

Electronic supplementary information

Enhancing interfacial thermal conductance of Si/PVDF by strengthening atomic couplings

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ESI 1. Structures details

The inorganic/organic material interface formed by PVDF and Si is shown in Fig. 1(a)-(f). The left and right silicon layers are face-centered cubic in the direction of [001] from left to right, and the left and right sides each contain 20 layers of silicon atoms with a cross-sectional area of $2.6 \text{ nm} \times 2.6 \text{ nm}$. PVDF is placed in the middle of two silicon substrates. The interface structure is sufficiently large to include most of the important phonon modes contributing to the interfacial thermal transport and thus can exclude the size effect¹.

The intrinsic silicon (In-Si) is structured, as shown in Fig. 1(a)-(c). To study the roles of hydroxyl groups in the interfacial heat transfer, the modified silicon (Mod-Si) surfaces facing PVDF are structured, as shown in Fig. 1(d)-(f). PVDF arrays are constructed by aligning 60 straight PVDF chains and placed in the middle of two silicon substrates, as shown in Fig. 1(a), (b), (d), and (e). For poled-PVDF (P-PVDF), as shown in Fig. 1(a) and (d), the orientations of all chains along the y direction are the same, generating a net dipole moment along x of the whole system. While for unpoled-PVDF (U-PVDF), as shown in Fig. 1(b) and (e), half the chains orientate oppositely with the other half along the x-direction (direction of dipole moment), the dipole moments of two parts cancel each other out, resulting in zero dipole moment of the whole system.

Besides, amorphous PVDF (A-PVDF) is also structured and placed in the middle of two silicon substrates, as shown in Fig. 1 (c) and (f). When constructing A-PVDF, a single PVDF chain contains 20 carbon atoms. Then 60 of these single PVDF chains are randomly packed into a supercell. After minimization, a NPT ensemble (a constant number of atoms, pressure and temperature) is used to increase the system temperature from 300 K to 600 K by a constant rate of 50 K/ns, and then a 12 ns NPT run at 600 K is used to generate PVDF melt with a fully relaxed amorphous structure. The system is then quenched to 300 K by a constant rate of 50 K/ns and equilibrated in the NPT ensemble for 1 ns to converge the density.

ESI 2. Molecular dynamics simulation details

The Non-equilibrium molecular dynamics (NEMD) simulation method is used to calculate the thermal transport properties of Si/PVDF interface. And the detailed setting parameters of all NEMD simulations are listed in Table S1. Noting that k_B is the Boltzmann constant, V is the system volume, T is the temperature, E is total kinetic energy of the group of atoms, N is the number of total atoms, and the angular bracket denotes an ensemble average. All NEMD simulations in this work are performed by the large-scale atomic/molecular massively parallel simulator (LAMMPS) package². The interactions between atoms are described by the polymer consistent force field (PCFF)³ which includes anharmonic bonding terms and is intended for applications in polymers and organic materials. Table S2 to S5 list the specific parameters of potential function in NEMD simulation. The long-range Coulombic force is ignored. Periodic boundary conditions are applied in the x and y directions, while nonperiodic boundary conditions are used in the z -direction. And the velocity Verlet algorithm is employed to integrate equations of motion. 0.25 fs and 10 Å are chosen as time step and cutoff distance for the Lennard-Jones interaction, respectively. In addition, 4 independent simulations with different initial conditions are conducted to get a better average. The simulation structures are simulated in NPT ensembles at target temperatures and 1 atm for 1ns to obtain the optimized structures and simulation cell sizes, then followed by NVT (for 1ns) and NVE (for 2ns) ensembles before collecting heat flux of z direction (across interface) in NVE ensembles for 5 ns.

Table S1 Non-Equilibrium molecular dynamics (NEMD) simulation details.

