

Electronic Supplementary Information for Raman Spectroscopic Investigation of Polycrystalline Structures of CVD-Grown Graphene by Isotope Labeling

Shengnan Wang *, Satoru Suzuki, and Hiroki Hibino

NTT Basic Research Laboratories, NTT Corporation, Atsugi, Kanagawa 243-0198, Japan

* E-mail: wang.shengnan@lab.ntt.co.jp

Methods

Synthesis and isotopic labeling of graphene on copper

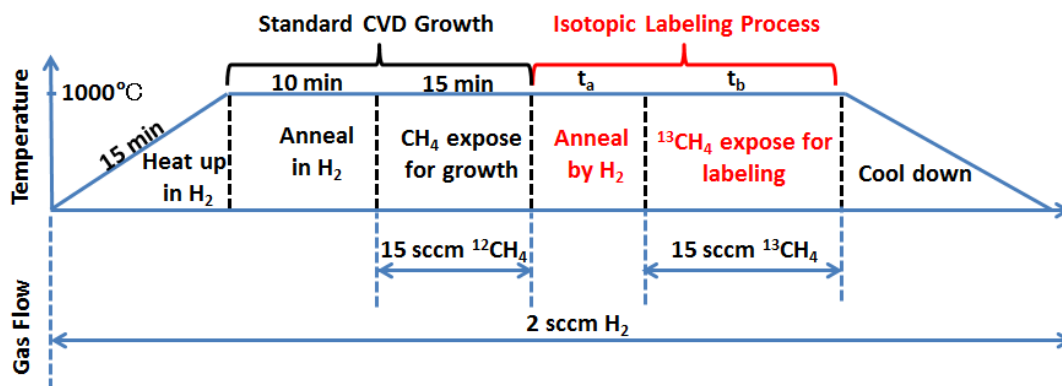


Fig. S1 Schematic process for LPCVD growth of graphene with labeled grain boundaries.

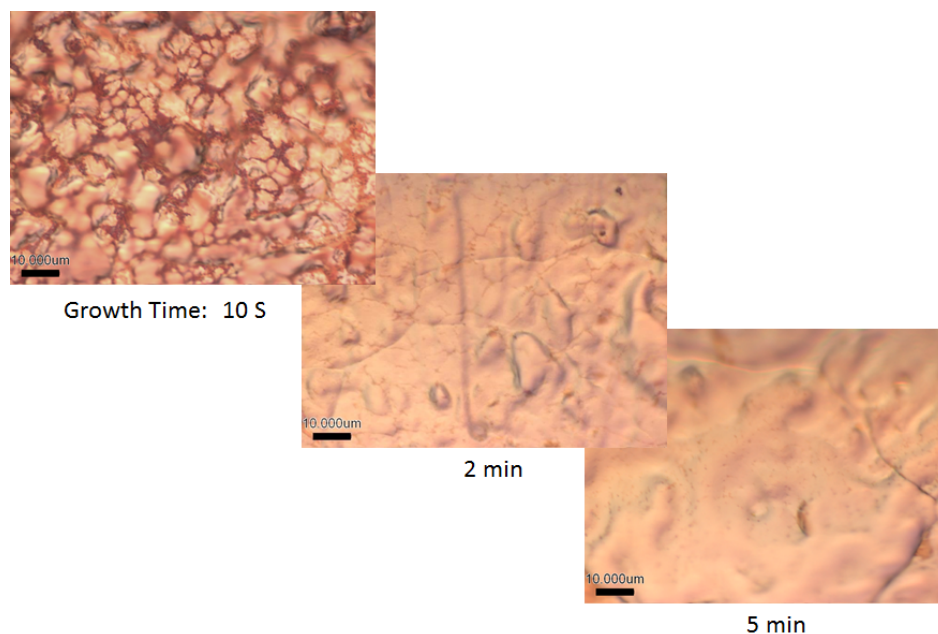


Fig. S2 Optical images of graphene on copper foil after heating at 160 °C for 6 min under ambient condition. The dark red trenches are the copper oxidized by air. The bright yellow areas are the pristine copper protected by the graphene on top. Characterization was done with Olympus BX51 microscopy.

