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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 electronic and structural properties of a clean GaAs surface upon deposition of submonolayer amounts of polyvalent metal atoms (e.g., Al) at low temperatures has long been recognized as central to the development of reliable microscopic models for the formation of Schottky barriers and the understanding of chemisorption-induced surface chemistry in heteropolar semiconductors.[1-12] A large diversity of theoretical methods has been applied to the problem, ranging from empirical tight-binding[3-5] (TB) to local semiempirical pseudopotentials[1,2] and coreless Hartree-Fock (HF) cluster methods.[6] Common to such models[1-5] is the underlying assumption that the physical and chemical characteristics of the initial interface (e.g., core shifts, valence-band photoemission spectra, Schottky-barrier pinning states, surface dipoles, and atomic relaxation) can be understood in terms of the postulated *short* (i.e., bulklike) chemisorption bonds between the adlayer and the substrate atoms. In the absence of total energy calculations, the computed sharp features in the one-electron density of states[2-5] or substantial accumulation of charge density along the adatom—substrate bonds[2] were taken as evidence for formation of *strong* chemisorption bonds. Previous theoretical studies have attempted to analyze the data within such strong chemisorption models in terms of either metallic bonds[1] or an ordered array of directional covalent bonds[2-5] between the adatoms and the substrate. Such chemisorption models, if correct, predict profound changes in the core and valence states of the semiconductor,[2-6] often accompanied by substantial surface relaxation.[3,4] They also result in the identification of the Fermi-level pinning states as arising from such chemisorptive bonds.

In this paper I show that a reexamination of the experimental data and of the previous theoretical calculations, together with the analysis of the new calculations reported herein (using *a priori* nonlocal pseudopotentials), shows that at low coverage and low-temperature deposition of Al on GaAs(110) the Al atoms do not bond strongly to either Ga or As. Instead, I suggest that Al atoms are likely to bond among themselves, forming small Al_n molecular clusters which interact only weakly and nondirectionally with the substrate, leaving its electronic and atomic structure largely unchanged relative to the clean surface. Since the formation of Schottky barriers is nearly complete at this low coverage (~ 1 Å) and low temperature, the model presented herein suggests that pinning of the Fermi energy is not induced by conventional chemisorption bonds, in contrast with other theoretical models.[1–6] Pinning by defect levels[7] is then a possible mechanism. This new model leads to several interesting predictions regarding the interface atomic structure and its spectroscopy discussed in Sec. V B.

While the understanding of the nature of the chemical bonds occurring at submonolayer coverages and low temperatures is central to modeling Schottky barriers (which are created under these conditions), the effects exhibited at higher temperatures (i.e., after annealing) show interesting chemistry. These are discussed separately in terms of an adlayer-substrate exchange reaction in Sec. VI. Recently, Skeath *et al.*[12] have independently presented an analysis of their previous experimental data[7,8]; their conclusions on Al/GaAs(110) are supported by the present theoretical study.

The present work is not intended as a conclusive study. Instead, it describes the basic elements of a new viewpoint on the subject resulting from both a critical assessment of the contemporary theoretical models (on which we build) and a close reexamination of the experimental data. At the time where the accepted theoretical model for the initial stage of the metal-semiconductor interface is an ordered array of chemisorption bonds[1–6] it seems appropriate to introduce and discuss the alternative view of the weakly interacting cluster model. For the first time, *ab initio* total-energy calculations are used to predict a geometry for an extended semiconductor chemisorption system. Crucial experiments and new predictions are then suggested. We find that this analysis strongly suggests the validity of the weakly interacting cluster model for describing the initial stage of formation of the metalsemiconductor interface.

I discuss first the initial stage of the interface formation (i.e., at low temperature and submonolayer coverage, Secs. III–V) during which the basic physical characteristics of the system (barrier heights, interface states, etc.) are already established.[7] Discussion follows in Sec. VI of the qualitatively different situation of the "exchanged system" where Al replaces the surface Ga (higher temperatures). This paper does not treat the properties of systems at thick coverages (i.e., multilayer coverage).

II. CALCULATION TOOLS

The calculation of the one-electron spectra as well as the total energy minimization is performed in a self-consistent repeated cell model[2,13] with nine layers of GaAs followed by three vacuum layers on each side. The nonlocal *a priori* density-functional pseudopotentials[14] and a plane-wave basis set consisting of 600 basis functions are used. The methods for the calculation of the one-electron spectra[2,14] and total energy[15] are analogous to those used previously. To facilitate understanding of the trends in the energies of the more localized interface states, we also examine the relevant atomic orbital energies. These calculations are performed with the same pseudopotentials, applying the "self-interaction correction"[14(b),16] which corrects systematically for the spurious interelectronic interactions included in the density functional formalism; the calculated energies are thereby brought into close agreement with experiment.[16]

Such first-principles calculations (i.e., the only empirical inputs are the atomic numbers and the geometrical degrees of freedom which are not obtained variationally) often yield band gaps that are too small.[17] The reasons for this have been discussed in great detail elsewhere.[16] To obtain an experimentally correct bulk band gap we have introduced a small *ad hoc* adjustment to the potential.[18–22]

Whereas the density-functional atomic pseudopotentials[14] are derived in an *ab initio* fashion, with their nonlocality retained, most previous pseudopotential calculations on metal-semiconductor,[1,2] semiconductor-semiconductor,[23] and semiconductor-vacuum[24] interfaces were performed with *semiempirical and local pseudopotentials* (SELP). These have usually produced very good agreement with the experimental results for systems such as the ideal[24(a)] and relaxed[24(b)] clean GaAs(110) surface, the interfaces of Ge/GaAs,[23(a)] AlAs/GaAs,[23(a),(b)] and GaAs/ZnSe,[23(b)] the jellium-GaAs interface,[1] and the Al/GaAs(110) interface.[2] In fact, these simple pseudopotentials have enabled self-consistent calculations for systems of such substantial structural complexity at a time where other computational schemes were intractable. Such simplified pseudopotentials, however, have certain limitations which become apparent when applied to the simpler systems, such as free atoms and bulk semiconductors. I have examined these SELP pseudopotentials for bulk GaAs, AlAs, and the corresponding free atoms in an attempt to understand the nature of the predictions for the more complex interface system[1,2] for which the electronic properties are expected to be intermediate between these two limits. The results show a number of undesirable features that are likely to affect the prediction of SELP calculating for interfaces. In part these findings have motivated the undertaking of an improved theoretical description of the system: (i) Perhaps the most significant difference in the electronic structure of the Al and Ga atoms is that while in their monovalent (s^2p^1) as well as trivalent (s^1p^2) 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.[4,25] This difference (associated with the existence of d core levels in Ga but not[26] Al) explains the qualitatively different conduction-band topologies in GaAs and AlAs. It is also largely responsible for the systematic differences in the stabilities of the corresponding elemental metals,[27] as well as the variations in the properties of the molecular compounds AlX, GaX, AlX_3, and GaX_3.[28] While the *nonlocal* first-principles atomic pseudopotentials[13,14] closely reproduce these variations in the atomic spectral features, the local semiempirical pseudopotentials,[1,2,23] yield a very small difference between the Al and Ga s and p energy levels, making Al appear more like Ga. Previous pseudopotential calculations for Al/GaAs(110) (Ref. 2) may thus reflect the situation pertinent to Ga/GaAs(110). (ii) Applying the SELP to the calculation of the bulk band structure of AlAs, I find an anomalously small indirect band gap of 0.95 eV as compared to the experimental value of 2.2 eV.[29] 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[17] or from the errors associated in the tight-binding schemes with fitting the observed band gaps.[3,4] 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 SELP 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 characters 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 an As-Al dangling bond near the valence-band maximum (VBM),[2] the spectroscopically correct nonlocal pseudopotentials yield this state near the conduction-band maximum (CBM), much like the empirical tight-binding result.[4]]

