Electronic Supplementary Information for

Electron Compensation Mechanism for Polymorphism of Boron Monolayers

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In order to simulate the boron monolayers growth on the metal substrates, we modeled the substrate using the five-layer slab with the bottom two layers fixed, considering a few possible configurations of boron monolayers on the substrates where the absolute value of lattice mismatch δ is under 2.5% (Table S1). To evaluate the interaction of various monolayer structures on metal substrates, the average adsorption energy(E_{ad}) is expressed as follows, $E_{ad} = (E_{tot} - E_{sub} - E_{sheet})/n$, where the E_{tot}, E_{sub} and E_{sheet} represent the total energy of the B/metal systems, the metal substrates and the B sheets respectively, and n is the number of atoms in the B sheets. In order to include the overall stability of different B monolayers deposited on Ag(111) substrate, we define the average formation energy as

$$E_{form} = \frac{1}{n}(E_{tot} - E_{sub} - n \times E_B),$$

where the E_{tot} , E_{sub} and n are the same as the defination in E_{ad}, E_B is the energy per atom in the boron solid of α phase.

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To reduce the influence of mismatch on the adsorption energy of boron monolayers on metal substrates, we have considered many possible configurations. In order to reduce the lattice mismatch, we have built boron monolayers using different supercell sizes to fit various metal substrates. The small lattice mismatches (Δa and Δb along two crystallographic orientations) between boron sheets and substrates are defined as: $\Delta a = \frac{|a_{sheet} - a_{sub}|}{a_{sub}}$, $\Delta b = \frac{|b_{sheet} - b_{sub}|}{b_{sub}}$, where a_{sheet}, b_{sheet}, a_{sub} and b_{sub} are the supercell parameters of the boron sheet and the metal substrates, respectively.

Table S1. The detailed structural information of various boron monolayers on the metal substrates.

Configurations	a_{sheet} (Å)	b_{sheet}(Å)	a_{sub}(Å)	b_{sub}(Å)	Δ_a (%)	Δ_b (%)
β_{arm}@Ag(111)	5.07	14.63	5.10	14.73	0.59	0.68
α_1@Ag(111)	20.28	5.85	20.41	5.89	0.64	0.68
β@Ag(111)	35.46	2.93	35.72	2.95	0.73	0.68
β_1@Ag(111)	20.28	5.85	20.41	5.89	0.64	0.68
$\eta_{1/8}$@Ag(111)	5.07	11.71	5.10	11.79	0.59	0.68
$\eta_{4/28}$@Ag(111)	35.49	5.85	35.72	5.89	0.64	0.68
$\eta_{2/15}$@Ag(111)	5.07	14.63	5.10	14.73	0.59	0.68
$\eta_{1/6}$@Ag(111)	20.28	8.76	20.41	8.84	0.64	0.90
β_{12}@Ag(111)	5.07	2.93	5.10	2.95	0.59	0.68
α@Ag(111)	20.28	20.28	20.62	20.62	1.65	1.65
χ_3@Ag(111)	25.17	5.84	25.52	5.89	1.37	0.85
$\eta_{4/33}$@Ag(111)	5.07	32.20	5.10	32.41	0.59	0.65

α@Au(111)	20.28	20.28	20.57	20.57	1.41	1.41
β_{arm}@Au(111)	5.07	14.63	5.09	14.69	0.39	0.41
β_{12}@Au(111)	5.07	2.93	5.09	2.94	0.39	0.34
χ_3@Au(111)	25.17	5.84	25.44	5.88	1.06	0.68
α@Cu(111)	5.07	5.07	5.16	5.16	1.74	1.74
β_{arm}@Cu(111)	5.07	30.36	5.16	31.10	1.74	2.38
β_{12}@Cu(111)	5.07	8.79	5.16	8.94	1.74	1.68
χ_3@Cu(111)	13.39	13.39	13.66	13.66	1.98	1.98

Table S2. The hexagonal vacancy concentration η and the average formation energy E_{form} calculated by different functionals for the corresponding boron monolayers.

