Appendix A

A-1 Convergence Test for Bulk Si

The calculations in this work are performed using the full-potential augmented plane wave plus local orbital method (Sec. 2.5.1 & 2.5.2) as implemented in WIEN2k computer code (cf. Sec. 2.8).

In order to obtain adequate accurate results and save as well computer time, one should first optimize the parameters which have a significant effect on the results. Here we present the convergence test for parameter which were used in the bulk Si and Si(001) surface calculations.

The main parameters which should de determined are the energy cutoff for the plane waves and the number of **k**-points in the irreducible part of the first Brillouin zone (1 BZ). In the surface calculations, additionally one needs to test the vacuum thickness and number of the layers in the slab. As it discused in Sec. 2.7, the surfaces of slabs should not have interaction with each other through the vacuum or the slab. On the other hand, the vacuum should not be very thick as this would make the calculations slow.

The calculations are done with the lattice constant of 5.47 Å for Si. The APW basis set is taken as follows: $R_{\mathrm{Si}}^{\mathrm{MT}}$ = 2.1 bohr, the maximum number of angular mometa for the wave function inside the muffin tin spheres up to $l_{\mathrm{max}}^{\mathrm{wf}}$ = 12. The results for the convergence test of the cohesive energy of Si bulk are shown in Fig. A-1.

Facilitate the comparison between plots, we compare cohesive energies. The energy of Si-atom is calculated in such way that we determine the total energy of and a single atom in a big box in size of $(20 \times 20 \times 20)$ bohr, for one **k**-point in the 1BZ and for a sufficiently big energy cutoff (here we took 16.4 [Ry]). In contrary to bulk, the calculation for the free atom is very slow which is due to the large size of the box which increases the size of the interstitial region.

We compare results for the **k**-point set of $(5\times5\times5)$, $(6\times6\times6)$, $(7\times7\times7)$, $(8\times8\times8)$ and $(10\times10\times10)$ and as well as for RK_{max} from 6 to 8.5 (bohr.Ry$^{1/2}$) which corresponds to E_{cut}^{pw} from 8 to 16.4 [Ry].

Finally, a (8×8×8) Monkhorst-Pack grid in the Brillouin-zone which corresponds to 29 **k**-points in the irreducible part of the Brillouin-zone and the energy cutoff of 12.8 [Ry] ($i.e.$ RK_{max} = 7.5 (bohr.Ry$^{1/2}$)) are chosen for bulk Si calculations. The differences in the cohesive energy for calculations using a higher number of **k**-points and larger E_{cut}^{pw} than above are smaller than 3 meV / atom.

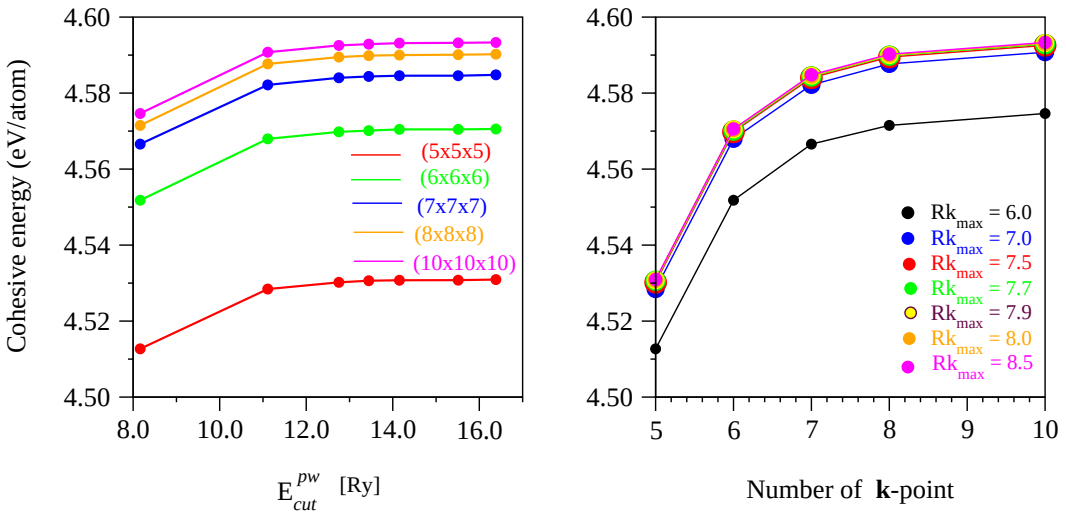

Fig. A-1: The cohesive energy as a function of (a) the cutoff of wave function, (b) the number of **k**-points in the 1BZ.

A-2 Convergence Test for The Si(001) Surface

The surface calculations are performed using a supercell containing a slab with inversion symmetry. The slab is oriented in *z* direction. The atoms in the two middle Si-layers are fixed at their bulk positions. All atoms in the remaining top and bottom layers are allowed to relax in each of the three directions (*x*,*y*,*z*). The geometry is relaxed until the residual forces on any atom are smaller than 30 meV / Å.

