

## Large-angle bond-rotation relaxation for CdTe(110)

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(Received 26 August 1994)

A combination of x-ray standing-wave measurements and first-principles total-energy calculations have determined the surface relaxation of the clean CdTe(110) surface. These two methodologies directly determine the local atomic geometry and therefore provide a model-independent means of verifying the results obtained indirectly from elastic low-energy electron diffraction (ELEED) studies. By comparing our results for this strongly ionic material (Phillips ionicity  $f=0.72$ ) with the results of numerous earlier studies of less ionic III-V compounds, we are able to assess the influence of ionicity on the degree of relaxation for the cleavage faces of zinc-blende semiconductors. Our measurements and calculations indicate that, contrary to a previous theoretical study but in agreement with ELEED, the relaxation is approximately independent of the semiconductor ionicity. Our model-independent measurements yield a vertical buckling  $\Delta_{1,1}=0.120\pm 0.023$  (in units of the lattice constant  $a=6.482$  Å), which agrees well with our calculated buckling of 0.114.

### I. INTRODUCTION

The (110) surfaces of the zinc-blende-structure III-V semiconductors are probably the most studied and best understood of all the semiconductor surfaces; numerous elastic low-energy electron-diffraction (ELEED) studies<sup>1-4</sup> and many calculations<sup>5-7</sup> have repeatedly confirmed their atomic and electronic structures. The local geometries of these surfaces conform to a universal topology, which consists approximately of a bond-length-conserving top-layer bond rotation characterized by a rotation angle  $\omega_1$  of approximately  $29^\circ(\pm 3^\circ)$ .<sup>1-7</sup> The surface anion moves up out of the surface relative to its ideal, bulk-terminated position, while the surface cation moves down into the surface. In the simplest approximation, the driving force for this relaxation is the rehybridization and lowering in energy of the doubly occupied anion-derived dangling-bond states. The detailed

structural parameters describing the relaxations are nearly independent of the compound when they are scaled by the respective bulk lattice constants.

There is compelling experimental<sup>2,3,8</sup> and theoretical<sup>9-11</sup> evidence that the relaxations of the (110) surfaces of the more ionic II-VI and I-VII semiconductors possess the same universal local topology as that of the III-V's. This circumstance raises the question as to the role played by ionicity. Clearly there must be a Coulomb energy cost for increasing the vertical separation (perpendicular to the surface plane) between the negatively charged surface anions and the positively charged surface cations. The effective charges on the anions and cations are larger for more ionic semiconductors and so the energy cost should also be larger. Therefore, in addition to the one-electron contribution to the total energy indicated above, there must also be a Coulomb contribution, which increases with ionicity and favors the bulk-terminated geometry.

Questions concerning the role of ionicity have been discussed in the literature.<sup>12</sup> Tsai *et al.*<sup>13</sup> predicted that the equilibrium bond-rotation angle  $\omega_1$  will decrease with increasing ionicity, going to zero for the I-VII semiconductor CuCl. However, this prediction for the CuCl(110) surface has recently been contradicted by an ELEED analysis<sup>8</sup> and a first-principles calculation,<sup>11</sup> both of which found a large-angle bond-rotation relaxation. Nonetheless, it remains true that all of the experimental evidence for a universal local topology, independent of ionicity, has come from ELEED data.<sup>13</sup> These data are difficult to analyze because they do not yield the atomic structure directly but require a model as input. In the case of the III-V (110) surfaces, several other techniques (e.g., ion scattering<sup>14</sup>) were applied before consensus was reached on the atomic structures; but, no techniques other than ELEED have been used for the more ionic II-VI's or I-VII's. In addition, for the CuCl ELEED study,<sup>8</sup> the surface was prepared *in situ* by congruent evaporation, which may raise uncertainties regarding the surface perfection, stoichiometry, and overall structure.

