Importance of bulk states for the electronic structure of semiconductor surfaces: implications for finite slabs

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Abstract

We investigate the influence of slab thickness on the electronic structure of the Si(1 0 0)-p(2 × 2) surface in density functional theory (DFT) calculations, considering both density of states and band structure. Our calculations, with slab thicknesses of up to 78 atomic layers, reveal that the slab thickness profoundly affects the surface band structure, particularly the dangling bond states of the silicon dimers near the Fermi level. We find that, to precisely reproduce the surface bands, the slab thickness needs to be large enough to completely converge the bulk bands in the slab. In the case of the Si(1 0 0) surface, the dispersion features of the surface bands, such as the band shape and width, converge when the slab thickness is larger than 30 layers. Complete convergence of both the surface and bulk bands in the slab is only achieved when the slab thickness is greater than 60 layers.

Keywords: density functional theory, silicon, surface state, bulk state, slab thickness, band structure

(Some figures may appear in colour only in the online journal)

1. Introduction

Semiconductor surfaces are of enormous importance both industrially, as the basis of the microelectronics industry, and scientifically, where they form the basis for studies of diffusion, growth and electronic structure. Moreover, recently a number of proposals for quantum information implementations based on isolated states in or near semiconductor surfaces have emerged [1]. In light of this, it is vital that our understanding of their atomic and electronic structure is as accurate and detailed as possible. We demonstrate in this paper that both the band gap and the character of the valence band depend strongly on the thickness of slabs used to model the system, and find that the slabs used in most calculations are much too small to describe the electronic structure of Si(100), the most common surface in industry.

Density functional theory (DFT) has become the standard approach to model the atomic and electronic structures of semiconductor surfaces. Although it is known to underestimate the band gap of solids, DFT generally reproduces the density of states (DOS) and band structure accurately. A surface is usually modeled by using a supercell consisting of a slab with two surfaces and a vacuum region. Since this approach gives a non-periodic system perpendicular to the surface (z direction), the accuracy of the resulting electronic structure will depend on the slab thickness. In the case of the Ge(100) surface, which bears a very similar structure to Si(100), the influence of slab thickness on the top of the valence band has...
been discussed in detail [2–5]. Some other physical properties, such as surface electronic structure [6], dielectric function [7], chemical reactivity [5], and transport properties [8], sensitively vary with cell size and slab thickness. Since recent improvements to experimental techniques allow measurements to be made with high energy resolution (∼meV), slab thickness is likely to become a key parameter in determining energy precision in DFT modeling.

However, it is still unclear how thick a slab is needed to reliably produce the electronic structure of a semiconductor surface; one study [5] suggested that slab thickness was unimportant, while another study of the basic (2 × 1) reconstruction [9] suggested, without giving detailed analysis, that at least 30 layers are required. Recently, we found that surprisingly thick slabs were required to obtain convergence of the electronic structure of silicon. In this paper, we report the critical slab thicknesses in the DFT calculation required to reliably produce the electronic structure of the Si(100) surface in terms of DOS and band structure.

2. Computational method

DFT calculations were carried out using the VASP code with a plane wave basis set [13, 14]. We employed PAW and the GGA PBE exchange correlation functional [15]. The Si(100)-p(2 × 2) surface layer was modeled using supercells consisting of a Si slab and vacuum layer of approximately 15 Å thick (this vacuum thickness was carefully converged). The bottom layer was terminated with hydrogen atoms and the bottom layer and hydrogen layer were fixed: this termination is convenient (as it allows small unit cells than a symmetrical termination) but does not change the resulting surface band structure, as shown in figure A1. Moreover, as the system is not polar, and the bottom surface is inert, no dipole corrections are required: we show a plot of the potential in the slab against depth in figure A2, which demonstrates that there is no field across the slab. For total energies and DOS, the tetrahedron method was applied [16]. Full details are given below.

2.1. Parameters used

We tested the influence of slab thickness between 6 and 78 atomic layers (L) on the electronic structure of the slab, in particular the dangling bond (DB) states. To ensure full convergence with respect to the basis set, we employed a plane wave cutoff energy of 312.5 eV throughout this study. Structural relaxation was done with Brillouin zone (BZ) sampling of 8 × 8 × 1 Monkhorst-Pack k-point mesh until the forces on each atom reached to below 0.01 eV Å−1. The relaxed lattice constant was a0 = 5.466 Å, which is slightly larger than experimental value (5.43 Å). For the total energies and DOS plots, the BZ sampling was increased to 22 × 22 × 1.