Boron Sheets	η	PBE E_{form}(eV/atom)	HSE06 E_{form}(eV/atom)	PBE0 E_{form}(eV/atom)
$(\eta_{4/28})$[36]	1/7	-5.977	-6.957	-7.294
$(\eta_{4/33})$[36,37]	4/33	-5.982	-6.950	-7.289
$(\eta_{1/8})$[10]	1/8	-5.981	-6.955	-7.293
$(\eta_{2/15})$[10]	2/15	-5.978	-6.950	-7.287
(α)[8]	1/9	-5.978	-6.947	-7.286
(β)[8]	1/7	-5.972	-6.953	-7.293
(α_1)[12]	1/8	-5.975	-6.947	-7.284
(β_1)[12]	1/8	-5.960	-6.931	-7.268
β_{arm}	2/15	-5.973	-6.950	-7.286

Table S3. The hexagonal vacancy concentration η, the average formation energy E_{form} and the AEC parameter (λ) of the corresponding boron monolayers.

Boron Sheets	η	PBE-E_{form}(eV/atom)	λ (e/atom)
Triangular Sheet	0	-5.651	-0.333
$\eta_{1/12}$	1/12	-5.912	-0.091

$\eta_{1/10}$	1/10	-5.948	-0.037
α	1/9	-5.978	0
$\eta_{4/33}$	4/33	-5.982	0.035
$\eta_{1/8}$	1/8	-5.981	0.048
α_1	1/8	-5.975	0
β_1	1/8	-5.960	0
$\eta_{2/15}$	2/15	-5.978	0.077
β_{arm}	2/15	-5.973	0.077
$\eta_{4/28}$	1/7	-5.977	0
β	1/7	-5.971	0
$\eta_{1/6}$	1/6	-5.970	0.1
β_{12}	1/6	-5.925	0.2
χ_3	1/5	-5.939	0.5

