*Supporting Information*

# Stability and Phase Transition of Metastable Black Arsenic under High Pressure

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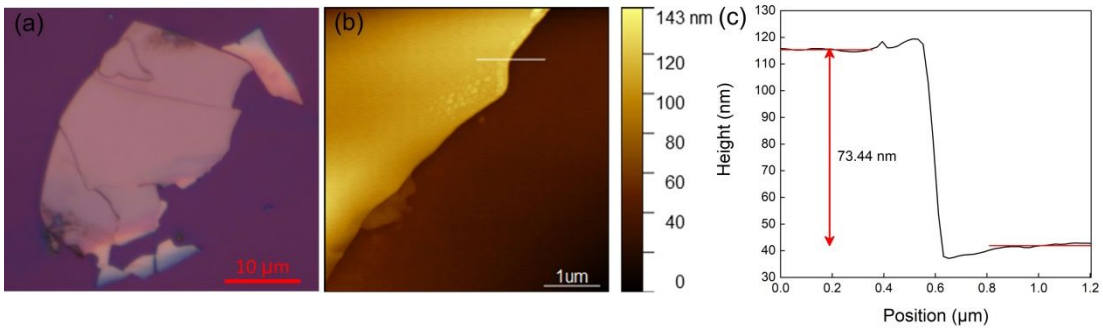


Figure S1. (a) Optical and (b) AFM images of bAs on $SiO_2$/Si substrate. (c) A height profile of bAs measured along the white solid line in (b).

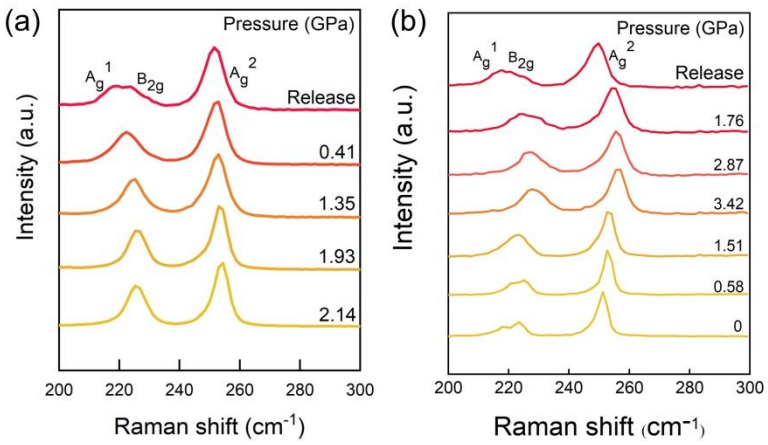


Figure S2. Pressure-dependence of the Raman shift. The pressure is firstly loaded to 2.14 (a) and 3.42 GPa (b), and then slowly released to ambient, respectively.

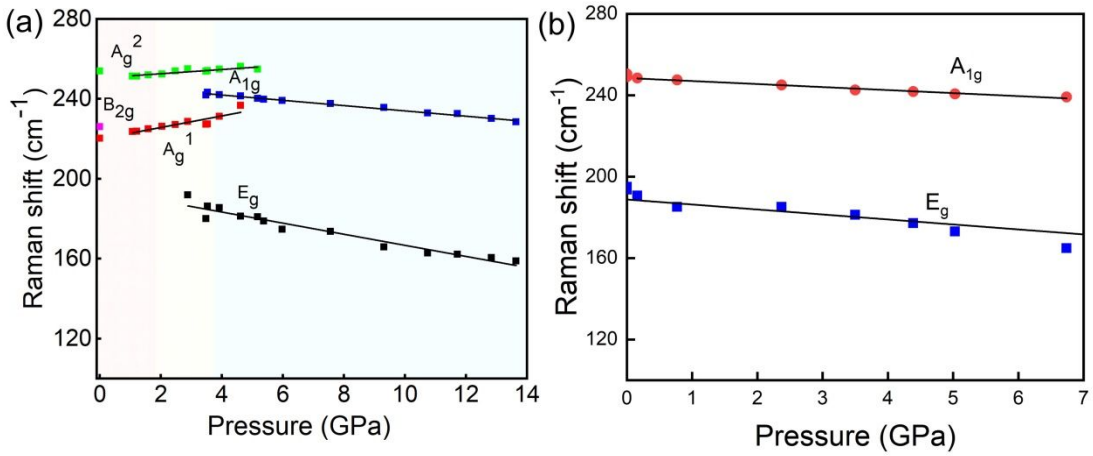


Figure S3. (a) Linear fitting pressure dependence of the Raman shifts for the $A_g^1$ and $A_g^2$ of bAs and the $E_g$ and $A_{1g}$ of gAs shown in figure 3a. (b) The linear fitting pressure dependence for the Raman shifts of $E_g$ and $A_{1g}$ of figure 3c.