Method	Non-Equilibrium molecular dynamics (NEMD)		
Potential	PCFF/Lennard-Jones/Tersoff	Time step	0.25 fs
Thermostat	Langevin	Heat source	350 K
		Heat sink	250 K
Simulation process			
Ensemble	Setting		Purpose
NPT	Boundary condition	x, y, z: p, p, p	Relax Structure
	Runtime	1 ns	
NVT	Boundary condition	x, y, z: p, p, f	Relax Structure
	Runtime	1 ns	
NVE	Boundary condition	x, y, z: p, p, f	
	Runtime	2 ns	
NVE	Boundary condition	x, y, z: p, p, f	Reach information
	Runtime	5 ns	
Recorded physical quantity			
Temperature	$\langle E \rangle = \sum_i \frac{1}{2} m_i v_i^2 = \frac{3}{2} N k_B T_{MD}$		
Heat flux	$J = \frac{1}{N_t} \sum_{i=1}^{N_t} \frac{\Delta \varepsilon_i}{2\Delta t}$		
Interfacial thermal conductance	$G = \frac{J}{A \cdot \Delta T}$		

Table S2 The types of atoms in PVDF chain and hydroxyl group.

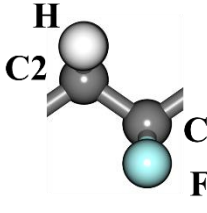
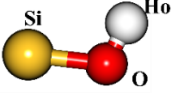
Structures	Atom types	Charge (e)
PVDF chain 	C	0.5
	C2	-0.106
	F	-0.25
	H	0.053
	O	-0.34
Hydroxyl group 	Ho	0.34
	O	-0.34

Table S3 The types of potential functions contained in PCFF force field.

Potential function in PVDF and hydroxyl group
Bond: class2
Angle: class2
Dihedral: class2
Improper: class2
Non-bonding potential: lj/class2/coul/cut 10.0
Special bond: lj 0.0 0.0 0.5 coul 0.0 0.0 0.5

Table S4 Bond parameters.

Bond	r_0 (Å)	K_{b2} (kcal·mol ⁻¹ Å ⁻²)	K_{b3} (kcal·mol ⁻¹ Å ⁻³)	K_{b4} (kcal·mol ⁻¹ Å ⁻⁴)
C-C2	1.5300	299.6700	-501.7700	679.8100
C-H	1.1010	345.0000	-691.8900	844.6000
C2-F	1.3900	403.0320	0.0000	0.0000
Si-O	1.6400	350.1232	-517.3424	673.7067
O-Ho	0.9494	540.3633	-1311.8663	2132.4446

Table S5 Angle parameters.

Angle	θ_0 (degree)	K_{a2} (kcal·mol ⁻¹ rad ⁻²)	K_{a3} (kcal·mol ⁻¹ rad ⁻³)	K_{a4} (kcal·mol ⁻¹ rad ⁻⁴)
C2-C-C2	112.6700	39.5160	-7.4430	-9.5583
C2-C-H	110.7700	41.4530	-10.6040	5.1290
H-C1-H	107.6600	39.6410	-12.9210	-2.4318
C-C2-C	112.6700	39.5160	-7.4430	-9.5583
C-C2-F	109.2000	68.3715	0.0000	0.0000
F-C2-F	109.1026	71.9700	0.0000	0.0000
Si-O-Ho	122.8000	23.7764	-19.8152	9.6331

Table S6 Interatomic Lennard-Jones potential parameters

	Pair coeff	ϵ (kcal·mol ⁻¹)	σ (Å)	cutoff (Å)
Between	Si-O	0.1013	4.230	10
Si and hydroxyl group	Si-Ho	0.1066	3.825	10
	Si-C	0.1013	4.230	10
Between	Si-C2	0.1013	4.230	10
Si and PVDF	Si-F	0.1066	3.825	10
	Si-H	0.0616	3.200	10
	O-C	0.1138	3.680	10
	O-C2	0.1138	3.680	10
	O-F	0.1198	3.275	10
Between	O-H	0.0693	3.1725	10
hydroxyl group and PVDF	Ho-C	0.0265	2.554	10
	Ho-C2	0.0265	2.554	10
	Ho-F	0.0279	2.149	10
	Ho-H	0.0161	2.0465	10

