
Supplementary Information

A novel atomic removal model for chemical mechanical polishing using developed mesoporous shell/core abrasives based on molecular dynamics.

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MD simulation details

Classical molecular dynamics model

All simulations were performed on Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS),¹ and OVITO² was used to analyze and visualize numerical results. In all MD models, β -cristobalite with lattice constant $a_0=7.16$ Å was employed as the original crystal structure of fused silica. The structure of fused silica was acquired by melting-quenching twice under canonical (NVT) ensemble and isothermal–isobaric (NPT) ensemble respectively.³ The heating rate and cooling rate are both 25 K/s, and the initial system temperature and target temperature are respectively 300 K and 5000 K.

To study material removal mechanism induced by NGME effect, a small part of actual contact of

abrasives was taken as the basis for modeling abrasive (shown in Fig. S1(a)).⁴ The classical MD model established in this work is shown in Fig. S1(b) which includes workpiece and the double tip representing NGME structure of abrasive. The d_1 represents the abrasive pore diameter of mesoporous structure, h is the pore depth, and a is the polishing depth of abrasive. The specific parameters of model are shown in Table S1.

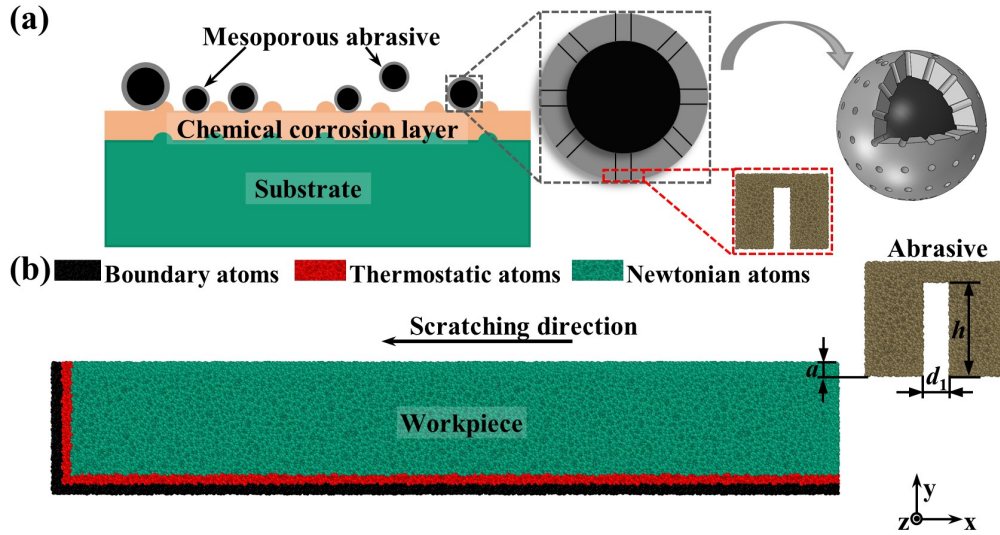


Fig. S1 Classical CMP MD model: (a) Schematic diagram of CMP with core/shell abrasive, (b) Classical MD model of fused silica with core/shell abrasive.

The workpiece is composed of three parts, including boundary atoms, thermostatic atoms and Newtonian atoms. The boundary atoms were fixed to prevent overall displacement of workpiece under inter-atomic force. The thermostatic atoms were kept at a constant temperature of 300 K under NVT ensemble to simulate heat transfer in actual processing. Under microcanonical (NVE) ensemble, Newtonian atoms were evolved correspondingly during CMP.⁵

Since the main purpose of this study is the deformation of material under nanotips, the abrasive was considered as rigid body. To study the possible effect of porous diameter on material removal process, d_1 is set as 0 nm, 1.5 nm, 1.8nm, 2 nm, 3 nm, 4 nm and 5 nm respectively. The Tersoff potential function, a three-body potential function, was used to describe interaction between Si-Si, Si-O, O-O in this system.^{6,7}

Table S1. Specific parameters of classical MD simulations of CMP.

Classical MD model parameters	Settings
The boundary conditions	Periodic boundary Z, fixed boundary X, Y

Timestep	0.8 fs
The size of workpiece	42 nm×7 nm×14.2 nm
The size of abrasive	7.5 nm×6 nm×7 nm
a	0.5 nm
d_1	0 nm, 1.5 nm, 1.8 nm, 2 nm, 3 nm, 4nm, 5nm
h	5 nm
The scratching velocity	50 m/s
The total scratching displacement	32 nm

A series of molecular dynamics scratching simulations were performed and the relative motion between abrasive and substrate during CMP was simulated. Then an 80 ps relaxation was carried out to enable system tend to be stable, and finally surface atoms were extracted in stable area of processed surface to calculate the arithmetic mean deviation of surface roughness (Sa) by Eq. (S1):⁸

$$Sa = \frac{1}{NM} \sum_{i=1}^N \sum_{j=1}^M |Z(x_i, y_j)| \quad (S1)$$

To prevent unstable interface between processed area and other surfaces from affecting roughness statistics, surface atoms in stable-scratching region with a certain distance from interface (the red region area of 10 nm×5 nm in Fig. S2) were extracted by OVITO construct surface mesh algorithm for roughness calculation.^{9,10} Moreover, the number difference of atoms in extracted region before and after CMP simulation is defined as the number of removed atoms.

