

## Calculation of surface core-level shifts within complete screening: Problems with pseudohydrogenated slabs

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By considering GaAs(110) and Si(100)(2×1) surfaces, it is shown that the use of the pseudohydrogen atoms to saturate the dangling bonds at one side of the slab modeling a free surface can lead to distorted surface core-level shifts within the complete screening picture. The effect is linked to the polarization of the slab and to the change in the bulklike electronic structure close to pseudohydrogenated part of the slab. It is demonstrated that these problems can be avoided if the pseudohydrogenated slab is large enough and the bulk reference layer is properly chosen. One easy way to control these errors is to monitor the planar-averaged potential energy curve of the slab.

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### I. INTRODUCTION

Core-level spectroscopy is a widely used method to determine the electronic and structural properties of various kinds of physical systems. It is a particularly powerful tool in the characterization of the semiconductor surfaces due to their manifold reconstructions. The surface core-level shift (SCLS), being a central quantity in core-level spectroscopy, is determined as the difference in the binding energy of the core-level photoelectrons emitted from the atoms that are located at the sample surface and deeper in the bulk. As semiconductor surfaces often undergo strong structural rearrangements, the identification of SCLSs provides important information about the atomic structures of such surfaces and the bonding and charge states of the surface atoms. However, resolving all of these SCLSs from a measured spectrum and interpreting their atomic origins are usually nontrivial tasks and, therefore, theoretical results can be very useful in the analysis of experimental data. Of course, several sources of inaccuracy both in the experimental and theoretical spectra and their interpretation can complicate the analysis, but trends can often be identified with great certainty. Moreover, the absence of a SCLS or a detection of an extra SCLS in experiments or in calculations acts as an indication of the incorrect identification of the surface structure.

Unfortunately, the theoretical evaluation of the SCLSs is far from being a straightforward procedure. This is mainly due to the fact that the SCLS is not a ground state property. However, in many cases, rather good approximations are obtained by analyzing ground state properties within the initial state model in which the quite complex final state effects due to the electronic relaxation after the core-level ionization are disregarded. On the other hand, for metallic systems, the inclusion of the final state effects has been demonstrated to lead to more accurate values for the SCLSs.<sup>1,2</sup> This is usually

done in the complete screening picture<sup>3–5</sup> in which the emitted electron is transferred to the Fermi level to act as the screening charge, which is supplied by the macroscopically large solid-state system. Therefore, at least two separate calculations (one for surface and one for bulk) are needed to determine a theoretical SCLS within the final state model. For semiconductors, however, the final state effects are not so clear. The complete screening SCLSs have been reported for GaAs(110) (Refs. 6 and 7) and for Sb on GaAs(110) (Ref. 8). Pehlke and Scheffler have shown that final state effects can be strong on semiconductor surfaces by considering Si(100)(2×1).<sup>9</sup> Similar systems have been studied by other groups.<sup>10–12</sup>

Theoretical SCLSs of semiconductors are usually calculated by using the repeated slab technique. It is a commonplace to use pseudohydrogen (or hydrogen) atoms in the bottom “surface” of the slab to decrease the actual size of the slab needed to model a free surface. Pseudohydrogen atoms saturate the dangling bonds of the bottom surface leading to semiconducting and bulklike behavior. The reconstructions of the semiconductor surfaces are often so complicated that it may be difficult to form symmetric slabs of not too large a size. In some cases, symmetric slabs cannot be formed at all.<sup>13–15</sup> Furthermore, stoichiometric symmetric slabs are often rare. For example, on the GaAs(100) surface, the only stoichiometric reconstructions are the so-called (2×4)– $\alpha$  (Refs. 16 and 17) and (2×4)– $\alpha 2$  (Refs. 18 and 19) structures. Mankefors has shown that pseudohydrogenated slabs contain unphysical charge density oscillations and, therefore, the reliability of the pseudohydrogenated slabs should be investigated whenever used.<sup>20</sup> In this paper, we give an important example of this effect by demonstrating that one must be cautious when SCLSs are calculated by pseudohydrogenated slabs. We show that due to the interaction of the ionized atom and the (pseudo)hydrogenated surface of the slab cell,

the theoretical SCLSs may be seriously underestimated within the complete screening picture if the bulk reference is spuriously determined. We also report on how to avoid these problems when pseudohydrogenized slabs are necessary.

