

Theoretical studies of the reconstruction of the (110) surface of III-V and II-VI semiconductor compounds^{a)}

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We have studied the reconstruction of the (110) surface of various III-V semiconductor compounds (GaAs, GaP, GaN, AlAs, AlP, AlN, BaS, BP, BN) by applying quantum chemical methods to small clusters representative of these surfaces. Application of these techniques to GaAs (110) leads to a surface shear (0.67 Å) in excellent agreement with experimental values (0.65–0.70 Å). The results lead to trends in the surface distortions and reconstruction consistent with those predicted from local valence considerations. Possibilities for the electronic structure of II-VI semiconductor compounds are also considered.

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I. INTRODUCTION

The reconstruction of the (110) surface of GaAs has attracted considerable attention in recent years, both experimentally¹⁻⁵ and theoretically,⁶ and by now is well understood. To study the systematics of the reconstruction, we have considered the reconstruction of the (110) surface of various III-V zincblende compounds, made up out of B, Al or Ga and N, P or As. The calculations were performed by applying quantum chemical methods to small clusters representative of the surface, as described in Sec. II.

We show that the reconstruction of these surfaces can be understood on the basis of local valence considerations, as presented in Sec. III. The results of our calculations are given in Sec. IV, together with a discussion of these results. Finally, in Sec. V, we discuss some of the features of the (110) surface of II-VI semiconductor compounds.

II. THEORETICAL METHODS

The methods used in these calculations are adaptations of well established methods of quantum chemistry. Their application to semiconductors⁷ and a comparison with other approaches⁸ is available in the literature. Here we only comment on the main features of our approach.

We start by creating a molecular cluster to mimic the surface chemical environment. Atoms at the edge of the cluster, which would have been connected to further atoms in the extended system, are connected to hydrogen atoms. This prevents artificial dangling bonds at the edge of the cluster from interfering with real dangling bonds on the surface and insures proper hybridization of the cluster atoms. Figure 1 shows the (110) surface of GaAs and Fig. 2 illustrates some of the models obtained with the above prescription.

Having approximated the surface by a finite cluster allows the use of the powerful techniques of molecular quantum mechanics.^{9,10} These techniques provide a microscopic and quantitatively accurate model for the surface. We can calculate the total energy of the cluster as a function of geometry and electronic configuration and so determine variationally

the minimum energy atomic geometry and its electronic configuration.

To make this approach feasible for clusters containing heavy atoms, we have replaced the inner core electrons of these atoms with *ab initio* effective potentials.¹¹ The basis sets are double zeta or split valence (that is, two contracted

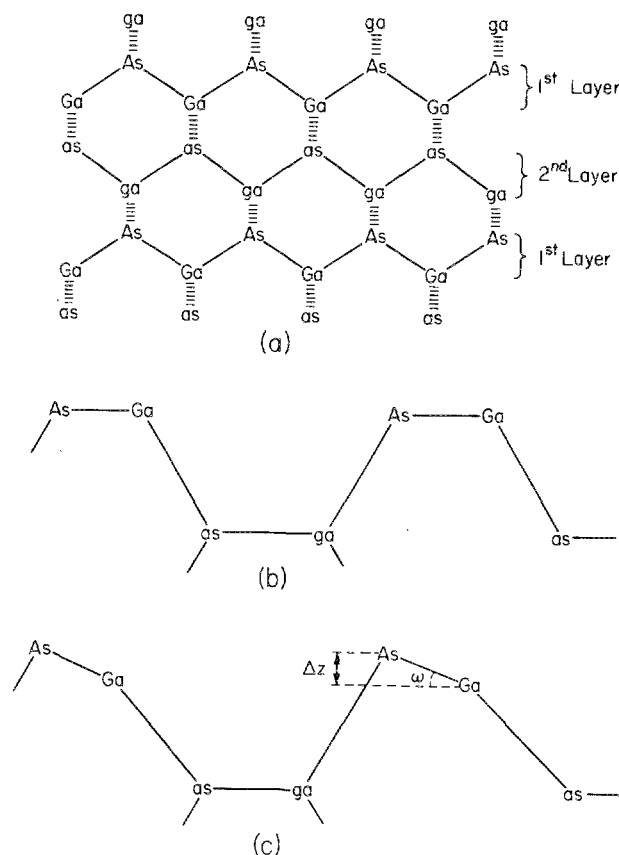


FIG. 1. (110) surface of GaAs. (a) Top view, (b) side view of projection in the (110) plane, unreconstructed, (c) side view of projection in the (110) plane, after reconstruction. ω is the reconstruction angle, Δz is the surface strain.

