
Supplementary information

Engineering interfacial thermal conductance across BAs/Epoxy boundaries via surface termination control and covalent bridging

Haoqiang Ai, Xiaohan Song, Liyin Feng, Hao Zhou, Luqin Hong, Zheng Cui, Ruiqiang Guo

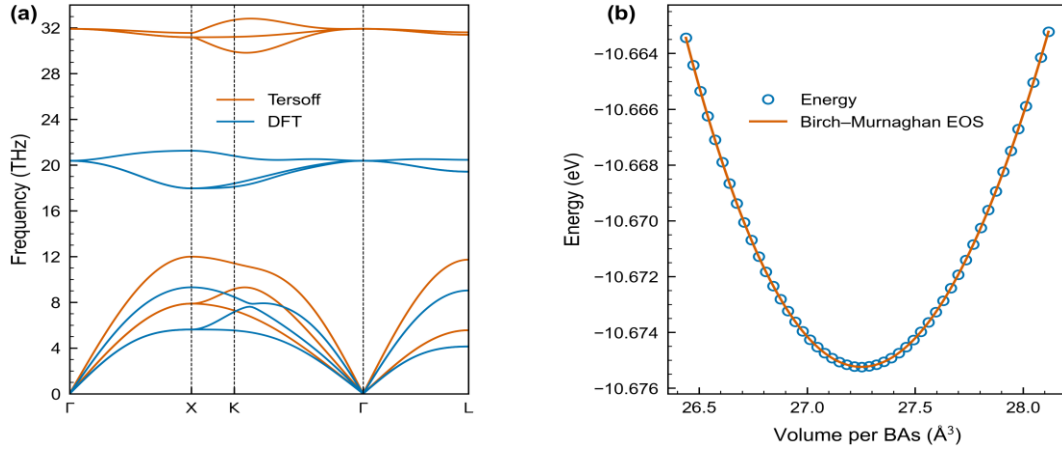


Figure S1. Validation of the BAs Tersoff potential. (a) Phonon dispersion along high-symmetry paths (Γ -X-K- Γ -L) of the Brillouin zone: Tersoff potential (solid lines) vs. DFPT reference (dashed lines). (b) Energy-volume relationship fitted to the third-order Birch-Murnaghan equation of state.

