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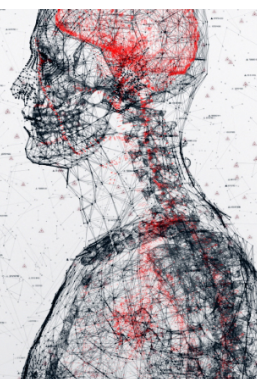
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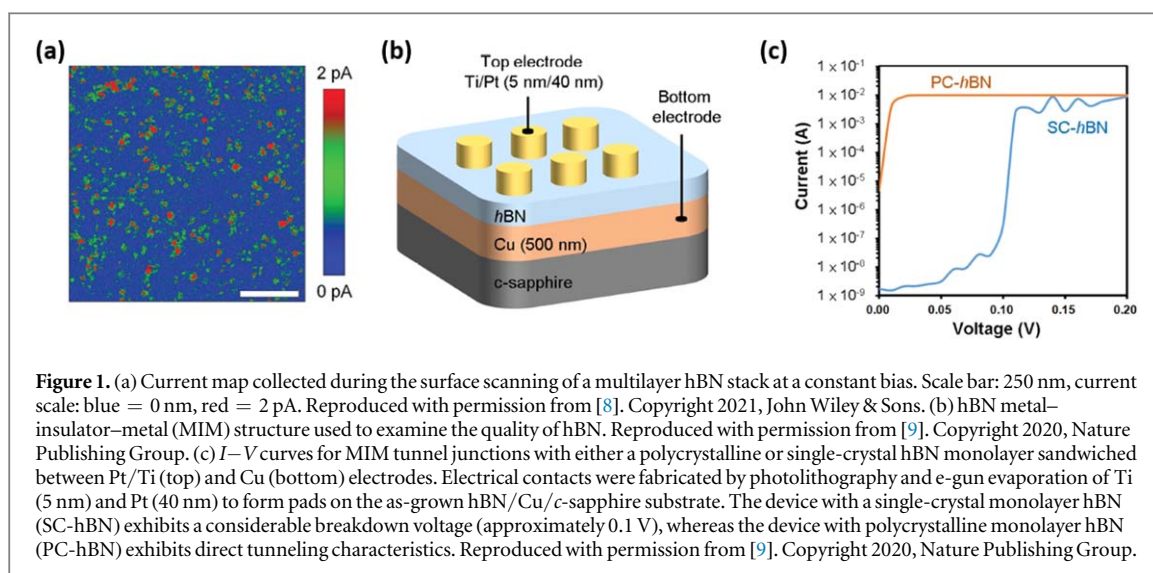
Toward growth of wafer-scale single-crystal hexagonal boron nitride sheets

Minsu Kim^{1,3}, Kyung Yeol Ma^{1,3} and Hyeon Suk Shin^{1,2} ¹ Department of Chemistry, Ulsan National Institute of Science and Technology (UNIST), Ulsan 44919, Republic of Korea² Low Dimensional Carbon Material Center, Ulsan National Institute of Science and Technology (UNIST), Ulsan 44919, Republic of Korea³ These authors contributed equally.E-mail: shin@unist.ac.kr**Keywords:** 2D materials, hexagonal boron nitride, single-crystal**Abstract**

Hexagonal boron nitride (hBN) has a two-dimensional planar structure without dangling bonds and is considered an insulator material that can overcome the limitations of SiO₂ and HfO₂, which typically exhibit large densities of dangling bonds and charged impurities at the interface. However, most of the reported hBN films prepared by chemical vapor deposition (CVD) are polycrystalline with grain boundaries. The grain boundaries of a polycrystalline hBN cause current leakage and gas permeability. A recent notable study reports the growth of wafer-scale single-crystal hBN monolayer, which could mitigate the aforementioned problems caused by polycrystalline hBN films. In this perspective, we discuss the recent progress in the research on single-crystal hBN and the direction to be taken for single-crystal hBN in future. The progress is closely related to the development of a single-crystal substrate and large area of monolayer single-crystal was grown on Cu (111). In terms of the hBN growth, the next step would be to grow multilayer single-crystal hBN, which is expected to expand the scope of applications.

