Electronic structure of the ideal Si (001) surface by first-principles calculations

M D Manyakin and S I Kurganskii
Department of Solid State and Nanostructure Physics, Voronezh State University, 1 Universitetskaya pl., Voronezh, 394018, Russia
E-mail: manyakin@phys.vsu.ru

Abstract. The electronic structure of Si nanofilms with an ideal unreconstructed surface (001) was modeled using the full-potential linearized augmented plane wave method. Total and local density of states spectra are calculated. The transformation of the electronic structure of nanofilms with an increase in their thickness from 1 to 10 silicon elementary cells along the crystallographic direction Z (4-40 monoatomic layers) is considered. A layer-by-layer analysis of a nanofilm electronic structure with a thickness of 40 atomic layers was performed.

1. Introduction
A significant number of modern scientific publications have been devoted to the study of the electronic structure and properties of the silicon (001) surface [1–3]. When the Si (001) surface is formed, two electronic bonds of the silicon atom in the tetrahedral crystal structure are broken and two unpaired electrons appear [4, 5]. This electronic configuration is not energetically stable. It is known from numerous experiments that the formation of the Si (001) surface is accompanied by its reconstruction with the formation of super structures 2×1, p(2×2) and c(4×2) symmetries [5, 6]. For this reason, when performing theoretical calculations of the Si (001) surface electronic structure, most authors consider various models of the reconstructed silicon surface. Noticeably less attention is paid to the calculations of unreconstructed surface electronic properties. Moreover, in such works [e.g. 4–6], calculated band structures and electronic charge densities distributions are mainly given. Such an important characteristic as the density of electronic states (DOS) for an ideal surface of Si (001) was almost not considered as the research object yet.

At the same time, a number of experimental studies have shown that the deposition of various chemical elements atoms (hydrogen, bismuth, antimony) on the reconstructed Si (001) surface leads to the restoration of a structure (1×1) close to the ideal one [7–10]. The atomic and electronic structure of solids experimental studies results reliable interpretation possibility is directly related to the need for their computer modeling [11, 12]. Considering an ideal unreconstructed surface as a source object for the structures mentioned above seems to be a rational step. Considering the above, conducting a detailed study of the electronic structure of the ideal surface Si (001) is a relevant scientific task of present work.

2. Calculation details
In this paper, the electronic structure of Si nanofilms with (001) surface orientation was calculated. The thickness of the nanofilms varied in the range from 1 to 10 unit cells of a bulk silicon crystal along the Z direction (4-40 monoatomic layers), which is ~ 6.4 to 55.3 Å. It is known that the silicon crystal structure is characterized by a Fd3m space group. Unit cell parameter in the simulation was chosen to
be 5.4309 Å [13]. Calculations of the electronic structure were performed using full-potential linearized augmented plane wave method (FP-LAPW), as implemented in the Wien2k software package [14]. To calculate the exchange-correlation energy, we used the Generalized Gradient Approximation (GGA) [15]. The parameter \( R_{\text{mt}} \cdot K_{\text{max}} \), which determines the number of plane waves, was taken to be equal to 6.0, where \( R_{\text{mt}} \) is the muffin-tin sphere radius (2.5 a.u.), and \( K_{\text{max}} \) is the boundary of the plane wave cut-off.

Calculations were performed using the Periodic Slab Geometry model [16]. This approach uses methods for calculating the electronic structure of three-dimensional periodic structures. The structure under study is represented as a system of thin films called slabs, periodically repeating in the direction perpendicular to the surface, and separated by vacuum intervals. Each of the cells consists of one slab and two vacuum regions equal in thickness to half of the total length of the vacuum region (\( d_{\text{vac}} \)) along the vertical direction. The total length of the vacuum region (\( d_{\text{vac}} \)) must be large enough to exclude interaction between neighboring slabs. In this paper, \( d_{\text{vac}} = 25 \) a.u.