The rest of the paper is organized as follows: in Sec. II the methods to calculate the SCLSs and the numerical details are described. Results are presented and discussed in Sec. III. We consider two important cases: GaAs(110) and Si(100)(2×1). These surfaces are examples of the most studied semiconductor surfaces and they are simple enough, which makes them most suitable to illustrate effects reported here. The paper ends with conclusions.

## II. CALCULATIONAL METHODS

The electronic structure calculations are performed using the *ab initio* total energy program Vienna *ab initio* simulation package<sup>21–24</sup> (VASP), which is based on the density functional theory.<sup>25,26</sup> Within this package, the projector augmented wave (PAW) method<sup>27,28</sup> and the local density approximation (LDA) of Ceperley and Alder,<sup>29</sup> as parametrized by Perdew and Zunger,<sup>30</sup> are used. The optimization of the atomic structure is performed using conjugate-gradient minimization of the total energy with respect to the atomic coordinates. The Ga and As 4*s* and 4*p* and the Si 3*s* and 3*p* electrons are treated as valence electrons. This is reasonable in the present study because in the complete screening calculations, the Ga 3*d* states, which are close to the valence states, should be included in the core. The GaAs(110) and Si(100)(2×1) surfaces are simulated by slabs of eight atomic layers (some larger slabs are also used, see Sec. III). The dangling bonds of the bottom surface atoms are passivated by pseudohydrogen and hydrogen atoms.<sup>31</sup> Theoretical lattice constants of 3.96 Å (GaAs) and 3.84 Å (Si) are used, and two bottom atomic layers of the slabs are fixed to the bulk positions. Small changes in the lattice parameters affect the surface core-level shifts very little. Other atoms, including the pseudohydrogen and hydrogen atoms, are relaxed until the remaining forces are less than 20 meV/Å. The energy cutoff is 350 eV (GaAs) and 280 eV (Si). The number of *k* points in the Brillouin zone is 36, corresponding to a *k*-mesh of 6×6×1. To avoid artificial interaction of the top and bottom surfaces of the slab construction due to three-dimensional periodicity, a dipole (and quadrupole) correction in the direction perpendicular to the surface is applied in all calculations. Additionally, a local potential correction was tested to eliminate all effects of the periodic boundary conditions. This additional correction changes the SCLSs by a few meVs at most.

The surface core-level shifts within the initial state model are evaluated by solving the Kohn–Sham equation inside the PAW spheres for core electrons after the self-consistency with the frozen core electrons has been attained.<sup>32</sup> The initial state values can also be calculated by considering electrostatic potentials within the core region.<sup>33</sup> Initial state SCLSs obtained by these two methods are estimated to differ from each other by 0.1 eV at maximum. The final state effects are included in the SCLSs calculated within the complete screening picture. In these calculations, a single core electron

is excited from the core to the valence by generating the corresponding core-excited PAW potential.<sup>32</sup> In the final state calculations, only the screening by valence electrons is included. Final state calculations are performed using (2×2) slabs and, in some cases, (4×4) slabs. The complete screening SCLS is obtained by equation

$$E_{SCLS} = E_{TOT,S} - E_{TOT,B}, \quad (1)$$

where  $E_{TOT,S}$  and  $E_{TOT,B}$  are total energies of the systems in which an atom is ionized on the surface and in the bulk, respectively (otherwise, the two systems are equivalent). We note that if different initial state systems would be used for the bulk and surface calculations, a significant uncontrollable error could easily be introduced. This definition is in accordance with the convention chosen, according to which, positive SCLS means larger binding energy on the surface atom than in the bulk.

