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

Supplementary Information

Band Engineering and Hybridization of Competing Arsenene Allotropes: A Computational Study

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COMPUTATIONAL DETAILS:

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The Vienna Ab initio Simulation Package (VASP)[1] within the framework of density functional theory (DFT) was adopted to perform structural relaxations and electronic structure calculations. The Perdew-Burke-Ernzerhof functional[2] in the generalized gradient approximation (GGA)[3] was used. The electron-ion interactions were treated using the projector-augmented-wave (PAW) method[4] with $4s^2 4p^3$ as the valence electrons of As. A plane-wave basis set cutoff of 500 eV and the Monkhorst-Pack (MP) scheme[5] with a dense *k*-point grid of $2\pi \times 0.03$ $Å^{-1}$ spacing in the Brillouin zone were adopted to ensure the energy converges to 1 meV/atom. The separation along the *c* direction is larger than 15 Å for all systems. During the structural relaxation, the energy convergent criterion was set to 10^{-5} eV per unit cell, and the atomic forces were smaller than 0.01 eV $Å^{-1}$. For multiple layers, van der Waals interaction was considered in the vdW-DF level using the optB88 exchange functional[6]. Phonon dispersions were calculated using Phonopy[7]. Ab-initio molecular dynamics simulations adopting the canonical (NVT) ensemble were performed with a time step of 1 fs for a total simulation time of 2 ps at 300 K, 600 K and 1000 K using a 3×5×1 supercell (60 atoms), a 3×3×1 supercell (72 atoms) and a 3×3×1 supercell (72 atoms) for γ-As, δ'-As and s/o-As, respectively. Band structures were calculated in the PBE and hybrid functional (HSE06) levels[8]. The simulated STM image was constructed on the basis of Tersoff−Hamann theory[9] and visualized using the p4VASP program[10]. Spin-orbit coupling (SOC) was neglected due to its minor effects on As[11]. The minimum energy pathway (MEP) between different allotropes was determined utilizing transition state theory as formulated in the generalized solid-state nudged elastic band (G-SSNEB) method[12] implemented in the VTST extension of VASP.

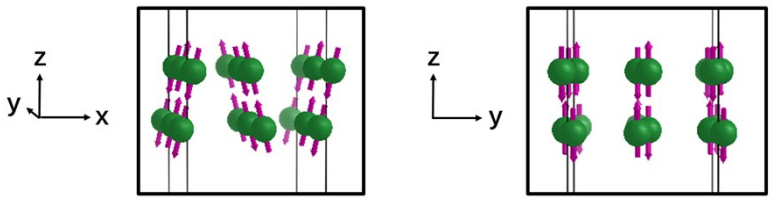
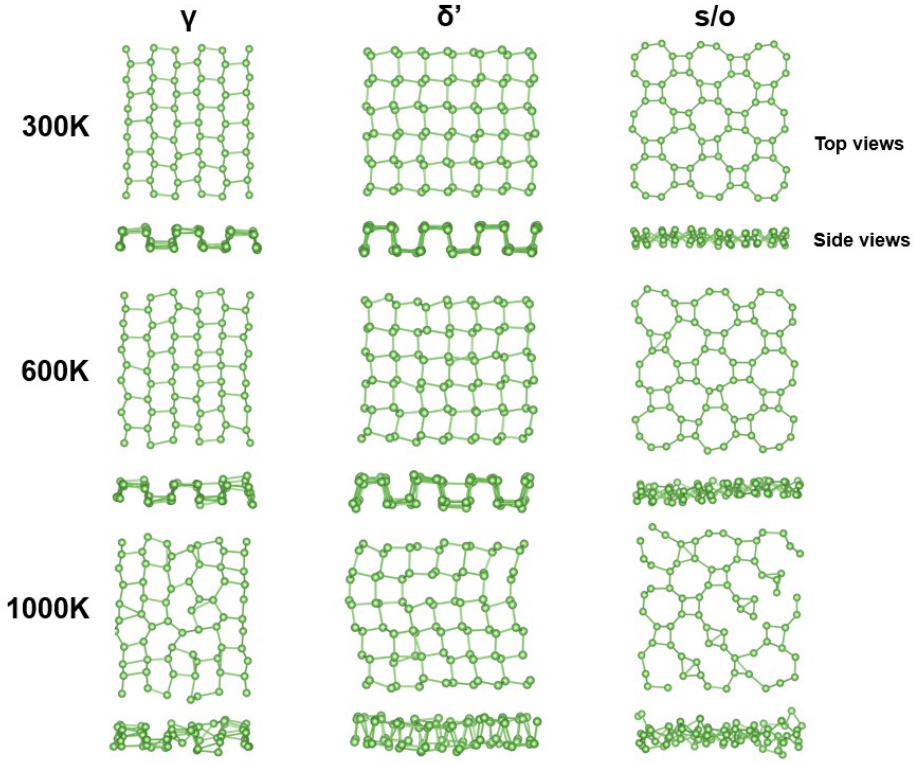
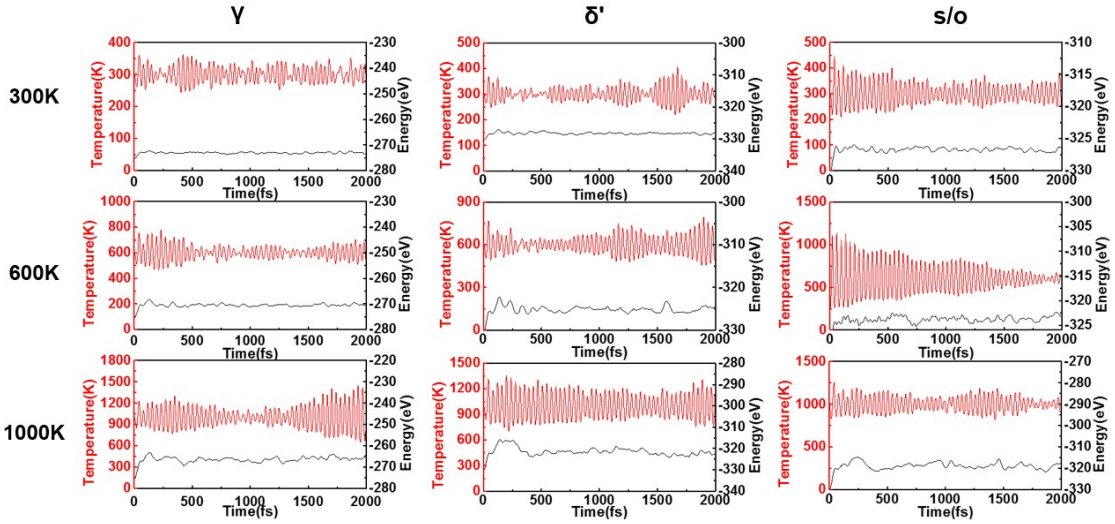