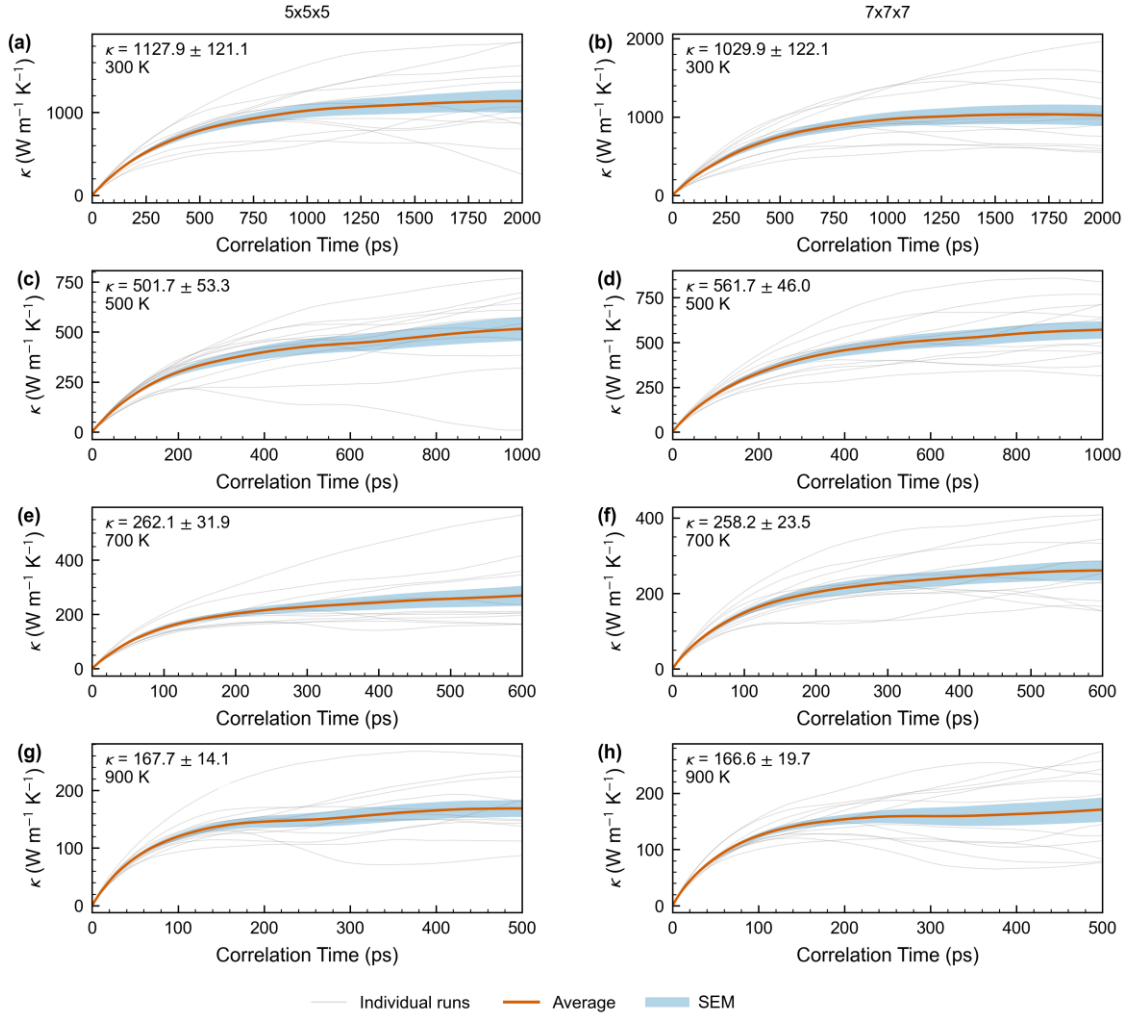


Figure S2. EMD thermal conductivity convergence analysis for bulk BAs at four temperatures (300, 500, 700, 900 K) and two supercell sizes ($5 \times 5 \times 5$, $7 \times 7 \times 7$). Gray curves are individual trajectories, the orange curve is the ensemble average, and the blue band represents the standard error of the mean (SEM).

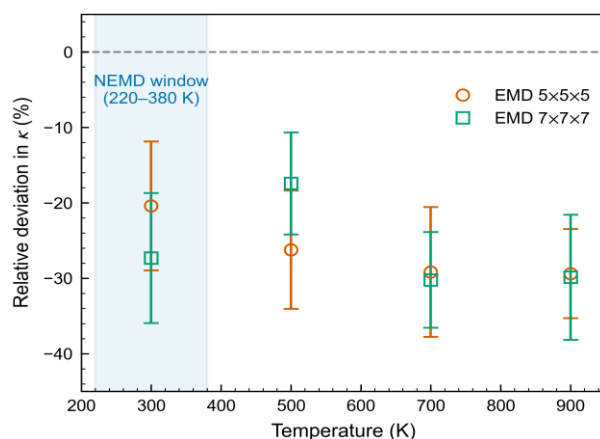


Figure S3. Relative deviation of the EMD thermal conductivity of bulk BAs from the first-principles reference (Feng *et al.*) as a function of temperature. The shaded region marks the 220–380 K temperature window of the interfacial NEMD simulations, and error bars represent the standard error of the mean.

