

Density Functional Theory Study of the Geometry, Energetics and Reconstruction Process of Si(111) Surfaces

*Santiago D. Solares^a, Siddharth Dasgupta^{a,b}, Peter A. Schultz^c, Yong-Hoon Kim^{a,d}, Charles B. Musgrave^{a,e}
and William A. Goddard III^{a*}*

^aMaterials and Process Simulation Center, California Institute of Technology, Pasadena, CA, 91125

^bCurrent address: Center for Neuromorphic Systems Engineering, California Institute of Technology, Pasadena, CA, 91125

^cMultiscale Computational Materials Methods Department, Sandia National Laboratories, Albuquerque, NM 87185

^dCurrent address: School of Computational Sciences, Korea Institute for Advanced Study, Seoul, 130-722 Korea

^eCurrent address: Department of Chemical Engineering, Stanford University, Stanford, CA, 94305

*Author to whom correspondence should be addressed (wag@wag.caltech.edu)

Supporting Information

1. Pseudopotentials and basis sets

The pseudopotentials used in these calculations are standard norm-conserving, non-separable pseudopotentials.¹ The LDA potentials for Si and H were generated using the generalized norm-conserving pseudopotential method.² The PBE potentials were generated using Hamann's new method for pseudopotentials.³ The silicon pseudopotentials included up to $l=2$ projectors (with standard settings) and the $l=2$ potential was used as the local potential. The hydrogen atom was also treated as a pseudopotential

(rather than with a bare-core potential), with only an $l=0$ potential. Multiple tests with hydrogen atoms, H₂ molecules and water molecules verified that the energetics of the bare core hydrogen potential and the hydrogen pseudopotential are almost indistinguishable.

The basis functions are double-zeta plus polarization quality, formed from contracted Gaussians. Hence the Si- s and Si- p , and the H- s have two radial degrees of freedom, and the Si- d and H- p angular polarization have only one. The PBE basis for Si is a contracted (4s3p1d/2s2p1d) basis, the LDA Si basis is (4s4p1d/2s2p1d), and both the LDA and PBE basis sets for hydrogen are contracted (4s1p/2s1p) basis sets. This nomenclature denotes, for H for example, that four Gaussian s -functions are contracted into two independent functions, and one Gaussian p -function is used as one independent radial degree of freedom. The d -functions are made up of the five pure $l=2$ functions, i.e., the s -combination is excluded. The Gaussians and contraction coefficients for hydrogen and silicon are listed in Tables S-1 and S-2.

Table S-1: Basis set for hydrogen. The Gaussian decay constants α ($1/\text{bohr}^2$), and associated contraction coefficients c_α for the contracted Gaussian basis functions (unnormalized).

H	s-functions			p-function	
	α_s	c_α (1 st zeta)	c_α (2 nd zeta)	α_p	c_α
LDA	0.112827	0.104600	0.083940	1.20	1.0
	0.407007	0.399225	0.145755		
	1.260443	0.394750	0		
	4.553255	0.380096	0		
PBE	0.102474	0.087388	0.075281	1.10	1.0
	0.372304	0.405344	0.120939		
	1.230858	0.485455	0		
	4.783324	0.397563	0		

Table S-2: Basis set for silicon. The Gaussian decay constants α ($1/\text{bohr}^2$), and associated contraction coefficients c_α for the contracted Gaussian basis functions (unnormalized).