## III. RESULTS AND DISCUSSION

The phenomena considered here were found for different surface systems including GaAs(110), Sb/GaAs(110), Si(100)(2×1), GaAs(100)(2×4) (Ref. 34), Bi/GaAs(100)(2×1) (Ref. 35), and Yb/Si(100)(2×4). First, as an important example, the core-level shifts of GaAs(110) are assessed in detail. The initial state and complete screening SCLSs for Ga 3*d* are 0.238 and −0.165 eV for the symmetric slabs, while the corresponding values are 0.252 and −0.294 eV for the pseudohydrogenated slabs. The As 3*d* initial state and complete screening SCLSs are −0.319 and −0.442 eV for the symmetric slabs and −0.295 and −0.590 eV for the pseudohydrogenated slabs. The experimental values are 0.28 eV for Ga and −0.37 eV for As.<sup>36</sup> Reported theoretical initial state values in literature vary from 0.14 to 0.18 eV for Ga and from −0.36 to −0.45 eV for As (Refs. 6, 7, 37, and 38), while the complete screening values of Schmidt, Käckell, and Bechstedt (Refs. 6 and 7) are −0.59 eV (Ga) and −0.76 eV (As). Discrepancy between theoretical and experimental Ga 3*d* SCLSs is well known<sup>6,7,39</sup> although the role of the final state effects in it is still unclear. In other words, the theoretical SCLS is too small even within the initial state model, whereas final state effects tend to decrease SCLS even more. One could think that the commonly used exchange-correlation functionals overestimate the electronic charge amount of the Ga atoms, which are situated closer to bulk atoms in the top surface layer than the As atoms are, leading to too small SCLS.

In Table I, various quantities including initial and complete screening Ga 3*d* SCLSs for the GaAs(110) are shown as a function of the depth from the surface (*z* coordinate) of the core-ionized Ga atom. The obtained trends are the same if the As atom is ionized instead of the Ga atom. The total energy of the system with a core-ionized atom in the bulk,  $E_{TOT,B}$ , has been determined as an average of the  $E_{TOT,BS}$  corresponding to systems, in which a Ga atom is ionized in the sixth and seventh layers. In general, it is suggested to use an average of the total energies of the systems having ionized atoms in bulklike layers in Eq. (1) (often, more than two layers can be used). It is realized that the initial state SCLSs

TABLE I. Initial and complete screening SCLSs for symmetric (15 atomic layers) and pseudohydrogenated (eight atomic layers) GaAs(110) slabs in which the position of the ionized Ga atom is varied in the direction perpendicular to surface. Total energies (ionization in the first layer determines the 0 eV value) and energy differences between systems including ionized atoms in adjacent layers ( $\Delta$ ) are also shown. The results for As 3*d* are shown in parentheses.

Symmetric slabs	Initial state SCLS (eV)	Total energy within complete screening (eV)	Complete screening CLS (eV)	$\Delta$ (eV)
Layer				
1	0.238 (−0.319)	0.000 (0.000)	−0.165(−0.442)	
2	−0.016 (0.019)	−0.014 (0.321)	−0.180(−0.121)	−0.014 (0.321)
3	−0.009(−0.029)	0.045 (0.350)	−0.120(−0.092)	0.059 (0.030)
4	−0.015(−0.005)	0.125 (0.384)	−0.041(−0.058)	0.080 (0.034)
5	−0.015(−0.007)	0.127 (0.412)	−0.039(−0.030)	0.002 (0.028)
6		0.167 (0.433)		0.041 (0.020)
7		0.164 (0.448)		−0.004 (0.015)
8		0.176 (0.446)		0.013 (−0.001)
Pseudohydrogenated slabs				
1	0.252 (−0.295)	0.000	−0.294(−0.590)	
2	−0.001 (0.045)	−0.006 (0.335)	−0.300(−0.260)	−0.006 (0.335)
3	−0.005(−0.006)	0.073 (0.382)	−0.221(−0.208)	0.073 (0.048)
4	−0.002 (0.014)	0.172 (0.425)	−0.122(−0.165)	0.099 (0.043)
5	−0.007 (0.007)	0.192 (0.499)	−0.102(−0.091)	0.020 (0.074)
6		0.266 (0.549)		0.074 (0.050)
7		0.322 (0.632)		0.056 (0.083)
8		0.445 (0.798)		0.123 (0.166)

are independent of the use of pseudohydrogens. However, the atoms adjacent to pseudohydrogens have more electrons than the atoms in the deepest layers of symmetric slabs (Table II). This leads to lower binding energies of the core-levels (because increased electronic charge increases Coulombic repulsion) and, therefore, the layer adjacent to pseudohydrogens is omitted when the core-level shifts are evaluated. Another thing is that the missing of the relaxation of the core levels in the initial state model diminishes the differences between the SCLSs in different layers. On the other hand, the total energy within complete screening satu-

rates to a bulklike value in symmetric slabs, while it increases monotonically for pseudohydrogenated slabs as the bottom surface is approached. This leads to too small SCLSs of the pseudohydrogenated slabs. Obviously the problems in calculating SCLSs seem to be related to the reliability of the bulk reference value.

