

**Supporting information for**

**How Graphene Crosses a Grain Boundary on the Catalyst Surface  
during Chemical Vapour Deposition Growth**

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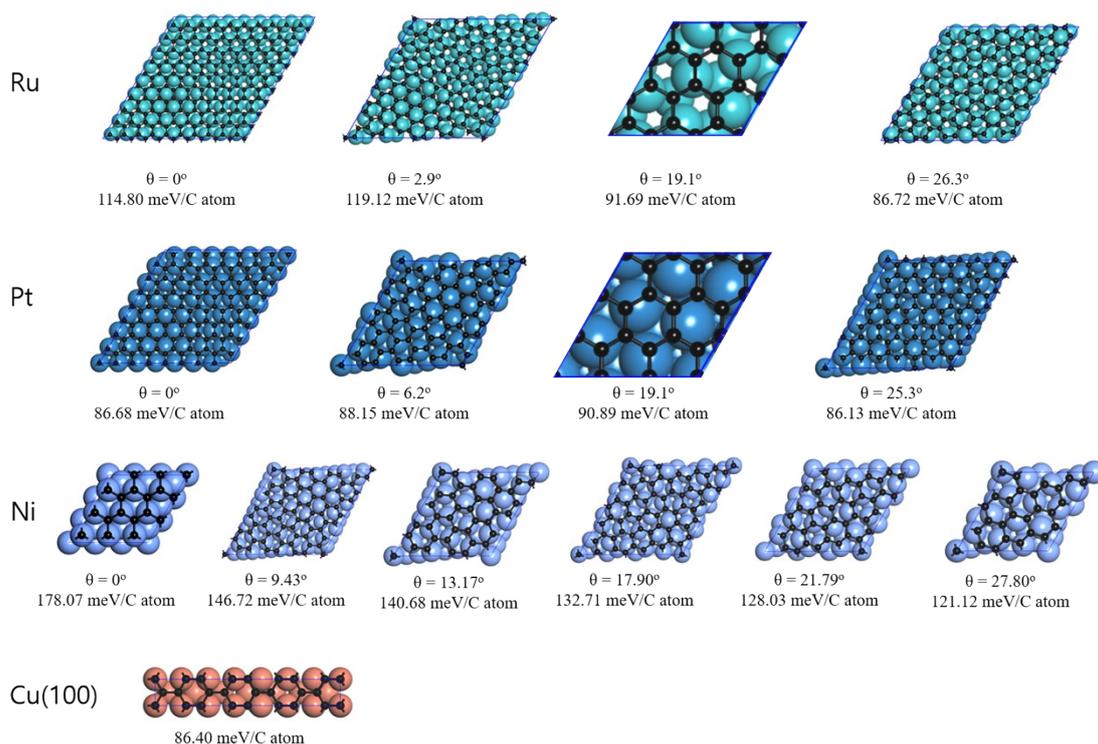
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**Methods**

**DFT calculations.** The DFT-D2 method which can describe the van der Waals interaction as implemented in the Vienna *ab initio* simulation Package (VASP) is used to calculate the binding energy of graphene adsorbed on the Cu substrate and the formation energy of a graphene domain growing across the substrate GB<sup>1-3</sup>. The Perdew-Burke-Ernzerhof generalized gradient approximation (GGA) is adopted for the exchange-correlation functional<sup>4</sup>. The interaction between valence electrons and ion cores is described by using the projected augmented wave (PAW) method<sup>5</sup>. The periodic structures for graphene adsorbed on the Cu(1 1 1) substrate are constructed through a previously reported method, in which the unit cell is described by a pair of

coprime indices,  $(m, n)$ , indicating its relation to the primitive hexagonal unit cell of graphene<sup>6</sup>. For graphene adsorbed on the Cu(1 0 0) substrate, the size of the orthogonal unit cell is  $2.468 \times 17.112 \times 20 \text{ \AA}^3$ . The substrate is modeled by three atomic layers. To obtain the Cu substrate with a twin GB, a Cu(1 1 1) slab of three atomic layers is first constructed, of which the in-plane unit cell vectors are  $(1, 4)$  and  $(-3, 2)$ , respectively. Then this unit cell is connected to its mirror to get the twin GB. All the substrates are separated by at least  $12 \text{ \AA}$  to avoid periodic imaging interaction. The Cu lattice constant is compressed by less than 4% to be commensurate with that of graphene. The k-point mesh is sampled by a separation of  $0.03 \text{ \AA}^{-1}$ . All the structures are fully relaxed until the force on each atom is less than  $0.01 \text{ eV/\AA}$ , with an energy convergence of  $10^{-4} \text{ eV}$ .

For the calculation of binding energy of graphene on Pt and Ru substrates, DFT-D3(BJ) method is used<sup>7</sup>. For each substrate, we choose four different rotation angles between graphene and the substrate (Figure S1). All these structures are chosen to ensure the mismatch between graphene and substrate is within 3%. For the calculation of binding energy of graphene on Ni substrate, DFT-D2 method is employed. The lattice constant of Ni is changed within 1% to keep commensurate with that of graphene. The binding energies of epitaxial and non-epitaxial graphene-substrate structures in Table 1 in the main text are chosen as the highest and lowest binding energies among the four structures.



**Figure S1** Structures and binding energies of graphene on Ru(111), Pt(111) and Ni(111) substrates with different misorientation angles and on Cu(100) substrate.