As shown in Fig. S2, full-coverage growth of graphene on copper foil was achieved in only 5 min. The growth time in the isotope-labeling experiment was set to 15 min to make sure the single-layer graphene fully covered the copper catalyst before the annealing and labeling steps. Scanning electron microscopy (SEM) images (Fig. S3) show the different morphology of graphene samples treated with various CVD processes. An additional hydrogen annealing step following standard CVD growth induced the partial etching of graphene on the copper foil. Similar as the narrowing of graphene from edges by oxidation and hydrogenation, the graphene was gradually etched into separated micrometer-size grain islands from the initial etched sites, as extending the hydrogen exposure time.^{2, 3} But the graphene sample did not show significant structural breaks after the whole process of isotope labeling on copper catalyst.

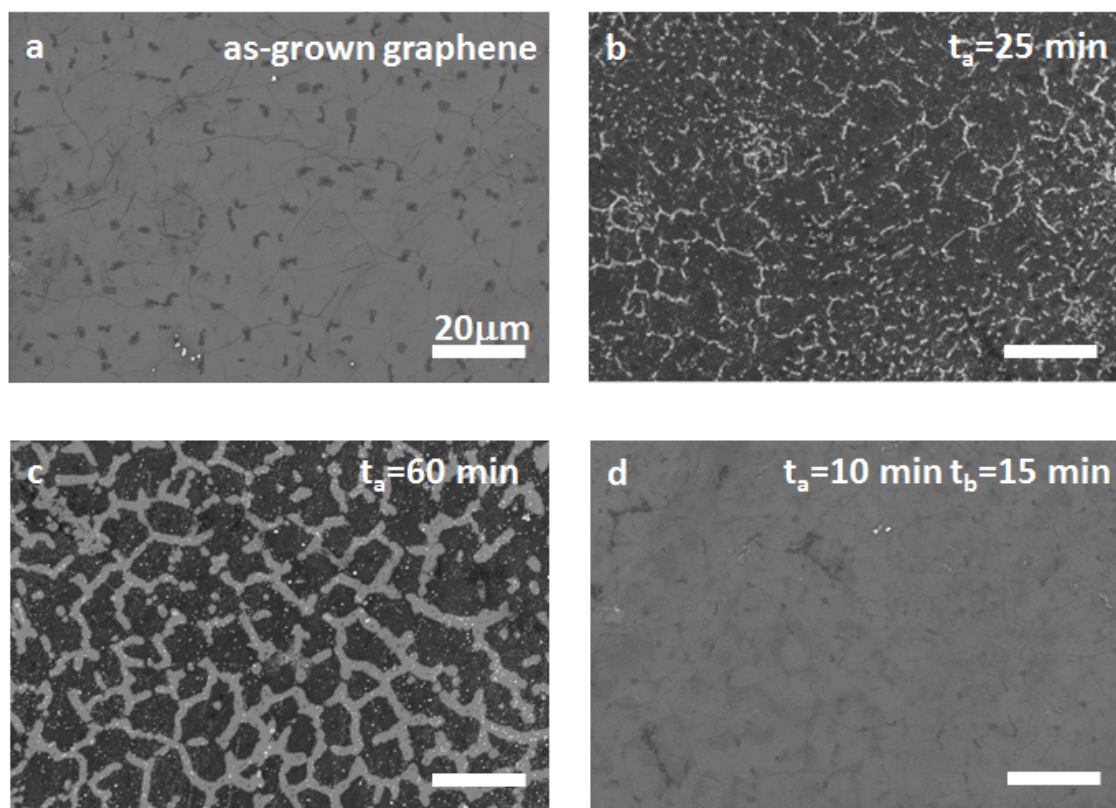


Fig. S3 SEM images of transferred graphene on SiO₂. (a) As-grown graphene with standard CVD process. The dark domains on single-layer graphene are related to several bilayer and multilayer islands. (b-c) Etched graphene induced by the hydrogen annealing step following the CVD growth process: (b) 25-min annealing, (c) 60-min annealing. (d) Labeled graphene treated with step-wise isotope-labeling CVD growth process: $t_a=10$ min, $t_b=15$ min. The standard CVD growth for all the graphene samples was 15 min. Characterization was done with Zeiss Ultra-55, and acceleration voltage was 5 kV.