III. THE METALLIC BONDING MODEL

The Schottky-barrier heights of metals on various semiconductors have been successfully calculated previously using the semiconductor-jellium interface model.[1] This model seeks the explanation for the barrier heights in terms of *metallic bonds* formed between the adlayer and the substrate. These bonds are then simulated by a relatively *thick* (10–20 Å) layer of jellium (with an average density of Al) in contact with an abrupt, *unrelaxed* surface.[1] Experimental evidence from photoemission studies suggests, however, that the barrier heights are already developed at less than $\frac{1}{2}$ monolayer (ML) coverage[7] when the adlayer is likely to be nonmetallic. This was illustrated convincingly for Au overlayers where it was found[7] that at the coverage where the Fermi energy is already stabilized (~ 0.2 ML) the spin-orbit splitting of the Au 5d shell (1.9 eV) is still much lower than the bulk metallic value (2.3 eV) but is larger than the atomic value (1.5 eV). This clearly indicates that the pinning adlayer is neither bulklike nor is it a free lattice gas of adatoms. Further, partial-yield experiments show that gap surface states (expected from an ideal unrelaxed surface) do not appear at low coverage,[7,11] suggesting an essentially relaxed surface geometry. In agreement with this, low-energy electron diffraction (LEED) studies[31] show at low coverage and room temperature (i.e., for unannealed samples) intensity patterns characteristic of the clean (i.e., relaxed) surface, with additional increased background signaling a disordered adlayer. This suggests that the model of a *thick* jellium layer over an *unrelaxed* substrate is inappropriate for the system at hand. One may then ask if one could test the metallic bonding hypothesis by using a *thin* ($\leq \frac{1}{2}$ ML) jellium layer on a *relaxed* surface. Perhaps not surprisingly, our self-consistent pseudopotential calculation shows that under these conditions *no Fermi-level-pinning metal-induced gap states* (MIGS) *occur.* In fact, such an ultrathin "metallic" layer is not even metallic; its bandwidth and Fermi surface are substantially different from those of the bulk metal. MIGS appear when the semiconductor initially has surface gap states (viz., unrelaxed substrate) which then hybridize with the well-developed tails of the metallic wave functions (viz., the thick metallic layer). Hence, although the thick jellium model[1] yields results that interestingly *correlate* well with the observed barrier heights, it does not explain their *physical origin;* the model fails to predict these barriers under the physical conditions in which they are actually formed. MIGS are expected[1] and found[32] to be spectroscopically important at high coverages. The basic physical characteristics of the interface (e.g., barrier heights, band bending, gap interface states) are, however, already established below a $\frac{1}{2}$ ML coverage.[7–11]

We will see below (Sec. V) that the jellium model shares an important feature with the final "weakly interacting cluster model" that we deduce: Both models stress the nondirectionality of the overgrowth adlayer. However, the jellium model is centered on a metallic nature of the bonding with the semiconductor atoms and perceives therefore the formation of a Schottky barrier as a result of the equilibration of a *bulklike* metallic Fermi energy with the semiconductor Fermi energy attendant upon charge transfer. Hence, if carried to the limit where barriers are experimentally formed (i.e., ultrathin overlayers over a largely relaxed substrate with no gap states), the model fails. In contrast, experimental evidence strongly suggests[7,11] that it is the local chemical potential of the essentially non-bulk-like adlayer, not of a well-developed metal overlayer, that dictates the electronic structure of the interface at the crucial stage where the barriers are formed. My final model makes this important distinction.

IV. THE STRONG-COVALENT-BONDING MODEL

A. Structure and stability

Consider next the theoretical models that assume an epitaxially ordered, *covalently* bonded Al adlayer. With the exception of the Hartree-Fock cluster models,[6] all such calculations[2–5] assume an Al—Ga or Al—As bond length taken from the bulk materials[33] (e.g., 2.43 Å, as in GaAs or AlAs). I first show that this Al—substrate bond length is grossly in error, making the predictions of these calculations questionable. I next show that calculations with a corrected bond length predict electronic spectra that are in sharp conflict with photoemission data. I then show that the physically correct bond distances imply that the interadatom bonds are stronger than the bonding to the substrate, favoring adatom cluster formation over adatom—substrate chemisorption bonds. Finally, I show that the weakly interacting cluster model agrees with the available experimental data and leads to a new and fundamentally different view of the morphology and spectroscopy of such interfaces.

The parametrization of the tight-binding Hamiltonian matrix elements[3–5] $H_{ij}(d)$ for Al, Ga, and As as well as the choice of adatom—substrate bond distances d for Al—As (Refs. 2 and 4), In—As (Ref. 5), and Ga—As (Refs. 3 and 4) in TB and pseudopotential calculations has previously been based exclusively on data obtained from the corresponding fourfold coordinated bulk semiconductors. In both the valence-bond picture and the configuration-interaction representation the electronic configuration of this multicoordinated bulk column-III atom is dominated by the excited form s^1p^2 [denoted here as A(III)]. On the other hand, the column-III atom adsorbed on the surface is likely to retain initially its monovalent ground-state atomic form s^2p^1 [denoted here as A(I)]. The choice between A(I)-like or A(III)-like matrix elements and characteristic bond lengths in surface electronic structure calculations is immaterial as long as the theory allows for a variational rearrangement of the electronic charge density (viz., self-consistent calculations with pseudopotentials that describe equally well all of the relevant electronic configurations) and of the bond distances (viz., a quantum-mechanical energy minimization). As neither type of variation was previously allowed in semi-infinite interface calculations,[1–5] the selection of an underlying electronic and structural configuration becomes important. I will first demonstrate the significant consequences of these different choices using simple semiclassical arguments and then present a quantitative self-consistent variational calculation of the equilibrium bond lengths. These considerations show that the Al-substrate bond is about 20% longer than previously assumed.