Fig. S1. Phonon vibrational mode of δ-As with imaginary frequency at Γ point.



(a)



(b)

Fig. S2. (a) Snapshots of canonical molecular dynamics simulations of the γ, δ’ and s/o phases at 300 K, 600 K, and 1000 K. (b) Temperature and total energy fluctuations of the γ, δ’, and s/o phases during AIMD simulations.

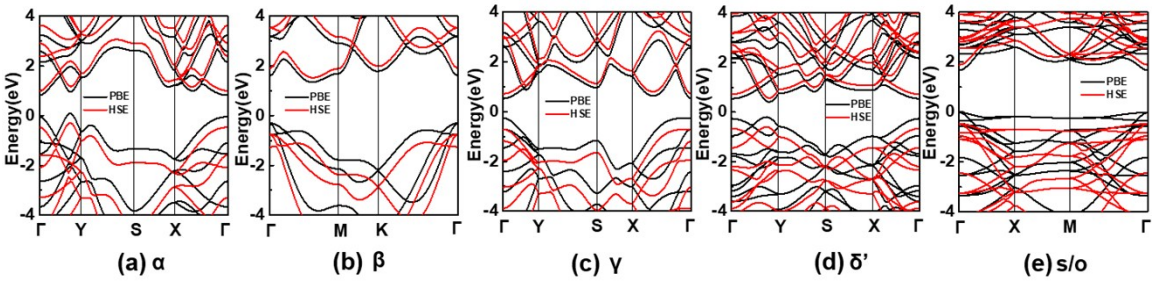
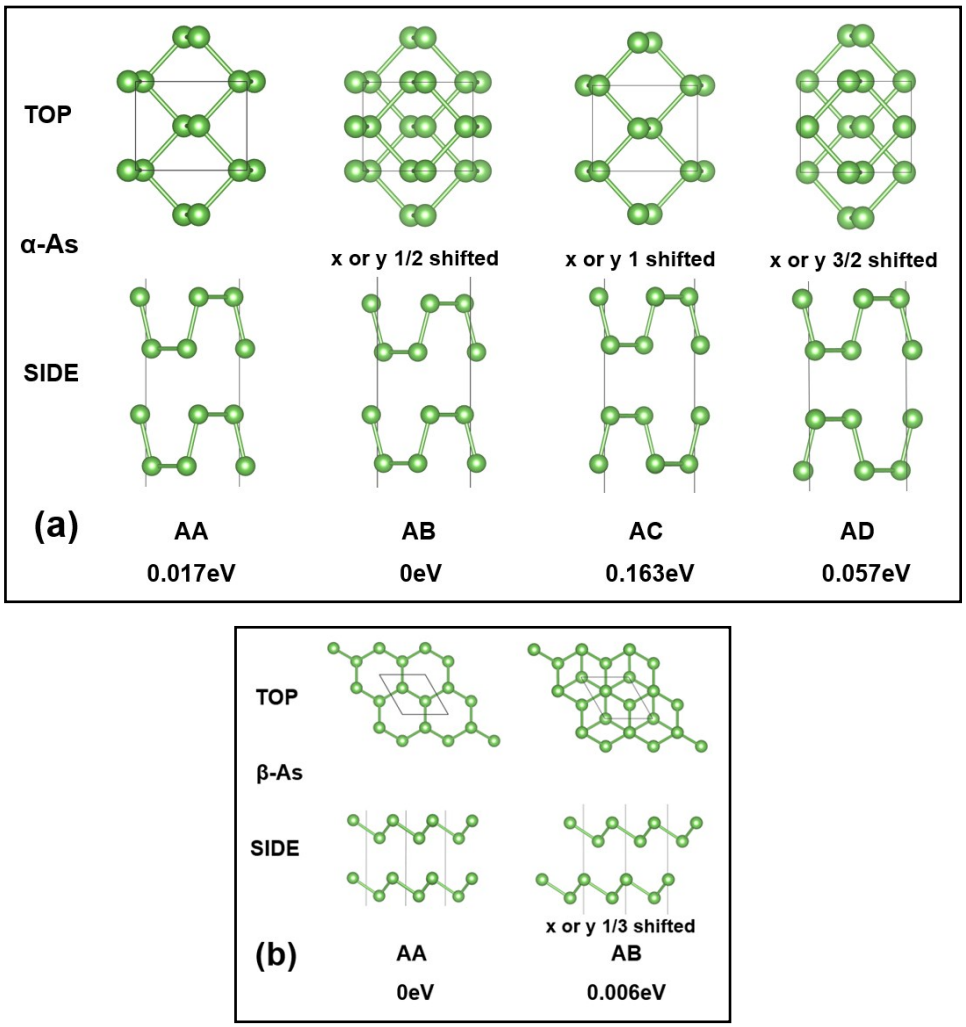
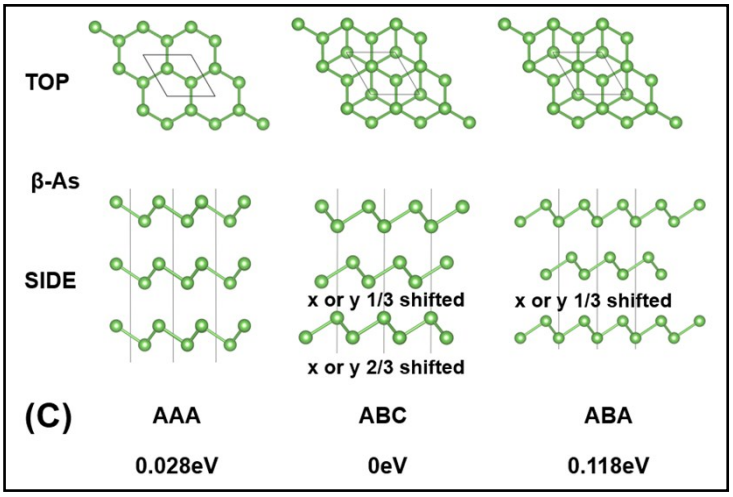
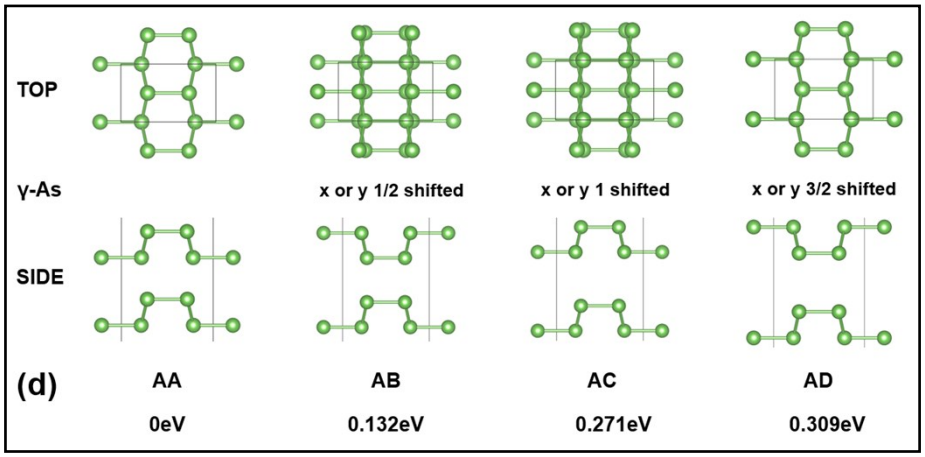
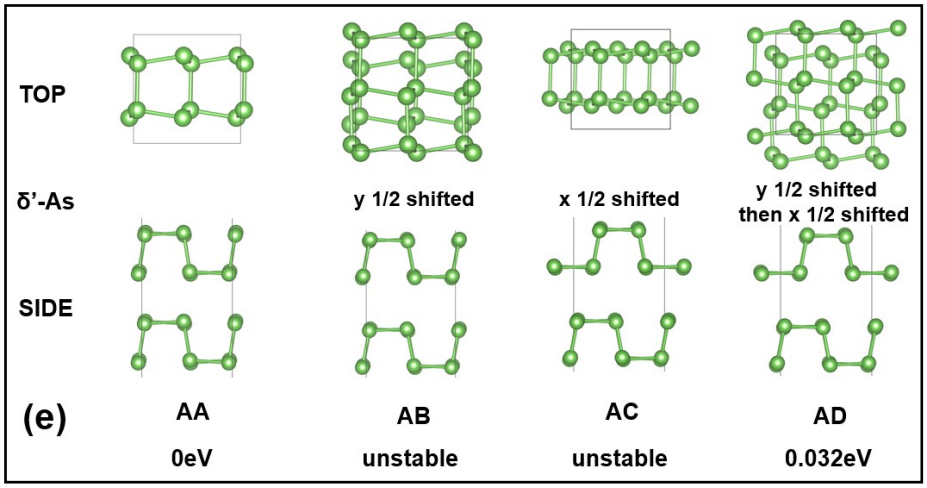