1. Introduction

Uniform large-scale single-layer hexagonal boron nitride (hBN) films are used as dielectric substrates for various two-dimensional (2D) material-based electronic devices [1]. The growth of large-scale hBN films by chemical vapor deposition (CVD) using Cu, Ni, and Pt foil substrates has been previously demonstrated [2–4]. However, hBN films grown on the general foil substrates are polycrystalline. Such polycrystalline films inevitably have grain boundaries that degrade the electrical and physical properties. In addition, the presence of grain boundaries affects the band gap and thermal conductivity, which do not satisfy the intrinsic properties of hBN [5–7]. In particular, the most important point is that defects such as grain boundaries cause leakage current in field effect transistor (FET) devices. When the surface of the CVD-grown polycrystalline hBN samples was scanned with the tip of a conductive atomic force microscopy (AFM) by applying a constant voltage, some defective locations were found to be much more conductive than others (figure 1(a)) [8]. This large leakage current makes hBN unsuitable as a gate insulator for scaled complementary metal–oxide–semiconductor technology because it significantly increases the off-state current of FET. However, single-crystal hBN growth can compensate for such leakage current problems to an extent [9]. Lain-Jong Li *et al* measured the I-V curves of the polycrystalline and single-crystal hBN samples using Pt/Ti (top) and Cu (bottom) electrodes, as shown in figure 1(b). The devices using polycrystalline hBN cause a leakage current due to defects and grain boundaries. However, the device using single-crystal hBN showed that the current does not flow significantly up to 0.1 V (figure 1(c)). Single-crystal hBN is not limited to applications of electrical devices but is expected to have advantages in various fields. For the gas-diffusion barrier application, water vapor transmission rate (WVTR) was measured for the hBN film transferred to polyethylene terephthalate (PET) film [10]. The WVTR values of the polycrystalline hBN and single-crystal hBN monolayer films were obtained as 1.01 and 0.60 g m⁻²·day⁻¹,



which are 30% and 58% lower than that of PET ($1.44 \text{ g m}^{-2} \cdot \text{day}^{-1}$), respectively. The single-crystal hBN monolayer films outperform the polycrystalline hBN monolayer films by approximately two times in the WVTR tests. As such, the importance of single-crystal hBN is gradually increasing, and large-area single-crystal hBN monolayers through the CVD method have been recently reported. Figure 2 shows a timeline of how hBN growth by the CVD method has evolved [2, 3, 9–14].

From this perspective, we review the trends in the growth method for large-scale single-crystal hBN and present a forward-looking view of this field. Herein, three issues of single-crystal growth are discussed: (1) preparation of a substrate for single-crystal growth in a considerably large area, (2) obtaining a high degree of alignment of hBN domains after nucleation and growth, and (3) seamless stitching of the hBN domain into a single-crystal through further growth.

