Surface topography of the Si(111)-7×7 reconstruction

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The surface structure of Si(111)-7×7 reconstruction is calculated by using *ab initio* pseudopotential total-energy technique adopting slab models of different geometries and different thicknesses. It is shown that the converged surface topography can be obtained only when the slab is thick enough: more than five Si layers are allowed to relax. The converged surface topography turns out to be consistent with the experimental results from low-energy electron diffraction, scanning tunneling microscopy, and noncontact atomic force microscopy. This result reasonably explains the discrepancy between the experimentally observed image contrasts and the previous results from *ab initio* calculations.

Si(111)-7×7 reconstructed surface is one of the most complex surfaces found so far. Since its discovery through low-energy electron diffraction (LEED) about 40 years ago,[1] an enormous amount of experimental effort[2–18] and theoretical effort[19–25] has been expended to understand the properties of this important surface. Now it is accepted that the geometry of this reconstruction is described by a dimer-adatom-stacking-fault model as proposed by Takayanagi *et al.*[7] This geometry has an extremely large area and vertical extent in its unit cell that contains a faulted half and an unfaulted half, with each half consisting of different sites: the corner hole, corner adatoms, center adatoms, rest atoms, and the dimers [see Fig. 1(a)]. In spite of the extensive studies, some ambiguity still remains in the detailed feature of the surface topography of the 12 adatoms.

An elaborate LEED analysis of the 7×7 reconstruction was reported by Tong *et al.*, adopting a method of combining symmetry in real and reciprocal spaces in solving the multiple-scattering problem.[12] The result showed that the heights of the adatoms are in the following decreasing order: *CoF*>*CeF*>*CoU*>*CeU*, where the *Co* and *Ce* denote the corner and the center adatoms, respectively, and the *F* and *U* denote the faulted and the unfaulted halves, respectively [see Fig. 1(b)]. The height difference for each step in the above inequality is 0.04 Å. Scanning tunneling microscopy (STM) is another technique for surface imaging. Although the quantity detected in STM is essentially the local density of states on surfaces rather than the surface topography itself, STM image contrasts are usually consistent with the real surface topography. In the case of the 7×7 reconstruction, the STM images[17,18] showed the same height sequence as mentioned above but with various height differences: 0.28, 0.10, and 0.15 Å for the three steps, respectively. In recent years, the noncontact atomic-force microscope (nc-AFM) was developed as a novel technique for obtaining atomic-scale images with true atomic resolution on surfaces of both conductors and insulators. Compared with the STM, the nc-AFM probes atomic tip-surface interaction that, in principle, is more directly related to the surface atomic structure. However, as demonstrated by some first-principles calculations,[26–28] the tip-surface interaction can induce remakable relaxations on both the tip and the surface. As a result, in some cases the image contrast may be inconsistent with the real surface topography and may be affected by the material of the tip. The complex structure and small difference between the inequivelent adatoms make the Si(111)-7×7 surface a very good stage for showing the power and characteristics of the nc-AFM. For a Si tip, a nc-AFM image[15] showed the same height sequence as obtained by the LEED and STM: *CoF*>*CeF*>*CoU*>*CeU*, but with various height differeces: 0.10, 0.10, and 0.05 Å for the three steps, respectively. Another experiment[16] showed a slightly different height sequence: *CoF*>*CeF*>*CoU*~*CeU*. For a *W* tip,[14] however, the image contrast is reversed: the center adatoms appear 0.13 Å higher than the corner adatoms.