It seems unlikely that an A(I)-As or A(I)-Ga bond will be similar to the A(III)-As and A(III)-Ga bond. In fact, while the monovalent form of boron B(I) (e.g., BF) does not occur in nature under normal conditions as a stable molecule or crystal,[28] one finds that, going down column III, the monovalent form of Al(I) (e.g., AlF) exists only at high temperature when bonded to strongly electronegative atoms such as fluorine[28] (Pauling's electronegativity of 4.0) and chlorine (electronegativity of 3.0) but not with Br or I (electronegativity of 2.8 and 2.5, respectively). In contrast, further down column III, indium and thallium form strong monovalent bonds both in the gas phase and in the solid state even with the least electronegative halogen atoms Br and I.[28,34(a)] Since the Al deposited on the GaAs(110) surface has an atomic ground state of Al(I) (s^2p^1) it seems unlikely that a strong covalent or ionic bond will be formed between Al(I) and arsenic (electronegativity of 2.0) or Al(I) and

TABLE I. Standard heats of formation [Ref. 34(a)] of the monovalent and trivalent forms of column-III halides in molecular and solid-state configurations (kcal/mol). Notice the increased strength of the monovalent bond as one proceeds down the column and the increased strength of the trivalent bond at the top of the column. The strength of the homopolar bond in column-III atoms, on the other hand, decreases as one goes down the column. This is evidenced in the bulk cohesive energies of B, Al, Ga, In, and Tl: −5.77, −3.39, −2.81, −2.52, and −1.88 eV/atom, respectively. The B−B, Ga−Ga, and In−In chemical bond energies are −3±0.2, −1.2±0.2, and 1±0.1 eV, respectively [Ref. 34(b)].

	Monovalent			Trivalent	
	Gas	Solid		Gas	Solid
BF	>>0		BF_3	−271.4±0.3	
BCl	>>0		BCl_3	−96.3±2.0	
BBr	>>0		BBr_3	−48.8±0.3	
BI	>>0		BI_3		
AlF	−63.4±0.8		AlF_3	−289.0±0.16	−361.0 ±0.3
AlCl	−12.3±1.0		$AlCl_3$	−139.7±0.7	−168.6 ±0.2
AlBr	+ 3.8±3.0		$AlBr_3$	−98.2±0.4	122.15±0.2
AlI	+ 14.3±2.0		AlI_3	−49.0±1.8	−73.9 ±1.5
GaF			GaF_3		
GaCl			$GaCl_3$		−125.4 ±1.1
GaBr			$GaBr_3$		−92.4 ±1.0
GaI			GaI_3		57.2 ±2.9
InF			InF_3		
InCl		−44.5 ±2.0	$InCl_3$		−128.4 ±2.0
InBr	−12.3±2.5	−41.9 ±2.0	$InBr_3$		−98.2 ±2.0
InI		−27.8 ±2.0	InI_3		−56.1 ±3.0
TlF		−77.8 ±1.1	TlF_3		−136.9 ±2.5
TlCl		−48.8 ±0.4	$TlCl_3$		−79.3 ±2.5
TlBr		−41.27±0.2	$TlBr_3$		
TlI		−29.6 ±0.2	TlI_3		

gallium (electronegativity of 1.6). Conversely, if a weak bond does exist, it will most likely be characterized by a bond length larger than the multivalent bulk Al−As or Ga−As bonds. These considerations are born out by the heat-of-formation data for the monovalent and trivalent forms of the column-III halides in their molecular and solid-state modifications, as presented in Table I.[34] Clearly, as one goes down column III, the monovalent form is stabilized and occurs even with weakly electronegative halides.

This pattern is readily understood in terms of the increase in energy required to promote the monovalent s^2p^1 form to the trivalent s^1p^2 form; our atomic total energy calculations yield 2.7, 3.3, and 4.7 eV for B, Al, and Ga, respectively. (Note that the promotion energy is adequately described as a difference in total energies of the two configurations rather than the difference in one-electron orbital energies in a single configuration.) Only a species far more electronegative than Ga or As could then stabilize a strong bond to Al(I) through ionic charge transfer. This has an immediate implication on the equilibrium bond length. Extrapolation to X=Ga in the linear plot of the AlX bond length (1.65, 2.13, 2.29, and 2.54 Å for X=F, Cl, Br, and I, respectively[35]) versus the X-atom electronegativity yields an Al(I)−Ga bond distance of $d=3.1$ Å, far larger than that previously inferred from Al(III) bulk data (2.43 Å).[2−5] Indeed, a cluster-type HF calculation[6] for Al(I) bonded to Ga in $GaAs_2$ yields d(Al−Ga)=3.04 Å [and a small binding energy of −(0.4−0.6) eV]. Since the two-center matrix elements $H_{ij}(d)$ appearing in surface calculations[2–5] scale approximately[36] as d^{-2}, the use of $d = 3.1$ Å rather than $d = 2.43$ Å (an error of a factor of 0.6 in H_{ij}) is likely to alter significantly the previous conclusions for Al/GaAs. While strongly localized interface states may be affected only weakly, the energy of adatom-substrate bonding-antibonding pairs, which often determine the pinning levels,[2,3] may be drastically affected (see below). In fact, much smaller changes in the geometry of surface Ga and As atoms attendant upon relaxing the clean ideal surface produces a drastic energy shift in the gap states, pushing them into the continuum.

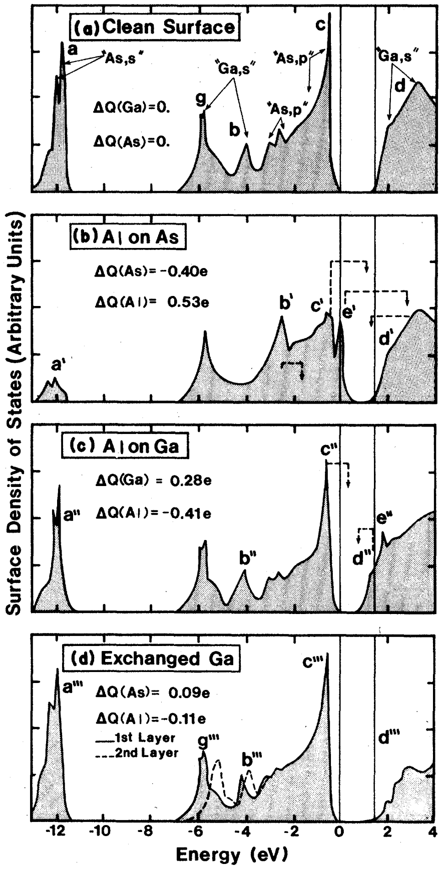

FIG. 1. Smoothed-surface density of states for different chemisorption models of Al on GaAs(110) obtained with a relaxed surface geometry and the calculated equilibrium Ga—Al and As—Al bond lengths. The dashed arrows indicate the positions of the main structures for an unrelaxed surface geometry and shorter (bulklike) adatom substrate bond lengths, used in previous calculations (see discussion in text).