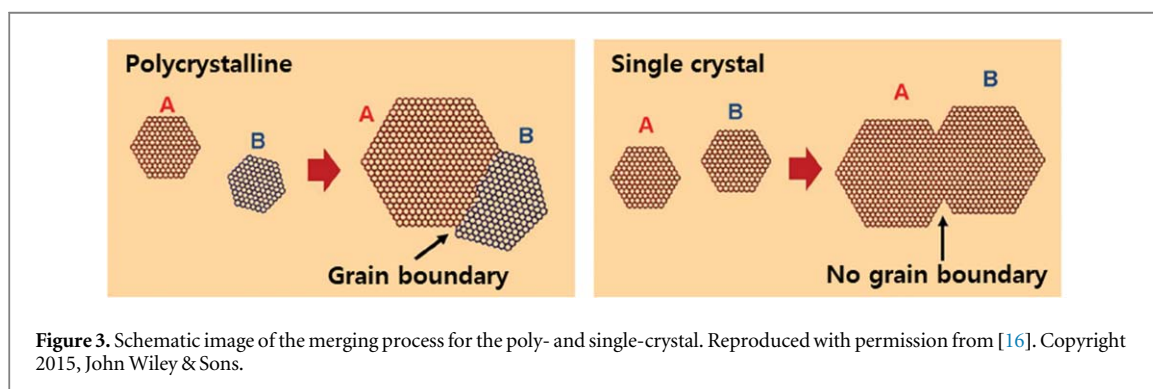
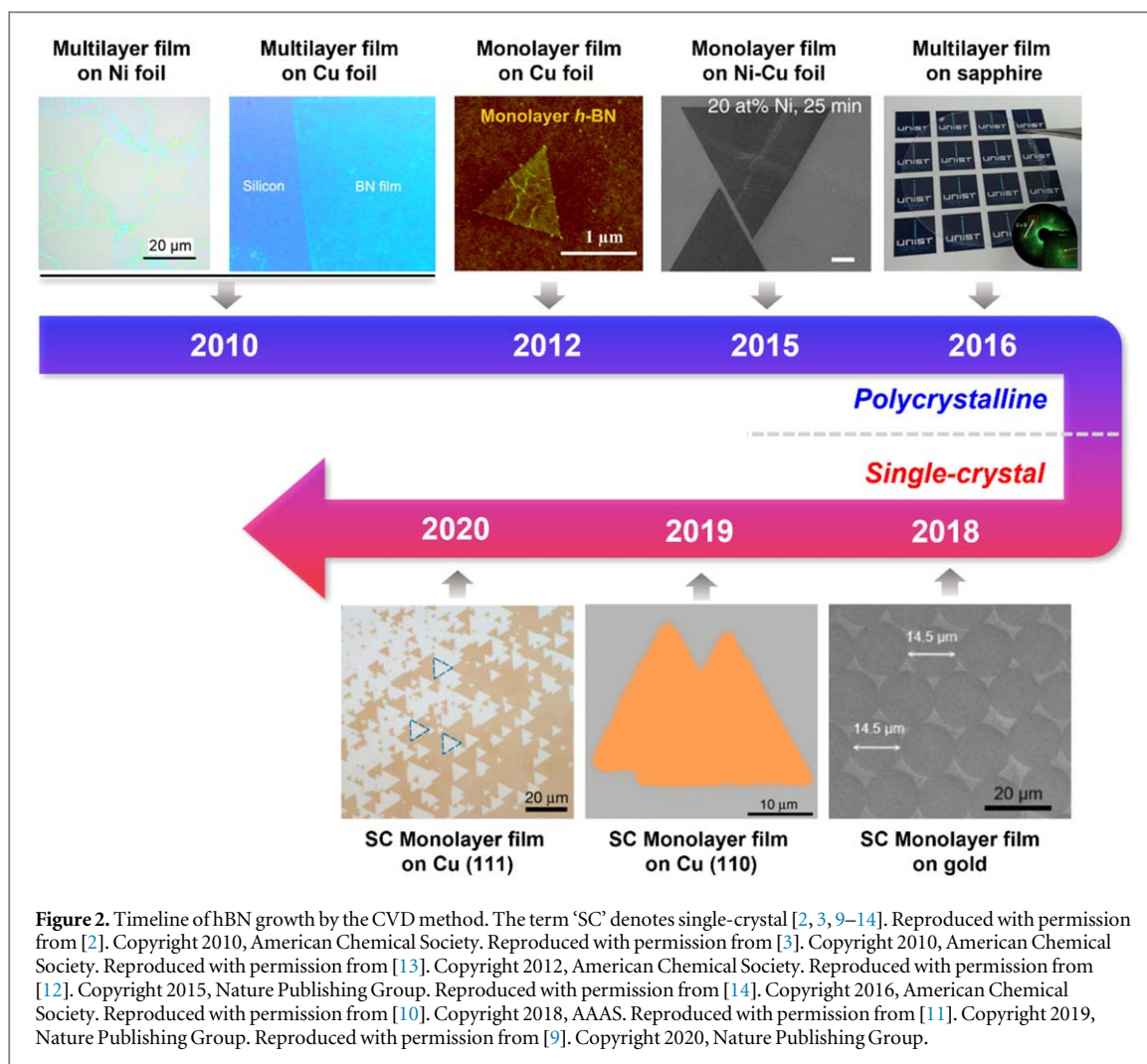
2. Epitaxial growth on substrate