ESI 3. Structures after relaxing

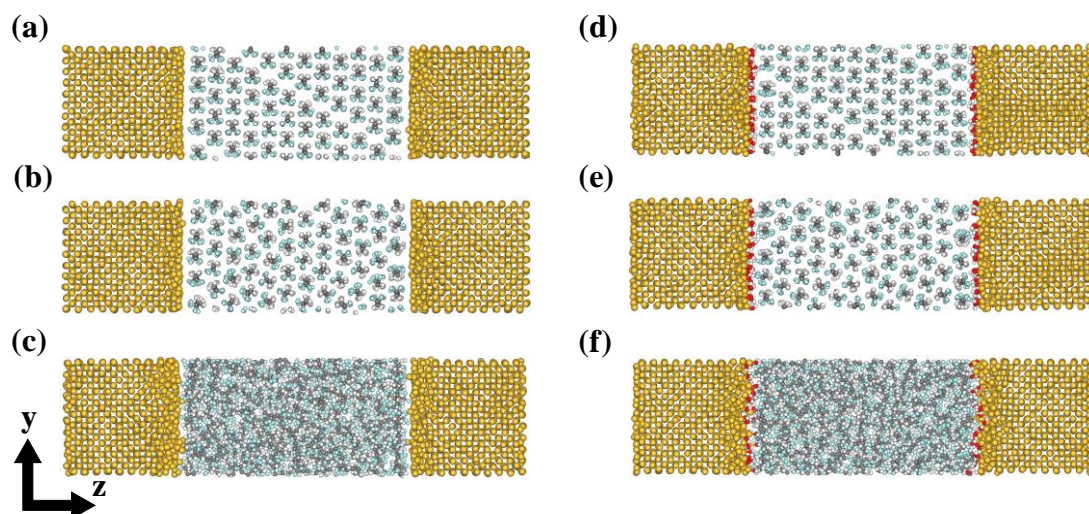


Fig. S1 Schematics of structure after relaxation at 300K of (a) intrinsic silicon/poled PVDF (In-Si/P-PVDF) interface, (b) intrinsic silicon/unpoled PVDF (In-Si/U-PVDF) interface, (c) intrinsic silicon/amorphous PVDF (In-Si/A-PVDF) interface, (d) modified silicon/poled PVDF (Mod-Si/P-PVDF) interface, (e) modified silicon/unpoled PVDF (Mod-Si/U-PVDF) interface and (f) modified silicon/amorphous PVDF (Mod-Si/A-PVDF) interface.

ESI 4. Temperature and heat flux

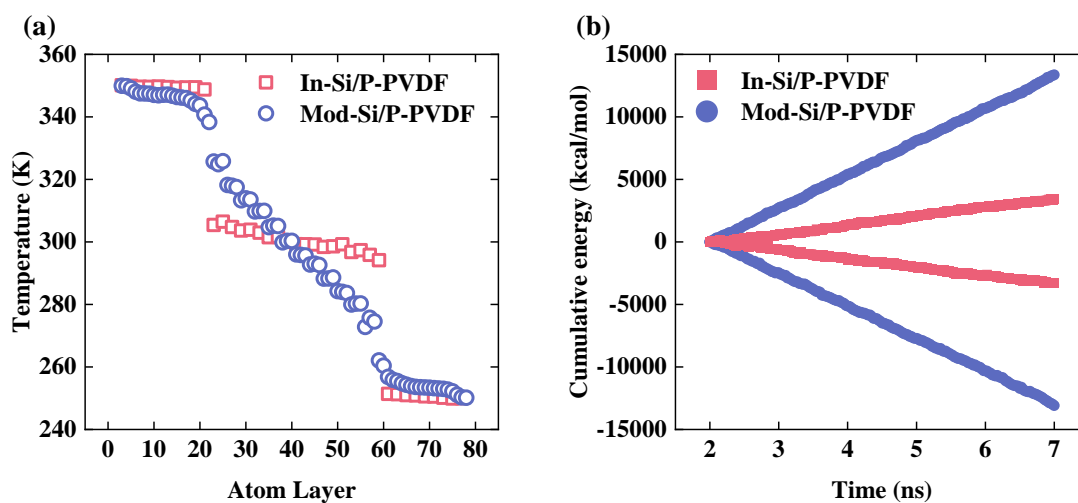


Fig. S2 (a) The temperature difference and (b) cumulative energy of the In-Si/P-PVDF and Mod-Si/P-PVDF structures along with z direction calculated by NEMD are recorded at 100K temperature difference.