2.2. Surface energies

Surface energies were calculated using both a reconstructed slab and a fully hydrogen terminated slab. The total energies were calculated for the p(2 × 2) slabs (the top was dimerised, the bottom was terminated with hydrogen) and hydrogen terminated slabs (both surfaces were terminated with hydrogen, using the same structure as the slab base) for thicknesses of 6L, 14L, 22L, 30L, 38L, 62L and 78L. All simulation cell sizes were constant (7.731 × 7.731 × 121.914 Å3). As the slab thickness was varied, so the amount of vacuum space also varied. Each p(2 × 2) slab was relaxed with a 8 × 8 × 1 k-point sampling, then the total energy was calculated with a 22 × 22 × 1 k-point sampling, with the tetrahedron method. By contrast, each hydrogen terminated slab was unrelaxed. The total energy was calculated with a 22 × 22 × 1 k-point sampling, again using the tetrahedron method. For all these calculations, the plane wave cutoff was increased to 600 eV.

To find a bulk silicon atomic energy, the total energy was calculated for a periodic 2 × 2 × 4 cell (16 Si atoms, bulk calculation), which was then divided by 16 to give the energy of a Si atom.

The surface energy was found by subtracting the energy for hydrogen termination (for one surface) and the energy of the bulk silicon atoms from the energy for the p(2 × 2) cell, divided by 2 to give eV/dimer.

2.3. Band structure

For band structures and densities of states, we performed a static calculation with 22 × 22 × 1 k-point sampling to produce a charge density (4 × 4 × 1 for the hybrid calculation).

To find a consistent energy zero for comparison between different slab thicknesses, all eigenvalues were shifted relative to the potential at the Si core, averaged over the first five layers from the surface. They were then all shifted by the same amount, so that the top of the valence band in the thickest slab (78L in figure 2 and 38L in figure 4) is zero.

2.4. Bulk band gap for a slab

The bulk band gap of a slab was found by considering the projected DOS (PDOS) of Si atoms in the middle layer of the slab. We found that it converged for 62L (interestingly,
when considering a periodic bulk two atom cell, we required a $k$-point mesh $31 \times 31 \times 31$, giving equivalent sampling).

### 2.5. Hybrid functional band structure

For the hybrid functional calculations, owing to the large computational cost, the charge density was found self-consistently using a $4 \times 4 \times 1$ $k$-point mesh.

## 3. Results and discussion

To start, we tested the influence of slab thickness on three key properties: the Si dimer bond length and buckling angle; and the surface energy. The structural properties are relatively weakly dependent on the slab thickness (table 1): the bond length and buckling angle both converge at 14 L. Performing calculations with a slab of less than 14 L is probably acceptable for the study of surface geometry, but will require some care. On the other hand, surface energy convergence is only obtained when the slab thickness is greater than 22 L, with the surface energy for a 14 L thick slab 114 meV per dimer higher than the converged value. We recall the discussion of the relative stability of the $c(4 \times 2)$ and $p(2 \times 2)$ reconstructions [10, 17, 18], which involved energy differences of a few meV, for which the error in surface energy, even at 14 L, is far from negligible. For calculations considering reaction, adsorption, or diffusion at the Si(1 0 0) surface, slab thickness needs to be tested and chosen carefully.

We now turn to the key electronic structure: DOS and the band gap, on which the slab thickness has a profound effect. Figure 1(a) shows the partial charge densities for each eigenstate at different $k$-points in the Brillouin zone (BZ) to assign the bands.

![Figure 1](image_url)

**Figure 1.** (a) PDOS of Si dimer calculated with Si(1 0 0) $p(2 \times 2)$ slabs. All energies are shifted so that the bottom of the potential of Si atoms averaged over the top five layer of each slab has the same value. (b) Surface (circle) and bulk (square) band gaps as a function of the slab thickness. The bulk band gap values were found from PDOS of the middle layer in each slab. The GGA bulk band gap value obtained by a converged bulk calculation is indicated by a broken line.

The second major effect of the increasing slab thickness is a reduction of the surface band gap. Figure 1(b) shows the surface and bulk band gaps (gap at the center of the slab) as a function of the slab thickness. The reduction of the surface band gap with slab thickness is strongly correlated with the reduction of the bulk band gap, and the development of the bulk bands. When the slab thickness is 38 L or greater, the bottom of the $\pi_1^*$ state overlaps with the top of the valence band, which has become a bulk state, and the surface band gap closes. It is perhaps not surprising that there is some dependence of gap on slab thickness, as a slab will behave as a form of quantum well; a thin slab will strongly confine its eigenstates, giving a larger band gap [20]. In our work, we calculated the fully converged bulk band gap of silicon to be $\sim 0.607$ eV, which is only reached when a slab calculation with 62 L or more is performed.

