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Relaxation of the clean and H-covered C(111) and the clean Si(111)-1×1 surfaces

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Well-converged plane-wave pseudopotential calculations using a steepest-descent method of finding the optimum atomic and electronic configuration have been applied to the clean and H-covered C(111)-1×1 and the clean Si(111)-1×1 surfaces in diamond structure to give new values of the surface relaxations. The small relaxation found for C(111)-1×1-H agrees with low-energy electron diffraction (LEED) studies of this diamond surface and supports the explanation that the surface was H covered. The other relaxation results differ from previous work due to use of sufficiently high plane-wave cutoffs to assure convergence, but also due to use of more **k** points in the surface Brillouin zone and to use of the *theoretical* bulk lattice constant in the surface problem. Close agreement is found with LEED results for the relaxation of the impurity stabilized Si(111)-1×1 surface. Indications of metastability are found for both clean (111)-1×1 surfaces.

I. INTRODUCTION

The structures of the (111)-1×1 surfaces of C, Si, and Ge in the diamond crystal structure are attractive for study because they are particularly simple, can be determined experimentally by low-energy electron diffraction (LEED) analysis when they are stable or metastable, and provide a test of current theory and computational power. The clean 1×1 Ge(111) and Si(111) surfaces are difficult to make experimentally, but Si(111)-1×1 has been stabilized by impurities and analyzed by LEED (Ref. 1) or stabilized by laser annealing and also analyzed by LEED.[2] The laser-annealed stabilized Si(111)-1×1 surfaces show considerable disorder,[3] but the LEED values of the relaxation in both stabilized surfaces are in moderate agreement with a previous first-principles calculation.[4] The structure of the C(111)-1×1 surface has also been determined by LEED analysis,[5] but the measured relaxations do not agree with the previous first-principles calculation of the relaxation of the clean surface[6] or with the results found here.

Both Ge(111)-1×1 and Si(111)-1×1 can be stabilized by a monolayer of H, and the Ge(111)-1×1-H surface structure has been found by LEED analysis[7] to give a relaxation of the first spacing (d_{12}) between Ge layers in good agreement with first-principles calculations.[4]

The present work uses a well-converged plane-wave basis calculation of the relaxation of clean C(111)-1×1 to repeat the calculation of Ref. 6, which employed a linear combination of atomic orbitals procedure based on Gaussian orbitals, and finds some differences. Notably the expansion of d_{23} is much larger in the present work. This expansion of d_{23} indicates a considerable rehybridization of the bonding of the surface C atoms already in the 1 × 1 structure. The present work goes on to find the relaxation of the H-covered C(111)-1×1 surface, which is shown to be in good agreement with the LEED results of Ref. 5.

In addition the geometry of the clean Si(111)-1×1 surface has been calculated, which can be compared with Ref. 4. The calculation made here increases the plane-wave energy cutoff to assure complete convergence and uses more **k** points in the surface Brillouin zone. Also the calculation here uses the theoretical bulk lattice constant in the surface calculation so the lattice is not under stress before the surface effects are considered, whereas Ref. 4 used the experimental lattice constant. The resulting relaxations show some differences from Ref. 4 and agree very well with the refined LEED results on the impurity-stabilized Si(111)-1×1 surface.[1]

II. COMPUTATIONAL PROCEDURE

The first-principles calculation on C(111)-1×1 used the Ceperley-Alder form[8] for the exchange-correlation potential and fully separable *ab initio* pseudopotentials;[9] s and p nonlocality was used for C, but only s nonlocality for H. The electron wave functions were expanded in plane waves with kinetic energies up to 60 Ry, which is required in order for carbon in the diamond structure to reach convergence in structural properties; graphite is also well converged with a 60-Ry cutoff. In a bulk calculation with the 60-Ry cutoff and 10 special **k** points in the irreducible part of the Brillouin zone, the equilibrium lattice constant is 6.69 bohr, which is 0.82% lower than experiment (6.745 bohr), part of which is due to zero-point motion; this discrepancy is typical of a well-converged calculation in the local-density approximation (LDA).