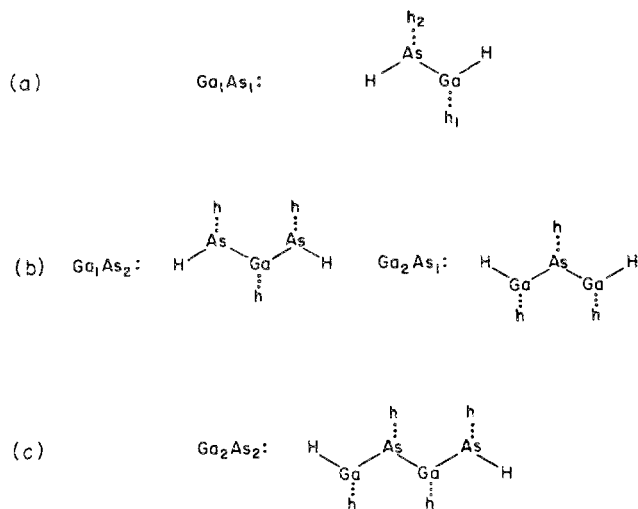


FIG. 2. Molecular models for the (110) surface. Lower case letters indicate subsurface atoms. (a) Two-site model, (b) three-site model centered on column III surface atom, (c) three-site model centered on column V surface atom, (d) four-site model

functions for each atomic valence orbital). The calculations on small models, containing only one column III and one column V surface atom, were performed with and without the use of *d*-polarization functions. It was found that in general the geometries were not sensitive to the use of these polarization functions, so that they were omitted in the calculations on larger models. The calculations reported here are for closed shell Hartree-Fock wavefunctions. For GaAs it was found that electron correlation had little influence on the geometry.

III. LOCAL VALENCE PICTURE

In this section we consider the behavior of the individual column III and column V atoms on the (110) surface. The idea that such considerations are important in describing the reconstruction of the (110) surface of GaAs has been introduced by Müller and Haneman^{4,12} and these ideas have been applied to the (110) surface of GaAs by several authors.^{1,4,12} Here we repeat the arguments to make clear how our results for the various III-V compounds are in agreement with, and validate these considerations. For convenience we discuss GaAs (110), although all the ideas are applicable to the other compounds as well.

Each surface atom has three ligands. Even for the unreconstructed surface (tetrahedral bond angles), calculations for GaAs show that the two dangling bonds broken at the surface coalesce into one lone pair of electrons localized on the As center (Fig. 3).¹³ Thus the surface Ga atom has three bonds with no electrons in the fourth valence orbital, and the surface As atom has the character of a normal trivalent As with a $(4s)^2$ lone pair. The situation for the surface atoms is similar to the situation for their respective trihydrides and the structure of the reconstructed surface should be closely related to that of the trihydrides.

First consider the Ga atom. It has a valence configuration $4s^2 4p$. Therefore GaH_3 will be planar, involving sp^2 hybridization, with a bond angle of 120° .

On the other hand, As has a $4s^2 4p^3$ valence configuration.

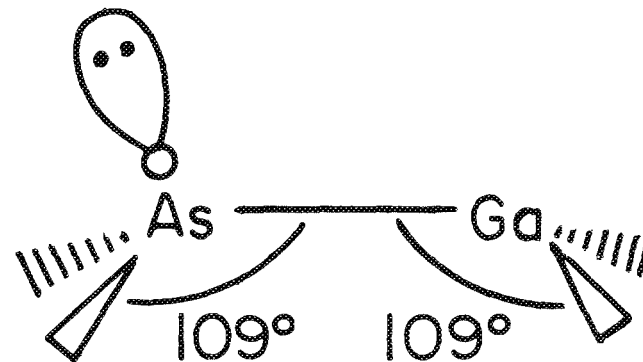


FIG. 3. Surface atoms of GaAs, with lone pair of electrons localized on the As center.

