Atomic Structures of CdTe and CdSe (110) Surfaces

K. Watari, J.L.A. Alves* and A.C. Ferraz

Instituto de Física da Universidade de São Paulo

Caixa Postal 66318, 05389-970, São Paulo, SP, Brazil

*Fundação de Ensino Superior de São João del Rei - DCNAT

Caixa Postal 110, São João del Rei, MG, Brazil

We report results based on the self-consistent density-functional theory, within the local-density approximation using *ab-initio* pseudopotentials of clean CdTe and CdSe (110) surfaces. We analyze the trends for the equilibrium atomic structures, and the variations of the bond angles at the II-VI (110) surfaces. The calculations are sensitive to the ionicity of the materials and the results are in agreement with the arguments which predict that the relaxed zinc-blende (110) surfaces should depend on ionicity.

I. Introduction

The non-polar (110) zinc-blende surface are thought to be the best understood among all semiconductor surfaces, from the electronic as well as the structural point of view. The study has been concentrated mainly on surfaces of Si, Ge and the III-V compounds[1], but the II-VI compounds have not been analyzed in detail. It is widely believed that the relaxations on these surfaces are determined virtually by covalent forces, and the surface anions rotate more-or-less rigidly out of surface through an angle $\omega \cong 29°$ for all zinc-blende (110) surfaces[2-4]. Recently, there has been a great deal of interest in wide-band-gap II-VI semiconductors mainly using these materials as pure or alloyed semiconducting compound in infrared detectors, solar cells and blue-light-emitting laser diodes[5]. Since the electron structures of different zinc-blende crystal compounds are generally very similar, one may hope that systematic comparison of data from different systems should resolve some of the ambiguities.

In the following paper, we present a theoretical study of the non-polar (110) cleavage face of CdTe and CdSe zinc-blende compounds. In particular, we will concentrate on the atomic surface geometry and on its correlation with the electronic and chemical properties of the surface. The driving mechanism for the atomic rearrangement will be analyzed in connection with the ionicity of the materials and another II-VI (110) surfaces.

II. Method of calculation

We use the first-principles density-functional-theory calculations for electronic structure and total energy[6,7] within the local-density approximation for the exchange-correlation functional[8]. Norm-conserving non local pseudopotentials are generated and Kleinman-Bylander (KB) type of fully separable pseudopotentials are constructed[9,10]. The wave functions are expanded in a plane-wave basis set with a kinetic-energy cut-off of 12 Ry. The $k_\parallel$ integration is replaced by a sum over four Monkhorst-Pack special points in the irreducible part of the surface Brillouin zone[11]. We treat the 4d electrons of Cd as core because the surface relaxations are mainly affected by the s and p valence electrons, but we generate a KB pseudopotential for a cadmium atom choosing suitable core radii and electron configuration $s^x p^y$.

The surfaces are modelled by a slab geometry of eight (110) atomic layers with a surface at each side plus a vacuum region equivalent to six atomic layers. The two central layers, representing the bulk CdTe and CdSe are frozen during the calculation. To determine the equilibrium atomic positions the three outermost layers on both sides of the slab are relaxed until optimum atomic coordinates are stablished by the calculated total energy and forces together with the Car-Parrinello approach[12]. At the equilibrium geometry

all forces are smaller than 0.005 eV/Å corresponding to an uncertainty of the atomic positions less than 0.05 Å.