Hydrogen etching of graphene on copper

The hydrogen etching of CVD graphene on copper foil is temperature-dependent.¹ To investigate the role of hydrogen in CVD growth process, we set the annealing temperature to 1000 °C in this experiment, the same as in the LPCVD growth condition. The LEEM/LEED analysis (Fig. S4) indicates that annealing treatment separates the whole graphene films into several single crystalline graphene domains with different lattice orientations, indicating the hydrogen etching preferentially starts from the grain boundaries of CVD graphene.

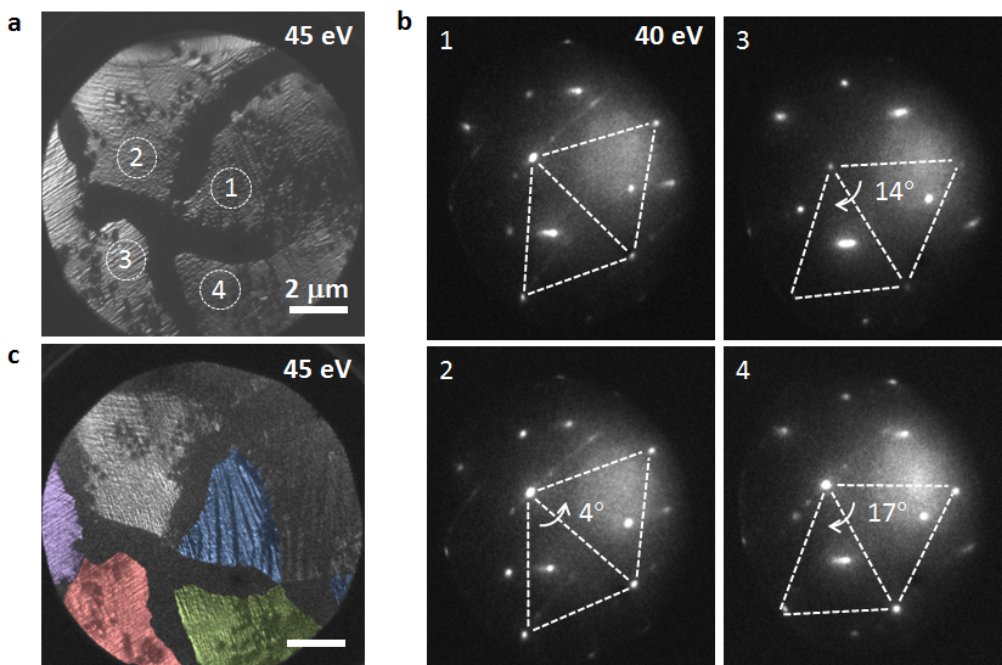


Fig. S4 (a) Bright-field LEEM image of hydrogen etched graphene on copper foil. $t_a = 60$ min. (b) LEED pattern collected from the selected area in (a). Because the copper surface has a faceted morphology, the LEED patterns presents some sets of diffraction spots from graphene grown on the facets. (c) Color-coded dark-field LEEM image of the sample in (a).

