Single-crystal two-dimensional material epitaxy on tailored non-single-crystal substrates

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The use of single-crystal substrates as templates for the epitaxial growth of single-crystal overlayers has been a primary principle of materials epitaxy for more than 70 years. Here we report our finding that, though counterintuitive, single-crystal 2D materials can be epitaxially grown on twinned crystals. By establishing a geometric principle to describe 2D materials alignment on high-index surfaces, we show that 2D material islands grown on the two sides of a twin boundary can be well aligned. To validate this prediction, wafer-scale Cu foils with abundant twin boundaries were synthesized, and on the surfaces of these polycrystalline Cu foils, we have successfully grown wafer-scale single-crystal graphene and hexagonal boron nitride films. In addition, to greatly increasing the availability of large area high-quality 2D single crystals, our discovery also extends the fundamental understanding of materials epitaxy.
After-scale single-crystal two-dimensional (2D) materials are highly desirable for the next generation of 2D material-based integrated electronics, optoelectronics and spintronics\textsuperscript{1–3}. By judiciously choosing single crystal substrates with the appropriate surface texture, epitaxial growth of large area single-crystal graphene, hexagonal boron nitride (hBN), and other two-dimensional (2D) materials have recently been realized\textsuperscript{4–16}. Despite significant progress in the synthesis of single-crystal substrates, such as Cu foils with different surface indices\textsuperscript{17–19}, the preparation of single-crystal substrates is still generally expensive. Thermodynamically stable twin boundaries are common in face centered cubic (FCC) metals and are easily created during annealing treatments\textsuperscript{20–22}. The presence of highly stable twin boundaries in Cu foils makes synthesizing high quality Cu single crystals challenging, and if possible, using polycrystalline substrates for 2D materials epitaxy would be highly beneficial.

Here we present a theoretical prediction and experimental demonstration of epitaxial growth of single-crystal 2D materials on tailored polycrystalline substrates. We have successfully annealed polycrystalline Cu foils into various types of inch sized twinned Cu foils. Following the theoretical prediction, inch-sized 2D materials (including graphene and hBN) single crystals on selected twinned Cu foils have been synthesized. This study opens a rapid, scalable and robust route for single crystal 2D materials growth on tailored polycrystalline substrates.

Results

Theoretical frame for alignment of 2D materials on twinned Cu foils. The epitaxial growth of a 2D single crystal on a polycrystalline substrate requires that all 2D islands grown on two sides of a grain boundary are perfectly aligned, which is obviously impossible for an arbitrary grain boundary. Let’s consider the alignment of 2D material islands on the two sides of a 60° <111> twin boundary. The schematic diagram of a 60° <111> twin of a Cu foil with FCC structure is shown in Fig. 1a with more details in Supplementary Fig. 1. Here, the angle between the twin plane and the foil surface, θ, and the in-plane rotation angle of the twin plane, ψ, are the two independent variables that fully describe the twinned structure. In the Supplementary Notes 1–2 and Supplementary Figs. 2 and 3, we demonstrate that (θ, ψ) are equivalent to Euler angles or surface indices for determining the orientation of a twinned crystal and their transformation. Such a twin boundary carries extremely low formation energy and can rarely be avoided during annealing of FCC metal\textsuperscript{20–22}. The position of some typical Cu twins containing at least one low-index surface plane in the (θ, ψ) map are presented in Supplementary Fig. 2c.

To explore the alignment of 2D islands on twinned substrates, it is necessary to know the principle that governs the alignment of 2D materials on arbitrary surfaces. Supplementary Fig. 4a shows two arbitrary (h k l) surfaces of an FCC crystal containing steps. Such steps are known to be active nucleation sites for 2D materials on arbitrary surfaces. Previous studies reported that the alignment of 2D material (such as graphene, hBN) islands on a single-crystal Cu (1 1 1) surface is determined by the alignment of a zigzag edge of the 2D island with respect to a Cu <110> step edge\textsuperscript{28,29}. However, an arbitrary FCC Cu surface may have many other types of step edges (<112>, <123>, etc.). Taking all these possible step edges into consideration makes it complicated to a priori determine the most favorable alignment of 2D material islands.