Before starting with the surface calculations, we perform tests concerning the energy cutoff, the number of **k**-points in the irreducible part of the first Brillouin zone (1 BZ), the vacuum thickness and the number of layers in the slab for an unreconstructed surface to determine the optimal parameters needed for the subsequent calculations. The values used for any of these parameters have a significant effect on the results.

Some details of the mentioned tests are as follows.

The convergence of the surface free energy (see Eq. 4.1) with respect to the plane wave energy cutoff, E_{cut}^{pw} is shown in Fig. A-2 (a) for the unrelaxed surface. In order to calculate the surface energy for each calculation, the energy values for both surface and bulk Si are taken using the same E_{cut}^{pw}. Choosing an energy cutoff of 13.8 Ry ensures an accuracy of about 0.6 meV / Å^2 . The number of **k**-points needed for an accuracy of 0.7 meV / Å , corresponds to a $(8 \times 8 \times 1)$ Monkhorst-Pack grid in a (1×1) surface unit cell. To obtain the bulk cohesive energy of silicon, a (8×8×8) **k**-point set is used. The dependence of the surface free energy on the **k**-points is displayed in Fig. A-2 (b).

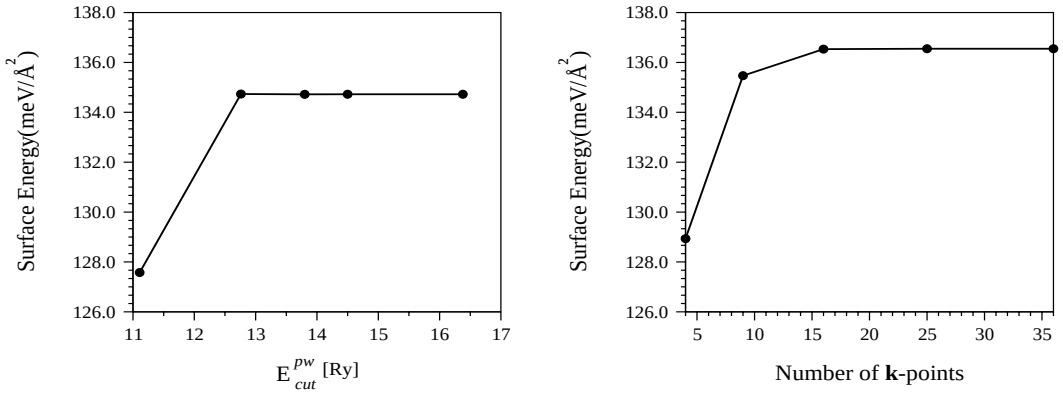

Fig. A-2: The surface free energy versus (a) the energy cutoff, (b) the number of **k**-points in the 1BZ for a slab of six Si layers and a vacuum of 15 Å.

The results of the convergence test concerning the number of Si layers in the slab and the vacuum thickness at E_{cut}^{pw}=13.8 Ry and with the $(8 \times 8 \times 1)$ **k**-point set in a (1×1) surface unit cell are shown in Fig. A-3. Using an 8 layer Si-slab and 14 Å vacuum thickness are sufficient to achieve an accuracy about 0.3 meV / Å^2 and 0.5 meV / Å^2 in the surface free energy convergence with respect to the slab and the vacuum thickness, respectively.

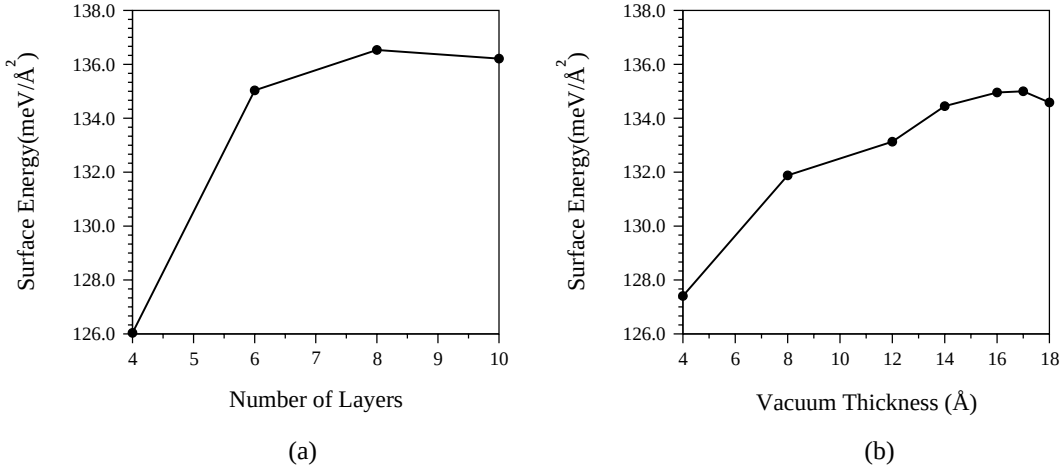

Fig. A-3: The surface energy as a function of the number of layers in the slab (a) and the vacuum thickness (b), using E_{cut}^{pw}=13.8 Ry and a $(8 \times 8 \times 1)$ **k**-point set.

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