

Modular assembly of graphene-skinned Cu(111) foils into large-scale laminates with tailored interfaces and enhanced conductivity

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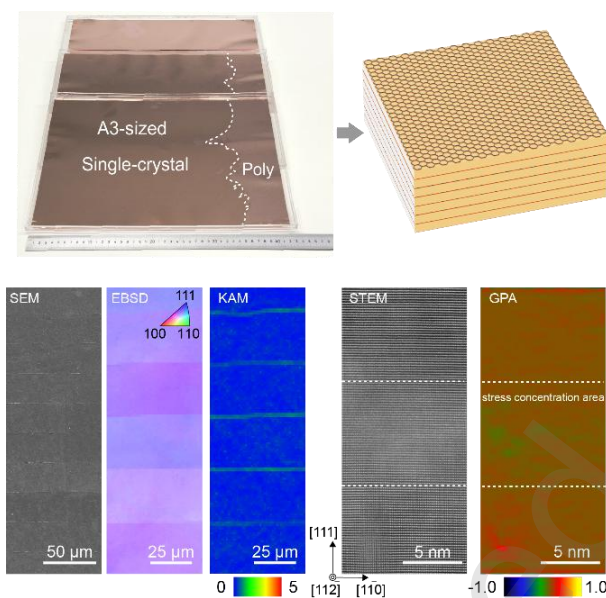
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A modular assembly strategy employing single-crystal graphene/Cu(111) building blocks facilitates the fabrication of bulk laminates featuring tailored interfaces and enhanced transport properties. This strategy capitalizes on the strong coupling that locks compressive strain at the graphene/Cu interfaces to enhance conductivity.

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ABSTRACT: Graphene-copper composites hold great promise for thermal and electrical management, yet their deployment is hindered by high grain boundary density, weak interfacial coupling, and limited scalability. Here we report a modular assembly strategy that transforms A3-sized single-crystalline graphene-skinned Cu(111) foils into bulk laminates with tailored interfaces and enhanced transport properties. The building blocks are synthesized via industrial-scale CVD system, combining temperature-gradient annealing with graphene epitaxial growth. Orientation-controlled stacking followed by spark plasma sintering yields dense laminates featuring only low-angle grain boundaries ($<2^\circ$), preserved coherent Gr(0001)/Cu(111) interfaces, and a continuous graphene channel. The laminates achieve electrical conductivity up to 103.7% IACS and thermal conductivity exceeding **422.3** $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, representing improvements of 5.5% and 8.2% respectively compared to commercial copper. Integrated heat spreaders exhibit substantially reduced thermal resistance ($0.88^\circ\text{C}/\text{W}$) with excellent stability. Extending this strategy to Gr/Ni(111) enables Cu-Gr-Ni heterostructures where graphene prevents intermetallic alloying. This work establishes a scalable paradigm for assembling macroscopic architectures from single-crystal, graphene-skinned building blocks for high-performance electronic packaging and multifunctional composites.

KEYWORDS: single-crystal Cu(111); chemical vapor deposition; graphene-copper composites; conductivity; thermal management

Introduction

Copper-based materials occupy an irreplaceable position in electronic packaging, power transmission, and thermal management applications owing to their exceptional electrical and thermal conductivity [1-3]. However, the escalating demands of artificial intelligence, 5G communications, and high-performance computing have pushed traditional copper to its limits, driving the need for advanced composites with superior performance. Among various candidates, graphene-copper (Gr/Cu) composites have emerged as a particularly promising direction, leveraging graphene's exceptional carrier mobility [4, 5], thermal conductivity [6, 7], and mechanical properties [8-10] to overcome copper's intrinsic property limitations.

Extensive efforts, including mechanical mixing[11-14], *in-situ* synthesis [15-19], and chemical vapor deposition (CVD) [20-27], have been dedicated to achieving uniform graphene dispersion. Yet, a critical oversight still persists: the detrimental effects of copper grain boundaries and poorly-bonded Gr/Cu interfaces are largely overlooked. High-angle grain boundaries (HAGBs) strongly scatter electrons and phonons, while non-functional, incoherent Gr/Cu interfaces introduce additional scattering that offsets graphene's benefits [8, 28-30]. Simply dispersing graphene within a polycrystalline matrix, without addressing these structural defects, cannot deliver the desired conductivity breakthrough.

An ideal Gr/Cu composite should simultaneously satisfy three criteria: (i) a matrix free from HAGBs, (ii) a coherent,

strongly coupled Gr/Cu interface minimizing scattering, and (iii) a continuous graphene channel. Single crystal Cu(111) foils meet the first requirement, as they are free of grain boundaries and possess minimum surface energy[31, 32]. Their close-packed (111) plane also offers minimal lattice mismatch with graphene (3–4%) [33], enabling epitaxial growth of high quality graphene films with coherent interfaces [34]. Such Gr/Cu(111) epitaxial interfaces uniquely accommodate the thermal expansion mismatch during cooling with minimal surface reconstruction [35–39], preserving a flat and strongly coupled interface. This feature has been shown to enhance conductivity by reducing electron-phonon coupling [40–43]. Despite these advantages, scalable fabrication of bulk composites from single-crystal Graphene-skinned Cu(111) foils has remained elusive, limited by foil dimensions and the challenge of preserving ideal structure during consolidation [21, 30, 44].

Here, we report a modular single crystal assembly strategy overcoming these barriers. We first achieve batch production of A3 sized (297 mm × 420 mm) single-crystal graphene-skinned Cu(111) foils by applying temperature gradient and texture-induced anomalous grain growth[34, 35] during the annealing process, followed by high-quality graphene epitaxial growth. These building blocks are then stacked with controlled orientations and consolidated *via* spark plasma sintering (SPS) into bulk laminates. The resulting composites feature ultralow grain boundary density (with only low-angle grain boundaries <2° between layers), preserved coherent Gr(0001)/Cu(111) interfaces that form a continuous graphene network, and interfacial compressive strain that enhances transport properties. The laminates attain an electrical conductivity of up to 103.7% IACS and a thermal conductivity exceeding 422.3 W·m⁻¹·K⁻¹, representing significant improvements over commercial copper and polycrystalline controls. To demonstrate practical utility, we fabricate integrated heat spreaders from these laminates and measure thermal resistance under chip- simulated conditions, showing stable performance over 30 thermal cycles. Beyond simple aligned stacking, controlled rotation of the building blocks allows tailoring of the crystallographic texture. Moreover, extending this strategy to graphene-skinned Ni(111) foils enables the construction of Cu–Gr–Ni heterostructures, where graphene acts as an effective diffusion barrier for immiscible metal lamination. This work establishes a scalable pathway to high-performance Gr/Cu composites and introduces a general paradigm for assembling macroscopic architectures from single-crystal, graphene-skinned building blocks for advanced thermal management, electronic packaging, and multifunctional composites.

Results and discussion

Figure 1 outlines the central concept and basic processes of the modular assembly strategy, which transforms single-crystalline Graphene-skinned Cu(111) foils into bulk laminates with controlled interfaces. The process begins with the annealing of texture-engineered polycrystalline copper foils in a multi-zone CVD system under a temperature gradient (Figure 1a, Figure S1 in the ESM). Driven by surface energy minimization, the Cu(111) facet emerges via abnormal grain growth and consumes

surrounding grains, ultimately yielding A3-sized single-crystal Cu(111) foils [34, 35]. Subsequently, epitaxial graphene growth is conducted at 1070 °C using methane (Figure 1b). The Cu(111) surface, with its favorable lattice match (3–4%) and crystallographic symmetry matching to graphene, enables the formation of high-quality single-crystalline monolayer graphene. During post-growth cooling, the thermal expansion mismatch between graphene and copper induces stress in both materials, which leads to the formation of step bunches on the copper substrate and wrinkles in the graphene layer[45, 46]. Fortunately, Cu(111) uniquely accommodates this stress with minimal surface reconstruction compared to other facets, preserving a flat and strongly coupled Gr/Cu interface[47]. To complete the assembly, the as-prepared Gr/Cu(111) foils are stacked with controlled orientations and consolidated *via* spark plasma sintering (SPS) at 800 °C under 35 MPa (Figure 1c, Figure S2 in the ESM). The resulting laminates feature a sandwich-like architecture with coherent Gr(0001)/Cu(111) interfaces and a continuous graphene network.

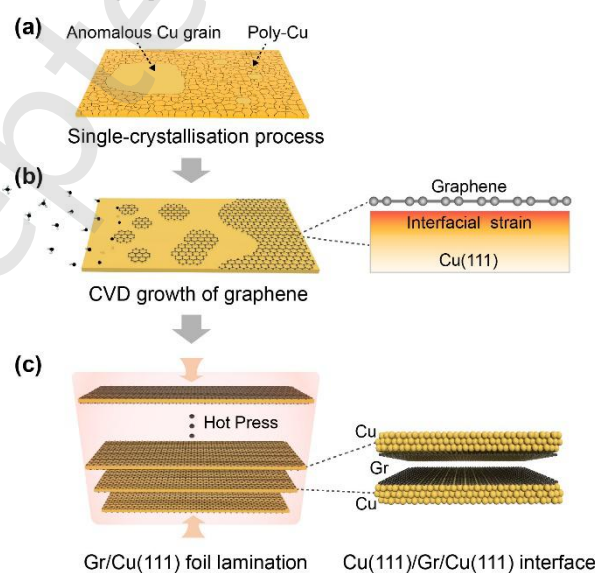


Figure 1 Modular assembly of Gr/Cu(111) laminates. (a) Schematic of abnormal grain growth transforming polycrystalline Cu foil into single-crystal Cu(111). (b) Epitaxial graphene growth on Cu(111). (c) Stacking of Gr/Cu(111) foils followed by spark plasma sintering (SPS), forming bulk laminates with coherent Gr(0001)/Cu(111) interfaces.