Si	s-functions			p-functions			d-function	
	α_s	c_α (1 st zeta)	c_α (2 nd zeta)	α_p	c_α (1 st zeta)	c_α (2 nd zeta)	α_d	c_α
LDA	0.109463	0.335647	1.0	0.077837	0.0395395	1.0	0.4604	1.0
	0.294700	0.501166	0	0.227532	0.212571	0		
	1.301011	-1.026687	0	0.565609	0.242187	0		
	2.602030	0.398914	0	1.131240	-0.174847	0		
PBE	0.104600	0.209953	1.0	0.094241	0.067616	1.0	0.45	1.0
	0.272263	0.559782	0	0.317679	0.318212	0		
	1.300508	-0.991282	0	1.561145	-0.066383	0		
	2.601030	0.334871	0					

2. Slab model calculations

Table S-3 contains the surface energy results for slab models of the 2x3H3T4 surface containing varying numbers of bulk layers, ranging from 2 to 14, and varying number of *fixed* bulk layers. All models were terminated on the bottom surface with a layer of fixed hydrogen atoms.

The results show that the surface energy calculations where all bulk layers are allowed to relax during the geometry optimization are the ones that most closely approach the value of the converged surface energy, and that six bulk layers are sufficient to obtain an accuracy better than 0.028 eV/1x1 cell. Since this convergence error is common to all models, it should not affect the relative energy differences between them.

Table S-3: Calculated surface energy (eV/1x1 cell) for the 2x3H3T4 surface using slab models with varying numbers of bulk layers and with varying numbers of fixed bulk layers. All models were terminated with a layer of fixed hydrogen atoms on the bottom surface. These results are depicted in Figure 4 of the paper.

Total bulk layers	No bulk layers fixed	2 bulk layers fixed	4 bulk layers fixed	6 bulk layers fixed
2	1.483	1.667	N/A	N/A
4	1.228	1.324	1.415	N/A
6	1.184	1.197	1.267	1.354
8	1.170	1.215	1.226	1.296
10	1.164	1.169	1.226	1.238
14	1.156	1.159	1.159	1.162

3. Comparison of PBE and LDA surface energies

Table S-4 compares the surface energies obtained using the PBE and LDA approximations for cell sizes up to 3x3. The results show that the LDA values are consistently higher than the PBE values with an average difference of 0.152.

Table S-4: Comparison of LDA and PBE surface energies for a selected group of surfaces. All energies are in eV/1x1 cell.

Surface	PBE surface energy, eV/1x1	LDA surface energy, eV/1x1 cell	LDA – PBE difference, eV/1x1 cell
1x1 relaxed	1.200	1.451	0.250
$\sqrt{3}\times\sqrt{3}\text{H3}$	1.360	1.487	0.127
$\sqrt{3}\times\sqrt{3}\text{T4}$	1.110	1.240	0.130
2x2H3	1.209	1.322	0.114

2x2T4	1.084	1.200	0.116
DAS3x3	1.070	1.241	0.172

4. Comparison of PBE DFT Si(111) surface energies to published values from empirical and semi-empirical calculations

Table S-5 compares the ab initio surface energies obtained from our PBE DFT calculations to previously reported empirical and semi-empirical results. Our results are in qualitative agreement with those of Takahashi et al.⁴ and Zhao et al.⁵, who used a modified embedded atom model and a building block energy contribution model, respectively.

Table S-5: Comparison of PBE-DFT surface energy for Si(111) surfaces with published results from empirical or semi-empirical methods. The reference energy is zero for the bulk crystal unless otherwise indicated, in which case it is the relaxed 1x1 unreconstructed surface. Energies are in eV/1x1 cell.

Surface	This work (<i>ab initio</i>)	Empirical surface energy, eV/1x1 cell				
		Takahashi et al. (1999) ⁴	Zhao et al. (1998) ⁵	Mercer and Chou (1993) ⁶	Khor and Das Sarma (1989) ⁷	Qian and Chadi (1987) ^{8,9}
Method	PBE-DFT	MEAM ^a	BBEC ^b	TB ^c	MD ^d	TB ^c
1x1 unreaxed	1.224			1.131	0 (ref.) ^e	0 (ref.) ^e
1x1 relaxed	1.200			1.1	-0.17	-0.17
√3x√3H3 hex.	1.353				-0.075	
√3x√3T4 hex.	1.102			0.860 - 1.338	-0.285	
2x2H3 hex.	1.209				-0.20	
2x2T4 hex.	1.083			0.790 - 1.198	-0.25	
2x2H3 rect.	1.264				-0.166	
2x2T4 rect.	1.085					
2x3H3T4	1.184					