In the other aspect, along with the advances in both massively parallel computing and algorithms for the implementation of total-energy pseudopotential calculations,[29] now it becomes possible to perform *ab initio* pseudopotential calculations to determine surface structures even for the large Si(111)-7×7 reconstruction.[20–25] Two elaborate *ab initio* pseudopotential calculations were reported by Brommer *et al.*[24] and Štich *et al.*[21] Their results showed that the height sequence of the adatoms is in the following decreasing order: *CoF*>*CoU*>*CeF*>*CeU*, being different from the results of the LEED and STM. However, probably due to the extreme success of the *ab initio* pseudopotential method in determining atomic structures of semiconductors, this theoretical result was still recently regarded as the real surface topography of the Si(111)-7×7 reconstruction and was used to analyze the nc-AFM image contrasts.[14–16] The conclusion of these analyses is that the nc-AFM images do not reflect the real surface topography but is dominated by the tip-surface interaction, including the differences in the chemical reactivity and the bond stiffness, etc. for the different adatoms.

In the previous two calculations, a supercell containing a Si slab of 400 atoms was adopted. The Si slab has two 7×7 surfaces that are arranged by imposing a mirror-image reflection in the vertical direction[24] or an inverse symmetry center[21] to the slab. In this geometry, only the adatom layer and the first three layers can be allowed to relax ($n=3$).

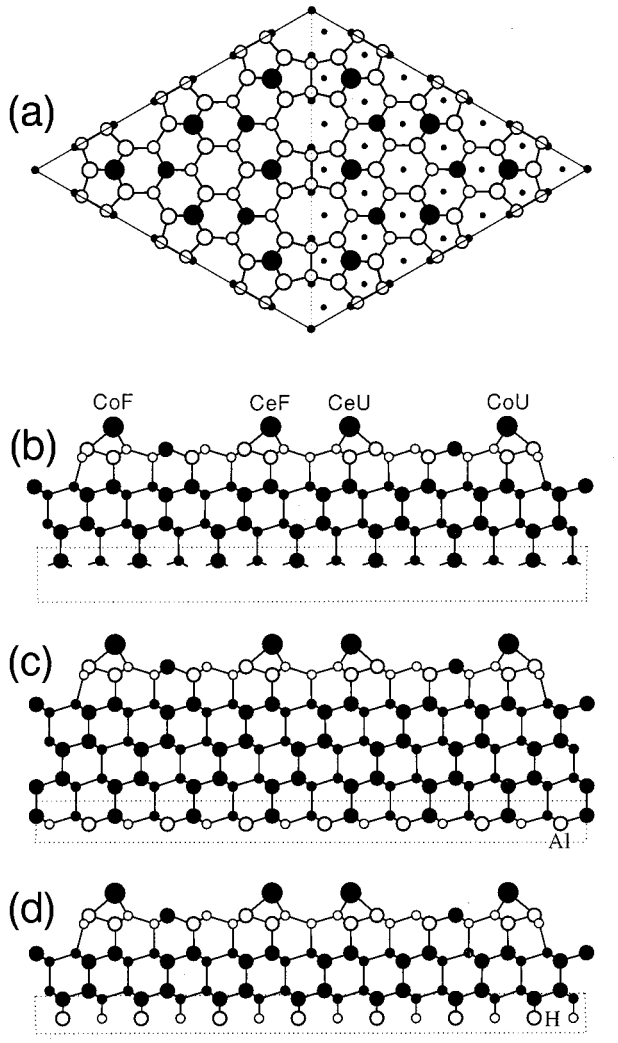

FIG. 1. Structures of the supercells used for the Si(111)-7×7 reconstruction: (a) top view where the faulted half and the unfaulted half are divided by a dotted line; (b) side view (half cell) where an inverse symmetry center is imposed to the Si slab ($n=6$); (c) side-view where the dangling bonds on the base layer of the slab ($n=8$) are saturated by Al atoms; (d) side view where the dangling bonds on the base layer of the slab ($n=5$) are saturated by H atoms. The atoms in the frame of dotted line are fixed during the relaxation.