The modular strategy demands large-area, high-quality building blocks. Using an industrial-scale CVD system, we achieved batch production of A3-sized (297 mm × 420 mm) single-crystal Gr/Cu(111) foils (Figure 2a). Optical contrast between single-crystal and residual polycrystalline regions arises from reduced surface roughness due to fewer step bunches and thermal grooves (Figure S3 in the ESM). Electron backscatter diffraction (EBSD) across five positions reveals uniform blue out-of-plane orientation (Cu(111)) and green in-plane orientation, confirming complete single-crystallization (Figure 2b). X-ray diffraction (XRD) shows a single sharp peak at 43° corresponding exclusively to the (111) plane (Figure 2c). Atomic force microscopy (AFM) confirms an atomically flat surface (Figure 2d). Raman spectroscopy of transferred graphene exhibits prominent G (~1580 cm⁻¹) and 2D (~2670 cm⁻¹) bands with negligible D band, indicating low defect density (Figure 2e). Raman mapping over 200 × 200 μm² areas shows uniform I_D/I_G

ratios, demonstrating the high quality and homogeneity of the monolayer graphene across the entire foil (Figure 2f).

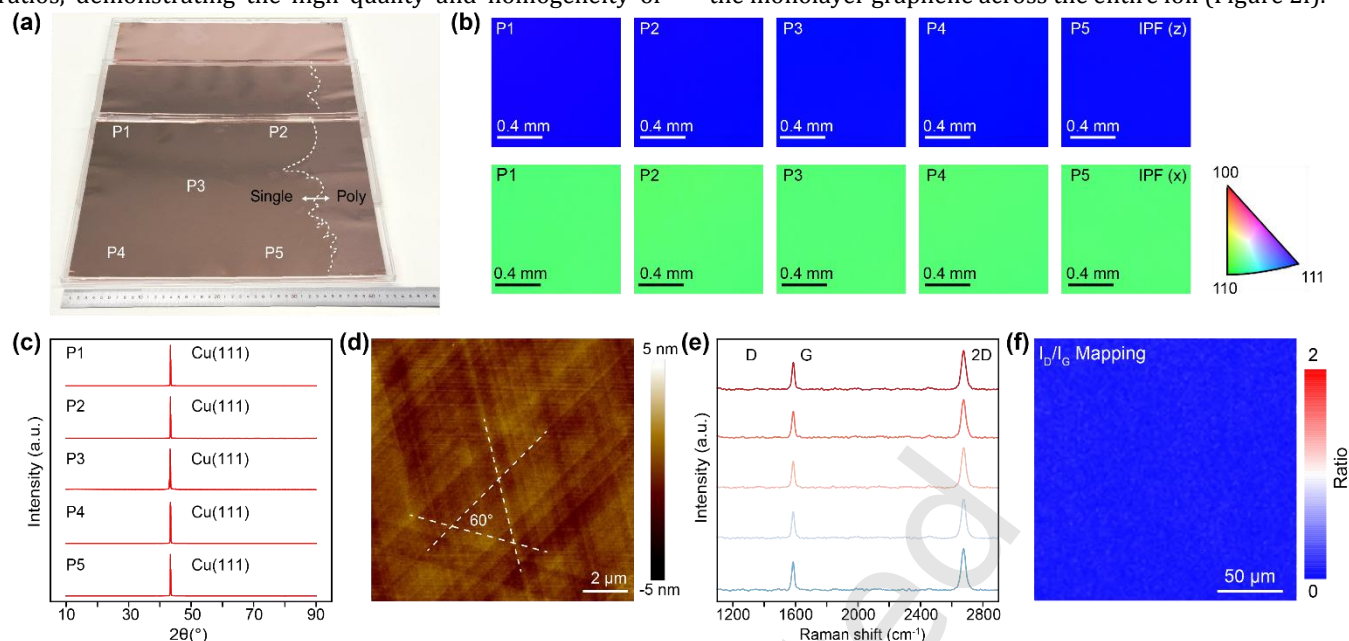


Figure 2 Scalable fabrication of single-crystalline Gr/Cu(111) foils. (a) Photograph of A3-sized single-crystalline Gr/Cu(111) foils. (b) EBSD IPF maps from five positions marked in (a). (c) XRD 2θ scans from corresponding positions. (d) AFM image of Cu(111) surface. (e) Raman spectra from five positions on transferred graphene. (f) Raman ID/IG map over $200 \times 200 \mu\text{m}^2$ area.

The Gr/Cu(111) foils were stacked and sintered into bulk laminates (Figure 3a, Figure S4 in the ESM). Through process optimization, the composite achieves tight interlayer bonding without porosity or melting (Figure S5 in the ESM). Cross-sectional EBSD reveals that all layers maintain a uniform (111) out-of-plane orientation with misorientation angles below 1° between adjacent layers (Figure 3b, Figure S6 in the ESM). Only low-angle grain boundaries (LAGBs, $<2^\circ$) are present, and high-angle grain boundaries (HAGBs) are completely eliminated. Scanning electron microscopy (SEM) shows a dense, pore-free lamellar structure with clear

graphene interlayers (Figure 3c). ToF-SIMS depth profiling and 3D reconstruction of C_2^- signals confirm continuous graphene distribution at the interface, forming a continuous conductive channel throughout the laminate (Figure 3d-f). The characteristic sp^2 carbon fragment ions C_2^- , C_4^- and C_6^- were all detected at the copper layer interface, confirming that the carbon signal originates from graphene (Figure S7 in the ESM). Multiple areas across the sample exhibit consistent graphene coverage with only occasional deformation-induced cracks (Figure S8 in the ESM), confirming the robustness of the interfacial structure under SPS conditions.

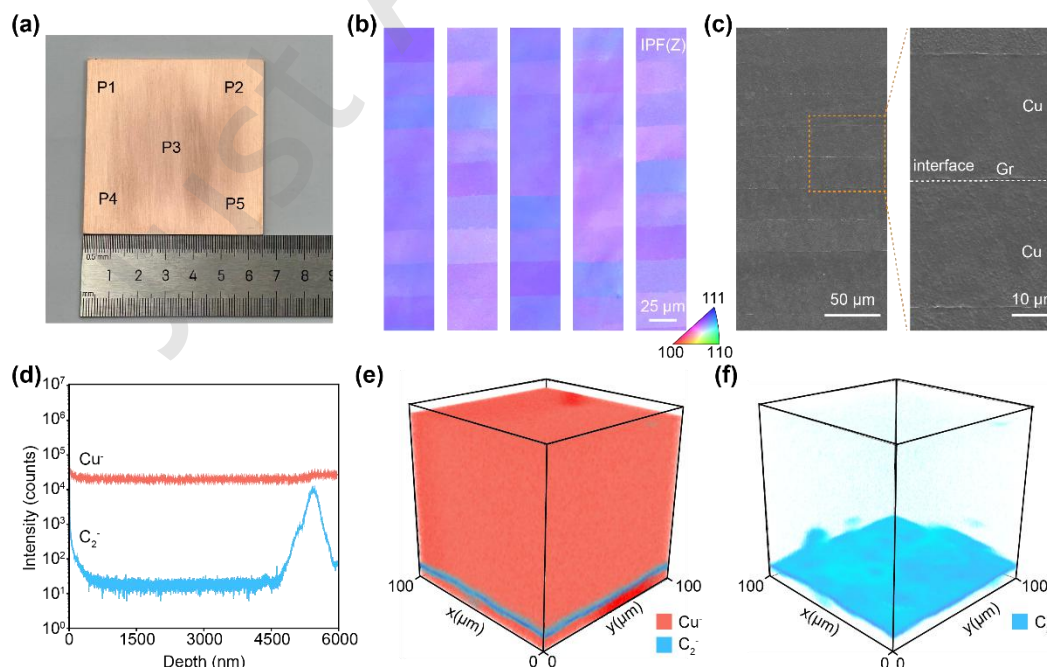


Figure 3 Microstructural characterization of Gr/Cu(111) laminates. (a) Photograph of as-sintered Gr/Cu(111) laminates. (b) Cross-sectional EBSD IPF maps from five positions marked in (a). (c) Cross-sectional SEM image showing lamellar structure with graphene interlayers. (d) ToF-SIMS depth profiles of Cu^- and C_2^- signals; (e-f) ToF-SIMS 3D reconstruction of Cu^- and C_2^- intensity (e) and individual 3D reconstruction of C_2^- intensity (f).

To elucidate the role of the Gr/Cu(111) interface, we compared laminates assembled from (i) annealed

polycrystalline Cu foils (without graphene), (ii) Gr/polycrystalline Cu foils, and (iii) Gr/Cu(111) single-crystal foils (Figure 4). EBSD orientation maps show that polycrystalline-derived laminates possess highly disordered

orientations with numerous HAGBs (Figure 4a,b,d,e). In contrast, Gr/Cu(111) laminates exhibit exceptional orientation consistency, with only LAGBs (misorientation $<2^\circ$) (Figure 4g,h).