To understand the mechanism of alignment of 2D material islands on an arbitrary Cu surface, we investigated the stability of the interfaces of various 2D material edges with different metal step edges\textsuperscript{30,31}. Taking graphene as an example, the interfacial formation energies of various graphene edge with respect to different metal step edge are calculated, see Supplementary Note 3 and Supplementary Fig. 4b. The deep valley observed along the diagonal of the map corresponds to an epitaxial relationship between graphene and the Cu surface. Based on this result, we deduced a simple geometric principle of graphene alignment on Cu surfaces. Where the most stable interfaces correspond to a graphene zigzag edge attaching to the longest (most predominant) <110> step edge segment of the Cu surface. More details are shown in the Supplementary Notes 4–5.

Here we selected the growth of two representative 2D materials, 3-fold symmetric hBN and 6-fold symmetric graphene, on twinned FCC Cu substrates as examples to demonstrate well-aligned 2D islands on both sides of a twin boundary. Including all possible twinned Cu foils, we calculated maps of misalignment angles between 2D material islands on the two sides of twin boundaries and the results are shown in Fig. 1b, c (see Supplementary Tables 1 and 2 for details). Figure 1d, e shows the predicted alignments of hBN and graphene islands on the two twinned Cu foil surfaces, where perfect alignment of the 2D islands on the twinned Cu surfaces is clearly seen. Our theoretical calculations predict that twinned surfaces that enable template-based epitaxial growth of hBN and graphene occupy significant portions of the maps, as shown by the blue regions in Fig. 1b, c (40.2% and 56.7% for hBN and graphene). This result shows that a majority of twinned Cu surfaces can be used as substrates for the uniaxial alignment of 2D material islands. Besides Cu substrates, the alignment maps (shown in Fig. 1b, c) are also applicable for graphene and hBN grown on other twin FCC metal substrates if the epitaxial relationship of a zigzag direction of a 2D material aligning along a high symmetric <110> direction of a substrate stands\textsuperscript{22,33}. For example, Au substrates are promising for the epitaxial growth of transition metal dichalcogenides (TMDCs)\textsuperscript{34,35}, sharing the same epitaxial relationship as that of hBN on Cu surface. Due to the same 3-fold symmetry of TMDCs and hBN crystal lattices, the alignment TMDCs on a twinned Au substrate is the same as that of hBN on a twinned Cu substrate of same type and, thus, the synthesis of single-crystal TMDCs on twinned Au surfaces is possible.

Preparation of polycrystalline Cu foils. Experimentally, a variety of twin structures can be obtained by subjecting raw Cu foils to deformation and annealing treatments. Figure 2a, d, g show the results of annealing a flat Cu foil, where electron backscatter diffraction (EBSD) mapping shows that the cold rolled foil forms a strong cube textured {001}<100> polycrystal\textsuperscript{22,36,37} associated with a small twinned grain. If an indented Cu foil is bent along the transvers direction (TD)\textsuperscript{38–41}, only one kind of twin structure is formed in the whole foil, as exhibited in Fig. 2b, e, h. Over the entire area of the foil, only two different optical intensities are seen, which arise from the different oxidation rates of the two different crystal orientations. EBSD mapping indicates that the dark and light areas in the optical image are approximately (1 1 6) and (1 1 1) surfaces, respectively. Except for the twin boundaries between these two areas, no other grain boundaries were detected in the foil. The pole and inverse pole figures in Supplementary Fig. 5 also confirm that no other orientations were present in the foil, implying that the inch-size Cu foil contained only (1 1 6)/(1 1 1) twin structures. To verify the role of the Cu foil surface structure in the annealing process, we selected another commercial polycrystalline copper foil for tailoring and obtained very similar results. This suggests that the key factors of twin boundary annealing are the bending and the indentation treatments, while the initial structure of the Cu foil is less important.

