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Surface relaxation of the $(10\bar{1}0)$ face of wurtzite CdS

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Abstract

Atomic geometry and electronic density of states of the wurtzite CdS $(10\bar{1}0)$ cleavage surface have been calculated. Calculations were carried out with two different self-consistent ab initio LDA methods leading to similar results. Surface relaxation is found to be strong: cations relax towards bulk and anions outwards from the surface. This is in accordance with experimental observations and other published calculations.

Keywords: Cadmium sulphide; Density-functional calculation; Semiconducting surfaces; Single crystal surfaces; Surface electronic phenomena; Surface relaxation and reconstruction

1. Introduction

Compound semiconductors and their interfaces with their specific physical properties are important for today's electronics. Optoelectronics is a typical example. Surfaces of compound semiconductors, in addition, have applications in catalysis, adsorption based processes and other areas of surface science technology [1]. Semiconductor gas sensors, for example, exploit the electric response to the adsorption and chemical processes at surfaces [2].

Cadmium sulphide is one of the II–VI compound semiconductors which has been found to be a useful material for gas sensors [3,4]. It subsists in two tetrahedrally coordinated crystallographic allotropes, wurtzite and zincblende. The more general hexago-

nal wurtzite form exhibits two cleavage faces $(10\bar{1}0)$ and $(11\bar{2}0)$, of which the former is more stable. Therefore, we have chosen to examine this surface, starting with the surface relaxation in this work.

Atomic geometries and electronic structures of tetrahedrally coordinated compound semiconductor interfaces and surfaces have recently been studied with computational methods [5–9]. CdS $(10\bar{1}0)$ wurtzite surface, in particular, has been considered both semi-empirically [7] and with ab initio methods [8,9]. Wang and Duke [7] found a strong surface relaxation, anions outwards from the surface, related to covalent bonding and surface electronic states. Furthermore, they found that the surface atomic geometry is “universal” among the II–VI wurtzite semiconductors but the extent of relaxation scales linearly with the bulk lattice constant [6,7]. Tsai et al. [8] considered the same $(10\bar{1}0)$ surface of ZnS and AlN but, on the contrary, suggested weak surface relaxation to the opposite direction: anion to-

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wards bulk, driven by ionic forces. We report here our self-consistent *ab initio* LDA calculations for the wurtzite (10 $\bar{1}0$) surface of CdS with two different methods [10,11]. These methods involve only a localised basis [10] or only a plane wave basis together with core level pseudopotentials [11]. Our results, like the other recent *ab initio* results [9] support those of Wang and Duke for the surface relaxation.

Our main goal here, however, is to test the models, methods and basis set effects in order to be able to investigate surface chemistry with adsorbates in future studies. Therefore, we are interested in both the surface relaxation and the electronic surface states and surface density-of-states (SDOS).

In the next two sections we describe our surface models and computational methods. Results will be given in the fourth section and conclusions drawn in the fifth and last one.

2. Surface models

The experimental bulk lattice parameters of the hexagonal wurtzite CdS are $a = 4.14$ Å and $c = 6.72$ Å [12] with the c/a ratio 1.623, which is close to the c/a ratio of ideal hcp structure 1.633. To be able to

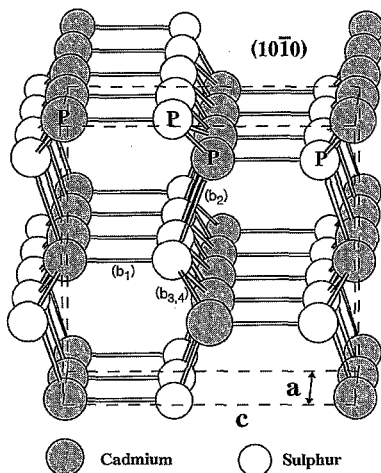


Fig. 1. Truncated bulk (or unrelaxed) geometry of the wurtzite CdS (10 $\bar{1}0$) cleavage face. The orthorhombic unit cell of the size of two primitive cells is marked with dashed lines, a and c are two of the lattice constants in notation ($a\ b\ -a-b\ c$) of the hexagonal wurtzite lattice and the symbol P shows the four atoms in a primitive basis.