Figure 1a shows a model of a Si (001) nanofilm with a thickness of 1 unit cell along the Z axis. A slab consisting of 4 atomic layers and two \( d_{\text{vac}}/2 \) vacuum gaps bounding the film on both sides. When translating such a cell along the Z axis, an infinite system of slabs separated by a \( d_{\text{vac}} \) interval is obtained. This is schematically shown in figure 1b for two adjacent nanofilm unit cells. The unit cells of nanofilms of greater thickness are similar to the one shown in figure 1a, with the only difference that the number of atomic layers in their slabs is proportionally greater and reaches 40 for a film with a thickness of 10 unit cells of a bulk silicon crystal.

![Figure 1](image)

**Figure 1.** a) Model of a nanofilm unit cell with a thickness of 1 unit cell along the Z axis. b) Schematic model of two unit cells of a four-layer nanofilm. The slab and vacuum region are shown.

### 3. Results and discussion

The results of the silicon nanofilms electronic structure calculations are shown in figure 2. Figure 2a shows the transformation of the silicon nanofilm total density of states (DOS) spectrum with an increase in the thickness from 1 to 10 elementary cells along the Z axis. It can be seen that for a film with a thickness of 1 cell, the DOS spectrum is radically different from the spectrum of a bulk silicon crystal, which is also shown in figure 2a for comparison. With increasing film thickness, this difference gradually reduces. The spectra of films with a thickness of 6 or more cells demonstrate the main features of the electronic structure of a bulk crystal. The most noticeable difference between the electronic structure of Si (001) nanofilms and a bulk crystal is the formation of an intense peak in the DOS spectrum, located directly near the top of the valence band. In the two thinnest films considered, this maximum is dominant. As the film thickness increases, its relative intensity reduces. Another important difference from the bulk crystal is the tightening of the band gap in the electronic spectrum of nanofilms. Analyzing the data in figure 2a, it can also be seen that near the valence band bottom of nanofilms, steps
characteristic of two-dimensional systems DOS are observed. The number of steps is equal to the number of elementary cells along the Z direction, which is most clearly visible for 1–4 cells thickness films.

Figure 2. a) Spectra of total DOS for Si (001) nanofilms with a thickness of 1 to 10 unit cells in comparison with the spectrum of a bulk crystal. b) Local DOS spectra of atoms lying in different layers of a nanofilm with a thickness of 10 elementary cells.

Figure 2b shows local DOS for atoms in different layers of a nanofilm with a thickness of 10 elementary cells (40 atomic layers). The surface layer of the film is marked as “layer 1”, the central layer as “layer 20”. Due to symmetry, we consider only the layers lying on one side of the XY plane that divides the film in half. It can be seen that the layers lying in the depth of the film have an electronic structure close to the bulk crystal. As we are approaching the surface of the film, the electronic structure begins to undergo more and more changes. The shape of the DOS spectrum for an atom in the surface layer of the film differs significantly from the DOS spectrum of a bulk crystal. Two maxima are observed in the surface atoms DOS spectrum: near the valence band top and at −7.2 eV. Analysis of local partial
DOS of the surface layer atom shows that $s$-states are dominant at the bottom of the valence band and up to the energy $–3.7$ eV (figure 3). Above $–3.7$ eV, the contribution to the spectrum is mainly made by $p$-states, which are also responsible for the formation of a peak near the valence band top. There is no band gap in the spectrum.

**Figure 3.** Partial DOS of an atom in the surface layer of an ideal Si (001) nanofilm with a thickness of 10 elementary cells.

The nature of the peak at the valence band top can be explained as follows. According to [4, 5], the formation of an ideal Si (001) surface is accompanied by the two unpaired electrons appearance for each atom in the surface layer. This leads to the formation of two narrow energy bands between the valence band and the conduction band [4], which correspond to the considered peak of the $p$-states. The localization of this peak at the valence band top and its high intensity are due to the fact that the electron in the surface layer of the film is located in a smaller potential well than inside the film bulk or in the crystal bulk.

4. Conclusion
In conclusion, we have compared the results of our calculations with previously published data. Figure 4 shows the calculated local DOS spectra of surface and central layer atoms for a 12-layer film in comparison with similar results obtained in [17]. There is a strong agreement between the data presented. Also, a good agreement is observed between the total DOS of the 12-layer film obtained by our group and the 13-layer film DOS from [18]. Such agreement between the results of calculations obtained by independent groups using various modeling methods (LAPW in our case and the pseudopotential method in [17, 18]) indicates the reliability of our results and their adequate description of the electronic structure of ideal silicon nanofilms (001).
Figure 4. Comparison of the 12-layer film DOS taken from [17] (left) and a similar calculation performed by our group (right).

