Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Phase Engineering of MoS_2 through GaN/AlN Substrate Coupling and Electron Doping

SUPPLEMENTARY INFORMATION

S1. Atomic configurations of different T Phases:

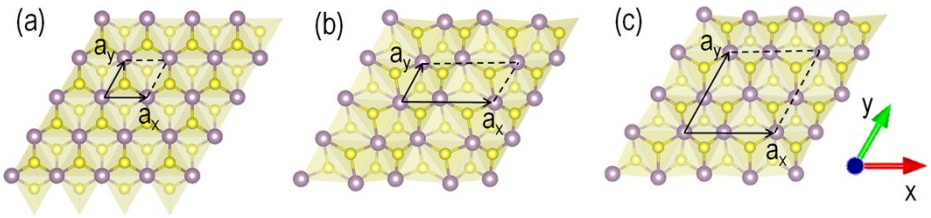

Fig. S1 (Color online): Atomic configurations of (a) 1T Phase; (b) 1T' Phase; (c) 1T'' Phase of MoS_2.

S2. Conformation of 1T' and 1T'' on top of GaN/AlN:

In order to conform with the 2×2 supercell of GaN (AlN) slabs, 2×2 supercell of 2H-MoS_2 and 1T-MoS_2, 1×2 super cell of 1T'-MoS_2 and 1×1 supercell of 1T''-MoS_2 is required. The corresponding atomic configurations are demonstrated by Fig. S2 below:

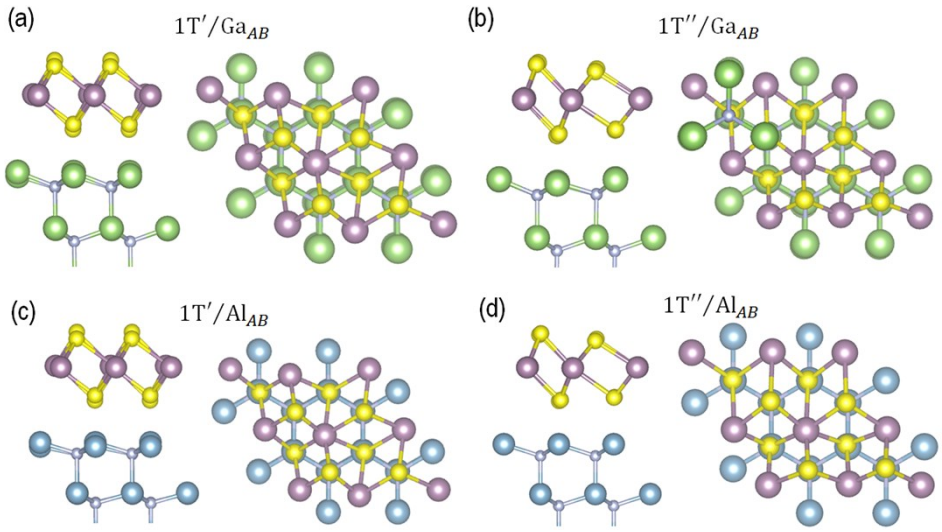

Fig. S 2 (Color online): Atomic configurations of $^{1T'}/Ga_{AB}$, $^{1T''}/Ga_{AB}$, $^{1T'}/Al_{AB}$, $^{1T''}/Al_{AB}$.

The equilibrium lattice parameters for different MoS_2 phases and [0001] facets of GaN and AlN are given in Table S1. The parameter a_x and a_y indicates the smallest

periodic distance in x and y directions.

Table S1: Lattice parameters of different MoS_2 phases and [0001] facet of GaN (AlN) in equilibrium.

Phase	2H	1T	1T'	1T''	GaN	AlN
a_x (Å)	3.18	3.19	3.18	6.44	3.21	3.13
	(3.18[1, 2])	(3.19[1, 2])	(3.18[1, 2])	(6.44[1, 2])	(3.22[3])	(3.13[3])
a_y (Å)	3.18	3.19	6.54	6.44	3.21	3.13
	(3.18[1, 2])	(3.19[1, 2])	(6.55[1, 2])	(6.44[1, 2])	(3.22[3])	(3.13[3])

S3. Stability of GaN/AlN substrate:

The relaxed structures of clean-surface GaN and AlN substrates are shown in Fig. S3. Our DFT calculations show that both GaN and AlN surfaces will be stable without external pertubation.