C2x8	1.184			0.780 - 1.189		-0.180
DAS3x3	1.070	1.243	1.196		-0.326	
DAS5x5	1.048	1.211	1.168	0.729 – 1.143	-0.344	-0.395
DAS7x7	1.044	1.206	1.153	0.728 – 1.138	-0.335	-0.403
DAS9x9	1.055	1.226	1.164		-0.325	-0.155

^aModified embedded atom model

^bBuilding block energy contributions

^cTight binding model

^dMolecular dynamics

^eAbsolute energies not provided

5. Spin states

Table S-6 contains the calculated high-spin surface energies for non-DAS surface structures. The results show that for the 1x1, $\sqrt{3}\times\sqrt{3}$ H3 and $\sqrt{3}\times\sqrt{3}$ T4 surfaces, the lowest energy state has a net spin of one. For all other non-DAS structures the lowest energy state has no net spin. Tables S-7, S-8 and S-9 contain the calculated surface energies for the DAS 3x3, DAS 5x5 and DAS 7x7 surfaces for different numbers of unpaired electrons (spin polarization), including zero. All models contained six bulk layers and were terminated with a layer of fixed hydrogen atoms on the bottom surface. The lowest surface energy was obtained for spin zero and increased monotonically with increasing spin polarization. Figures S-1 and S-2 depict the results of tables S-7 and S-9 (the results of table S-8 are shown graphically in Figure 5 of the paper).

Table S-6: Calculated high-spin surface energy for non-DAS surface structures with respect to the zero spin state.

Surface	Spin Polarization	Surface energy, eV/1x1 cell
1x1 unrelaxed	1	-0.129
1x1 relaxed	1	-0.106

$\sqrt{3}\times\sqrt{3}\text{H3 hex.}$	1	-0.007
$\sqrt{3}\times\sqrt{3}\text{T4 hex.}$	1	-0.008
2x2H3 hex.	2	0.012
2x2T4 hex.	2	0.068
2x2H3 rect.	2	-0.002
2x2T4 rect.	2	0.051
2x3H3T4	2	0.008
c2x8	4	0.001

Table S-7: Calculated surface energy for the DAS 3x3 surface as a function of the spin polarization, with respect to the singlet state. These results are shown graphically in Figure S-1.

Spin polarization	Surface energy, eV/1x1 cell
0	0
1	0.011
2	0.019

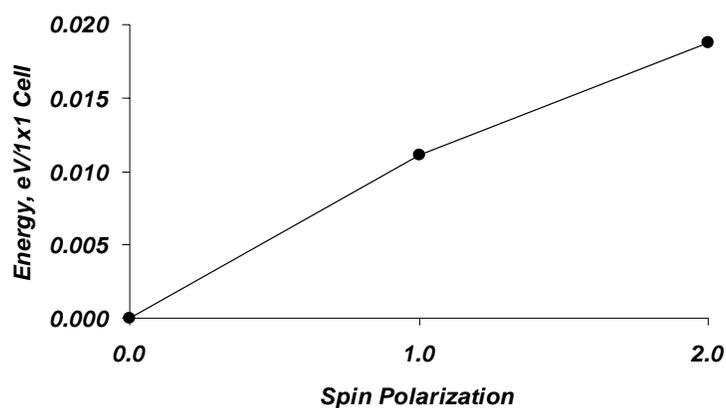


Figure S-1. Calculated surface energy of the DAS 3x3 surface as a function of the spin polarization, with respect to the singlet state (Table S-7). Note: the DAS 3x3 surface contains 2 dangling bonds.

Table S-8: Calculated surface energy for the DAS 5x5 surface as a function of the spin polarization, with respect to the singlet state. These results are shown graphically in Figure 6 of the paper.

