

## Anion-terminated zinc-blende CdS(100) surface

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Using the local-orbital density-functional molecular-dynamics method, we have studied the surface structure of the strain-stabilized zinc-blende monolayer anion-terminated CdS(100) surface. By analogy with the GaAs(100) surface, we have considered four structural models and found that the structure with a  $(2 \times 4)$  unit cell, in which there are a two-dimer unit and a two-shifted-dimer unit, is the most favorable. These results can be understood in terms of physical properties associated with ionicity. [S0163-1829(97)04739-5]

Recently, there have been investigations of wurtzite CdS (0001),<sup>1</sup> (10 $\bar{1}$ 0), and (11 $\bar{2}$ 0) (Refs. 2 and 3) surfaces. It was found that the strain due to mismatched lattice parameters between epilayers and substrate surfaces can generate dislocations that may spread and cutdown the device performance.<sup>4,5</sup> These problems suggested that the cubic zinc-blende structure may be a better alternative for device applications. Though the zinc-blende structure is not the thermodynamically most stable structure for bulk CdS, this structure can be stabilized by the strain on a cubic substrate. And Niles and Höchst<sup>6</sup> have grown cubic CdS epilayers on the GaAs(100) substrate. The availability of the zinc-blende CdS films suggests that it may be worthwhile to study the surface structures of these films. A knowledge of the surface structure is needed for further studies of film growth mechanism.

It is well known that on the Si(100) surface the surface atoms form long dimer rows. However, long dimer rows have been shown to be unfavorable on the As-terminated GaAs(100) surface.<sup>7-9</sup> Recently, Tsai, Lin, and Chang found instead that the favorable surface structure of the monolayer As-terminated GaAs(100) surface may have a  $(2 \times 4)$  unit cell with a three-dimer unit and a shifted dimer.<sup>9</sup> In other words, the dimer rows have an optimal length of three dimers. The shifted single dimer can be regarded as an interruption and for a coverage less than one monolayer this single dimer becomes a missing dimer. Though recently, Hashizume *et al.*<sup>10</sup> have concluded from scanning tunneling microscopy measurements that the missing-dimer containing As-terminated GaAs(100) surfaces have a two-dimer basic unit, here we are only interested in the smooth monolayer anion-terminated surfaces. Since GaAs is not a pure covalent material and contains partial ionic bonding, while Si has pure covalent bonding without charge transfer, we wonder if ionicity may play an important role in limiting the length of the dimer rows. By a simplified electrostatics argument, the repulsive Coulomb interactions will tend to disperse the charged surface dimers, which tend to reduce the length of the surface dimer row. In this line of thought, the material

with a larger ionicity will have shorter dimer rows. This has actually been demonstrated for GaN(100), in which the surface dimer row has a length of two dimers.<sup>11</sup> CdS with a Phillips' ionicity of 0.685 is much more ionic than GaAs with a Phillips' ionicity of 0.31 and is slightly more ionic than GaN with an ionicity of 0.5,<sup>12</sup> and CdS(100) may have a dimer-row length of two dimers or even just one dimer. To show that this is the case, we have carried out this study using the local-orbital density-functional molecular-dynamics (MD) method.<sup>13-15</sup>

The MD method<sup>13-15</sup> used is based on the norm-conserving pseudopotential method.<sup>16,17</sup> This method was developed originally by Sankey and Niklewski<sup>13</sup> for covalent solids and later extended by Tsai, Dow, and Sankey<sup>14</sup> to more ionic materials by including charge transfer. Most recently, Tsai and Hass<sup>15</sup> have improved this method to calculate the charge density and potentials self-consistently without the use of spherical approximation. The original non-self-consistent Harris-functional treatment of Sankey and Niklewski was no longer used. We have chosen  $s$ ,  $p_x$ ,  $p_y$ , and  $p_z$  local orbitals, which are obtained by solving the atomic one-electron Schrödinger equation with pseudopotentials, for each atomic species in the system. Bloch sums of these orbitals are constructed and the matrix elements of the one-electron Hamiltonian within the Hohenberg-Kohn-Sham density-functional theory<sup>18</sup> are calculated. Diagonalization of the Hamiltonian matrix yields eigenenergies and eigenvectors. Charge density and electronic potentials are then obtained from them. The long-ranged Coulomb potentials due to charge transfer are treated by a modified Ewald technique.<sup>14</sup> And the Ceperley-Alder<sup>19</sup> local-density exchange-correlation potential is implemented. Charge density and potentials are determined self-consistently using the Johnson's mixing scheme<sup>20</sup> with a tolerance of  $0.001e$  (where  $e$  is the magnitude of the electronic charge) for each atom. The force acting on each atom is calculated by the modified Hellman-Feynman theorem<sup>13</sup> using the calculated derivatives of the total energy with respect to atomic posi-