In a similar manner, by changing the experimental parameters (such as radius of curvature, indentation type and depth, and
rotation angle), a variety of twin structures can be obtained. For example, if an indented Cu foil was bent along a direction 45° to the TD direction, the whole foil showed another kind of twin plane. The crystal axial of the two crystal lattices on both sides of the twin boundary (A and B) and their $<111>$ co-axis is also shown. The nature of coherent twins is confirmed by the transmission electron microscopy (TEM) in Fig. 2j−l.

**2D materials growth and characterization.** Figure 3 shows experimentally observed and theoretically predicted hBN and graphene islands grown on different twinned Cu surfaces. Figure 3a−b and e−f show perfectly aligned hBN and graphene on four different twinned Cu surfaces. Two more cases where we observed the formation of misaligned hBN and graphene are presented in Fig. 3c, g, and more results with various twin boundaries are shown in Supplementary Figs. 6–7, Supplementary Tables 1 and 2. Figure 3d, h show the theoretical prediction and experimental statistics of the misalignment angle of hBN and graphene grown on different substrates. The results indicated that the predicted misalignment angles of all the islands are strikingly consistent with the measured values within the range of measurement error ($\pm0.5$ degree). This excellent agreement validates our theoretical model used to determine the alignment of 2D material islands on arbitrary surfaces.
The aligned domains on twinned Cu substrates eventually coalesce to form a thin film. To confirm this, we performed high-resolution TEM to characterize the merging area of domains at the atomic scale. The scanning TEM-annular dark-field (STEM-ADF) image and intensity profile of the merging area in Fig. 4a–c show the homogeneous nature of the single layer hBN film, which is also verified by atomic force microscopy (AFM) measurement in Supplementary Fig. 8a, b. Hexagonal selected area electron diffraction (SAED) patterns were collected at different positions around the merging area of two well-aligned hBN domains, shown in Fig. 4d. The Second Harmonic generation (SHG) mapping clearly show that the parallel hBN domains are seamlessly stitched together, as shown in Supplementary Fig. 9a. Two sets of SAED patterns were observed in the merging area of two misaligned hBN domains in Supplementary Fig. 9. In addition, hydrogen etching was used to analyze the crystallinity of the samples on the macroscopic scale. No etching lines were observed between aligned hBN domains in Supplementary Fig. 8e. In contrast, for domains formed by the merging misaligned hBN islands, etched boundaries are clearly visible, as shown in Supplementary Fig. 8f. The above results confirm that well-aligned hBN domains can be seamlessly stitched into a large single-crystal hBN film.

For graphene, the D band Raman map of two merged islands in Supplementary Fig. 10b can be used to further confirm the absence of defects at the merging area. Low-energy electron microscopy (LEEM) and micro-low energy electron diffraction (μLEED) measurements were also performed. The μLEED patterns of selected areas confirmed that the graphene grains are precisely aligned on both sides of the twin boundary in Fig. 4f. Besides, the recently proposed seamless coalescence criteria were adopted and we further confirmed the seamless coalescence of well-aligned graphene islands, nucleated on both sides of the Cu twin boundary in Supplementary Fig. 11a. Aligned graphene domains were seamlessly stitched together to form a single crystal film (the graphene growth process, Supplementary Fig. 12), as shown in Fig. 4g. The crystallinity of randomly chosen 5 × 5 mm²...
areas of the as-grown graphene/Cu sample was tested by low-energy electron diffraction (LEED) (Supplementary Figs. 11d, e). The Raman spectrum of the continuous as-grown graphene film showed a high I_{2D}/I_{G} ratio and a negligible D peak (Supplementary Fig. 11c). Furthermore, a series of field effect transistor (FET) devices with 10 μm-wide channels and channel lengths ranging from 50 μm to 2 mm were fabricated to evaluate the electrical transport characteristics as shown in Supplementary Fig. 13a, b. No large changes in the carrier mobility of the devices (Supplementary Fig. 13c, d) were observed when the graphene channel length was varied by two orders of magnitude (Fig. 4h).

