Electronic Supplementary Information

Controlling the orientations of h-BN during growth on transition metals by chemical vapor deposition

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1. Schematic adsorption sites and alignments of BN clusters on the same terrace of metals stacked in the hexagonal close packed form.

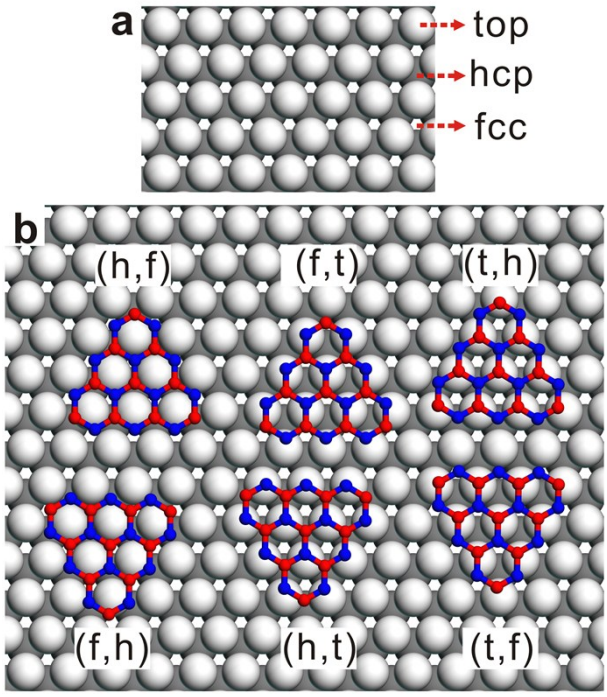

Fig. S1 Schematic adsorption sites and alignments of BN clusters on the (0001) facet of metals stacked in hexagonal close packed form. (a) Three high-symmetry sites, and (b) alignments of six possible configurations, which are identified with the first letters of adsorption sites occupied by B and N atoms. The boron and nitrogen atoms are shown in red and blue, respectively. The substrate atoms are shown in white-, gray-, and black in order of ascending depth from the top.

2. A representative model used in simulations.

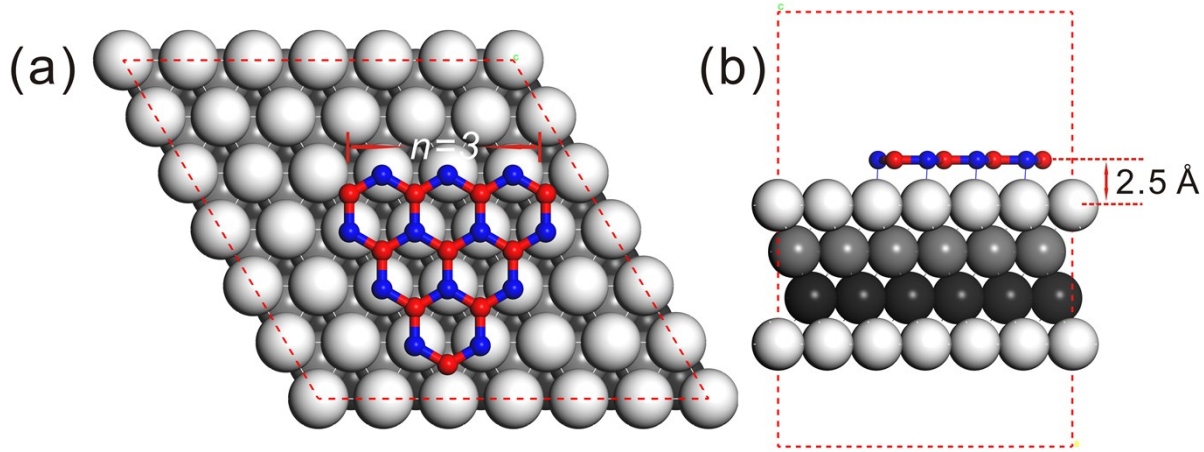

Fig. S2 Representative model of N-terminated BN clusters (n = 3) with B and N adopting hcp and top sites of the (111) facet of face-centered cubic metals: (a) top view and (b) side view. n is the number of hexagonal rings on each edge. Boron and nitrogen atom is shown in red and blue, respectively. The substrate is shown in white-grey-black seen from top.

3. The formation energies and energy differences between B_hN_t and B_fN_t of BN clusters on various metals.

Table S1 The formation energies (E_f) of BN clusters with six configurations and energy difference (ΔE) between B_hN_t and B_fN_t of BN clusters (n = 2, 3, 4) on Ag(111), Au(111), Co(0001), Cu(111), Ir(111), Ni(111), Pd(111), Pt(111), Rh(111), and Ru(0001). BN clusters on Ag(111) and Au(111) are calculated with configurations of B_hN_t and B_fN_t.