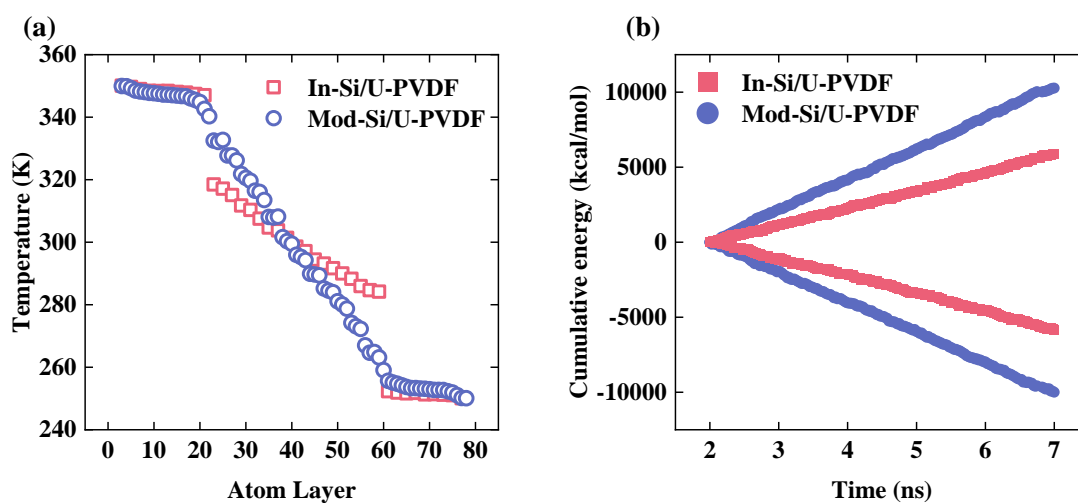


Fig. S3 (a) The temperature difference and (b) cumulative energy of the In-Si/U-PVDF and Mod-Si/U-PVDF structures along with z direction calculated by NEMD are recorded at 100K temperature difference.

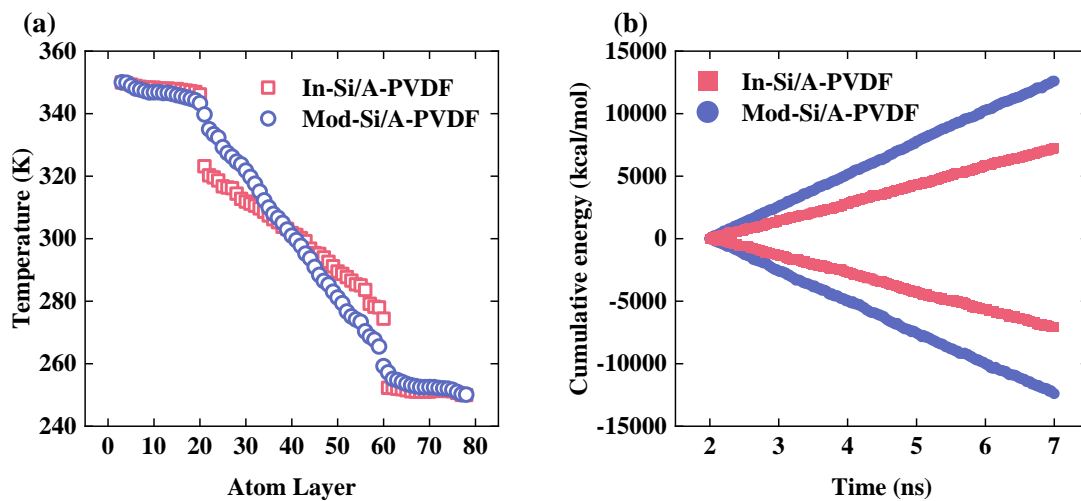


Fig. S4 (a) The temperature difference and (b) cumulative energy of the In-Si/A-PVDF and Mod-Si/A-PVDF structures along with z direction calculated by NEMD are recorded at 100K temperature difference.