The average electron and hole mobility was found to be $2.2 \times 10^{4}$ cm$^2$V$^{-1}$s$^{-1}$ and $2.8 \times 10^{4}$ cm$^2$V$^{-1}$s$^{-1}$ at room temperature, while the corresponding values for FETs with polycrystalline graphene is only $0.6 \times 10^{4}$ cm$^2$V$^{-1}$s$^{-1}$ and $0.8 \times 10^{4}$ cm$^2$V$^{-1}$s$^{-1}$.

It is worth noting that, in our proposed method, the twin structures are highly stable after annealing and generally don’t change during graphene/hBN growth. The in-situ SEM observation of the graphene growth process shown in Supplementary Fig. 14 clearly confirms this. In addition, our experimental observations show that, different from the well explored normal grain boundaries, no apparent grooves appear near a twin boundary of the Cu foil and no enhanced graphene nucleation near the twin boundary area are observed (Supplementary Fig. 15). This can be understood by the high stability of the twin boundaries and the closed packed atomic arrangement near the twin boundaries.

**Discussion**

In summary, we established a geometrical model to determine the alignment of 2D material islands on an arbitrary substrate and validated it through numerous experimental observations. Based on our concise model, we predicted that single-crystal 2D materials can be epitaxially grown on various twinned substrates. Experimentally, we have successfully synthesized a number of differently twinned Cu foils and demonstrated the growth of single-crystal hBN and graphene films on these substrates. In addition to demonstrating our theoretical model, this study provides a viable approach to synthesize 2D films with tailored grain boundaries for future applications.

**Methods**

**Modeling techniques.** Calculations of the interfacial formation energy of graphene with different edges attached to Cu steps were performed within the framework of the DFT-D3 method as implemented in the Vienna ab initio simulation package (VASP). Exchange-correlation functions were treated according to the generalized gradient approximation (GGA), and the interaction between valence electrons and ion cores was modeled by the projected augmented wave (PAW) methods. Along the direction of the interface of a graphene edge attached to a Cu step edge, the lattice mismatch between the graphene edge and the step edge in the supercell was limited within 3.0%, and the graphene lattice was used to avoid extra...
strain on graphene. Along the direction perpendicular to the step edge, the distance between parallel step edges was maintained at a constant value of ~20 Å. In the out of plane direction, the vacuum space between neighboring images was kept at least 12 Å to avoid periodic imaging interactions. A force on each atom of less than 0.01 eV/Å with an energy convergence of $10^{-4}$ eV, was used as the criterion for structural relaxation. Computational details are discussed in the supplementary information.

**Preparation of twinned Cu substrate.** In this study, we used commercial oxygen-free high conductivity (OFHC) Cu foils with a purity of 99.99 wt% from CHINALCO Shanghai Copper Company. The cold-rolled oxygen-free high purity polycrystalline Cu foils had a thickness of 46 µm and hardness of 132 HV (measured using a load of 50 g). X-ray diffraction measurements showed that the initial texture is composed of typical rolling components of S {123}<634> (34.6%, volume fraction), Cu {112}<111> (16.6%), Brass {011}<211> (19.7%) and Goss {011}<001> (5.8%). The annealing treatments were conducted in a 100 mm-diameter furnace in H2/Ar (30/500 sccm) ambient gas under atmospheric pressure. A quartz tube with a diameter of 80 mm was used to load the samples into the furnace. The Cu foil was bent to fit the quartz tube and annealed at 1010 °C for 1 h; a central hardness indent was created using a pyramid-shaped diamond hardness indenter under 300 g load and 10 s dwell time at the center of the Cu foil.

**hBN epitaxy.** hBN film was grown on a twinned Cu substrate by a chemical vapor deposition method. BNH4 (Alfa Aesar, 99.9%) served as the B and N source. The growth was performed after completing the Cu annealing process to obtain a twinned Cu substrate. The gas ambient was H2/Ar (10/200 sccm) under 200 Pa pressure for 45 min at 1010 °C to grow a single crystal hBN film, while heating the precursor at 65 °C within 10 min using a water bath.