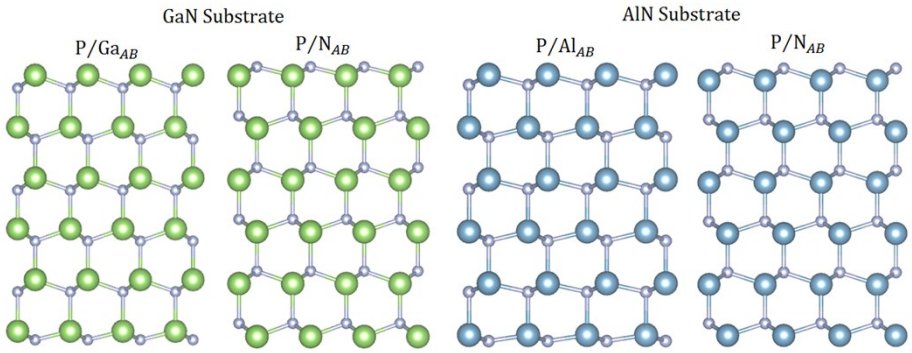

Fig. S3 (Color online): Relaxed structures of clean-surface GaN and AlN substrates.

S4. Electron localization functions of selected configurations:

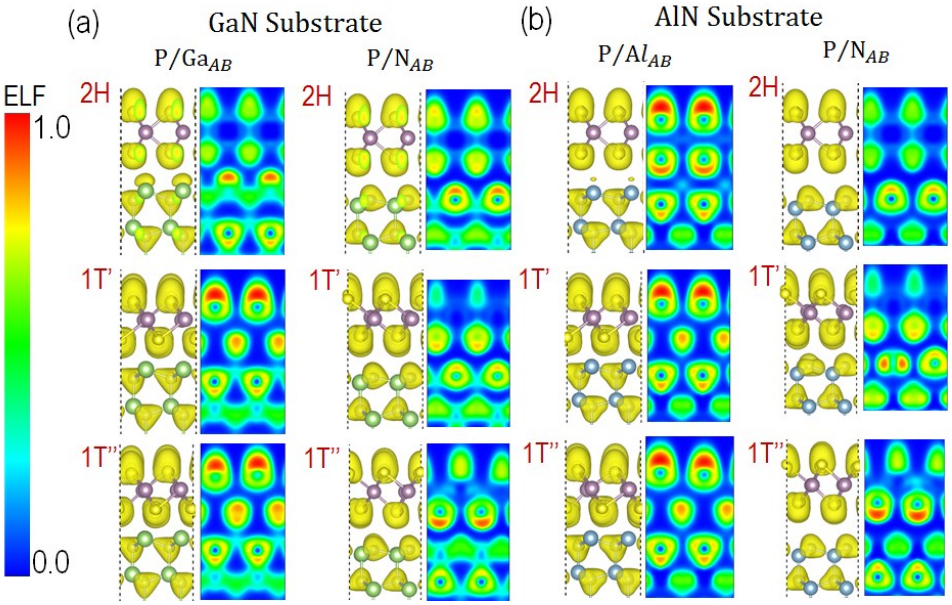

Fig. S4 (Color online): Representative electron localization function (ELF) plots for MoS_2 phases on (a) Ga-terminated and N-terminated c-plane GaN substrates, and (b) Al-terminated and N-terminated c-plane AlN substrates. For each phase, the subfigure on the left shows the 3D isosurfaces

while the right subfigure illustrate the 2D slices with respect to top atom of GaN/AlN.

S5. Calculated total energies of different configurations:

Table S2: Calculated total energies normalized by number of unit cell for MoS_2/GaN heterostructures.

Stacking	Ga termination (eV)				N termination (eV)			
	2H	1T	1T'	1T''	2H	1T	1T'	1T''
T_{AB}	-96.14	-95.55	-96.64	-96.66	-95.97	-95.14	-95.45	-95.44
T_{AC}	-96.28	-95.87	-96.31	-96.29	-95.95	-95.20	-95.42	-95.40
T_{BA}	-96.58	-96.28	-96.65	-96.67	-95.96	-95.38	-95.77	-95.77
T_{BC}	-96.22	-95.92	-96.34	-96.34	-95.95	-95.38	-95.52	-95.49
T_{CA}	-96.53	-96.25	-96.63	-96.66	-95.94	-95.40	-95.79	-95.78
T_{CB}	-96.18	-95.78	-96.65	-96.67	-95.97	-95.27	-95.43	-95.44

Tab. S 3: Calculated total energies normalized by number of unit cell for MoS_2/AlN heterostructures.