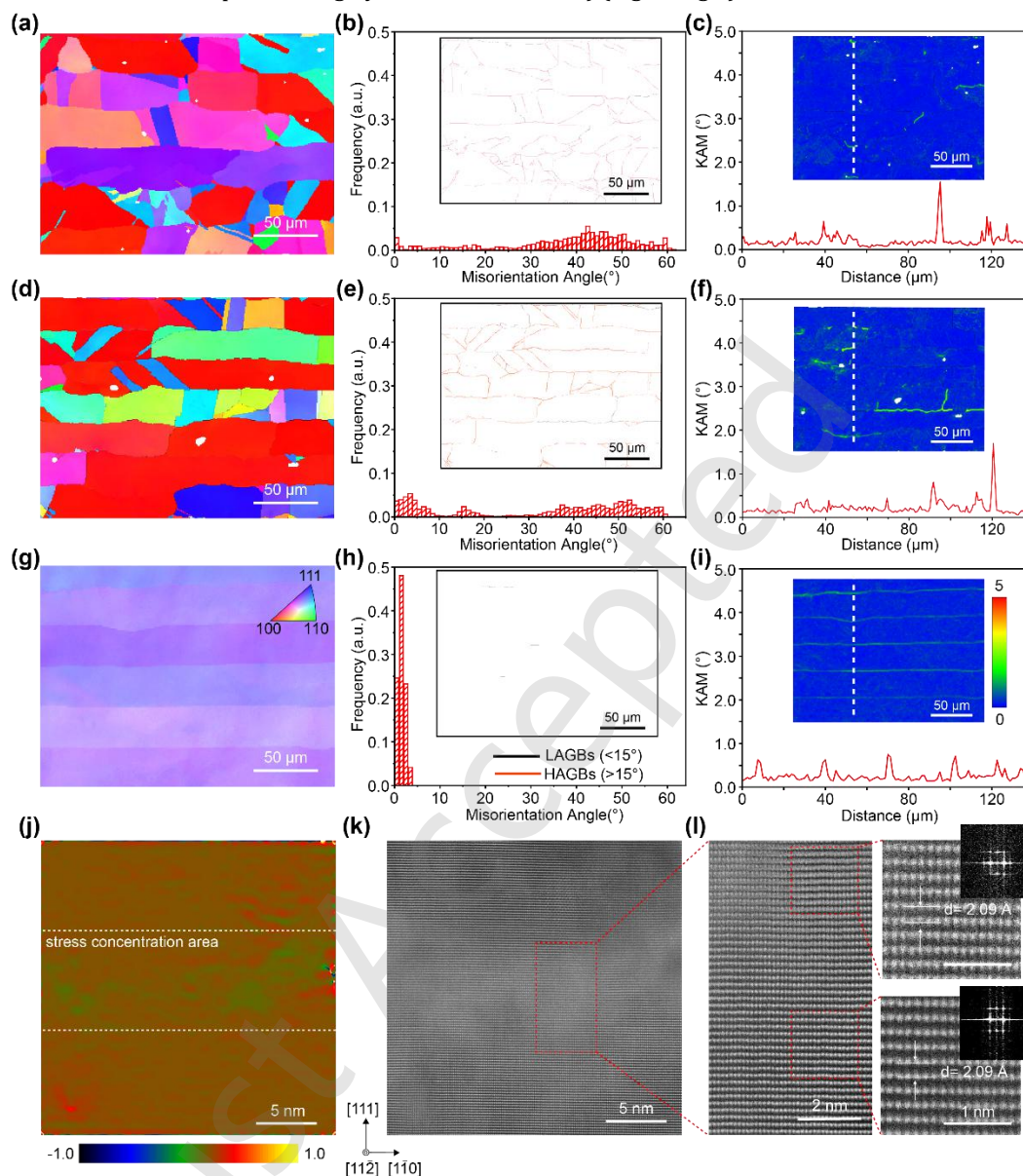


Figure 4 Interfacial structure and strain analysis. (a–c) EBSD IPF map (a), grain boundary map (b), and KAM map (c) of laminates from annealed polycrystalline Cu foils. (d–f) EBSD IPF map (d), grain boundary map (e), and KAM map (f) of laminates from Gr/polycrystalline Cu foils. g–i) EBSD IPF map (g), grain boundary map (h), and KAM map (i) of laminates from Gr/Cu(111) foils. j) In-plane strain map (ϵ_{xx}) obtained by GPA of HAADF-STEM image in (k); k,l) Cross-sectional STEM images of Gr/Cu(111) interface; insets in (l) show FFT patterns from both sides.

Kernel average misorientation (KAM) mapping reveals distinct distributions arising from the different interface behaviors during SPS process. While all samples show comparable average KAM values (~ 0.2) due to similar thermal histories, only Gr/Cu(111) laminates display a periodic strain pattern with intensity peaks precisely at the Gr/Cu interfaces (Figure 4i). Cross-sectional scanning transmission electron microscopy (STEM) combined with geometric phase analysis (GPA) confirms compressive strain concentrated along the interface region (Figure 4j). High-resolution STEM images show atomic lattice spacings of 2.09 Å on both sides of the interface, corresponding to Cu(111) planes, with slight lattice distortion at the Cu/Gr/Cu interface (Figure 4k, l, additional STEM-GPA analysis from a

different laminate see Figure S9 in the ESM, the compressive strain pattern is consistently reproduced). The monolayer graphene is not directly resolved as a discrete layer due to the low atomic contrast and strong electronic coupling at the coherent interface. For comparison, the same graphene layer remains clearly visible on the Cu(111) surface prior to stacking (Figure S10 in the ESM). This distortion originates from the thermal expansion mismatch between graphene and copper during the heating and cooling process of SPS. Critically, the strong interfacial coupling between graphene and Cu(111) allows the interface to ‘grip’ each other through the thermal process, minimizing surface reconstruction and preventing defect formation or interface tearing. As a result, the thermally induced compressive strain is preserved and

localized at the interface rather than being relaxed, giving rise to the periodic strain pattern observed in KAM and GPA.

The structural advantages of Gr/Cu(111) laminates, namely the elimination of high-angle grain boundaries (HAGBs), the preservation of coherent interfaces, and the beneficial interfacial strain, directly lead to improved transport properties. The in-plane Electrical conductivity measured by the van der Pauw method (experimental setup see Figure S11 in the ESM) reaches $103.7 \pm 0.2\%$ IACS, a 5.5% enhancement over commercial copper and nearly 2% improvement over polycrystalline Gr/Cu controls (Figure 5a). The in-plane thermal conductivity follows a similar trend, achieving $422.3 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, an 8.2% increase relative to commercial copper (Figure 5b). A parallel comparison among four configurations further reveals the hierarchical contributions: single-crystal Cu(111) laminates without graphene already reach 102.6% IACS and $414.1 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$,

accounting for roughly 70% of the total enhancement and demonstrating that HAGB elimination is the predominant factor. Introducing graphene into the single-crystal matrix further raises the conductivity to 103.7% IACS and $422.3 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, an additional gain attributed to the strongly coupled, coherent interface that locks in compressive strain and minimizes residual scattering. By contrast, incorporating the same graphene interlayers into a polycrystalline Cu matrix yields only 102.2% IACS and $408.0 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, confirming that the benefit of graphene is largely offset when HAGBs remain. Thus, the single-crystal matrix serves as the prerequisite and dominant enabler, while the graphene interface acts as an indispensable secondary enhancer. Mechanical testing shows exceptional ductility (53.5%) compared to commercial copper (30.5%) (Figure S12 in the ESM), and the material can be readily processed into various shapes and wires (Figure S13 in the ESM).