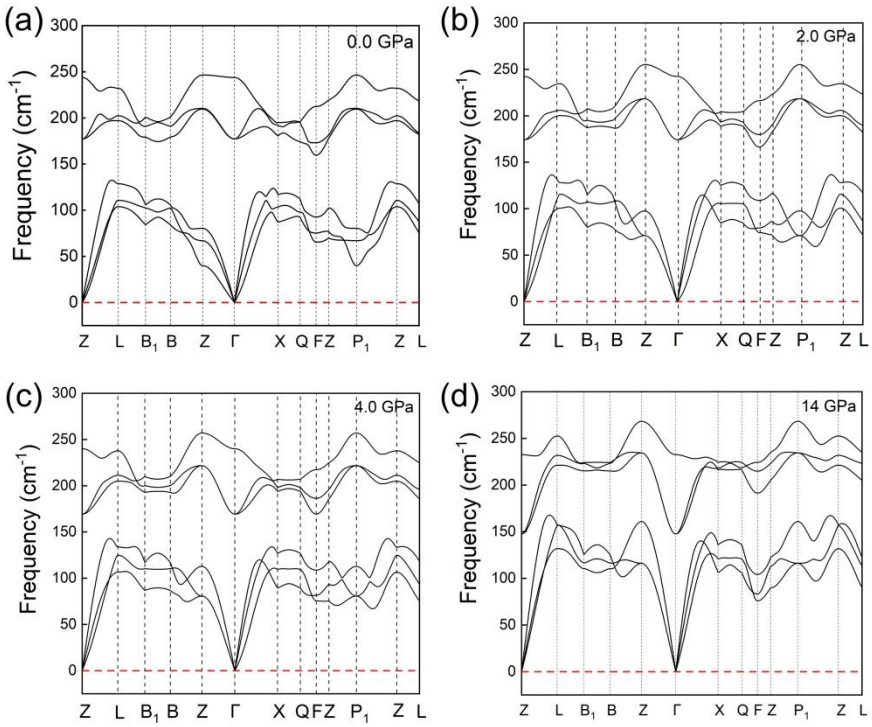


Figure S4. The calculated phonon dispersions for gAs at (a) 0, (b) 2, (c) 4, and (d) 14 GPa.