ESI 5. Thermal conductivity of PVDF.

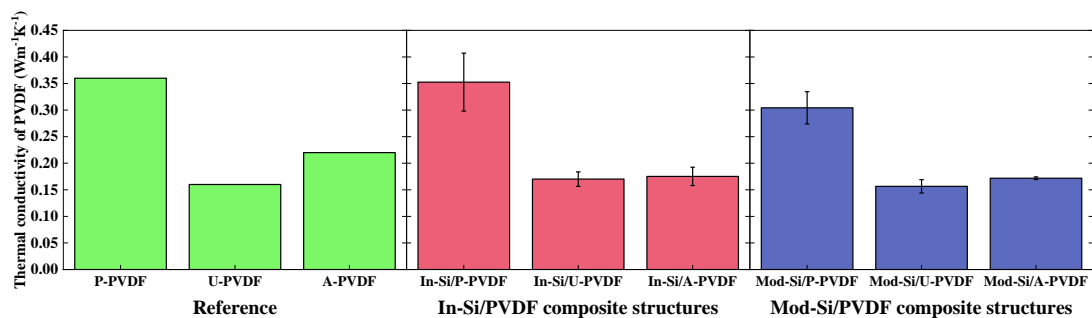


Fig. S5 Thermal conductivity of PVDF in all Si/PVDF composite structures. The thermal conductivity of U-PVDF and A-PVDF is comparable, while the thermal conductivity of P-PVDF exceeds both. The value of reference is from the previous study⁴.

ESI 6. The interaction between Mod-Si and PVDF.

The interaction between the F atom and the OH group in Fig. 4 (b) and (c) is similar to that between the C atom and the OH group. Firstly, there is also a higher interaction between the OH group and the C atom in PVDF. As shown in Table S2, the high charge of the C atom ($0.5e$) in PVDF results in a stronger Coulombic force with the OH group.

Secondly, when averaging and calculating the value of force in MD simulation, all atoms are considered and counted. For instance, shown in Fig. R1, when averaging the interaction between an F atom, both the nearest neighbor F atom (F1) and the next nearest neighbor F atom (F2) to the interface are counted, the values are averaged of these two interactions. As a result, the force between the OH group and the F atom is not much higher than that between the OH group and the C atom.

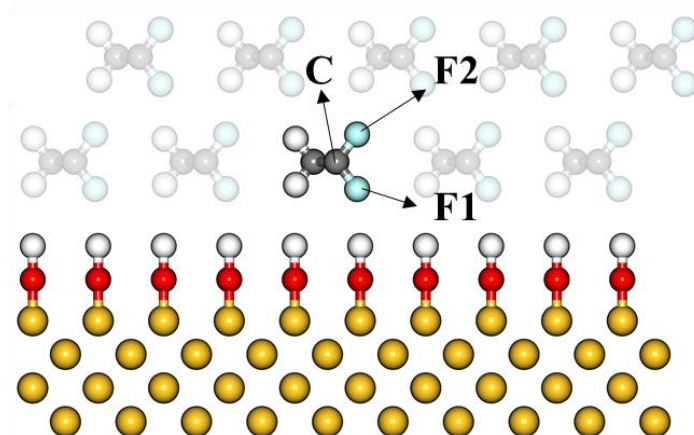


Fig. S6 Schematic of atomic force in Mod-Si/P-PVDF composite structures. Both the nearest neighbor F atom (F1) and the next nearest neighbor F atom (F2) to the interface are counted.

ESI 7. Phonon density of states in the full frequency range.