**Graphene growth.** Graphene film was grown on twinned Cu substrate by a chemical vapor deposition. Growth was performed after completing the annealing process to obtain twinned Cu. The gas ambient was CH4/H2/Ar (0.1/40/500 sccm) under atmospheric pressure and growth was carried out for 15 min at 1010 °C to obtain single crystal graphene film. Using a CH4 concentration of 185 ppm, it took approximately 15 min to fully cover the Cu surface with monolayer single-crystal graphene. To investigate the grain structure of graphene, the reaction was
terminated before the Cu surface was completely covered by adjusting the experiment time from 1 to 15 min.

Raman spectroscopy measurements. Raman spectroscopy and mapping were performed using a HeCd laser (458 nm wavelength) excitation source at 1 mW power. The objective lens 50X was used and the spatial resolution was 1 μm. The accumulation time for each spectrum was 0.5 s for image scanning and 1 s for a single spectrum.

Etching of graphene and hBN. Etched hexagonal holes appeared on graphene after 10-min etching at 800 °C with 10/500 sccm H2/Ar under atmospheric pressure. To visualize the etched areas, each sample was oxidized in air on a hot plate at 190 °C for 5 min. Oxygen passed through the etched regions to react with the underlying Cu substrate to form CuO while the Cu substrate under other areas remained unreacted.

SEM and EBSD measurements. SEM and EBSD measurements were performed with a JEOL 7600F/Oxford EBSD nano system. The working voltage was 10 kV.

TEM measurements. TEM was performed on twinned Cu structures and merging hBN domains. The twinned Cu was cleaned by chemical electropolishing, followed by conventional ion milling using a Gatan Model 911IPS. HR-TEM images and the corresponding SAED patterns were obtained on an aberration-corrected TEM (FEI Titan3 G2) with an acceleration voltage of 300 kV. A double-tilt analytical holder was used. In the twin structure measurement, rotation angles α and β were 20.56° and −7.75°, respectively. After α and β rotations, the twin boundary was perpendicular to the sample holder, making the twin structure easier to observe.

LEED and LEEM/μLEED measurements. Low Energy Electron Diffraction (LEED) images were obtained from single-crystal graphene film on twinned Cu foil using a BLD600IR system from Omicron. A 1 cm × 1 cm section of the sample was cut and attached to a metal holder and introduced to a chamber under ultrahigh vacuum with operating pressure at 1×10−10 Torr. The LEEM/μLEED measurement was performed on The LEEM III system (Technische Universität, Clausthal) with operating pressure at 4×10−10 Torr.

Transfer of hBN and graphene films. After CVD growth, hBN and graphene were transferred onto a 300-nm SiO2/Si substrate by a wet transfer process using 4 wt% polyvinyl alcohol (PVA) in deionized water for 5 h. The PMMA/hBN and graphene from the backside of the Cu foil were treated to float on the substrate of a Cu etching solution (10 mol% H2O2, 15 mol% HCl and 300 mol% DI water) for 6 h. The PMMA/hBN/(Graphene)/Cu was transferred into another solution (250 mol% DI water, 10 mol% HCl), allowed to stand for 30 min. The PMMA/hBN/(Graphene) was then transferred onto the target substrate. The PMMA/hBN/(Graphene)/substrate was heated on a hot plate at 100 °C for 30 min, followed by soaking in acetone, alcohol, and finally in DI water.