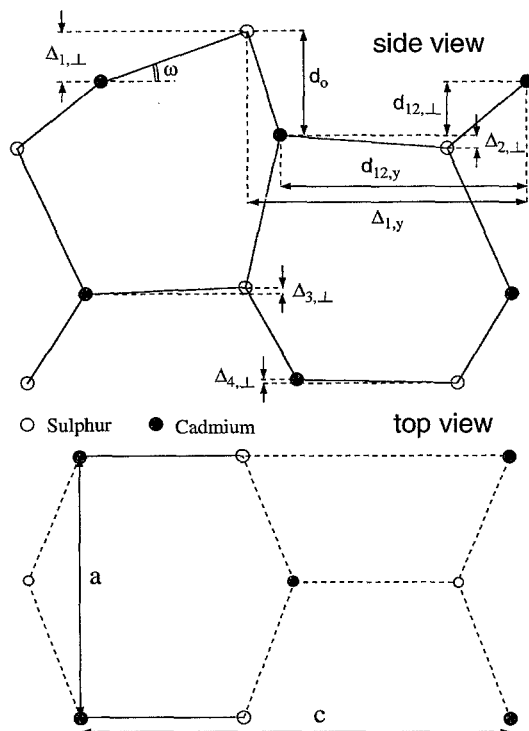


Fig. 2. Side view (four layers) of the relaxed surface geometry of CdS (10 $\bar{1}0$) surface and top view of the two uppermost layers. The structural parameters specifying the atomic relaxation are shown. The lattice constants a and c define the surface unit cell.

conveniently treat the (10 $\bar{1}0$) surface we chose the orthorhombic unit cell with eight atoms (two primitive cells), shown in Fig. 1. An attempt to optimise the bulk lattice parameters with a fixed c/a ratio was made using total energy minimisation. Though both methods described below resulted in lattice constants which deviated less than 0.1% from the experimental ones, the exact evaluation suffered from numerical inaccuracies related to the varying lattice size. Therefore, we chose to use the experimental bulk lattice constants for the surface unit cell. The experimental value of the internal parameter u is 0.375, but the total energy minimisation for the chosen bulk unit cell led to small deviations from this.

The wurtzite (10 $\bar{1}0$) surface is nonpolar and built up by a series of double layers. The chosen orthorhombic unit cell in Fig. 1 contains two of such double layers. Each atom has one bond within a layer (b_1), one to the next double layer (b_2) and two

bonds to the other plane of the same double layer ($b_{3,4}$). Thus, the surface layer atoms have one dangling bond each. As compared with the bulk, a surface atom has lost four and a subsurface atom two of their twelve next-nearest neighbours of the same element. The surface unit cell cut from the bulk is not expected to undergo an actual reconstruction with symmetry break but only strong relaxation to minimise the surface energy [7]. This will be shown to lead to large relative changes in atomic positions (> 0.5 Å), but only in a plane perpendicular to the surface and containing the c -axis of wurtzite lattice, see Fig. 2.

For calculations the $(10\bar{1}0)$ surface was modelled with slab constructions, where supercells of different sizes were tested as described below.

3. Computational methods

The Car–Parrinello (CP) approach [13] has successfully been used in the first principles calculations for both bulk and surface properties of metals and semiconductors. Most often the method employs plane wave (PW) expansion and local-density approximation (LDA) for the valence electrons with the core electrons treated using pseudopotentials (PP). Here we use the fhi94md code package [11], which is similar to the usual CP codes. The main difference is that in fhi94md the electronic degrees of freedom are subject to energy minimisation at each nuclear configuration. The Williams–Soler algorithm [14] is used to relax the electronic system, whereas the ionic positions are optimised on the Born–Oppenheimer surface using damped molecular dynamics. LDA with the Perdew–Zunger parametrisation [15] of the Ceperley–Alder Monte Carlo data [16] is employed.