Spin polarization	Relative surface energy, eV/1x1 cell
0	0
1	$< 10^{-3}$
2	0.001
3	0.003
4	0.011
5	0.013
8	0.029

Table S-9: Calculated surface energy for the DAS 7x7 surface as a function of the spin polarization, with respect to the singlet state. These results are shown graphically in Figure S-2.

Spin polarization	Relative surface energy, eV/1x1 cell
0	0
1	$< 10^{-3}$
2	$< 10^{-3}$
3	$< 10^{-3}$
4	$< 10^{-3}$
5	0.001
19	0.029

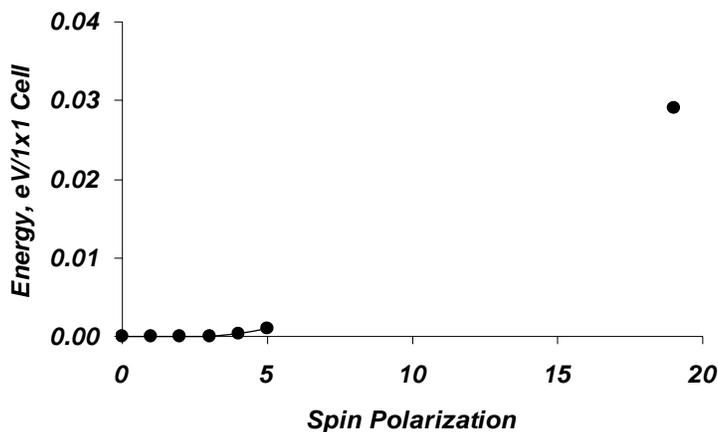


Figure S-2: Calculated surface energy of the DAS 7x7 surface as a function of the spin polarization, with respect to the singlet state (table S-9). Note: the DAS 7x7 surface contains 19 dangling bonds.

6. Comparison of 2x2 hexagonal and rectangular surfaces

Tables S-10 and S-11 provide a comparison of the surface energy, sub-surface strain energy and adatom snap bond energy (as defined in section 4.2 of the paper), and adatom geometry for hexagonal and rectangular 2x2H3 and 2x2T4 surfaces. The results show that the surface energy is significantly different between the hexagonal and rectangular structures for the 2x2H3 surface, but not for the 2x2T4 surface. The surface energy of the 2x2H3 surface is ~ 0.22 eV/2x2 cell higher for the rectangular surface, primarily due to lower adatom bond energy (Table S-10). A Mulliken populations analysis of these surfaces (Figures S-3 and S-4) shows that there is significant charge separation in both cases, but that the geometry of the hexagonal cell allows this separation to remain local (thus providing an overall uniform charge distribution when many cells are considered), while the rectangular cell exhibits charge separation between infinite parallel lines in the green (3rd) layer (again considering an infinite number of unit cells), with non-uniform charge distribution around the 2nd layer dangling bond atoms (brown), thus leading to a less favorable energy. Figures S-5 and S-6 show that charge separation also takes place for the 2x2T4 rectangular surface in a

similar way, but that the charge distribution remains more uniform in the green layer (except for the green atom directly below the adatom). The adatom in the 2x2T4 rectangular surface can be stabilized by the 3rd layer (green) atom directly below it, which allows the 3rd layer atoms surrounding a 2nd layer dangling bond atom (brown) to all have the same charge and provide a more uniform charge distribution, similar to that of the hexagonal surface, leading to a negligible energy difference between the two surface structures.

Table S-10: 2x2H3 hexagonal and rectangular electronic structure and geometry calculations. All energies are in eV per 2x2 unit cell.

