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Title
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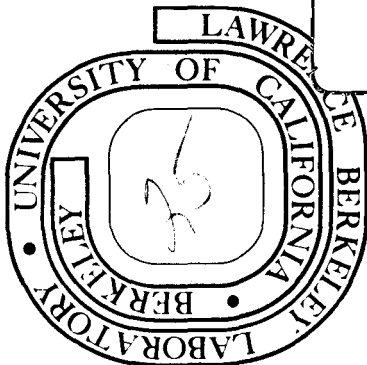# INTRINSIC SURFACE STATES OF (110) SURFACES OF GROUP IV AND III-V SEMICONDUCTORS

J. D. Joannopoulos and Marvin L. Cohen

August, 1974

DISCLAIMER

Intrinsic Surface States of (110) Surfaces

of Group IV and III-V Semiconductors*

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Abstract

Electronic local and total density of states calculations have been performed using tight binding models on the (110) surface of a group IV and III-V semiconductor . Ge and GaAs are taken as prototypes and the surface is assumed to be unrelaxed. Several new surface states are obtained near the bottom of the valence bands. The origin, localization, and character of the surface states are examined.

I. Introduction

Recently tight binding models with only sp^3 hybrids[1,2] (or s and p orbitals[3]) and with all nearest neighbor interactions included have been found very useful in studying the (111) surfaces of group IV[1,2] and III-V[3] semiconductors. This usefulness results not only from the simplicity and calculational convenience of the methods but also because these models are very appealing from a physical point of view. They can reproduce results obtained from experiment[4] and from more elaborate theoretical methods.[5]

We wish to extend some of these models to study the (110) surfaces of semiconductors. This ∧is of interest since it is the thermally stable cleavage face of III-V compounds and remains unreconstructed. Moreover it is of intrinsic interest since two different types of atoms can exist simultaneously on the surface so that the surface states can exhibit the individual characteristics of each atom.

Using this method we recently briefly reported[6] the existence of new states for <u>unrelaxed</u> (110) surfaces of Ge and GaAs. In this paper we develop the method in detail and examine the origin, localization and character of the surface states. We also present local density of states calculations for atoms in various surface layers. The results presented here are generally of wider validity than just for the cases of Ge and GaAs, i.e. Ge and GaAs will be considered as prototypes.

The format of the paper is as follows. In Section II we discuss the tight binding model, describe the structural aspects of the system we are studying and discuss the calculational methods involved. In Section III we present the results of our calculations for Ge and GaAs and discuss their ramifications. Finally in Section IV we make some concluding remarks.

The model we use to study the (110) surface of a diamond structure or zincblende semiconductor is similar to a model used first by Hirabayashi[1] for (111) and (100) surfaces. The

method involves studying a system of atoms which is finite
in one dimension and periodic in the other two dimensions.
We are thus dealing with a "slab" of material with two
surface layers which can be chosen to have N periodic layers
of atoms. It is found[1] that generally reliable results can
be obtained with $N \geq 10$ so that one need not worry about
spurious results caused by the finiteness and double surface
characteristics of the system.

This system will now be conveniently and "realistically"
studied using a tight binding model with sp^3 (or s and p)
orbitals including all interactions between nearest neighbor
atoms. These interactions can be parametrized and fit to
realistic (e.g. pseudopotential) band structures with very
good precision. In general the filled valence bands are
obtained much more accurately than the conduction bands.
This is reasonable because of the plane-wave like nature of
the conduction bands, this should have relevant consequences
only for the detailed structure of the surface states in
the fundamental gap.

II. Calculational Procedures

In Fig. 1 we show a sketch of (110) layers of atoms
lying parallel to the $\hat{x}$-$\hat{y}$ plane. Two different types of
atoms are shown as they would occur in a zincblende structure.
We also show schematically four sp^3-like directed orbitals
on each of the two atoms in a surface unit cell (ABCD). For
a zincblende structure the (110) surface thus contains one

dangling orbital from the cation and one from the anion per unit cell. In the case of a diamond structure (110) surface the two atoms and dangling orbitals are identical but there are still two atoms in a surface unit cell.

In the tight binding model we are considering, we saturate the number of nearest neighbor interactions. Using the orbital notation (to be discussed shortly) shown in the bottom of Figure 1, we must specify the following interaction parameters for a homopolar system.

$$
\begin{aligned}
V_0 &= <I|H|I> \\
V_1 &= <I|H|N+I> \\
V_2 &= <I|H|4N+I> \\
V_3 &= <I|H|5N+I> \\
V_4 &= <N+I|H|6N+I> \\
V_5 &= <N+I|H|5N+I>
\end{aligned}
\tag{1}
$$

For all practical purposes V_0 can be taken as zero since it simply involves a reference energy for all the bands. For Ge these parameters where fit to pseudopotential band structures[7] and the agreement is fairly good. The values obtained (in eV) are $V_0 = 0$, $V_1 = -2.0$, $V_2 = -5.0$, $V_3 = -0.2$, $V_4 = -0.4$ and $V_5 = 0.6$.