Dark-field LEEM images of transferred graphene on epitaxial graphene/SiC

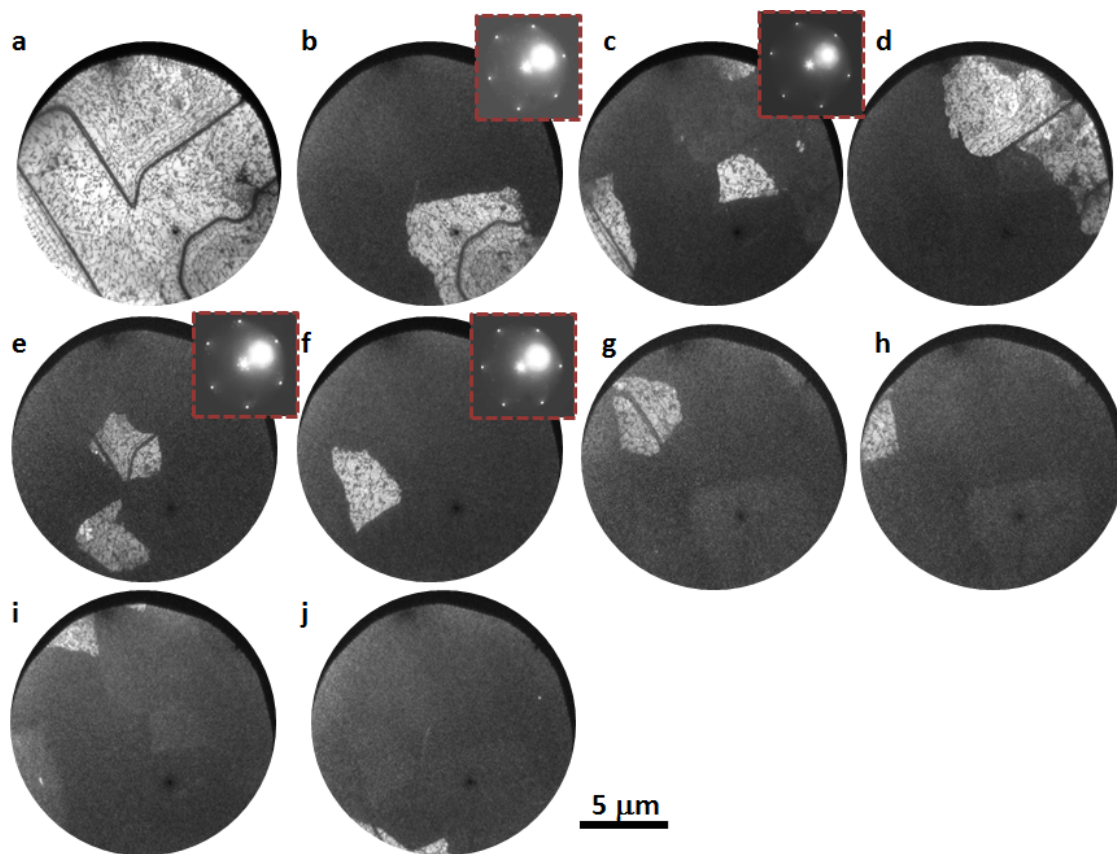


Fig. S5 Bright- (a) and dark-field (b-j) LEEM images and typical LEED patterns of graphene transferred onto epitaxial graphene/SiC. The set of raw dark-field image for nine different lattice orientations, used to create the final composite color-coded image in Figure 1d in the manuscript. The electron beam energy was 44.5eV for images and 40 eV for diffraction patterns.

Raman spectrum of isotope-labeled CVD graphene transferred onto epitaxial graphene grown on pre-patterned SiC

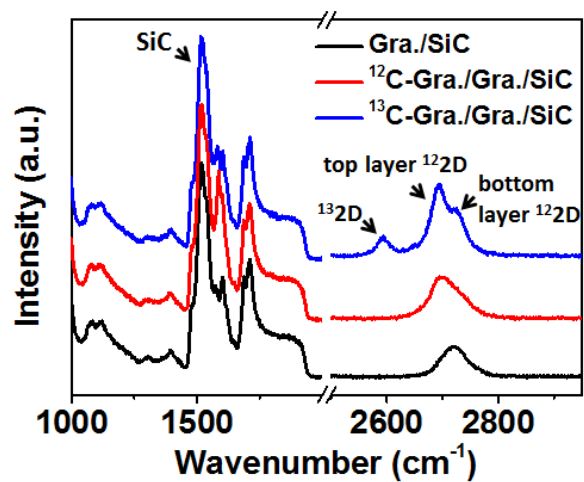


Fig. S6 Raman spectrum of labeled graphene on epitaxial graphene/ SiC. The ¹³D band (~2593 cm⁻¹) was used to achieve grain-boundary mapping of transferred labeled graphene. The SiC feature peak (~1518 cm⁻¹) was used to achieve the mark-pattern mapping for the sample location.