In order to gain further insights into the influence of the slab thickness on the electronic structure, we have examined the band structure of the Si(1 0 0)- $p(2 \times 2)$ surface with various slab thicknesses. Figure 2 shows valence band diagrams near the Fermi level along the dimer row direction ($\Gamma - \frac{1}{2}J\bar{T} - \frac{1}{2}J\bar{T}$ line). We plotted the partial charge densities for each eigenstate at different $k$-points in the Brillouin zone (BZ) to assign
the character (bulk, DB, back-bond) to the band as it moves through the BZ. Typical isosurfaces of the charge density for the 78L slab are shown in figure 3 and in figure A4. The major surface states are the DB states \( \pi_1 \) and \( \pi_2 \) (red open circles). Both the \( \pi_1 \) and \( \pi_2 \) bands show intense charge densities on the Si dimer atoms, though the decay into the bulk depends strongly on the band and the \( k \)-point. The \( \pi_1 \) state bears charges localized on the up atom of the Si dimer, while the \( \pi_2 \) state has most of charges on the up atom and some extended onto the down atom as well.

We observe that the band shape and width of \( \pi_1 \) drastically changes with the increase of the slab thickness, while those of \( \pi_2 \) are only slightly changed by the slab thickness. The surface band maximum (SBM) appears half way along the \( \Gamma - \frac{1}{2} \Gamma \) line for 6L. Correspondingly, the \( \pi_1 \) band width is only 0.13 eV. With increasing thickness, the SBM moves toward the \( \Gamma \) point and the band width also widens. Eventually, the SBM reaches to the \( \Gamma \) point when the slab thickness is greater than 20L and the band width converges, to approximately 0.40 eV, for thickness greater than 30L (see table 1).
The convergence of the surface states relies on more than just slab thickness: it also requires precise reproduction of the bulk electronic structure in the slab. In figure 2, the eigenstates with no charge density on the Si dimers (i.e. pure bulk bands) are plotted with black dots. For comparison, conventional bulk bands, calculated at $k_z = 0$ with a repeated cell consisting of four Si atoms, are superimposed as thick gray curves and labeled as $\Sigma_1$, $\Sigma_1'$, and $\Sigma_2$. As might be expected, the 6 L slab calculation does not produce any bulk bands near the surface bands (figure 2(a)). With increasing slab thickness, the bulk bands develop, and the VBM becomes dominated by a bulk state, instead of the DB state, when the slab thickness is greater than 30 L. Full agreement between bulk valence bands in slab and bulk calculations is only obtained for a slab thickness of 60 L or more. This thickness matches with that of the slab calculation in which the bulk band gap agrees with the value of a repeated cell bulk calculation, as seen in figure 1(b).
In a slab calculation, where the electronic states in the sample have no periodicity perpendicular to the surface and Bloch’s theorem does not apply, extra bands appear and develop with increasing slab thickness (in contrast to a bulk calculation which requires increasing BZ sampling for convergence). The increase in number of bands and the development of their shape is seen clearly in figure 2. Some of the bands that appear with increasing thickness have charge density on both the Si dimers and the bulk atoms, as seen in figure 3(b). These bands are hybridized between surface and bulk states. These hybridizations are prominent for the $\pi$ band, particularly near the $\Gamma$ point, where the surface states extend into the bulk. As the slab thickness, and hence number of additional bands, becomes greater, more band mixing occurs: a thicker slab shows a larger number of hybridized bands. This causes the charge density of the $\pi$ band near the $\Gamma$ point to redistribute into the slab, resulting in an apparent absence of the $\pi$ band near the $\Gamma$ point, while the same band near the $\frac{1}{2}J\Gamma$ point, and the $\pi_2$ band across the BZ, are well localized at the surface regardless of slab thickness (see figure A5).