The vibrational density of states (VDOS) is calculated based on Parseval's theorem, the mass weighted power spectra $P(\omega)$ are calculated based on velocities. Then VDOS is expressed as

$$P(\omega) = \frac{1}{N} \sum_{i=1}^N m_i \left| \frac{1}{\sqrt{2\pi}} \int v_i(t) e^{-i\omega t} dt \right|^2$$

here ω is the angular frequency, N is the number of atoms, m is the atomic mass, v is the velocity, and t is the time interval. We recorded the trajectory of Mod-Si/P-PVDF structures, then performed fast a Fourier transform and multiple time average to obtain the power spectra. VDOS in the full-frequency range is given in Fig. S10.

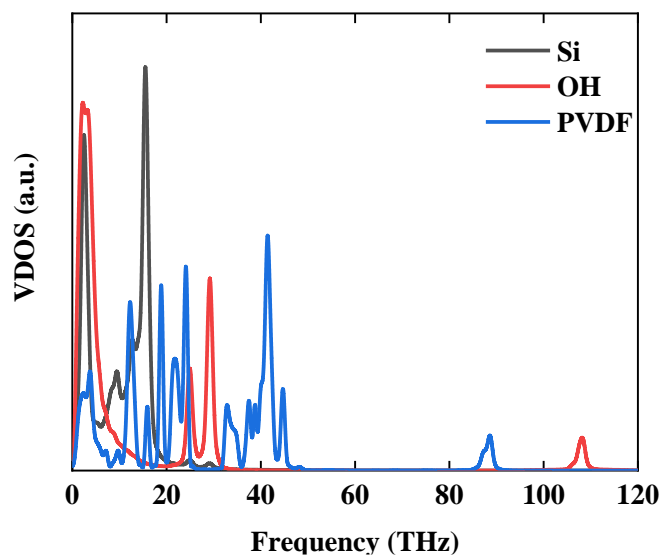


Fig. S7 VDOS comparison between atom groups of Si, OH, and PVDF in full frequency range.

ESI 8. Interfacial thermal conductance of Si/Z-PVDF.