For GaAs we would, in principle, need to break down some of the parameters in (1) into additional parameters because of the lack of inversion symmetry. It is however quite simple, convenient and adequate, for our purposes, to

describe GaAs with only one additional parameter. Namely we take $V_0 = \pm\Delta$ depending on whether $|I\rangle$ in (1) is a cation $(+\Delta)$ or anion $(-\Delta)$ orbital. With $\Delta = 3.2$ eV we obtain an "antisymmetric" gap in the filled valence band which is in satisfactory agreement with pseudopotential calculations.[7] As we have already mentioned our results are generally valid so that Ge and GaAs can be considered as prototypes. Therefore it is unnecessary to obtain fits which are in excellent agreement with experiments.

In the structural model the most important parameter to specify is the number N of layers of atoms. Once this is done the labels of each orbital in the unit cell for any layer I can be very conveniently specified as shown in the bottom of Figure 1. In addition the tight binding Hamiltonian matrix can be obtained easily and involves essentially only two matrices for any layer I. Given the unit cell (ABCD) and the $\hat{x}\hat{y}$ coordinate system as shown in Fig. 1 we obtain the following Hamiltonian submatrices for any layer I.

	I	N+I	2N+I	3N+I	4N+I	5N+I	6N+I	7N+I
I	$-\Delta$	V_1	V_1	V_1	$V_2+V_5 n^*$	$V_3+V_3 n^*$	$V_3+V_4 n^*$	$V_3+V_4 n^*$
N+I		$-\Delta$	V_1	V_1	$V_3+V_3 n^*$	$V_5+V_2 n^*$	$V_4+V_3 n^*$	$V_4+V_3 n^*$
2N+I			$-\Delta$	V_1	$V_3+V_4 n^*$	$V_4+V_3 n^*$	$V_4+V_4 n^*$	$V_5+V_5 n^*$
3N+I				$-\Delta$	$V_3+V_4 n^*$	$V_4+V_3 n^*$	$V_5+V_5 n^*$	$V_4+V_4 n^*$
4N+I					Δ	V_1	V_1	V_1
5N+I						Δ	V_1	V_1
6N+I							Δ	V_1
7N+I								Δ

$$(2)$$

and

	$4N+I-1$	$5N+I-1$	$6N+I-1$	$7N+I-1$	$4N+I+1$	$5N+I+1$	$6N+I+1$	$7N+I+1$
I	H_5^I	H_4^I	H_4^I	H_3^I	H_5^I	H_4^I	H_3^I	H_4^I
$N+I$	H_4^I	H_5^I	H_4^I	H_3^I	H_4^I	H_5^I	H_3^I	H_4^I
$2N+I$	H_3^I	H_3^I	H_3^I	H_2^I	H_4^I	H_4^I	H_3^I	H_5^I
$3N+I$	H_4^I	H_4^I	H_5^I	H_3^I	H_3^I	H_3^I	H_2^I	H_3^I

$$(3)$$

where

$$\eta = e^{ik_y a/\sqrt{2}} \quad , \quad \xi = e^{ik_x a} \qquad (4)$$

and

$$H_n^I = \frac{V}{2}(1+\eta^*\xi^*) - \frac{V}{2}(-1)^I(1-\eta^*\xi^*) \ . \qquad (5)$$

Here a is the lattice constant and expression (5) is different depending on whether I is an even or odd numbered layer. We define all odd numbered layers to be analogous to the ABCD layer shown in Fig. 1 where there is always one basis atom at the origin. The information contained in (2) and (3) is all that is necessary to build up the complete hermitian Hamiltonian matrix for any given number of layers N. Care however must be taken if I is a surface layer (i.e. I = 1 or I = N). In this case some of the elements in submatrix (3) must be treated differently depending on what type of relaxation is imposed. In our calculations we assumed an unrelaxed surface and just set the appropriate matrix elements to zero.