In AsH_3 the hydrogens will bind to the three singly occupied *p*-orbitals, leading to a bond angle close to 90° . Because the different bond pairs must be orthogonal¹⁴ (due to the Pauli principle) the bond angles increase slightly, forcing the $(4s)^2$ lone pair to move slightly away from the ligands, as shown schematically for AsH_3 in Fig. 4. The results for the various trihydrides are given in Table I. We see that the bond angle is 120° for trihydrides of column III elements, whereas for PH_3 and AsH_3 the bond angle is indeed close to 90° . For NH_3 the bond angle is substantially greater than 90° (106.5°), which is due to the shorter bond distance, resulting in a greater effect of orthogonality of bond pairs.¹⁴

On the basis of these results for the trihydrides, one expects the surface reconstruction to be such that the column III element moves toward a more planar geometry (average bond angle close to 120°) and that the column V element moves toward a more pyramidal geometry (average bond angle $\sim 94^\circ$ for P and As, and $\sim 106^\circ$ for N). As shown in Fig. 1, this requires the column III surface atom to move slightly towards the subsurface and the column V surface atom to move slightly away from the unreconstructed surface. The surface strain Δz is defined as the *z*-projection (perpendicular to the unreconstructed surface) of the total displacement of the surface As relative to the surface Ga. The reconstruction angle ω corresponds to the angle between the unreconstructed surface (110) plane and the line connecting a surface Ga to a surface As, measured in the $(1\bar{1}0)$ plane perpendicular to the surface plane.

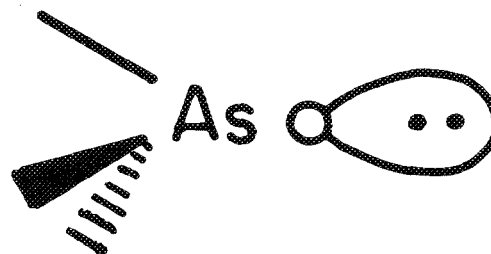


FIG. 4. The orbital character of trivalent As. Orthogonality of the bond pairs forces the lone pair to move slightly away from the ligands.

TABLE I. Bond angles for the various trihydrides considered in this work.

	Theory	Experiment ^{a)}
BH ₃	120°	...
AlH ₃	120°	...
GaH ₃	120°	...
NH ₃	106.5°	106.7°
PH ₃	94.8°	93.3°
AsH ₃	94.3°	92.1°

^{a)} Ref. 15

IV. THEORETICAL RESULTS AND DISCUSSION

We have considered the following models for the (110) surface of the various III-V compounds: (i) the X_1Y_1 -model, consisting of one column III surface atom X and one column V surface atom Y, and (ii) the X_2Y_2 -model, consisting of two column III and two column V surface atoms (see Fig. 2). The surface reconstruction was obtained by carrying out the following geometric variations: the positions of the (virtual) subsurface atoms were kept fixed and the surface atoms were allowed to move in the (110) plane through their unrelaxed positions in such a way that the distance to the subsurface nearest neighbor remained constant. Thus we do not take into account second or third layer reconstructions; these reconstructions have been found to be very small for GaAs,³⁻⁵ and should not affect the basic picture for the reconstruction sketched in Sec. II.

In Table II we give our results for GaAs (110) and compare these with the experimental results. Notice that the results for the Ga_1As_1 -model are very close indeed to the results of the Ga_2As_2 -model (differing by 0.005 Å), indicating rapid convergence of these results with cluster size. This holds true for all cases where we have compared the results of the X_1Y_1 -model with those of the X_2Y_2 -model. Furthermore the agreement with experimental values for GaAs is excellent (0.67 Å from theory, 0.65 to 0.70 Å from experiment). Having established that in the case of GaAs the small clusters used in our calculations do represent the surface adequately, we proceed to apply the same methods to small clusters representative of the other III-V compounds. In these cases no experimental or theoretical results are available for comparison, but on the basis of the above results for GaAs we expect the calculations for the other compounds to be accurate as well.