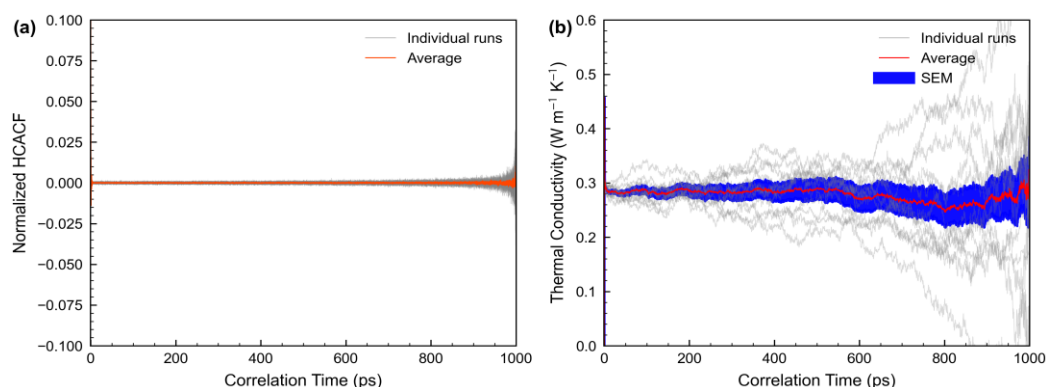


Figure S4. EMD thermal conductivity analysis of the cross-linked epoxy resin (DGEBF/DETDA) at 300 K. (a) Normalized HCACF. (b) Running thermal conductivity (Green-Kubo integral) as a function of correlation time. The correlation length is 1 ns. Gray curves are individual trajectories, the red curve is the average, and the blue band represents the standard error of the mean (SEM).

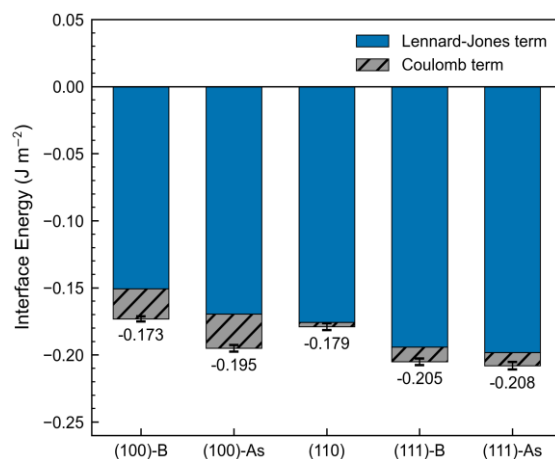


Figure S5. Interface energies of the five pristine BAs/epoxy interfaces. Each bar is stacked by the Lennard-Jones contribution (base segment) and the Coulomb contribution, both negative, with the total value annotated, and error bars represent the standard deviation over 30 snapshots.

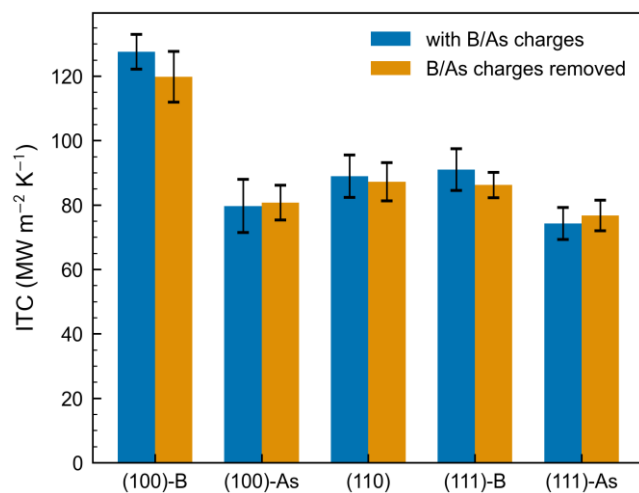


Figure S6. ITC of the five pristine interfaces. Blue bars are results of the full force field, and orange bars are results of the charge-removal control in which the B and As charges are set to zero, averaged over ten independent trajectories, and error bars represent the standard deviation.