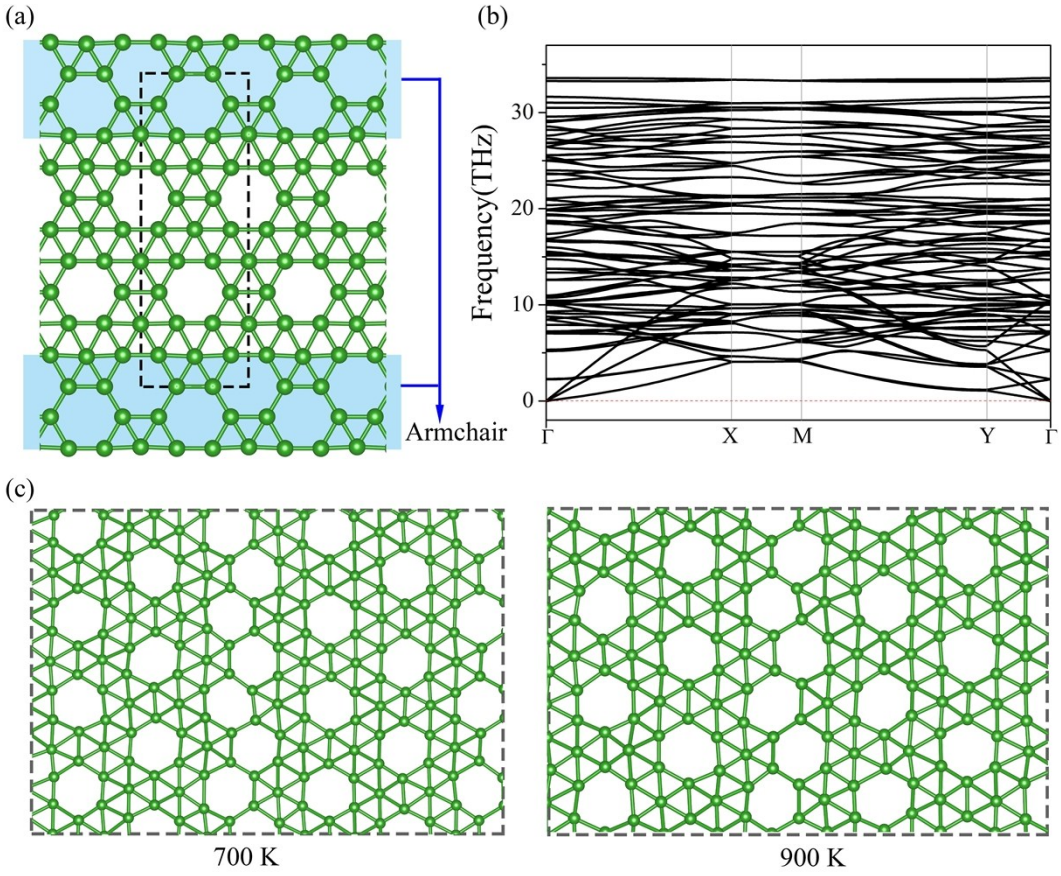

Fig. S1. (a) The atomic structure of the β_{arm}, and the black dash lines represent the unit cell of the boron monolayer. (b) The phonon dispersions along the high-symmetry line of β_{arm} monolayer. (c) The AIMD snapshots at the temperature of 700/900 K (10 ps) for β_{arm} monolayer. All the data in this figure are calculated by PBE functional.