BN@Ag	B-terminated			N-terminated		
	n = 2	n = 3	n = 4	n = 2	n = 3	n = 4
B_hN_t	*15.19*	**23.64**	**31.32**	**10.50**	***16.82***	22.27
B_fN_t	15.24	*23.65*	**31.24**	***10.51***	**16.83**	22.30
ΔE (eV)	-0.05	-0.01	**0.08**	-0.01	-0.01	-0.03
BN@Au	B-terminated			N-terminated		
	n = 2	n = 3	n = 4	n = 2	n = 3	n = 4
B_hN_t	12.84	**20.55**	26.17	11.71	***20.13***	24.56
B_fN_t	12.83	***20.77***	26.57	11.75	**20.13**	24.57
ΔE (eV)	0.01	-0.22	-0.04	-0.04	0.00	-0.01
BN@Co	B-terminated			N-terminated		
	n = 2	n = 3	n = 4	n = 2	n = 3	n = 4
B_fN_h	***9.53***	*15.36*	*18.75*	**8.16**	10.57	**10.89**
B_tN_f	*10.13*	*15.58*	*18.75*	-	-	11.08
B_hN_t	*10.13*	***14.28***	***16.65***	8.29	**10.39**	11.08
B_tN_h	-	15.40	18.83	-	-	-
B_hN_f	**9.59**	15.40	18.82	***8.21***	*10.88*	*11.14*
B_fN_t	10.27	**14.52**	**17.09**	*8.30*	***10.37***	***11.02***
ΔE (eV)	-0.14	-0.24	-0.44	-0.01	-0.02	-0.06
BN@Cu	B-terminated			N-terminated		
	n = 2	n = 3	n = 4	n = 2	n = 3	n = 4
B_fN_h	12.64	**18.42**	26.12	*10.63*	***13.14***	***17.25***
B_tN_f	12.98	-	26.72	*10.91*	*14.10*	*18.84*

B_hN_t	**12.46**	18.67	**26.03**	***10.54***	*14.25*	*18.18*
B_tN_h	*12.90*	***18.49***	*27.19*	10.60	13.71	18.59
B_hN_f	*12.76*	-	*26.29*	10.65	**13.03**	**17.25**
B_fN_t	***12.53***	*18.79*	***26.15***	**10.52**	14.16	18.15
ΔE (eV)	-0.07	-0.12	-0.12	0.02	0.09	0.03
BN@Ir	B-terminated			N-terminated		
	$n = 2$	$n = 3$	$n = 4$	$n = 2$	$n = 3$	$n = 4$
B_fN_h	9.90	14.72	**17.26**	*8.83*	-	-
B_tN_f	9.62	14.34	-	*9.73*	*12.74*	-
B_hN_t	**8.49**	**14.03**	17.38	***7.54***	***10.90***	***13.33***
B_tN_h	*9.55*	*14.39*	***17.16***	9.77	-	-
B_hN_f	*9.73*	*14.48*	*18.25*	9.77	13.46	15.94
B_fN_t	***8.46***	***14.34***	*17.94*	**7.70**	**11.14**	**13.40**
ΔE (eV)	0.03	-0.31	-0.56	-0.16	-0.24	-0.07
BN@Ni	B-terminated			N-terminated		
	$n = 2$	$n = 3$	$n = 4$	$n = 2$	$n = 3$	$n = 4$
B_fN_h	-	14.43	18.19	*9.21*	***10.44***	-
B_tN_f	**9.65**	14.45	18.19	***7.87***	*11.20*	***11.58***
B_hN_t	9.94	**13.71**	**17.13**	*8.63*	*11.20*	*13.09*
B_tN_h	-	*14.70*	-	**7.85**	11.29	11.65
B_hN_f	***9.50***	*14.24*	*17.94*	9.10	**10.48**	**11.63**
B_fN_t	*9.93*	***13.67***	***17.14***	8.68	11.29	13.13
ΔE (eV)	0.01	0.04	-0.01	-0.05	-0.09	-0.04
BN@Pd	B-terminated			N-terminated		
	$n = 2$	$n = 3$	$n = 4$	$n = 2$	$n = 3$	$n = 4$
B_fN_h	10.71	**13.15**	**19.07**	-	-	***11.89***
B_tN_f	**9.68**	13.86	19.09	*10.26*	-	-
B_hN_t	10.30	13.47	19.40	***9.88***	***11.85***	***17.60***
B_tN_h	*11.27*	*13.82*	***18.99***	**9.84**	13.28	18.61