In contrast to ELEED data, x-ray standing-wave (XSW) measurements provide a model-independent means of directly determining the surface atomic geometry.<sup>15,16</sup> In this work, we use the XSW technique to study the atomic structure of the clean CdTe(110) surface. CdTe is the most ionic of all the zinc-blende II-VII's (Phillips<sup>17</sup> ionicity  $f=0.72$ ), and comparable in ionicity to CuCl ( $f=0.75$ ). CdTe is suitable for XSW studies because Cd and Te possess strong surface sensitive Auger peaks at 370 and 490 eV, respectively. The (220) Bragg energy of 2707 eV (for the back-reflection configuration at the Bragg angle of 90°) is also easily accessible experimentally. Good quality crystals of this easily cleaved material can be selected. (Our XSW measurements directly determine if the crystal is twinned, as is very commonly the case.)

In addition to the XSW measurements, we have also carried out first-principles total-energy calculations for the CdTe(110) surface. The accuracy of the first-principles methods [based on the local-density approximation (LDA)] in the determination of surface atomic structures is well established.<sup>6,7,11</sup> Our combined XSW measurement and first-principles calculation of the surface structure, therefore, provides an independent test of the prior ELEED analyses.<sup>18,19</sup>

The remainder of this paper is organized as follows. In Secs. II and III, we describe our experimental and theoretical methods, respectively. Our combined results are presented and compared to previous work in Sec. IV. Finally, Sec. V contains a short summary.

## II. EXPERIMENTAL METHOD

The XSW technique has been used to measure the vertical displacement of the surface In and P atoms on non-polar (110) planes of InP.<sup>15</sup> This earlier work established the applicability to surface structure problems of the back-reflection diffraction geometry combined with the detection of Auger electrons. The use of low-energy elastic photoelectrons or Auger electrons results in extreme

surface sensitivity, as is well known from low-energy photoemission studies. The surface sensitivity is further enhanced by our experimental geometry in which the central axis of the double-pass cylindrical-mirror analyzer (CMA) is parallel to the surface. The advantage of the back-reflection configuration lies in the fact that the Bragg condition is achieved at the lowest possible energy, minimizing problems with secondary effects induced by energetic electrons excited in the bulk of the sample. These electrons could induce Auger or fluorescence transitions, which are also frequently used to measure the standing-wave patterns.

The XSW method relies on the change of phase and hence the electric-field intensity of a standing wave near a Bragg condition. As the photon energy is swept through the Bragg energy, the electric-field intensity relative to the diffracting planes varies spatially. The analysis of changes in the absorption of the surface atoms provides information on the separation between these atoms and the diffracting planes. As in EXAFS, the absorption can be measured through a secondary channel proportional to the absorption. In this work, we use the Auger yield of the Cd and Te MNN transitions. Contrary to adsorbate studies, which are often performed with XSW, there is no elemental discrimination of the signal because both surface and bulk are made of the same atoms. In order to extract information about the surface relaxation, the extreme surface sensitivity of the yield from the elastic electrons has to be referenced against the bulk sensitive yield of secondaries or against the total yield. For surfaces of compound materials, elemental discrimination exists in the sense that displacement of different atoms making up the surface can be individually established. Specifically for CdTe, the positions of the Cd and Te surface atoms are determined separately and the difference gives the vertical buckling of the top-layer chains.

The present XSW experiment was performed on the beamline X-24A of the National Synchrotron Light Source in a standard UHV chamber equipped with a double-pass CMA. Data from cleaved CdTe crystals were obtained by scanning a pair of Si(111) monochromator crystals through the CdTe 220 Bragg energy, which occurs at around 2707 eV for the back-reflection geometry. The Cd and Te MNN Auger yields and the respective background spectra at kinetic energies 50 eV above the Auger peaks have been measured around the Bragg condition. The background spectra from the inelastically scattered electrons are representative of the bulk substrate standing waves and give the same signatures as the total yield. Since the elastic component is a sum of surface and bulk contributions, the analysis is performed by fitting the ratio of the "on peak" and background scans, as described in our previous paper.<sup>15</sup> In this way, no prior knowledge of the electron escape depth is required to determine distances, provided that the energy dependence of the background is indeed a unity standing wave and the surface has low disorder. This was established to be the case by the direct fitting of the background data. The reflectivity spectra were measured by monitoring the variation of the current from the incident flux monitor, which consists of an 80% transmitting Ni