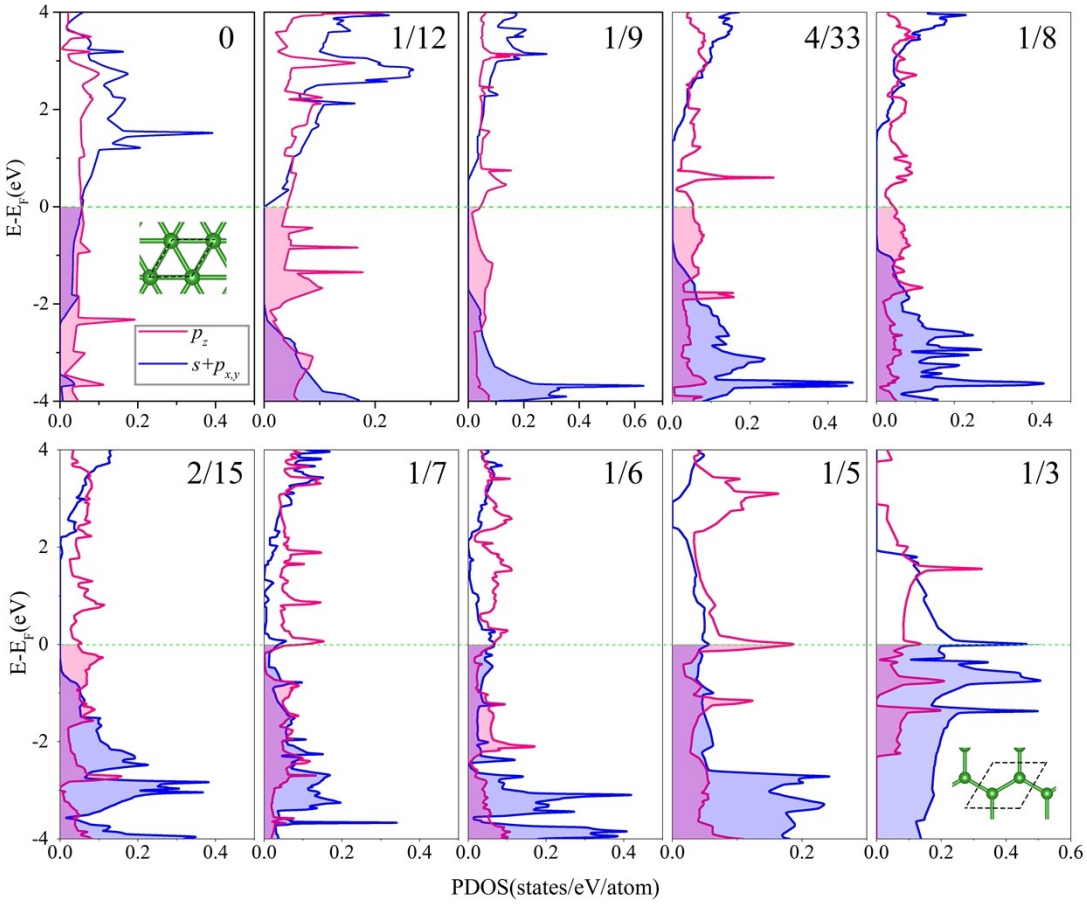

Fig. S2. Projceted density of states (PDOS) for a few most stable boron monolayers at given η, the pink lines represent the out-of-plane p_z orbitals, and the blue lines represent the in-plane $s+p_{x,y}$ orbitals. The density plots in this figure are calculated by PBE functional.

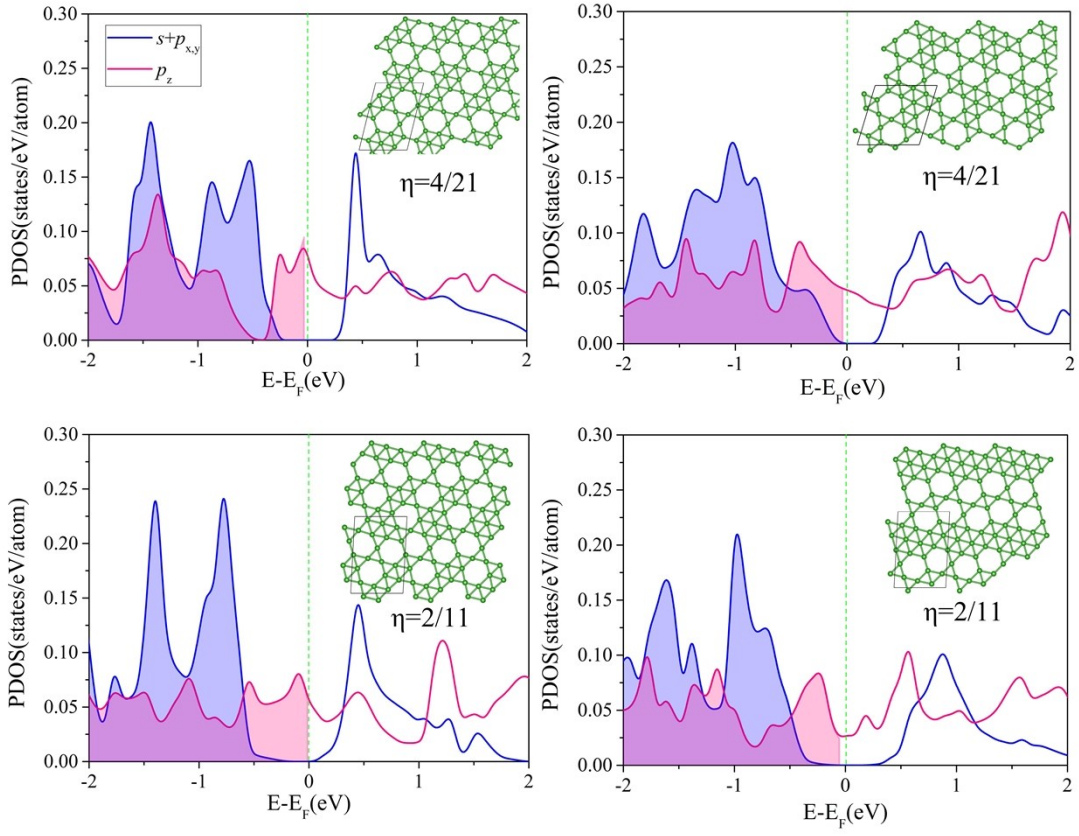

Fig. S3. Projceted density of states (PDOS) for a few unstable boron monolayers, the pink lines represent the out-of-plane p_z orbitals, the blue lines represent the in-plane s+$p_{x,y}$ orbitals, and the atomic structures of the boron monolayers are shown in the insets. The density plots in this figure are calculated by PBE functional.

