Surface reconstruction on stishovite SiO_2, HfO_2 and rutile TiO_2 (001)*

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This paper systematically investigates the surface reconstruction processes and patterns on stishovite SiO_2, HfO_2 and rutile TiO_2 (001) by using classical molecular dynamics. It is found that these three surfaces relax instead of reconstruction at 0 K, and have little possibility to reconstruct below 40 K. Above 40 K, surface reconstructions take place as collective atomic motion which can be speeded by higher temperature or compressed strain. Several reconstruction patterns with approximate surface energies are found, and electrostatic potentials on them are also provided in comparison with possible microscopic results.

Keywords: surface reconstruction, molecular dynamics, oxides

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1. Introduction

Stishovite SiO_2, HfO_2 and rutile TiO_2 have the same tetragonal lattice structure (space group: $P42/mnm$). The first one is a manmade compound after Sergey M. Stishov and then by Chao *et al.*[1] The later two are new functional materials: HfO_2 is a high κ (dielectric constant) material which can replace SiO_2 to reduce the size of microelectronic components in the semiconductor industry;[2] TiO_2 is a common catalyst[3] and is an important photoelectric material which converts sunlight into electric energy.[4,5] Some experimental, classical simulations[6,7] and *ab initio* calculation methods[8] had been used to understand their lattice structures and surface reconstruction.

The most stable surface on rutile TiO_2 is (110) surface, which had been thoroughly investigated.[9] Some experimental studies were performed on its surface structure.[10,11] A (2×1) surface reconstruction was reported by quantitative low energy electron diffraction[10] and by elevated temperature scanning tunneling microscopy.[11] A few studies focused on rutile TiO_2 (001) surface: two types of (1×3) surface structures were found by classical simulation[12] and by first principle calculation.[13] The geometries and the electronic structures of tetragonal HfO_2 (space group: $P42/nmc$) and those of its (001) surface had been studied by first principle calculations, which find that this surface is not reconstructed. The first principle calculations also find that the surface reconstructions on SiO_2 (110) are similar to those on rutile TiO_2.[14,15]

Though experimental, classical simulations and *ab initio* calculation results were obtained to understand the surface structures on the above three oxides,[10−15] there are still some interesting and important points that remain unclear: (i) How surface atoms (Si, Hf, Ti and O) move from their equilibrium positions in the bulk to their new equilibrium positions on the surface after cleavage? (ii) Are there any other possible reconstruction models, especially on their (001) surfaces, in comparison with surface reconstructions on (110) surfaces? (iii) When we cleave the bulks to obtain high quality surfaces, which technical parameter(s) we should consider? For investigating above three questions, we used classical molecular dynamics (MD) to study the reconstruction process and the atomic distribution on stishovite SiO_2, HfO_2

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and rutile TiO_2 (001).

2. The molecular dynamics method

The molecular dynamics simulations were performed in canonical ensemble with periodic boundary on surface models. Before MD simulation, lattice structures were thermally expanded by lattice dynamics to the structures at MD simulation temperature. Surface models containing 400 to 2000 free atoms were constructed using the expended lattices as done in Refs. [16]–[18]. The time step in MD is 2 femtoseconds (fs, 10^{-15} s). Because the reconstruction processes are always finished in a few picoseconds (ps, 10^{-12} s), MD simulations within equilibrium period other than production period are performed. The Buckingham potential parameters for SiO_2, HfO_2 and TiO_2[19] were obtained at 0 K by an empirical method (known as the "relaxed" fitting approach). We adjusted these potentials for stishovite or rutile structures to precisely reproduce experimental lattice parameters and bond lengths.[6,19] During MD simulations, shell mass in the core-shell model is set as 15% of the total mass of Si, Hf, Ti or O ions. Details of this method and the surface models can be seen in Refs. [16] and [18].