grid upstream of the monochromator. Near the Bragg energy, the back-reflected signal is superimposed over a constant incident flux. The measurement of reflectivity, which provides information on energy calibration and resolution, is critical for reliable data analysis.

### III. THEORETICAL METHOD

We use a full-potential linear-muffin-tin orbital (FP-LMTO) method,<sup>11,20–22</sup> which makes no shape approximation for the crystal potential. The crystal is divided up into regions inside atomic spheres, where Schrödinger's equation is solved numerically, and an interstitial region. As in all LMTO methods, the wave functions in the interstitial are Hankel functions. The interpolation procedure we use for evaluating interstitial integrals involving products of Hankel functions is accurate for close packed but still nonoverlapping atomic spheres. As is customary for the zinc-blende structure, we include empty atomic spheres at the interstitial sites, producing an overall sphere-packing equivalent to that in the bcc structure. However, these empty spheres do not contribute to the basis but merely improve the accuracy of the interpolation procedure.

The basis is composed of one set of  $s$ ,  $p$ ,  $d$ , and  $f$  LMTO's per atom with Hankel function kinetic energy  $-\kappa^2 = -0.7$  Ry plus two additional sets of  $s$ ,  $p$ , and  $d$  LMTO's per atom with Hankel function kinetic energies of  $-\kappa^2 = -1.0$  and  $-2.3$  Ry, for a total of 34 orbitals per atom. The Hankel functions decay exponentially as  $e^{-\kappa r}$ ; we find that taking energies  $-\kappa^2$  closer to zero leads to an inaccurate description of the exponential decay of the charge density just outside the surface. We also find that a layer of empty spheres is needed outside the surface in order that the interpolation procedure be sufficiently accurate in this region. The charge density beyond this layer of empty spheres is small so that only a single layer is needed. The angular-momentum sums involved in the interpolation procedure are carried up to a maximum of  $l=6$  for all of the spheres.

The calculations presented here are based on the LDA, using the exchange-correlation potential of Hedin and Lundqvist.<sup>23</sup> The scalar-relativistic Schrödinger equation (without spin-orbit interactions) was solved self-consistently for the (110) surfaces of CdTe. The Cd 5s, 5p, 4d, and 4f states and the Te 5s, 5p, 5d, and 4f states were all treated as valence. The semicore Cd 4p and Te 4d states were treated as full band states by carrying out a two-panel calculation. The second-panel band calculation for the semicore states included the Cd 5s, 4p, and 4d states and the Te 5s, 5p, and 4d states. The Cd 5d states were not included in either the first or second panel. The Brillouin sums were carried out using 12 irreducible  $\mathbf{k}$  points in the first panel and 4 irreducible  $\mathbf{k}$  points in the second panel. The (110) surface was approximated by a supercell consisting of seven CdTe layers and the equivalent of nine vacuum layers. The surface calculations were carried out using the theoretical equilibrium lattice constant in order to avoid spurious nonzero pressures, which could alter the calculated atomic geometries. The accuracy of our FP-LMTO method for

surface calculations has been demonstrated previously.<sup>11,22</sup>

The  $1 \times 1$  symmetry of the relaxed CdTe(110) surface reduces the number of independent degrees of freedom per atom from 3 to 2. These are conventionally referred to as the  $y$  coordinate, measured parallel to the (110) planes and perpendicular to the zig-zag chains, and the  $z$  coordinate, measured perpendicular to the (110) surface. We have minimized the total energy with respect to five independent degrees of freedom: the  $y$  and  $x$  coordinates of the surface Cd and Te plus the rotation angle for a bond-length-conserving second-layer counter rotation.

