

Supplementary Materials for

The Unrevealed 3D Morphological Evolution for Annealed Nanoporous Thin Films

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I. Volume dependence of critical radius r_c and r_m

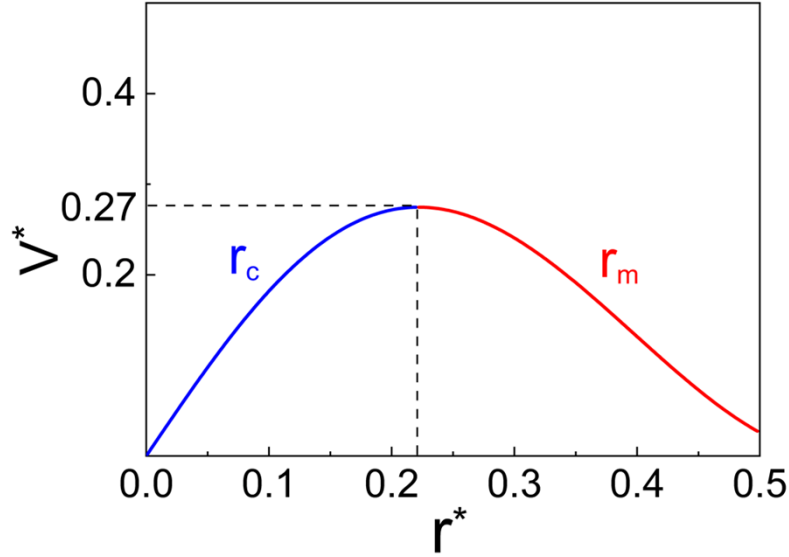


Figure S1 The normalized volume V^* dependence of critical radius r_c and r_m .

Set the derivative of surface free energy change ΔF^* with respect to the radius r^* in Eq. (2b) to zero. The resulting critical radius expressions contain V^* , which can be formulated as follows:

$$V^* = \frac{2\pi^2 r^{*5} - 4\pi r^{*3} + 2r^*}{1 + \pi r^{*2}} \#(S1)$$

And the $V^* - r^*$ functional relationship is plotted in Figure S1. It can be concluded that when the V^* is greater than 0.27, the critical radius r_c and r_m disappears, and the ΔF^* in Figure 1C increases monotonically with the increase of the r^* .

II. Sample preparation and high-temperature annealing experimental process

The 70-nm-thick Si thin film used in the annealing study came from the device layer of a silicon-on-insulator (SOI) substrate. The film was released from the

substrate by etching away the buried oxide layer in diluted hydrofluoric acid.

Nanopores of different sizes were drilled with a Ga⁺ Focused Ion Beam (FIB). The beam voltage and current for the milling process were chosen to be 30 keV and 7.7 pA.

The annealing was carried out in a furnace with nitrogen protection throughout the entire process. A higher flow rate was used to purge the annealing chamber before processing and then maintained at 10 scfm. The temperature was ramped up to the setpoint (annealing temperature) at a rate of 5 K/min to minimize the thermal stress inside the film and then maintained at the annealing temperature for 2-3 hours. Then the temperature was ramped down to the ambient at the same rate.

Electron microscopy studies were carried out before and after the annealing to study the morphology of the nanopore. The STEM/TEM images were taken with the Hitachi HF-5000 TEM. The SEM images were taken with the FEI Helios NanoLab 660.

III. EMD simulation process and parameter settings

The equilibrium molecular dynamics (EMD) method is used to simulate structural deformation [1, 2]. All EMD simulations in this work are performed by the large-scale atomic/molecular massively parallel simulator (LAMMPS) packages [3]. The interactions between atoms are described by a modified Tersoff potential, which reproduces a wide range of properties of silicon such as surface energies and reconstructions, melting temperature [4]. The free and periodic boundary conditions are applied in the z-axis and other two directions, respectively. And the velocity Verlet algorithm is employed to integrate equations of motion [5]. Here 0.2 fs and 3.2 Å are chosen as time step and cutoff distance for the Tersoff potential, respectively.