Fig. S3. Band structures of monolayer arsenic allotropes (a) α-As, (b) β-As, (c) γ-As, (d) δ’-As, and (e) s/o-As calculated in the PBE and HSE levels. Fermi levels are shifted to 0 eV.




TOP
β-As
SIDE
x or y 1/3 shifted
x or y 1/3 shifted
x or y 2/3 shifted
(C)
AAA
ABC
ABA
0.028eV
0eV
0.118eV


TOP
γ-As
SIDE
x or y 1/2 shifted
x or y 1 shifted
x or y 3/2 shifted
(d)
AA
AB
AC
AD
0eV
0.132eV
0.271eV
0.309eV


TOP
δ'-As
SIDE
y 1/2 shifted
x 1/2 shifted
y 1/2 shifted
then x 1/2 shifted
(e)
AA
AB
AC
AD
0eV
unstable
unstable
0.032eV

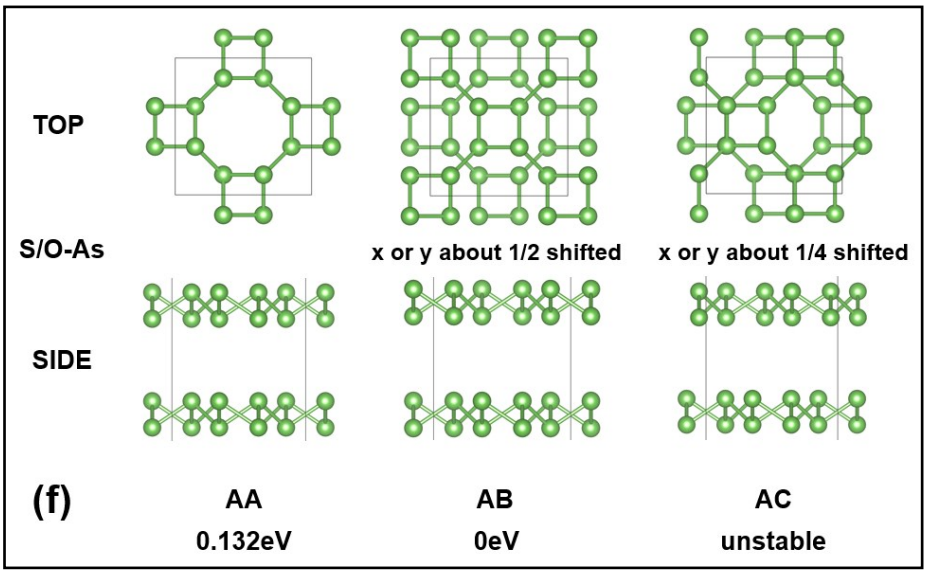


Fig. S4. Top and side views of various stacking orders of bilayer/tri-layer arsenene allotropes; relative energies with respect to the most favorable stacking orders are also given. The unstable stackings transform to other stacking orders after structural optimization.