B_hN_f	***9.91***	*13.53*	*19.45*	9.91	11.90	-
B_fN_t	*10.70*	***13.50***	*19.31*	9.98	**11.85**	**17.75**
ΔE (eV)	-0.40	-0.03	0.09	-0.10	0.00	-0.15
BN@Pt	B-terminated			N-terminated		
	$n = 2$	$n = 3$	$n = 4$	$n = 2$	$n = 3$	$n = 4$
B_fN_h	9.84	**13.37**	16.48	**9.70**	13.72	18.43
B_tN_f	11.28	13.51	**16.31**	11.13	13.72	**17.97**
B_hN_t	**9.84**	13.38	16.83	9.73	**13.71**	18.09
B_tN_h	10.28	**13.33**	16.52	9.79	14.47	18.21
B_hN_f	*9.73*	*13.34*	***16.33***	*14.48*	*15.26*	***17.56***
B_fN_t	***9.73***	*13.83*	*17.07*	***9.79***	***13.92***	*18.25*
ΔE (eV)	*0.11*	*-0.45*	*-0.24*	*-0.06*	*-0.21*	*-0.16*
BN@Rh	B-terminated			N-terminated		
	$n = 2$	$n = 3$	$n = 4$	$n = 2$	$n = 3$	$n = 4$
B_fN_h	**9.10**	13.35	17.24	*7.89*	-	-
B_tN_f	10.23	13.86	**17.19**	*9.13*	-	-
B_hN_t	9.26	**12.55**	17.32	***7.85***	***9.55***	***11.20***
B_tN_h	*10.18*	*13.86*	***17.14***	-	-	-
B_hN_f	*9.23*	***13.25***	***17.14***	9.11	-	13.83
B_fN_t	***9.17***	*13.28*	*17.23*	**7.95**	**9.66**	**11.28**
ΔE (eV)	-0.09	-0.73	0.09	-0.10	-0.11	-0.08
BN@Ru	B-terminated			N-terminated		
	$n = 2$	$n = 3$	$n = 4$	$n = 2$	$n = 3$	$n = 4$
B_fN_h	*9.04*	*14.07*	*17.95*	6.60	-	9.99
B_tN_f	*9.33*	*14.82*	*18.06*	-	-	-
B_hN_t	***8.09***	***12.20***	***15.04***	**6.09**	**7.57**	**7.96**
B_tN_h	8.86	14.01	18.08	-	-	-
B_hN_f	8.73	14.01	17.81	*6.77*	-	-
B_fN_t	**8.33**	**12.35**	**15.45**	***6.11***	***7.65***	***7.80***

ΔE (eV)	-0.24	-0.15	-0.41	-0.02	-0.08	0.16

Notes: 1. "–" represents the configurations turn into the stable one after relaxations;

2. The energy difference, $\Delta E = E_{f, BhNt} - E_{f, BfNt}$;

3. Two local minima are emphasized with black body and the global minima are emphasized with bold.

4. The metal lattices and lattice mismatches between h-BN and metal substrates.

Table S2 The metal lattices and lattice mismatches between h-BN and metal substrates.

Metals	Lattice parameters (Å)	Mismatching (%)	Metals	Lattice parameters (Å)	Mismatching (%)
Cu(111)	2.556	1.71	Pt(111)	2.775	10.43
Ni(111)	2.492	-0.84	Ag(111)	2.889	14.96
Rh(111)	2.690	7.04	Au(111)	2.884	14.76
Ir(111)	2.72[1]	8.00	Ru(0001)	2.706	7.68
Pd(111)	2.751	9.47	Co(0001)	2.507	-2.39

$a_{B\text{-}N}$: 2.513 Å; Mismatch = $(a_M - a_{BN})/a_{BN}$, the lattice parameters are taken from the default ones provided by the software Material Studio 6.