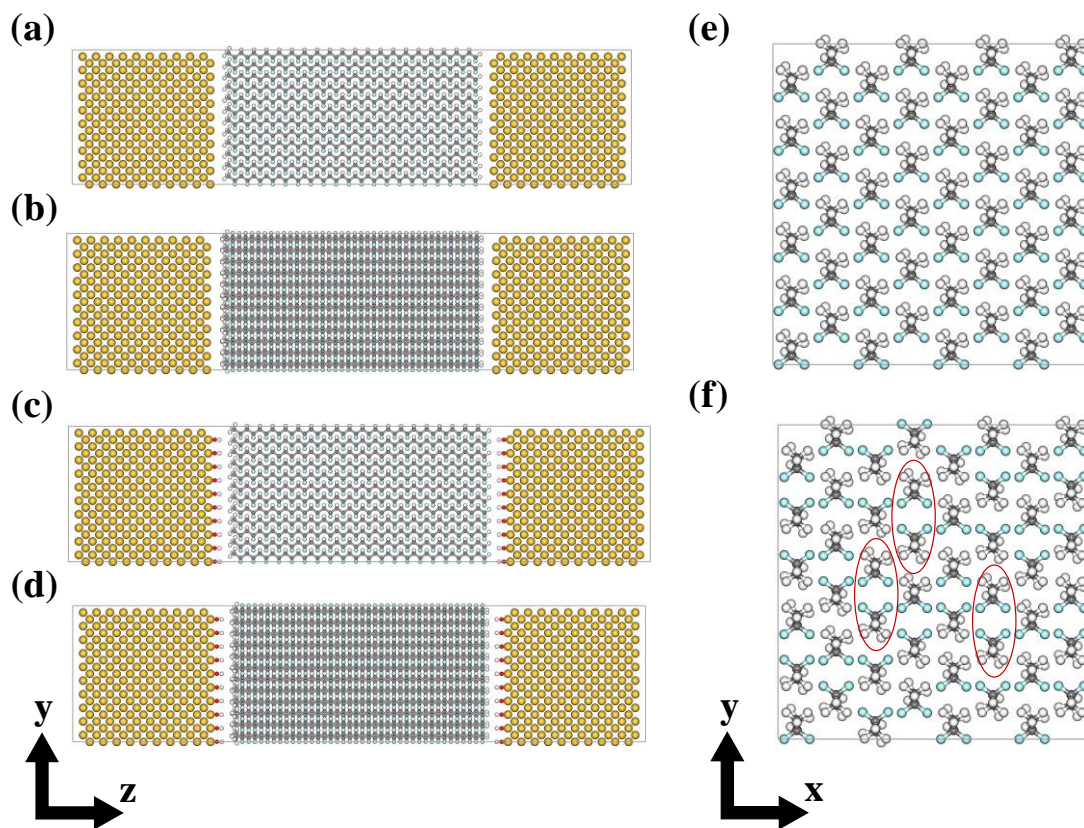


Fig. S8 Schematics of the interface structure are shown in the yz plane: (a) intrinsic silicon/poled PVDF chain oriented in the z-direction (In-Si/PZ-PVDF) interface, (b) intrinsic silicon/unpoled PVDF chain oriented in the z-direction (In-Si/UZ-PVDF) interface, (c) modified silicon/poled PVDF chain oriented in the z-direction (Mod-Si/PZ-PVDF) interface, (d) modified silicon/unpoled PVDF chain oriented in the z-direction (Mod-Si/UZ-PVDF) interface. Schematics of the PVDF structure are shown in the xy plane: (e) PZ-PVDF and (f) UZ-PVDF. The chain length of PVDF in the structure is 20 units.

In the case of finite-length PVDF, the terminal ends of PVDF segments are consistently designated as hydrogen atoms. Specifically, at one end, the carbon atom is bonded to three hydrogen atoms (CH₃), while at the other end, it is bonded to two fluorine atoms and one hydrogen atom (CF₂H).

Even for different end atoms of PVDF chains, the strategy to enhance interface thermal conductivity remains effective. As shown in the structures in Fig. S6, the left end of PVDF is CH₃ and the right end is CF₂H. As shown in Fig. S7 and Fig. S8, it is observed that a decrease in temperature gap at interfaces and an increase in heat flux, with hydroxylation of the silicon surface. Thus the interface thermal conductance is enhanced.

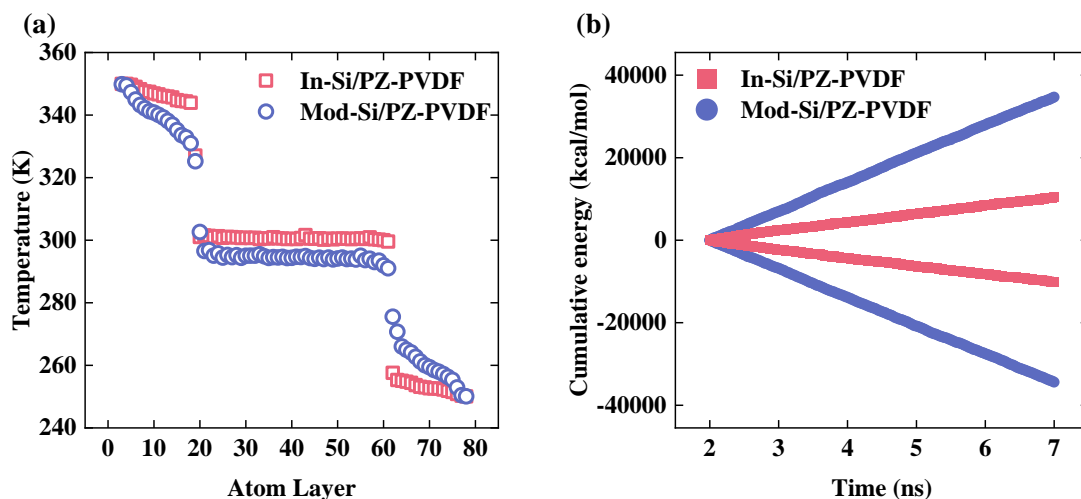


Fig. S9 (a) The temperature difference and (b) cumulative energy of the In-Si/PZ-PVDF and Mod-Si/PZ-PVDF structures along with z direction calculated by NEMD are recorded at 100K temperature difference.