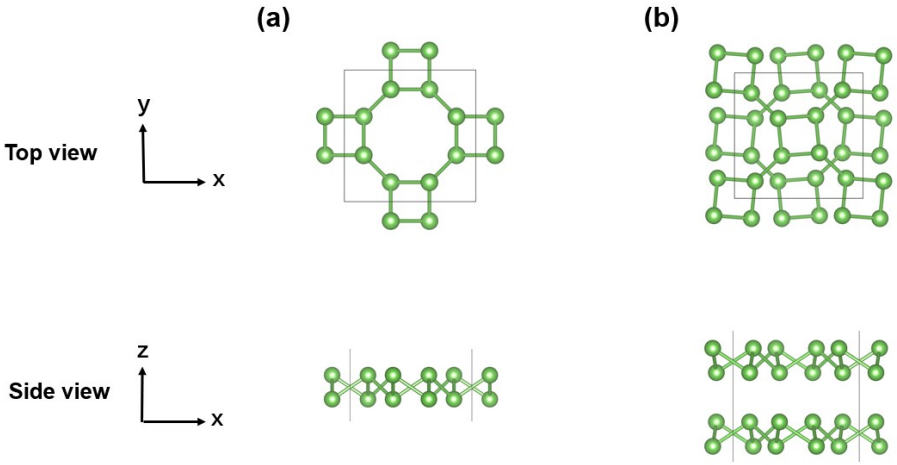


Fig. S5. Top and side views of (a) monolayer s/o-As and (b) bilayer AB stacking s/o-As after structural optimizations.

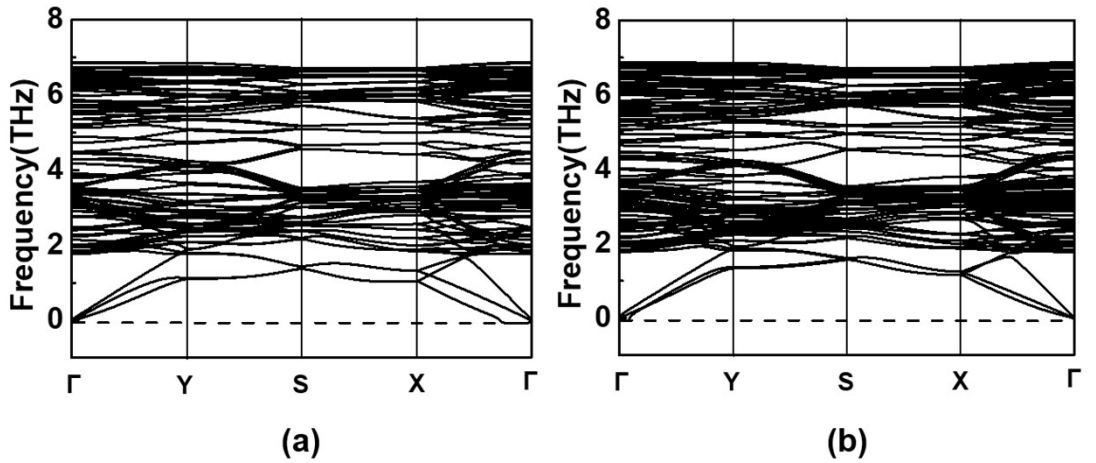


Fig. S6. Phonon dispersions of (a) 4-layer AA stacking δ-As and (b) 5-layer AA stacking δ-As.

