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Nonlocal pseudopotential calculation of the electronic properties
of relaxed GaAs (110)surface

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The electronic structure of a semiconductor surface is studied for the first time using self-consistent nonlocal (first-principles) pseudopotentials. In agreement with the recent local pseudopotential as well as tight-binding studies, no
intrinsic surface states are obtained in the gap of GaAs for the relaxed surface. However, in contrast with the
previous approaches, new features of the electronic structure are obtained, including a pronounced downwards displacement of the low As-derived surface states, the appearance of an additional As p state near the valence-band maximum, the reordering of the states near X with a different order of. wave-function parity, and the development
of pronounced d-orbital character (in addition to s and p) in the highest occupied and lowest empty surface states.

I. INTRODUCTION AND CONCLUSIONS

All of the pseudopotential electronic-structure
calculations of semi- infinite semiconductor sur-

faces known today have used local pseudopoten-tials. Qn the other hand, all pseudopotentials are inherently nonlocal. ~ Until recently, nonlocal
pseudopotentials which are usable in self-con-
sistent calculations were not available. Empirical nonlocal-like corrections to otherwise local
pseudopotentials" have shown substantial changes
both in the band structure as well as in the elec-tronic charge densities of zine-blende semicon-ductors. ~ Since, however, in this approach the screened pseudopotential, rather than the bare
pseudopotential, has been empirically parame-
trized, '

these potentials were not expressible in
terms of the calculated

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of the nonloca/ pseudopotential is appreciably
deeper than the s component for both Ga and As
(Fig. 1) (reflecting a weaker pseudopotential can-
cellation due to the existence of only one core state
of d symmetry compared to three of s symmetry),
the local pseudopotential approach constrains both s and d states to sample a common potential. This raises artif icially the energy of the d-containing states to the higher conduction bands, outside the energy region of conventional interest.

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Similarly one may select V„(r)to be e(lual to the local semiempirical pseudopotential v,

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V(k + G, k + G') = V„(G—G') + V„(G—G') + V,(G —G')

+ I S,(G —6')(E ~(G —6')+ $)„.g(k+ Gk+G')),

a

and the various terms are given by Eqs.— (10a), (10b), (10c), (6), and (4), respectively.
The input to the calculation is {v~'$ for & =Ga, As and I =0, 1, 2, as well as the geometry {II„,7]. The matrix elements F, 0(G) and E,(k+ G, k+ G') are then calculated once and for all on a given grid in
momentum space by performing the one-dimensional numerical integrations indioated in Fqs. (6) and (4), respectively. To solve (13), an intial guess for V„(G)+ VQG)+ V,(Q) is needed. This guess does not affect the final self-consistent result but rather the computing speed with which it is obtained. One can use an initial guess taken from previous empirical pseudopotential studies or by first solving an atomic pseudo-
potential equation with v' "(r)for Qa and As:

{- v + v„[no (r)] + v„[no (r)] +v, [go(r)] + v

' "(r)P,] y„,(r) =q„,p„,(r) (15)

using standard atomic structure programs, 34 and
then use the linearly superposed atomic screening
as a first guess to the crystal screening:

W."„'(r)=,P g ~„,„„[~,(r- a„- 7.)],
where v„„,(r) denotes collectively v„+v„+v,. Qiven this initial guess, Eq. (13) is solved for four special k points in the surface Brillouin zone. 35 To obtain a convergence of 0.25 eV in the eigenvalues e&(k) with respect to the sum over Q' in Eq. (13), I use 600 plane waves at I' (which de-compose into two 300x300 matrices due to the symmetrization) plus a,n additional 1167 plane waves in a second-order Lowdin perturbation technique. ~ These correspond to energy cutoff values of 4.1 and 9.5 Ry, respectively. Those large cutoff values are required because the first-principles pseudopotentials (Fig. 1) are rather steep in coordinate space.
From the wave functions x&(k, r) evaluated at points k& in the irreducible zone [Eq. (12)] one calculates the symmetrized wave function x&(k, r) over the full zone. The charge density is then given as

(16)

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n(r) =g g ur +)x& (k&, r)x&(k, r),,
using the statistical weights u (kP for the four special k points k&.35 The density Fourier com-ponents are

(17)

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n(G) =g g g u (k,)B, (k~ + G')B, (k +Q). 0'
(18)

From (18) I obtain the interelectronic Coulomb potential V„(Q) using Eq. (10a). The individually divergent V„(G=O) and E,,

(Q=O) terms are
arbitrarily set to zero, redefining thereby the posit:ion of the vacuum level.. From the coordinate
space charge density in Eq. (17), tabulated over

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about 65000 grid points {r,.]

in the unit cell, I

calculate m(r,.)' ', and via a fast Fourier trans-form, 3~1 obtain from this the V„(G) term in (10b). The correlation potential (10c) is similarly cal-culated by fast Fourier transforms of V,(r,.). Using this updated screening W, (G) = V„(G) + V„(G)
+ V,(Q), and the fixed pseudopotentials E„o(G) and E,„(G,G'), Eq. (13) is solved again. The pro-cess is repeated iteratively until the screening IV„,(G) agrees to within 10 Hy in successive iterations. Starting from the initial guess (16) and using extensively iteration-damping tech-. niques, this requires nine iterations.

III. PSEUDOPOTENTIALS

Our basic method for obtaining nonempirical

atomic pseudopotentials {v~,"' (r)) in the density-
functional formalism has been previously de-scribed. 4
The nonlocal density-functional pseudopotentials
for Ga and As are displayed in Fig. 1, where they are compared with the semiempirical local pseudo-potentials used previously for surface calcula-
tions.