2.1. Preparation of single-crystal substrate

The alignment of hBN domains on a substrate is related to its interaction with the substrate. In other words, the edge of the hBN domain is terminated by an active metal substrate, where the strong interaction between the edge of the hBN domain and the pristine substrate facet determines the alignment of the 2D material and its epitaxial growth [15]. When the hBN domains are arranged in a certain crystal orientation and merged, a perfect single-crystal hBN without any grain boundary can be realized (figure 3) [16]. To control the orientation of the hBN domains, a single-crystal growth substrate such as Cu (111) and Ni (111) is required. However, it is difficult to prepare such a single-crystal substrate over a large area. Recently, studies on the fabrication methods of single-crystal metal substrates have been conducted [17, 18]. The methods for preparing single-crystal metal substrates include T-gradient-driven annealing, contact-free annealing, and domain seed annealing, which are summarized in figure 4 and table 1. In the initial stage of preparing a single-crystal substrate, the size was limited to approximately 2 inches. However, the single-crystal substrates can be produced only by heat treatment, and the limitation on scalable size has been solved. In particular, the roll-to-roll method for Cu (111) in 2017 made continuous processes possible, which can be adapted to the CVD growth of graphene and hBN [19]. The development of this single-crystal substrate is expected to accelerate the growth of graphene and transition metal dichalcogenides as well as single-crystal hBN [20–22].

2.2. Alignment of the hBN domain on the surface

Since Cu substrates have low solubility of B and N atoms and are suitable for monolayer growth, Cu (111) is considered a candidate substrate for single-crystal hBN growth [25, 26]. The lattice constants of Cu (111) and hBN are not significantly different— $a_{\text{Cu}(111)} = 2.6 \text{ \AA}$ and $a_{\text{hBN}} = 2.5 \text{ \AA}$, with a 3.8% lattice mismatch [9]. The triangular-shaped hBN domain is well aligned on the Cu (111) surface with a six-fold symmetry; the relative orientation difference can be expressed as a multiple of 60° [27]. The hBN domain on Cu (111) is predominantly formed in two directions, 0° and 60° ; that is, the hBN domain is aligned along the twinned Cu (111) structure [27]. However, the twin boundary of Cu (111) causes the hBN domains to grow aligned in two directions, 0° and 60° ; however, when they are merged, an hBN film with undesirable grain boundaries is formed. To avoid this



issue, Lain-Jong Li *et al* prepared a novel single-crystal Cu (111) film devoid of twin grains on a 1-inch c-plane sapphire wafer [9]. In their work, high-temperature CVD using ammonia borane as a precursor produces a monolayer of the single-crystal hBN film. This method is successfully realized via scanning tunneling microscopy, which reveals numerous step edges on the Cu (111) film. First-principles calculations indicate that these step edges affect the binding energy of hBN on the Cu (111) surface. The energy difference between the favorable and unfavorable configurations is sufficiently large to ensure mono-oriented epitaxial growth. Moreover, the step edge alignment for the growth of single-crystal hBN films is not limited to Cu (111). The Cu (110) single-crystal substrate is ‘vicinal’ because of the existence of steps and the step edges play a crucial role in the unidirectional alignment of hBN domains [11]. The epitaxial growth was achieved by the coupling of Cu step edges with hBN zigzag edges, which breaks the equivalence of antiparallel hBN domains and enables unidirectional domain alignment over 99%.