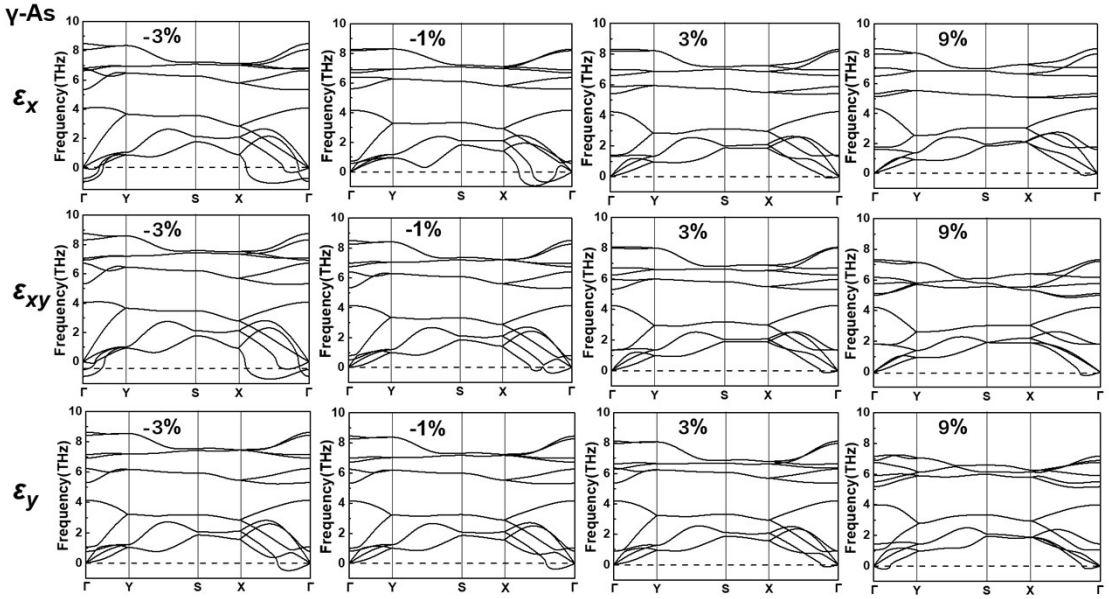


Fig. S7. Phonon dispersions of γ-As under strains. Negative and positive strains represent compressive and tensile strains, respectively.

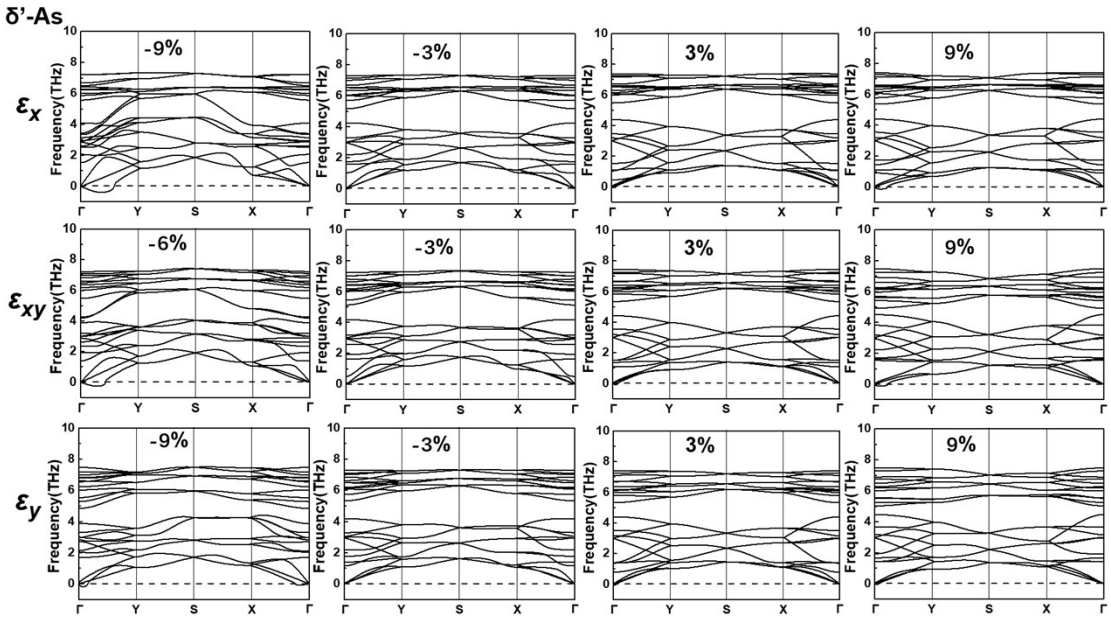


Fig. S8. Phonon dispersions of δ'-As under strains. Negative and positive strains represent compressive and tensile strains, respectively.

