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Perspective

Progress and perspective on the growth of two-dimensional single crystals

Xiaozhi Xu [a,*], Kaihui Liu [b,c,*]

[a] Guangdong Provincial Key Laboratory of Quantum Engineering and Quantum Materials, Guangdong-Hong Kong Joint Laboratory of Quantum Matter, School of Physics and Telecommunication Engineering, South China Normal University, Guangzhou 510006, China
[b] State Key Laboratory for Mesoscopic Physics, Frontiers Science Center for Nano-optoelectronics, School of Physics, Peking University, Beijing 100871, China
[c] Songshan Lake Materials Laboratory, Institute of Physics, Chinese Academy of Sciences, Dongguan 523808, China

Consisting of one to a few atomic layers, two-dimensional (2D) materials have atomically perfect surfaces that are free of dangling bonds and exhibit various exotic physical and chemical properties [1]. Even more exciting, one can construct new materials by stacking different 2D layers as they are generally bonded by van der Waals interactions [2]. Therefore, in the past decade, 2D materials have attracted much interest in the field of materials science, physics, chemistry and electrical/optical engineering. To implement the most anticipated applications of the 2D materials-based devices in the future, the growth of large-scale 2D single crystals is a prerequisite. Only single crystals can ensure the ultimate intrinsic performance of the materials and the uniformity of the devices.

Generally, there are two ways to realize the growth of 2D single crystals: (1) controlling the nucleation. One should ensure the material grows gradually from only one nucleus, which could eventually grow into a large single crystal [3,4]. (2) Controlling the orientation. There are massive nuclei formations during the growth and one should ensure that the lattice orientations of all the 2D islands are the same. When these islands meet each other, they can seamlessly merge together and form large single-crystal films [5–11]. After more than ten years efforts, the epitaxy of 2D single crystals by controlling the orientation has been widely chosen due to its high efficiency, general applicability, stable controllability and better compatibility with industrial production.

The realization of epitaxial growth of 2D single crystals relies on suitable single-crystal substrates. Driven by the urgency of preparing large 2D single crystals, the production of large-size single-crystal substrates has been developed rapidly in recent years. Taking copper (Cu) as an example, the size of single-crystal Cu foils increases quickly from millimetre- to meter-scale, and the surface index also develops from only low index to a lot of high indices through recently developed temperature-gradient-driven [5], contact-free annealing [12] or seeded growth techniques [13].

Having a single-crystal substrate, it is then necessary to select applicable epitaxy substrates and proper mechanisms to achieve the unidirectional alignment of 2D islands according to the lattice symmetry of the 2D materials and substrates. For centrosymmetric graphene, the identical orientations can be achieved by van der Waals coupling between graphene islands and the triple symmetric Cu(111). Regulated by the periodic potential fields on Cu(111) surface, all graphene islands exhibit the same orientation and then seamlessly merge into a single-crystal film (Fig. 1a) [5]. Later, this epitaxy has also been extended to the Cu_xNi_y (111) substrates, where the presence of minor nickel can enhance the catalytic activity of Cu, and realize the rapid growth of graphene single crystals [6].

For non-centrosymmetric hexagonal boron nitride (hBN), due to its C_{3v} lattice symmetry, two equivalent antiparallel islands would always appear synchronously on most high symmetric surfaces, leading to the formation of twin boundaries, which greatly increases the difficulty in the epitaxy of hBN single crystals. To break this equivalence, researchers introduced the parallel atomic steps to reduce the surface symmetry of the substrate to C_1. The unique edge coupling between atomic steps and hBN islands ensured unidirectional alignment and the later seamless stitching (Fig. 1b). Under this mechanism, wafer-scale single-crystal hBN films have been synthesized on vicinal Cu(110), Cu(111) and many other high-index surfaces with steps [7,8].