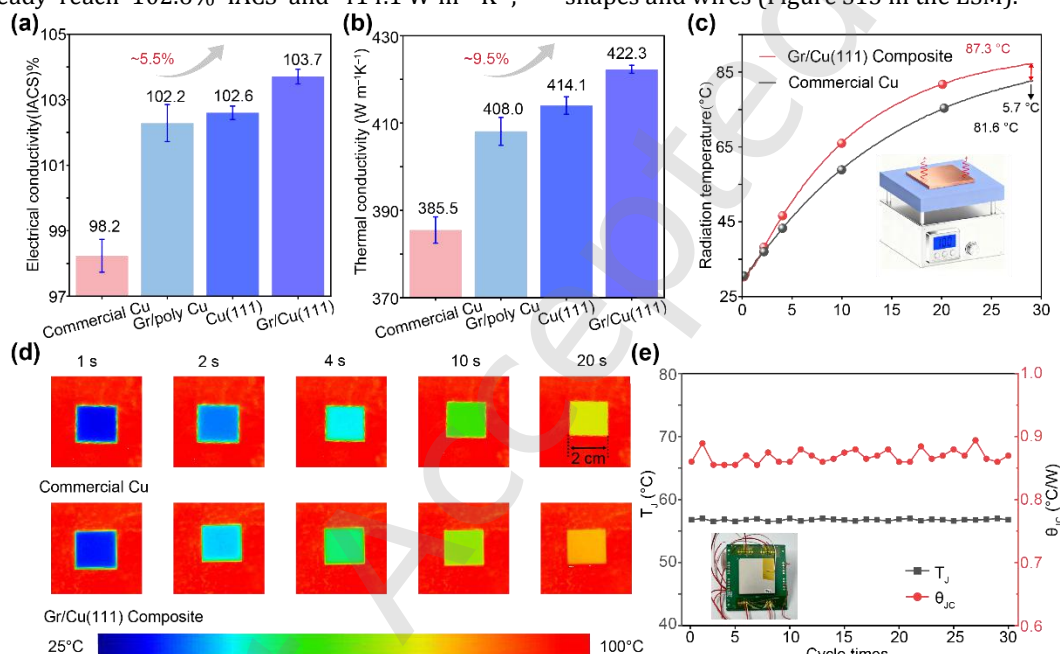


Figure 5 Transport properties and thermal management performance. a-b) Electrical conductivity (a), thermal conductivity (b) of commercial Cu, Gr/polycrystalline Cu foil laminates, single-crystal Cu(111) foil laminates, and Gr/Cu(111) foil laminates. c) Infrared camera images of commercial Cu (top) and Gr/Cu(111) (bottom) laminates on a 100°C hot plate. d) Surface temperature evolution with heating time. e) Thermal resistance stability of integrated heat spreaders (IHS) over 30 thermal shock cycles. Inset: photograph of IHS on test chip and measurement setup.

To demonstrate practical utility, we compared heat transfer performance using infrared imaging. When placed on a 100 $^{\circ}\text{C}$ heat source, Gr/Cu(111) laminates reach higher surface temperatures more rapidly than commercial copper: after 30 seconds, the temperature difference reaches 5.7 $^{\circ}\text{C}$ (Figure 5c, d). Fabricated into integrated heat spreaders (IHS, experimental setups see Figure S14 in the ESM) and tested with chips, the Gr/Cu(111)-based spreaders exhibit substantially lower thermal resistance (0.88 $^{\circ}\text{C/W}$) compared to commercial copper controls (1.66 $^{\circ}\text{C/W}$), with

excellent stability in both thermal performance and structural integrity over 30 thermal shock cycles (Figure 5e, S15 in the ESM). This deliberately anisotropic design is aligned with the application requirements. Electronic packaging necessitates in-plane current flow and heat spreading, while the short through-plane path is seldom rate-limiting. Consequently, the inherent advantages of our laminate architecture are maximized. These results underscore the material's promise for high-performance electronic packaging.

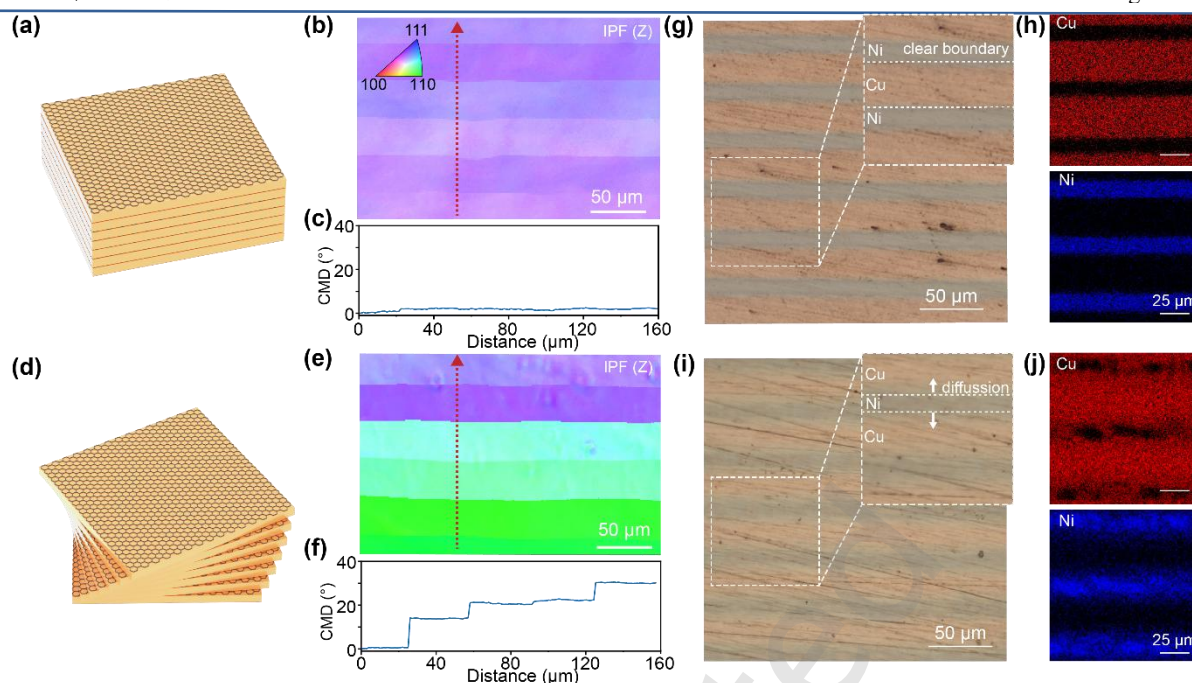


Figure 6 Architectural versatility: twisted stacking and heterometallic laminates. a) Schematic of aligned stacking; b) Cross-sectional EBSD IPF map of aligned-stacked laminate; c) Cumulative misorientation distribution (CMD) along line in (b); d) Schematic of angular stacking; e) Cross-sectional EBSD IPF map of angular-stacked laminate; f) CMD along line in (e); g-i) Optical images (g, i) and EDS mappings (h, j) of laminates from Cu-Ni (g, h) and Cu-Gr-Ni (i, j) foils, respectively.

The modular assembly approach enables structural designs beyond simple aligned stacking. By cutting and stacking Gr/Cu(111) foils with controlled rotational angles, we fabricated laminates with tailored crystallographic textures. Aligned stacking produces a structure resembling a single crystal, with cumulative misorientation below 2° across the entire cross-section (Figure 6a-c). In contrast, sequential rotation yields a progressive color gradient in EBSD orientation maps and step-like cumulative misorientation distributions (Figure 6d-f), demonstrating precise control over the three-dimensional crystallographic architecture.

Extending this strategy to other metal systems, we employed Gr/Ni(111) building blocks to construct Cu/Gr/Ni heterostructures. Alternating stacking of Gr/Cu(111) and Gr/Ni(111) foils followed by SPS yields sharp, well-defined interfaces (Figure 6g). EDS mapping confirms that graphene acts as an effective diffusion barrier, preventing intermetallic alloying between copper and nickel layers (Figure 6h). In the absence of graphene, extensive interdiffusion occurs, producing a diffuse interface and visible alloy formation (Figure 6i, j). This ability to laminate immiscible metals without alloying creates opportunities for multifunctional composites that integrate the high conductivity of copper with the magnetic and mechanical properties of nickel, a combination that was previously unachievable because of their complete mutual solubility. More broadly, this approach addresses a fundamental challenge in metal matrix composites: preventing undesirable reactions or interdiffusion between matrix and reinforcement without compromising the intrinsic properties of each constituent. Graphene, as the thinnest possible barrier, achieves this isolation, offering a versatile platform for designing multifunctional metal-based architectures.

Conclusion

In summary, this work reports a modular assembly strategy for fabricating bulk graphene-copper laminates from single crystalline Graphene-skinned Cu(111) foils. The resulting materials feature a grain boundary free structure within the layer, coherent Gr(0001)/Cu(111) interfaces, and a continuous graphene channel. Leveraging the strong interfacial coupling inherent to the Gr/Cu(111) epitaxial system, the sintering-induced compressive strain is effectively locked at the interfaces rather than relaxed through defect formation, contributing directly to the enhanced transport properties. Consequently, the Gr/Cu(111) laminates exhibit outstanding electrical conductivity, thermal conductivity, and ductility, demonstrating superior performance in electronic packaging applications. The strategy extends to Gr/Ni(111) building blocks, enabling Cu-Gr-Ni heterostructures where graphene serves as an effective diffusion barrier. This work establishes a scalable paradigm for assembling macroscopic architectures from single crystal, graphene coated building blocks for advanced thermal management and multifunctional metal matrix composites.

Experimental

Preparation of Single-crystal Cu(111) Foils and Ni(111) Foils: Commercially available Cu foils (28 μm) were placed on a 6 inches quartz tube or our home-made five-zone industrial CVD system. The entire annealing process was conducted under a H_2 (1000 sccm) atmosphere. The sample was first heated to 900 $^\circ\text{C}$. And then, a temperature gradient was established by setting the different zones to 1070 $^\circ\text{C}$, 1040 $^\circ\text{C}$, and 1010 $^\circ\text{C}$ to initiate abnormal grain growth. Subsequently, the temperature across all zones was raised to 1070 $^\circ\text{C}$ for a 1-hour anneal to promote uniform grain growth (Figure S1 in the ESM). Single-crystal Ni foils were prepared via a

contact-free annealing method. A polycrystalline Ni foil was suspended in a vertical annealing furnace and held at 1350 °C for 15 h under a bottom-to-top Ar/H₂ mixed gas flow, where Ar serving as the protective atmosphere, H₂ reducing trace surface oxides on the Ni foil and the upward gas flow direction helped maintain a stable furnace pressure. After this treatment, single-crystal Ni foils were obtained.