### IV. RESULTS

Figure 1 shows the best fits to the normalized XSW data. These fits place the topmost Cd and Te atoms 0.75 Å below and 0.03 Å above their respective truncated surface positions (errors  $\pm 0.1$  Å). Taken together, these XSW data indicate a 16% mean contraction of the topmost bilayer. The corresponding vertical shear between the surface Cd and Te atoms, labeled  $\Delta_{1,1}$ ,<sup>10,18</sup> is 0.78 Å ( $\pm 0.15$  Å) or 0.120 ( $\pm 0.023$ ) in units of the bulk lattice constant ( $a = 6.482$  Å). This value is in excellent agreement with our FP-LMTO calculations which give  $\Delta_{1,1} = 0.114$  and a corresponding tilt angle  $\omega_1 = 29.5^\circ$ .

The results obtained from our XSW measurements and first-principles calculations are compared to previous experimental and theoretical studies in Table I. The listed structural parameters are illustrated in Fig. 2 and are the same as those defined in Refs. 10 and 18. All of the distances are given in terms of the bulk lattice constant.

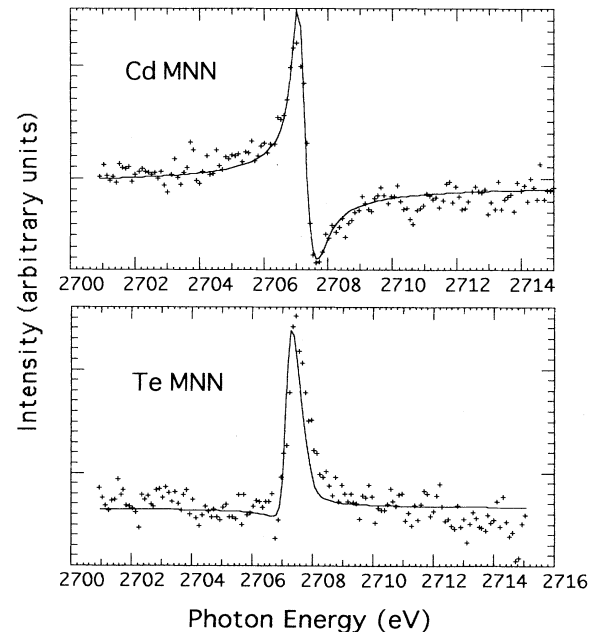


FIG. 1. Photon-energy dependence of the Cd MNN and Te MNN ratiored XSW data near the CdTe(220) Bragg back-reflection condition. Solid lines represent fits to the data points (see text).

TABLE I. The structural parameters that describe the relaxation of the (110) surface of CdTe (the parameters are illustrated in Fig. 2 and are the same as those defined in Refs. 10 and 18). All of the distances are given in terms of the bulk lattice constant while the angle  $\omega_1$  is in degrees. The values obtained from our XSW measurements and first-principles calculations (FP-LMTO) are compared to two earlier ELEED analyses and a previous tight-binding calculation. The XSW value of  $\omega_1$  corresponds to a bond-length-conserving rotation.

	$\Delta_{1,\perp}$	$\Delta_{1,y}$	$d_{12,y}$	$d_{12,\perp}$	$\Delta_{2,\perp}$	$d_{23,\perp}$	$\omega_1$
ELEED 1 <sup>a</sup>	0.127	0.784	0.594	0.241	-0.028	0.367	30.5
ELEED 2 <sup>b</sup>	0.127	0.784	0.560	0.245	-0.013	0.362	30.5
TB <sup>c</sup>	0.117	0.791	0.580	0.247	-0.039		29.3
XSW	0.120						(28.7)
FP-LMTO	0.114	0.798	0.573	0.255	-0.020	0.363	29.5

<sup>a</sup>See Ref. 18.

<sup>b</sup>See Ref. 19.