Raman maps of intrinsic CVD graphene

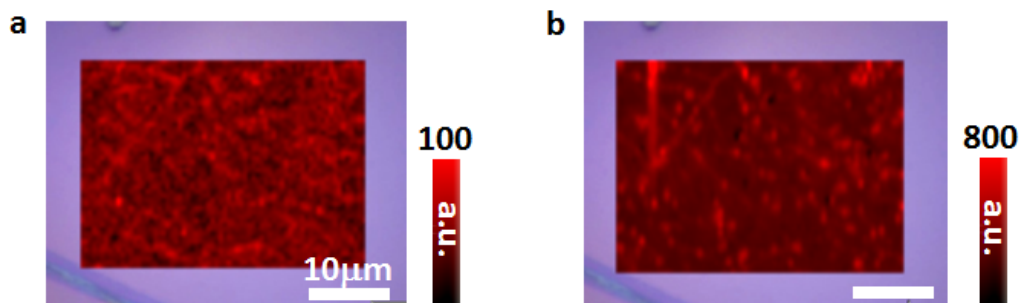


Fig. S7 Raman intensity maps of as-transferred CVD grown-graphene on SiO₂/Si: (a) D band; (b) G band. The network-like patterns are not found in the G and D band intensity maps, indicating the grain boundaries are invisible in intrinsic CVD graphene before the labeling treatment.

Raman peak position maps of labeled CVD graphene

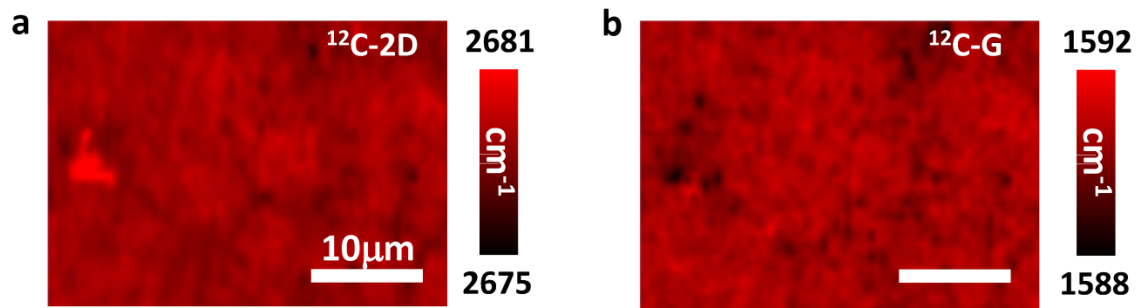


Fig. S8 Raman ^{12}C -band position mapping results of labeled graphene: (a) 2D band; (b) G band.

Time-dependent ^{12}C - ^{13}C atom exchange of graphene by isotope labeling process