5. Relaxed geometries of B_hN_t on Ir(111).

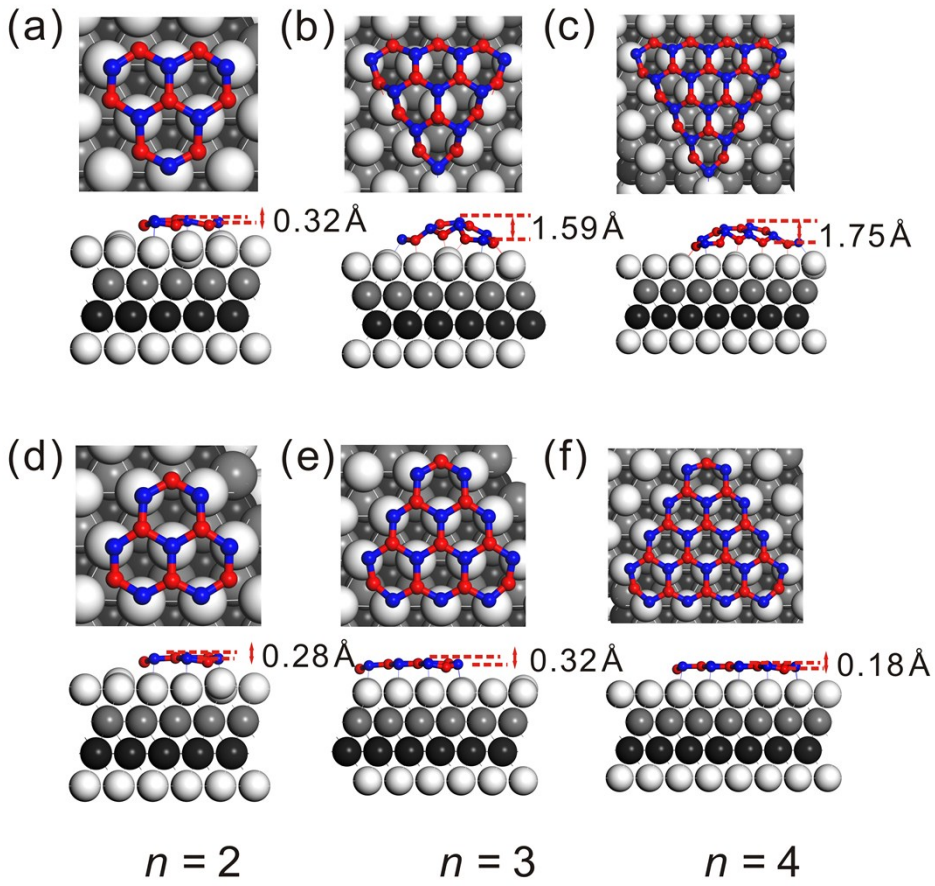

Fig. S3 Relaxed geometries with configuration of B_hN_t on Ir(111) seen from the top and side: B- (a-c) and N- (d-f) terminated BN clusters.

6. Relaxed B_hN_t geometries of N-terminated BN clusters on Ru(0001).

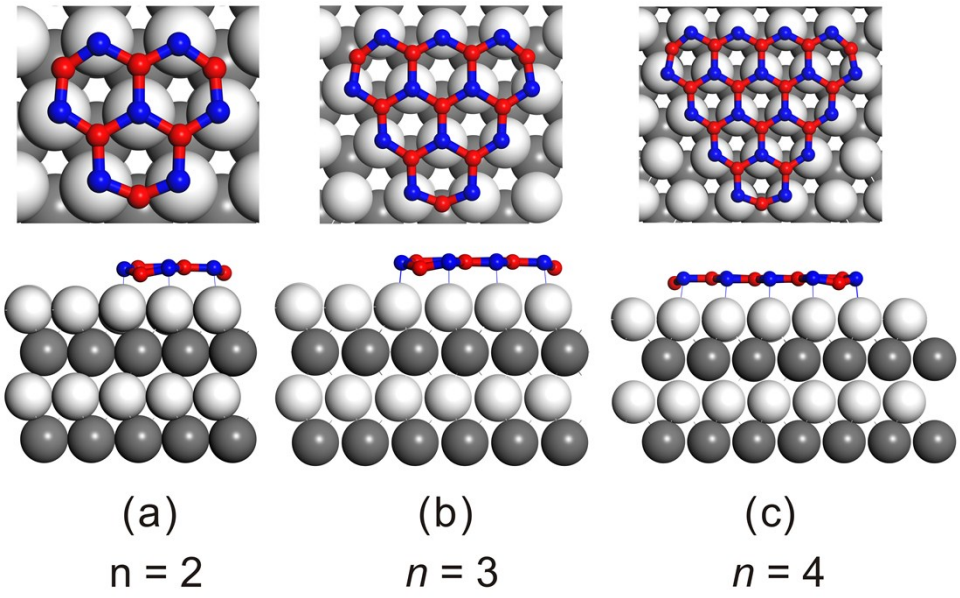

Fig. S4 Relaxed geometries of N-terminated BN clusters, B_hN_t (n = 2-4) on Ru(0001) seen from the top and side.