This analysis and the findings indicated in Ref. 30 and Sec. II suggest the undertaking of new quantitative self-consistent calculations to reexamine the predictions of the covalent bonding hypothesis. Using the distances $d = 2.8$, 3.0, 3.2, and 3.4 Å and a relaxed surface geometry, a total energy minimization was performed (method described in Ref. 15) in a repeated-cell model for $\frac{1}{2}$ ML of Al bonded to either Ga or As, where Al is located in a symmetry plane perpendicular to the surface; positioning of Al along the dangling bonds yields similar results for the energy levels. The large basis set used in this calculation (600 plane waves in the direct Hamiltonian matrix plus an additional 1000 waves in a Löwdin perturbation) is sufficient to locate the minimum of the binding curve with a precision of a ± 0.1 Å; however, the relative precision in the absolute binding energy is only ± 0.3 eV. This yielded at equilibrium $d(\text{Al—Ga}) = 3.1 \pm 0.1$ Å and $d(\text{Al—As}) = 3.0 \pm 0.1$ Å, in good agreement with my semiclassical estimates but in disagreement with the values ($d = 2.43$ Å) assumed in previous calculations. The binding energy to the Ga site is calculated to be at equilibirum -0.4 ± 0.3 eV, with a somewhat lower value of -0.3 ± 0.3 eV on the As site, confirming the weakness of the bonds to the substrate. Despite the apparent high precision of the calculated bond lengths it seems only fair to assume that the overall surface geometry is in fact not known very accurately at this time; this will require an extensive optimization of *all* the structural degrees of freedom including the Al—Al distance in a nonperiodic model for the adlayer. While the present results are likely to be far closer to the correct singly-coordinated bond lengths than the values inferred from bulk data, I base my major conclusions below on results obtained from the two extreme sets of bond distances bracketed in Fig. 1. Figures 1(a)—1(c) show the predicted one-electron spectra of the Al and first substrate layer calculated with the equilibrium bond lengths. The dashed arrows point to the positions of the main peaks obtained in calculations assuming short bonds and an unrelaxed ideal substrate. Figure 1(a) shows for comparison the results for the clean surface.[13] I summarize below the salient features of the spectra, indicating the major points of disagreement between my calculated spectra and experiments. I discuss the various structures a' to e' (As site bonding) and a'' to e'' (Ga site bonding) in decreasing order of binding energies.

B. Spectroscopy of *Al* bonded to As [Fig. 1(b)]

I note the following.

(i) The lowest state a' is a substrate As s state, strongly attenuated relative to the corresponding clean-surface state a due to the capping of the surface As by A(I). The local density of states on the second subsurface layer shows this peak to be restored 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[13] [Fig. 1(a)]. Since the state b' is strongly localized, one may expect that at zero order the energy separation $\Delta_{b'g}$ of b' from g will scale with the difference in the corresponding atomic orbital energies $\Delta\epsilon_{ss}(A)=\epsilon_s[\mathrm{Ga(III)}]-\epsilon_s[A(\mathrm{I})]$. One indeed finds in the calculation by Mele and Joannopoulos[4] that b' is 3.5 eV above g for $A=\mathrm{Al}$, while my simple atomic prediction yields $\Delta\epsilon_{ss}(\mathrm{Al})$ of 3.5 to 2.8 eV for spin down and up, respectively. Similarly, Chadi and Bachrach[3] find for $A=\mathrm{Ga}$ that b' is about 1.8 eV above g, while the atomic prediction yields $\Delta\epsilon_{ss}(\mathrm{Ga})=2.1$ to 1.6 eV, and Huijer *et al.*[11] find for $A=\mathrm{In}$ that b' is about 1.5 eV above g, compared with the atomic value $\Delta\epsilon_{ss}(\mathrm{In})=1.9$ to 1.4 eV. A notable exception is the pseudopotential result of Chelikowsky *et al.*[2] for Al on GaAs: Their state b' seems to lie within 1.2 eV of the substrate Ga state g, in contrast with both the TB result of Mele and Joannopoulos[4] (3.5 eV) and the atomic estimate (this observation is due to Joannopoulos[37]). This is consistent with the findings of Ref. 30 and Sec. II indicating that the local semiempirical pseudopotential for Al is more appropriate to Ga.

Experimentally, one finds $\Delta_{b'g}$ to be 1.5 eV for In [binding energy relative to the valence-band maximum of $E_{b'}=-5$ eV (Ref. 5)] and 0.9–1.3 eV for Ga [$E_{b'}=-5.6$ eV (Ref. 10)]. For Al, which is expected to have the largest shift, no reproducible b'-like structure was found by Skeath *et al.*[8] and Huijer *et al.*,[11] whereas Bachrach *et al.*[10] found a weak structure at $E_{b'}=-6.1$ eV ($\Delta_{b'g}\cong 1.5$ eV) that has not been reproduced in other experiments.[8,11] However, even if experimentally $\Delta_{b'g}\neq 0$ for Al, we notice that the *trend* in the binding energies—$E_{b'}=-6.1$, -5.6, and -5 eV for Al, Ga, and In, respectively—is the reverse of that obtained both in the interface calculations and from the atomic estimates. The state b' hence cannot have the same origin for Al, Ga, and In. This is consistent with the known chemical trend discussed above indicating a change in the stability of the singly coordinated bond between a column-III atom and the substrate as one proceeds down the column. Recent careful experiments[11] showing $\Delta_{b'g}\approx 0$ for Al indicate that no bonding of Al(I) to the substrate occurs. This experimental finding also conflicts with the structural relaxation model constructed in Ref. 4 to produce $\Delta_{b'g}=1.5$ eV for Al. Since the Ga(I) atomic s level lies about 1.5 eV above both the Ga(III) and the Al(III) s levels, Mele and Joannopoulos[4] suggested that one can explain a shift $\Delta_{b'g}=1.5$ eV by assuming that Al is exchanged with the Ga and the exchanged Ga(I) is bonded to the substrate Al(III); hence $\Delta_{b'g}=\epsilon_s[\mathrm{Al(III)}]-\epsilon_s[\mathrm{Ga(I)}]\cong 1.5$ eV. I note, however, that even if $\Delta_{b'g}$ were 1.5 eV, this shift could be equally well explained as an Al(III) s level above the substrate Ga(III) s level. Such Al(III)-like levels may exist in Al_n clusters residing on the substrate. This distinction is not easily made by a TB theory which in its standard form the matrix elements are deduced from bulk data (i.e., exclusively for multivalent species).