Stacking	Al termination (eV)				N termination (eV)			
	2H	1T	1T'	1T''	2H	1T	1T'	1T''
T_{AB}	-111.42	-110.91	-112.17	-112.19	-111.31	-110.61	-110.78	-110.79
T_{AC}	-111.76	-111.38	-111.79	-111.80	-111.14	-110.50	-110.62	-110.75
T_{BA}	-112.13	-111.70	-112.18	-112.18	-111.13	-110.48	-110.55	-110.70
T_{BC}	-111.73	-111.51	-111.78	-111.78	-111.13	-110.60	-110.82	-110.84
T_{CA}	-112.09	-111.76	-112.17	-112.18	-111.13	-110.47	-110.69	-110.78
T_{CB}	-111.46	-111.03	-112.18	-112.19	-111.15	-110.37	-110.52	-110.61

S6. Strain influence of calculated energetics

Since 1T' and 1T'' phases were made to conform to 2H-MoS_2, their lattices were strained. This straining leads to strain energies, which are calculated to be (per supercell) 0.096 eV and 0.064 for 1T' and 1T'' phases respectively. Suppose that the above strain energies are relieved because of the incommensurate interface, one would expect (*a*) for MoS_2 on a metal-terminated GaN or AlN, the 2H→1T'/1T'' transition will be slightly enhanced due to the lowering of energy states in 1T'/1T'' (see Fig. 2); (*b*) for MoS_2 on a N-terminated GaN or AlN, the relative phase stability will not be altered as the magnitude of strain energy is smaller than the energy gap between 2H and 1T' (or 1T") (being 0.15~0.55 eV and 0.29~0.63 eV per supercell respectively, see Fig. 2, Tab. S2 and Tab. S3). Thus the presence of strain will not change the general picture of phase stability and transition.

S7. Calculated DOS for 2H/Ga_{AB} and 2H/N_{AB} for MoS_2 on top of GaN

The electronic properties are certainly modified by the underlying GaN (AlN) substrate. Such modification is illustrated below in Fig. S5, where we presented (as representatives) the DOS plots of 1T'/Ga_{AB}, 1T''/Ga_{AB}, 2H/N_{AB} (for MoS_2 on GaN), 1T'/Al_{AB}, 1T''/Al_{AB}, 2H/N_{AB} (for MoS_2 on AlN) and the DOS plot of a free-standing 2H-MoS_2, 1T'-MoS_2 and 1T''-MoS_2.