	HEX	RECT	RECT – HEX difference
Surface energy	4.838	5.058	0.220
Surface strain energy (below adatom)	0.883	0.804	-0.079
Stabilization due to adatom snap bond energy	-6.399	-6.100	0.299
Adatom bond angle, degrees	85.4	85.5	0.1
Adatom bond length	2.61	2.60	-0.01

Table S-11: 2x2T4 hexagonal and rectangular electronic structure and geometry calculations. All energies are in eV per 2x2 unit cell.

	HEX	RECT	RECT – HEX difference
Surface energy	4.333	4.341	0.008
Surface strain energy (below adatom)	0.798	0.923	0.125
Stabilization due to adatom snap bond energy	-6.819	-6.936	-0.117
Adatom bond angle, degrees	94.7	94.1	-0.6
Adatom bond length	2.49	2.47	-0.02

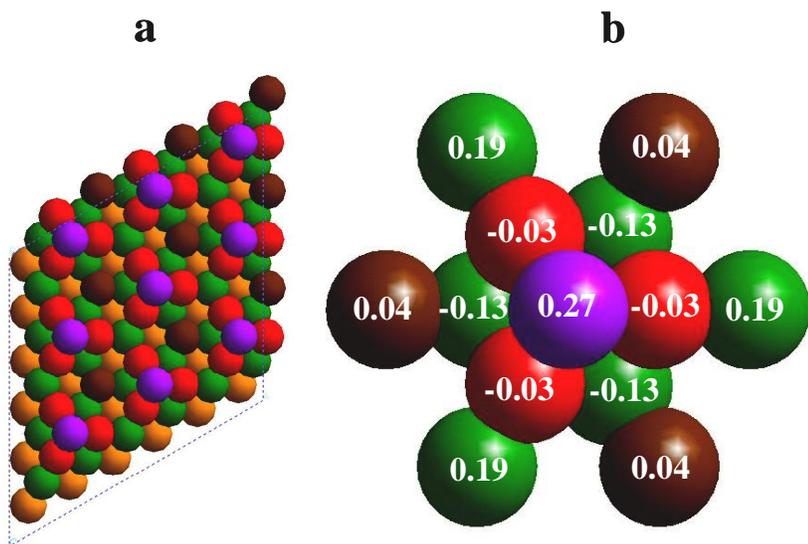


Figure S-3. 2x2H3 hexagonal surface partial atomic charges from Mulliken populations analysis. The results show significant charge separation in the unit cell, but the hexagonal symmetry allows the overall charge distribution to be uniform when large surface regions are considered.

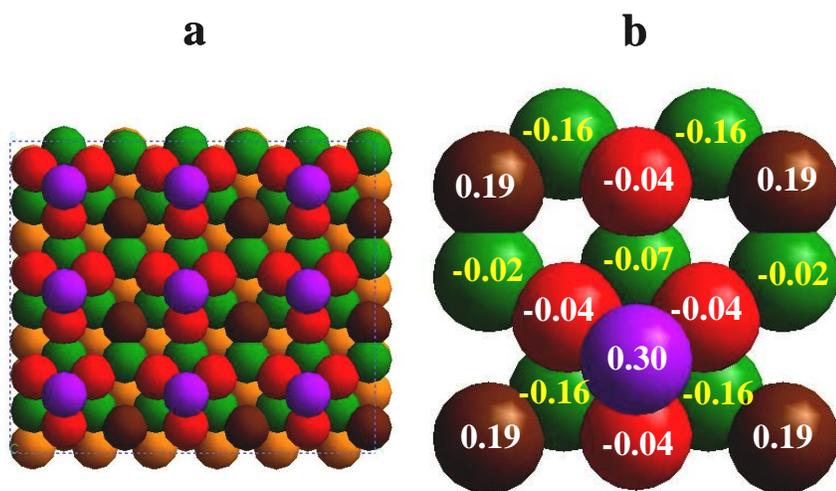


Figure S-4. 2x2H3 rectangular surface partial atomic charges from Mulliken populations. The results indicate that charge separation takes place in the 3rd layer (green with charge values highlighted in yellow) in a non-uniform manner, leading to dipoles between infinite parallel lines oriented with the size of the unit cell. This surface also has uneven charge distribution around the 2nd layer dangling bond atoms (brown).