I conclude that the experimental structure b' is inconsistent with the model of Al(I) bonded to the substrate As, and an Al-Ga exchange is not needed to explain it.

(iii) The peak c' is an As-A(I) p-like dangling-bond state replacing the clean-surface As state c.[13] Its position with respect to the valence-band maximum depends critically on the strength of the $A(\mathrm{I})-\mathrm{As}$ bond: For Al, where the s state is closer to c' than the Ga s state, the c' state lies below the conduction-band minimum, using[4] $d=2.43$ Å (but below the VBM with the present geometry). For Ga, having a lower-lying orbital energy, the c' state is nearly unshifted from the clean-surface As dangling-bond state c, lying at the VBM.[3] Since the free-atom In(I) s state is even higher in energy than the Al(I) s state, one expects the c' state for In-GaAs to lie at the bottom (or above) the conduction-band minimum. These trends are born out by the TB calculation of Mele and Joannopoulos[4] (Al-GaAs and Ga-GaAs) as well as by the calculation of Chadi and Bachrach[3] (Ga-GaAs). In both calculations the state c' is below the Fermi energy. The calculation by Chelikowsky *et al.*[2] for Al-GaAs places the c' state below the VBM, as expected for Ga-GaAs but not for Al-GaAs. This is consistent with the findings discussed in Sec. II.

Experimentally, no strong emission is observed from filled gap states such as c' for Al-GaAs, Ga-GaAs, or In-GaAs.[5,8,11] Since the c' state is predicted to be localized on the substrate As, one does not expect that the sharp c' peak obtained in the TB calculation will be broadened by Al-Al interactions, leading to a weak and experimentally undetectable predicted structure. I conclude that the calculated state c' in the covalent-bond model for Al disagrees with experiment for either of the bond lengths used in the calculation.

(iv) The peak d' is a substrate cation state appearing in the TB calculations at E_F for $A = \text{Al}$,[4] Ga,[3] and In,[5] and just above the CBM in the present calculation for Al. Since the bonding of A(I) to As does not alter significantly the cation states, d' is close to d. In the TB calculations for Al the state d' is responsible for the pinning of the Fermi energy at ~ 0.2 eV below the CBM. Experimentally the pinning occurs at 0.75–0.95 eV below CBM.[7]

(v) The state e' is an interadatom A-A p-like state appearing in pseudopotential calculations below the substrate cation state d' and leading to pinning at 1 and 1.3 eV below the CBM for $d = 2.43$ Å (Ref. 2) and $d = 3.1$ Å, respectively. The tight-binding model,[3,4] failing to include any direct interadatom interactions (which stabilize e' but leave d' unchanged), places e' *above* d' and hence leads to a fundamentally different pinning mechanism. Experimentally,[7–11] however, one does not find any evidence in the photoemission spectra for sharp and partially occupied gap states such as d' or e'; one would have to attenuate the calculated peaks by an unlikely factor of nearly 2 orders of magnitude (e.g., due to averaging over a number of surface layers) to explain their absence in the observed spectra.

C. Spectroscopy of A(I) bonded to Ga [Fig. 1(c)]

The major differences from the previous case are as follows.

(i) The As s state a'' is unattenuated relative to the clean-surface state a since in this geometry A(I) does not cap the surface As.

(ii) The peak b'' is unshifted but has a somewhat increased intensity.

(iii) The cation p-like bonding state d'' is now stabilized by bonding of A(I) to Ga and appears in the gap below the A(I)-A(I) state e'', predicting pinning at much too low energies: 0.4 eV below the CBM for $d = 3.1$ Å relative to the observed value of 0.75–0.95 eV. Owing to its two-center (A-Ga) nature (and resulting mixed angular momentum content) and substantial predicted intensity, matrix element effects are not expected to reduce the intensity of the d'' state below detection. Further, this strong bond to the surface Ga will tend to change considerably the Ga 3d exciton state occuring at the same final energy as d''. In contrast, however, d'' is not observed experimentally in the gap[8]; the Ga 3d exciton is unshifted in energy and unchanged in shape upon Al deposition.[8,11]

D. Charge transfer

The insets to Fig. 1 show the calculated charge transfer ΔQ associated with surface atoms with respect to the clean-surface and atomic Al, obtained by integrating the calculated charge densities in spheres. (Such point charges, much like Mulliken charges, are therefore nonobservables; only their signs, which indicate the direction of the overall charge transfer, are used in the argument below.) The calculated values are consistent with a simple chemical model: When Al is placed on the substrate As [Fig. 1(b)] the As lone-pair orbitals overlap with the Al empty p orbitals, leading to negatively charged[6] Al (a physically improbable situation due to the higher electronegativity of As). When Al is placed on Ga [Fig. 1(c)], the Al p electrons are delocalized into the empty Ga orbitals, leading to positively charged Al. In case 1(b) one expects a shift of the As (Al) core states to higher (lower) ionization energies, whereas in situation 1(c) the As (Al) core states are expected to shift to lower (higher) ionization energies. In contrast, Huijer *et al.*[11] found that for $\sim \frac{1}{3}$ ML of Al deposited at room temperature, the Ga 3d core emission and the surface-sensitive core exciton are weakened in intensity but unshifted relative to the clean surface. In agreement with this, Skeath *et al.*[8] found at very low coverages a *rigid* shift (i.e., band bending, not a chemical shift) of the Ga and As 3d emission towards lower binding energies by 0.6 ± 0.1 eV, without any change in the line shapes. The significant point here is that all theoretical models that assume either an adatom–substrate covalent bond [Figs. 1(b) and 1(c)] or a metallic bond predict a charge exchange between the substrate and adlayer; the net charge then has an opposite sign on both sides of the interface. These models hence lead inevitably to (substantial[4,6]) core shifts, having opposite signs for both sides of the interface, a result that is in sharp conflict with experiment.

I conclude that the epitaxial covalent-bonding model, if carried out with physically correct adatom–substrate bond lengths and accurate pseudopotentials, leads to one-electron spectra that cannot be reconcilded with experimental results.