The pseudopotentials are of generalised norm-conserving type [17]. They consist of 1s-, 2s- and 2p-potentials for sulphur, with s being treated as the nonlocal component in the Kleinman–Bylander [18] picture. The cadmium PP contains s, p and d-type functions (1s–4d) with sp-nonlocality. Linear core-valence exchange-correlation functionals are used. The size of PW basis is determined by the simulation cell size, if the maximum PW energy (cut-off) is fixed. Here the number of plane waves varied depending on the slab thickness from 4000 to 16 000,

as the cut-off of 20 Ry was adopted after careful testing. For integrations over the reciprocal space the Γ -point ($k = 0$) value was taken as the representative average. The original code was modified to accommodate the simple orthorhombic unit cell.

The other computational method, DSolid, is commercially distributed software. It allows self-consistent ab initio computation of periodic structures within the LCAO (linear combination of atomic orbitals), i.e., localised basis set, and LDA. We have chosen to use the same LDA as above [16], here parameterised by Vosko, Wilk and Nusair [19]. The basis functions are one-electron orbitals of free atoms and free ions computed and stored in numerical form prior to the solid state calculation. The typical extent of radial functions is 5–6 Å. This type of basis allows one to use high quality but relatively small basis set compared to the use of Gaussian basis, but the drawback is the consequent numerical integration of matrix elements [20] instead of the analytical one, and laborious solving of the Coulomb potential.

For sulphur we use the following basis set: $(1s^2)$, $(2s^2)$, $(2p^6)$, $3s^2$, $3p^4$, $3s^{0*}$, $3p^{0*}$, $3d^{0*}$, where those in parentheses form a “frozen core” and those denoted with an asterisk are generated in ions rather than in neutral atoms. With the same notations the basis set for cadmium is $(1s^2)$, $(2s^2)$, $(2p^6)$, $(3s^2)$, $(3p^6)$, $(3d^{10})$, $(4s^2)$, $(4p^6)$, $4d^{10}$, $5s^2$, $4d^{0*}$, $5s^{0*}$, $5p^{0*}$. Thus, the highest in energy of the inactive (frozen) set of basis functions is Cd 4p at about -65 eV (the free atom eigenvalue). In particular, the Cd 4d functions were kept active to see if their role is important [9] in energetics of geometric relaxation. Note that with fhi the Cd 4d is described by a pseudopotential.

Periodic boundary conditions are invoked simply by summing up the periodic part of one-electron functions from the localised basis functions at the sites throughout the whole periodic system. As a matter of fact this leads to the same Γ -point approximation as above, with the feature that the larger the computational unit cell, the smaller the first Brillouin zone and the better the approximation becomes. In our case here we always have eight or sixteen atoms in a unit cell. Therefore, we expect the description of the SDOS to become qualitatively representative, or at least, revealing the differences between the bulk and surface.

4. Results

The bulk unit cell in Fig. 1, optimised with DSolid, contains eight (4 Cd + 4 S) atoms and increase of the cell size was found to drastically increase the computational task. With fhi, a 16-atom (8 Cd + 8 S) unit cell (two adjacent unit cells of Fig. 1) was used. This was advantageous in bringing the orthorhombic cell geometry closer to cubic that was found to stabilise the internal bulk geometry very close to the experimental internal structure. Furthermore, it increases the accuracy of the Γ -point approximation. Energy optimisations for bulk CdS, from the internal redistribution of the ideal configuration, were 0.24 and 0.28 eV/primitive cell with corresponding values 0.358 and 0.376 for the internal parameter from DSolid and fhi, respectively.

The surface calculations were carried out in various supercell geometries. A supercell structure with four vacuum layers and four atomic layers was found to be relatively good for a quantitative description of the relaxation of the first two surface layers (on two rigid layers). The relaxed geometry is given in Table 1 together with the structure parameters from the studies of Wang and Duke [7] (WD) and by Schröer, Krüger and Pollmann [9] (SKP). The results are compared also with those of the ideal truncated bulk surface. The results from both of our calculations show a bond-length-conserving relaxation in which the top-layer cations move towards bulk and the anions move outwards from the surface plane. The nearest-neighbour distance within the surface layer is

slightly changed to 2.41 and 2.37 Å (ideal: 2.51 Å) with DSolid and fhi, respectively. The rotation angle ω between the bond direction of the surface layer atoms and the surface plane is 17.8° and 14.3° in the same order. The calculated relaxation is driven by the same energy gain of 0.56 eV/surface unit cell (Fig. 1) with both methods. Both obtained structures are close to those of WD and SKP.