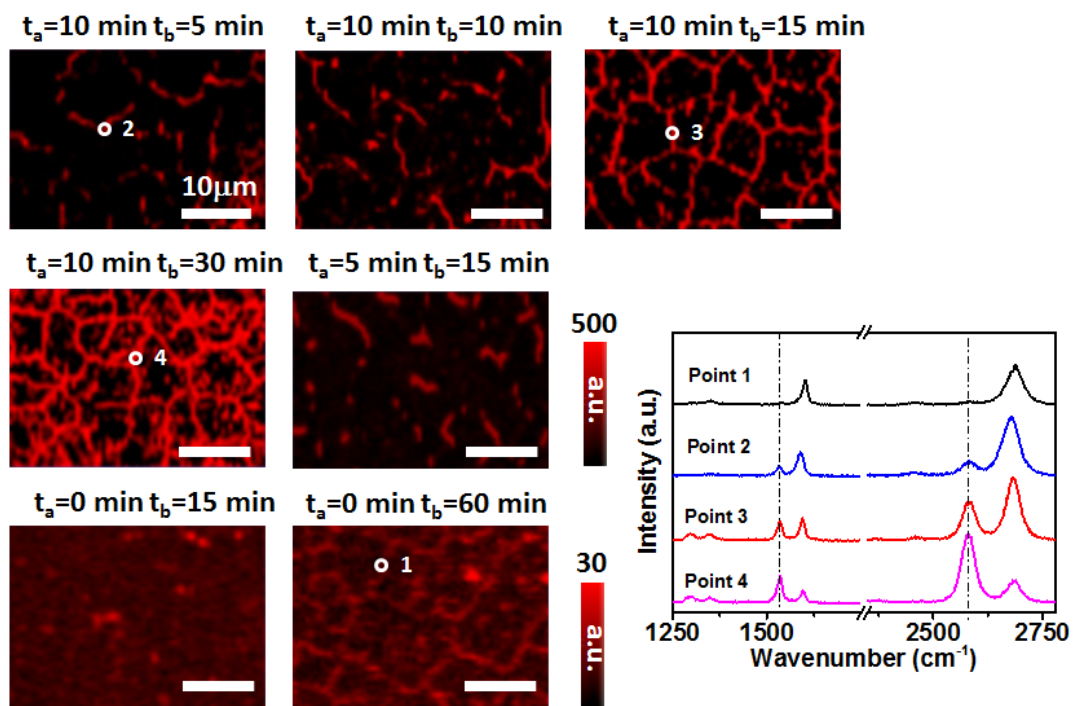


Fig. S9 Raman ^{13}C -G intensity mapping results for labeled graphene with various hydrogen pre-annealing times (t_a) and isotopic methane gas exposing times (t_b). The typical Raman spectra are collected from the graphene samples at the points shown in the maps. The dash-dot lines are employed to trace the evolution of ^{13}C -2D and ^{13}C -G band.

Raman data of isotope-labeled graphene with wrinkle structure

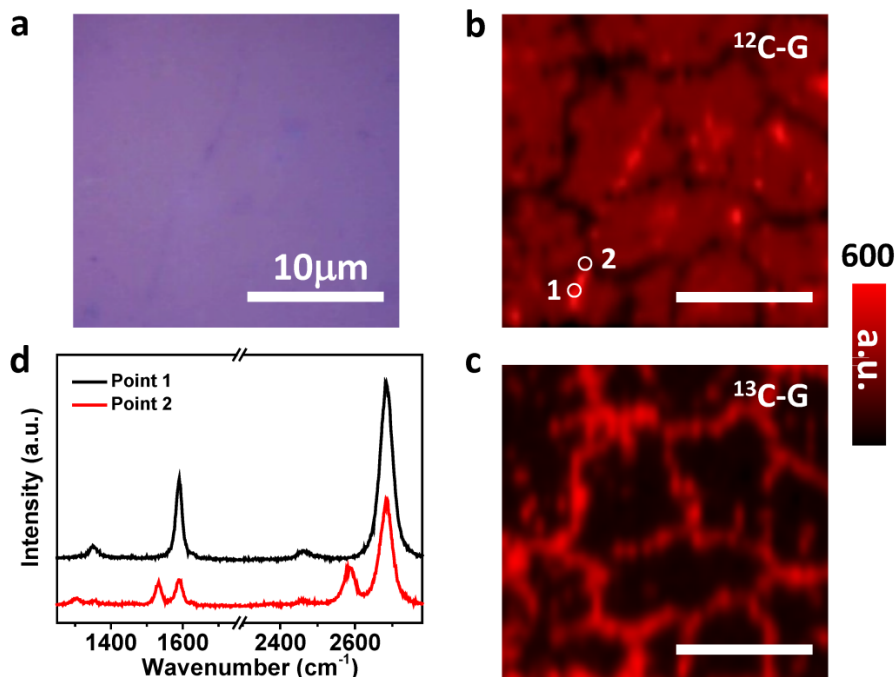


Fig. S10 (a) Optical image of labeled-graphene transferred on SiO₂. (b-c) ¹²C- and ¹³C-G band intensity maps of labeled graphene shown in (a), respectively. (d) Raman spectra of labeled graphene with and without wrinkle structure. The point 1 and 2 are corresponding to the circle sites in (b). It is clear to distinguish the line-shape structure of wrinkle in the optical image and ¹²C-G band intensity map. In the ¹³C-G band intensity map, the cross sites between wrinkles and grain boundaries exhibit ¹³C-related signal as the boundaries area without wrinkles. The Raman spectra also present the ¹³C-related characteristic in the grain boundary site with wrinkles.

References:

1. Y. Zhang, Z. Li, P. Kim, L. Zhang, and C. Zhou, *ACS Nano* 2011, **6**, 126.
2. X. R. Wang, and H. J. Dai, *Nat. Chem.*, 2010, **2**, 661.
3. L. Xie, L. Jiao, and H. Dai, *J. Am. Chem. Soc.*, 2010, **132**, 14751.