Once the band structure is known the total density of states can be obtained using the expression

$$N(E) = \frac{1}{MN} \sum_{\underset{\sim}{k}} \sum_{n} \delta(E-E_n(\underset{\sim}{k})) \qquad (6)$$

where N_a is the number of atoms in the primitive cell, M
is the number of primitive cells and N(E) is normalized to
the number of states per atom. The local density of states
of an orbital is defined as

$$N_{ij}(E) = \frac{1}{MN_a} \sum_{\underset{\sim}{k}} \sum_{n} |<\psi_{\underset{\sim}{k},n}|\phi_{\underset{\sim}{k},ij}>|^2 \delta(E-E_n(\underset{\sim}{k})) \qquad (7)$$

where $\psi_{\underset{\sim}{k},n}$ is an eigenfunction of the total Hamiltonian and
$\phi_{\underset{\sim}{k},ij}$ is the jth bloch function orbital centered at atom i.
The local density of states of an atom is then obtained from

$$N_i(E) = \sum_j N_{ij}(E) \qquad (8)$$

Physically the local density of states $N_i(E)$ is just equal
to a product of the total density of states N(E) multiplied
by an average probability that an electron is at atom i
when the electron has an energy E in the total system.

The method used to evaluate the integrals in (6) and
(7) is due to Gilat and Raubenheimer.[8] The energy derivatives
required by this method were obtained using $\underset{\sim}{k} \cdot \underset{\sim}{p}$ perturbation
theory. In the next section we show the results of our
calculations for a system with 12 layers of atoms. The local
densities of states that will be shown will involve an
additional factor of 2N in order to make the normalization
the same as for the total density of states and hence ease
comparisons.

III. Results

In Fig. 2(a) and (b) we show the total density of states
of Ge and GaAs in the diamond and zincblende structures
respectively. The filled valence bands are shown at negative
energies. The shapes of these curves are in very good overall
agreement with the densities of states obtained from pseudo-
potential calculations.[7] The biggest discrepancy in the
valence band results from an inability to reproduce the dip
in the p-like states between Σ_1^{min} and X_4 which would lie near
-4 eV. This is, however, unimportant and can actually be
obtained by introducing a second nearest neighbor interaction.[9]

In Fig. 2(c) and (d) we show the total density of states
for Ge and GaAs in the 12 layer structure respectively. The
fermi levels for Ge and GaAs are around 0.4 and 0 eV respectively.
These are unsmoothed computer plots so that the wiggles along
the curves should be considered as noise. The step like
structure around -12 eV is however real and is caused by the
two dimensional singularities of a finite number of two-
dimensional layers. Figures 2(c) and (d) reveal a composite
effect of bulk and surface properties. They can, for instance,
be compared readily with their completely bulk counterparts
shown in Figs. 2(a) and (b). The labels A and B represent
surface states obtained for Ge and GaAs in these calculations.
We now proceed to analyze them in detail.

A. Ge

In Fig. 3 we show a plot of the local densities of states
of a Ge atom in various layers of atoms in the 12 layer system.

The second basis atom in each layer is identical to the first
so that their local densities of states are equivalent. In
Fig. 3(a) we show the local density of states for a Ge atom
in the sixth layer from the surface. This then is essentially
a bulk density of states as is readily observed by comparing
Fig. 3(a) with Fig. 2(a). Let us now examine what happens
as we approach the surface. Nothing really happens until we
get to the third layer of atoms shown in Fig. 3(b). We can
now distinguish clearly the onset of two types of surface
states shown by arrows in the figure. When we go to the
second layer the former states become more pronounced and we
have the onset of two other additional surface states also
designated by arrows in this figure. Finally when we reach
the outer surface layer (Fig. 3(d)) the states in the fundamental
gap become very strong and go off the scale. Actually the
number of states in the fundamental gap of Fig. 3(d) is around
1.5 states/atom. These states are labelled A_1 and are the
usual states obtained in the gap from other calculations.
They consist of two surface bands and represent the dangling
bond states of Ge atoms at the surface. In our calculations
we find approximately 85% of the charge is concentrated in
the first layer with 98% of this charge in the first three
surface layers. This is of course consistent with the trends shown in Fig. 3.
The states labelled A_2 designate new surface states[6] which
originate near $\bar{M}$ and along $\bar{M}$ to $\bar{X}'$ and are concentrated
primarily in the first three layers. This concentration is

also observed by comparing (a), (b), (c) and (d) in Fig. 3.
These states represent bond states that lie in the layers with
roughly 30% of the charge localized in each layer. The states
labelled A_3 are also new[6] and occur mostly at and near $\overline{X}'$ but
extend along $\overline{X}'$ to $\overline{\Gamma}$ and $\overline{X}'$ to $\overline{M}$ with a total band width of
around 1 eV. These states represent essentially Ge s-like
states with about 64% of the charge concentrated in the first
layer with additional concentrations in either the second
($\overline{X}'$ to $\overline{\Gamma}$) or third ($\overline{X}'$ to $\overline{M}$) layers.