The planar-averaged (averaged in planes parallel to the surface) potential energy of an electron for GaAs(110) is shown in Fig. 1 for systems where no ionization has taken place (solid line) and where a Ga atom is ionized in the seventh layer (dotted line). The real surface is on the left side

TABLE II. Averaged total number of electrons (Ga+As) per atom (radius is 1.60 Å) in the atomic layers of pseudohydrogenated GaAs(110) (eight atomic layers) for the nonionized slab and the slab in which a Ga atom is ionized in the seventh layer. Differences between the considered electron numbers are also shown. Positive value means that there are more electrons in the atom of the nonionized system.

	<i>N</i> Nonionized slab	Ga atom ionized in the seventh layer	$\Delta N$
1 layer	31.669	31.661	0.008
2 layer	31.866	31.855	0.011
3 layer	31.867	31.863	0.004
4 layer	31.879	31.875	0.004
5 layer	31.882	31.879	0.003
6 layer	31.885	31.883	0.002
7 layer	31.892	31.881	0.009
8 layer	31.969	31.971	−0.002

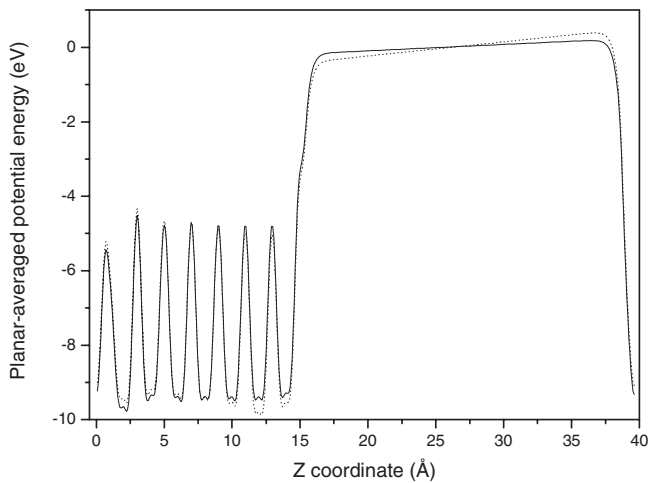


FIG. 1. Planar-averaged potential energy of the GaAs(110) for slabs of eight atomic layers in which ionization has not taken place (solid line), and a Ga atom is ionized in the seventh layer (dotted line). The  $z$  direction is perpendicular to the surface.

of the figure. Eight atomic layers are shown as eight potential energy wells. The pseudohydrogen layer is shown only as a slight bend in the steep rise of the potential energy at the bottom surface. The vacuum region corresponds to the potential energy around 0 eV. Changes in the planar-averaged potentials can be connected to the charge densities. The charge density difference between considered systems in the  $(-110)$  plane ( $y$ - $z$  plane), including the ionized Ga atom, is shown in the Fig. 2. Although the valence charge density is increased around the ionized Ga atom, the total electronic charge around the Ga atom is decreased because one electron has been taken away from the core. This is shown in Table II. The charge density in the  $y$ - $z$  plane is larger near the bottom surface in the nonionized system, whereas the charge density near the top of the real surface is larger in the ionized system. These differences are reflected in the planar-averaged potential energy of an electron shown in Fig. 1. The planar-averaged potential energy of an electron is remarkably lower

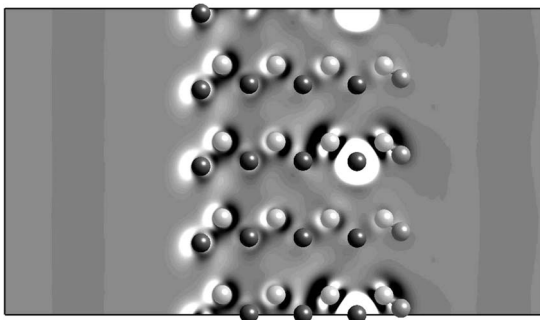


FIG. 2. Valence charge density difference of the GaAs(110) slabs of eight atomic layers in which ionization has not taken place, and a Ga atom is ionized in the seventh layer. Black areas show increased charge density in the nonionized system, whereas white areas show increased charge density in the ionized system. The positions of the atoms are also shown: Ga (black), As (light gray), and pseudohydrogens (dark gray). The real surface is on the left side of the figure.