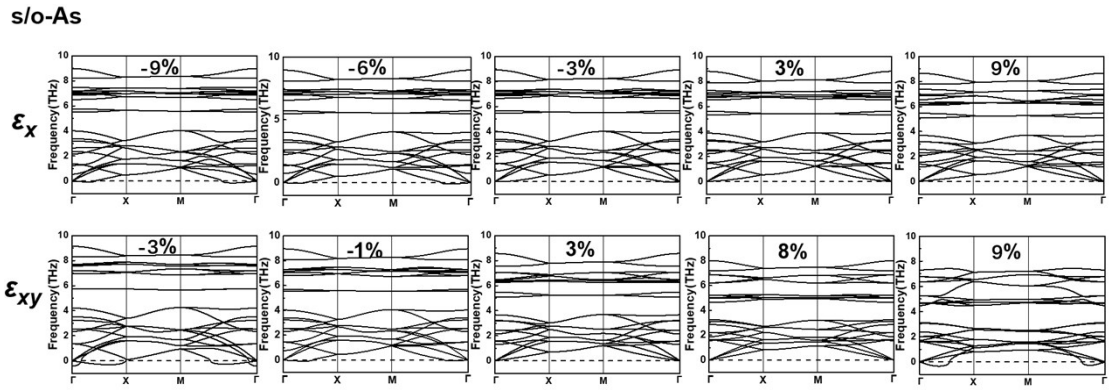


Fig. S9. Phonon dispersions of s/o-As under strains. Negative and positive strains represent compressive and tensile strains, respectively.

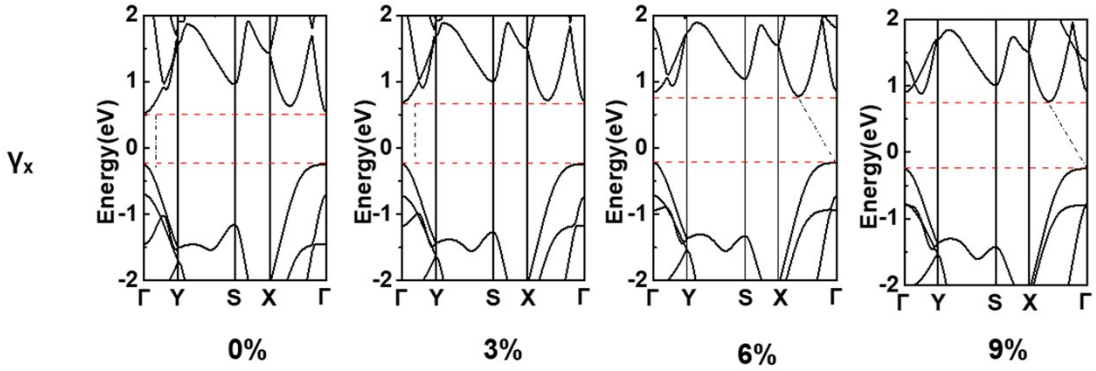
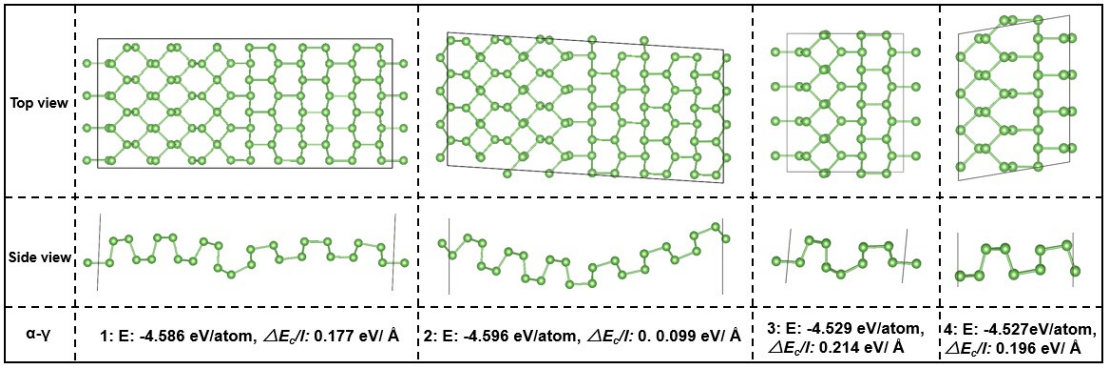
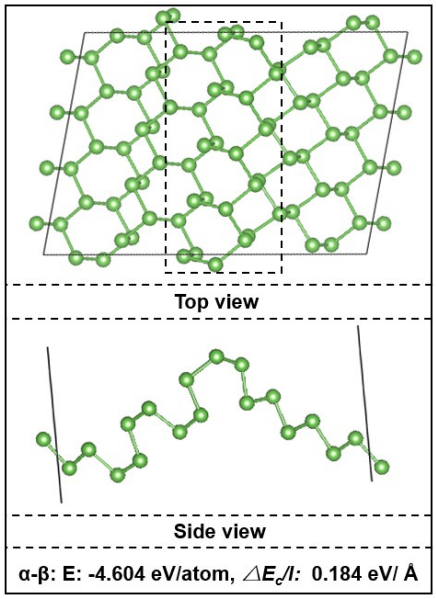


Fig. S10. Band structures of γ-As under different uniaxial *x* tensile strains. Fermi levels are shifted to 0 eV.