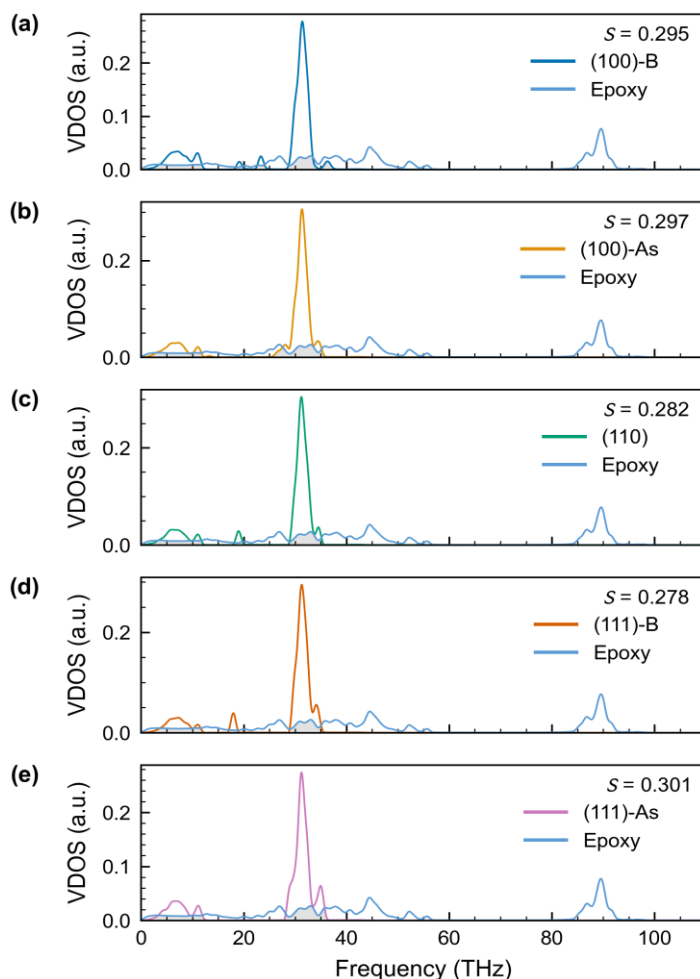


Figure S7. Normalized vibrational density of states (VDOS) at five pristine BAs/epoxy interfaces: (a) (100)-B, (b) (100)-As, (c) (110), (d) (111)-B, (e) (111)-As. The correlation factor S is annotated in each subplot.

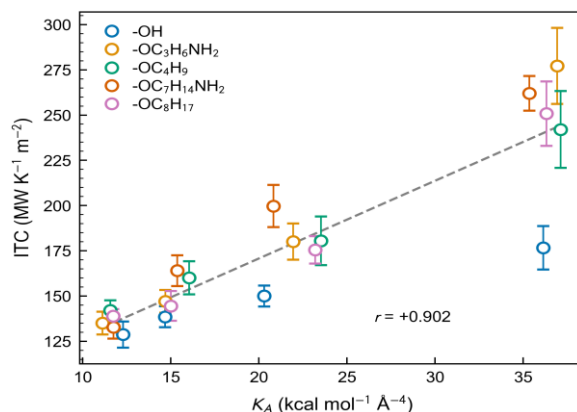


Figure S8. ITC versus the interfacial coupling stiffness K_A for the twenty functionalized BAs(100)-B/epoxy interfaces, color-coded by molecular species. Error bars represent the standard error of the mean from ten independent NEMD trajectories, and the dashed line is a linear fit.