III. Results and analysis

Figure 1 shows a top view of the surface and the side view of the outermost layers of the clean relaxed surface. Also the structural parameters are defined in Table I and II. The atomic relaxation on both CdTe (110) and CdSe (110) surfaces have a similar pattern of the III-V (110) surfaces: the surface-layer anions move out of the surface and the cations move inward. Under the coordination conditions of the surface, the cation atom prefers a more planar, sp^2-like bonding situation with its three anions neighbors and the anion prefers a p-bonding with its three cations neighbors. The calculated equilibrium cubic lattice constant is 6.203 Å for CdTe and 5.783 Å for CdSe and are about 4% smaller than the experimental values of 6.486 Å and 6.052 respectively.
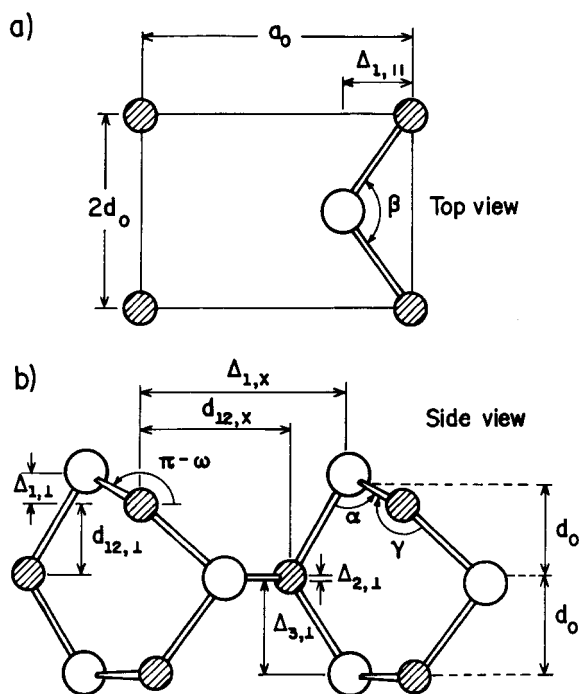
Figure 1. Atomic geometry for II-VI semiconductor (110) surfaces. (a) Top view of the surface unit cell. (b) Side view of the first three layers of the (110) surface. Open circles are anions and the hatched circles are cations. a_0 is the theoretical bulk lattice constant and $d_0 = \sqrt{2}a_0/4$.

Table I shows the displacements of atoms from the ideal zinc-blende positions for the clean surfaces CdTe

Table I. Structural parameters for the surface relaxation as defined in Fig. 1. For each compound the first line corresponds to the LEED analysis (Ref. 13).

	$\Delta_{1,\perp}$ (Å)	$\Delta_{1,x}$ (Å)	$\Delta_{2,\perp}$ (Å)	$d_{12,\perp}$ (Å)	$d_{23,\perp}$ (Å)	$d_{12,x}$ (Å)	ω (°)
CdTe	0.81	5.08	0.00	1.71	2.29	3.84	30.0
	0.72	4.96	0.14	1.55	2.31	3.56	30.2
CdSe	-	-	-	-	-	-	-
	0.59	4.63	0.12	1.49	2.15	3.28	27.1

Table II. Displacements perpendicular to the surface of the cations and anions at the top layer. The positive direction is taken along (110). The changes of the cation-anion distances (labeled $c_i a_j$) between neighboring atoms in the first two layers ($i, j = 1,2$) of our slab are given in the last three columns.

	$\Delta_{1,\perp}$ anion (Å)	$\Delta_{1,\perp}$ cation (Å)	Bond-Lenght Change (%)		
			$c_1 a_1$	$c_2 a_1$	$c_1 a_2$
CdTe	↑0.19	↓0.53	-2.43	-0.62	-2.42
CdSe	↑0.13	↓0.46	-3.29	-0.94	-2.60

(110) and CdSe (110). The results for CdTe (110) are in very good agreement with low-energy electron diffraction (LEED) analysis[13] while for zinc-blende CdSe (110) there is no available data. The relative displacement is the most accurately determined by LEED intensity analysis to within ± 0.05 Å. The tilt angle ω is also in very good agreement with the experimental one.

From Table II it can be seen that the surfaces relax with the surface anions moving out of the surface and the surface cations moving inward. The calculated changes in the bond lengths of the surface atoms relative to the bulk lengths are smaller than 3.3%. The change in the cation-anion distance at the first layer of the surfaces ($c_1 a_1$) is larger for CdSe. While the $c_2 a_1$ bond length is almost unchanged (less than 1%), the $c_1 a_2$ bond length is shortened around 2.5%. These bond length variations are bigger than the observed values for III-V (110) surfaces[3] and agree well with the results for other II-VI (110) surfaces[4,14].

The bond angles obtained in our present calculations are shown in Table III. As it was pointed out on reference 4, the angle α is bigger in II-VI compounds

Table III. Calculated tilt angle ω, relative displacement $\Delta_{1,\perp}$ in % of the lattice constant a_0, bond angles at the anions and at the cations located at the first layer, and $Z^2 e^2/\epsilon a_0$ in eV.