<sup>c</sup>See Ref. 10.

The experimental lattice constant is 6.482 Å; this value was also used in the tight-binding (TB) calculations. The theoretical value obtained from our FP-LMTO calculations is 6.426 Å. The TB entry for  $\omega_1$  is *not* the one listed by Wang *et al.*<sup>10</sup> in their Table II, but is calculated from their values of  $\Delta_{1,\perp}$  and  $\Delta_{1,y}$ . The present XSW study only determined displacements perpendicular to the surface plane and, therefore, the listed XSW angle  $\omega_1$  assumes a bond-length-conserving rotation. The FP-LMTO calculations minimized the total energy with respect to only five independent degrees of freedom so that one of the distance parameters involving the second layer is redundant (as is the angle  $\omega_1$ ).

Until now, the surface relaxation of CdTe has been measured by only two independent ELEED studies. Duke *et al.*<sup>18</sup> reported  $\Delta_{1,\perp}=0.127$  and  $\omega_1=30.5^\circ$  and almost identical values were reported by Cowell and de Carvalho.<sup>19</sup> Our XSW data and calculations for the vertical shear are well within the experimental errors of both techniques. The tight-binding total-energy calculation of Wang *et al.*<sup>10</sup> gave  $\Delta_{1,\perp}=0.117$  and  $\omega_1=29.3$ ; again in excellent agreement with our data and calculations as well as the ELEED results. All of these results contradict Tsai *et al.*<sup>13</sup> who calculated a value of  $\omega_1=7^\circ$ .

The Phillips<sup>17</sup> ionicity for CdTe is 0.72, which is almost as large as that of CuCl at 0.75. We have deter-

mined the tilt angle  $\omega_1$  to be approximately  $29^\circ$ , which confirms the results of the earlier ELEED analyses. A large body of literature<sup>1-7</sup> has demonstrated convincingly that the tilt angles for the less ionic III-V compounds are approximately  $29^\circ \pm 3^\circ$ . The ionicities for these compounds are as low as the value of 0.26 for GaSb. Thus, it is clear that the tilt angle and, therefore, the gross features of the relaxation are essentially independent of ionicity over a large range. It is still true that there is an ionicity-dependent Coulomb contribution to the total energy but evidently the one-electron contribution still dominates for the II-VI and I-VII compound semiconductors.

## V. SUMMARY

We have presented the results of XSW measurements and first-principles total-energy calculations, which both yield a large-angle bond-rotation relaxation for the CdTe(110) surface. Our results have provided model-independent verification of earlier ELEED analyses, which determine the atomic structure only indirectly. By comparing the relaxation of CdTe(110), with a Phillips ionicity of 0.72, to the well-established relaxations of the less ionic III-V compounds, we are able to conclude that the gross features of the local atomic structure for zincblende (110) surfaces are essentially independent of ionicity.

## ACKNOWLEDGMENTS

We would like to thank Ron Morris and Barry Karlin for excellent technical assistance. The XSW measurements were carried out at the National Synchrotron Light Source, which is supported by the U.S. Department of Energy, Office of Materials Science. This part of the work was performed under ONR Contract No. N00014-92-J-1280 with additional support from the National Institute of Standards and Technology and the Stanford Synchrotron Radiation Laboratory. The first-principles calculations were carried out at the National Energy

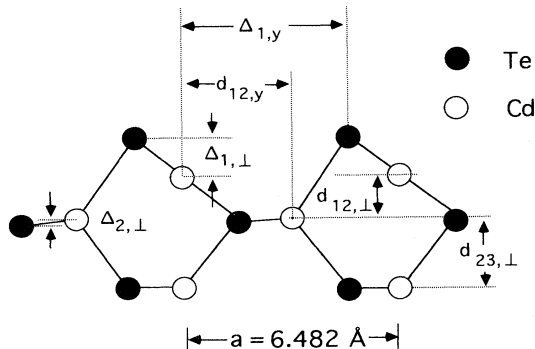


FIG. 2. Schematic drawing of the CdTe(110) surface illustrating the structural parameters in Table I.