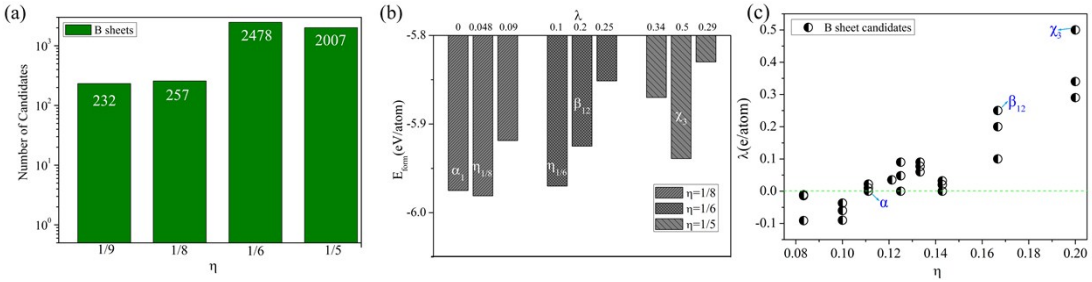

Fig. S4. (a) The number of inequivalent boron monolayer candidates at fixed vacancy concentration η. (b) The formation energies E_{form} as a function of AEC parameter λ for several boron monolayers at fixed η. (c) The relationship of AEC parameter λ and vacancy concentration η. The formation energies in (b) are calculated by PBE functional.