The results of these calculations are presented in Table III, where we give for each compounds the values obtained for Δz and ω . Furthermore, to check the ideas concerning control of the reconstruction by local valence forces, we give in Table III the average bond angles, α and β , around the column III and column V elements respectively. We see that in all cases the average angle around the column III element is always within 2° of 120°, so that the column III element has a more planar geometry on the reconstructed surface. Similarly, the angle β is in all cases within 3° of the value obtained with the corresponding trihydrides. Thus the reconstruction of the (110) surface of III-V zincblende compounds can indeed be understood on the basis of the local valence considerations

presented in Sec. III. This is an important result which hopefully can be useful in *predicting* (before calculations or experiments) the reconstruction of other surfaces. The energy lowering per pair of surface atoms between the fully reconstructed and the unreconstructed surface, ΔE , is also given in Table III. Values range from 0.8 to 1.5 eV per pair of surface atoms.

The results in Table III show certain trends. First consider the arsenides. In this group the results for AlAs and GaAs are very similar, but the results change for BAs. This is probably due to the smaller size of the B atom and the shorter bond distance in BAs compared to AlAs and GaAs. Similarly, for the phosphides, the results for AlP and GaP are very similar, but BP is different. As a group though, the phosphides are slightly different from the arsenides. This seems to indicate that the reconstruction is dominated by the anion, although the cation also has an effect. This conclusion is confirmed by the results for the nitrides, which as a group differ from the previous two but with similar trends apparent within the group.

V. THE (110) SURFACE OF II-VI SEMICONDUCTOR COMPOUNDS

The situation for the (110) surface of II-VI semiconductor compounds is entirely different from that of the III-V compounds discussed before. The column II and column VI elements do not form trihydrides, so that one cannot use the trivalent chemistry of these elements to gain insight in the surface reconstruction of these compounds.

Consider for instance Zn as a typical example of a column II element. Zn has a $(4s)^2$ valence configuration, so that it will bind at most two hydrogen atoms to form ZnH_2 , with a bond angle of 180°. On the other hand Se, as an example of a column VI element, has a $(4s)^2(4p)^4$ valence configuration, with only two of the 4p orbitals singly occupied. Therefore Se will also bind only two hydrogen atoms to form SeH_2 , with a bond angle of 90.6°.¹⁵

What then will be the electronic structure of the perfect (110) surface of ZnSe? There are two possibilities, as shown in Fig. 5. In the first case [Fig. 5(a)] the surface atoms are all bonded covalently to subsurface atoms, while the bonds between surface atoms are alternating between a covalent bond

TABLE II. Surface strain, Δz , and reconstruction angle ω for GaAs (110).

A. Theory Model		Δz (Å)	ω
Ga ₁ As ₁		0.660	26.8°
Ga ₂ As ₂		0.665	27.2°
B. Experiment		Δz (Å)	ω
Ref. 1	1976	0.64 < Δz < 0.81	27° < ω < 35°
Ref. 2	1978	0.65	27.2
Ref. 3	1978	0.70	26.4
Ref. 4	1978	0.65	28.5
Ref. 5	1979	0.65	27.3

TABLE III. Theoretical results for the various III-V compounds. α is the average angle around the column III element, β is the average angle around the column V element, Δz is the surface strain, ω is the reconstruction angle, and ΔE is the energy lowering per pair of surface atoms upon reconstruction.

Compound	α	β	Δz (Å)	ω	ΔE (eV)
GaAs	119.4	95.1	0.665	27.2	1.18
AlAs	119.4	95.0	0.667	27.2	1.10
BAs	119.3	96.1	0.554	27.3	1.50
GaP	119.2	96.2	0.606	26.1	1.06
AlP	119.1	96.5	0.594	25.7	0.97
BP	119.2	96.8	0.517	27.1	1.47
GaN	118.1	104.0	0.315	19.4	0.77
AlN	118.3	105.5	0.295	19.3	0.81
BN	118.7	103.5	0.276	21.7	1.11

and a donor-acceptor bond. Of course for the infinite system the structure shown in Fig. 5(a) would be in resonance with a similar structure in which the position of the covalent bond and the donor-acceptor bond between surface atoms are interchanged. A second possibility, shown in Fig. 5(b), is the case where all the bonds between surface atoms are covalent bonds, while each surface atom is bonded to a subsurface atom by a donor-acceptor bond.

In either case one expects new and interesting properties for these surfaces as compared to the (110) surface of III-V compounds. Calculations are presently under way to inves-

tigate the above two cases for the electronic structure of the (110) surface of II-VI compounds.