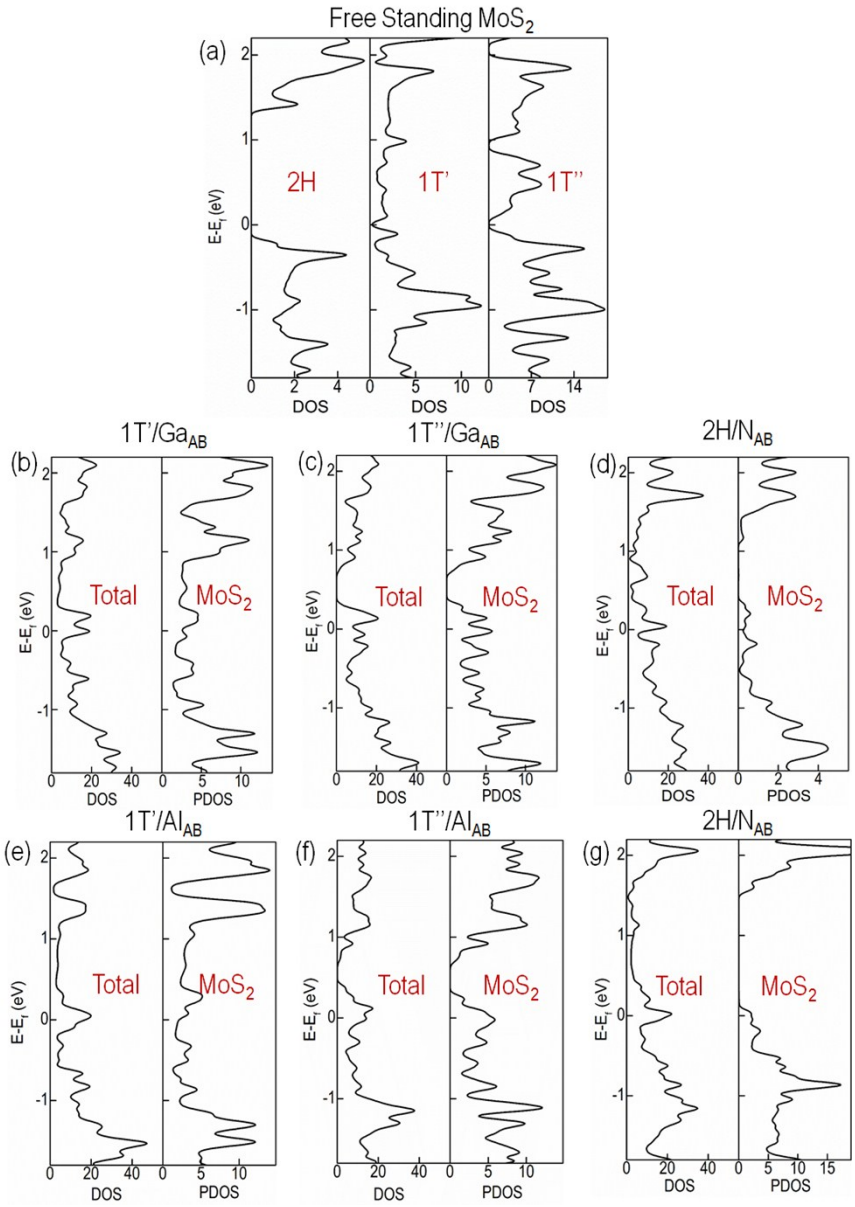

Fig. S5: (a) DOS of free standing 2H-MoS_2 monolayers; (b) Partial DOS and total DOS for 1T'/Ga_{AB} (GaN Substrate); (c) Partial DOS and total DOS for 1T''/Ga_{AB} (GaN Substrate); (d) Partial DOS and total DOS for 2H/N_{AB} (GaN Substrate); (e) Partial DOS and total DOS for 1T'/Al_{AB} (AlN Substrate); (f) Partial DOS and total DOS for 1T''/Al_{AB} (AlN Substrate); (g) Partial DOS and total

DOS for 2H/N_{AB} (AlN Substrate).

S8. Work of adhesion for different stacking conditions.

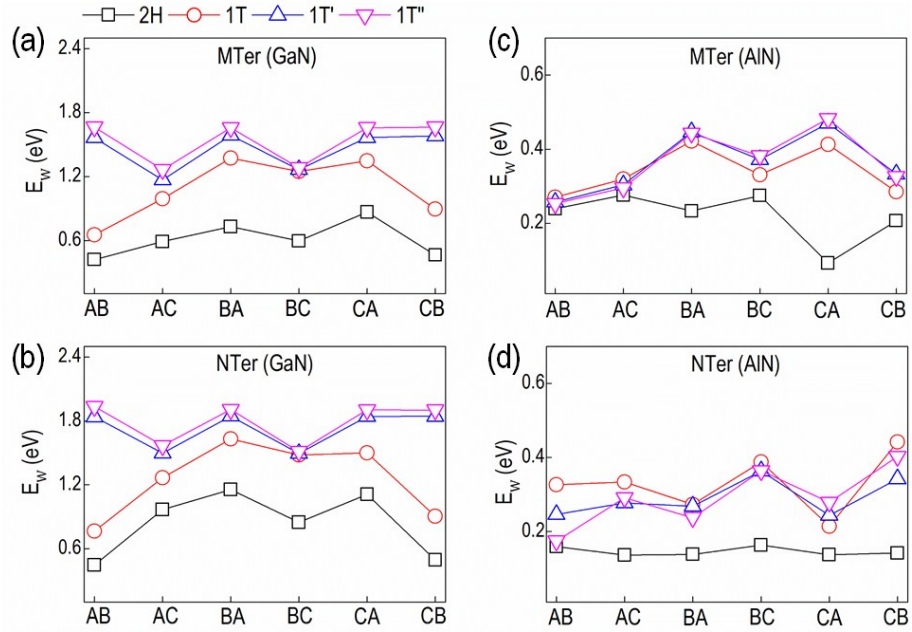

Fig. S6 (Color online): Work of adhesion for all stacking sequences at different surface termination (a) Ga termination; (b) N termination; (c) Al termination; (d) N termination.