However, the LEED result[12] showed that the height differences among the atoms in the fourth layer can be as large as 0.15 Å. This indicates that the slab thickness adopted in the two calculations is, in principle, not sufficient for obtaining the converged surface topography of the adatoms, although it may be enough for determining the bond lengths in the first three layers. In order to perform reasonable analyses on the image contrasts from the STM and nc-AFM, and to show the power and characteristics of these advanced microscope technologies, we should first consider more carefully the real surface topography. For this purpose the theoretical calculation must be well converged, especially to the slab thickness. On the other hand, the converged theoretical surface topography enables us to see whether the *ab initio* pseudopotential method works well even for this very subtle problem that, however, can still be possibly solved by the modern technologies.

In this paper, we carefully performed *ab initio* pseudopotential calculations that show convincingly the converged surface topography of the Si(111)-7×7 reconstruction. We have considered three different geometries for the supercell of the slab model: (1) an inverse symmetry center is imposed to the supercell, as used in Ref. 21 [see Fig. 1(b)]; (2) the surface system is cut inside a Si bilayer and the dangling bonds (three per atom) are saturated by 49 Al atoms [see Fig. 1(c)]; and (3) the surface system is cut between two Si bilayers and the dangling bonds (one per atom) are saturated by 49 H atoms [see Fig. 1(d)]. By adopting the three different geometries we can have a look at the effect from the boundary of the supercell and eventually exclude it in the conclusion about the subtle problem we want to investigate. For each supercell geometry, we have considered several different slab thinknesses from $n=3-8$. Between the slabs, a vacuum region of 11 Å is introduced. The supercells contain from 298 to 694 atoms, or eqivalently about 700 to 1100 bulk atoms in total.

The energies and atomic forces are calculated in the framework of density-functional theory in its plane-wave pseudopotential formulation.[29] The electronic orbitals are expanded at the Γ point of the Brillouin zone with a cutoff energy of 9 Ry or 12 Ry, which is significantly higher than those values used in the previous calculations.[24,21] Optimized Troullier-Martins-type pseudopotentials are used for the atomic cores. Both the local-density approximation (LDA) and the generalized gradient approximation (GGA, in its version of PW91)[30] to the electron exchange correlation are considered. The convergence criterion for the forces on the atoms is set to be 0.01 eV/Å, which is much stricter than those adopted in the two previous calculations: 0.15 eV/Å in Ref. 24 and 0.1 eV/Å in Ref. 21. The calculations were carried out on a Fujitsu VPP700E machine with eight processors.

The calculated height differences among the four adatoms along the long diagonal are listed in Table I together with the experimental results and the theoretical results from the two previous *ab initio* pseudopotential calculations.[21,24] We should notice in Table I that for $n=3$, the present LDA calculation for the inverse-symmetry system gives the same height sequence as obtained by the two previous LDA calculations: *CoF*>*CoU*>*CeF*>*CeU*, although the quantitative values are somewhat different among the three calculations. The difference may be due to the different computational details. Because of the much stricter convergence criteria, the present result can be expected to be more reliable.

Let us first have a look at the result of the LDA calculation for the Al-terminated system. For $n=3$, the obtained height sequence is the same as that of the inverse-symmetry system. As the value of n is increased from 3 to 5, the height sequence of *CeF* and *CoU* is actually reversed, and the height difference between *CoU* and *CeU* decreases remarkably, indicating that the surface topography is not yet converged. However, from $n=5$ to $n=8$, these changes become very small ($\leqslant 0.01$ Å) and the height sequence of the four adatoms remains unchanged. These results show that the converged surface topography will be reached in the case

TABLE I. Experimental and theoretical results of the height differences among the four adatoms along the long diagonal of the Si(111)-7×7 surface (in units of Å): ΔH_1=height(*CoF*)−height(*CeF*), ΔH_2=height(*CeF*)−height(*CoU*), ΔH_3=height(*CoU*)−height(*CeU*). ''Al-'' and ''H-'' mean that the dangling bonds on the base layer of the Si slab are saturated by Al and H atoms, respectively, and ''Si-'' means that the Si slab has an inverse symmetry center.