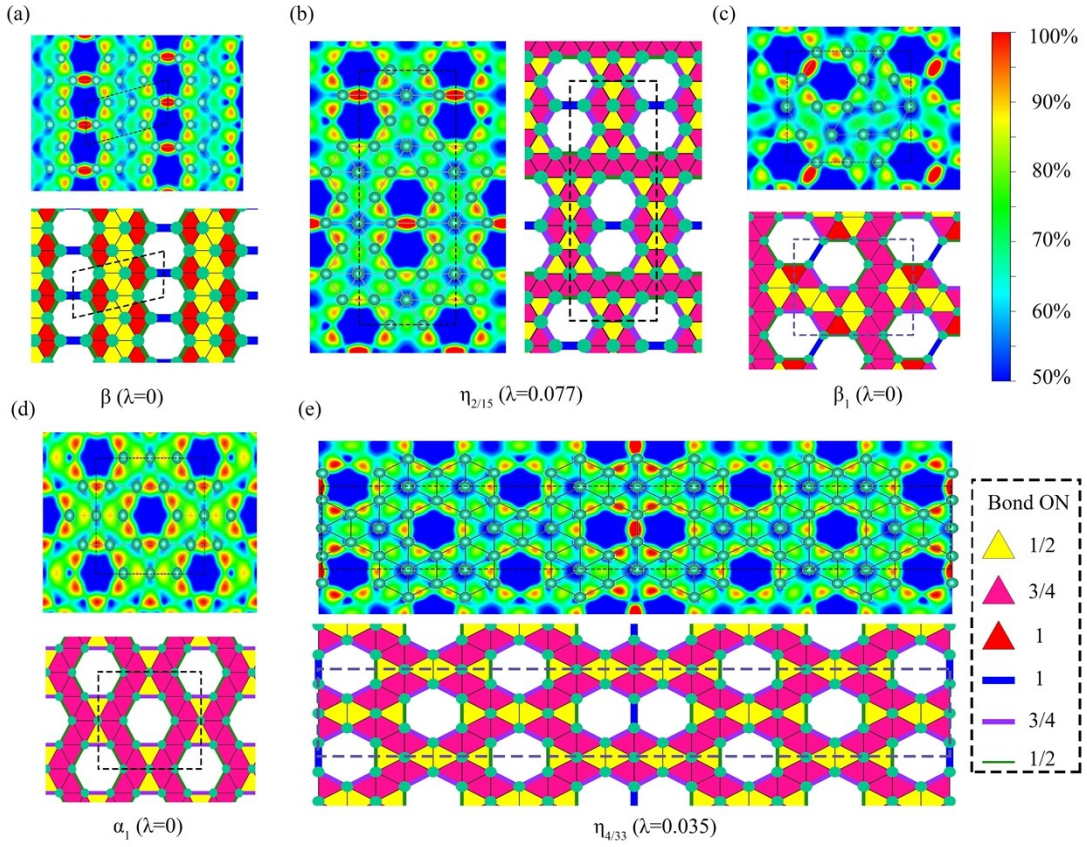

Fig. S5. Bonding analysis for a few stable boron monolayers. The left part of (a-c) and upside of (d,e) presented the charge difference of the corresponding boron monolayers, the rest part of (a-e) presented the possible 2c-2e and 3c-2e bond distributions. The percentages of the colorbar are signed with the peak amplitude value for the isosurface, and the occupation numbers (ON) of the 2c-2e and 3c-2e bonds are both listed on the right side of the figure. The above charge differences are calculated by PBE functional.