As shown in Figure 1B, one of the simulation cells is built by 12×12×3 silicon single crystal cells, which means that the periodic length l is 6.52 nm and the thickness h is 1.63 nm. The atomic arrangement is in line with the regular diamond structure with a bond length of 0.235 nm. In the LAMMPS approach, the size of the simulation box

is $6.52 \times 6.52 \times 41.62 \text{ nm}^3$, which is the same with silicon supercell in x and y directions and much larger in the z-direction. The nanoporous silicon structure was firstly equilibrated at 300K for 0.15 ns in the canonical ensemble (*NVT*) and then in the microcanonical ensemble (*NVE*) for 0.15 ns. Afterward, the Langevin thermostat is used to increase the system temperature from 300 K to 1300 K and higher temperature. Then Langevin thermostat runs for 1.5 ns to record atomic coordinates and calculate the pore area.

Table S1 Parameter settings in MD simulation.

Method		Equilibrium MD			
Potential		Tersoff			
Boundary conditions		x y z: periodic, periodic, periodic			
Simulation process					
Ensemble	Settings				Purpose
NVT	Time step (fs)	0.5	Runtime (ns)	0.15	Relax structure
	Temperature (K)	300	Thermostat	Nose-Hoover	
NVE	Time step (fs)	0.5	Runtime (ns)	0.25	Relax structure
NVE	Time step (fs)	0.5	Runtime (ns)	0.1	Raise temperature
	Temperature (K)	300-1500	Thermostat	Langevin	
NVE	Time step (fs)	0.5	Runtime (ns)	1.5	Data process
	Temperature (K)	1500	Thermostat	Langevin	