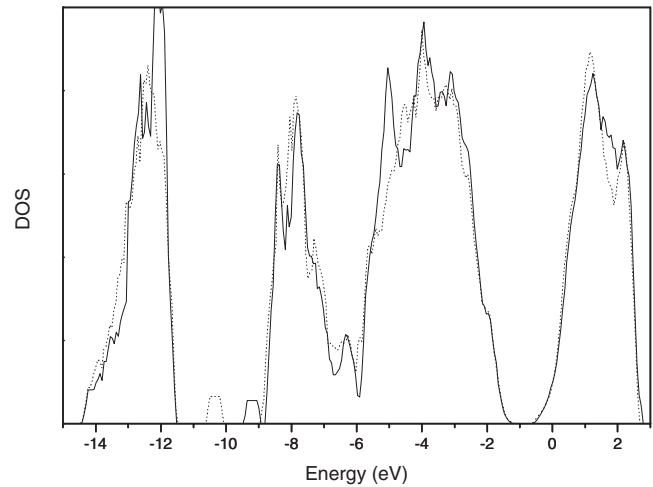


FIG. 3. Total density of states of GaAs(110) slabs with pseudohydrogens on both surfaces. A Ga atom is ionized in the center of the atomic slab (solid line) and in the atomic layer next to pseudohydrogens (dotted line).

in the seventh layer in the ionized system because the missing electron from the core is not fully compensated by the screening, making the potential energy much more negative around the ionized atom.

While averaged quantities give important information, it is also illustrative to consider what happens to individual atoms because the covalent bonds are highly directional. It is found that the nearest As neighbors of the ionized Ga atom donate some amount of electronic charge (which is shown in the Fig. 2 by black areas close to As atoms in the sixth and eighth layers), leading to deeper local potential energy at these sites. This phenomenon is observed both in the symmetric and pseudohydrogenated slabs, and it is mediated to the other atoms in the neighboring atomic layers, too. This phenomenon seems to be destructive for the bulk reference in the pseudohydrogenated slabs for two reasons. First, the symmetric slab is thicker if the number of the nonequivalent atomic layers is kept constant. Second, the bonds connecting pseudohydrogens to the bottom surface are affected. This effect seems to be quite strong probably because there are no atoms beyond the pseudohydrogens, i.e., the bulk is simulated by the pseudohydrogenated surface.

We carried out additional test calculations for an atomic slab, which was pseudohydrogenated on both surfaces. The total energy increases as the position of the ionized atom gets closer to pseudohydrogens. This could be interpreted as a tendency of the pseudohydrogenated bulklike surface to transform into a real surface, which increases the energy due to the surface energy. The total density of states (DOS) is shown in the Fig. 3 for this slab in cases: (i) Ga atom in the center of the atomic slab is ionized, and (ii) Ga atom next to pseudohydrogens is ionized. A marked difference in the DOS curves is found in the energy range from  $-9$  to  $-11$  eV. The peak in this energy region is at the higher binding energy if the ionization happens close to pseudohydrogens. This DOS structure is attributed to the bonds including pseudohydrogens by examining the local DOS, and it is peculiar to systems including real and pseudohydrogenated surfaces, too.



TABLE III. Initial and complete screening SCLSs for symmetric (13 atomic layers) and hydrogenated (eight atomic layers) Si(100)(2×1) slabs in which the position of the ionized atom is varied in the direction perpendicular to surface. Total energies (ionization in the first layer up Si atom determines the 0 eV value) and energy differences between systems including ionized atoms in adjacent layers ( $\Delta$ ) are also shown.

Symmetric slabs	Initial state SCLS (eV)	Total energy within complete screening (eV)	Complete screening CLS (eV)	$\Delta$ (eV)
Layer				
1 up	-0.238	0.000	-0.544	
1 down	0.565	0.392	-0.153	
2	0.153	0.504	-0.040	0.504
3	0.315 0.028	0.812 0.379	0.267 -0.166	0.307
4	0.222 -0.181	0.763 0.288	0.219 -0.256	-0.048
5	0.044	0.599	0.054	-0.164
6		0.593		-0.006
7		0.495		-0.098
Pseudohydrogenated slabs				
1 up	-0.270	0.000	-0.850	
1 down	0.542	0.348	-0.502	
2	0.127	0.520	-0.329	0.502
3	0.277 0.002	0.854 0.415	0.004 -0.435	0.334
4	0.181 -0.208	0.846 0.364	-0.003 -0.486	-0.008
5	-0.005	0.730	-0.120	-0.117
6		0.860		0.130
7		0.840		-0.020
8		0.857		0.017

The ionization close to pseudohydrogens affects the bonds at the bottom surface and destroys the bulk reference because the bonds do not simulate the bulk properly in the ionized case. This means simply that the pseudohydrogenation suitable to nonionized slab is not valid to the ionized slab anymore.