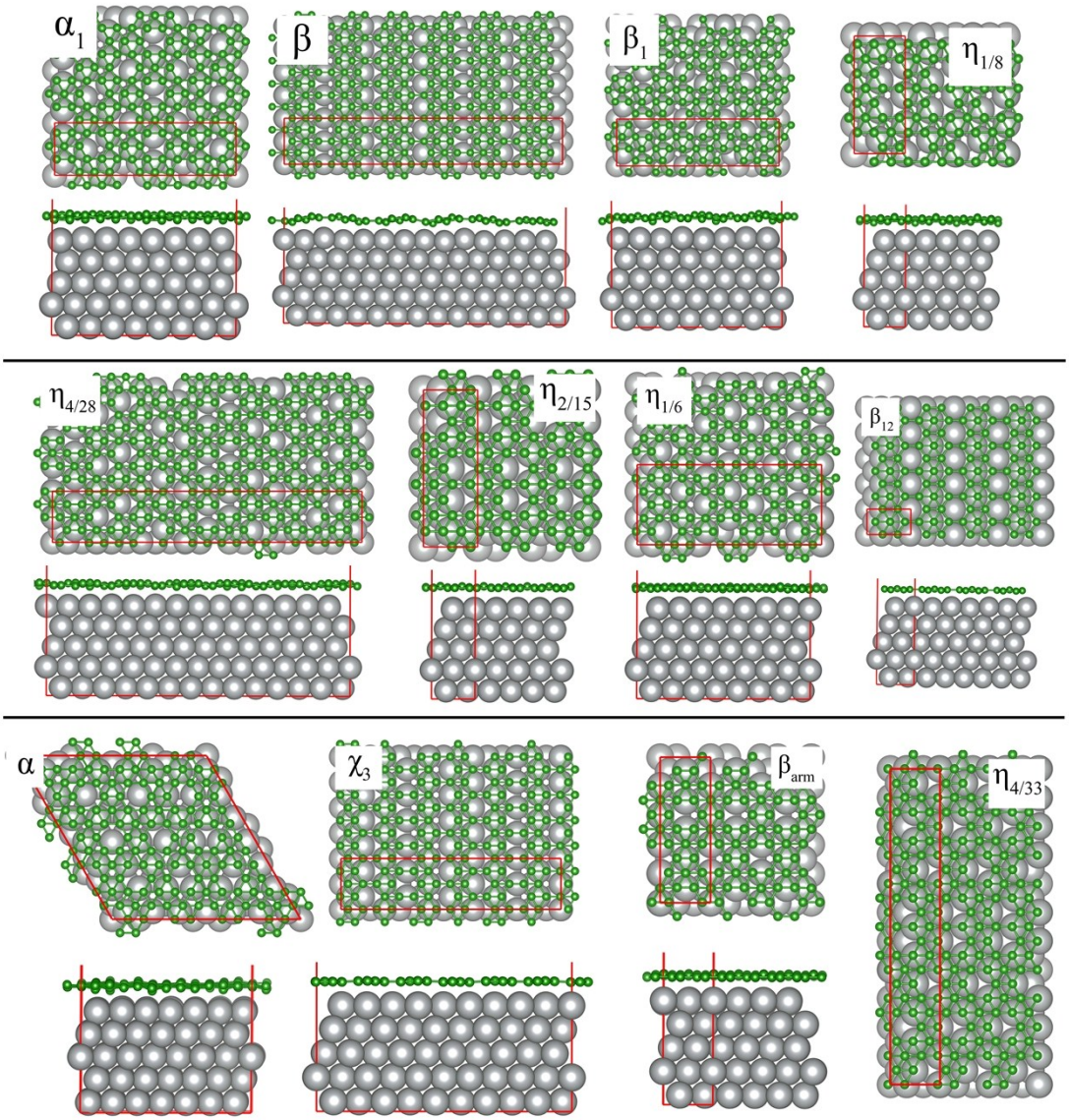

Fig. S6. The atomic configurations of various boron monolayers on Ag(111) surface. The bigger gray atoms represent the Ag substrates, and the red solid frames represent the unit cell of the B/Ag systems in our calculations. The above configurations are fully relaxed by PBE functional.

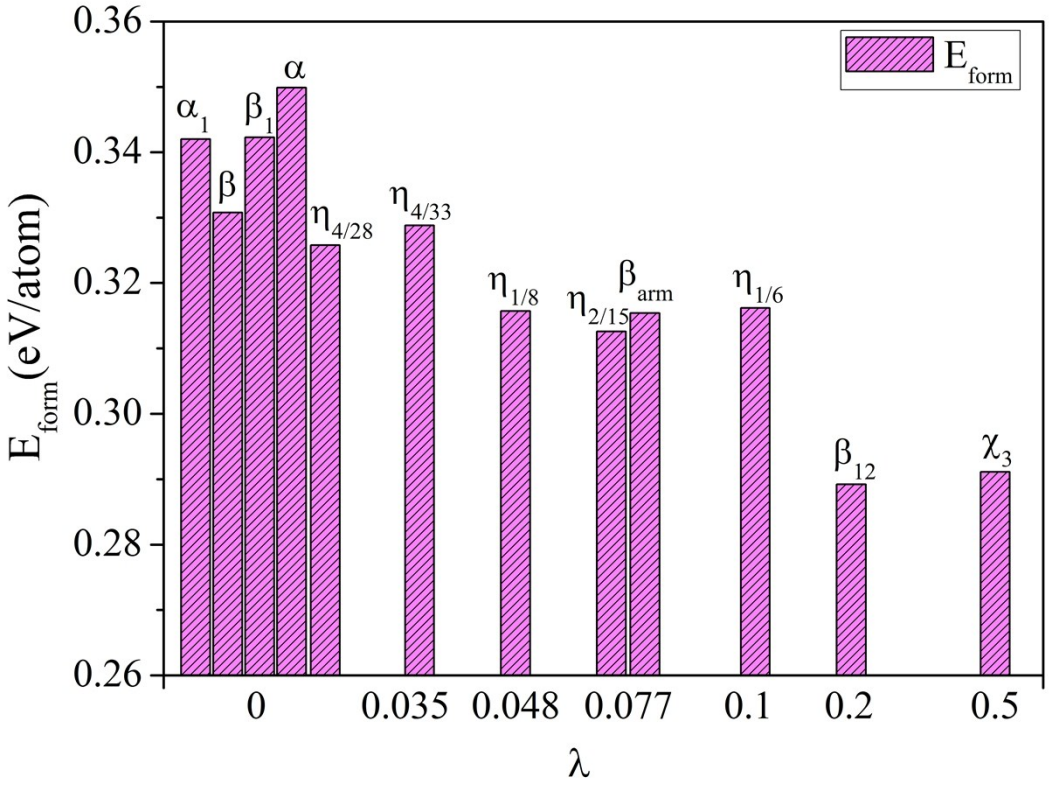

Fig. S7. The average formation energy(E_{form}) of various boron monolayers on the Ag(111) substrate. The average formation energies are calculated by PBE functional.