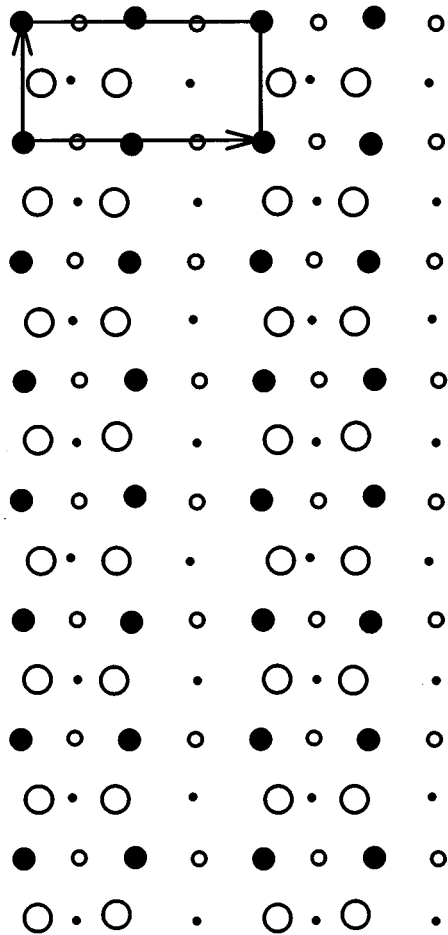


FIG. 1. Top view of the  $(2 \times 1)$  S-terminated CdS(100) surface [i.e., model (1)]. Large open circles and small open circles are the surface- and third-layer S atoms, respectively. The large filled circles and small filled circles are the second- and fourth-layer Cd atoms, respectively.

tions. We do not use pair or fixed interatomic potentials. This method has been shown to work well for semiconductor systems.<sup>21,23–25</sup>

For MD calculations, we first determine the theoretical lattice constant of the bulk CdS crystal using the cubic unit cell, which has four Cd and four S atoms, and sample only the  $\Gamma$  point. The theoretical lattice constant obtained is 5.832 Å, which differs only +0.24% from the experimental value of 5.818 Å.<sup>26</sup> This theoretical lattice constant and a repeated six-layer-slab (i.e., supercell) model with a vacuum region of about 7 Å wide are then used for our structural models. By analogy with the anion-terminated GaAs(100) surface, we have considered four structural models. They are (1) the  $(2 \times 1)$  dimer structure shown in Fig. 1, (2) the  $(2 \times 4)$  structure with a three-dimer unit and a shifted-dimer shown in Fig. 2, (3) the  $(2 \times 4)$  structure with a two-dimer unit and a two-shifted-dimer unit shown in Fig. 3, and (4) the  $(2 \times 2)$  dimer structure shown in Fig. 4. For all four models, we have chosen the same  $(2 \times 4)$  unit cells in order to compare total energies on the same footing and sampled the  $\bar{\Gamma}$  point in MD calculations. The bottom-layer atoms are assigned an arbitrarily large mass so that they are essentially motionless

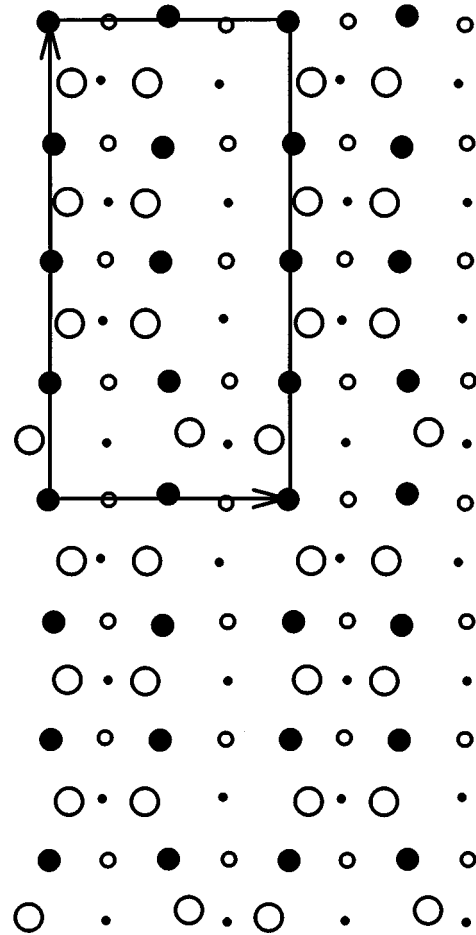


FIG. 2. Top view of the three-dimer-one-shifted-dimer model of the  $(2 \times 4)$  S-terminated CdS(100) surface. Large open circles and small open circles are the surface- and third-layer S atoms, respectively. The large filled circles and small filled circles are the second- and fourth-layer Cd atoms, respectively.