S9. Minimum reaction path of phase transitions.

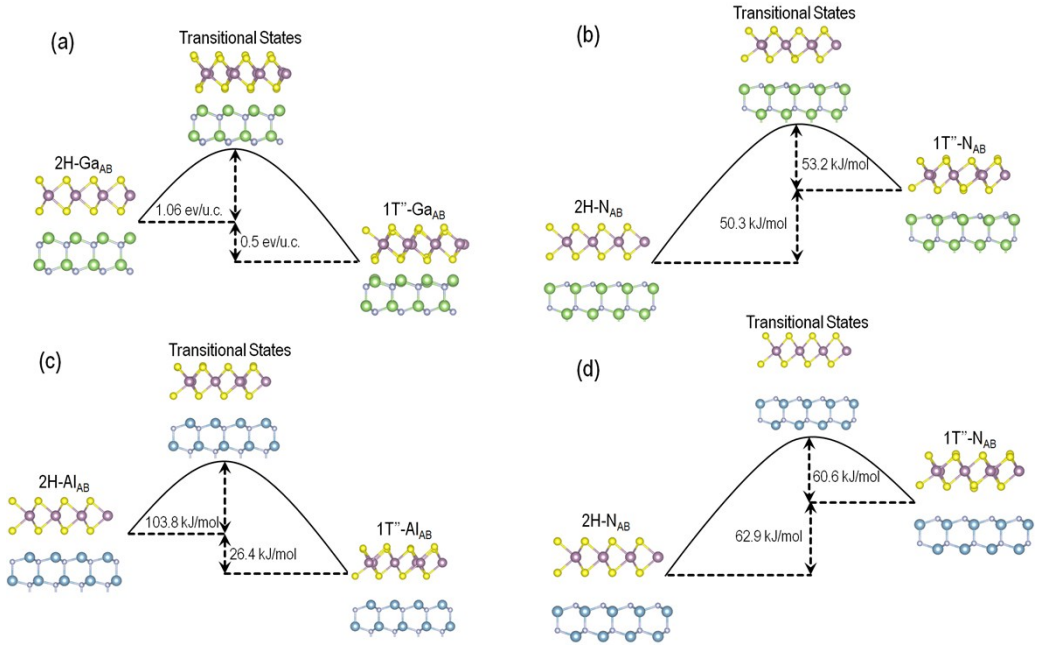

Fig. S7 (Color online): Minimum reaction paths for (a) 2H/Ga_{AB} (GaN) → 1T''/Ga_{AB} (GaN); (b) 2H/N_{AB} (GaN) → 1T''/N_{AB} (GaN); (c) 2H/Al_{AB} (AlN) → 1T''/Al_{AB} (AlN); (d) 2H/N_{AB} (AlN) → 1T''/N_{AB} (AlN).

S10. Energetic profile with electron injection within other Metal termination.