					ΔH_1	ΔH_2	ΔH_3
		LEED[a]			0.04	0.04	0.04
		STM[b]			0.28	0.10	0.15
		STM[c]			+	+	+
		nc-AFM[d]			0.10	0.10	0.05
		nc-AFM[e]			+	+	~0
		Cal.[f] (Si-, LDA, 8 Ry, $n=3$)			0.054	−0.007	0.038
		Cal.[g] (Si-, LDA, 7 Ry, $n=3$)			0.039	−0.001	0.003
This work	Si-	LDA	9 Ry	$n=3$	0.054	−0.057	0.065
				$n=6$	0.040	0.054	0.015
	Al-	LDA	9 Ry	$n=3$	0.051	−0.018	0.034
				$n=4$	0.049	−0.005	0.034
				$n=5$	0.055	0.046	0.012
				$n=6$	0.056	0.049	0.011
				$n=8$	0.061	0.056	0.015
			12 Ry	$n=6$	0.053	0.051	0.011
		GGA	9Ry	$n=3$	0.069	−0.034	0.049
				$n=6$	0.070	0.047	0.014
	H-	LDA	12 Ry	$n=3$	0.052	−0.020	0.041
				$n=5$	0.040	0.045	0.015

[a]Reference 12.
[b]Reference 17.
[c]Reference 18.
[d]Reference 15.
[e]Reference 16.
[f]Reference 24.
[g]Reference 21.

that more than five Si layers on the surface are allowed to relax. However, we must keep in mind that here we are dealing with a very subtle problem: the quantity is only several percentages of an angstrom. So we should check the result very carefully for the following items besides the slab thickness: (1) cutoff energy; (2) approximation to the electron exchange-correlation (LDA or GGA); and (3) the boundary condition of the slab in the supercell approach.

For checking the convergence to the cutoff energy, we have carried out a further calculation for $n=6$, adopting a higher cutoff energy of 12 Ry for the Al-terminated system. It appears that the difference between the results from the 9-Ry calculation and the 12-Ry calculation is as small as negligible, indicating that the surface topography obtained has well converged with respect to the cutoff energy. For checking the effects of LDA and GGA to the electron exchange correlation, we have further performed GGA calculations for the Al-terminated system ($n=3$ and $n=6$). The results show the same variation tendency with the increase of n as in the case of LDA, and the difference from the LDA result is minor. For checking the effect of the boundary condition, we can see in Table I that for $n=3$, the results for the inverse-symmetry (9 Ry, LDA), Al-terminated (9 Ry, LDA or GGA), and H-terminated systems (12 Ry, LDA) are qualitatively the same, and the differences among the slab-thickness-converged results ($n\geq 5$) for the three boundary conditions are also just minor. This convincingly shows that the effect from the boundary condition on the height sequence of the adatoms is fairly small and does not affect the conclusion.

The slab-thickness-converged surface topography for all of the three supercell geometries turns out to be qualitatively consistent with the experimental results from the LEED,[12] STM,[17,18] and the nc-AFM.[15,16] Especially, the present result is in very good agreement with the LEED and nc-AFM results. This good agreement comfirms further the real topography of the adatoms on the Si(111)-7×7 reconstructed surface. It also indicates that the *ab initio* pseudopotential calculation is successful even for this very subtle problem.

In summary, we have performed careful *ab initio* calculations for the surface topography of the Si(111)-7×7 reconstruction. By considering different slab thicknesses, different boundary conditions of the slab model, different cutoff energies, and different schemes for the electron exchange correlation, we obtained the converged surface topography that turns out to be consistent with the experimental results of LEED, STM, and nc-AFM (Si tip), indicating that the *ab initio* plane-wave pseudopotential method does work well even for this very subtle problem of only several percentages of an angstrom. The fact that the converged surface topography can only be obtained when more than five layers on the surface are allowed to relax explains reasonably the discrepancy between the experimental results and the theoretical results from the previous *ab initio* calculations.

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