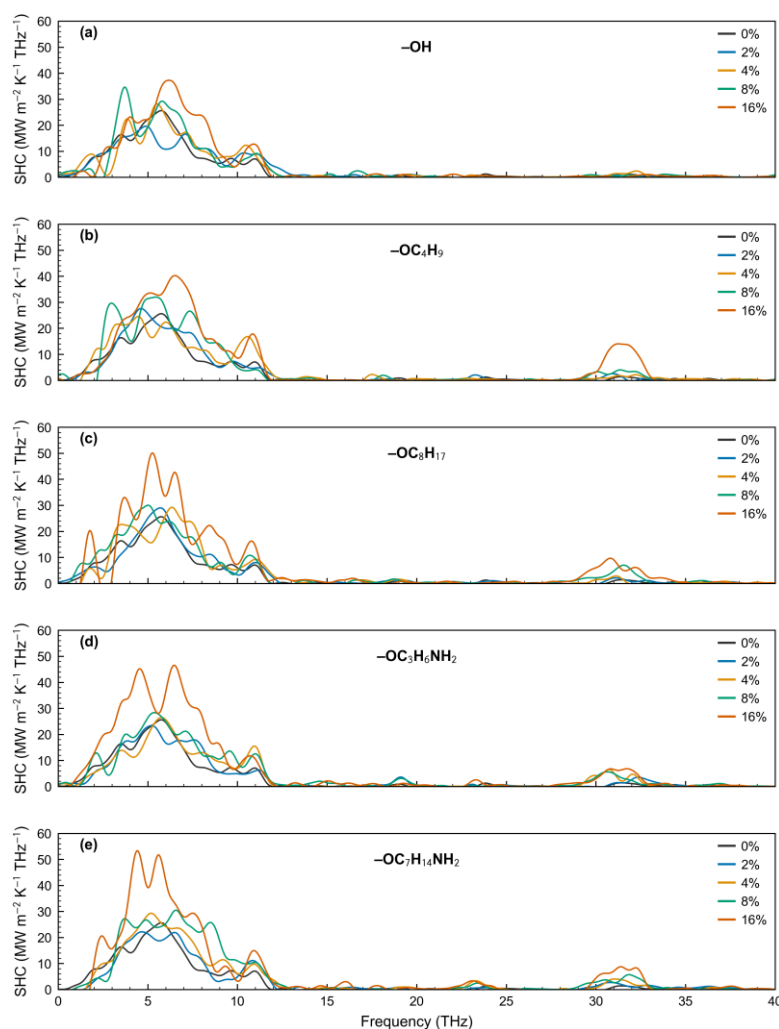


Figure S9. Spectral heat conductance (SHC) as a function of frequency for five functional molecules at different coverages on the BAs (100)-B/epoxy interface. Each panel corresponds to one functional group: (a) -OH, (b) -OC₄H₉, (c) -OC₈H₁₇, (d) -OC₃H₆NH₂, (e) -OC₇H₁₄NH₂. Black solid lines represent the pristine interface (0%); colored curves correspond to 2%, 4%, 8%, and 16% coverages.

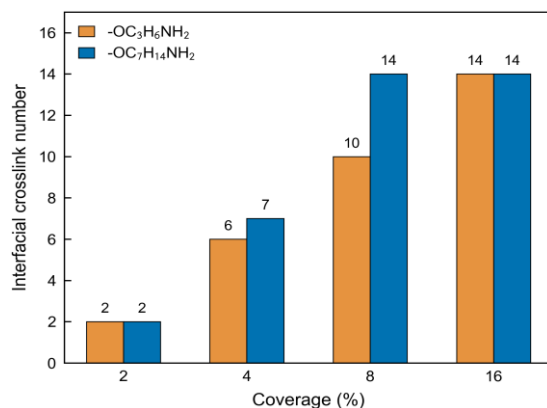


Figure S10. Number of interfacial cross-links between aminoalkoxy-functionalized BAs (100)-B surfaces and the epoxy matrix as a function of coverage. Orange: -OC₃H₆NH₂; blue: -OC₇H₁₄NH₂.

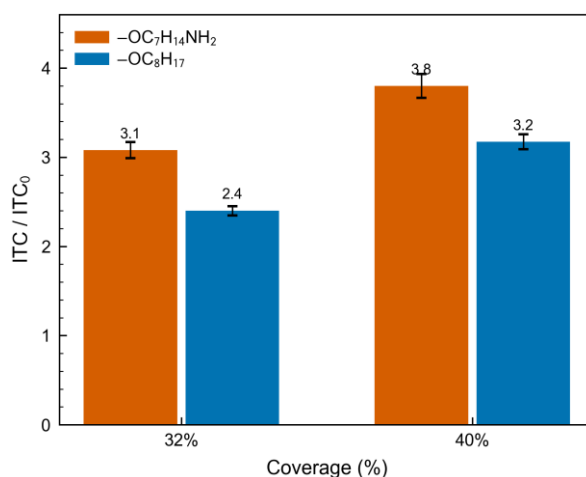


Figure S11. Normalized ITC of the functionalized interfaces at 32% and 40% coverage, referenced to the pristine (100)-B interface. Error bars represent the standard error of the mean from ten independent NEMD trajectories.

