

Supplementary Information for

Ultrafast Diffusive Cross-sheet Motion of Lithium through Antimonene with a 2+1 Dimensional Kinetics

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Supplementary text
Figs. S1 to S6

Other supplementary materials for this manuscript include the following:

Movies S1 to S4

S1. The band structure and details of charge transfer for Li adsorption on antimonene

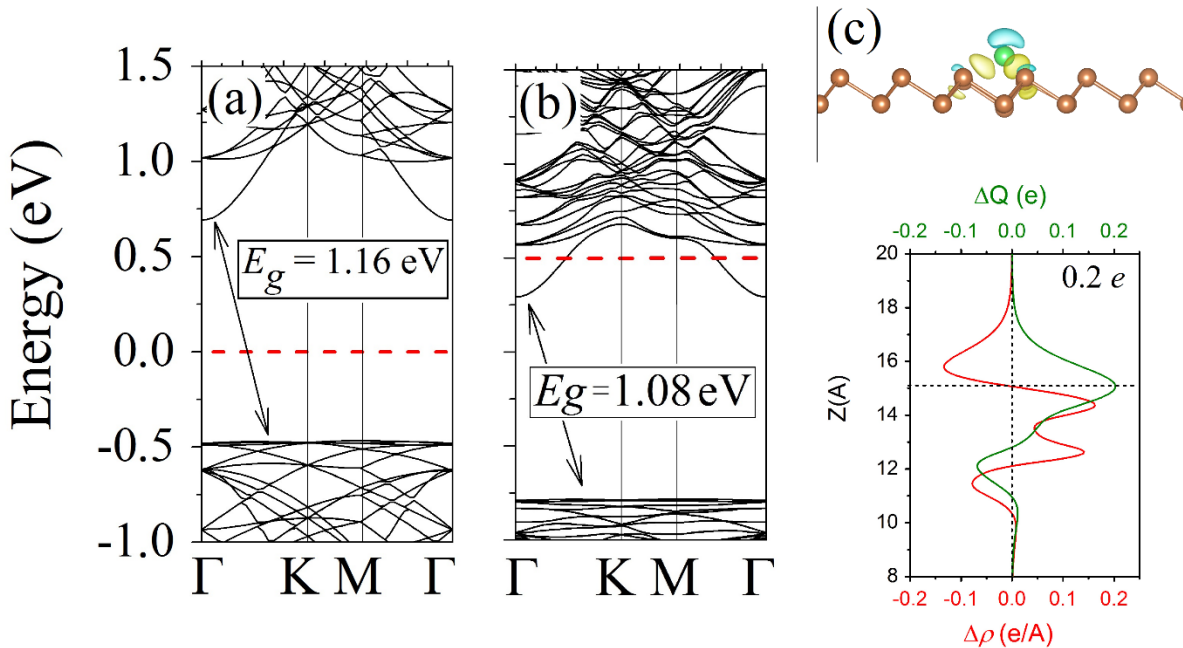


Figure S1. The band structure of (a) pristine and (b) Li-adsorbed antimonene. The red dashed line shows the Fermi level. (c) The upper panel: the atomic structure and the charge redistribution (side views of the 0.02 \AA^{-3} DCD isosurface); the lower panel: the plane-averaged differential charge density $\Delta\rho(z)$ (red line) and the amount of transferred charge $\Delta Q(z)$ (green line) (bottom panel) between the Li atom and antimonene sheet. The Li and Sb atoms are coloured in green and brown, respectively. The yellow (blue) colour denotes depletion (accumulation) of electrons.