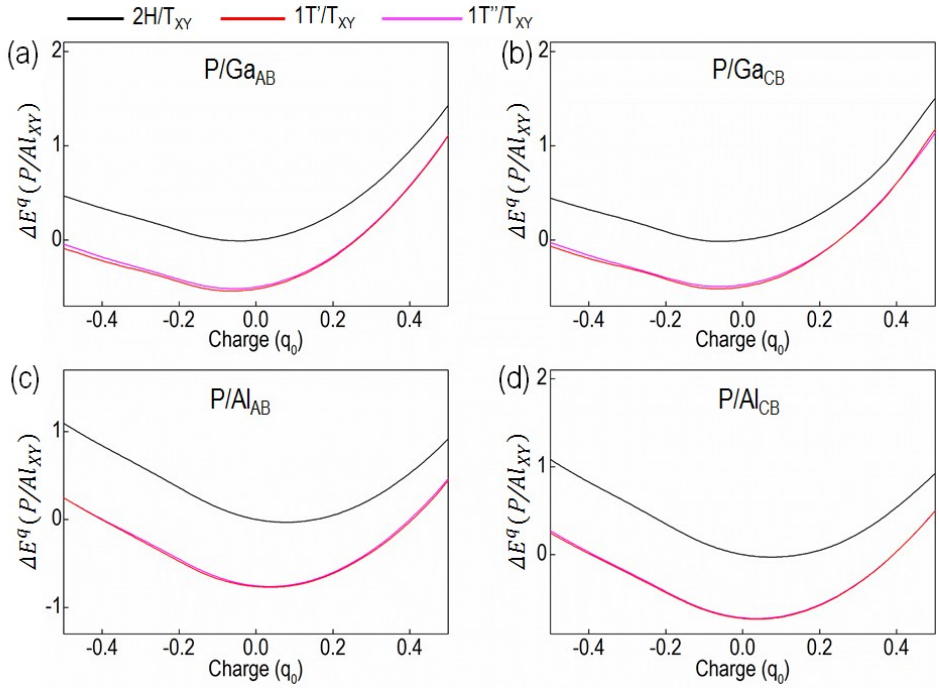

Fig. S8 (Color online): Charge engineering of phase stabilities of MoS_2 growing at (a) Ga_{AB}; (b) Ga_{CB}; (c) P/Al_{AB}; (d) P/N_{AB}.

S11. Energetic profile with electron injection of GaN with Nitrogen termination.

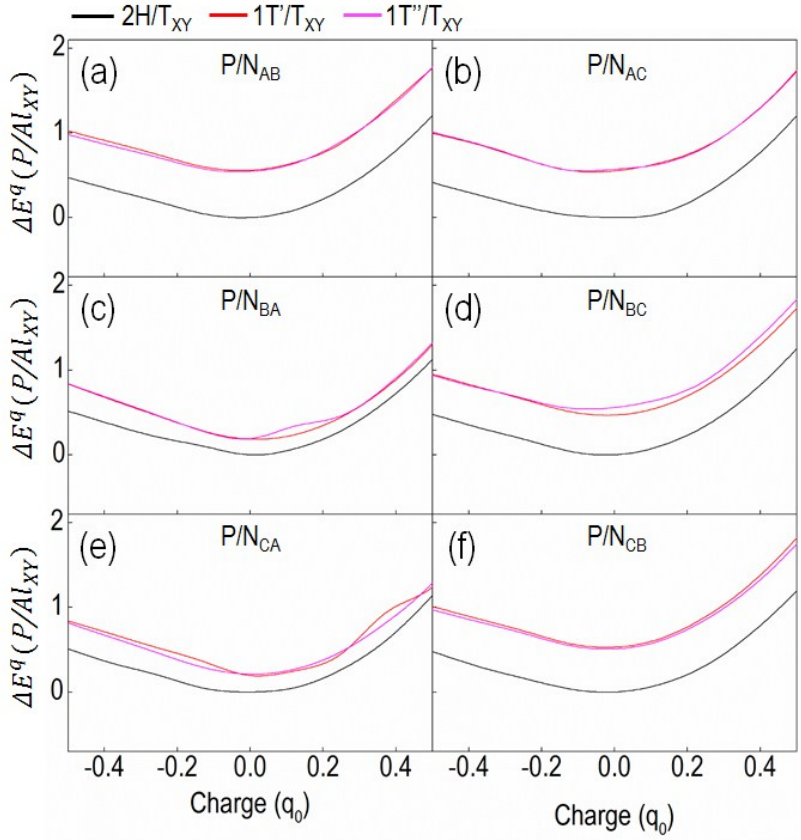

Fig. S9 Charge engineering of phase stabilities of MoS_2 growing on GaN at (a) N_{AB};

(b) N_{AC}; (c) N_{BA}; (d) N_{BC}; (e) N_{CA}; (f) N_{CB}.

S12. Energetic profile with electron injection of AlN with Nitrogen termination.