**MD simulations.** The simulation model is the same as that used in the DFT calculation. A graphene nanoribbon is first placed on the substrate as a seed. The simulation is performed at 1200 K with a time step of 0.5 fs. A C atom is added to the uncovered substrate areas near the graphene edge about every 5 ps. The Sutton-Chen potential is used to describe the Cu-Cu interaction<sup>8</sup>. The C-C interaction is treated by the second generation Reactive Empirical Bond Order (REBO) potential<sup>9</sup>. We employ our previously developed Metal-Carbon potential for the Cu-C interaction, which has been proved to successfully describe the CVD growth process of graphene on transition metal substrates<sup>10</sup>. During the MD simulation process, a basin-hopping strategy is employed to find the local energy minima, instead of overcoming the energy barriers between local energy minima, which was successfully used in our previous studies<sup>10</sup>. The basin-hopping strategy is performed every after the addition

of 4 C atoms.

### Derivation of equation (1) in main text

The critical length,  $\Delta L_C$ , is defined at which the total (formation) energies of these two systems of Path 1 and Path 2 become equal. Therefore, we can easily write down the following equation:

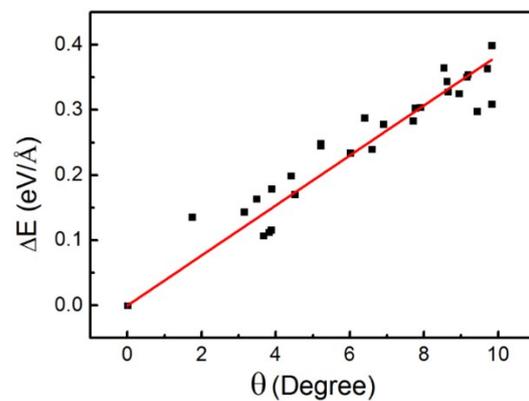
$$\Delta\varepsilon \times \Delta L_C \times w/S_C = \Delta E \times w \quad (\text{S1})$$

where  $w$  is the width of the system,  $\Delta E$  is the formation energy of graphene GB, and  $\Delta\varepsilon$  is the binding energy difference between epitaxial graphene and non-epitaxial graphene on the substrate per carbon atom.

### Linear fitting of the graphene GB at small misorientation angle

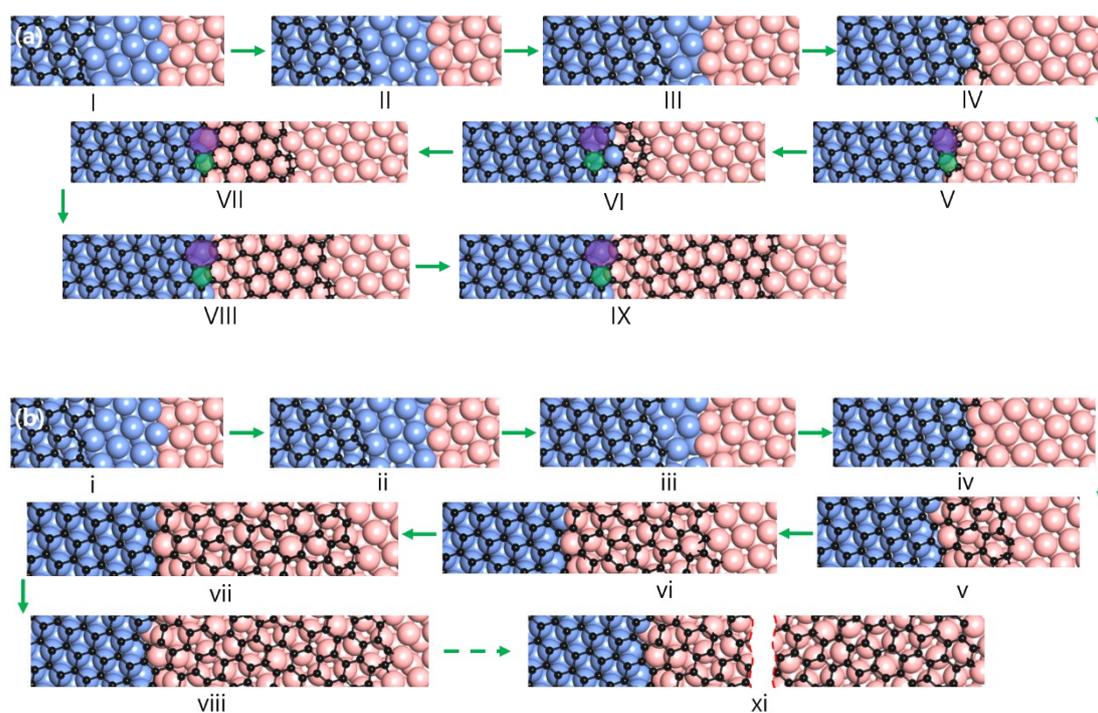
Our previous studies have shown that the formation energy of graphene GB increases linearly with its misorientation angle when the misorientation angle is small <sup>11</sup>, as shown in Figure S2. The linear fitting is

$$\Delta E = 0.038\theta \text{ eV/\AA} \quad (\text{S2})$$



**Figure S2** Formation energy of graphene GB as a function of its misorientation angle less than  $10^\circ$  and its linear fitting.

### Growth of graphene across the GB of Ni substrate



**Figure S3.** Structures for the DFT calculation on the epitaxial growth of graphene across the Ni substrate GB. (a) Growth along **Path 1**—forming a GB in graphene at the GB of substrate, (b) Growth along **Path 2**—single crystalline graphene crossing the GB of the substrate. The twin Ni grains are denoted by blue and orange. Carbon atoms are denoted in black. The models are similar to those for graphene on Cu, except that the Cu substrates are replaced by Ni. The carbon pentagons and heptagons of the graphene GB are shadowed in purple and green, respectively. Due to the large size of the unit cell of structure (xi), its middle part is replaced by a white strip.

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