Finally let us also briefly discuss for completeness the
A_1' surface states obtained in the conduction band. These
originate from two areas in the irreducible zone. The states
at 4.4-4.6 eV originate from a region near the center of the
irreducible zone. They are mostly concentrated in the first
two atomic layers and are essentially antibonding s-like
states in nature. The states between 4.0 and 4.4 eV originate
mainly around $\overline{X}'$ and contain roughly 80% of the charge in the
first layer. They are localized on hybrid orbitals lying
along the surface. The concentrations of the A_1' states are
also rescaled in the local density of states plots in Fig. 3.

B. GaAs

In Figs. 4 and 5 we show plots of the local densities
of states of an As and Ga atom respectively in various layers
of atoms in the 12 layer structure. Again as in Ge we con-
centrate on the sixth, third, second and outer layers of atoms.
Since the local densities of states of layer 6 can be essentially

interpreted as a bulk local density of states, Figs. 4(a)
and 5(a) reveal the As and Ga character of the various regions
of the bulk or crystalline (Fig. 2(b)) density of states.
We notice that the filled valence band is mostly of As nature.
This is particularly true in the s-like region of the density
of states (around -12 eV). The region around -6 eV is
essentially equally shared between As and Ga states while
the top of the valence band is again predominantly As-like.
In the tight binding model the lower energy conduction band
states are also equally Ga and As-like while the higher
energy conduction band states are strongly Ga in nature.

Let us now examine what happens as we approach the
surface. In Figs. 4(b) and 5(b) we show the local density
of states of an As and Ga atom respectively in the third layer.
We can distinguish clearly the onset of four types of surface
states shown by arrows in the figures. The states near -11 eV
and -2 eV are very strongly As in nature, while the states
near 1 eV are predominantly Ga in character. Finally the
surface states near -7 eV seem to be equally shared between
the As and Ga atoms. When we reach the second layer (Figs.
4(c) and 5(c)) we now obtain new surface states in the
conduction bands which seem to be of a stronger Ga nature.
In addition the surface state at -2 eV now has some Ga
character. Another interesting effect that has occurred is
the rapid strengthening of the As character of the surface
states near 1 eV. In this layer the As nature of these states

is stronger than the Ga nature. Finally when we reach the surface (Figs. 4(d) and 5(d)) all the surface states become more pronounced but there are also some very rapid changes. First the As character of the B_1 states becomes very strong while the Ga character does not change very much. There are approximately 1.4 states/atom in the B_1 states of Fig. 4(d). Secondly the character of the B_1' states has now become more Ga-like. This is difficult to see from the figures since both peaks have gone off the scales, however, we find about 0.4 states/atom for the B_1' peak in Fig. 4(d) and about 1.0 states/atom for the B_1' peak in Fig. 5(d). Finally the B_3 states in Fig. 4(d) have also become very strong now with about 1.3 states/atom between -11.6 eV and -10.7 eV.

The band structures of these surface states are plotted in Fig. 6 along the symmetry lines of the irreducible zone given by $\overline{\Gamma X}'\overline{MX}$ in the notation of Jones.[10] The labels on the right hand side of the figure identify the various bands with the appropriate types of surface states. The dashed lines represent the band edges as obtained from Fig. 2(b) and the first and second numbers in parenthesis represents roughly the fraction of charge on the As and Ga atoms respectively. The B_1 and B_1' states are the usual states obtained in the fundamental gap of a polar compound. They essentially result from a splitting of the two A_1 surface bands caused by the differences in potential of the cation

and anion. In our calculations we find that the B_1 states represent As dangling bond states with roughly 80% of the charge localized in the first layer. From Fig. 6 we notice that the surface bands cross the bulk edge around $\bar{\Gamma}$. However it is the $\bar{M}$ and $\bar{X}$ regions that contain the strongest localization. The B_1' states are also localized more strongly at $\bar{M}$ and $\bar{X}$. These states contain roughly 80% of the charge in the first layer with 60% on the Ga atoms and 20% on the As atoms. This is also consistent with the local density of states plots in Figs. 4 and 5. The B_1' states represent dangling bond Ga states along with As bonding states which lie along the surface layer.

The B_2 states are new[6] and originate from a rather small region of the irreducible zone around $\bar{M}$. This is shown in Fig. 6 where we also notice that at $\bar{M}$ we have 80% of the total. Charge localized in the first layer which is shared equally between the As and Ga atoms. As we go away from $\bar{M}$ the charge is primarily concentrated in the first three layers. This is also what was observed in the local densities of states in Figs. 4 and 5. These states represent GaAs bonding states which lie primarily along the surface layer bonds.