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These latter potentials are obtained by
fitting the spectra of the bare ions Ga'3 and As' to experiment without constraining the shaPe of the
wave functions. For comparison, Fig. 1 also
shows the local pseudopotential developed by Frensley and Kroemer38 (FK) by fitting orbital energies and using realistic Hartree-Fock-type atomic charge densities. gt is seen that the semi-empirical local pseudopotential" is qualitative1y different from the two other potentials which in-corporate realistic charge densities: Its mini-
mum is displaced to larger r values and is sub-
stantially shallower. Having also an attractive character in the core region, the semiempirical pseudopotential tends to accumulate charge in the core (where a pseudopotential description of the
wave function is least valid).

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V. RESULTS

The (110) projected band structure of GaAs to-
gether with the calculated surface bands are dis-
played in Fig. 2(a). A schematic drawing of the
experimentally observed surface states
plotted with the calculated projected band structure is given in Fig. 2(b). The surface states have been denoted by the chemical symbol of the atom (Ga/As) that forms the predominant orbital character in the corresponding wave function, followed by a number in parentheses, in increasing order from the bot-tom of the bands that labels the different slates. Fifteen calculated k points in the surface Brillouin zone have been used, and the wave functions of the lowest 60 bands at each point have been analyzed by calculating the wave function's planar average (which indicates the region of space perpendicular to the surface where the wave function is mostly localized) as well as an angular momentum pro-jection of the wave function [~B,(k+.C)j,(~ (k+ G) ~ r ~)1;] around spheres (with r ~R, where R, is the tetrahdral radius~6) centered on surface atoms. This can be used to establish the predominant orbital character in each state, and when nor-malized, this yields the percentage of a given angular momentum species in each state. As both s as well as P, d-type pseudopotentials wave func-

tions have zero amplitude at the origin, such a de-composition is an important tool in analyzing the orbital character. In addition, a large number of the calculated wave functions have been subjected to a symmetry reflection operation in the mirror plane to examine their parity.
The two lowest surface states labeled As(1) and As(2) (83 and B„respectively, in the notation of Ref. 13 and Ref. 16) are As s-like. The As(1) state was observed experimentally at -12eV(Ref. 30) and is predicted to have its region of maximum band flatness (i.e., peak density) at

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by the former method.

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More detailed experiment-
al data are needed to assess the calculated disper-sion and energy separation between these states. The Ga(1) and Ga(2) pair of bands appearing at —(5.8-6.0) eV at M (B2 in the notation of Hef. 13) are Qas-like with a 10'%%uo AsP-like contribution. Similarly to the As(1)-As(2) pair, Ga(1) is local-ized on the second layer, whereas Qa(2) is local-ized on the first layer. Only one state at —6.5 ep (Hef. 23) is observed experimentally in this energy region. Both pairs As(1)-As(2) and Ga(1)-Ga(2) are split by an interaction induced by the surface

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the problem by avoiding the use of

d basis functions

and neglecting intersite overlap. As indicated be-fore, whereas local-pseudopotential studies allow, in principle,

d character in the wave functions (as
the plane-wave basis used can produce all angular symmetries), the neglect of nonlocality effects tends to destabilize

d states and push them to high
energies.
The empty surface states Ga(3) and Ga.(4) obtained in this study are localized on the surface layer and agree closely in location with the corresponding states found in the local-pseudopotential study. '5 As indicated by others, '3'" the Qa(4) state lies in the gap for the unrelaxed geometry, whereas Qa(3) lies above it. Relaxation effects reverse their order and place both of them in the conduction band, partial-yield photoemission studies '

in-

dicate that transitions from As 3p and Qa3d to empty surface states have comparable intensities, whereas the As 3d-to-empty-state transitions are extremely weak. It was assumed" that if cross transitions coupling the two sublattices are weak, the As character in the empty states is s-like and the Qa character is P-like, in agreement with the present study. However, the absence of transi-tions from As 3d is also naturally explained by the fact that the present study finds Asd character in the empty

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W«, [n(r), P2 (r)]= U«[n(r)] + Ug n(r)]

+ U.[n(r)1- U«[4)(&)]

—U„[P,(r), $

.=1]

—U.[C', (~), (=1], (19)

where g denotes spin polarization. Applications
to many atoms have shown that the orbital ener-

gies obtained with (19) are 1-3 ep lower than those obtained with Eq. (7), even for the valence electrons. In addition, many of the systematic anomalies characterizing the local-density for-malism have been shown to be removed by this self- interaction corrected scheme.

states in the density-functional approach, relative to diffused itinerant states (which have a vanishing self- interaction).
&t has been recently pointed out4 that one can go beyond the local-density formalism by defining a new energy functional in which self-interaction effects are canceled self-consistently. This leads to a modified state-dependent screening which re-places Eq. (7):

Since some of the surface states obtained for
semiconductors have a localization range char-
acteristic of an atomic scale [e.g., states ap-pearimg in gaps in. the projected band structure such as Ga(1) and Ga(2) in Fig. 2], one may ex-pect that self-interaction corrections for these states would be a non-negligible fraction of that
found for atoms. Indeed, the energy of the Ga(1)-
Ga(2) states calculated here is about 0.5-0.7 ep higher than the experimental value. 3 Hence, whereas many electronic-structure calculations for semiconductor surfaces using a density-func-tional screening Eq. (7) (e.g., Ref. 49 and refer-ences therein) have produced an overall agreement
with experiment (sometimes via semiempirical
parametrization of the pseudopotential or scaling
the exchange potential), as pointed out first by Schrieffer, 5 non-negligible corrections can result from the physical mechanisms underlying Eq. (19).

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