V. THE WEAKLY INTERACTING CLUSTER MODEL

A. Stability arguments

Previous models of the Al/GaAs(110) interface, imposing simplistically short and bulklike Al—substrate bonds,[1–5] have led naturally in calculations with a single fixed bond length to the notion that the source of stability of the system lies in these chemisorption bonds. We have seen that far longer bonds—consistent with the fact that the adsorbed Al retains largely its monovalent atomic configuration rather than the excited bulklike multivalent configuration—are obtained in a variational total energy calculation. When such long bonds are used in an epitaxially ordered bonded model calculation for $\frac{1}{2}$ ML of Al bonded to either Ga or As, we have seen that one obtains one-electron spectra that contradict in many respects the experimental data. It will be argued now that the epitaxially ordered model is unlikely to be physically correct also because it is unstable with respect to the formation of Al_n clusters. The importance of interadatom interactions was first stressed by Chelikowsky *et al.*[2]

Bonding of Al to any of the semiconductor sites results, even at coverages as high as $\frac{1}{2}$ ML, in a very large Al—Al separation of 3.96 Å (next-nearest-neighbor substrate distance) and small binding energy $\mathrm{BE}\sim-(0.3-0.6)$ eV.[6] These values are well outside the stability range of Al systems: For metallic Al and the diatomic Al_2, respectively, $d(\mathrm{Al-Al})=2.86$ and 2.50 ± 0.1 Å and $\mathrm{BE}=-3.4$ and -0.85 ± 0.15 eV/atom. (The values for Al_2 were obtained from a self-consistent nonlocal pseudopotential calculation for the $^3\Sigma_g$ ground state.)

In the absence of strong bonds with the substrate, it is unlikely that a long (3.96 Å) and weak Al—Al bond will be stable. Since the present calculation shows that the adatom—substrate bonds are weak, a configuration of a lattice gas of adsorbates which are mutually noninteracting is likely to be unstable towards partial condensation in which the above mentioned Al-Al energy is released. These considerations suggest that, while at thermal equilibrium a certain fraction of Al may be bonded to the substrate, the stress induced by the lateral spreading pressure will induce decoupling of some atoms from sites to form the stabler Al_n clusters. In doing so the system loses an energy $E_{\mathrm{ad}}^{(m)}$ required to desorb m atoms from their sites, it then needs to overcome an activation barrier E_D for surface diffusion and eventually gains the bonding energy $E_b^{(n)}$ released upon forming a n-atom cluster. The net energy associated with cluster formation is hence $\Delta(n,m)=E_b^{(n)}-E_{\mathrm{ad}}^{(m)}$. Note that in general $n\neq m$ since an Al_n cluster may still have $n-m$ of its atoms in an adsorptive contact with the substrate (for planar clusters $m=0$ while for three-dimensional clusters $n>m\neq0$). Our foregoing discussion permits a simple evaluation of the magnitude of $\Delta(n,m)$. One expects that the Al—Al bond lengths and binding energy per atom in an Al_n cluster to be intermediate between the values of the diatomic Al_2 and the bulk metal Al_∞; i.e., 2.50—2.86 Å and $-(1-3)$ eV/atom, respectively. On the other hand, the range of the average desorption energy per site $E_{\mathrm{ad}}^{(m)}/m$ can be estimated from the total energy calculation of Swarts *et al.*[6] for a single Al atom adsorbed on the substrate Ga, or from the present calculation for $\frac{1}{2}$ ML of Al bonded to all surface Ga sites. The range obtained is -0.45 ± 0.15 eV/site. Clearly, for any $n>m$ the clustering reaction is exogenic. The kinetics of the process is then dictated by E_D/kT, the jump attempt frequency ω, and the average adsorption site separation d (the average diffusion velocity being $\sim\omega d e^{-E_D/kT}$).

It is important to realize that in the present model the substantial excess energy $\Delta(n,m)$ is available at the surface to promote both chemical reactions and defect formation. This has not been previously recognized because the chemisorption models permit only the relatively small condensation energy (i.e., chemisorption energy plus the deexcitation energy of the impinging particles) to be available for promoting surface chemistry.[7,9] This then leads in the chemisorption models to an unexplained puzzle: Since the Al—substrate bonds are weak (on the scale of bulklike Al—Al bonds) the condensation energy falls short of activating the formation of surface vacancies [$\sim$2 eV (Ref. 38)] or an Al-Ga exchange. The situation with Al is fundamentally different from the one encountered for *strongly* chemisorptive species such as oxygen[39] and chlorine[40] on GaAs(110) or aluminum on the polar surface GaAS(100).[41,42]

When one proceeds down column III from B and Al to Ga, In, and Tl, the interadatom bond energy $E_b^{(n)}$ decreases. For example, the present calculation for In_2 yields a binding energy of -0.45 eV/atom while the value for Al_2 is -0.85 ± 0.15 eV/atom. The same trend is apparent in the bulk cohesive energies $E_b^{(\infty)}$ for column-III solids: For B, Al, Ga, In, and Tl the values[43] are -5.77, -3.39, -2.81, -2.52, and -1.88 eV/atom (notice that cluster binding energies for $n\simeq 2-7$ are typically only 10–20% of the bulk values). At the same time the stability $E_{\text{ad}}^{(m)}$ of the monovalent bond $A-X$ increases (Table I and the arguments surrounding it in Sec. IV). This suggests that down the column $\Delta(n,m)$ may eventually become positive: At the bottom of column III (In or Tl) a singly coordinated bond to the substrate may be favored over interadatom clustering while at the top (B or Al) the ground state of the system is likely to involve clustering. Indeed, the loss spectrum of adsorbed In shows no indication for metalliclike In clusters: The *d*-exciton doublet has the same position as in InAs.[5] The former situation (In,Tl) is in essence similar to that encountered for Cs/GaAs(110) (Ref. 44): The large *s-p* promotion energy makes Cs and Tl effectively monovalent. Despite the large differences in electronegativities and orbital character (Cs is s^1 and Tl is p^1) both atoms are expected to form monovalent chemisorptive bonds and not show either clustering or a chemical exchange with surface atoms.[44] Although detailed variational calculations[45] of $E_{\text{ad}}^{(m)}$ and $E_b^{(n)}$ (i.e., optimizing both Al–Al, and the Al–substrate distances as well as the *n* value) will be necessary to establish the precise magnitude of $\Delta(n,m)$ and the transition point (if it exists) between clustering $[\Delta(n,m)<0]$ and chemisorption $[\Delta(n,m)>0]$, there seems to be little doubt that the indicated *trend* is correct. In assuming a chemisorption behavior for *all* column-III elements on GaAs(110), previous models[1–6] have ignored this important distinction between the two fundamentally different regimes.

One could similarly estimate the trends in bonding characteristics for different substrates: With a more covalent low-band-gap substrate (e.g., silicon) one knows[46] that Al initially forms intermediate structures, (i.e., between that of the macroscopic epitaxial film and that of the substrate film) followed eventually by an ordered epitaxy. On the other hand, for very ionic substrates (e.g., alkali halides[47]) one finds three-dimensional clusters of the adatoms rather than a multilayered ordered epitaxy. Between the two limits one expects a phase transition (much like that observed in the variation of other Schottky-barrier properties with ionicity[48]) between the ordered epitaxy regime and the isolated three-dimensional cluster regime. Our foregoing discussion strongly suggests that Al on GaAs(110) belongs to the more ionic side of this phase diagram.