For another class of typical 2D materials, the transition metal dichalcogenides (TMDs), the growth mechanism is similar to that of hBN because they have the same in-plane lattice symmetry. However, due to the weak interaction between step edges and TMDs islands on insulating substrates, it is very difficult to achieve unidirectional alignment of TMDs only by steps edge coupling [10]. In this case, single-crystal TMDs can be produced by the so called dual-coupling-guided mechanism. The sapphire surface-TMDs interaction will lead to two preferred antiparallel orientations of the TMDs islands, and then sapphire step edge-TMDs interaction breaks the energy equivalence of the antiparallel orientations (Fig. 1c). This technique has been proved to be feasible for a variety of 2D materials, and the production of wafer-scale TMDs single crystals has become a reality [11].

Over the past 15 years efforts, the preparation of 2D single crystals has made breakthrough progress. The size of three representative 2D single crystals, conducting graphene, semiconducting

* Corresponding authors.
E-mail addresses: xiaozhixu@scnu.edu.cn (X. Xu), khliu@pku.edu.cn (K. Liu).

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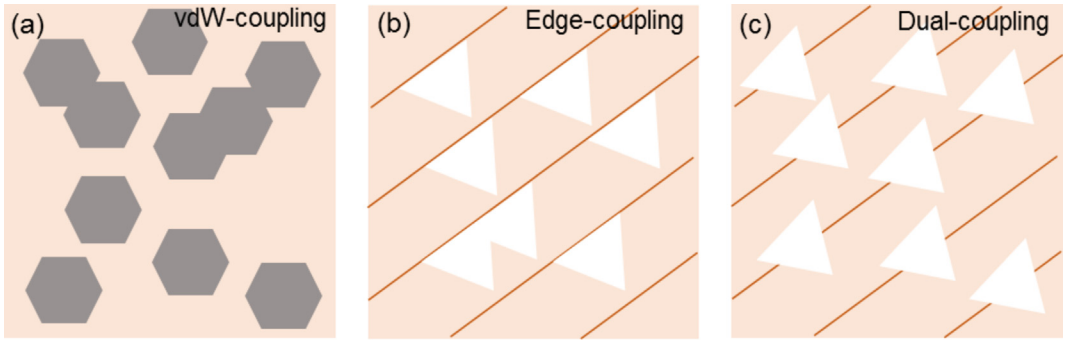

Fig. 1. (Color online) Schematic diagrams of three growth mechanisms of 2D single crystals. (a) van der Waals (vdw)-coupling, (b) edge-coupling and (c) dual-coupling guided growth.

TMDs and insulating hBN, has increased from nanometre-scale to industrially acceptable wafer scale. However, the research on the production of 2D single crystals is far from being over. There are still considerable fields waiting for researchers to explore and great challenges to overcome, including controllable doping, layer number, stacking order, twist angle and heterostructure (Fig. 2). In the following, we will make an outlook on the challenges in the production of 2D single crystals in the future.

Despite lots of excellent properties, the zero-bandgap nature of graphene has seriously limited its application in the field of electronics. Among the many attempts, doping is considered to be a promising method to modify the band structure of graphene without reducing the electrical performance and stability. For example, by doping graphene with boron and nitrogen, it is expected to produce a new semiconducting material with continuously tunable bandgap, named boron carbonitride or BCN [14]. So far, the direct growth of well-doped large 2D single crystals is still a big challenge due to the uncontrollable doping level and dopant configurations.

In addition to a single layer, controlled growth of 2D single crystals with different layers is another important aspect. For most 2D materials, their electronic band structures are extremely sensitive to the layer number. Monolayer graphene is a conductor, but AB stacked bilayer graphene would transform into a semiconductor when a vertical electric field is applied. When MoS_2 changes from monolayer to bilayer, a transition from direct bandgap to indirect bandgap can be observed. All these indicate that the electronic band structure of 2D materials can be tuned by layer number, and the growth of 2D single crystals with controllable layers is obviously an attractive topic. However, due to the self-limited growth mode of graphene/hBN and the Volmer-Weber growth behaviour of TMDs, the production of layer-controlled 2D single crystals is still waiting to be realized.