Graphene growth: 1000 sccm hydrogen (H₂, 99.999% purity) and 0.8 sccm methane (CH₄, 99.999% purity) are introduced into the chamber at pressure of 2000 Pa for Graphene growth on single-crystal Cu(111) surface. After a growth duration of 120 minutes, high-quality graphene films were obtained.

Preparation of Graphene/Cu(111) composite: The A3-size Gr/Cu(111) foil was cut into equal-sized square pieces, and typically 40 pieces were placed into a customized graphite die. Then, the assembly was sintered in a SPS furnace at 800 °C under a pressure of 35 MPa, under a vacuum of 10⁻⁴ Pa. The sintering was conducted with a heating rate of 400 °C/min, while the pressure was linearly ramped to 35 MPa over 30 minutes and then maintained for 60 minutes to enhance densification. The resulting bulk laminate had a final thickness of approximately 1 mm.

ToF-SIMS measurements: Fresh interfaces of Gr/Cu Composite were prepared for Time-of-flight secondary ion mass spectrometry ((ION-TOF GmbH TOF.SIMS5-100, Germany) analysis. A 2 keV Cs⁺ primary ion beam was used for surface sputtering, and then a 30 keV Bi⁺ ion beam was employed for compositional imaging, acquiring images at 128 × 128 pixels over areas of 100 × 100 μm² (Figure S3 in the ESM). Under these conditions, the spatial resolution in the XY plane, which is defined by the 25%-75% signal rise at a graphene domain boundary, was approximately 0.2 μm, and the depth resolution was about 1 nm. All measurements were performed at a base chamber pressure of approximately 10⁻⁸ mbar. The instrument's proprietary SurfaceLab 7.0 software (ION-TOF) was used to perform the final data processing, including characteristic peak identification and image reconstruction.

Electrical conductivity measurements: The Van der Pauw method is employed to assess the electrical conductivity of samples. Regular square Gr/Cu composite samples with clean and flat surfaces was placed on a test stage equipped with four metal electrodes. A known current applied through two electrodes and measured the voltage across the other two. The sample thickness was determined by dividing its volume, measured via Archimedes' principle, by its length and width. Using the measured current, voltage and thickness, the calculation of resistivity employs the Van der Pauw formula:

$$\rho = \frac{\pi * R * d}{\ln 2}$$

where R is the measured resistance (Ω), d is the composite thickness (meters; its measurement is shown in Figure S11), ρ is the resistivity (Ω • m). The conduct is compared to the conductivity of pure copper (58 MS m⁻¹) to calculated the sample's IACS%:

$$\sigma = \frac{1}{\rho}$$

$$IACS\% = \frac{\sigma}{5.8 * 10^7} * 100$$

Laser flash method for thermal conductivity measurements: The thermal conductivity is determined using the following formula:

$$\kappa = \alpha \times \rho_{sample} \times C_p$$

Where κ is the thermal conductivity, ρ_{sample} is sample density measured with a density balance (intermediate density measurement process and data see Tables S1–S4), C_p is the heat capacity (PerkinElmer, DSC8000). The thermal diffusivity (α, mm²s⁻¹) of the samples was measured using an LFA 467 HyperFlash apparatus (Netzsch, Germany).

Characterizations: The crystal orientation of the Gr/Cu(111) foil and composite was characterized by OM (Nikon, LV100ND), SEM (FEI Quattro S, acceleration voltage 10 kV), XRD (Bruker D8 ADVANCE, with a Cu Kα radiation, 40 kV and 40 mA), AFM (Bruker Dimension Icon, with ScanAsyst mode), EBSD (AMETEK EDAX Digi View Camera in combination with EDAX's TEAM, 20 kV). Static tensile tests of Gr/Cu composites, processed into a dog-bone shape, were tested by the universal mechanical testing machine (MTS, UTM E43.504).

Electronic Supplementary Material: Supplementary material (including Figure S1 to S15 and Table S1 to S4) is available in the online version of this article at <https://doi.org/10.26599/NR.2026.94908969>.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request."

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Declaration of competing interest

All the contributing author(s) report(s) no conflict of interests in this work.

Author contribution statement

Z.L. and L.S. supervised and convinced the project. L.S., S.Z., and X.W. designed the experiments and carried out the synthesis and sample preparation. L.Q. drew the schematic diagrams. B.C., S.Z., and X.W. performed the STEM characterizations. X.S., Y.D., C.W., P.B., J. D. and Z.W. conducted the optical microscopy image and Raman characterizations. J.W. performed the thermal conductivity measurements and corresponding analysis. S.Z. and P.L. performed the ToF-SIMS characterizations. All authors discussed the results and wrote the paper. †These authors contributed equally. (Sicong Zheng, Xinpeng Wang, Buhang Chen).

Use of AI statement

None.

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Electronic Supplementary Material

Modular assembly of graphene-skinned Cu(111) foils into large-scale laminates with tailored interfaces and enhanced conductivity

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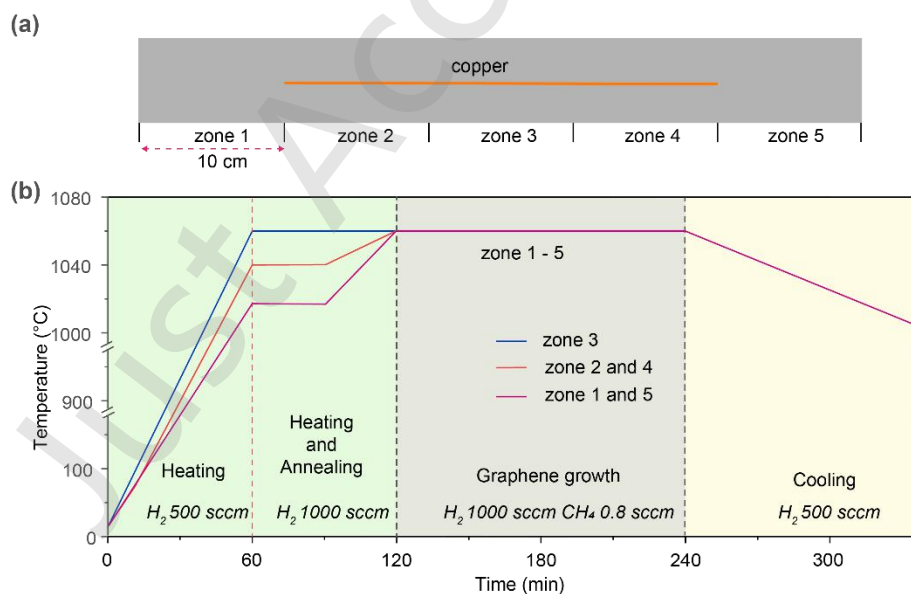


Figure S1 (a) Schematic diagram of five-zone CVD system; (b) Protocols and typical CVD parameters for the synthesis of Gr\Cu(111) foils.

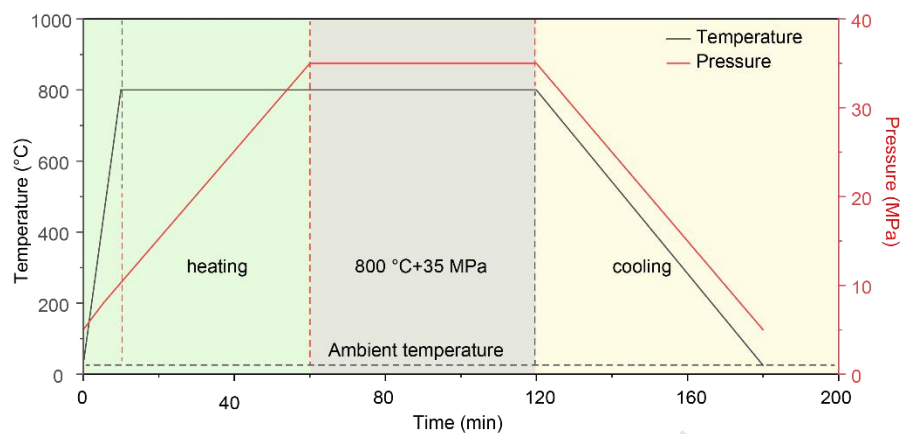


Figure S2 Protocols and typical SPS parameters for the fabrication of Gr\Cu(111) laminates.