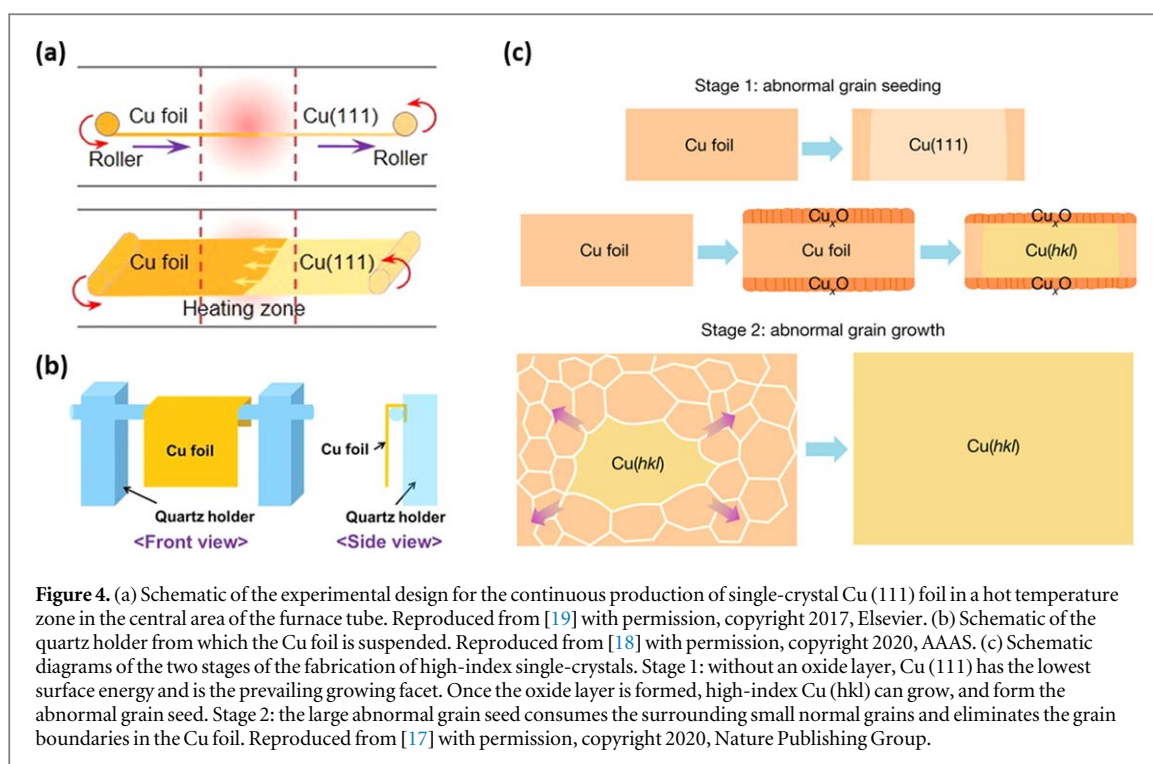


Figure 4. (a) Schematic of the experimental design for the continuous production of single-crystal Cu (111) foil in a hot temperature zone in the central area of the furnace tube. Reproduced from [19] with permission, copyright 2017, Elsevier. (b) Schematic of the quartz holder from which the Cu foil is suspended. Reproduced from [18] with permission, copyright 2020, AAAS. (c) Schematic diagrams of the two stages of the fabrication of high-index single-crystals. Stage 1: without an oxide layer, Cu (111) has the lowest surface energy and is the prevailing growing facet. Once the oxide layer is formed, high-index Cu (hkl) can grow, and form the abnormal grain seed. Stage 2: the large abnormal grain seed consumes the surrounding small normal grains and eliminates the grain boundaries in the Cu foil. Reproduced from [17] with permission, copyright 2020, Nature Publishing Group.

3. Seamless stitching of the hBN domain

Mono-oriented epitaxy enables seamless stitching without the formation of grain boundaries (figure 3) [16]. The seamless stitching was realized by merging the hBN domains in the same orientation on surface and verified via atomic-scale images by scanning tunneling microscopy (STM) and transmission electron microscopy (TEM) at the corner formed by two edges of the merged domains [9]. Moreover, ultraviolet-light oxidation was performed to confirm the presence of the grain boundary in a large area [9]. The aforementioned verifications confirm that unidirectionally aligned hBN domains can be seamlessly stitched into an intact piece of single-crystal film.

4. Non-epitaxial growth on the substrate

In addition to the epitaxial growth on the single-crystal substrate, single-crystal hBNs can be grown using a liquid gold surface without using the single-crystal substrate. Kim *et al* synthesized a single-crystal hBN monolayer using the phenomenon of self-collimation, wherein the domains of BN are formed in the same direction on the liquid gold surface [10]. In the self-collimation phenomenon, the N and B atoms generate electrostatic interaction by pushing or pulling each other, thereby maintaining an appropriate distance on the liquid gold surface. A circular hBN domain of uniform size was synthesized by simply adsorbing and moving the hBN domain onto a smooth liquid gold surface. Each hBN domain moved randomly, and an electrostatic interaction was induced between N and B at the edge of the domain. As a result, the grains were aligned to grow single-crystal hBN.

5. Outlook

As recent studies have reported that the single-crystal hBN films can mitigate the problems caused by polycrystalline hBNs to an extent, we expect that single-crystal hBN exhibits better results in applications than polycrystalline hBN. However, the current status is that the growth of single-crystal hBN in large area is limited to a monolayer as we discussed above. The significantly thin thickness of the monolayer hBN film is not sufficient to block the tunneling or leakage current, which is a disadvantage to the actual devices. For an example, it is expected that the monolayer of hBN is too thin to act as a gate insulator in FETs [1]. Therefore, thicker than monolayer hBN films are required for practical applications; however, the growth of multilayer single-crystal hBN is even more challenging because the catalytic reaction on metal substrates for the multilayer growth does not work any longer.