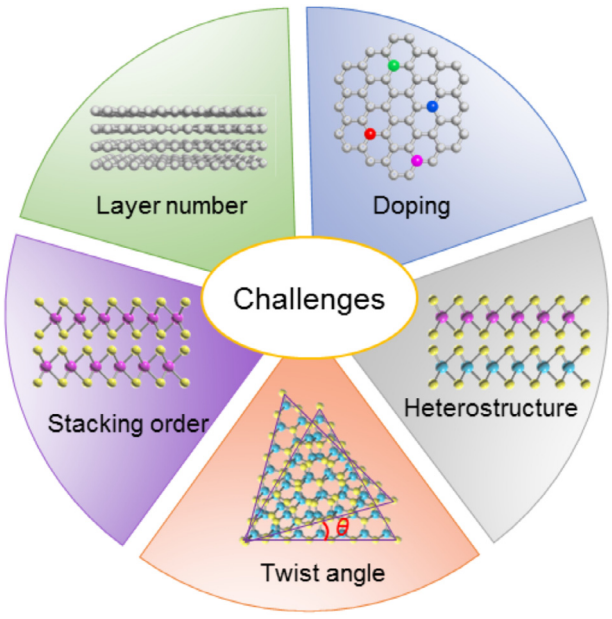

Fig. 2. (Color online) Future challenges for the growth of 2D single crystals.

For these multilayer 2D materials, it is necessary to consider the stacking order between different layers, as different stacking configurations often exhibit distinct properties. AA-stacked multilayer TMDs can exponentially increase the nonlinear response while AB-stacking structure can only show nearly zero signal. Also, AA-stacked bilayer TMDs show significantly enhanced electrical transport performance than AB-stacked ones. Nevertheless, like the epitaxy of hBN on high-symmetric surfaces, there are always both AA and AB structures during growth as they are nearly energetically degenerate. How to break this equivalence to achieve controllable stacking of 2D single crystals is certainly an important direction in the future.

The twist angle between 2D materials provides a completely new freedom to tune properties. At present, the researches on twisted 2D materials have swept the world, and a series of novel phenomena like superconductivity, moiré excitons and quantum anomalous Hall effect have been reported successively [15]. Obviously, the production of single-crystal materials with controllable twist angle will be a very important field in the future. However, it is still a technological gap so far since the materials with a small twist angle are usually not energetically favourable during growth at high temperature.

Except for the same kind of 2D materials, the van der Waals interaction between 2D layers makes it possible for the vertical stacking of different 2D materials (or heterostructures) beyond the limitation of the lattice constant [2]. Surprisingly, the properties of these 2D heterostructures are usually very different from the superposition of all constituent materials, and many specific 2D physics phenomena have been observed in these systems. In addition to the basic research, new electronic and optoelectronic devices based on 2D heterostructures have also been developed. However, most 2D heterostructures are prepared by transfer method so far, which is not conducive to industrial applications. Up to now, the alignment control of both the lower and upper layer of 2D materials is still a technical gap. Therefore, how to achieve controllable production of large single-crystal 2D heterostructures directly is another interesting point in the future.

In summary, the emergence of 2D materials has provided new possibilities to update the existing materials in many fields and up to now the production of monolayer 2D single crystals has made great progress. However, there are still many interesting

research areas that deserve continuous exploration. It is believed that 2D materials may usher in the industrial applications in the near future.

Conflict of interest

The authors declare that they have no conflict of interest.

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Xiaozhi Xu received his Ph.D. degree (2017) in Condensed Matter Physics from Peking University. He then joined the group of Prof. Kaihui Liu at Peking University as a postdoctoral fellow from 2017 to 2019. He is now a professor and a group leader at South China Normal University. His research interest mainly focuses on the production and characterization of low-dimensional single crystals, surface physics and surface catalysis.

Kaihui Liu received his Ph.D. degree in Condensed Matter Physics from the Institute of Physics, Chinese Academy of Sciences in 2009 and afterward worked as a postdoctoral research fellow at UC Berkeley, USA, until 2014. He is currently a professor and principle investigator in the State Key Laboratory for Mesoscopic Physics, School of Physics, Peking University. His current research interest is the growth, characterization, and applications of meter-scale single crystals.