Grow Up and Grow Out:
van der Waals Epitaxy and In-Plane Epitaxy of Two-Dimensional Materials

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Abstract (Arial 10)
Both van der Waals (vdW) solids[1] consisting of two-dimensional (2D) sheets and in-plane hetero-structures[2,3] of 2D materials promise new physics and novel applications. The synthesis and characterization of these novel structures and, more importantly, the physical insight into their growth are prerequisites to the experimental exploration of the new physics. Here, we report a combined experimental-theoretical study that has gained insight into the determination of orientational order in vdW epitaxy, as well as a demonstration of in-plane heterostructures of 2D materials by adapting common wisdom accrued in the art of conventional epitaxy.

We experimentally show that hexagonal boron nitride (h-BN) grown on a (100)-oriented Cu foil surface strictly aligns to the underlying Cu lattice (Fig. 1). This behavior is in sharp contrast to the orientational disorder of the graphene/Cu(100) system observed in previous work,[4] despite the close crystallographic similarity between h-BN and graphene. Our first-principles calculations reveal the origin of this curious contrast between the two crystallographically similar 2D materials. We show that strong C-Cu interactions (relative to B- and N-Cu interactions) actually lead to misalignment, a conclusion that runs counter to the conventional wisdom that stronger epilayer-substrate interactions enhance orientational order.

The choice of the h-BN/Cu(100) system as the platform for this case study of vdW epitaxy provides the following advantages: (1) The epilayer and substrate are of different symmetries, therefore the physical picture we get from this study is more general than vdW epitaxies of epilayer-substrate pairs of the same symmetry already documented in the literature. (2) Comparison between h-BN and crystallographically similar graphene leads to physical insight: In vdW epitaxy, interactions between the cluster ***edges*** and the substrate at the early nucleation stage steer the cluster's orientation, which later determines the orientation of the crystallite that the cluster grows into. In this picture, stronger edge-substrate interactions may reduce orientational order.

Using the same archetypical 2D materials – graphene and h-BN, we also demonstrate a single-atomic layer, in-plane heterostructure, by projecting the concept of heteroepitaxy to 2D space.[5] Monolayer h-BN grows from fresh edges of monolayer graphene with lattice coherence, forming an abrupt boundary, or 1D interface (Fig. 2). More importantly, the crystallography of the h-BN is ***solely*** determined by that of the graphene seed; in this 2D heterostructure, the h-BN forgoes the aforementioned orientations it would assume if grown independently on the supporting Cu substrate.

This demonstration is of fundamental significance. Due to the inherent 3D nature of the interactions between the 2D crystals and their surroundings, it is not clear whether a 2D crystal can grow from the edge of a 2D seed crystal ***epitaxially***, i.e., adapting to the crystallography of the seed, while overcoming energetic factors in its 3D environment. Our work unambiguously answers this fundamental question. On the technical side, our method (Fig. 2a) was inspired by the common practice in conventional epitaxy in 3D. We view the graphene seed crystal as the "substrate" in 2D space, while the Cu supporting substrate merely confines the growth process to its surface – the 2D space where the epitaxy happens. This new vantage point inspires us to adapt the good practice commonly used in conventional epitaxy simply by reduced-dimension analogy.

Moreover, by adapting homoepitaxy to 2D space, we also demonstrate multiple millimeter-sized graphene single crystals.