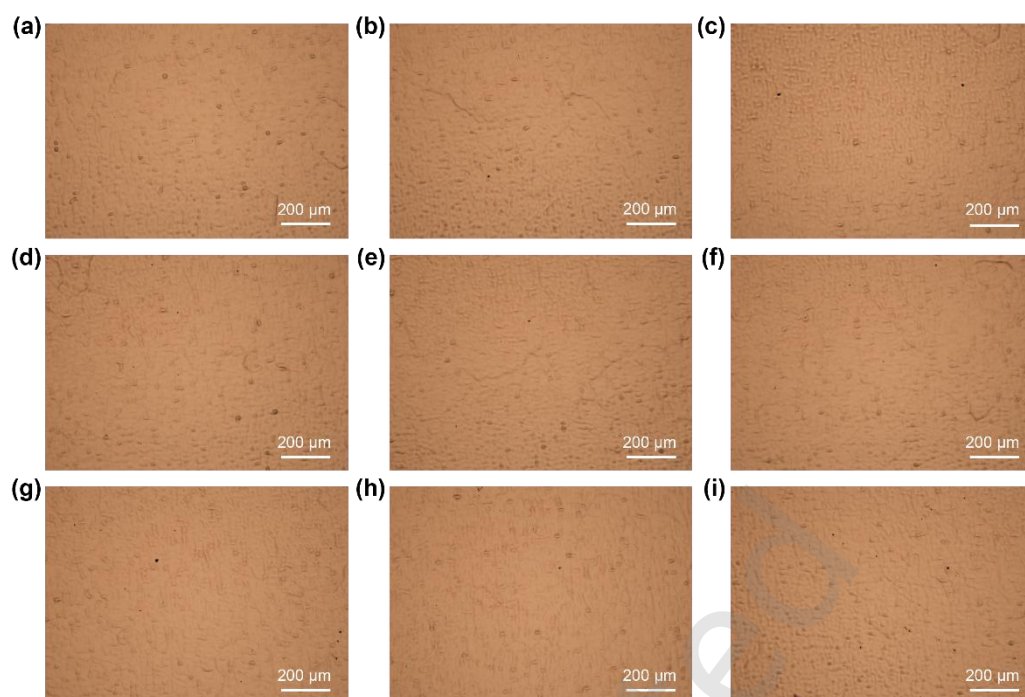


Figure S3 Typical optical photograph of as-obtained Gr/Cu(111) foils.

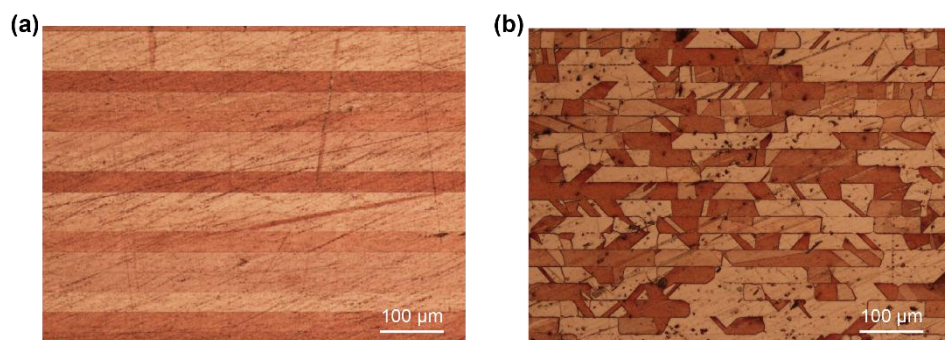


Figure S4 (a) Cross sectional optical microscope image of composite prepared via Gr/single-crystal Cu(111) foil. (b) Cross sectional optical microscope image of composite prepared via Gr/polycrystalline Cu foil.

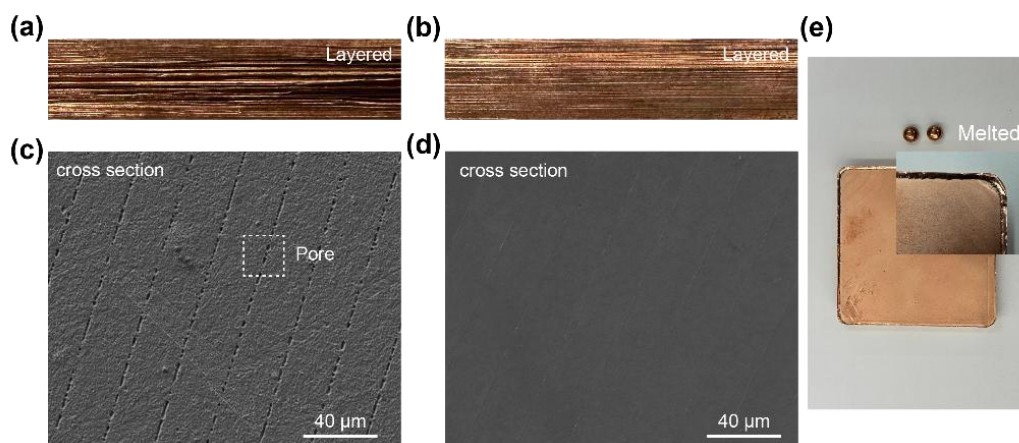


Figure S5 (a) Cross-section below 800 °C showing delamination. (b) Cross-section at 800 °C showing tight bonding. (c) SEM image corresponding to (a) with pores. (d) SEM image corresponding to (b) without pores. (e) Sample melted at 800 °C and 1000 °C.

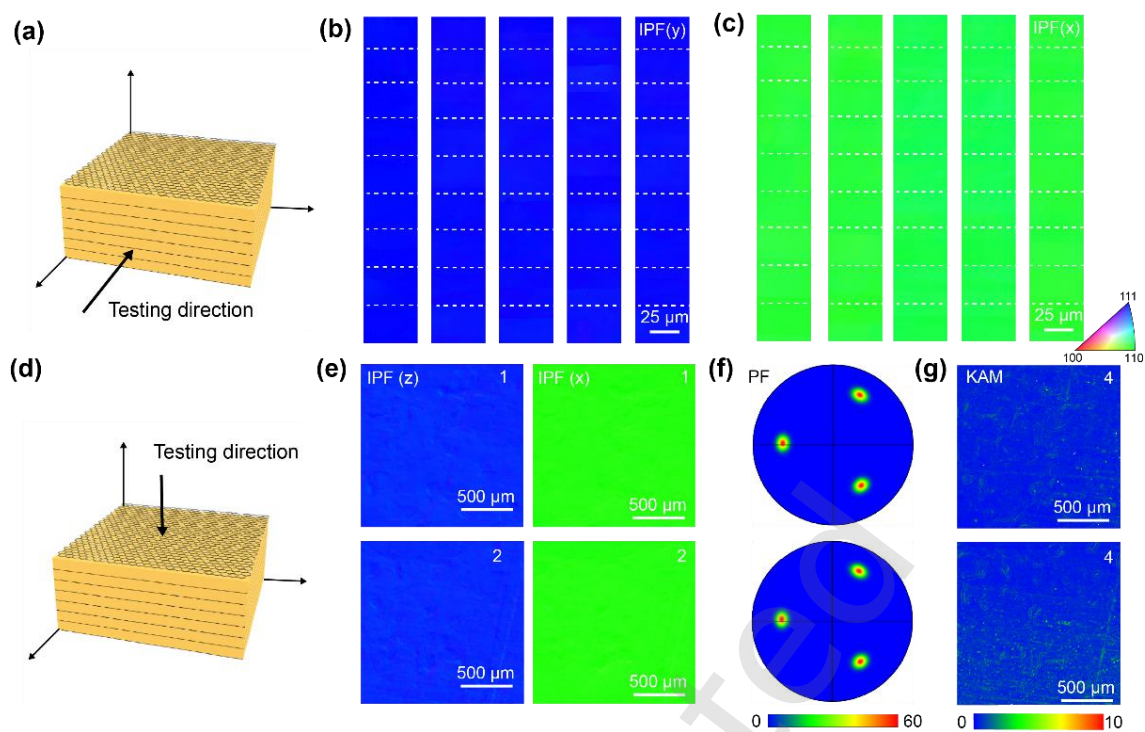


Figure S6 EBSD characterization of the Gr/Cu(111) composite. (a)(a-b) EBSD IPF maps in y direction and in x direction. (f) The pole figures of the (001) poles. (g) KAM maps.

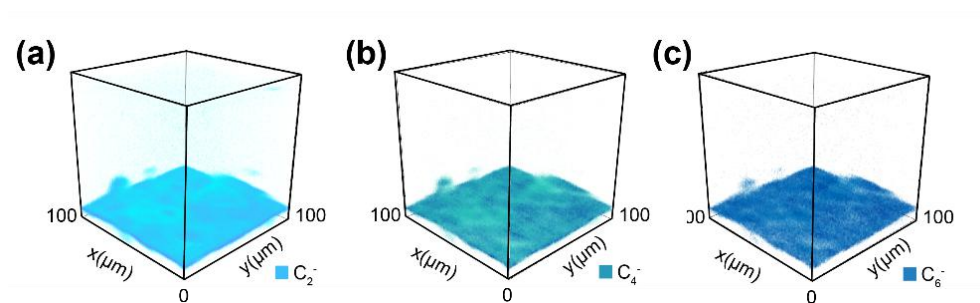


Figure S7 ToF-SIMS 3D reconstruction of C_2^- intensity(a), C_4^- intensity(b) and C_6^- intensity(c).

