D materials could be synthesized with large area single crystalline substrates with low symmetry," says Prof. Feng Ding. Notably, hBN is the most representative 2-D insulator, which is different from the conductive 2-D materials, such as graphene, and 2-D semiconductors, such as molybdenum disulfide (MoS_2). The vertical stacking of various types of

2-D materials, such as hBN, graphene and MoS_2, would lead to a large number of new materials with exceptional properties and can be used for numerous applications, such as high-performance electronics, sensors, or wearable electronics."

More information: Epitaxial growth of a 100-square-centimetre single-crystal hexagonal boron nitride monolayer on copper. *Nature*. DOI: 10.1038/s41586-019-1226-z

Provided by Institute for Basic Science