	ω (°)	$\Delta_{1,\perp}/a_0$ (%)	α (°)	β (°)	γ (°)	$Z^2 e^2/\epsilon a_0$ (eV)
CdTe	30.2	11.6	90.8	113.6	122.6	0.888
CdSe	27.1	10.2	93.1	115.2	121.3	0.904

than in III-V compounds and the angle α is closer to 90° as one goes from sulphur compound to selenium compound and then to tellurium compound. Here the *pyramidal* angle α at the anion goes from 93.1° for CdSe to 90.8° for CdTe in agreement with the Zn compounds. The *planar* angle γ at the cation is close to 120°, and the *in-plane* angle β is lower, close to the tetrahedral bond angle (109.47°).

The attractive Coulomb forces between the outward surface anions and the inward surface cations should reduce the relaxation caused by covalent forces, for the more ionic zinc-blende semiconductors. The Philipps ionicities[15] for CdSe (wurtzite) and CdTe are 0.699, 0.675, respectively. We compare in Table III the trends of the angle α and the Coulomb energy[16] $Z^2 e^2/\epsilon a_0$, where a_0 is the zinc-blende theoretical lattice constant, Z is the longitudinal effective charge[17], e is the electronic charge, and ϵ is the dielectric constant. For the calculation of the Coulomb energy of CdSe (110) surface, we have used the parameters Z and ϵ of the wurtzite structure. As can be seen in Table III, for compounds with common cation, the angle α decreases, getting closer to 90°, when the Coulomb energy decreases. The tilt angle ω increases when the Coulomb energy decreases. The calculated relative displacement $\Delta_{1,\perp}$ in % of the theoretical lattice constant a_0, is smaller for higher Coulomb energy. The *planar* angle γ increases above 120° as the Coulomb energy decreases, while the *in plane* angle β goes above the tetrahedral angle.

The calculated bond angles at the II-VI (110) surfaces are bigger than the bond angles at the III-V (110) surfaces[4] as the ionic forces try to reduce the relaxation caused by the covalent forces. The dependence on ionicity of the (110) surface relaxations of zinc-blende semiconductors is stablished, as our calculations are

sensitive to the ionicity of the materials, and in good agreement with the arguments which predict that the tilt angle should depend on ionicity[16].

References

1. A. Kahn, Surface Sci. Rept. **3**, 193 (1983).

2. C. B. Duke, J. Vac. Sci. Technol. **A6**, 1957 (1988).

3. J. L. A. Alves, J. Hebenstreit and M. Scheffler, Phys. Rev. **B44**, 6188 (1991).

4. J. L. A. Alves, K. Watari and A. C. Ferraz, Solid State Comm. **87**, 1001 (1993).

5. H. Jeon, J. Ding, A. V. Nurmikkco, W. Xie, D. C. Grillo, M. Kobayashi, R. L. Gunshor, G. C. Hua and N. Otsuka, Appl. Phys Lett. **60**, 2045 (1992).

6. P. Hohenberg and W. Kohn, Phys. Rev. **136**, B 864 (1964).

7. W. Kohn and L. J. Sham, Phys. Rev. **140**, A 1133 (1965).

8. D. M. Ceperley and B. I. Alder, Phys. Rev. Lett. **45**, 566 (1980); J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

9. L. K. Kleinman and D. M. Bylander, Phys. Rev. Lett. **48**, 1425 (1982).

10. X. Gonze, R. Stumpf and M. Scheffler, Phys. Rev. B **44**, 8503 (1991).

11. H. J. Monckhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).

12. R. Car and M. Parrinello, Phys. Rev. Lett. **55**, 2471 (1985).

13. C. B. Duke, *Surface Properties of Electronic Materials*, D.A. King & D.P. Woodrif eds. - Elsevier, 1986 - Chapter 3.

14. A. C. Ferraz and G. P. Srivastava, J. Phys. C **19**, 5987 (1986).

15. F. Bechstedt and R. Enderlein, *Semiconductor Surfaces and Interfaces* (Akademic Verlag, Berlim, 1988).

16. R. V. Kasowski, M.-H. Tsai and J. D. Dow, J. Vac. Sci. Technol. B **5**, 4, 953 (1987).

17. G. Lucovsky, R. M. Martin and E. Burstein, Phys. Rev. B4, 1367 (1971).