(a)



(b)

Fig.S11. Other potential hybridizations of different arsenene allotropes with relatively higher energies.

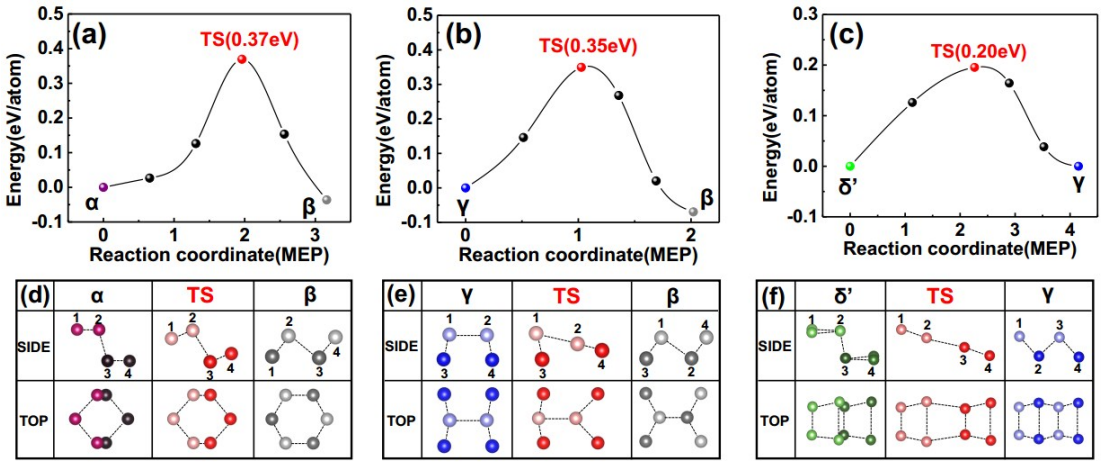


Fig.S12 The calculated transition minimum energy paths (MEP) between (a) α-As and β-As, (b) γ-As and β-As, and (c) δ'-As and γ-As, as determined using VTST[12].

References

1. Kresse, G.; Furthmüller, J., Efficient Iterative Schemes for Ab Initio Total-Energy Calculations Using a Plane-Wave Basis Set. *Phys. Rev. B* **1996**, *54*, 11169-11186.
2. Perdew, J. P.; Burke, K.; Ernzerhof, M., *Generalized Gradient Approximation Made Simple*, *Phys. Rev. Lett* **1996**, *77*, 3865-3868.
3. Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Singh, D. J.; Fiolhais, C., Atoms, Molecules, Solids, and Surfaces: Applications of the Generalized Gradient Approximation for Exchange and Correlation. *Phys. Rev. B* **1993**, *46*, 6671-6687.
4. PE, B., Projector Augmented-Wave Method. *Phys Rev B Condens Matter* **1994**, *50*, 17953-17979
5. Chadi, D. J., Special Points for Brillouin-Zone Integrations. *Phys. Rev. B* **1977**, *16*, 5188--5192.
6. Klime, J. í.; Bowler, D. R.; Michaelides, A., Van Der Waals Density Functionals Applied to Solids. *Phys. Rev. B* **2011**, *83*, 772-772.
7. Togo, A.; Oba, F.; Tanaka, I., First-Principles Calculations of the Ferroelastic Transition between Rutile-Type and $CaCl_2$-Type SiO_2 at High Pressures. *Phys. Rev. B* **2008**, *78*, 134106.
8. Heyd, J.; Scuseria, G. E., Hybrid Functionals Based on a Screened Coulomb Potential. *J. Chem. Phys.* **2003**, *118*, 8207-8215.
9. Tersoff, J.; Hamann, D. R., Theory of the Scanning Tunneling Microscope. *Phys. Rev. B* **1985**, *31*, 805.
10. See (http://www.p4vasp.at/).
11. Pizzi, G.; Gibertini, M.; Dib, E.; Marzari, N.; Iannaccone, G.; Fiori, G., Performance of Arsenene and Antimonene Double-Gate Mosfets from First Principles. *Nat. Commun.* **2016**, *7*, 12585.
12. Sheppard, D.; Xiao, P.; Chemelewski, W.; Johnson, D. D.; Henkelman, G., A Generalized Solid-State Nudged Elastic Band Method. *J. Chem. Phys.* **2012**, *136*, 074103.

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