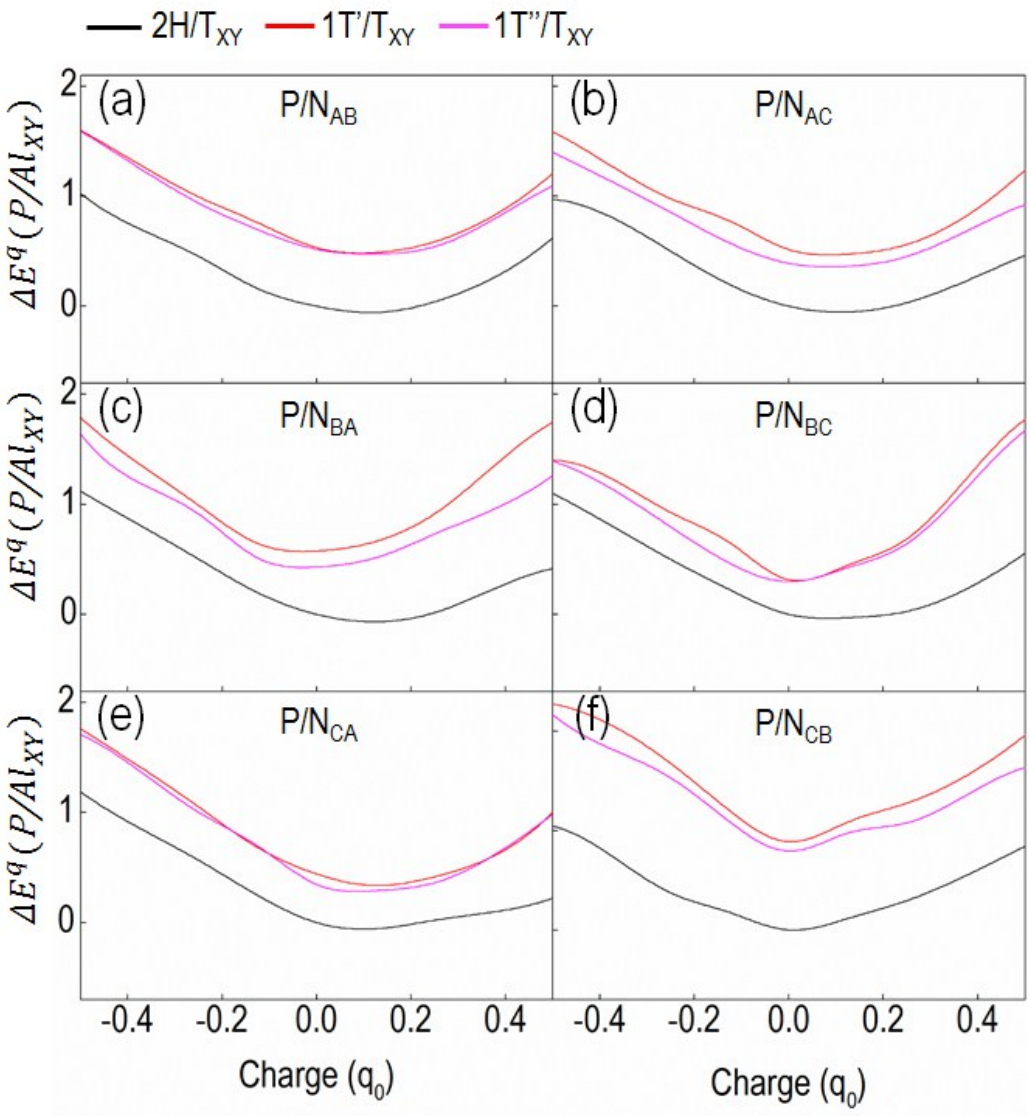

Fig. S10 Charge engineering of phase stabilities of MoS_2 growing on AlN at (a) N_{AB}; (b) N_{AC}; (c) N_{BA}; (d) N_{BC}; (e) N_{CA}; (f) N_{CB}.

Reference:

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2. M. Kan, J. Y. Wang, X. W. Li, S. H. Zhang, Y. W. Li, Y. Kawazoe, Q. Sun and P. Jena, *J. Phys. Chem. C*, 2014, 118, 1515-1522.
3. L. Gordon, J. L. Lyons, A. Janotti and C. G. Van de Walle, *Phys. Rev. B*, 2014, 89, 085204.