S2. The motion of the Li atom through antimonene

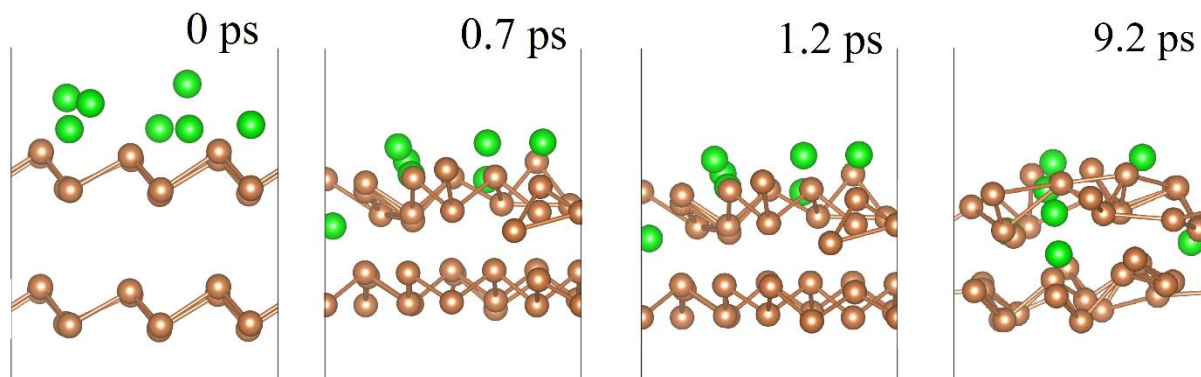


Figure S2. The snapshots of the Li atomic motion on free-standing bilayer antimonene calculated by AIMD at 300 K. The Sb and Li atoms are coloured in brown and green, respectively.

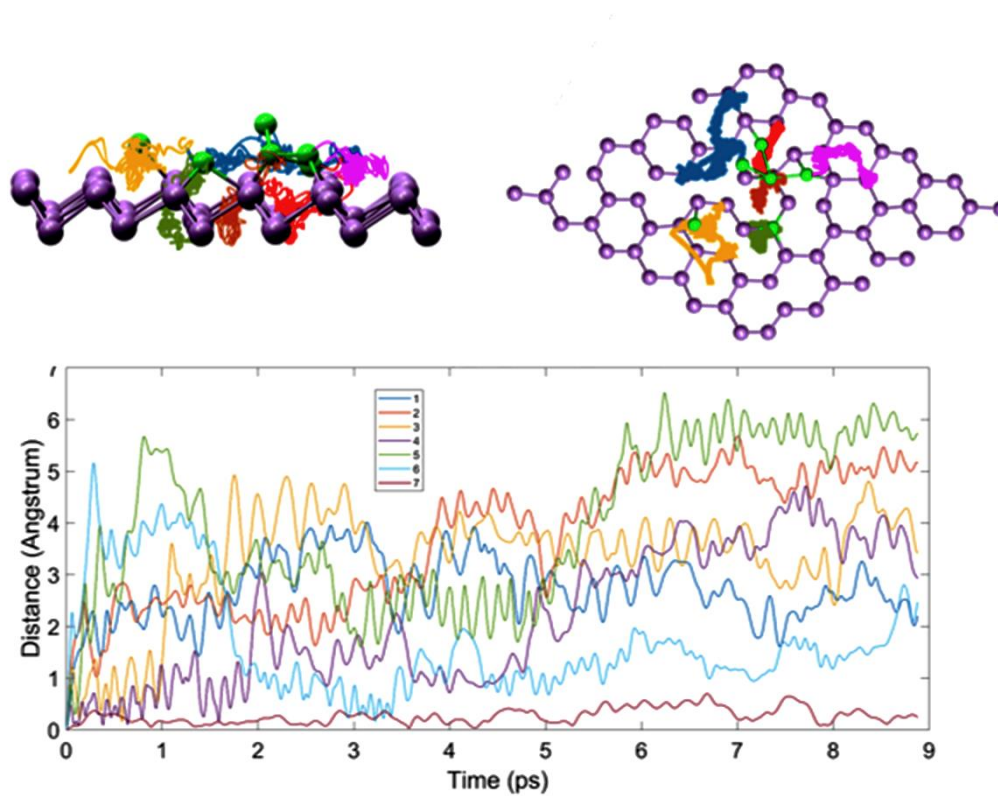


Figure S3. The kinetics of the Li atoms on antimonene by AIMD simulations at 300 K. The cumulative distance as a function of time for Li atoms 1 (red curve), 2 (red curve), 3 (red curve), 4 (red curve), 5 (red curve), and 6 (red curve) on free-standing monolayer antimonene.

