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Al on GaAs(110) interface: Possibility of adatom cluster formation

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A reexamination of the experimental data and previous electronic-structure calculations on the prototype Schottky system Al/GaAs(110), together with new calculations, indicates that at low coverages and temperatures neither a covalent bond nor a metallic bond is likely to be formed between Al and the substrate. Instead, the predominant species is likely to be Al clusters which interact only weakly and largely nondirectionally with the substrate. In contrast with all previous theoretical models which assume an epitaxially ordered array of chemisorption bonds even at submonolayer coverage, it then appears that the formation of a Schottky barrier as well as other physical and chemical characteristics of the interface (e.g., core level and exciton shifts, valence-band photoemission spectra, gap states, surface atomic relaxation) are not explainable in terms of strong and ordered chemisorption bonds. This weakly interacting cluster model leads to several interesting predictions regarding the atomic structure and spectroscopy of this metal-semiconductor interface at the initial stages of its formation; The properties of the interface at higher temperatures (i.e., after annealing) are discussed in terms of an Al-Ga exchange reaction.

I. INTRODUCTION

The understanding of the changes in the elec-
tronic and structural properties of a clean GaAs surface upon deposition of submonolayer a'mounts of polyvalent metal atoms (e.g., Al) at low tem-
peratures has long been recognized as central to the
development of reliable microscopic models for the
formation of Schottky barriers and the understand-
ing of chemisorption-induced surface chemistry in
heteropolar semiconductors. ' ' A large diversity of theoretical methods has been applied to the problem, ranging from empirical tight-binding (TB) to local semiempirical pseudopotentials' and
coreless Hartree-Fock (HF) cluster methods.
Common to such models' is the underlying as-
sumption that the physical and chemical charac-teristics of the initial interface (e.g., core shifts, valence-band photoemission spectra, Schottky-barrier pinning states, surface dipoles,

semicj ET 5/Xi0 8.95 T2 Tic reliabtion) relcTj E Inste ET BT /Xi0 9.05 Tf 22074 Td .49 8d (the)Tj ET BT /Xi0 8.62 Tf 12614 25 .49 8d (theabse-ba ET BT /Xi0 10.33 Tf 89.118 29 .49 9d (of)Tj ET BT /Xi0 8.75 2f 2 the

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in contrast

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prediction of SELP calculating for interfaces. In
part these findings have motivated the undertaking
of an improved theoretical description of the sys-
tem: (i) Perhaps the most significant difFerence in
the electronic structure of the Al and Ga atoms is

that while in their monovalent (s p') as well as trivalent (s'p

) configurations their

p energy levels
are nearly degenerate, the Al

s level lies above the
Ga

s level in both configurations by 1.

3

—1.

5

eV. ' This difference (associated with the ex-istence of d core levels in Ga but not Al) explains
the qualitatively different conduction-band topolo-
gies in GaAs and AlAs. It is also largely responsi-ble for the systematic differences in the stabilities of the corresponding elemental metals, as well as the variations in the properties of the molecular compounds A1X, GaX, AlX3, and GaX3. While the nonlocal first-principles atomic pseudopoten-
tials' '

closely reproduce these variations in the
atomic spectra1 features, the local semiempirica1

pseudopotentials, ' '

yield

a very small difference
between the Al and Ga

s and
p energy levels, mak-
ing Al appear more like Ga. Previous pseudopo-tential calculations for Al/GaAs(110) (Ref. 2) may thus reflect the situation pertinent to
Ga/GaAs(110). (ii) Applying the SELP to the cal-culation of the bulk band structure of A1As, I find
an anomalously small indirect band gap of 0.95 eV
as compared to the experimental value of 2.

2 eV.

This discrepancy results from the SELP: It is much larger than the errors resulting from the underlying density-functional theory used to
describe the screening in the system' or from the
errors associated in the tight-binding schemes with fitting the observed band gaps. '

Interface states

lying near or in the conduction bands (e.g.

,

the

Ga-Al states) may be affected by this spuriously low Al level in the SELF description.
These findings as well as those indicated in Ref. 30 suggest that the description of interface gap states as well as the proportions of

s to
p charac-
ters in the wave functions is likely to be distorted
by such pseudopotentials. [For example, while the
SELP produce for Al chemisorption on the As site

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ties of the interface (e.g., barrier heights, band
bending, gap interface states) are, however, already
established below a —, ML coverage.

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TABLE I. Standard heats of formation [Ref. 34(ta)] of the monovalent and trivalent forms of column-III halides in molecular

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calculations2

—5

scale approximately as d, the

use of

d =3.

1

A rather than

d =2.43

A (an error
of

a factor of 0.

6 in H;1

) is likely to alter signifi-
cantly the previous conclusions for AllGaAs. While strongly localized interface states may be af-fected only weakly, the energy of adatom-substrate bonding-antibonding pairs, which ofzed

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strongly attenuated relative to the corresponding
clean-surface state

a due to the capping of the sur-
face As by A(I). The local density of states on the
second subsurface layer shows this peak to be re-
stored to its shape in the bulk material. The chemisorption-induced change from

a to a' was
not observed experimentally.