The values of the relaxation-structure parameters from the fhi method in Table 1 are a little smaller than the WD and SKP values, except for $\Delta_{1,y}$, while the values from the DSolid method are a little larger than the WD and SKP values, except for $\Delta_{1,\perp}$, $\Delta_{1,y}$ and $d_{12,y}$. The values of $\Delta_{1,\perp}$ and $\Delta_{1,y}$ from DSolid are between the WD and SKP values. The value 17.8° from the DSolid method for the rotation angle ω , especially, is very close to the WD and SKP values 17.5° and 16.4°, respectively. The relative difference between our calculations and the earlier WD and SKP results is largest for $\Delta_{2,\perp}$ (about 100% and –75% from DSolid and fhi, respectively). However, the corresponding absolute differences are only 0.08 and –0.06 Å. The origin for these differences is already present in our optimised internal bulk structure where the bulk $\Delta_{\perp}$ values (differences between the anion and cation coordinates of the same layer in the $[10\bar{1}0]$ direction) are 0.04 and –0.03 Å with DSolid and fhi, respectively.

To test slab models calculations were also made with different vacuum thicknesses in the surface supercell. The case of only two vacuum layers on four atomic layers was found inadequate and resulted in very large deviations in relaxation parameters, up to the Å range. With increasing vacuum thickness from four to eight layers on the four atomic layers, the parameter values from both DSolid and fhi methods increased of order of 10%. Table 2 shows the calculated values of the relaxation parameters for six and eight vacuum layers with DSolid and fhi, respectively. The fhi values are now closer to the WD and SKP values, while the larger DSolid values deviate further from these results.

The supercell structure with eight atomic CdS layers was used to evaluate deeper subsurface relaxations. The bulk structure was taken to correspond to the optimised one. Results from the DSolid calculation with a supercell with four vacuum layers on eight atomic layers, where the four uppermost atomic

Table 1
Relaxation parameters of CdS (10 $\bar{1}0$) surface, as defined in Fig. 2, from models with two uppermost relaxing layers^a

	Unrelaxed	DSolid 4/2+2	Fhi 4/ 2+2	WD [7]	SKP 4/2 +6 [9]
$\Delta_{1,\perp}$	0.00	0.73	0.58	0.74	0.72
$\Delta_{1,y}$	4.19	4.43	4.44	4.41	4.43
$d_{12,y}$	3.35	3.80	3.73	3.86	3.82
$d_{12,\perp}$	1.19	0.90	0.60	0.62	0.62
$\Delta_{2,\perp}$	0.00	0.16	0.02	0.08	0.08
d_0	1.19	1.63	1.18	1.19	1.26
ω	0.0°	17.8°	14.3°	17.5°	16.4°

^a The size of the super cell is given as “vacuum layers/relaxing atomic layers + rigid atomic layers”. Except for ω , all quantities are given in units of Å.

layers were free to relax, are given in Table 2. These parameter values are only a little larger than the corresponding DSolid values in Table 1, except for $d_{12,\perp}$. Relaxation of the third and fourth atomic layers, parameters $\Delta_{3,\perp}$ and $\Delta_{4,\perp}$, are only 0.03 and 0.0016 Å, respectively. Thus, the relaxation of the fourth atomic layer (from the optimised bulk geometry) is negligible. The general trend in the fhi results is the same as in DSolid results, the relaxation increase to some extent.

The relaxation of a wurtzite (10 $\bar{1}0$) surface is equivalent to the bond-angle rotation at a zincblende (110) surface and the above relaxation model is very similar to that of zincblende (110) surfaces, which is experimentally established for III–V compound semiconductors. A structure model of CdS (10 $\bar{1}0$) surface from experimental LEED data has not been proposed [9]. However, a LEED analysis for CdSe (10 $\bar{1}0$) surface has been carried out with a determination of the structure parameters [21]. Schröer et al. [9] found that these values, when scaled by the ratio of the respective lattice constants, fit nicely their calculated results for CdS (10 $\bar{1}0$). From the similarity of CdS and CdSe, in addition to the above general agreement with CdSe (10 $\bar{1}0$), they conclude that their energy-optimised relaxation geometry for CdS (10 $\bar{1}0$) is the most probable. In this sense, our results are also in close agreement with the experimental findings for nonpolar surfaces of related heteropolar covalent semiconductors. Their surface relaxation is driven by a downward shift of an anionic dangling-bond band [7,9].