3. Results and discussions

As we have done in Ref. [16], the surface energies of stishovite SiO_2, HfO_2 and rutile TiO_2 (001) have been calculated and shown in Table 1. Our simulated surface energies qualitatively agree with some other experimental or theoretical results.[20−25] It is found that the fresh surfaces (after cleavage) have the largest surface energies ($E^{\rm a}$ in Table 1). (In Table 1 and Fig. 1, $m \times n$ means that the surface model is obtained by multiplying unit cell of the surface by m and n times along X and Y axes,[16] respectively.) After relaxation (optimized at 0 K), surface energies reduce to $E^{\rm b}$ which are smaller than the values ($E^{\rm c}$) of reconstructed surfaces at 300 K. After MD surface reconstruction and relaxation again, surface energies of reconstructed surfaces reduce to the least values $E^{\rm d}$. Surface energies in Table 1 demonstrate that (001) surfaces of the above three oxides have a thermodynamic tendency to reconstruct after overcoming an energy barrier at higher temperature (300 K).

The initial (001) top layer is shown in Fig. 1(a): Si/Hf/TiO_2 molecules are arranged along [110] or [$\bar{1}$10] direction. Figure 1(b) shows the reconstructed pattern of 4×4 SiO_2 (001). On the top layer, every two adjacent SiO_2 molecules are combined to form one diamond and two separated Si–O bonds. Horizontal diamonds (along dot line A) and vertical diamonds (along dot line B) appear alternatively. For 6×6 structure (Fig. 1(c)), two ranks of horizontal diamonds and one rank of vertical diamonds appear alternatively. The 4×4 structures have smaller surface energies than those of 6×6 structures, but the energy differences are less than 0.05 J·cm^{-2} (Table 1).

Table 1. Surface energies (J·m^{-2}) of stishovite SiO_2, HfO_2 and rutile TiO_2 (001), compared with some experimental and simulation results.

	SiO_2	HfO_2	TiO_2
$E^{\rm a}/E^{\rm b}$	5.84/2.83	4.88/3.73	4.77/2.92
$E^{\rm c}/E^{\rm d}$ (4×4)	2.87/2.55	4.06/3.61	3.24/2.76
$E^{\rm c}/E^{\rm d}$ (6×6)	3.23/2.59	4.02/3.64	3.29/2.78
$E^{\rm c}/E^{\rm d}$ (4×6)	3.04/2.61	4.02/3.66	3.25/2.78
$E^{\rm c}/E^{\rm d}$ (5×5)	3.09/2.67	4.11/3.69	3.35/2.85
$E^{\rm c}/E^{\rm d}$ (5×6)	3.17/2.67	4.13/3.70	3.28/2.84
other results	4.17[20]	2.17[22]	2.40[24]
	1.50[21]	1–10[23]	1.75[25]

[a]Surface energy after cleavage (average value of the $m \times n$ surface models).

[b]Surface energy after 0 K optimization (average value of the $m \times n$ surface models).

[c]Surface energy after 300 K MD simulation until reconstruction.

[d]Surface energy after reconstruction then after 0 K optimization.

Reconstructions on HfO_2 (Figs. 1(d) and 1(e)) are similar to that of SiO_2, but the diamond lines are along [1$\bar{1}$0] direction. 7×7 structure of HfO_2 (Fig. 1(e)) contains intercepted diamond lines (for example, the dot line C). Compared with Si/HfO_2 (001), rutile TiO_2 (001) has an incomplete surface reconstruction (Fig. 1(f)).

Stishovite SiO_2, HfO_2 and rutile TiO_2 (001) surfaces manifest similar and interesting reconstruction processes as seen via direct MD observation. Because the top layer atoms reconstruct with larger displacements, while the second or the third layer atoms relax slightly, we take atomic motion on the top layer of HfO_2 (001) as an example. Figure 2 shows the trajectories of two adjacent HfO_2 molecules on 4×4 HfO_2 (001).