The theoretical lattice constant was used in the slab supercell, which consisted of a slab 10 C(111) layers thick and a rectangular $\sqrt{3}$×1 surface unit cell 8.19 × 4.73 bohr containing two atoms (see Fig. 1). The slabs were 21 bohr thick, separated by 10 bohr of vacuum. The irreducible part of the surface Brillouin zone was sampled at six special **k** points. Only one side of the slab was relaxed, with the back side always passivated by a layer of H atoms. The asymmetric treatment was done to avoid long-range interaction between identical surface states. The artificial electric field thus produced was corrected

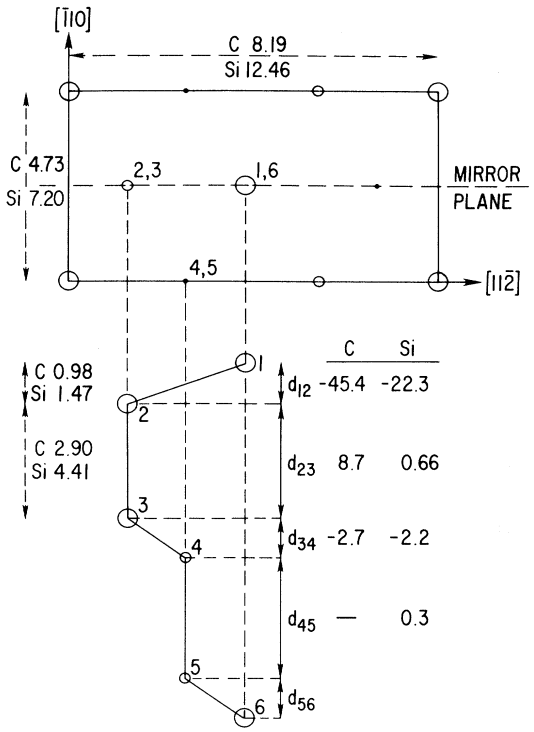

FIG. 1. Bulk geometry drawn to scale of the two-atom surface cell of C and Si used in the relaxation calculations; top view above and side view below show atoms down to the sixth layer. The new calculated changes in layer spacings for the clean relaxed C(111)-1×1 and Si(111)-1×1 surfaces are given next to the corresponding spacing in %. Smaller circles indicate atoms further from the plane of the plot (three sizes). Distances are in bohrs.

for.[10]

The first three C(111) layers and also the H layer (if present) were always relaxed, using a damped steepest-descent method[11] and imposing one mirror plane perpendicular to the slab face and parallel to the [11$\bar{2}$] direction (see Fig. 1) as a symmetry constraint. The calculation converged to a relaxed 1×1 structure for both the clean and H-covered surface. Since the clean unreconstructed surface was semimetallic, the electronic states were occupied according to a Fermi distribution. In order to stabilize convergence we use kT_{el} of 0.05 eV. The clean C(111)-1×1 system reacted very stiffly to occupation changes and easily started to oscillate in successive iterations, but was successfully converged to a final value of E within 10^{-5} eV on successive iterations.

The calculations on Si(111)-1×1 used the same two-atom cell, but used the Si parameters (Fig. 1), 10 layers of Si(111), Si pseudopotentials[9] with s and p nonlocality, a 16-Ry plane-wave cutoff (twice the value used in Ref. 4 for the primary calculation, which was supplemented then by a perturbation procedure using plane waves up to 16 Ry), six **k** points in the irreducible part of the surface Brillouin zone. Four Si layers were relaxed on one side and the other side was kept fixed. Again the electric-field correction was made.[10] The theoretical lattice constant was 10.175 bohr, 0.83% less than experiment (10.26 bohr).

III. RESULTS AND DISCUSSION

The results of calculations on C(111) are summarized in Table I. The calculations here on the clean C(111)-1×1 surface show moderate agreement[12] with Ref. 6 for the relaxation of d_{12}, 45% contraction here versus 33% in Ref. 6, but a larger discrepancy in the relaxation of d_{23}, 8.7% expansion versus 2.1% expansion. In addition to the use of a different basis set, Ref. 6 makes approximations (in the representation of the potential and in the estimation of the interatomic charge transfer involving surface atoms), which are avoided in the plane-wave calculation; Ref. 6 also uses the experimental bulk lattice constant, which is larger than the theoretical value used here that minimizes the total energy. The use of the experimental lattice constant means that the assumed lattice is under stress even before surface effects are considered, and hence changes the calculated relaxations determined by reducing the forces on surface layers to zero.