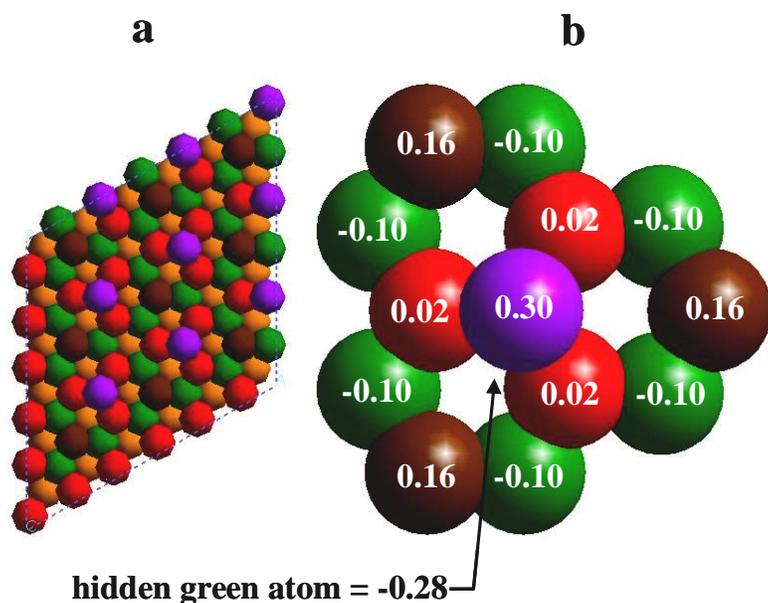


Figure S-5. 2x2T4 hexagonal surface partial atomic charges from Mulliken populations analysis. As with the 2x2H3 hexagonal surface, this structure shows significant charge separation in the unit cell, but the cell symmetry allows the overall charge distribution to be uniform when large surface regions are considered.

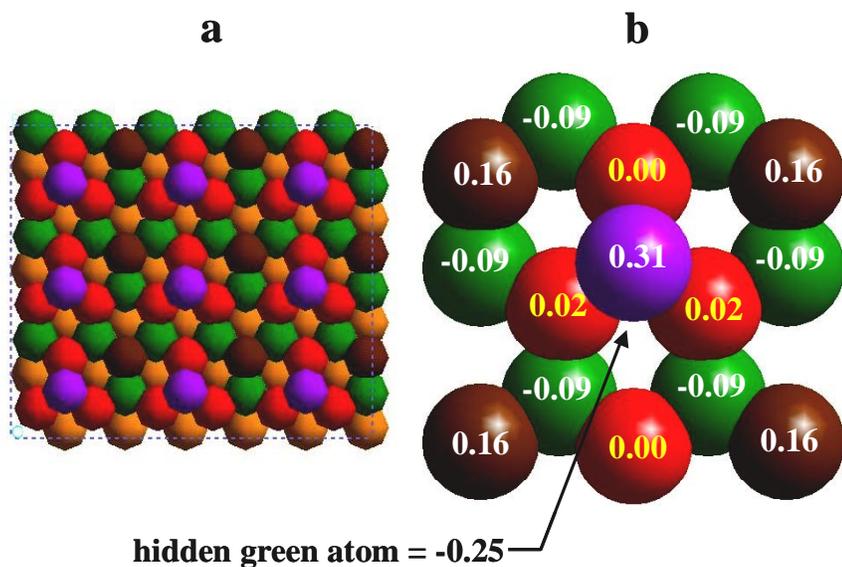


Figure S-6. 2x2T4 rectangular surface partial atomic charges from Mulliken populations analysis. The results show a nearly uniform charge distribution in the 2nd layer (red with charges highlighted in yellow), and also in the green layer (except for the atom directly below the adatom).

8. References

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