VI. SUMMARY

We have shown that the theoretical results for the reconstruction of GaAs (110) are in good agreement with the experimental values, indicating that the small models used in these calculations do represent the surface adequately. This is also confirmed by the fact that the results converge rapidly with cluster size. Furthermore, it was shown that the recon-

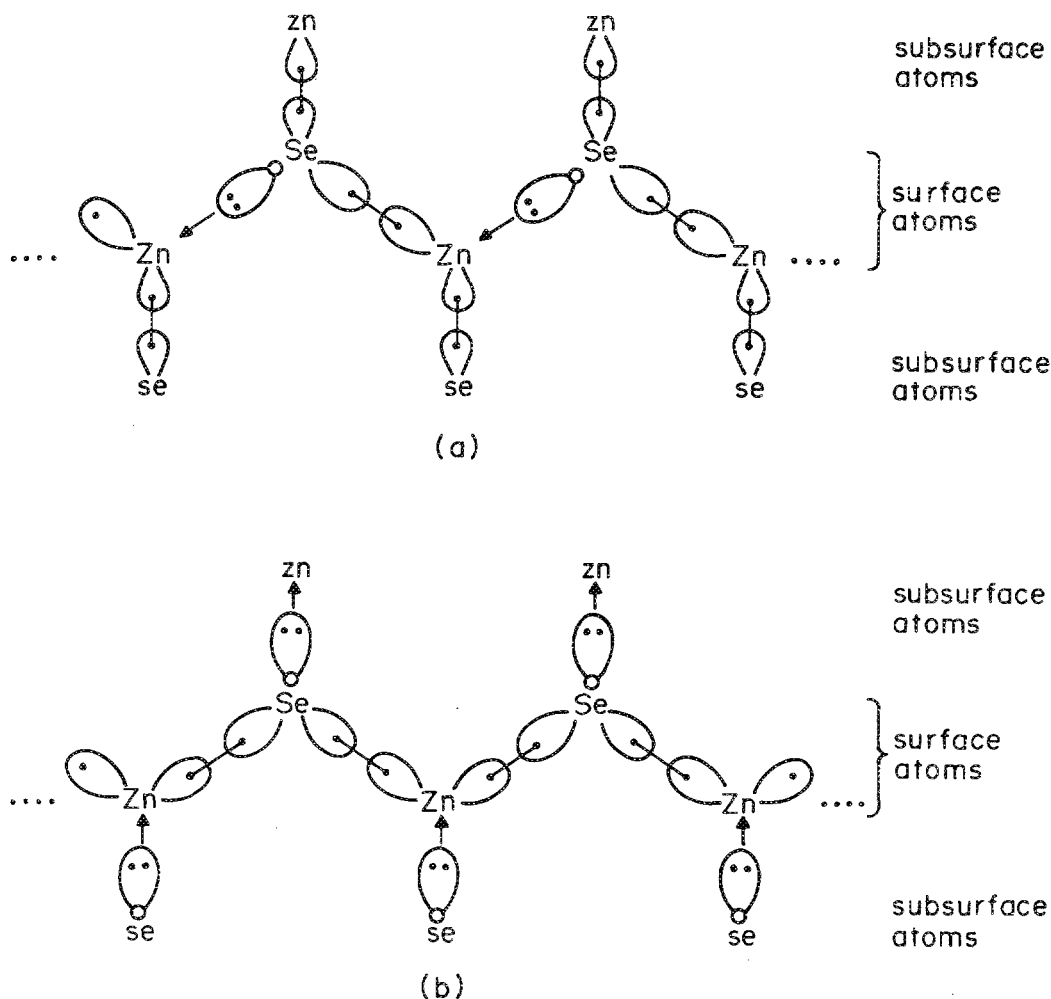


FIG. 5. Possible electronic structures for the (110) surface of II-VI compounds. Lower case letters indicate subsurface atoms. (a) Covalent bonds to subsurface, donor-acceptor and covalent bonds between surface atoms, (b) donor-acceptor bonds to subsurface, covalent bonds between surface atoms.

struction of the (110) surface of III-V compounds can be understood on the basis of local valence considerations, and that the details of the reconstruction are dominated by the column V element.

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