IV. Structural dependence of melting point of the silicon membrane

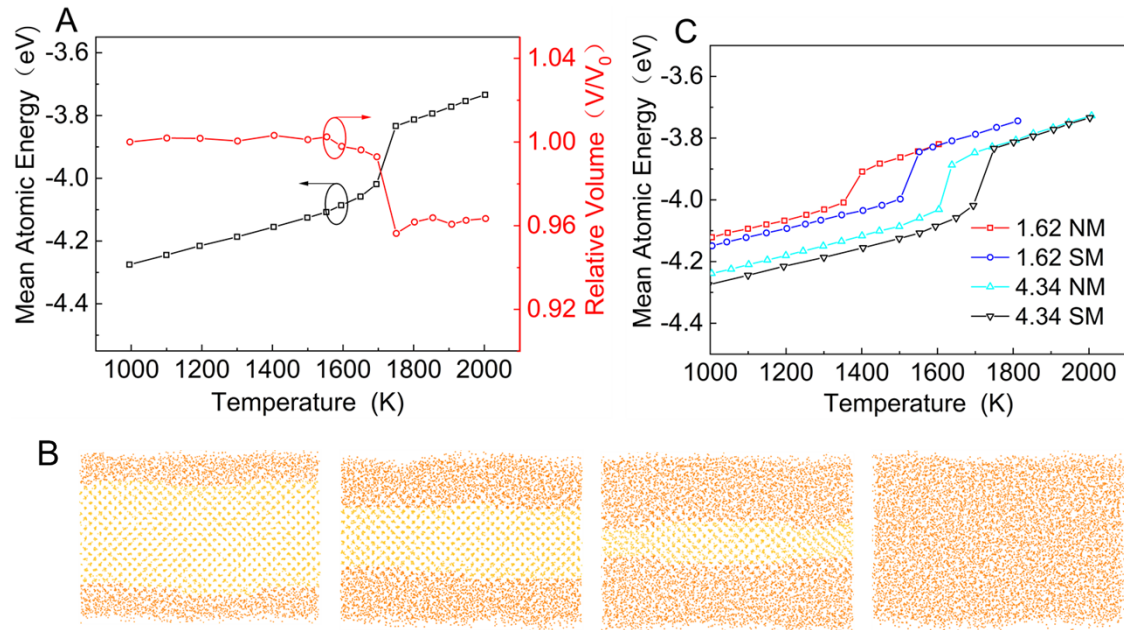


Figure S2 (A) The changes in the mean atomic energy and structural volume of 4.34 nm thick silicon solid membrane with increasing temperature. The temperature of the membrane in simulation is initially 1000 K and increases every 50 K to 2000 K. (B) Snapshots of MD simulation of the membrane in Figure S3A at 0.05, 0.2, 0.4, and 0.6 nanoseconds. The temperature is maintained around 1750 K by the Langevin thermostat. The orange area indicates that the silicon membrane has melted, whereas the yellow area retains a crystalline silicon structure. (C) Mean atomic energy versus temperature for different structures. The red, blue, cyan and black curves represent 1.62 nm thick nanoporous membrane (NM)/solid membrane (SM) and 4.34 nm thick NM/SM, respectively.

The phase change plays an important role in the subsequent deformation process and is simulated by MD. The temperature of the silicon membrane is initially 1000 K and increases every 50 K until the structure melts. The melting point of the porous membrane is essential in the simulation of deformation, which is obtained by recording the mean atomic energy and volume. As shown in Figure S2A, the total energy of atoms increases linearly with temperature, which reflects the rising process of the internal energy of silicon. The total energy of atoms increases sharply around 1750 K and then keeps increasing linearly. It can be concluded that the melting point of this structure is

around 1750 K and the structure absorbs extra energy during melting due to the latent heat of fusion [6]. From the ordinate value on the right, it can be seen that the volume of the membrane decreased by about 4% at 1750 K. Changes in volume indicates that the covalent bonds between silicon atoms and crystal structure are destroyed, resulting in volume reduction and density increase.

Figure S2B shows the melting process of the silicon membrane. Compared with atoms in the bulk of solid, surface atoms have lower cohesive energy because of weaker bond networks and fewer neighbors [7]. It can be seen that the atoms on the surface are close to each other to form new bonds at high temperatures due to the less binding than the bulk atoms. There is a surface melting layer at a temperature below the melting point. As the temperature rises, this melting layer gradually thickens and eventually leads to the melting of the silicon crystal membrane. The Lindemann criterion states that the fraction of thermal displacement atoms reaching 10% - 15% can result in the melting of the entire solid [8].

The melting point of silicon membranes shows an obvious size dependence, which is shown in Figure S2C. Membrane with a higher surface-to-volume ratio is more unstable due to extra surface energy. It is calculated that the surface-to-volume ratio of the membrane with nanopore reaches 0.79, and the value of membrane of the same thickness without nanopore is only 0.67. The higher surface-to-volume ratio results in a lower melting point due to much more defective surface atoms and higher surface energy, which can be proved by the difference in mean atomic energy as shown in Figure S2C.