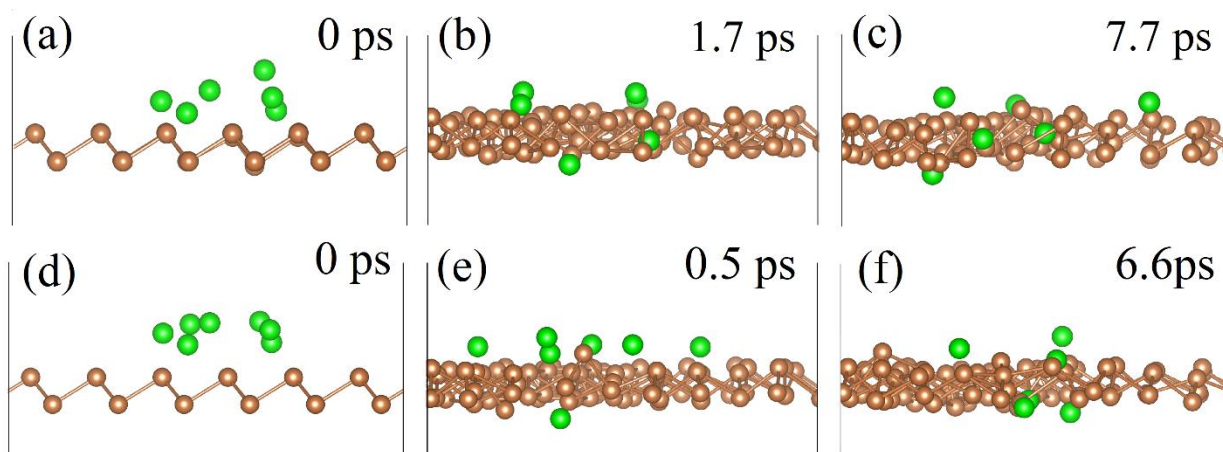


Figure S4. The snapshots of the Li atomic motion on (a)–(c) free-standing and (d)–(f) stretched (tensile strain 4%) monolayer antimonene calculated by AIMD at 300 K. The Sb and Li atoms are coloured in brown and green, respectively.

S3. CE prediction of Li occupation on antimonene

We measured the relative preference of adsorption on these sites based on the site occupancy ratio $O = n_c / n_b$, where n_c and n_b denote the number of occupied hexagonal centre and buckle sites per unit cell, respectively. In the limit of isolated adsorption, $O = 0$ since Li preferentially occupies the buckle site due to its slightly more negative binding energy (Fig. S5).

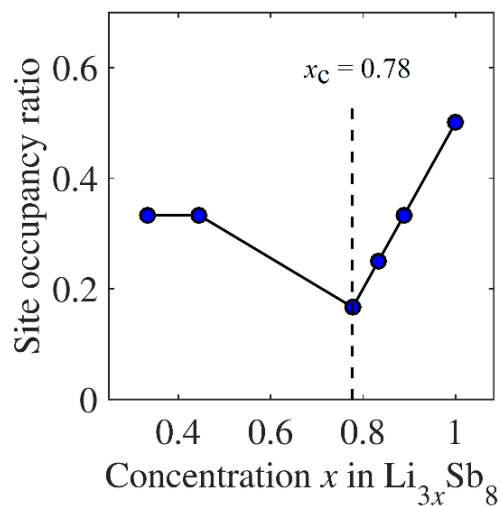


Fig. S5. The site occupation as a function of Li concentration x .

Computational Details.

The adsorption energy E_a of the Li atom on antimonene was calculated as

$$E_a = E_{Sb+Li} - E_{Sb} - E_{Li}, \quad (1)$$

where E_{Sb+Li} , E_{Sb} , and E_{Li} are the energies of the Li-adsorbed antimonene, the isolated antimonene, and the Li atom, respectively.

Charge transfer analysis was conducted by the calculation of the differential charge density (DCD) $\Delta\rho(r)$, which is defined as

$$\Delta\rho(r) = \rho_{Sb+Li}(r) - \rho_{Sb}(r) - \rho_{Li}(r), \quad (2)$$

where $\rho_{Sb+Li}(r)$, $\rho_{Sb}(r)$, and $\rho_{Li}(r)$ are the charge densities of the Li-adsorbed antimonene, the isolated antimonene, and the Li atom, respectively. The exact amount of the charge transfer between the Li atom and the antimonene was calculated by integrating $\Delta\rho(r)$ over the basal plane at the z point for deriving the plane-averaged DCD $\Delta\rho(z)$ along the normal direction z of the sheet. The amount of transferred charge at the z point is given by $\Delta Q(z) = \int_{-\infty}^z \Delta\rho(z') dz'$. Based on the $\Delta Q(z)$ curve, the total number of electrons donated by the Li atom was read at the interface between the Li atom and antimonene where $\Delta\rho(z)$ shows a zero value.