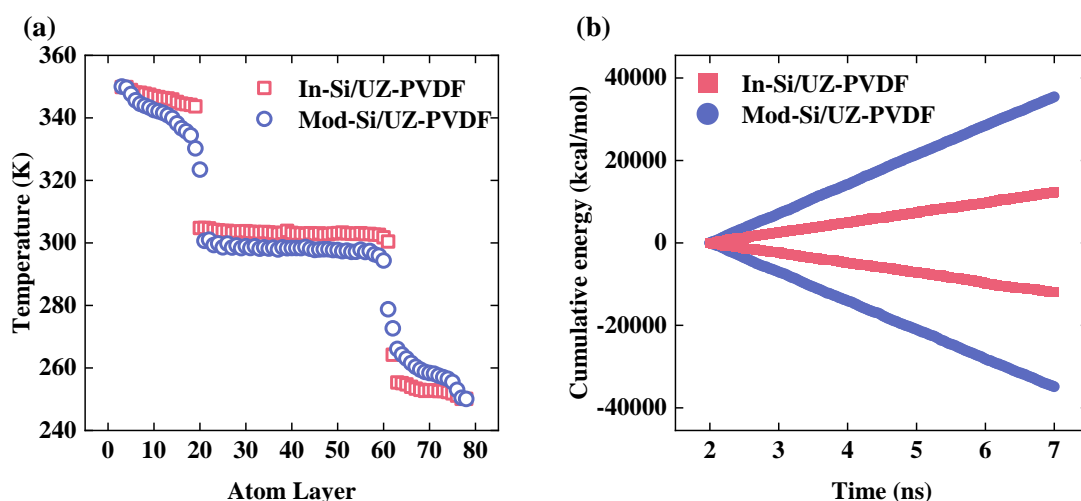


Fig. S10 (a) The temperature difference and (b) cumulative energy of the In-Si/UZ-PVDF and Mod-Si/UZ-PVDF structures along with z direction calculated by NEMD

are recorded at 100K temperature difference.

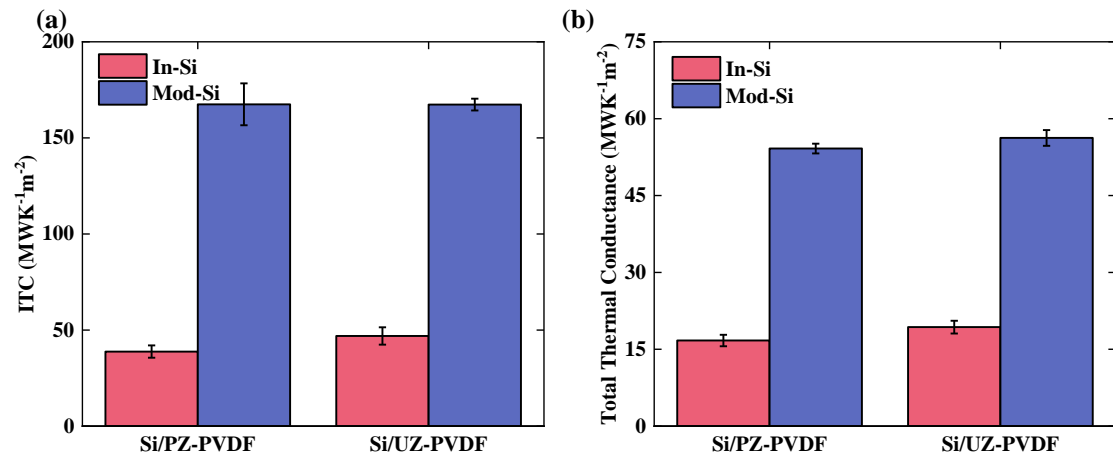


Fig. S11 (a) ITC of Si/Z-PVDF interface: For Si/PZ-PVDF and Si/UZ-PVDF, through modification of Si surface ITC can be increased by 331% and 256%. (b) Total conductance of composite structures: For Si/PZ-PVDF and Si/UZ-PVDF composite structures, through modification of the Si surface total conductance of composite structures can be increased by 224% and 191%.

Reference

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