To investigate what causes this change in surface band energy and shape, we simplified the problem. We calculated bands for $2 \times 1$ symmetric (flat) and asymmetric (buckled) dimers with 6L, 14L and 38L slabs. The major effect that causes the surface band to change shape is hybridization with the bulk bands. The $\pi$ band of the symmetric dimer in figures 4(a), (c) and (e) only slightly changes its shape near the $\Gamma$ point even though the slab thickness increases from 6L to 38L: since the $\pi$ band is situated in the bulk band gap, the hybridization is weak. On the other hand, the $\pi$ band of the asymmetric dimer changes its shape with slab thickness and this is not due to any structural change, but mainly due to the band mixing between the $\pi$ and the bulk bands. The increase in slab thickness develops the bulk bands and raises their energy predominantly around the $\Gamma$ point; simultaneously, the hybridization lifts the $\pi$ band’s energy near the $\Gamma$ point as well.

These hybridizations are clearest between the $\Gamma$ point and a point halfway to the $J$ point. This tendency is kept when the bands are folded and transformed in the surface Brillouin zone by switching the surface cell from $2 \times 1$ periodicity to the $p(2 \times 2)$. Correspondingly, the $\pi_2$ band, which originates from the second half of the $\pi$ band in the smaller cell, does not change in its shape with slab thickness. Hybridization between surface and bulk bands is inevitable in slab calculations, so a precise calculation of surface states will require the convergence of bulk states. It is interesting to note that hybridized bands associated with bulk states, back bond and dimer bond are also found in figure 2.

We also note that the change in the shape of the DB band is partly caused by surface state confinement in a thin slab. Surface states decay into the bulk, with different decay lengths. For a slab that is not thick enough for the wave function of the surface state to decay sufficiently, its energy will shift due to the well known quantum confinement effect. We can see in figure A5 that the tails of the $\pi_1$ band in a 38L slab spread at least 20 Å into the bulk. Thin slabs, such as the 6L and 14L also shown in figure A5, are too thin to produce the electronic structure precisely.

We have also examined the effect of slab thickness on the band structure along other high symmetry lines in the BZ. A comparison of band structures of Si(100) between 10L and 38L is displayed in figure 5. With a slab that is 10L or thinner, as is typically used to model the Si(100) surface, the SBM tends to appear in the $J = \frac{1}{2}KJ$ line (figure 5(a)). This result can be found in previous reports [10–12, 21]. However, the SBM is actually located at the $\Gamma$ point in converged band structures calculated with a sufficiently thick slab (figure 5(b)). This agrees with the observations of direct transition of the surface band gap [22, 23].

Due to the narrowing of the bulk band gap with the slab thickness, the bottom of the unoccupied DB band ($\pi_1^*$) overlaps the top of the valence band when the slab thickness is greater than 30 layers. It might be that this overlap affects the development of the bands, so to check this, we carried out a band calculation for the 38L slab with a screened hybrid exchange-correlation functional (HSE06) [24–26]. These functionals generally alleviate the standard DFT problem with band gaps that are too small. The results are shown in figure 5(c), where it is clear that the band gap has opened. There are no other differences in the band structure between the conventional and hybrid functional calculations. Our discussions, based on standard DFT, are therefore valid and unaffected by the band gap.

4. Conclusion

We have shown that DFT calculations for the electronic structure of the Si(100) surface require a much thicker slab than is conventionally used. A study for simple geometrical structures will be adequate with a thin slab of around 15 layers, though 20-25 layers are required for convergence of the surface energy. Treatment of the precise surface electronic structure needs a slab of at least 30 layers, while the full convergence of both surface and bulk electronic structure requires a slab of 60 layers or more. The reason that such thick slabs are needed lies in the fact that penetration of some surface states into the semiconductor extends several nanometers from the surface and accordingly hybridizations between surface and bulk states inevitably occur. Thus, a precise calculation for a surface state simultaneously requires the precise calculation of bulk states in the slab. The source of the dependence of the penetration length on position in the BZ is still an open question. It is important to determine which properties need to be calculated and choose an appropriate slab size. With advances in experimental techniques, the desired accuracy from DFT modeling has reached an energy resolution in the meV range, suggesting that calculations should be performed with a significantly thicker slab than is the norm.

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Appendix. Extra figures and tables

The figures below are not central to our study, but add extra detail in some areas, and are included for completeness and information.

A.1. Slab termination

Figure A1. Band structure calculated with: (a) 38 layers and hydrogen termination of the bottom surface; (b) 76 layers and a clean Si(001) surface on both sides of the slab. Note that the number of bands has doubled with the symmetric slab as the number of atoms has doubled, but that the overall band structure is essentially identical.

A.2. Experimental data

Figure A2. Electrostatic potential in the slab as a function of z coordinate, averaged in x and y, for both six and fourteen layer slabs. Note that there is no field across the slabs.