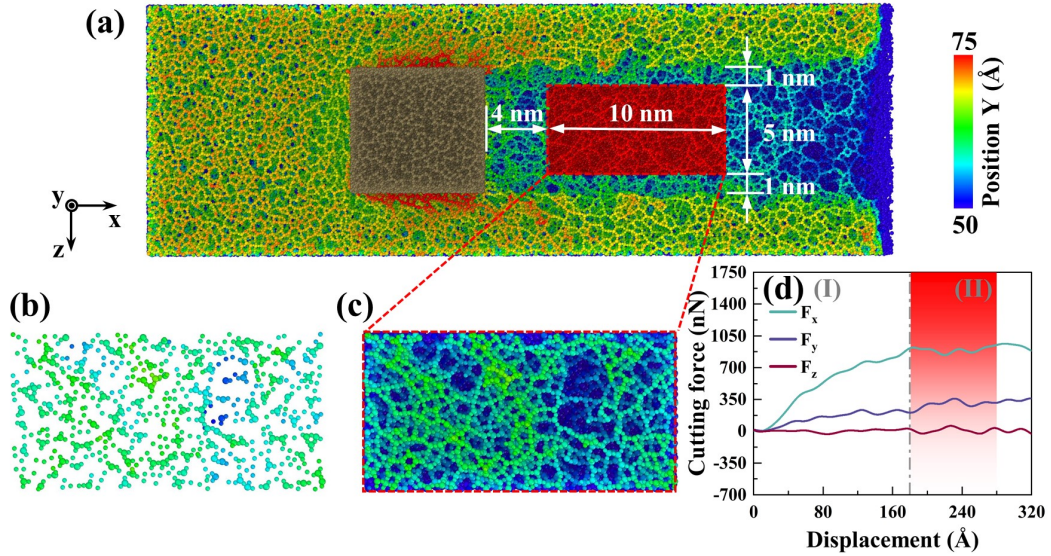


Fig. S2 Information of extraction area on workpiece surface: (a) Y-direction position cloud image of workpiece surface induced by sSiO₂ after simulation, red rectangle part is extracted area, (b) Extracted atoms from extracted area, (c) Magnification of the red area, (d) The curve of abrasive cutting force changing with cutting displacement during scratching process, (II) is the stage where cutting force is

relatively stable in all directions, the red region corresponds to (a).

Reactive force field molecular dynamics model

The ReaxFF MD model includes five parts: the rigid layer, abrasive free layer, slurry layer, substrate free layer, and fixed substrate layer (Fig. S3). Both substrate and abrasive materials are fused silicas, and polishing slurry layer was directly constructed by Materials Studio 7.0, containing 400 H₂O molecules and 11 H₂O₂ molecules. The d_2 represents the aperture of mesoporous structure, and d_2 is respectively set as 0 nm, 2 nm, 2.5 nm, 3 nm to investigate NGME influence on chemical reaction. The overall size of model is 71.6 Å×57.3 Å×60 Å.

The Si/O/H potential function developed by Fogarty was employed to simulate the interatomic interactions of system.¹¹ The timestep was set as 0.25 fs, the X and Y directions were set as periodic boundaries, and the Z direction was set as a fixed boundary. All simulations of this model were carried out under NVT ensemble, and a Nosé-Hoover thermostat was used to keep system temperature at about 300 K.^{12,13}

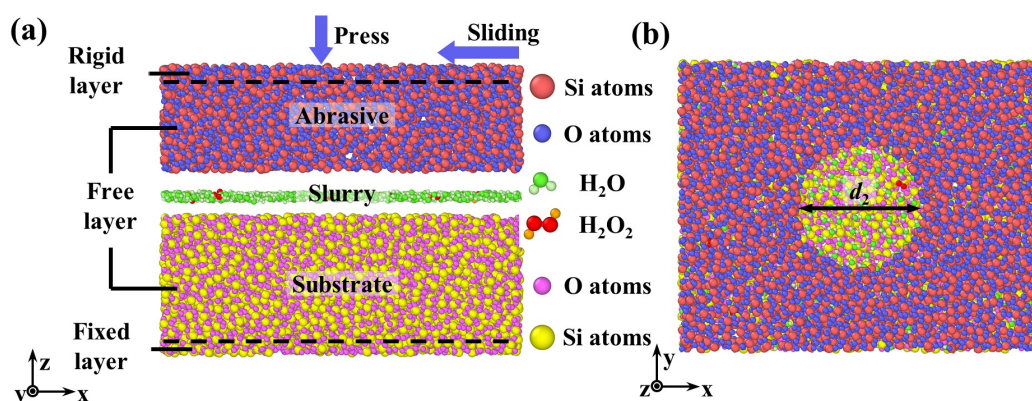


Fig. S3 ReaxFF MD model of CMP: (a) CMP model and its components, (b) Top view of CMP model, with d_2 representing the pore diameter of abrasive shell.

The CMP process are simulated by this model in following three steps. Firstly, the fixed layer and rigid layer were kept stationary, and the system relaxed for 100 ps to achieve a sufficient reaction between the slurry layer and surrounding interface. Then, with a pressing force of 100 nN, the rigid layer was controlled to drive abrasive to slide along negative direction of X axis at 40 m/s for 200 ps. After reaching destination, the abrasive was withdrawn from substrate.

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