The B_3 states are also new[6] and of particular interest since this surface band extends across the bulk edge into the "antisymmetric" or "heteropolar" gap. This is shown quite clearly in Fig. 6 where the band crosses the edge at $\bar{M}$, $\bar{X}$ and $\bar{\Gamma}$. These states extend approximately 0.2 eV across this

edge. The strongest localization occurs at $\overline{M}$ and $\overline{X}$ with roughly 70% and 60% respectively of the charge localized in the first layer. The B_3 states represent As s-like states and at $\overline{\Gamma}$ they are concentrated roughly equally in the first three layers. These states remain extended into the "hetero-polar" gap even with small changes in the tight binding parameters. In particular the less ionic the material the more they extend into the gap.

Finally for completeness let us also briefly examine the B_2' states which are found in our tight binding conduction bands and also extend across a bulk edge. This is again shown in Fig. 6 where we obtain a crossing in the region around $\overline{\Gamma}$. The B_2' states are a combination of Ga dangling bond states along with charge localized on Ga hybrid orbitals lying along the bonds. The strongest localization is at $\overline{X}'$ and $\overline{M}$ with roughly 80% and 78% respectively of the charge concentrated in the first layer. The Ga nature and localiza-tion of the B_2' states is also clearly revealed in Figs. 4 and 5.

IV. Summary and Conclusions

We have studied the (110) surface of a diamond and zincblende semiconductor using Ge and GaAs as prototypes. The method used involved a model structure consisting of a finite number of (110) layers of atoms. The surface layers of this structure were assumed to be unrelaxed and the system was studied using a tight binding model including all

interactions between nearest neighbor atoms. Taking the
structure to contain 12 layers produces reliable results
while keeping the computational aspects simple.

Using the tight binding model whose parameters were
fit adequately to pseudopotential band structures[7] we have
calculated local densities of states of atoms for various
surface layers. These calculations are very useful and
appealing because they reveal in a very natural way how the
states behave as one approaches the surface from the bulk.
In particular we have found new surface states which we
designate by A_2 and A_3 for Ge and B_2 and B_3 for GaAs. By
surface states we mean states which are very well localized
on the surface. We make no distinction here between bona
fide surface states and strong resonances. The A_2, A_3, B_2
and B_3 states lie in the lower energy regions of the filled
valence bands where the tight binding description is most
valid. The surface states A_2 and B_2 states are quite similar.
They both involve states that originate around $\bar{M}$ and repre-
sent bond-like states which lie along the surface layers.
The A_3 and B_3 states are also similar in that they both
involve s-like surface charge distributions. Of particular
interest are the B_3 states, since they extend into the
"heteropolar" gap of an ionic compound. This extention should
decrease with the increasing ionicity of the material. This
diminution of the surface effect with increasing ionicity is
of course related to a general feature of systems which can

be described with very localized states. Such systems are affected rather weakly by long range perturbations.

Finally it should be emphasized that the simplicity and "realspace" nature of the tight binding model makes it a very useful tool in treating more involved aspects of surface studies. For instance relaxation and reconstruction effects as well as influences of adsorbates can be studied in rather simple and physical ways.

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Figure Captions

Figure 1. A drawing (top) of (110) layers of atoms shown
parallel to the $x\hat{y}$ axis for a zincblende structure.
The dots and open circles represent atoms and the heavy
lines signify bonds. ABCD defines the surface unit cell
and four sp^3-like directed orbitals are sketched on each
of the two basis atoms. Below we show the notation used
in the text to label the orbitals for any given layer I
in a total system of N layers.

Figure 2. Total densities of states for Ge and GaAs in the
diamond and zincblende structures ((a) and (b)) and in
structures consisting of 12 layers of atoms with unrelaxed
(110) surfaces ((c) and (d)) respectively. These densities
of states are obtained using the tight binding model
discussed in the text. The labels A and B represent
surface states for Ge and GaAs respectively and are also
described in the text.

Figure 3. Local densities of states for a Ge atom in the
sixth (a), third (b), second (c) and outer surface (d)
layers of the 12 layer structure. The arrows in the
figures represent the onset of surface states as the
surface layer 1 is approached from within the bulk. The
labels A_1, A_2, A_3, and A_1' refer to surface states
discussed in the text.

Figure 4. Local densities of states for an As atom in the
sixth (a), third (b), second (c) and outer surface (d)

layers of the 12 layer structure. The arrows in the figures represent the onset of surface states as the surface layer 1 is approached from within the bulk. The labels B_1, B_2, B_3, B_1' and B_2' refer to surface states discussed in the text.