A.3. Spread of bands into slab

Figure A3. Tunneling spectrum (black) and DFT–PDOS (red) of Si dimer on the Si(100) surface. Tunneling spectrum was obtained at 78 K with a setpoint of $V_s = +1.5$ and $I = 3.5$ nA. PDOS was obtained with a 62L slab.

Figure A4. Isosurface charge density distributions of eigenstates indicated by labels in the band diagram of Si(100)- p(2 × 2)-78L. Isosurface value is $1 \times 10^{-3}$ e Å$^{-3}$. 

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Figure A5. Distribution and integration of charge density for the $\pi_1$ and $\pi_2$ bands as a function of $z$ position in slabs with 6, 14 and 38 layers. Charge densities are selected from the numbered $k$ points in the band diagrams shown at the top. The integrated value of the charge is set to be two in the vacuum region (for a fully occupied band). The origin in $z$ position corresponds to the upper atom of the Si dimer. Note that the charge distribution of the $\pi_1$ band in the 38L slab varies with $k$-point and that the charge spreads more than 20 Å (corresponding to 14L of silicon) near the $\Gamma$ point. A surface state with this extent will hybridize with the bulk states easily, resulting in a change of shape of the band. Also, for thin slabs such as 6L and 14L, these charges are compressed by the narrow slab size, causing a shift of energy. On the other hand, the $\pi_2$ band tends to localize in the surface across the BZ, which results in weak hybridization with bulk bands. This band hardly changes its shape with slab thickness.

References

[1] Veldhorst M et al 2015 Nature 526 410
[2] Radny M W, Shah G A, Schofield S R, Smith P V and Curson N J 2008 Phys. Rev. Lett. 100 246807
[3] Yan B, Yam C, da Rosa A L and Frauenheim T 2009 Phys. Rev. Lett. 103 189701
[4] Radny M W, Shah G A, Schofield S R, Smith P V and Curson N J 2009 Phys. Rev. Lett. 103 189702
[5] Shah G A, Radny M W, Smith P V and Schofield S R 2012 J. Phys. Chem. C 116 6615
[6] Smeu M, Guo H, Ji W and Wolkow R A 2012 Phys. Rev. B 85 195315
[7] Vazhappilly T and Micha D A 2014 J. Phys. Chem. C 118 4429
[8] Martinez A, Kalna K, Shugur P V, Barker J R and Asenov A 2009 IEEE Trans. Nanotechnol. 8 159
[9] Shah G A, Radny M W, Smith P V and Schofield S R 2012 J. Phys. Chem. C 116 6615
[10] Fritsch J and Pavone P 1995 Surf. Sci. 344 159
[11] Zhu Z, Shima N and Tsukada M 1989 Phys. Rev. B 40 11868
[12] Ramstad A, Brocks G and Kelly P J 1995 Phys. Rev. B 51 14504
[13] Kresse G and Hafner J 1993 Phys. Rev. B 47 558
[14] Kresse G and Furthmuller J 1996 Phys. Rev. B 54 11169
[15] Perdew J P, Burke K and Ernzerhof M 1996 Phys. Rev. Lett. 77 3865
[16] Blöchl P E, Jepsen O and Andersen O K 1994 Phys. Rev. B 49 16223
[17] Inoue K, Morikawa Y, Terakura K and Nakayama M 1994 Phys. Rev. B 49 14774
[18] Nakamura J and Natori A 2005 Phys. Rev. B 71 113303
[19] Okada H, Fujimoto Y, Endo K, Hirose K and Mori Y 2001 Phys. Rev. B 63 195324
[20] Delley B and Steigmeier E F 1995 Appl. Phys. Lett. 67 2370
[21] Zhou M, Liu Z, Wang Z, Bai Z, Feng Y, Lagally M G and Liu F 2013 Phys. Rev. Lett. 111 246801
[22] Goldmann A, Koke P, Mönch W, Wolfgarten G and Pollmann J 1986 Surf. Sci. 169 438
[23] Enta Y, Kinoshita T, Suzuki S and Kono S 1987 Phys. Rev. B 36 9801
[24] Heyd J, Scuseria G E and Ernzerhof M 2003 J. Chem. Phys. 118 8207
[25] Heyd J and Scuseria G E 2004 J. Chem. Phys. 121 1187
[26] Heyd J, Scuseria G E and Ernzerhof M 2006 J. Chem. Phys. 124 219906