Surface diffusion of Cu mediated by graphene coverage

Haitao Zhang[1], Qi Zhang[1], Baixue Bian[1*], Yue Liu[1*], Tongxiang Fan[1*], Mingyu Gong[1,2]

[1]State Key Lab of Metal Matrix Composites, School of Materials Science and Engineering, Shanghai Jiao Tong University, Shanghai 200240, China

[2]Institute of Medical Robotics, Shanghai Jiao Tong University, Shanghai 200240, China

1. Comparison of step configurations and formation energies of Gr/Cu interfaces from molecular dynamics and density functional theory

We validated the LJ potential against DFT for both {100}- and {111}-type steps under Gr coverage. As presented in Figs. S1-S3 and Table S1, the step configurations obtained from MD relaxation closely resemble those from DFT, and the step formation energies show reasonable agreement across different moiré registries (top-fcc and hcp-fcc). These comparisons confirm that the LJ potential adequately describes the geometric and energetic features of Gr-covered Cu steps.

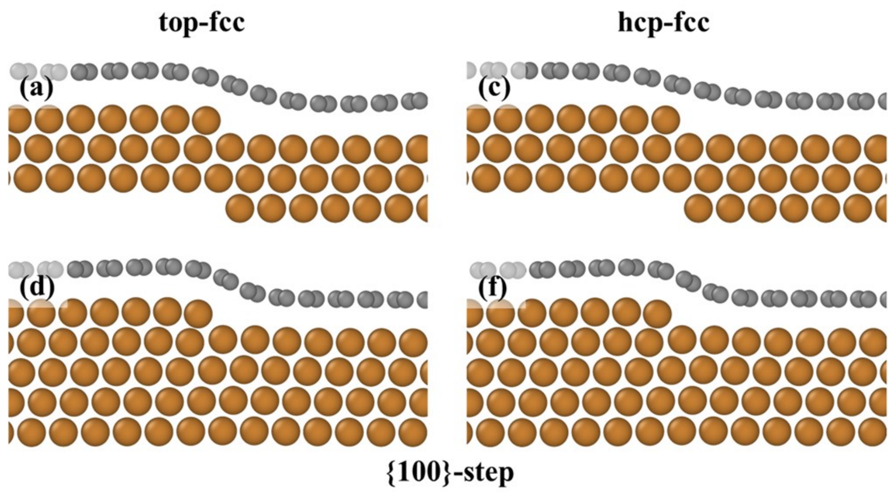

FIG. S1 Side view of the models of Gr on Cu(111) surface {100}-step. (a) and (b) top-fcc and hcp-fcc step configuration obtained by DFT. (c) and (d) top-fcc and hcp-fcc step configuration obtained by MD.

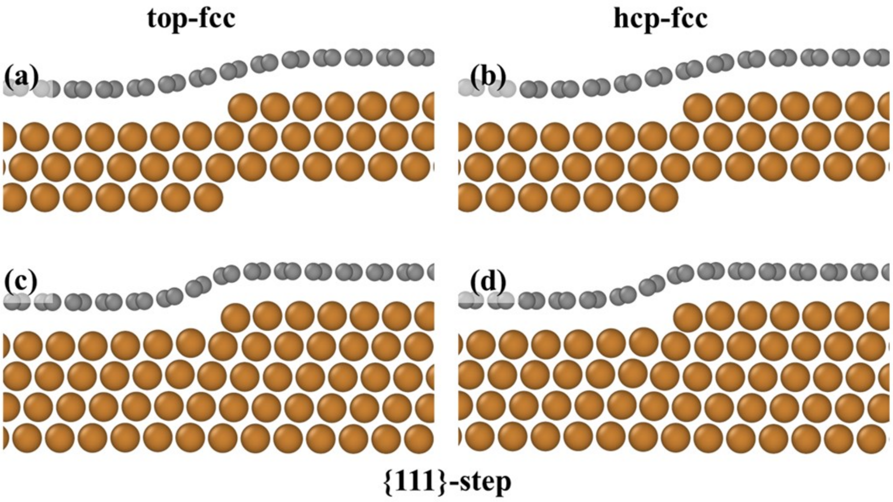

FIG. S2 Side view of the models of Gr on Cu(111) surface {111}-step. (a) and (b) top-fcc and hcp-fcc step configuration obtained by DFT. (c) and (d) top-fcc and hcp-fcc step configuration obtained by MD.