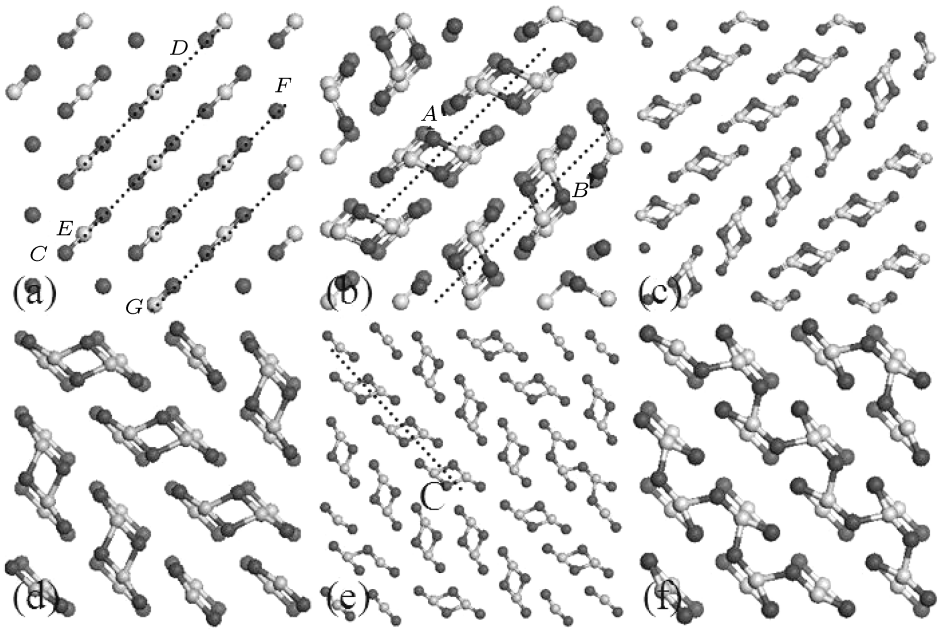


Fig. 1. Original surface structures of 4×4 (001) (a), 4×4 SiO_2 (b), 6×6 SiO_2 (c), 4×4 HfO_2 (d), 7×7 HfO_2 (e), and 4×4 TiO_2 (f) reconstruction patterns. Gray balls denote O atoms; dark balls denote Si, Hf or Ti atoms. Figures (a), (c) and (e) show the top layer, while figures (b), (d) and (f) show the top layer before (covered balls) and after (uncovered balls) reconstruction.