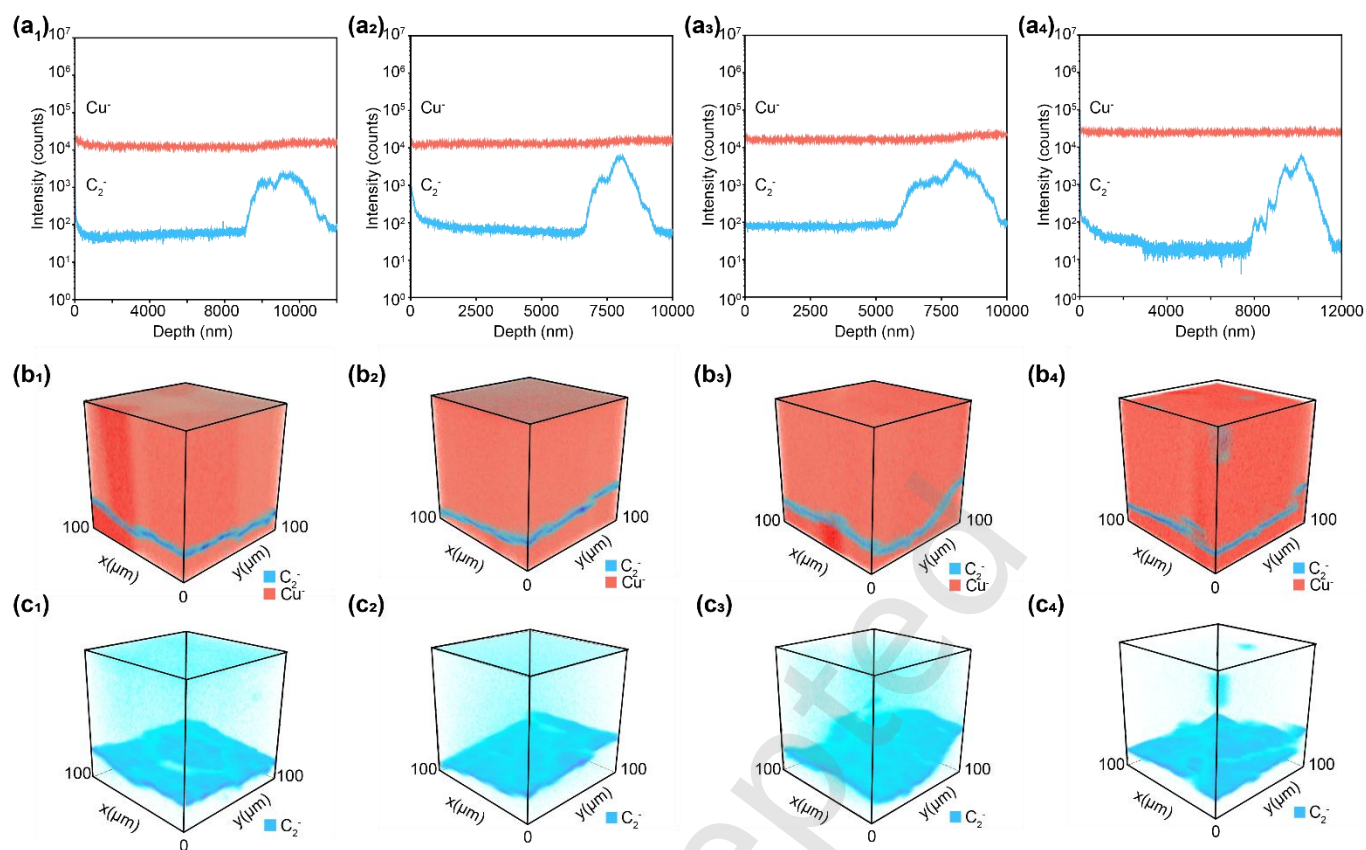


Figure S8 ToF-SIMS characterization of Gr/Cu(111) interfaces across multiple random regions. (a₁-a₄) Depth profiles of Cu^- and C_2^- secondary ion signals; (b₁-b₄) Corresponding 3D distribution maps of Cu^- and C_2^- intensity; (c₁-c₄) Individual 3D distribution maps of C_2^- intensity.

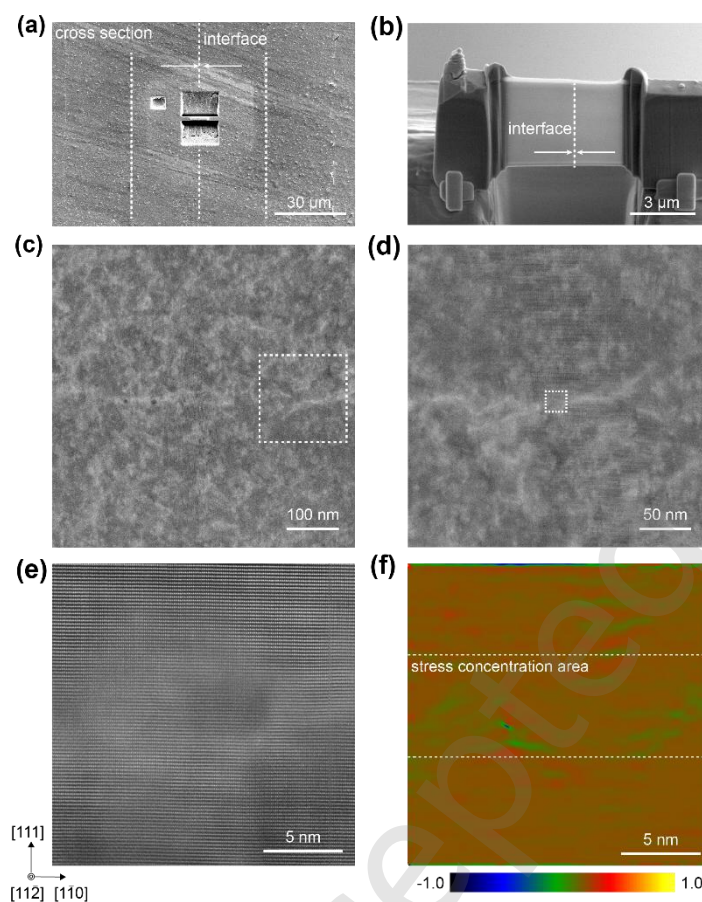


Figure S9 a) FIB sampling location. b) Prepared cross-sectional sample. (c-e) STEM images of the interface at different resolutions. (f) In-plane strain map (ϵ_{xx}) obtained by GPA of HAADF-STEM image in (e).

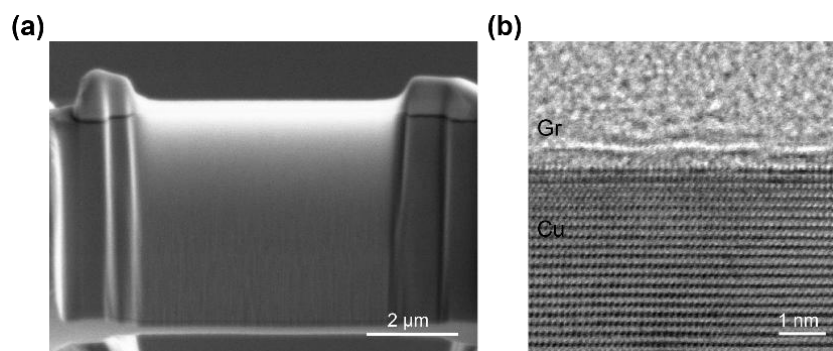


Figure S10 a) SEM image of graphene on copper foil prepared by FIB. b) (b) STEM image of epitaxial graphene on copper foil.

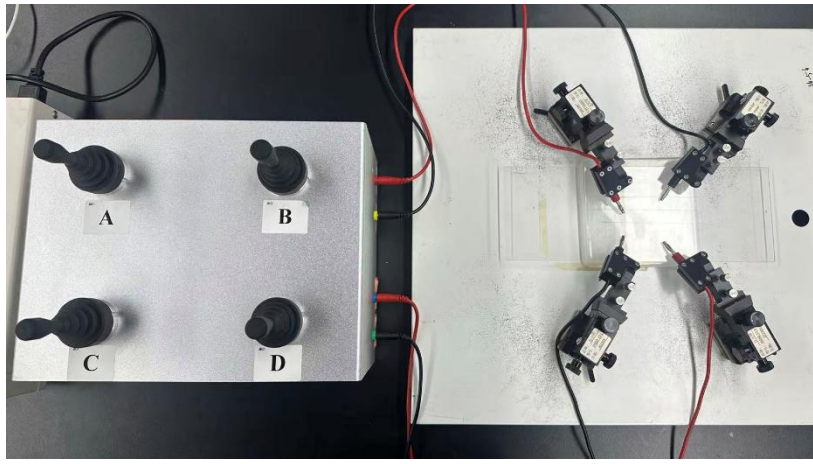


Figure S11 Experimental setup for van der pauw conductivity measurements.

The sample is clamped between the four probes on the right, and the direction of the applied current is controlled by the lever (ABCD) on the left, which permits the acquisition of voltage from terminals CD and AD, and current from terminals AB and BC, thus facilitating resistance computation. Calculate using the following formula:

$$\rho = \frac{\pi h}{21n2} \left(\frac{U_{CD}}{I_{AB}} + \frac{U_{DA}}{I_{BC}} \right)$$

The sample thickness was determined by the Archimedes drainage method. A regular square sample with clean and flat surfaces was weighed in air and then fully submerged in deionized water at 25 °C. The volume was obtained by dividing the mass difference between the two measurements by the density of water, and the average thickness was then calculated by dividing the volume by the measured surface area. Five repeated measurements were performed for each specimen to obtain the mean value. Calculate using the following formula:

$$d_{sample} = \frac{(m_{air} - m_{liq})\rho_{water}}{L \cdot W}$$

Where d_{sample} is sample thickness, m_{air} is the mass of the sample in air, and m_{liq} is the mean apparent mass when fully submerged in the reference liquid. Their difference $m_{air} - m_{liq}$ equals the mass of displaced liquid, which numerically gives the displaced volume. L and W are the sample length and width, respectively.