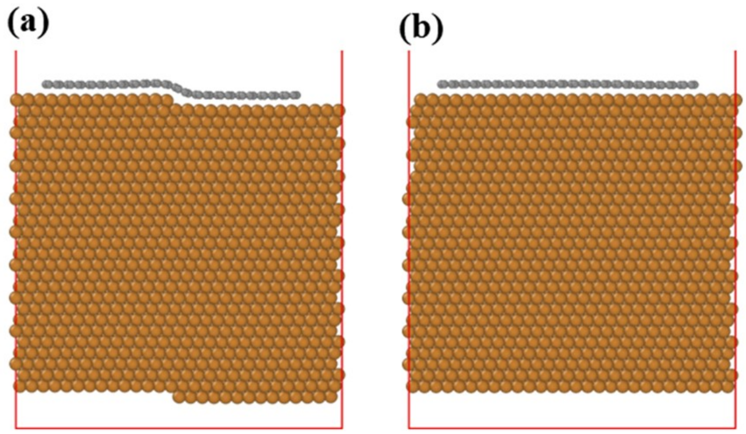

FIG. S3 Models for Gr/Cu step formation energies calculation. (a) Stepped Gr/Cu model. (b) Flat Gr/Cu model. Step formation energy is defined as $E^{GrCu}_{\{100\}step} = E^{GrCu}_{step} - E^{GrCu}_{flat} - E^{Cu}_{\{100\}step} - 2E^{Cu}_{\{111\}step}$ or $E^{GrCu}_{\{111\}step} = E^{GrCu}_{step} - E^{GrCu}_{flat} - E^{Cu}_{\{111\}step} - 2E^{Cu}_{\{100\}step}$. E^{GrCu}_{step} and E^{GrCu}_{flat} represents the total energy of the stepped and flat model. $E^{Cu}_{\{111\}step}$ and $E^{Cu}_{\{100\}step}$ represents the {111} and {100} step formation energies on Cu surface. Similar methods are also used in DFT calculations with smaller models.

TABLE. S1 Calculated Gr/Cu step formation energies obtained by MD and DFT.

Step	Structure	Step Formation Energy	
		MD	DFT
{100}-step	top-fcc	0.14 eV/Å	0.13 eV/Å
	hcp-fcc	0.15 eV/Å	0.20 eV/Å
{111}-step	top-fcc	0.13 eV/Å	0.10 eV/Å
	hcp-fcc	0.16 eV/Å	0.10 eV/Å