For the differentiation of the characteristics of the kinetic motion of Li atoms, the cumulative distance d_a for the atom a at the i^{th} MD step along the path l_a was calculated as

$$d_a(N_i) = \int_{N_0}^{N_i} dl_a. \quad (3)$$

Cluster expansion method for screening the configurational energy. The lithiation of antimonene was investigated under the cluster expansion (CE) formalism by evaluating the configurational dependence of the structural energies with the aid of DFT calculations. In combination with DFT-based calculations, CE technique serves as a well-established tool for the

prediction of intermediate ground states of multicomponent alloys with different compositions. The surface adsorption of lithium adatoms on antimonene is analogous to the case of binary alloys, whereby two pure components – lithium (Li) and vacancies (V) – are present in variable fractions across pre-allocated adsorption sites on a spectator substrate of antimonene. Since each adsorption site may either be occupied or vacant, the concentration x of lithium can be expressed as $\text{Li}_x\text{V}_{1-x}$, where $0 \leq x \leq 1$. Furthermore, occupation variables σ_i are defined to take on discrete value of +1 or –1 depending on whether the i^{th} adsorption site is Li- or V-occupied, respectively. In its essence, the CE formalism involves the parametrization of the total energy (per atom) E for any given configuration of Li and V of arbitrary concentration in terms of the occupation variables $\sigma = \{\sigma_1, \sigma_2, \dots, \sigma_n\}$, as $E(\sigma) = \sum_{\alpha} m_{\alpha} J_{\alpha} \langle \prod_{i \in \alpha'} \sigma_i \rangle$. Here, a summation was performed over a set of α -type symmetry-inequivalent cluster configurations of sites i (i.e. pairs, triplets, etc.) and the occupational product was averaged over all α -equivalent clusters, known as α' -type clusters. The multiplicities of α -type clusters are denoted by m_{α} , while J_{α} refers to its corresponding effective cluster interaction (ECI). The ECIs are determined from a fit of $E(\sigma)$ to a training dataset of DFT-calculated energies for various Li-antimonene configurations. The cross-validation (CV) score provides a progressive assessment of the predictive capability of the cluster expansion and was given by

$$CV = \left(\frac{1}{n} \sum_{i=1}^n (E_i^{\text{DFT}} - E_{(i)}^{\text{CE}})^2 \right)^{1/2}, \quad (4)$$

where E_i^{DFT} is the DFT-calculated energy of structure i and $E_{(i)}^{\text{CE}}$ is the CE-predicted energy of the same structure from a least-squares fit of $(n-1)$ structural energies without including the contribution of E_i^{DFT} . The cluster expansion (with ECIs known) was employed in the ground state search by finding the most energetically favourable configuration at different Li concentrations x based on the formation energy E_f , as

$$E_f = E_{\text{Li}_x\text{V}_{1-x}} - (xE_{\text{Li}_1\text{V}_0} + (1-x)E_{\text{Li}_0\text{V}_1}) \quad (5)$$

where $E_{\text{Li}_1\text{V}_0}$ and $E_{\text{Li}_0\text{V}_1}$ refer to the total energies of fully lithiated and pristine antimonene, respectively.

Discrete geometry analysis.

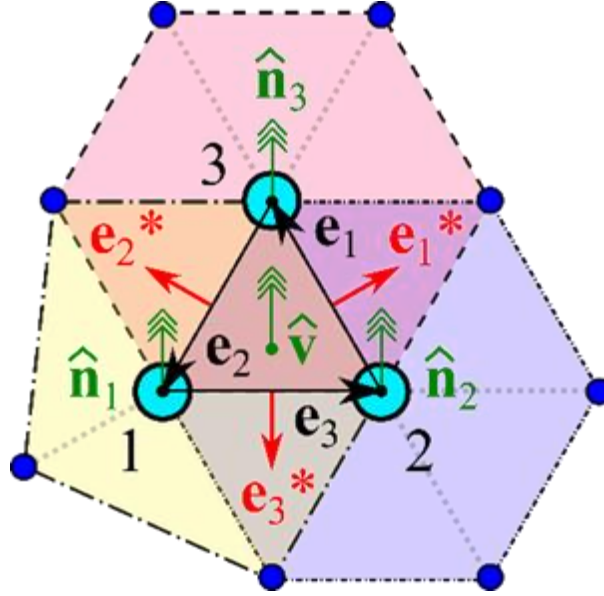


Figure S6. Schematic representation of a 2D lattice (top view) containing a triangulated element defined by the atoms $p = 1, 2,$ and 3 (cyan), and all other nearest-neighbour atoms (blue). The in-plane vectors e_p (black) and e_{p^*} (red) are denoted by single arrowheads, while the surface normal vectors \hat{n}_p (green) and \hat{v} (green) are indicated using multiple arrowheads. Dashed lines specify the boundary of the polygon enclosure for each atom p .

S4. Brief legend for supporting movies

movie S1: Li diffusion on freestanding bilayer antimonene (no strain).

movie S2: Li diffusion on freestanding monolayer antimonene (no strain).

movie S3: Li diffusion on stretched monolayer antimonene.

movie S4: AIMD calculations for the stability of Li-adsorbed antimonene structure (Li_3Sb_8) obtained by the cluster expansion method.