TABLE I. Relaxation results on clean and H-covered C(111)-1×1. All distances in bohrs.

Structural parameter	Bulk value[a]	Relaxed clean[a]	Bulk value[b]	Relaxed clean[b]	Relaxed H-covered[a]
$d_{C\text{-}H}$	2.119[c]				2.127
b_{12}	2.897	2.781	2.91	2.82	2.881
Δb_{12} (%)	0	−4.0	0	−3.1	−0.6
d_{12}	0.966	0.527	0.97	0.66	0.916
Δd_{12}	0	−0.439	0	−0.32	−0.050
Δd_{12} (%)	0	−45.4	0	−33.5	−5.2
d_{23}	2.897	3.148	2.91	2.98	2.923
Δd_{23}	0	0.251	0	0.06	0.026
Δd_{23} (%)	0	8.7	0	2.1	0.9
d_{34}	0.966	0.940			0.971
Δd_{34}	0	−0.026			0.005
Δd_{34} (%)	0	−2.7			0.5

[a]This work; lattice constant 6.690.
[b]Reference 6; lattice constant 6.730.
[c]Theoretical value for relaxed H on the rigid truncated bulk crystal.

TABLE II. Relaxation results on clean and H-covered Si(111)-1×1. All distances in bohrs.

Structural parameter	Bulk value[a]	Relaxed clean[a]	Bulk value[b]	Relaxed clean[b]	Relaxed H-covered[b]	Relaxed H-covered[c]
d_{Si-H}	2.90[d]		2.80[e]		2.918	2.88
b_{12}	4.406	4.308	4.441	4.32	4.40	
Δb_{12} (%)	0	−2.2	0	−2.7	−0.9	
d_{12}	1.469	1.141	1.480	1.08	1.36	
Δd_{12}	0	−0.328	0	−0.40	−0.12	−0.047
Δd_{12} (%)	0	−22.3	0	−27.2	−8.0	−3.2
d_{23}	4.406	4.435	4.441		4.38	
Δd_{23}	0	0.029	0		−0.06	
Δd_{23} (%)	0	0.66	0		−1.3	
d_{34}	1.469	1.437				
Δd_{34}	0	−0.032				
Δd_{34} (%)	0	−2.2				
d_{45}	4.406	4.419				
Δd_{45}	0	0.013				
Δd_{45} (%)	0	0.30				

[a]This work; lattice constant 10.175.
[b]Reference 4; lattice constant 10.255.
[c]Reference 14; lattice constant unknown.
[d]Theoretical value for relaxed H on the rigid truncated bulk crystal.
[e]Sum of covalent radii.

Note the deep range of the relaxation, which shows a 2.7% contraction of d_{34}. Comparison with the Si(111)-1×1 results (see Table I and Fig. 1) indicates that the relaxation probably extends significantly deeper. The relaxed clean 1×1 surface was tested for metastability by giving the relaxed structure a set of small random displacements ($\leq$0.08 bohr) and allowing the system to relax to equilibrium. The two-atom cell and the mirror plane were retained, however. In all cases the same 1×1 structure was recovered upon relaxation.

The H-terminated surface shows a drastically reduced relaxation with a contraction of d_{12} of only 5.2%, or 0.05 bohr (0.026 Å). The LEED analysis of Ref. 5 reported no relaxation, but gave no error bound and was never refined. Since even refined LEED structure analyses have error bounds of ±0.03 Å, the theory of the H-covered C(111)-1×1 surface may be considered in agreement with the LEED result. A later LEED study[13] of C(111)-1×1 agreed well with the *I-V* spectra of Ref. 5, but did not make an intensity analysis; this study stated that the surface was saturated with H.