Figure 5. Local densities of states for a Ga atom in the sixth (a), third (b), second (c) and outer surface (d) layers of the 12 layer structure. The arrows in the figures represent the onset of surface states as the surface layer 1 is approached from within the bulk. The labels B_1, B_2, B_3, B_1' and B_2' refer to surface states discussed in the text.

Figure 6. Surface bands for GaAs along important symmetry directions. The irreducible zone and symmetry points are sketched in the lower left-hand side of the figure. The numbers (f_1, f_2) represent the fraction of charge f_1 and f_2 concentrated in the first surface layer for an As and Ga atom respectively for the various surface states and symmetry points. The labels B refer to surface states discussed in the text and identify their corresponding band structures. The dashed lines represent band edges of the bulk and can be compared with those in Fig. 1(b).
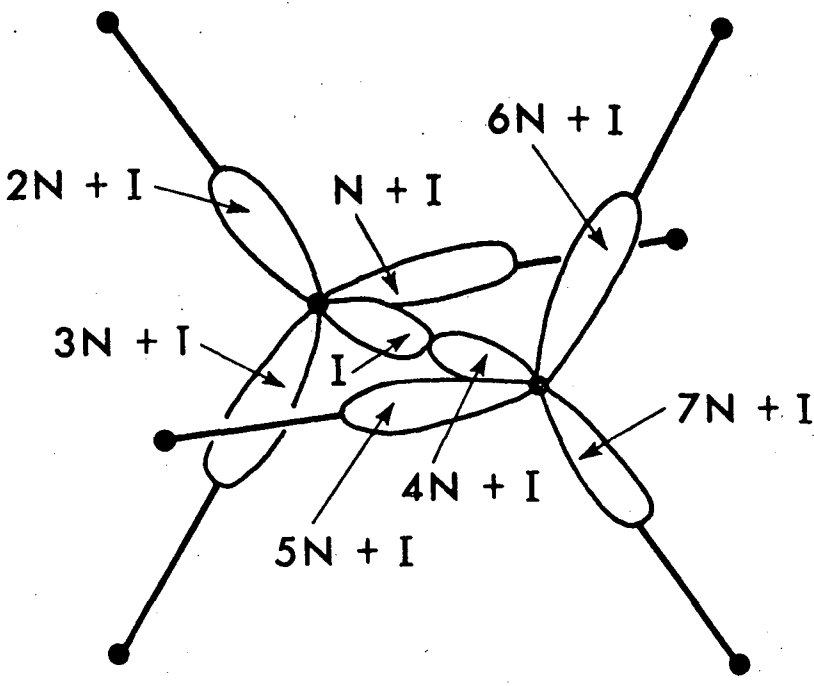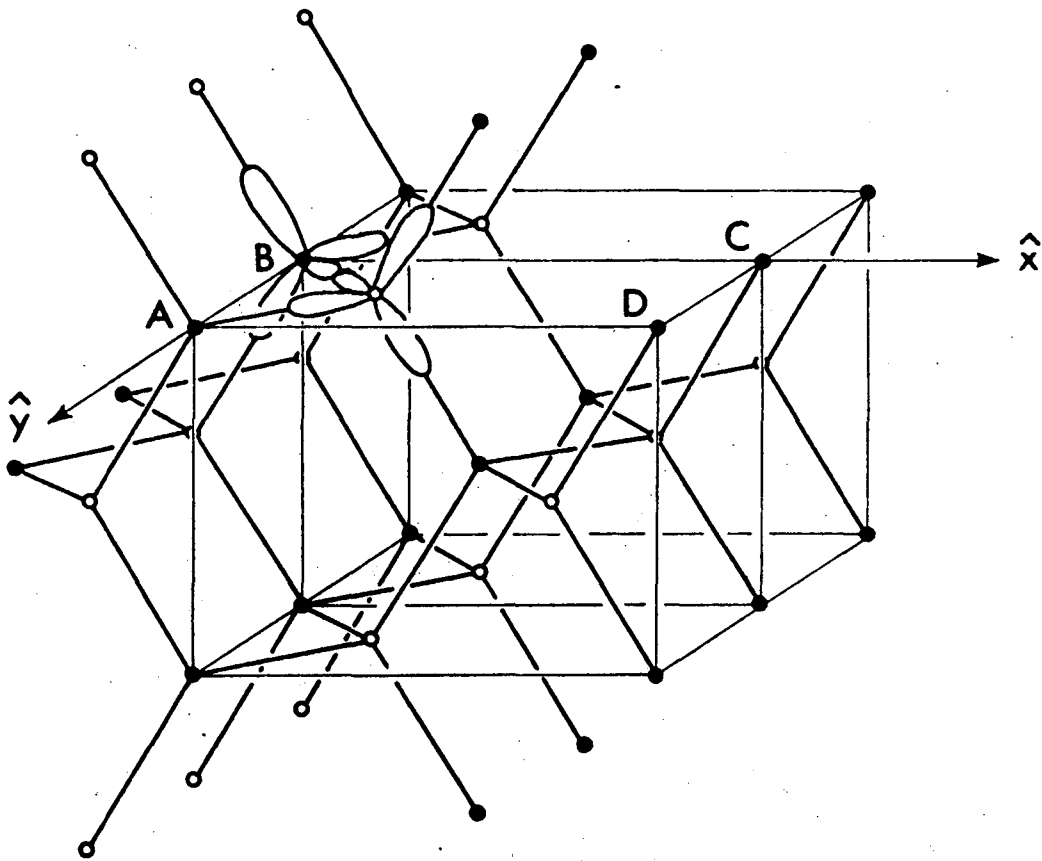
Figure 1