Graphene FETs fabrication. Graphene field-effect transistors were fabricated by ultraviolet light lithography. Graphene films on Cu were transferred onto a 300 nm SiO2/Si substrate by wet transfer method. Electron beam evaporation and thermal evaporation methods were used to form electrical contacts (Cr/Au, 3 nm/45 nm), while oxygen plasma etching (30 W, 15 sccm) for 60 s to remove the hBN and graphene from the backside of the Cu foil. The treated samples were allowed to float on the surface of a Cu etching solution (10 mol% H2O2, 15 mol% HCl and 300 mol% DI water) for 4 h. The PMMA/hBN/(Graphene)/Cu was transferred into another solution (250 mol% DI water, 10 mol% HCl), allowed to stand for 30 min. The PMMA/hBN/(Graphene) was then transferred onto the target substrate. The PMMA/hBN/(Graphene)/substrate was heated on a hot plate at 100 °C for 30 min, followed by soaking in acetone, alcohol, and finally in DI water.

Carrier mobility measurements. The transfer curve (Lμ-Vμ) of the graphene FET was measured on a probe station with a Keithley 4200 semiconductor characterization system at room temperature under normal pressure. The widely-used Kim model based on nonlinear fitting was used to calculate the mobility:

\[ R_{\text{total}} = \frac{V_{\text{fb}}}{I_{\text{rb}}} \]  
\[ R_{\text{total}} = R_{\text{contact}} + \frac{L}{W} \frac{1}{n + \frac{n}{e} \sqrt{\frac{W}{e}}} \]  
\[ V_{\text{g}} = V_{\text{fb}} - \frac{L}{W} \frac{1}{n + \frac{n}{e} \sqrt{\frac{W}{e}}} \]  

where \( L_{P} \) is the current source and drain electrodes, \( V_D \) is the drain voltage with source grounded, \( V_{\text{fb}} \) is the back-gate voltage, \( R_{\text{contact}} \) is the resistance between the source and drain electrodes, \( R_{\text{contact}} \) is the contact resistance of the source and drain, \( L \) is the graphene channel length ranging from 50 μm to 2 mm, \( W \) is the graphene channel width fixed at 10 μm, \( n \) is the carrier density at the Dirac point (residue carrier density), \( \mu \) is the carrier density induced by the back-gate bias away from the Dirac point, \( y \) is the Fermi velocity of carriers in graphene, which is \( 1.0 \times 10^6 \text{cm/s} \). Three parameters, namely, the mobility (\( \mu \)), carrier density (\( n \)), and contact resistance (\( R_{\text{contact}} \)), were fitted. To improve fitting consistency, we measured more than seven graphene FET devices for each channel length.

In situ CVOD growth experiments. In situ CVD growth experiments were performed inside the chamber of a modified commercial ESEM (FEI Quantum 200). After sample loading, the chamber was pumped out to around 10−3 Pa, purged with pure nitrogen and pumped again to 10−3 Pa successively for several times. Under CVD growth conditions, the pressure is six orders of magnitude higher than the base pressure and constitutes mostly H2 (99.9995% purity) and CH4 (99.95% purity). The substrate is pretreated 50 μm-thick Cu foil (99.999% purity). CVD growth was performed at temperatures ranging from 700 degree to 1000 degree, with a pressure in the chamber ranging from 10−3 Pa to 25 Pa.

Data availability

The data that support the findings of this study are available from the corresponding authors upon reasonable request.

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Author contributions
H.S. supervised the project. H.S. and X.L. conceived and designed the experiments. F. D., L.Zhang, and J.D. developed the theoretical model. X. H., G.W., T.H., X.L., Y.D. J.G. and D.H. contributed to treatment of Cu substrate, X.L.., D.H., Y.L., R.Z., J.Y. and H.S. performed graphene growth experiments; R.S.R. provided suggestions about further experiments. J.S., Y.L., R.Z. and W.X. performed the FET devices and measured carrier mobilities. G.W., M.L., L.Zhu. and T.H. performed EBSD measurements. W.T., K.M.Y. and G.W. performed LEEM and pLEED experiments. Z.W. performed the in situ CVD growth experiments. Y.L., L.Zhang, F.D. and H.S. wrote the paper. M.S.A., R.S.R., W.T. and X.H. reviewed and edited the manuscript. All co-authors discussed and commented on the manuscript.

Competing interests
The authors declare no competing interests.

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