The results of calculations on Si(111) are summarized in Table II. The relaxation of the clean Si(111)-1×1 surface may be compared with the values obtained in Ref. 4, which also used a plane-wave basis, but with a lower cutoff energy, fewer **k** points in the irreducible part of the surface Brillouin zone, fewer atomic layers, and relaxation of both sides of the slab. Reference 4 also used the experimental lattice constant rather than the theoretical value that minimizes the bulk total energy. The new calculations find a contraction of d_{12} of 22% compared to 27% in Ref. 4, and an *expansion* of d_{23} of 0.66% compared to a contraction of 1.3% in Ref. 4. We assume that in Ref. 4 the lattice is under tensile stress before surface effects are introduced and wants to contract. This is further confirmed by the results of Ref. 4 for the contraction of the top-layer spacing of the H-covered Si(111)-1×1 surface. It is 8% according to Ref. 4 and only 3.2% according to a recent calculation,[14] which is of comparable quality to that reported here.

Note that the 22% contraction is now quite close to the LEED relaxation value for the change in d_{12} found in Ref. 1 of (20.5±3.8)%; also the 0.66% expansion of d_{23} agrees with the LEED finding of tendency toward a slight expansion by about 1.5%. Note that the relaxations alternate in sign, unlike Ref. 4, and extend to the fourth spacing d_{45}, which expands 0.3%.

A test of metastability of the 1×1 structure for Si(111) was made by giving the structure small random displacements which preserved the two-atom surface cell and the mirror plane; the system returned to the 1×1 structure. A test with no mirror plane and the $2\sqrt{3}\times2$ surface cell using one special **k** point in the irreducible part of the Brillouin zone also showed a return to the 1×1 structure. However, a calculation with a two-atom surface cell with only the Γ point gave a transformation to the 2×1 chain structure. These results differ from Ref. 15 in showing that the 1×1 surface is retained with the more accurate calculation made here, whereas Ref. 15, which started with the truncated bulk 1×1 surface and used the molecular-dynamic technique, found the system evolved dynamically into the 2×1 chain structure with no apparent barrier. The present calculations used a higher cutoff energy (16 Ry versus 8 Ry) and more points in the surface Brillouin zone (six points compared to use of only the Γ point of a $\sqrt{3}\times4$ supercell, where a band splitting occurs upon relaxation to the 2×1 structure); also the calculation of Ref. 15 uses the experimental lattice constant.

IV. SUMMARY

Calculations have used the accurate plane-wave basis and pseudopotential procedure for treating the bulk and (111)-1×1 surfaces of crystalline C and Si in the diamond structure with higher cutoff energies than previous calculations to assure convergence. These calculations bring both crystals into the status of well-converged LDA calculations. Supercell calculations of the relaxations of this simplest semiconductor surface for both clean and H-covered C and for clean Si give significantly different relaxations from previous calculations. In the case of C(111)-1×1-H, which has not been calculated previously, the new small relaxation found agrees with the results of LEED studies of the diamond (111) surface, whereas the large relaxation of the clean surface does not agree, even though in the experiment the surfaces were not deliberately covered with H. In addition to the higher-energy cutoff for plane waves, differences from previous calculations arise from use of a larger number of **k** points in the surface Brillouin zone and from the use of the theoretical bulk lattice constant found in a separate well-converged bulk calculation. At this lattice constant the bulk of the lattice is not under stress before surface effects are introduced. The new Si(111)-1×1 relaxations agree very well with the LEED analysis of the impurity stabilized 1×1 surface. Exploitation of the capability of the technique used here to take account of all degrees of freedom of a system, including the nuclear positions, provides indications of the metastability of the clean C and Si (111)-1×1 relaxed surface structures. However these results are within the constraints of a surface cell of given size.

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[12] This moderate agreement between the two theoretical calculations on the clean C(111)-1×1 surface and disagreement with the LEED result was confused by an error in Table I of Ref. 7, which gave the contraction of d_{12} found in Ref. 6 as 3% instead of 33%, i.e., gave the contraction of the b_{12} bond rather than the d_{12} spacing. The same table also overlooked the refined value of $(\Delta d_{12}/d_{12})$ of 20.5% in Ref. 1.

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