In Table III information about the SCLSs of the Si(100)(2×1) as in Table I is gathered. It is remarkable that the SCLSs are more significant in the deeper layers than in the case of GaAs (Table I), which is realized particularly well in the initial state values. (Some Si atoms also in the second Si layer of the bottom surface of the hydrogenated slab have too many electrons due to hydrogen, and they were not taken into account in the calculation of the bulk Si reference value.) This is indicative of the deeper reconstruction on the Si(100)(2×1) surface as compared to the GaAs(110). For Si(100)(2×1), the complete screening SCLSs are in a better agreement with the experimental values<sup>40</sup> [-0.49 eV (up atom) and +0.06 eV (down atom)] than the initial state values. It should be noted that the present SCLSs are obtained from calculations where the numerical errors are kept at a very low level (see Sec. II). This may explain the slight difference between the present and the earlier results [-0.48 eV (up atom), -0.09 eV (down atom), and +0.13 eV (second layer atom)].<sup>9</sup> It is interesting that the core-level shift (CLS) between the up Si and down Si (closer to surface) atoms is obtained quite well using symmetric and pseudohydrogenated slabs. [The same phenomenon is found

also on Sb/GaAs(110)]. In Table III, two values are given for the SCLS of the nonequivalent Si atoms in layers three and four.

It would be advantageous to find a way to obtain reliable complete screening SCLSs also for pseudohydrogenated slabs because in some cases, complex reconstructions on semiconductor surfaces do not permit the use of symmetric slabs. This is due to computational reasons because the reconstruction pattern is frequently rotated between the top and bottom surfaces of the symmetric slabs by 90°, making symmetric slabs larger and calculations heavier. Moreover, it may be difficult or impossible to maintain correct composition with symmetric slabs.

It is possible to find quite reliable complete screening SCLSs also using pseudohydrogenated slabs but this is not straightforward. Naturally, one thinks that increasing the slab size could help in that case since one is not forced to ionize the bulk reference atom too close to pseudohydrogens. This seems to be the case, indeed. However, one has to take into account the characteristics of the considered system. For example, the interlayer distance is smaller on (110) surfaces than on (100) surfaces. Therefore, the Si(100) slab has to be enlarged in the horizontal direction (i.e., within the surface plane), whereas the GaAs(110) slab can be enlarged also in the vertical direction (i.e., in direction perpendicular to the surface), which is a computationally easier task. Moreover, one has to know also the initial state SCLSs (which are more easily evaluated) to determine suitable position in the  $z$  di-

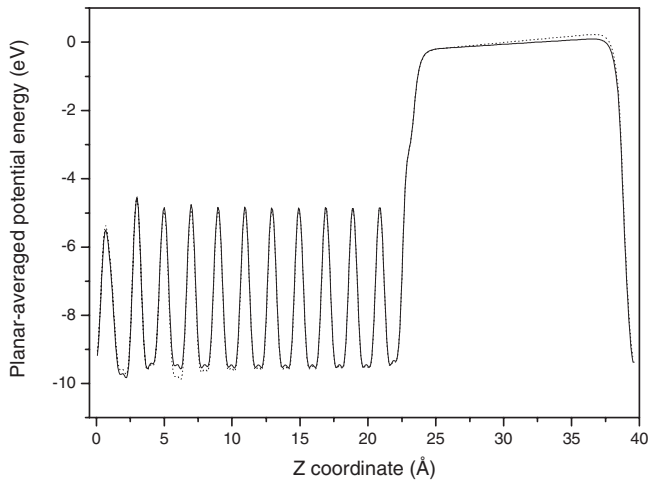


FIG. 4. Planar-averaged potential energy of the GaAs(110) for slabs of 12 atomic layers in which ionization has not taken place (solid line) and a Ga atom is ionized in the fourth layer (dotted line). The  $z$  direction is perpendicular to the surface.

rection for the bulk reference. It is found that a useful way to avoid errors due to pseudohydrogens is to monitor the planar-averaged potential energy. If the potential energy does not change appreciably at the pseudohydrogenated surface due to ionization, the resulting complete screening SCLSs are quite reliable. This is an easy and useful test.