At this time, little is known experimentally about cluster stability. One expects, however, to have a distribution of cluster sizes $n(T,D)$ depending on the temperature T and the average deposition thickness D. The cluster binding energy per atom $E_b^{(n)}$ is usually a nonmonotonic function of *n*, as can be deduced from simple models for both two-[49] and three-dimensional[50] clusters. A simple application of statistical mechanics and kinetic theory[51–53] permits the deduction of the distribution of cluster sizes as a function of $\Delta(n,m)$ and temperature, as well as the calculation of the most probable nucleus size and the nucleation rate. Clusters of sizes $n=5-10$ are very often predicted[51,52] and observed[54–59] in various systems.

I note here that the cluster phenomena cannot be adequately modeled by the jellium approach[1]; such models not only make the excitation spectra of the adlayer continuous, smooth, and metallic, but they also inevitably introduce substantial bonding with the substrate through the long-range tails and Friedel oscillations of the abrupt jellium layer.[60,61] In fact, it is the *discreteness* of the cluster size *n* which plays a major role in determining its spectrum, formation energy, and interaction with the substrate.

Various phase transitions may occur among the different structures in the surface phase diagram. As the temperature increases the condensation of the attractive particles is enhanced, resulting in larger clusters. Increasing the average coverage leads to a decrease in interisland separation and a rapid increase in average island size. Clusters of different sizes may likewise have varying Al–Al bond lengths ranging from the diatomic value of 2.50 Å to the bulk metallic value of 2.86 Å.

I close this section by making a few observations on the clustering kinetics and morphology based on the characteristics of the function $E_b^{(n)}$ versus *n* (cluster cohesion per atom versus cluster size). Precise calculations of $E_b^{(n)}/n$ are available for some s^1 and s^2 elements [e.g., Li (Ref. 62), Be (Ref. 63), Mg (Ref. 64)], but to the author's knowledge, no such calculations are available for Al_n. The feature of central importance here is that $E_b^{(n)}/n$, as calculated for structure-optimized clusters is often a *nonmonotonic function of n* for small *n* and may even change sign at some critical cluster size n^*. For Be_n clusters, for example, large-basis-set Hartree-Fock calculations[63] yield $E_b^{(n)}/n$ 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_n configuration-interaction calculations[62] yield values of 0.0, -0.45, and -0.43 eV/atom, respectively, for $n=1$, 2, and 3 [the bulk cohesive energy being -1.63 eV (Ref. 43)]. All values are given here with respect to the ground-state atoms; positive $E_b^{(n)}/n$ values indicate, therefore, clusters which are unbound relative to the dissociated system.

The nonmonotonic behavior of $E_b^{(n)}$ has a number of immediate implications to the present discussion.

(i) If the smallest cluster size which leads to a system that is bound relative to its fragments is denoted by n^*, then at the absence of external stabilizing mechanisms a simultaneous n^*-body encounter is necessary to produce a stable cluster. For $n^*>2$ the probability of such an event (decreasing as a power law[51]) is exceedingly small; the clustering reaction may then be vanishingly slow. For Be_n clusters, for example, the data given above show that $n^*=4$ (i.e., $Be_2 \rightarrow 2Be$, $Be_3 \rightarrow Be_2+Be$, and $Be_3 \rightarrow 3Be$, but Be_4 is stable with respect to 4Be, $2Be_2$, and Be_3+Be) so that the clustering from monomers is an unlikely event. My calculation of $E_b^{(2)}$ for Al_2 and In_2 yields $E_b^{(2)}<0$ so that for these systems $n^*=2$ and clustering is possible.

(ii) For some elements one may find a second critical cluster size n^{**} (equal or larger than n^*): Clusters of size n^{**} are more stable than some *larger* clusters (i.e., $E_b^{(n^{**})}<E_b^{(m)}$ for a few m values with $m>n^{**}$). In this case, cluster growth is inhibited above the size n^{**} by the low probability of the simultaneous $n^{**}-m$ events. For example, the Be data show $n^{**}=5$, i.e., Be_5, if formed, will disproportionate into Be_4+Be. In such cases the distribution of cluster sizes will have a peak at n^{**}. At present, no information is available on possible n^{**} values for clusters formed from column-III elements.

(iii) The properties indicated in (i) and (ii) above suggest that, in general, one may expect to find forbidden cluster sizes, e.g., $n=2$, 3, and 5 for Be_n or $n=3$ for Li_n. No comparable information exists for column-III clusters.

(iv) Cluster stability calculations indicate that for polyvalent elements with fewer than four valence electrons, three-dimensional clusters are far more stable than the planar two-dimensional clusters for obvious chemical reasons (e.g., Ref. 63). For example, a planar Be_4 cluster is unbound ($E_b^{(n)}>0$) for all interatomic distances while a tetrahedral cluster is stable; the stability of three-dimensional boron polyhedra (e.g., Ref. 65) is likewise well documented. Two-dimensional Al or Ga rafts suggested in Ref. 12 seem unlikely to occur on GaAs(110) at low coverage.

The possible occurrence of $n^*>2$, $n^{**}\geq 2$, and forbidden cluster sizes [points (i)—(iii) above] is a manifestation of the nonmonotonic nature of the function $E_b^{(n)}/n$. Note that this behavior is intimately connected with the existence of important *multibody interaction* terms within a cluster: The simplistic view that $E_b^{(n)}$ can be modeled by pairwise additive two-body interactions usually leads to a monotonic function $E_b^{(n)}$. Analysis of the calculated $E_b^{(n)}$ values in terms of multibody terms, $E_b^{(n)}=E(2,n)+E(3,n)+\cdots+E(n,n)$, shows[63] for Be_4 that the two-body term is $E(2,n)=3.83$ eV, the three-body term $E(3,n)$ is -5.88 eV, and the four-body term $E(4,n)$ is 1.21 eV while the total binding $E_b^{(n)}$ is -0.84 eV. In fact, the multibody terms are exclusively responsible for the extra stability of the three-dimensional clusters relative to the planar clusters.[63] These features should be considered in any detailed discussion of the energetics of the weakly interacting cluster-semiconductor interface.

B. Predictions of the weakly interacting cluster model

This model based on weakly interacting clusters for the initial stage of the low-temperature (unannealed) Al deposition on GaAs(110) leads to a number of interesting predictions regarding the spectroscopy [points (i)—(iii) below] and structures [points (iv)—(vii) below] of the interface, all of which conflict with the ordered covalent-bonding model.