Research Supercomputer Center and were performed in part under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under Contract No. W-7405-ENG-48. J.E.K. and C.M.

would also like to acknowledge the support of the Office of Basic Energy Sciences, the Division of Materials Science. M.v.S. was supported by ONR Contract No. N00014-89-K-0132.

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- <sup>1</sup>A. Kahn, *Surf. Sci. Rep.* **3**, 193 (1983).  
<sup>2</sup>A. Kahn, *Surf. Sci.* **168**, 1 (1986).  
<sup>3</sup>C. B. Duke, in *Surface Properties of Electronic Materials*, edited by D. A. King and D. P. Woodruff (Elsevier, Amsterdam, 1988), p. 69.  
<sup>4</sup>C. B. Duke, *J. Vac. Sci. Technol. A* **10**, 2032 (1992).  
<sup>5</sup>C. Mailhot, C. B. Duke, and D. J. Chadi, *Surf. Sci.* **149**, 366 (1985).  
<sup>6</sup>G.-X. Qian, R. M. Martin, and D. J. Chadi, *Phys. Rev. B* **37**, 1303 (1988).  
<sup>7</sup>J. L. A. Alves, J. Hebenstreit, and M. Scheffler, *Phys. Rev. B* **44**, 6188 (1991).  
<sup>8</sup>A. Kahn, S. Ahsan, W. Chen, M. Dumas, C. B. Duke, and A. Paton, *Phys. Rev. Lett.* **68**, 3200 (1992).  
<sup>9</sup>Y. R. Wang and C. B. Duke, *Phys. Rev. B* **36**, 2763 (1987).  
<sup>10</sup>Y. R. Wang, C. B. Duke, K. O. Magnusson, and S. A. Flodström, *Surf. Sci.* **205**, L760 (1988).  
<sup>11</sup>J. E. Klepeis, C. Mailhot, M. van Schilfgaarde, and M. Methfessel, *J. Vac. Sci. Technol. B* **11**, 1463 (1993).  
<sup>12</sup>C. B. Duke, R. J. Meyer, and P. Mark, *J. Vac. Sci. Technol.* **17**, 971 (1980).  
<sup>13</sup>M.-H. Tsai, J. D. Dow, R. P. Wang, and R. V. Kasowski, *Phys. Rev. B* **40**, 9818 (1989).  
<sup>14</sup>L. Smit and J. F. van der Veen, *Surf. Sci.* **166**, 183 (1986).  
<sup>15</sup>J. C. Woicik, T. Kendelewicz, K. E. Miyano, P. L. Cowan, C. E. Boulbin, B. A. Karlin, P. Pianetta, and W. E. Spicer, *Phys. Rev. Lett.* **68**, 341 (1992).  
<sup>16</sup>J. Zegenhagen, *Surf. Sci. Rep.* **18**, 199 (1993).  
<sup>17</sup>J. C. Phillips, *Bonds and Bands in Semiconductors* (Academic, New York, 1973), p. 26.  
<sup>18</sup>C. B. Duke, A. Paton, W. K. Ford, A. Kahn, and G. Scott, *Phys. Rev. B* **24**, 3310 (1981).  
<sup>19</sup>P. G. Cowell and V. E. de Carvalho, *J. Phys. C* **21**, 2983 (1988).  
<sup>20</sup>M. Methfessel, *Phys. Rev. B* **38**, 1537 (1988).  
<sup>21</sup>M. Methfessel, C. O. Rodriguez, and O. K. Andersen, *Phys. Rev. B* **40**, 2009 (1989).  
<sup>22</sup>M. Methfessel, D. Hennig, and M. Scheffler, *Phys. Rev. B* **46**, 4816 (1992).  
<sup>23</sup>L. Hedin and B. I. Lundqvist, *J. Phys. C* **4**, 2064 (1971).