Table 2

Comparison of the slab models; relaxation parameters, other notations and units as in Table 1

	DSolid 6/2+2	Fhi 8/ 2+2	DSolid 4/4+4	Fhi 8/ 4+4
$\Delta_{1,\perp}$	0.79	0.60	0.86	0.77
$\Delta_{1,y}$	4.43	4.44	4.43	4.49
$d_{12,y}$	3.64	3.74	3.96	3.87
$d_{12,\perp}$	1.04	0.58	0.81	0.47
$\Delta_{2,\perp}$	0.18	0.04	0.22	0.18
d_0	1.65	1.18	1.67	1.24
ω	19.0°	14.9°	20.5°	19.0°

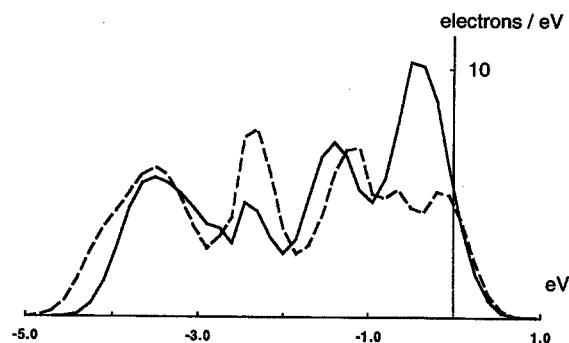


Fig. 3. Density of states of the CdS (10 $\bar{1}0$) surface (SDOS) at the two surfacemost atomic layers (solid curve) compared with the bulk CdS density of states (dashed curve). Only the occupied valence band is shown.

In Fig. 3 we compare the bulk DOS and SDOS of (10 $\bar{1}0$) surface obtained with the fhi method. The SDOS is evaluated from the eigenenergy spectrum of a four layer slab allowed to fully relax throughout all layers. Thus, it corresponds to the one-electron levels of the two surfacemost layers at both sides (though not on top of the third layer but on its own mirror image). For graphical presentation the discrete spectra of eigenenergies are convoluted by a Gaussian shape of 0.6 eV width and both density-of-states curves are shifted in energy to set the top of the valence band (highest occupied one-electron level) to 0 eV.

Both of the DOS curves in Fig. 3 are similar to those obtained by Wang and Duke [7] and the bulk DOS matches well with the X-ray photoemission spectrum of the valence band [22]. Major reason for the remaining differences may be our sparse sampling of the k -space. The lowest unoccupied levels locate at 1.7 and 2.4 eV above the valence band in the bulk and at the surface, respectively. The next lowest levels in both structures are found at about 3.4 eV. The development of surface states to the top of valence band can be clearly seen and the energy relaxation of these states has been explained to be responsible for the geometrical relaxation of the surface layers [7,9]. Furthermore, the strong enhancement of SDOS leads to considerable increase in chemical activity and catalytic properties that will be the subject of our further studies.

5. Conclusions

Both of our self-consistent *ab initio* LDA methods give the relaxation of wurtzite CdS (10 $\bar{1}$ 0) surface in close agreement with the earlier semiempirical results of Wang and Duke [7] and *ab initio* results of Schröer et al. [9]. It was also found that the relaxation is very small in the third atomic layer and negligible in the fourth layer. Four vacuum layers on four atomic layers, where the two uppermost are free to relax, is a minimum sized model, which can be improved by increasing the thickness of vacuum. Use of two adjacent surface unit cells rather than one as a computational unit makes the system more square like, and depending on the method, may result in more reliable description of the relaxation. The size of the surface supercell with the number of relaxing atomic layers in the slab model is, however, related to the computational effort. The explicit role of Cd 4d electrons was not found to be essential in the relaxation. Finally, the obtained densities-of-states for both bulk and surface electronic levels are close to those of previous calculations and support the idea that the surface relaxation is driven by energy relaxation of surface states.

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