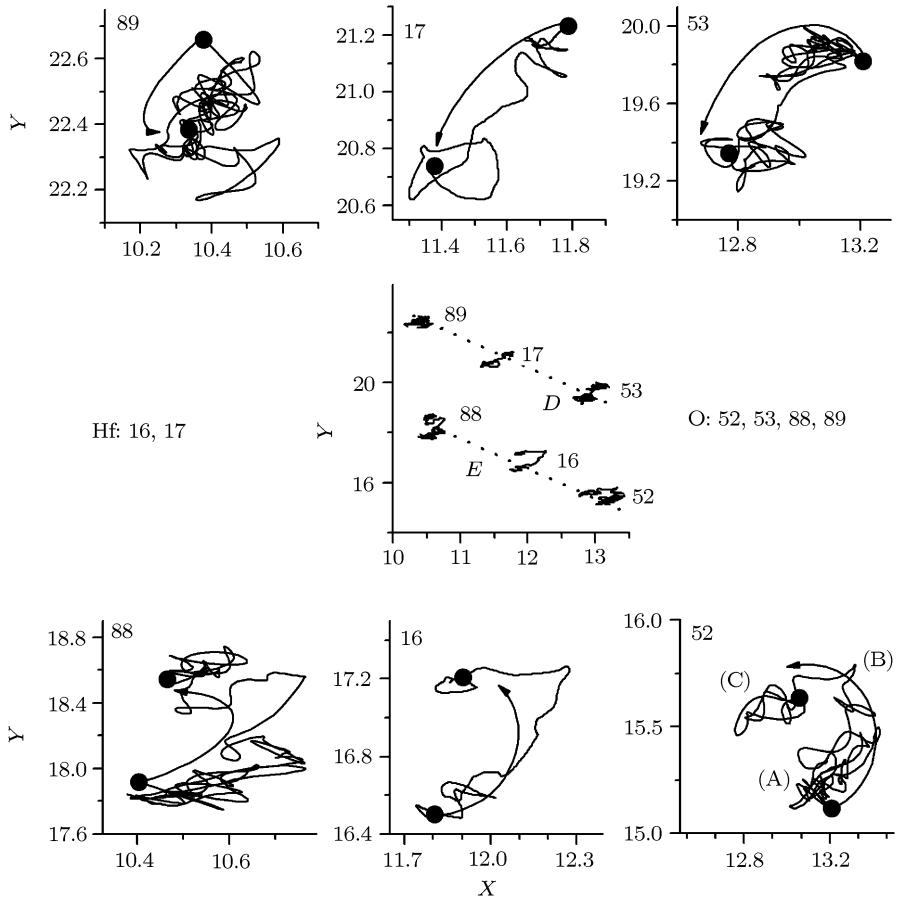


Fig. 2. Collective atomic motion during HfO_2 (001) reconstruction. The arrowy curve indicates the vibration direction of an atom from the beginning point (the equilibrium position in bulk) to the end area (around the equilibrium position on the reconstructed surface). Unit of X and Y coordinates is in unit Å (1 Å=0.1 nm).

Generally, the motion of an atom during the reconstruction process can be divided into three steps in our (001) surface MD simulations: (A) vibrating around its equilibrium position in the bulk (we can consider this step as the continuation of bulk atomic vibration); (B) moving and always overreaching to a new vibrating area; (C) turning back to a new equilibrium position. These three steps are illustrated for an oxygen atom (No. 52) in Fig. 2. In Fig. 2, the traces of O atoms are more complex than those of Hf atoms, and this can be contributed to Hf's larger atom mass and lower velocities. At the same time, the distance that an O atom travels during the reconstruction process is about three times of that of an Hf atom. For O atoms, the motion areas of steps (A), (B) and (C) have similar sizes. But, for Hf atoms, the size of motion area of step (B) is much larger than those of steps (A) and (C). For all atoms, step (A) consumes about 90% of reconstruction time (total time of steps (A), (B) and (C)), and the other two steps consume roughly equal reconstruction time.

We also note that (001) surface reconstructions of these oxides are collective atomic motions. In Fig. 2, the atoms on $[1\bar{1}0]$ (the dot line D, atoms with Nos. 89, 17, 53) move along similar curves with $[\bar{1}\bar{1}0]$ direction. The atoms on the adjacent line $[1\bar{1}0]$ (the dot line E, atoms with Nos. 88, 16, 52) move along similar curves with [110] direction. Generally, surface reconstructions are completed once and for all. But, a special case is found on TiO_2 (001) at 250 K in Fig. 1(a): firstly, line D attracts line E, line F attracts line G, to form an instantaneous reconstruction pattern. Subsequently, they depart from each other. Finally, line D attracts line G and line E attracts line F to form a permanent reconstruction pattern.

It is also found that the reconstruction process depends on two factors: reconstruction temperature and lattice strain. The 4×4 surface models with zero lattice strain were simulated from 10 K to 1200 K (Fig. 3(a)). If the temperature is less than 40 K, 10-ps MD simulation reaches to an equilibrium station without reconstruction. If the temperature increases from 45 K to 1200 K, surface reconstruction time reduces from several ps to about one-fifth ps. At higher temperatures, atoms have larger velocities and vibration area. This is the reason why reconstruction time reduces. The 4×4 surface models with different lattice strains were simulated at 300 K (Fig. 3(b)). It can be seen that negative strains (compressing the surface along X and Y axes) reduce reconstruction time and positive strains (expanding the surface lattice) increase reconstruction time. Negative strains can reduce atomic distances and increase atomic interactions, so less reconstruction time is needed. When positive lattice strains are larger than 0.9%, the surface model reaches to an equilibrium situation without reconstruction even MD time is up to 10 ps. If negative lattice strains are larger than –1.8%, the surface model becomes unstable and collapses. Surface reconstructions formed at high temperature (or with compressed strains) are stable, that is, they will not disappear when temperature decreases to 0 K (or when the compressed strains are released). This means that higher temperature and negative strain are helpful to obtain high quality (001) surfaces from their bulks.