2.Effects of Gr/Cu moiré superstructures on adatom diffusion barriers

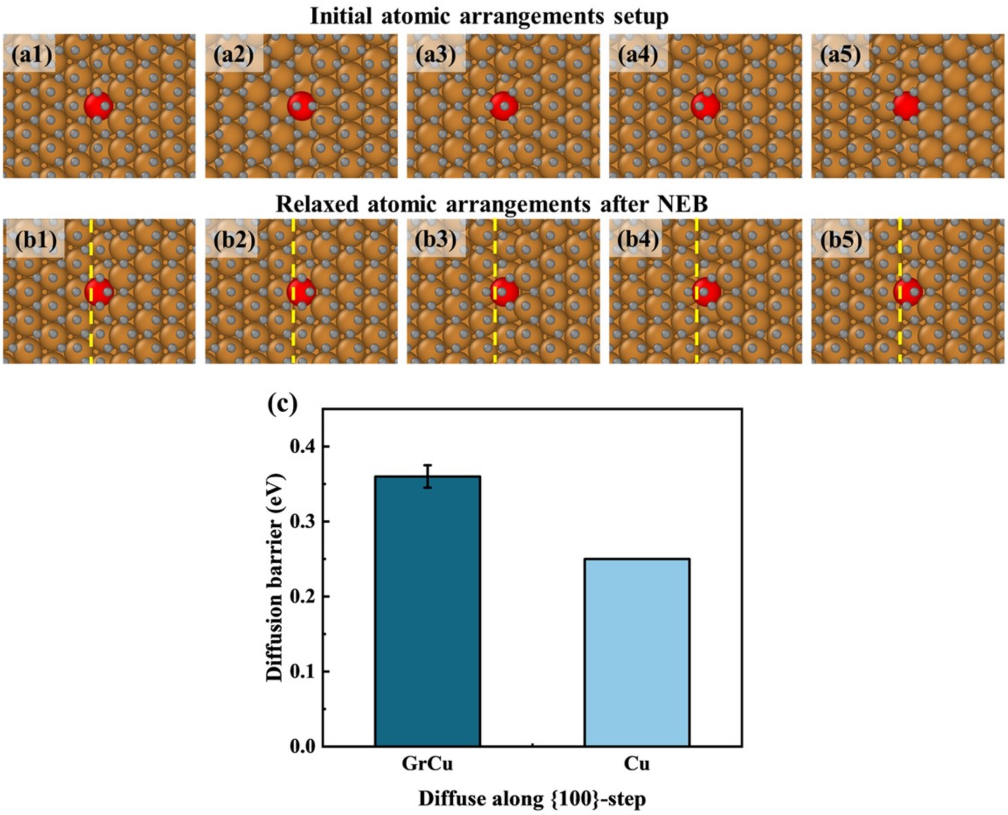

FIG. S4 Effects of Gr/Cu moiré superstructures on barriers of diffusing along {100}-step. (a1)-(a5) Initial atomic arrangements setups with uniform intervals within one superlattice period of Gr/Cu at the direction vertical to step edges. (b1)-(b5) Relaxed atomic arrangements after calculating diffusion barriers using NEB. The yellow dashed line marks the position of the center of the Gr hexagonal ring parallel to step edges, indicating the same local atomic arrangements at the direction vertical to step edges. (c) Comparison of diffusion barriers between Gr/Cu and Cu. The error bars of barriers stem from different local atomic arrangements parallel to step edges. Adatoms in (b1), (b2) and (b5) locate at the center of Gr hexagonal ring above the adatom while (b3) and (b4) at the junction of two adjacent hexagonal rings.

3.Calculation of adatom diffusion kinetic barrier on Gr/Cu terrace

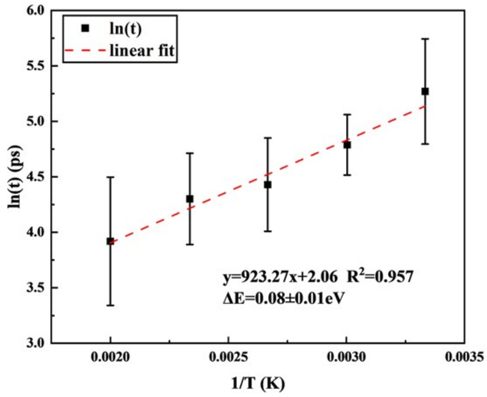

FIG. S5 Fitting of Arrhenius-plot to determine the barrier of diffusing on Gr/Cu terrace through exchange diffusion mechanisms. The time required for an interstitial atom on Gr/Cu terrace to diffuse the same distance is *t*, and it follows: $\frac{1}{t}=\frac{1}{t_0}\exp\left(-\frac{\Delta E}{kT}\right)$, where the t_0 is the prefactor for the diffusion time, ΔE is the barrier of an interstitial atom diffusing on Gr/Cu surface by exchange, k and T is the Boltzmann constant and the temperature, respectively. In the calculation of adatom diffusion kinetic barrier on Gr/Cu terrace via Arrhenius-plot fitting, we employed sufficiently extended simulation durations and statistically representative sampling of diffusion sites. This approach ensures that the derived barrier values reflect the average behavior across the entire terrace, and the error bars inherently incorporate the influence of moiré superstructures on the diffusion process. The error bars indicate that the variation in barriers induced by moiré superstructures is negligible when compared with barrier differences between bare Cu and Gr/Cu, similar to the case of adatom diffusion near steps on Gr/Cu.