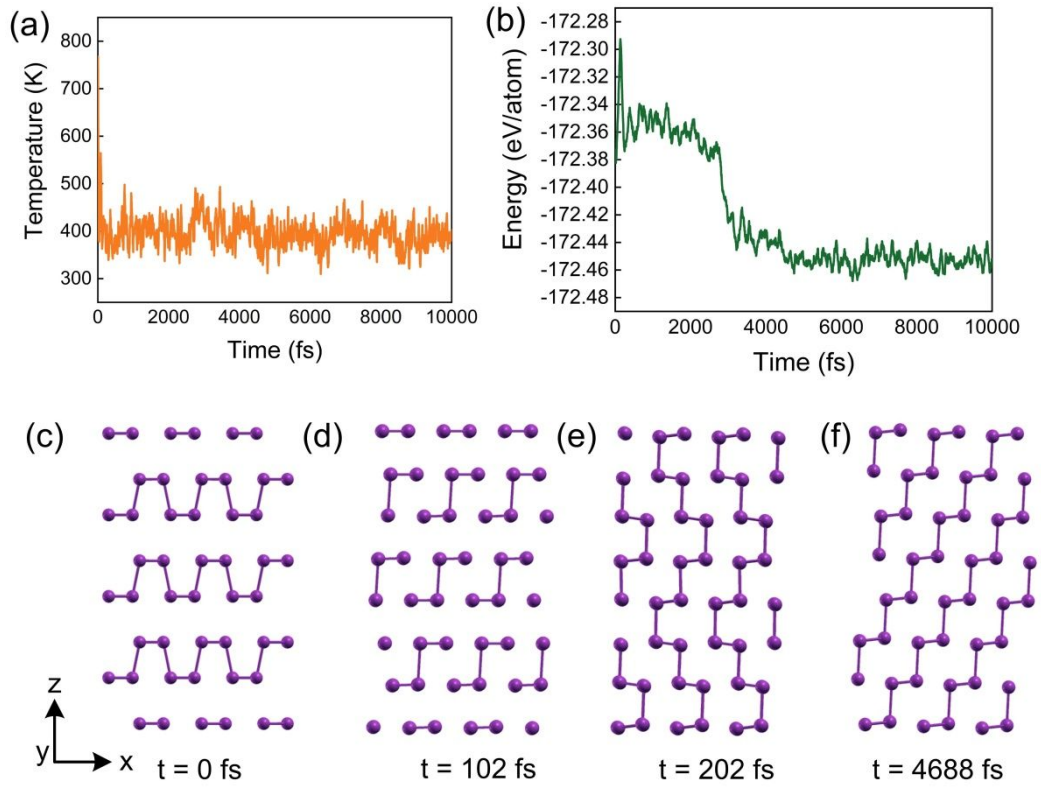


Figure S5. Mechanism and process for the phase transition from bAs to gAs at 5 GPa and 400 K in the *NPT* ensemble. (a) Temperature and (b) potential-energy change in the MD simulations. (c) The initial structure of bAs with a 3×3×2 supercell (t = 0 fs). (d) Structure of the intermediate state for the phase transition process at 102 fs showing intralayer As-As bonds breaking. (e) Structure of the intermediate phase transition state at 202 fs where the interlayer As-As bonds formed and (f) crystal structure after transformation to the gAs phase at 4688 fs.

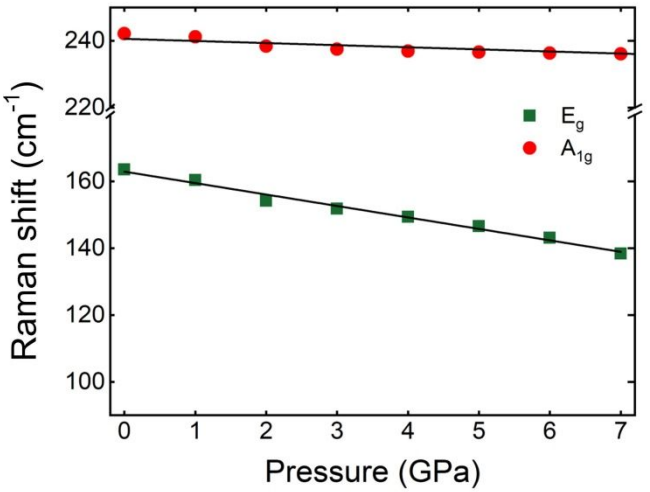


Figure S6. Calculated pressure dependence of the Raman shifts for gAs up to 7 GPa.

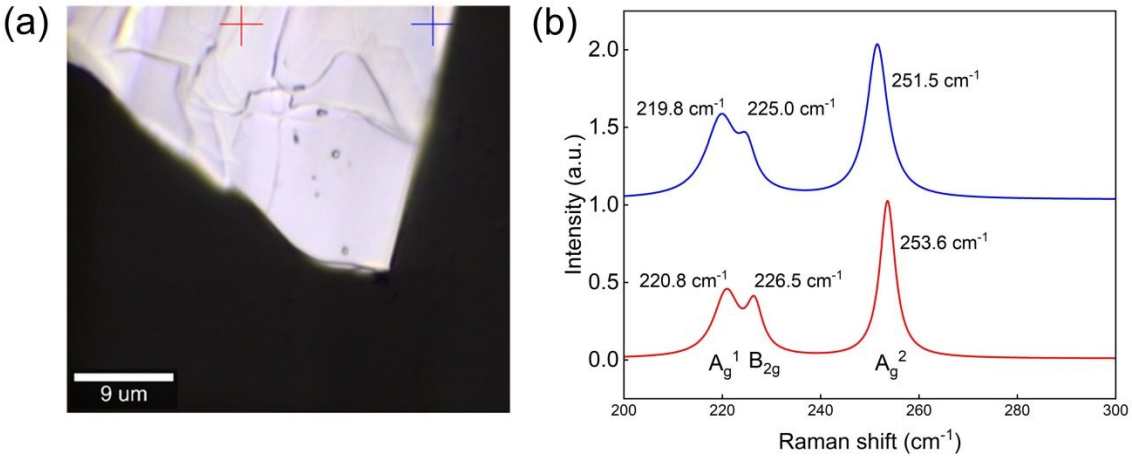


Figure S7. (a) Optical micrograph of the thick bAs sample. (b) Raman spectra for two different points on the sample.