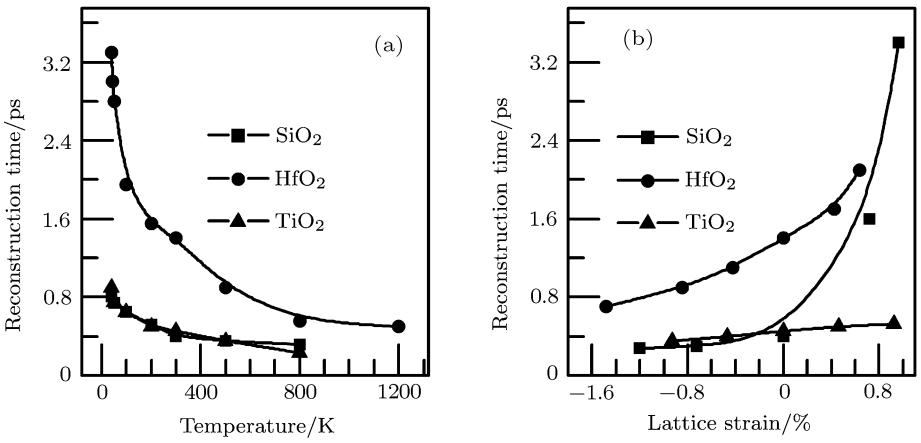


Fig. 3. Temperature (a) and strain (b) dependence of reconstruction time.

Electrostatic potentials of 6×6 SiO_2 (001) were calculated and shown in Fig. 4. Figure 4(a) shows elec-

trostatic potentials on the original (before reconstruction) surface, and figures 4(b)–4(f) show electrostatic potentials on the reconstructed surface of Fig. 1(a) with different heights. As the height above the surface increases (Figs. 4(c)–4(f)), the values of electrostatic potentials decrease. If the height is larger than 4 Å, electrostatic potentials become totally negative. At the height larger than 5 Å (Figs. 4(e) and 4(f)), locations of atoms on the surface cannot be distinguished by stripe-like electrostatic potentials. Figures 4(b)–4(f) can be compared with (for example, atomic force) microscopical images.

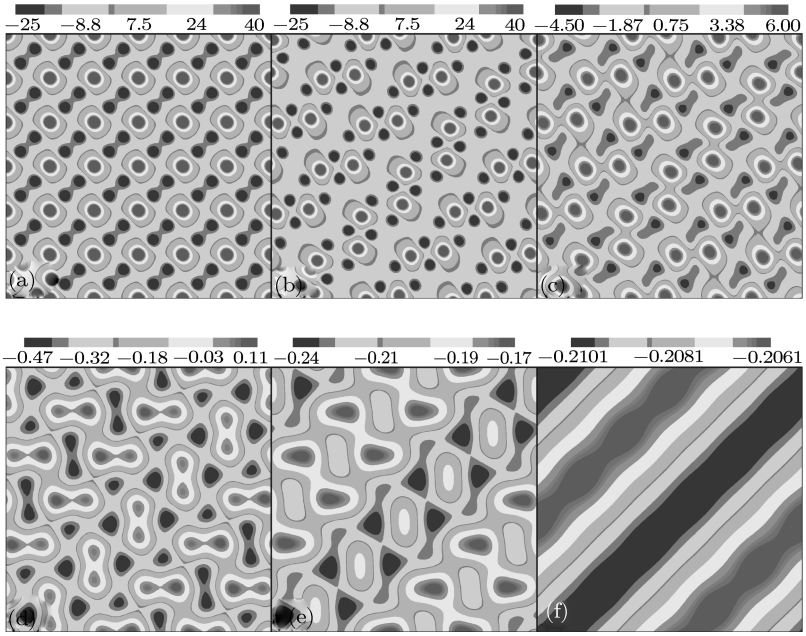


Fig. 4. Electrostatic potentials: 0 Å (a) and (b), 1 Å (c), 3 Å (d), 5 Å (e), and 10 Å (f) above 6×6 SiO_2 (001). Figure (a) shows the original surface while others the reconstructed surface with different heights. Unit is in eV.

4. Conclusion

Using classical MD simulations, reconstruction processes and reconstruction patterns on stishovite SiO_2, HfO_2 and rutile TiO_2 (001) were systemically investigated. The main findings are the followings. (i) These three surfaces relax but do not reconstruct at 0 K, and have little tendency to reconstruct at temperatures below 40 K. (ii) Above 40 K, they reconstruct as collective atomic motion. (iii) Higher temperature and compressed strain are important parameters to reduce reconstruction time, and may be helpful to obtain high quality cleaved surfaces. (iv) Surface electrostatic potential maps by atomic simulation can be compared with microscopy results.

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