References

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Figures

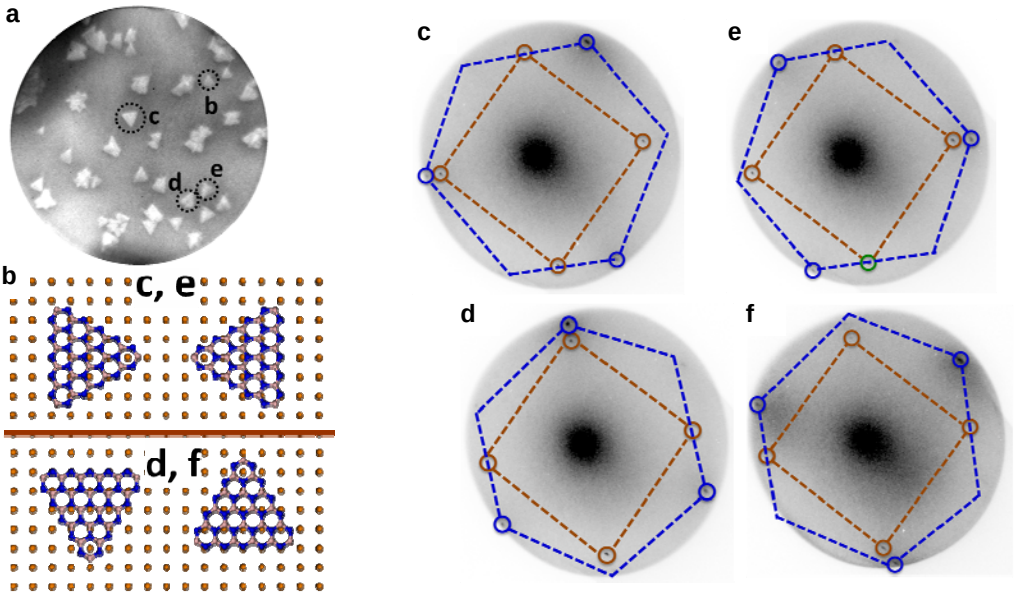

Fig. 1. (a) Low-energy electron microscopy (LEEM) image (25 μm diameter field of view) of h-BN crystallites on (100) surface of Cu foil. (c-e) Selected-area LEED patterns obtained in circled areas labeled c-e in (a), respectively. (b) Real space model of h-BN crystals on Cu(100). Four and only four equivalent orientations are observed.

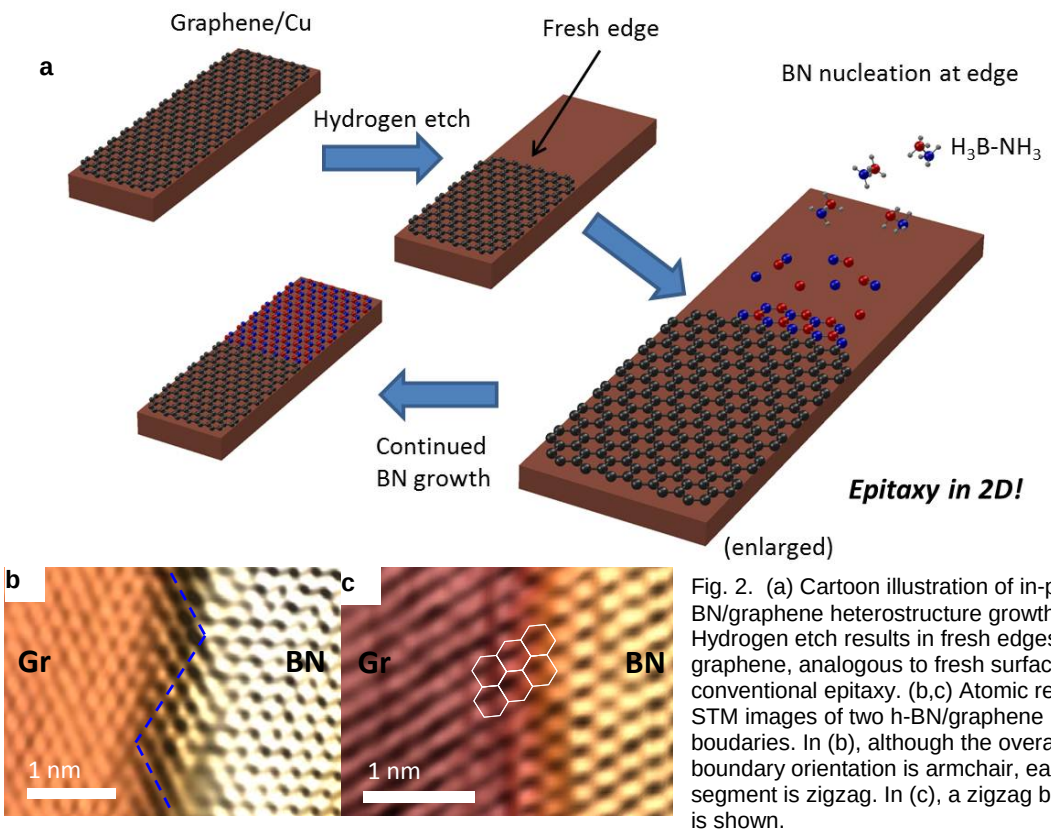

Fig. 2. (a) Cartoon illustration of in-plane h-BN/graphene heterostructure growth. Hydrogen etch results in fresh edges of graphene, analogous to fresh surfaces in conventional epitaxy. (b,c) Atomic resolution STM images of two h-BN/graphene boudaries. In (b), although the overall boundary orientation is armchair, each segment is zigzag. In (c), a zigzag boundary is shown.