to simulate bulk atoms.<sup>21</sup> For all four structural models, the starting atomic positions are chosen similar to Figs. 1–4 with the initial dimer bond lengths roughly equal to twice the covalent radius of the S atom.<sup>22</sup> The Newtonian equation of motion is solved numerically for a time step of 0.296 fs using the fifth-order Gear algorithm.<sup>27</sup> We do not use simulated annealing but use a quenching scheme<sup>14,21</sup> to let atoms settle to their stable or metastable positions. The principle of the quenching scheme is that the overall kinetic energy of the system is maximum when all the atoms reach their equilibrium (stable) or metastable positions, at which the total electronic energy or the total atomic potential energy is minimum (or local minimum). Thus, we calculate the total kinetic energy of all atoms in the unit cell for each time step. When the total kinetic energy starts to decrease between two successive time steps, we know that the atoms just pass their stable or metastable positions. Then the motions of all atoms are quenched by setting their velocities to be zero to prevent them from moving further away from the stable or metastable positions. Due to the finite time step interval, the atoms at this time step may not be exactly at their stable or metastable positions and the forces acting on them may not be small. The MD calculation is continued and the forces

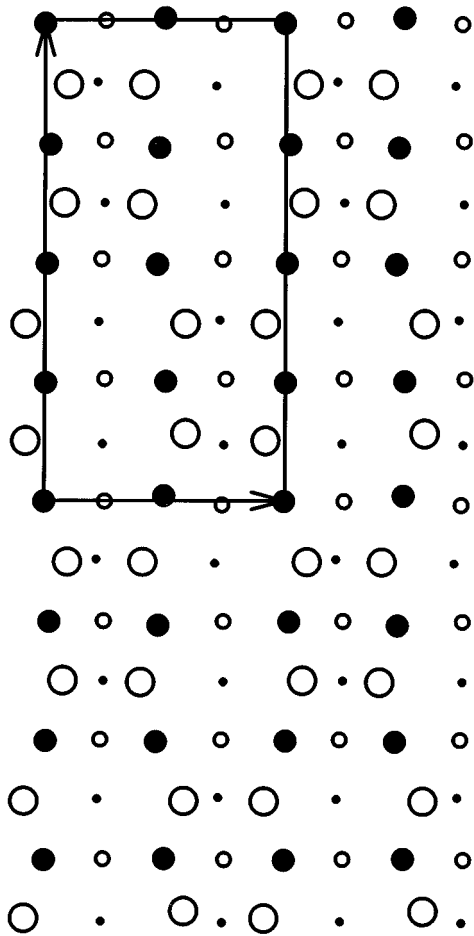


FIG. 3. Top view of the two-dimer-two-shifted-dimer model of the  $(2 \times 4)$  S-terminated CdS(100) surface. Large open circles and small open circles are the surface- and third-layer S atoms, respectively. The large filled circles and small filled circles are the second- and fourth-layer Cd atoms, respectively.

will drive the atoms to move back toward their stable or metastable positions and the total kinetic energy will start to accumulate. When the total kinetic energy starts to decrease, the motions of atoms are quenched again. It is expected that the forces will become smaller and the atoms will become closer to their stable or metastable positions when the quenching procedure is repeated. In this study, we consider that the atoms are close enough to their stable or metastable positions when the forces are smaller than about  $0.2 \text{ eV}/\text{\AA}$ . This method was applied to the (110) surface of the relatively ionic II–VI semiconductor ZnTe,<sup>23</sup> and yielded a geometry in agreement with previous theoretical calculations using the conventional first-principles electronic structure and total-energy calculational method.<sup>28</sup> After the stable or metastable atomic positions are found, we sample four special  $\mathbf{k}$  points in the irreducible Brillouin zone for a two-dimensional rectangular lattice<sup>29</sup> to calculate the total energies.