Figure 4 represents the planar-averaged electronic potential energy of two GaAs(110) systems with 12 atomic layers in which ionization has not taken place (solid line) and in which a Ga atom is ionized in the fourth layer (dotted line). The potential energies are quite the same outside the region where the ionized atom is located, and the distortion of the potential energy around the ion is quite local. According to Table I, the fourth layer is deep enough to be used as the bulk reference layer for the initial state SCLS. The Ga complete screening SCLS is  $-0.152$  eV, which is in a good agreement with the value ( $-0.124$  eV) obtained by symmetric slabs if the bulk reference is in the fourth layer. If the bulk reference is in the fifth layer, the obtained SCLS is almost the same ( $-0.160$  eV). In fact, with these bulk reference layers, the slab of eight atoms is already quite acceptable, yielding SCLSs of  $-0.172$  and  $-0.192$  eV for pseudohydrogenated and symmetric slabs, respectively. In the case of the Si(100)( $2 \times 1$ ), the initial state SCLSs are quite large in layers 1–4 and, therefore, the bulk reference must be in the fifth layer or below it. If one uses ( $4 \times 4$ ) slab with eight Si layers, the planar-averaged potential energy does not change appreciably with the position of the ionized atom. The complete screening SCLS of the up Si atom is  $-0.569$  eV,  $-0.632$  eV, and  $-0.550$  eV if the ionized bulk Si atom is in the fifth, sixth, and seventh layers, respectively. These values are again in a quite good agreement with the values obtained by the symmetric slab ( $-0.599$  eV,  $-0.593$  eV, and  $-0.495$  eV, ionization in the fifth, sixth, and seventh layers, respectively). In case of Si(100)( $2 \times 1$ ), enlarging the hydro-

genated slab in the vertical direction does not help. A ( $2 \times 2$ ) slab of 16 Si layers yields complete screening SCLSs of  $-0.684$  eV,  $-0.745$  eV, and  $-0.719$  eV for cases in which the ionized bulk Si atom is in the fifth, sixth, and seventh layers, respectively.

Finally, we consider some previously not reported SCLSs: the Ga SCLSs (first Ga layer) of Sb/GaAs(110) and Bi/GaAs(100)( $2 \times 1$ ). These are interesting examples of adsorbate systems. It turns out again that ( $4 \times 4$ ) slabs has to be used for the (100) surface, whereas on the (110) surface, this is not necessary. Planar-averaged potential curves reveal that the proper bulk reference is around the fourth Ga layer of these slabs of eight atomic layers. If the bulk reference is fixed to the fourth layer, the Ga SCLS of Sb/GaAs(110) is  $-0.232$  eV. The initial state SCLS is  $-0.081$  eV. In the same way, the Ga SCLS of the Bi/GaAs(100)( $2 \times 1$ ) is  $-0.527$  eV. The initial state value is only  $-0.053$  eV (if the Ga  $3d$  electrons are included in the valence, DOS curves reveal that the initial state SCLS is about  $-0.15$  eV), whereas the experimental value is  $-0.42$  eV.<sup>35</sup> The error bar caused by the pseudohydrogens in the complete screening SCLS value of the Bi/GaAs(100)( $2 \times 1$ ) is estimated to be about 0.1 eV. We also mention that the complete screening SCLSs of the GaAs(100)( $2 \times 4$ ) surface are in a better agreement with the experimental values than those of the GaAs(110). Most of the complete screening SCLSs of the GaAs(100)( $2 \times 4$ ) are only 0.1 eV or smaller (some complete screening SCLSs are about 0.20–0.25 smaller) than the initial state SCLSs.

#### IV. CONCLUSIONS

By using GaAs and Si surfaces, we have demonstrated that if the bulk reference is close to the pseudohydrogen atoms in complete screening calculations, the SCLSs are underestimated by about 0.2–0.4 eV. This is due to the polarization of the slab and the change in the bulklike electronic structure close to pseudohydrogens after the core ionization. We have shown that the pseudohydrogenated slab can be, nevertheless, used in calculations, assuming that the size of the slab is large enough and the bulk reference is properly chosen. It is important to know the initial state SCLSs to determine the proper position(s) for the bulk reference. We propose that the effect of ionized atom on the slab can easily be monitored by investigating the planar-averaged electronic potential energy.

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