DENSITY OF STATES (states/eV-atom)

ENERGY (eV)
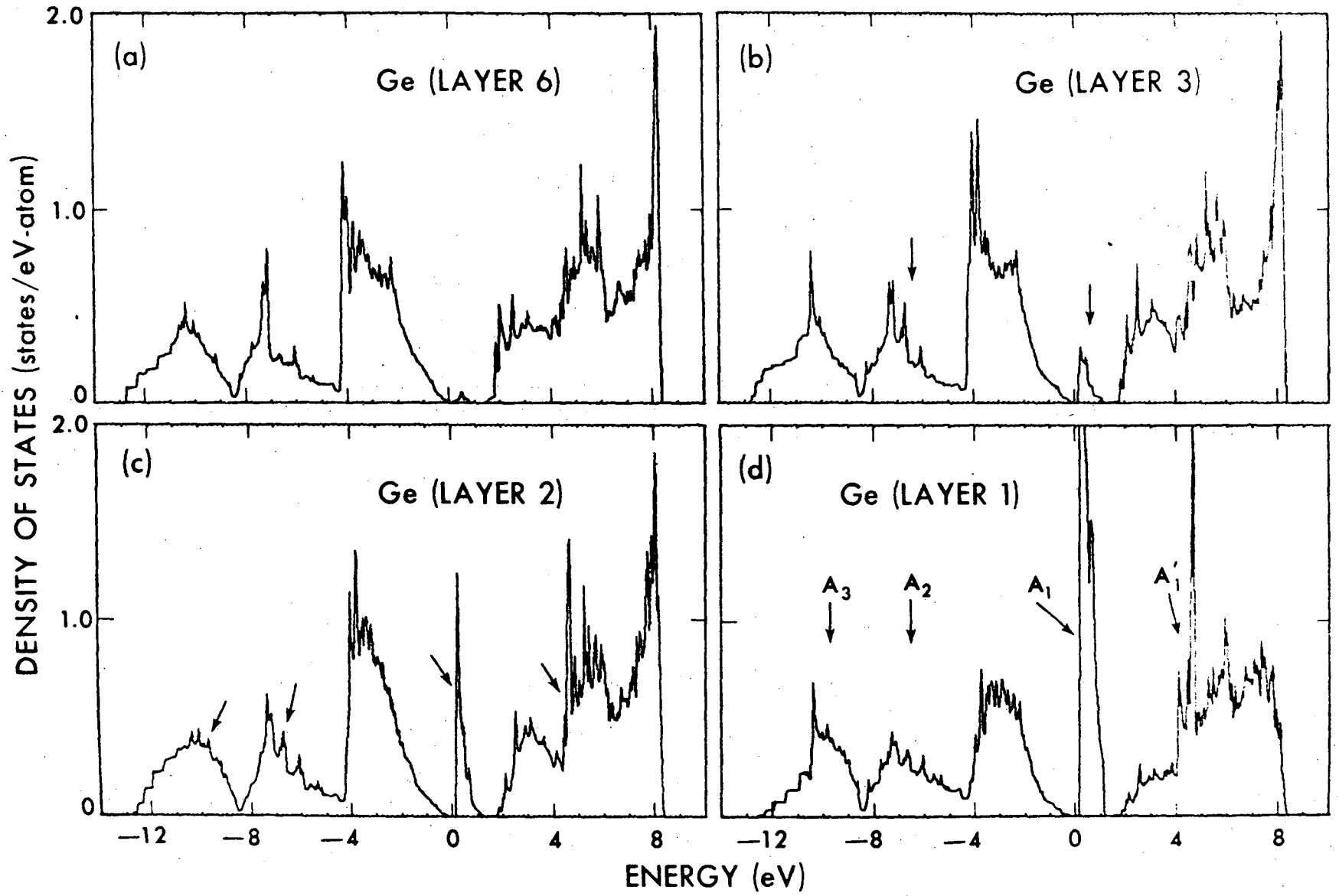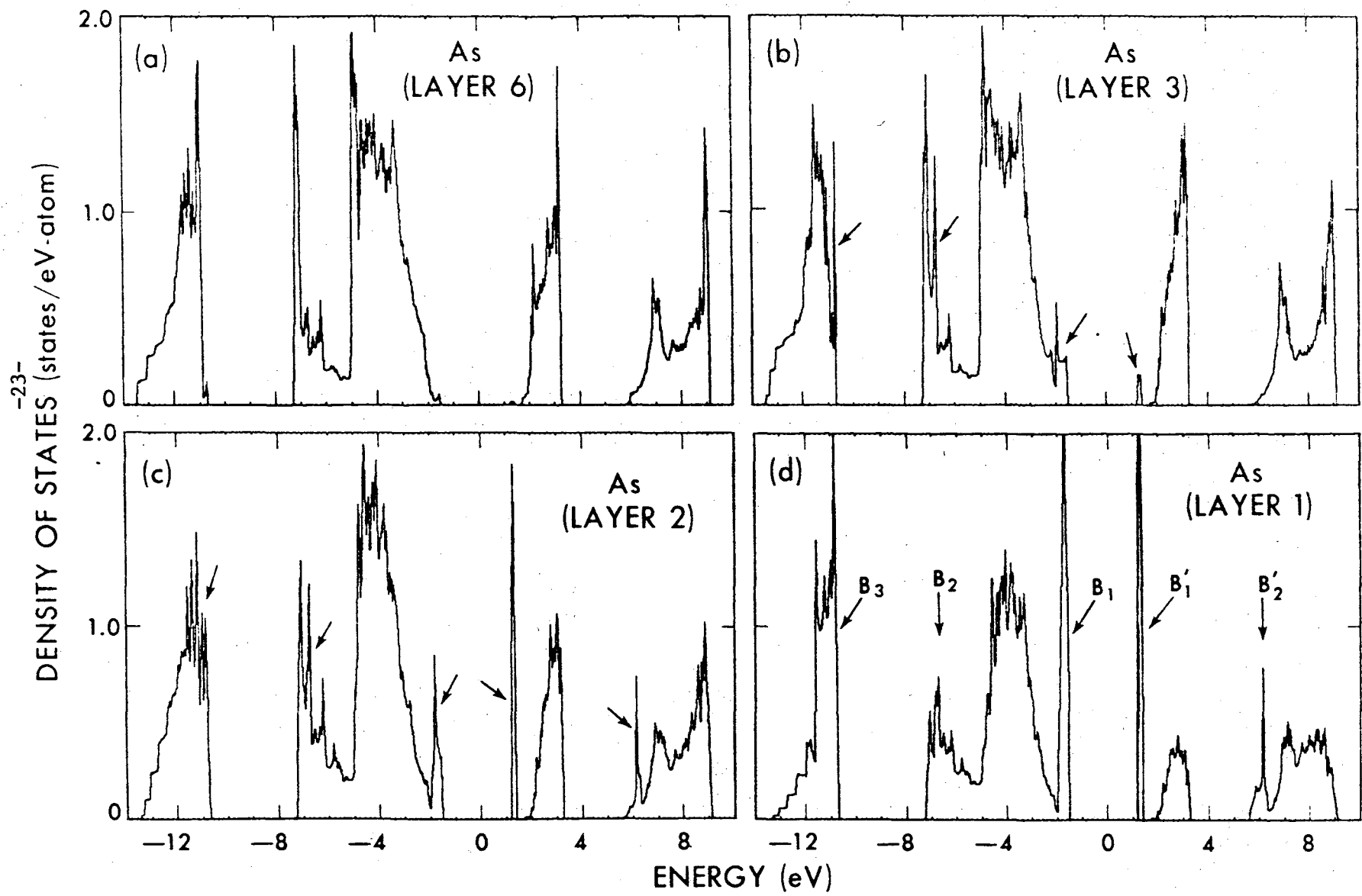
(a) Ge (BULK)

(b) GaAs (BULK)

(c) Ge TWELVE (110) LAYERS

(d) GaAs TWELVE (110) LAYERS

Figure 2

Figure 3

-22-

Figure 4

-23-

Figure 5

-24-

Figure 6