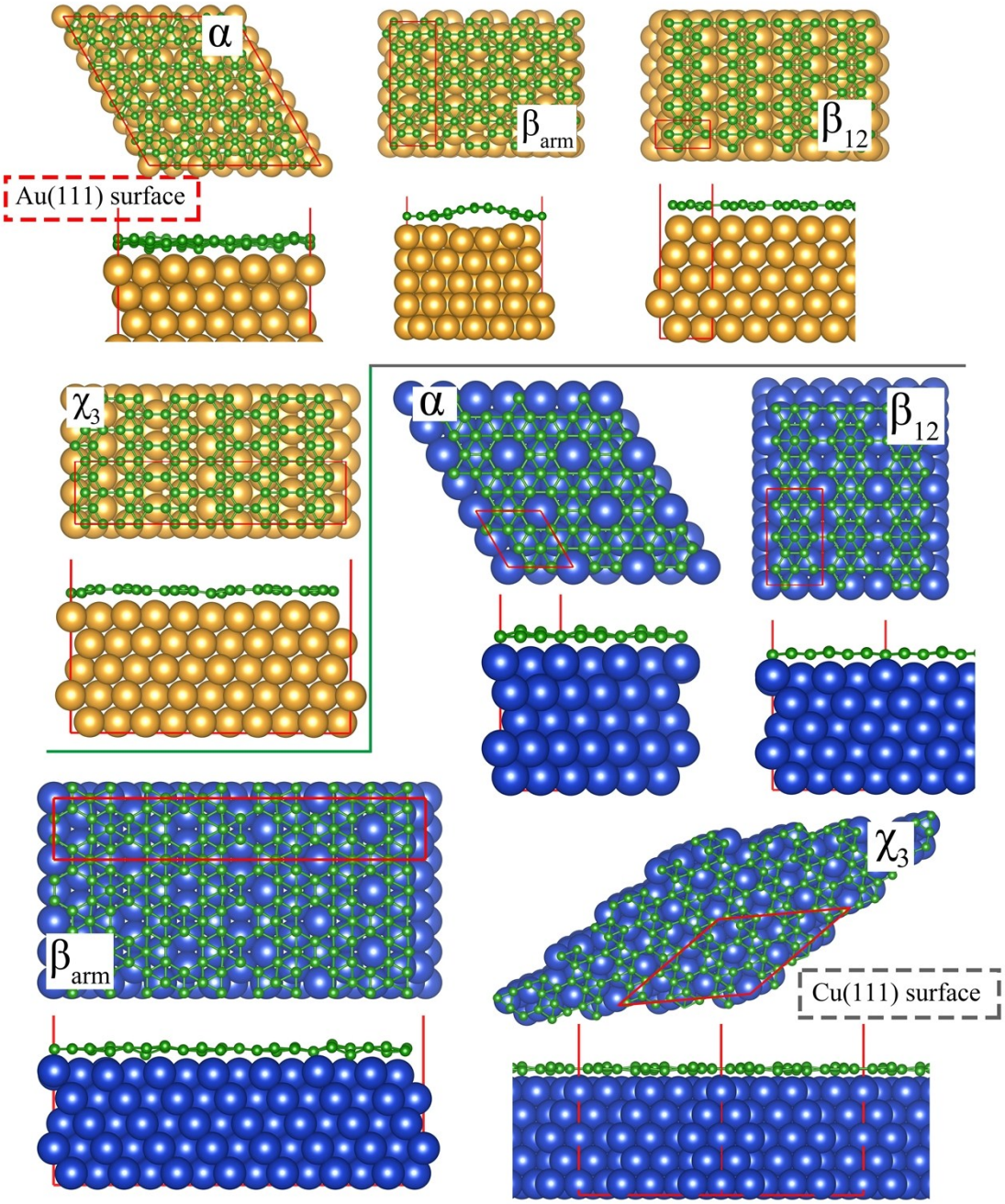

Fig. S8. The atomic structures (top view and side view) of the boron monolayers (β_{12}, χ_3, β_{arm}, α) on the Au/Cu(111) surfaces. The above configurations are fully relaxed by PBE functional.