4. Calculation of step kink formation energies

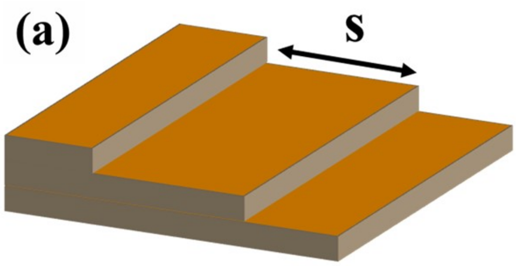

FIG. S6 Dual-step models for calculating step kink formation energies. A row of r atoms is transferred from the second to the first step, leading (a) the perfect step model to (b) the kinked step model. A step kink formation is given by: $4E_{kink} = E_{kinked} - E_{perfect}$. E_{kinked} and $E_{perfect}$ are the system energy of (b) the kinked step model and (a) the perfect step model, respectively. Step spacing s rows and kink spacing r atoms are big enough that step-step interaction and kink-kink interaction can be neglected.

5. Molecular dynamics simulations of step dissociation

Molecular dynamics (MD) simulations were performed using LAMMPS with the empirical potentials described in the Methods. A canonical ensemble (NVT) was used with a time step of 1.0 fs. To ensure statistical robustness, simulations were performed using multiple independent random seeds for initial velocity distribution. The system was first energy-minimized and then equilibrated at 300 K for 3 ns to establish a stable baseline configuration (Fig. S7a-b). Subsequently, the temperature was raised to 750 K to activate the dissociation process.

As shown in Fig. S7c-d, the double-atomic steps began to dissociate into mono-atomic steps via inward exchange diffusion at the step edges within 1.20 ns at 750 K. The dissociation was essentially complete by 4.80 ns (Fig. 74e), and the newly formed mono-atomic steps remained stable for the subsequent 5 ns of simulation (Fig. S7f). These results, now reinforced by longer simulation times and multiple independent runs, indicate that step dissociation is a thermally activated process with a reduced barrier under Gr coverage, observable on a nanosecond timescale at 750 K.

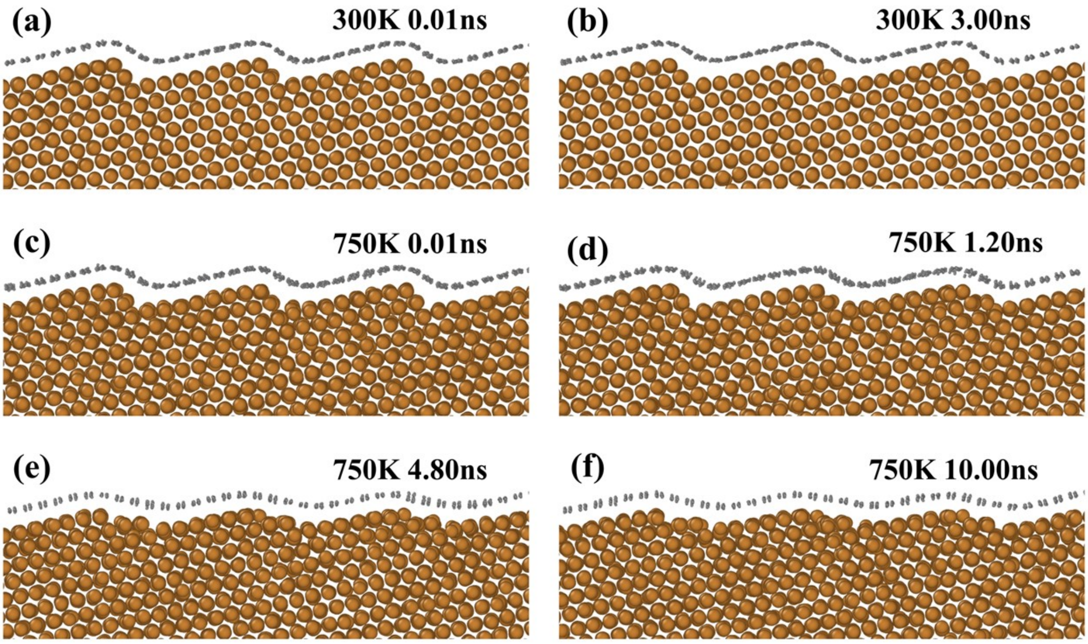

FIG. S7 (a)-(f) Snapshots of Gr/Cu step structures from MD simulations.