Table 1. Representative fabrication methods of single-crystal metal substrates for epitaxial growth.

No	Substrate	Method	Detailed procedure	References
1	Cu (111) on c-plane sapphire	Heteroepitaxial deposition	The Cu film was deposited onto the c-plane α -Al ₂ O ₃ by a radio frequency magnetron sputtering machine.	[23]
2	Cu (111)	Repeated chemical-mechanical polishing and annealing	The Cu foil was annealed at 1075 °C with 1000 sccm Ar and 500 sccm H ₂ for 2 h and was polished using the chemical-mechanical polishing (CMP) method	[16]
3	Cu (111)	Temperature gradient driven annealing	The central region of the furnace was maintained at 1030 °C with 500 sccm Ar when the Cu foil was continuously slid through the furnace center.	[19]
4	Cu/Ni (111)	Thermal annealing	The desired amount of Ni was electroplated onto the Cu (111) and it was then annealed at 1050 °C for 4–6 h	[24]
5	Cu (111), Ni (111), Pt (111)	Contact-free thermal annealing	The Cu foil was suspended over the rod in a typical annealing process. The Cu foil was heated to 1323 K for 12 h in an atmosphere. Subsequently, Cu was cooled at the following average cooling rates: approximately 82 K min ⁻¹ from 1323 to 373 K and approximately 9 K min ⁻¹ from 373 K.	[18]
6	Cu (110)	Thermal annealing	First, the foil was annealed at 1,060 °C for 2–10 min under a mixed-gas flow (Ar, 500 sccm, H ₂ , 50 sccm; sccm; then, the temperature was quickly decreased to 1,040 °C and the Cu foil was annealed at this temperature for 3 h.	[11]
7	Single-crystal high-index Cu foils	Pre-oxidation-guided seeded growth of single-crystal Cu foils	The furnace was slowly heated to 150 °C–650 °C for 10–60 min and then maintained at this temperature for 1–4 h to oxidize the Cu surface. Subsequently, the pre-oxidized Cu foil was heated to 1,020 °C for 1 h and maintained at this temperature under a gas flow of 800 sccm Ar and 50 sccm H ₂ for 3–10 h, and was naturally cooled to room temperature.	[17]

Ni, Fe, and Ni-Fe alloy substrates have so far been used for multilayer hBN films. Ni exhibits a higher solubility for B (~0.3%) and lower solubility for N (~0.004%) atoms, which complicate the precipitation of different contents of the B and N atoms during the film growth [2, 28, 29]. Furthermore, the solubility of B and N atoms changes according to the growth temperature; thus, their quantitative evaluation is difficult. To solve this problem, Ni-Fe alloy substrate is used for the growth of multilayer hBN film [29]. In contrast to Ni, Fe exhibits higher solubility for N atoms than B atoms. Combining Ni and Fe metals tunes the solubilities of B and N atoms and facilitates metal crystallinity, which stimulates the uniform segregation of multilayer hBN. However, the multilayer hBN grown till date is polycrystalline. Thus, new approaches, which are different from simple catalytic and precipitation mechanisms mentioned above, are required for the growth of multilayer single-crystal hBN films. It would not be pessimistic. Until just a few years ago, it was very difficult to grow a single-crystal graphene with controllable thickness. However, bilayer and trilayer of single-crystals graphene can now be grown on Cu-Ni(111) alloy substrates [20]. The Ni content is important to control the thickness of single-crystal graphene, because the higher Ni content causes the higher amount of dissolved carbon in the alloy substrate—the carbon solubilities in Cu and Ni at ~1000 °C are 75 ± 0.5 ppm and 1.3 atom %, respectively [30]. This example of the single-crystal graphene growth with controllable thickness can be applied for the hBN growth—but, the growth of hBN would be more complicated because it is a result of reactions by two elements. Therefore, we need to intensively explore to find suitable substrates and growth parameters by novel growth mechanism for multilayer single-crystal hBN.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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