V. The rounding process of the nanopore

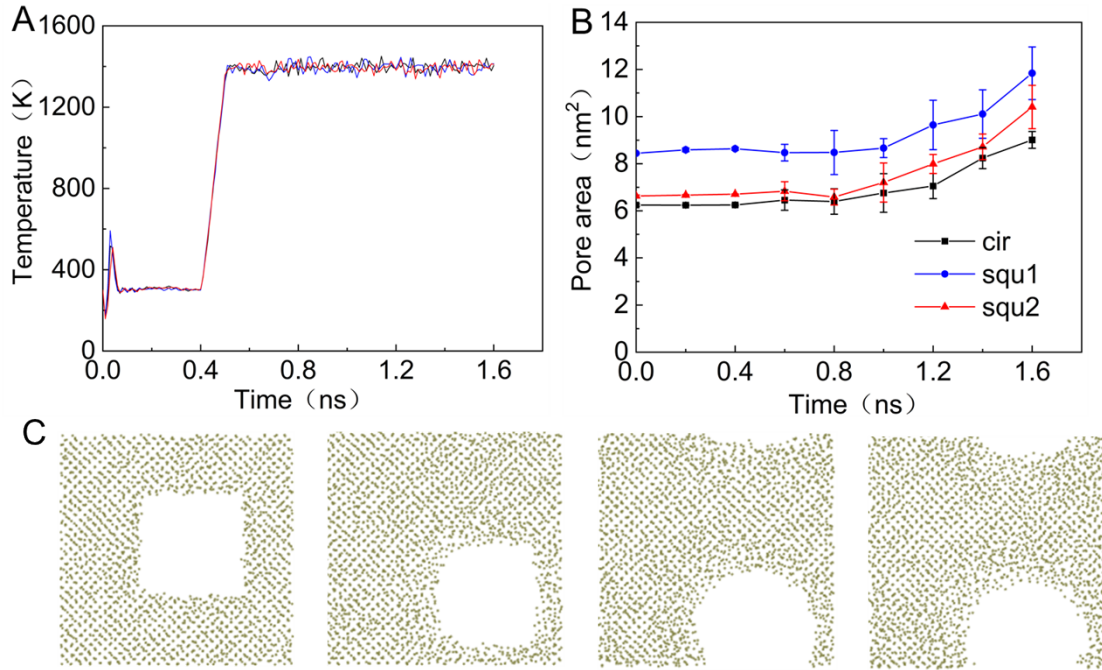


Figure S3 (A) (B) Temperature and pore area evolution for square and round pores. The black curve represents the membrane with a round nanopore, and the red and blue curves represent membranes with square pores with the Si (1 0 0) and Si (1 1 0) surface plane respectively. (C) Snapshots of MD simulation of Si (1 0 0) square nanopore at 0, 0.2, 0.4, and 0.6 nanoseconds since raising the temperature.

A curved surface under the surface tension results in a pressure difference over the interface [9]. Due to the pressure difference, the atoms along the pore edge on the surface would be pushed away from the nanopore at first. This pressure difference can also be used to explain the rounding process of a square pore in Fig S3, where the atoms in the corners will migrate to round off the edges.

Nanopores are usually non-circular before high-temperature annealing due to the highly anisotropic nature of the wet etch in silicon membranes[10]. As shown in Figure S3B, both round and square pores have the same expansion trend. It can be concluded that the geometry of pores does not affect expansion or shrinking trends. From the images in different stages shown in Figure S3C, it can be observed that the corners of square pores quickly round off since raising the temperature.

The rounding process can be explained by considering local forces generated by

surface tension. The curved surface under tension leads to pressure difference. Atoms in the corners will move under the greatest force due to the strongest curvatures. For round pores, the force is directed away from the axis of the pore. The pore area has little change since the internal atomic arrangement remains the original crystal structure. Over time, the number of thermally displaced atoms gradually increases, which leads to the entire crystal structure melting. After 1.0 ns, pores of all three shapes will expand under surface tension directed away from the axis of the pores. Therefore, high-temperature annealing can not only accurately control the size of nanopores, but also round the original irregularly shaped nanopores.

VI. The original data for nanoporous membranes

Table S2 The original data for nanoporous membranes in experiments and simulations.

Exp.	V^*	p (nm)	V (10^6 nm^3)	h (nm)	r (nm)	F (10^6 eV)
1	0.11	600	22.02	70.0	120.9	4.48
				97.7	207.2	3.84
2	0.14	400	8.94	70.0	101.4	1.97
				143.1	176.2	1.81
3	0.28	200	2.20	70.0	52.2	0.56
				68.7	50.4	0.56
4	0.33	150	1.10	70.0	46.7	0.34
				48.9	0	0.30
5	0.42	400	26.4	220.0	112.6	2.58
				187.8	78.6	2.46