(ii) The next chemisorption state b' is identified as an adatom (predominantly s-derived} bonding

state, lying above the clean-surface Ga(III) state g' [Fig. 1(a)]. Since the state b' is strongly localized, one may expect that at zero order the energy

separation Ebs of b' from

g wi11 scale with the
difference in the corresponding atomic orbita1 ener-gies b,

4380 '

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dopotentials, leads to one-electron spectra that can-not be reconcicbdopotentials,

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ter size n*. For Be„clusters, for example, large-
basis-set Hartree-Fock calculations yield Eb"'/n
values of 0.0, 0.01, 0.14, —0.21, and —0.07
eV/atom for n =0, 1, 2, 3, 4, and 5, respectively
[the bulk cohesive energy being —3.32 eV (Ref.
43)], while for Li„configuration-interaction calcu-lations yield values of 0.0, —0.45, and —0.43 eV/atom, respectively, for n

for

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the observed valence-band photoemission
results

We note that the attenuation of the GaAs energy distribution curve (EDC) structure with

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state observed in surface photovoltage spectroscopy
at an energy of 0.6 eV above the VBM. More ef-
fort in this direction is clearly called for.
(iv) Since in this model the molecular clusters
Al„ interact only weakly and largely nondirection-
ally with the substrate, the adlayer will be disor-dered above a translational freezing temperature; the atomic structure of the substrate (i.e.,

relaxa-

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stage of the formation of the Al/GaAs(110) inter-
face. %e now consider the system's properties
after annealing takes place. Central to our discus-
sion here is the realization that different theoretical
models are

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VII. SUMMARY AND IMPLICATIONS
- ON FERMI ENERGY PINNING

DifFerent theoretical models that describe the

low-temperature and low-coverage stage of the for-
mation of the Al/GaAs(110) interface have been
examined. Central to these models is the assump-tion that the basic physical properties of the inter-face (e.g., valence-band photoemission, charge transfer, Schottky-barrier heights, and the surface atomic structure) can be explained in terms of the properties of an ordered epitaxial array of either metallic' or covalent chemisorption bonds between the adatoms and the substrate. The cen-

tral deduction of this paper is that, when carried out properly, such models cannot be reconciled with the experimental data. A difFerent viewpoint —that at the initial stage of the forma-tion of the interface no such bonds occur but that Al„clusters, which interact only weakly with the substrate prevail —is shown to be more likely. Analysis of the data leads to the following con-
clusions.

(i) Although the semiconductor-jellium model
works well for thick overlayers, if carried to the
limit where barriers are actually formed (thin over-
layers over a relaxed substrate), it fails.
(ii)

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ious (only)Tj ET BT /Xi1419.57 87 402.Tf 840.85 Td ((thin)Tj ET BT /Xi14 8.96 T5 32.Tf 840.85 Td (the)Tj ET BT /Xi14 8.81 Tf 21.Tf 367.e3aTd (epita (only)Tj ET BT /

over

substrate

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and iT td (mation)Tj ET BT /Xi14 9.9274 564.Tf 972.51 Td (of)Tj ET BT /Xi14 9.05 Tf 3913T110414.3 Td (the)Tj ET BT /Xi1698.56 Tf 74.0i14 9.23 T(preabltrate)Tj ET BT /Xi17

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exam(the)Tj ET BT /Xi14 8.93 Tf 118i46 691.01 (thin

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110),

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be responsible for Fermi energy pinning. We brief-

ly discuss this possibility below. I have already indicated (Sec. V A) that in my
model clusters and AIDS are intimately related—
cluster formation releases sufficient energy to create. AIDS. Since most clusters have band gaps which are smaller than that of the semiconductor (e.g.

,

for
A15, A19, Al&9, Alzs, and A143 the calculated band gaps are 0.14, 0.07, 0.05, 0.2, and 0.03 eV, respec-tively} cluster states are likely to overlap the sem-iconductor gap region. The low-energy density of cluster states (typically

1
—S states/eV) and the low
surface density of the clusters make their direct ex-perimental identification diAicult. The Fermi ener-gy may, however, be pinned at these gap cluster levels following

a small charge transfer. Notice
that the cluster states may act both as acceptor and donor states: They may exist both in negatively and in positively charged states to pin the Fermi energy at different positions for n-type and p-type samples, respectively.
The alternative possibility is that AIDS may be responsible for Fermi energy stabilization. Such

a

model was first put forward by Spicer

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S. G. Louie, J. R. Chelikowsky, and M. L. Cohen,
Phys. Rev. 8 15, 2154 (1977);J. Vac. Sci. Technol.
13, 790 (1976); S. G. Louie and M. L. Cohen, Phys.
Rev. 8 13, 2461 (1976).
2J. R. Chelikowsky, S. G. Louie, and M. L. Cohen,
Solid State Commun. 20, 641 (1976).
D. J. Chadi and R. Z. Bachrach, J. Vac. Sci. Technol. 16, 1159 (1979).
4E. J. Mele and J. D. Joannopoulos, Phys. Rev. Lett.
42, 1094 (1979);J. Vac. Sci. Technol. 16, 1154 {1979). 5J. Van Laar, A. Huijer, and T. L. Van Rooy, J. Vac. Sci.. Technol. 16, 1164 (1979);A. Huijer, Ph.D. thesis, Philips, Eindhoven, Holland, 1979 (unpublished).
C. A. Swarts, J.J. Barton, W. A. Goddard, and T. C. McGill, J. Vac. Sci. Technol.