The fully relaxed atomic arrangements for the top four layers for models 1–4 are shown in Figs. 1–4, respectively. For model 1, the dimer has a bond length of  $2.513 \text{ \AA}$ . The dimer bond lengths for model 2 are on an average  $2.512 \text{ \AA}$  for the three-dimer unit and  $2.64 \text{ \AA}$  for the shifted dimer. For

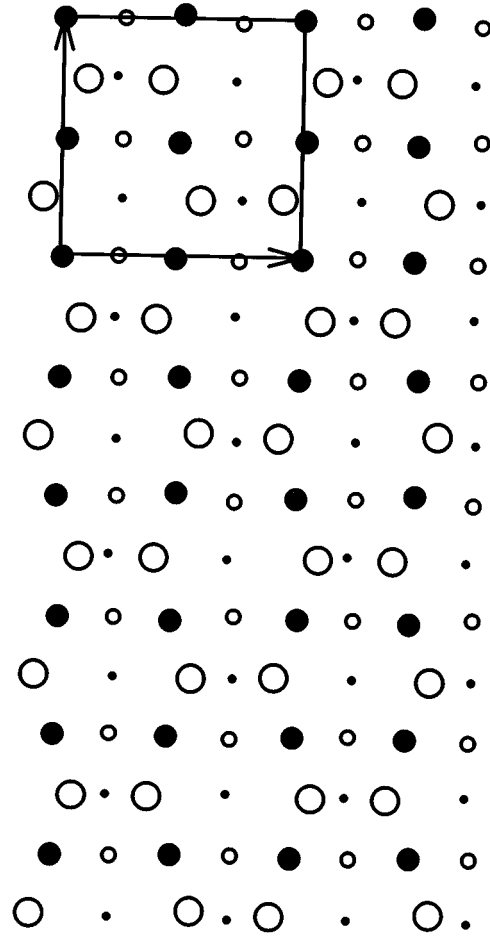


FIG. 4. Top view of the  $(2 \times 2)$  S-terminated CdS(100) surface. Large open circles and small open circles are the surface- and third-layer S atoms, respectively. The large filled circles and small filled circles are the second- and fourth-layer Cd atoms, respectively.

model 3, the two-dimer pairs have different dimer bond lengths; one pair has an average dimer bond length of  $2.514 \text{ \AA}$ , while another one has  $2.651 \text{ \AA}$ . For Model 4, the two dimers have different bond lengths of  $2.473 \text{ \AA}$  and  $2.685 \text{ \AA}$ . Using the total energy of model 1 as a reference, models 2, 3, and 4 have total energies of  $-0.048$ ,  $-0.132$ , and  $-0.126 \text{ eV}$  per  $(1 \times 1)$  cell, respectively. These results show that the structural model 3 with a two-dimer unit and a two-shifted-dimer unit has the lowest total energy and is the most favorable among the four models considered. However, model 4 with a  $(2 \times 2)$  dimer structure, in which all dimers are isolated dimers and do not couple into rows or any unit with more than one dimer, has an energy only slightly higher than that of model 3 by  $0.06 \text{ eV}/(1 \times 1)$  cell. This small energy difference is only 2.3 times the room-temperature thermal excitation energy. Thus, for the usual crystal-growth conditions, structural model 4 may coexist with structural model 3. The surface S atoms have a negative effective charge of around  $0.09e$ . The repulsive Coulomb forces among dimers tend to keep dimers away from one another. However, the covalent forces tend to cause dimers to form long rows as on the Si(100) surface. The most favorable surface structure will result from a detailed balancing between these two opposing forces. In the limit of strong Cou-

lomb repulsion for highly ionic compound semiconductors, the structural model 4 will be expected to be the most favorable. CdS is indeed a compound semiconductor with a high ionicity. But it is not as highly ionic as I–VII compound semiconductors and its bonding between neighboring atoms still has a significant covalent content. So that the structural model 3 with a basic dimer-pair unit, or a dimer row of length two, becomes slightly more favorable.

The effective charge on the surface anions is related to ionicity of a given compound semiconductors. Thus, ionicity may approximately be a guideline for determining the surface structure. Besides the nonvanishing effective charge on the surface anions, ionicity is also a measure of the ionic content in the bonding with neighboring atoms. The larger the ionicity the larger the ionic content and the smaller the covalent content in the bonding. Since the driving force for the surface atoms to form dimers in long rows as on Si(100) is the covalent bonding, larger ionicity means a reduced ten-

dency for the surface atoms to form long dimer rows. Coulomb repulsion further suppresses this tendency. Our finding of the most favorable dimer-row length of two dimers from our total-energy calculations indeed is consistent with our prediction stated previously based on ionicity and the trend of the surface structures of Si(100) and anion-terminated GaAs(100) and GaN(100).

In summary, our molecular-dynamics studies find that surface atoms of the anion-terminated CdS(100) surface do not form long dimer rows. Instead, the surface anions may form a ( $2 \times 4$ ) surface structure with a two-dimer unit and a two-shifted-dimer unit with a dimer-row length of two dimers. This result is consistent with the prediction based on ionicity and the trend of the surface structures of Si(100) and anion-terminated GaAs(100) and GaN(100).

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