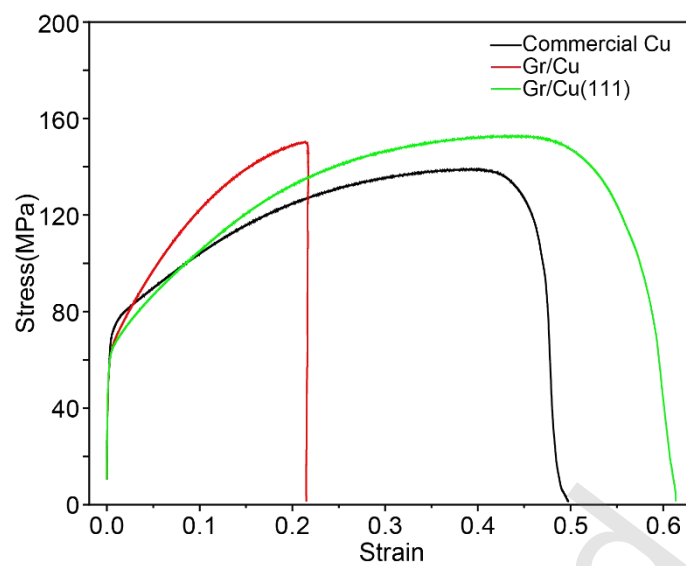


Figure S12 Tensile strength and ductility measurements of commercial Cu, Gr/polycrystalline Cu, and Gr/Cu(111).

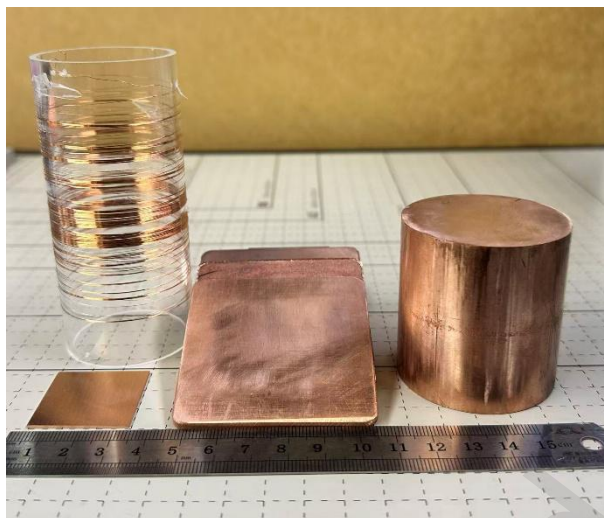


Figure S13 Various forms of as-obtained graphene-copper composites.

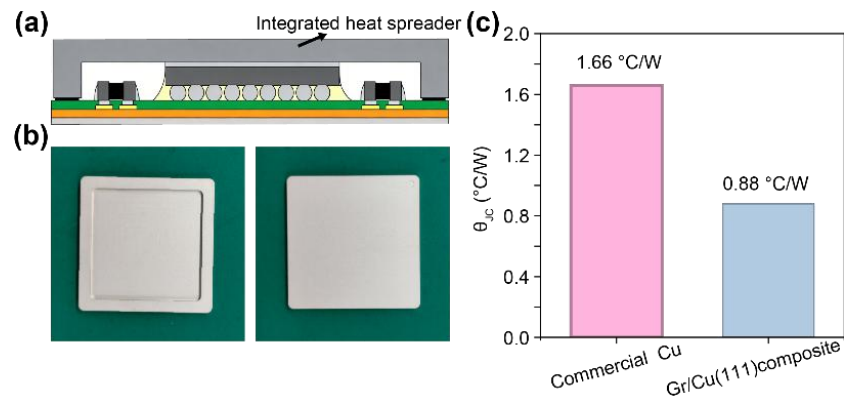


Figure S14 a) Schematic of integrated heat spreader (IHS). b) Photograph of HIS. c) Thermal resistance measurement results.

The thermal resistance is calculated using the following formula:

$$\theta_{jc} = (T_j - T_c) / P$$

Here, T_j is obtained from the forward voltage drop (K-factor method), T_c is recorded by a thermocouple embedded in the cold plate contacting the package surface, and P represents the heating power dissipated in the device.

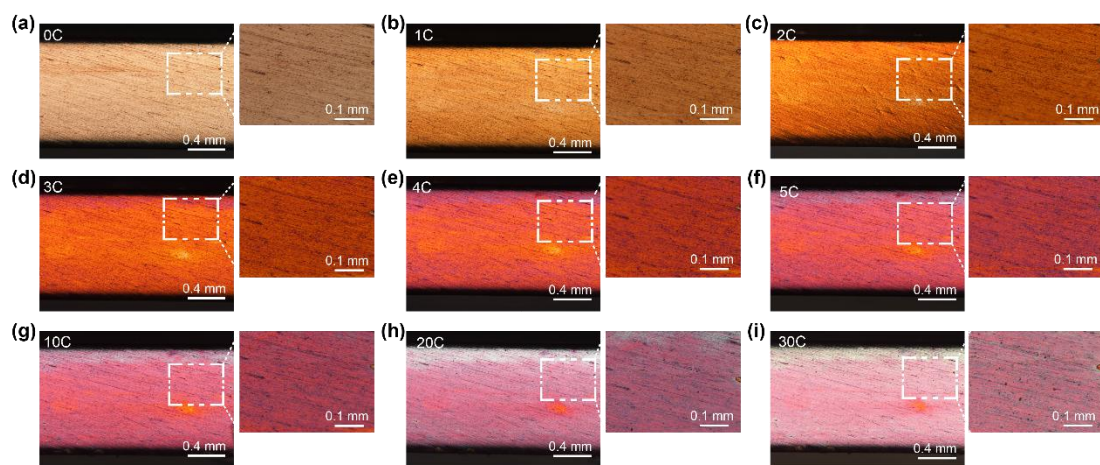


Figure S15 Cross- sectional optical photograph of the Gr/Cu(111) laminates after various thermal cycles at 200°C: (a) 0C, (b) 1C, (c) 2C, (d) 3C, (e) 4C, (f) 5C, (g) 10C, (h) 20C, (i) 30C.

Table S1 Archimedes density measurements of commercial Cu.

Sample number	M _{air} (g)	M _{liq} (g)	(M _{air} - M _{liq}) (g)	Density (g·cm-3)
1	7.9248	7.0408	0.8840	8.9378
2	8.1648	7.2529	0.9120	8.9260
3	7.5508	6.7078	0.8431	8.9294
4	7.5247	6.6831	0.8416	8.9143
5	7.9523	7.0640	0.8883	8.9253
6	8.1913	7.2765	0.9148	8.9302
7	7.5007	6.6631	0.8376	8.9279

Table S2 Archimedes density measurements of Gr/polycrystalline Cu foil laminates.

Sample number	M _{air} (g)	M _{liq} (g)	(M _{air} - M _{liq}) (g)	Density (g/cm3)
1	7.9920	7.0998	0.8922	8.9312
2	8.2736	7.3507	0.9229	8.9381
3	7.7032	6.8435	0.8597	8.9331
4	7.7568	6.8909	0.8659	8.9316
5	8.6441	7.6788	0.9653	8.9282
6	7.9129	7.0292	0.8837	8.9273
7	7.7122	6.8507	0.8615	8.9254

Table S3 Archimedes density measurements of single-crystal Cu(111) foil laminates

Sample number	M _{air} (g)	M _{liq} (g)	(M _{air} - M _{liq}) (g)	Density (g/cm3)
1	7.5958	6.7482	0.8476	8.9344
2	7.4909	6.6546	0.8363	8.9307
3	7.5840	6.7377	0.8463	8.9341
4	7.8836	7.0029	0.8808	8.9241
5	7.9457	7.0574	0.8883	8.9180
6	7.8980	7.0166	0.8814	8.9338
7	7.7372	6.8728	0.8644	8.9241

Table S4 Archimedes density measurements of Gr/Cu(111) foil laminates.

Sample number	M _{air} (g)	M _{liq} (g)	(M _{air} - M _{liq}) (g)	Density (g/cm3)
1	7.5508	6.7078	0.8431	8.9294
2	7.7566	6.8902	0.8664	8.9258
3	7.9248	7.0408	0.8840	8.9387
4	7.5994	6.7511	0.8483	8.9316
5	7.5935	6.7454	0.8480	8.9300
6	7.6655	6.8098	0.8557	8.9325
7	7.9744	7.0848	0.8896	8.9367

The relative density of each sample was determined using the Archimedes principle, i.e., by measuring the mass difference of the sample in air and in a liquid at 25 °C to calculate its density ($\rho=0.997$ g·cm-3). Calculate using the following formula:

$$\rho_{sample} = \frac{M_{air}}{V} = \frac{M_{air}}{(M_{air} - M_{liq})} \rho_{liq}$$

Where ρ_{sample} is sample density , M_{air} is the mass of the sample in air, and M_{liq} is the mean apparent mass when fully submerged in the reference liquid. Their difference $M_{air}- M_{liq}$ equals the mass of displaced liquid, which numerically gives the displaced volume. All masses are averaged from five repeated measurements for each specimen.