Acknowledgments
The study was supported by Russian Science Foundation (Project 19-72-20180).

References
[1] Seo H, Hatch R C, Ponath P, Choi M, Posadas A B and Demkov A A 2014 Critical differences in the surface electronic structure of Ge(001) and Si(001) Ab initio theory and angle-resolved photoemission spectroscopy Phys. Rev. B 89 115318
[2] Li H, Ji A, Zhu C and Mao L-F 2018 Structure properties and electrical mechanisms of Si (001)/SiO$_2$ interface with varying Si layer thickness in nano-scale transistor Current Applied Physics 18 1020–1025
[3] Domashievskaya E P, Terekhov V A, Turishchev S Yu, Prijimov A S, Kharin A N, Parinova E V, Rumyantsev N A, Usoltseva D S, Fomenko Yu L and Belenko S V 2015 Atomic and Electronic Structure of Amorphous and Nanocrystalline Layers of Semi-Insulating Silicon Produced by Chemical-Vapor Deposition at Low Pressures Journal of Surface Investigation, X-ray, Synchrotron and Neutron Techniques 9 1228–1236
[4] Appelbaum J A, Baraff G A and Hamann D R 1975 The Si (100) surface: A theoretical study of the unreconstructed surface Phys. Rev. B 11 3822–3831
[5] Eastman D E 1980 Geometrical and electronic structure of Si (001) and Si (111) surfaces: a status report Journal of Vacuum Science & Technology 17 492–500
[6] Uchiyama T and Tsukada M 1993 Step-induced state of a Si (001) reconstructed surface Surface Science 282 152–162
[7] Tromp R M, Smeenk R G and Saris F W 1981 Ion Beam Crystallography at the Si (100) Surface, Phys. Rev. Lett. 46 939–942
[8] Fan W C, Wu N J and Ignatiev A 1992 Determination of a Bi-induced (1×1) structure of the Si (100) Surface, Phys. Rev. B 45 14167–14170
[9] Hu X and Lin Z 1995 Surface structure of Si (100) – (1×1)-2H determined by tensor LEED: Substrate interlayer relaxations Phys. Rev. B 51 10164–10166
[10] Mitsui T, Hongo S and Urano T 2001 LEED structure analysis of Sb adsorbed Si (001) surface Surface Science 482–485 1451–1456
[11] Manyakin M D and Kurganskii S I 2019 Electronic structure of stishovite SiO$_2$, IOP Conf. Series Journal of Physics: Conf. Series 1352 012032
[12] Manyakin M D, Kurganskii S I, Dubrovskii O I, Chvenkova O A, Domashevskaya E P, Ryabtsev S V, Ovsyannikov R, Parinova E V, Sivakov V and Turischev S Yu 2019 Electronic and atomic structure studies of tin oxide layers using X-ray absorption near edge structure spectroscopy data modelling Materials Science in Semiconductor Processing 99 28–33
[13] Hom T, Kiszenick W and Post B 1975 Accurate Lattice Constants from Multiple Reflection Measurements II. Lattice Constants of Germanium, Silicon and Diamond J. Appl. Cryst. 8 457–458
[14] Blaha P, Schwarz K, Madsen G K H, Kvasnicka D, Luitz J, Laskowski R, Tran F and Marks L D 2018 WIEN2k, An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties (Karlheinz Schwarz: Techn. Universität Wien, Austria)
[15] Perdew J P, Burke K and Ernzerhof M 1996 Generalized Gradient Approximation Made Simple Phys. Rev. Lett. 77 3865–3868
[16] Lannoo M and Friedel P 1991 Atomic and Electronic Structure of Surfaces. Theoretical Foundations (Berlin: Springer-Verlag)
[17] Kerker G P, Louie S G and Cohen M L 1978 Electronic structure of the ideal and reconstructed Si (001) surface Phys. Rev. B 17 706–715
[18] Obreshkov B and Thumm U 2007 Nonresonant formation of H$^-$ near unreconstructed Si (100) surfaces Phys. Rev. A 76 052902