Simu.	V^*	p (nm)	V (nm^3)	h (nm)	r (nm)	F (eV)
1	0.21	6.52	58.93	1.63	1.41	569.96
				2.12	2.16	553.66
2	0.28	6.52	79.93	2.17	1.34	599.43

				2.60	1.94	604.08
3	0.31	6.52	86.64	2.72	1.84	618.77
				2.63	1.75	616.32
				2.72	1.40	628.51
4	0.35	6.52	98.53	2.32	0	557.26
				4.34	1.35	719.75
5	0.57	6.52	159.60	3.76	0	557.26

VII. A comparison of the validity of the CVM and CTM

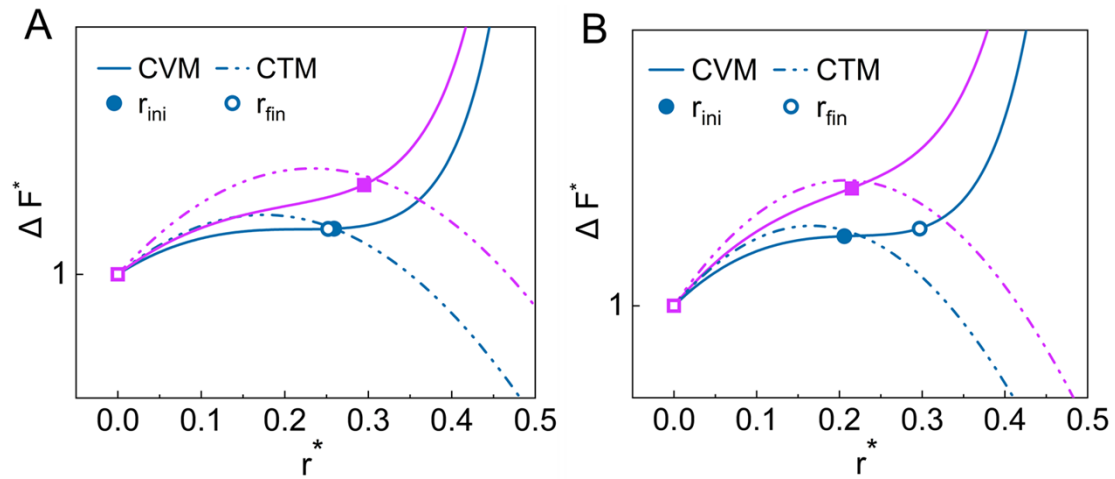


Figure S4 Experimental (A) and simulation (B) results on the evolution of nanopore size, as well as CVM and CTM model predictions.

VIII. The characteristic length for soft silicon

Generally, the shape of soft materials is determined by both the surface tension and gravity. For the sake of argument, a cube with sides d is used to discuss the effects of both. When deformation is driven by surface tension, the average strain of the cube (α) is on the order of [11]

$$\alpha = \frac{\gamma}{\mu d} \#(S2)$$

where γ is the surface tension and μ is the small strain shear modulus. And the average strain of the cube due to gravity (β) is on the order of

$$\beta = \frac{\rho g d}{\mu} \#(S3)$$

where ρ is the mass density and g is the acceleration of gravity.

The dominant forces that drive the deformation can be determined by comparing the magnitude of the two dimensionless strain parameters α and β . When $\alpha \gg \beta$, the effect of gravity is negligible and surface tension is dominant. For the value of α/β is 10^3 , it is equal to

$$\frac{\gamma}{\rho g d_c^2} = 10^3 \#(S4)$$

For soft silicon, γ is 0.733 N/m, ρ is 2.42×10^3 kg/m³ and g is 9.8 N/kg. The characteristic length (d_c) is on the order of 100 μ m obtained by Eq. (S4). The surface tension is dominant for both experiments and simulations, because both their size are much smaller than 100 μ m. Both the simulations and the measured results can validate the predicted trend by the constant volume model, i.e., expansion or contraction of nanopores for different starting diameters (Fig. 4).

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