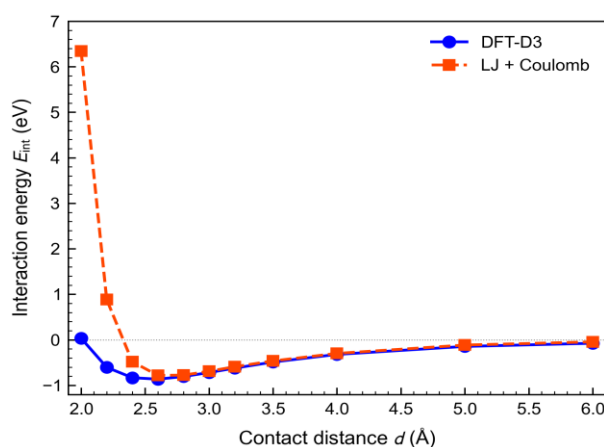


Figure S12. Interaction energy between a DGEFB molecule and the BAs(100)-B surface as a function of the contact distance, obtained by rigid scans with DFT-D3 and with the force field used in this work. The interaction energy is referenced to the isolated state at a contact distance of 12.0 Å, and the adsorption energy is read from the minimum of each curve.

Table S1. Acoustic-branch contribution to the interfacial thermal conductance (ITC) of the five pristine BAs/epoxy interfaces, expressed as a percentage of the total ITC.

Interface	SHC fraction in the acoustic-branch frequency range (%)
(100)-B	95.9
(100)-As	98.9
(110)	97.5
(111)-B	93.5
(111)-As	99.0

Table S2. Acoustic-branch contribution to the interfacial thermal conductance of the functionalized BAs(100)-B/epoxy interfaces at coverages from 2% to 16%, expressed as a percentage of the total ITC.

Molecule	0% (pristine)	2%	4%	8%	16%
-OH	95.9	92.3	96.4	95.9	98.2
-OC ₄ H ₉	95.9	94.5	92.2	93.3	86.1
-OC ₈ H ₁₇	95.9	92.7	96.1	89.2	84.1
-OC ₃ H ₆ NH ₂	95.9	92.0	90.5	86.9	89.2
-OC ₇ H ₁₄ NH ₂	95.9	91.5	92.2	91.7	87.1

To assess the ability of the Tersoff potential to describe BAs surfaces quantitatively, we constructed slab models of the five low-index terminations, in which the upper and lower ends of the slab are terminated by the same atomic species, with a vacuum of 15 Å on each side. The slab and the bulk energy reference were both constructed at the equilibrium lattice constant of the potential itself. For each surface, two initial configurations were adopted, namely the ideal cleaved surface and a randomly perturbed one. The middle three atomic layers were fixed to mimic the bulk environment, and the atoms at the two ends were fully relaxed by energy minimization. The surface energy was calculated using the same definition as Ref. [1],

$$\gamma = \frac{E_{\text{slab}}^{\text{relax}} - NE_{\text{bulk}}}{2A}, \quad (\text{S1})$$

where $E_{\text{slab}}^{\text{relax}}$ is the total energy of the relaxed slab, N is the number of atoms in the slab, E_{bulk} is the energy per atom of bulk BAs computed with the same Tersoff potential, A is the in-plane area of the slab, and the factor of 2 arises from the two surfaces terminated by the same atoms at the upper and lower ends of the slab. The resulting surface energies of the five surfaces are listed in Table S3. The Tersoff values range from 4.6 to 8.1 J m⁻² and are systematically higher than the DFT values^[1], with an average overestimation of about two to three times. This deviation is consistent with the parameterization of the potential, in which the BAs Tersoff parameters were

fitted only to bulk properties without including any surface information^[2]. The absolute values of the BAs surface energies calculated with the Tersoff potential are therefore not accurate.