7. Relaxed B_hN_f geometries of N-terminated BN clusters on Ir(111).

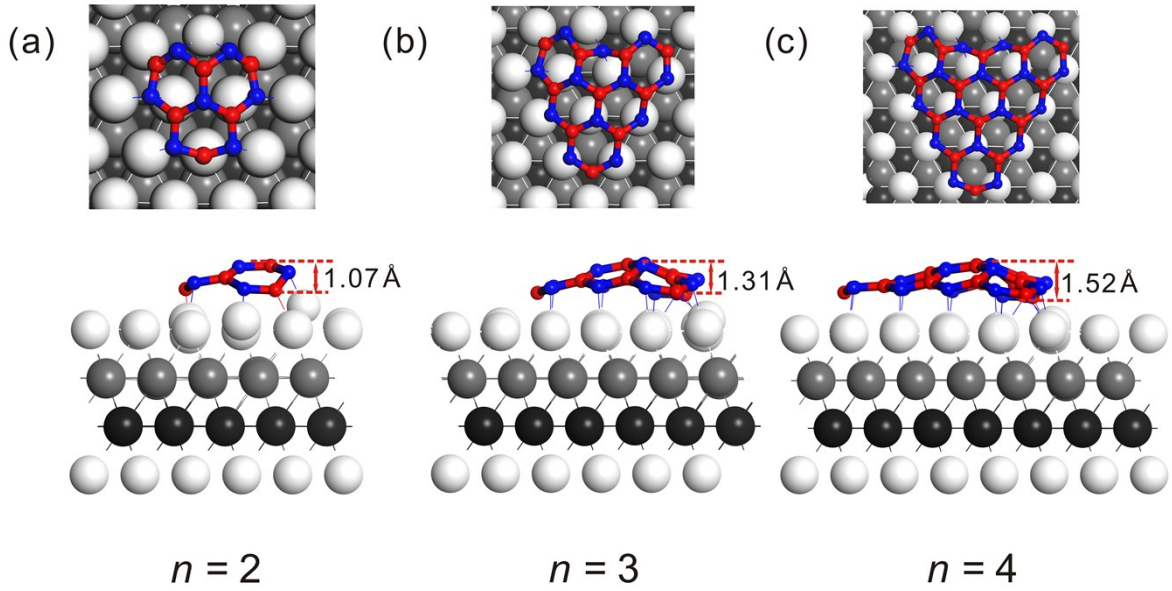

Fig. S5 Relaxed geometries of N-terminated BN clusters, B_hN_f, (n = 2-4) on Ir(111) seen from the top and side.

8. Defects formed as BN domains grow and merge.

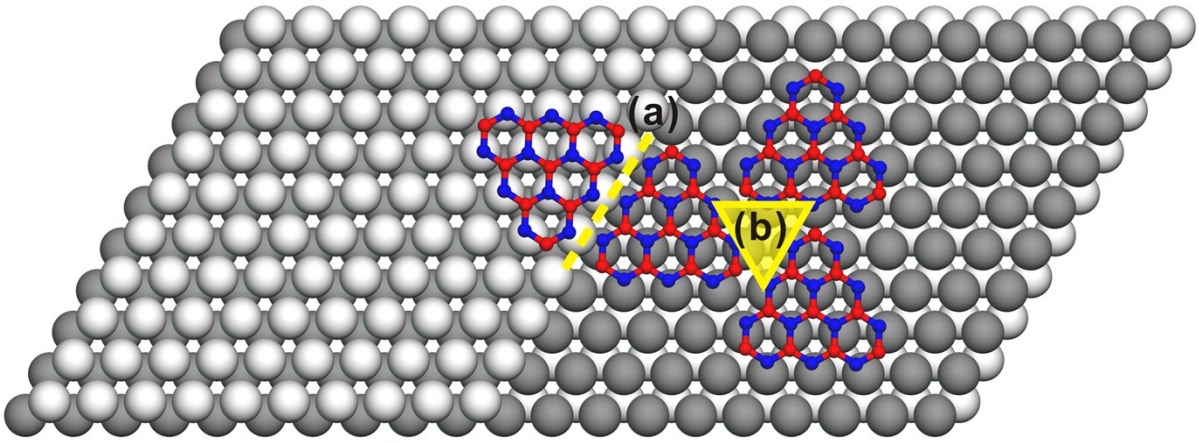

Fig. S6 Defects formed as triangular BN domains grow and merge: (a) Line defects (formed by anti-parallel domains) and (b) triangular voids (formed by parallel domains).