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ters (e.g.

, cutoff values) used in self-consistent calcula-
tions. If, for example, one performs a fully converged
calculation with this pseudopotential (i.e.

, 169 plane
waves in the basis set, including all nonzero com-

ponents in the pseudopotential up to a momentum of q =3 a.u. '

indicated in Table

I of Ref. 23(a) and
iterating over 10 special

k points), one obtains [for an
exchange coeAicient

a =0.

8 (Refs. 1, 2, 23, and 24)]
an indirect band gap

I 25 „~h], of 0.95 eV. Experi-
mentally, this material has a direct band gap
T'25 „~I&, of 1.52 eV. More specifically, such

a cal-
culation produces the band energies (in eV, taken with respect to the valence-band maximum, internal pre-

cision of 0.03 eV): 1 &„(—12.14), I ~,(1.31), I i5,(3.56), I),(7.17);X),(—9.73), X3„(—6.64),

X5„(

—2.56), X~,{1.02), X3c(1.04), X5,(11.03); and
Li„(

—10.52), Lgt,

(

—6.51), L3„(

—1.03),

L),(1.04),
Ls,(4.09). The experimental results are I'i„[—13.

1

{Ref. 19),

—13.8 (Ref. 20)),

I i,[1.52,1.63 (Ref. 19)],
I'», [4.72 (Ref. 19), 4.49 (Ref. 21)], I' t,[8.33 (Ref. 19)];Xi„[—10.

7 (Refs. 19 and 20)], X3„[—6.

7 (Ref.
19),

—7.

1 (Ref. 20)], Xs„[—2.

8 (Ref. 19),

—2.

5 (Ref.
20)], X&,[2.18 (Ref. 19), 1.95 {Ref.21)], X3,[2.58 (Ref. 19), 2.35 (Ref. 21)]; and L&„[—11.2 (Ref. 19),

—12

(Ref. 20)], L2„[

6 7(Ref—. 19.),

—7.

1 {Ref.20)],
Lsr[1.

3 (R—ef. 19),

—1.4 (Ref 20)], Li,[1.85 (Ref. 19),
1.95 (Ref. 21)], L3,[5.

6 (Ref. 21)]. Clearly, the calcu-
lated lower conduction band is about 1 eV too low in
the

6 and

A directions. In practice, however, com-
puter storage limitations have prohibited the use of
such

a large basis set when supercells are considered (Refs. 1, 2, 23, and 24); more often

a basis of -27
plane waves per primitive unit cell has been used. If
one repeats

a self-consistent calculation with the same
parameters as before, but with

a 27 plane-wave basis
set (i.e.

, an underconverged basis) one still obtains an indirect

I 25„~hi, band gap (0.

6 eV) with

I &,{1.30),
Xi,(0.69), and Li,(0.92). To get

a physically correct
band structure one needs to truncate the pseudopoten-tial to include only the first six nonzero reciprocal-

lattice vectors (6 =3, 4, 8, 11, 12, and 16, equivalent to the first 65 plane waves, or q,„=2.36 a.u. ') but
to artificially extend the screening potential to include

the first -181plane waves Using 2.

7 plane waves in

the basis, one then gets the "optimal" results I i,(1.53), X&,(1.42), and L &,(1.36); i.e., a I 2~,„~A,
indirect band gap, but within -0.

2 eV of the magni-
tude of the direct gap. (This calculation has been
checked independently by J. R. Chelikowsky who ob-
tained results which are within 0.1 eV of the present results for the lowest five bands.

) Such

a fine control

of the internal computational parameters may not have been exercised previously in all of the

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3720 (unpublished) ~ Also quoted by C. Kittel, Intro-

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P. Petrol (private communication).
J. F. Hamilton and P. C. Logel, Thin Solid Films 23, 89 (1974).
R. F. C. Farrow, A. G. Cullis, A. J. Grant, and J. E. Pattison, J. Cryst. Growth 45, 292 (1978).
U. Landman and M. F. Shlesinger, Phys. Rev. 8 16, 3389 (1977); U. Landman, E. %'. Moritroll, and M. F.

Shlesinger, Phys. Rev. Lett. 38, 785 (1977).
M. S. Daw and D. L. Smith, Phys. Rev. 8 20, 5150 (1979).
R. E. Allen and A. Zunger, SERI Report No. PR-611-737, p. SS-12 (unpublished); Bull. Am. Phys. Soc. 75, 194 (1980), and unpublished results.