Table S3. Surface energies of the five low-index BAs surfaces obtained with the Tersoff potential in this work, together with the DFT values reported by Chen *et al.*^[1] (in units of J m⁻²).

Surface	γ (this work, Tersoff)	γ (DFT) ^[1]
(100)-B	4.57	1.99
(100)-As	6.92	3.00
(110)	4.72	2.18
(111)-B	4.96	2.21
(111)-As	8.10	2.37

To further assess the ability of the Tersoff potential to describe the structure of BAs surfaces, we examined the surface reconstruction of the (100)-B and (111)-B terminations. The calculations used the same slab models as the surface energy calculations described above, in which the upper and lower ends of the slab are terminated by the same atomic species, the middle three atomic layers were fixed, and the atoms at the two ends were fully relaxed. For each termination, two initial configurations were adopted, namely the ideal cleaved surface and a randomly perturbed one. The DFT reference calculations were performed with VASP using the PBE functional, a plane wave cutoff energy of 420 eV, and a 4×4×1 k point mesh. Both methods produced B–B dimers formed by pairs of B atoms exposed on the outermost surface, and this reconstruction pattern is consistent with the B-terminated surface reconstruction reported in Ref. [1]. The dimer bond lengths given by DFT are 1.64 Å for the (100)-B termination and about 1.7 Å for the (111)-B termination. The dimer bond lengths given by the Tersoff potential are 2.08 Å and 2.15 Å, respectively. The dimer bond lengths obtained with both methods are much shorter than the nearest neighbor B–B distance of about 3.4 Å in the bulk, indicating that the Tersoff potential qualitatively reproduces the dimer reconstruction of the exposed B atoms.

To assess the accuracy of the classical force field used in this work for the nonbonded interactions between BAs and epoxy, we compared it with DFT calculations including the D3 dispersion correction^[3]. The comparison system was the adsorption of a DGEBF molecule on the BAs(100)-B surface. DGEBF is the monomer component of the epoxy network, and its interaction with the BAs surface is exactly the cross interface interaction described by the LJ and Coulombic terms in the interfacial simulations. The calculation adopted a rigid scan, in which the molecule was translated along the surface normal to 11 contact distances between 2.0 and 6.0 Å, and an isolated reference state was defined at a contact distance of 12.0 Å. At each position, a

single point calculation was performed with DFT-D3 and with the force field used in this work, and the interaction energy was defined as the energy at that position minus the energy of the reference state. As shown in Figure S12, both curves exhibit a typical adsorption well. The minimum of the DFT-D3 curve is located at 2.57 Å with an adsorption energy of -0.87 eV, and the minimum of the force field curve is located at 2.70 Å with an adsorption energy of -0.82 eV. The well depth is shallower by about 6% and the equilibrium distance is longer by 0.13 Å, and the two curves agree well in the well region and at intermediate distances. The two curves differ noticeably only in the strongly repulsive short range region, whereas the molecules in the interfacial simulations always stay near the equilibrium position at the bottom of the adsorption well, so this difference does not affect the well region interaction on which the simulations rely. These results indicate that the force field provides an acceptable description of the well region parameters that determine the interfacial binding and heat transfer.

References

- [1] Z. Chen, J. Zhao, L. Yin, Z. Chen, B-terminated (111) polar surfaces of BP and BAs: promising metal-free electrocatalysts with large reaction regions for nitrogen fixation, *J. Mater. Chem. A* 7 (2019) 13284–13292. <https://doi.org/10.1039/C9TA01410A>.
- [2] F. Benkabou, C. Chikr. Z, H. Aourag, P.J. Becker, M. Certier, Atomistic study of zinc-blende BAs from molecular dynamics, *Phys. Lett. A* 252 (1999) 71-76. [https://doi.org/10.1016/s0375-9601\(99\)80004-8](https://doi.org/10.1016/s0375-9601(99)80004-8).
- [3] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu, *J. Chem. Phys.* 132 (2010) 154104. <https://doi.org/10.1063/1.3382344>.