(i) Since the Al atoms in Al_n clusters are multicoordinated and have most of their bonds chemically saturated, one expects that the bonding of the cluster to the substrate will be weaker and less directional than in the chemisorption of independent adatoms. Such clusters will be spread across the surface due to their low diffusion barrier. The model predicts therefore, that the valence-band spectral features will be similar to those of the *clean surface,* lacking the sharp structures characteristic of strong chemisorption bonds. This is the only model so far which agrees on this issue with the observed valence-band photoemission results.[8–11]

We note that the attenuation of the GaAs energy distribution curve (EDC) structure with increasing Al or Ga (Refs. 7 and 12) coverage (without changing the spectral shapes) is consistent both with the formation of two-dimensional adlayer rafts[12] or three-dimensional clusters. Assuming, for simplicity, spherical clusters with an average Al—Al bond distance equaling the covalent radius, one finds that even at $\frac{1}{2}$ ML coverage, clusters of size $n=5-9$ atoms will "shadow" as much as 35% of the substrate area. Taking the conservative estimate that only substrate atoms shadowed directly by the clusters will show a spectral attenuation (i.e., neglecting the long-range Coulomb screening), this amount of attenuation accounts for the observed data.[66] While attenuation data do not determine the geometry of the clustered adlayer (two- versus three-dimensional clusters), stability considerations[62–65] strongly suggest that three-dimensional (i.e., multicoordinated) metallic clusters are far more stable than two-dimensional arrays of metal atoms.

(ii) The model predicts that the core energy levels of the Al adlayer (e.g., $2p$ levels) will change with coverage between 0.1 ML and $\sim\frac{1}{2}$ ML, reflecting the changing chemical environment with the average n value attained at each coverage and temperature. In contrast, the epitaxial covalent model predicts a constant core level energy in this coverage range because just more of the same Al—substrate bonds are formed. Furthermore, the latter model predicts that the observed Al $2p$ energy will correspond to an Al—As or Al—Ga bond. Interpolation of the Al $2p$ binding energy for nine AlX compounds[67] places this energy at 74.5 ± 0.5 eV (i.e., 1.5 ± 0.5 eV below the bulk metallic value). In contrast, the present model predicts this value to be *above* the bulk metallic value [72.6 eV (Ref. 67)] and *below* the value corresponding to bonding with the substrate (74.5 ± 0.5 eV); as the average n value changes from small values (covalent molecular clusters) to $n>100$ (metallic drops) and finally to a coalesced metallic phase, the Al $2p$ level is predicted to converge to the metallic limit. In agreement with this, one finds experimentally[8,10] that (a) the Al $2p$ level changes with coverage in the range of 0.4—1.5 Å ($\approx\frac{1}{2}-1$ ML) by as much as 0.3 eV (over and above band bending), and (b) the change is bracketed by the limits predicted by the present model; at somewhat higher coverage the level converges to the bulk metallic value, not the value expected from Al—substrate bonding.

(iii) The model predicts that the spectral features above the VBM and below E_F will be characteristic of cluster states, not of chemisorptive bonds. The electronic structure of isolated small Al$_n$ clusters ($n=5,9,13,19,25,43$) was previously calculated by Salahub and Messmer.[68]

There exists a rich literature on the observed spectral properties of small "free" Al clusters (e.g., Refs. 69—73). It is possible that the nature of the clusters at the early stage of Al adsorption on GaAs(110) may be elucidated by considering the known special properties of such clusters. The main salient features of the theoretical[68] and experimental spectroscopic studies[69–73] are the following. (a) The clusters are nonmetallic until a critical size of about 50—150 atoms is reached.[55,68] Compared with larger clusters, the smaller clusters have a substantially narrower valence-band width, smaller interband splittings, more localized structures near E_F, and often even finite band gaps.[68] The density of states of the small clusters and the directionality of the electronic charge density are poorly approximated by the free-electron jellium model.[68] (b) As the cluster size increases one observes a transition from the molecular limit ($n\lesssim40$) to a metallic-drop limit, followed eventually by a true bulk metal.[55,68] (c) The Debye temperature of small Al particles is considerably reduced relative to the bulk metal; surface-related phonon softening and an enhancement of the superconducting transition temperature are apparent.[69] (d) The far-infrared (0—150 cm^{-1}) absorption spectra of small Al particles[69–72] shows an unusual parabolic frequency dependence possibly related to the Gorkov-Eliashberg theory of periodic frequency dependence of the electronic susceptibility of small metallic particles. (e) Small Al$_n$ clusters show in the visible spectrum an absorption band which does not occur in the free atom or bulk metal.[73] (f) The x-ray photoemission spectra of small metallic particles show an increase in the linewidth with decreasing particle size due to the reduced screening of the core hole.[74] (g) The plasmons exhibited by small metallic particles are shifted to higher energies and show distinctive secondary structure above the plasma frequency.[75]

While at present the spectral resolution attained at the energy region between the VBM and E_F seems too low to establish spectroscopically the transition between the molecular-cluster and metallic-drop limits, the experimental results do indicate some weak structures[8] and a new localized state observed in surface photovoltage spectroscopy at an energy[9] of 0.6 eV above the VBM. More effort in this direction is clearly called for.

(iv) Since in this model the molecular clusters Al_n interact only weakly and largely nondirectionally with the substrate, the adlayer will be disordered above a translational freezing temperature; the atomic structure of the substrate (i.e., relaxation) will be largely unchanged relative to the clean surface. This agrees with the low-energy electron diffraction (LEED) observations[31] at room temperature which show the same spot patterns as the clean (i.e., relaxed) surface except for a general decrease in intensity and an increased background, signaling motional disorder. This conflicts, however, with the ordered covalent-bonding model, which assumes an epitaxial arrangement even at low coverage and predicts a binding energy to the substrate many times larger than the thermal energy.

Direct observation of the growth kinetics and morphology of the initially formed clusters via transmission electron microscopy (TEM) is difficult even with improved lattice imaging techniques.[76] Such experiments may, however, ultimately elucidate the nature of the overgrowth at the initial stages where Schottky barriers are formed. Similar experiments at higher coverages (10 – 200 Å) for different systems have indeed clearly shown cluster formation: Sn deposited on GaAs has been seen to form isolated islands with incomplete surface coverage even at an average deposition thickness of 200 Å.[77] Similar thicknesses of Al on GaAs(110) results in a rough surface with isolated pyramidal clusters on it.[78]

(v) Al_n clusters with (Poisson-distributed[79]) small values of n will reside in the (110) surface troughs that have their base on the *second* subsurface layer. Under conditions in which Al is exchanged with the substrate cations[11] (e.g., annealing at temperatures of ~450 °C; see Sec. VI below), the present model leads to the possibility that *second-layer* cations will be exchanged. The epitaxial covalent-bonding model, on the other hand, requires that, at low coverage, bonds be formed only with the surface atom (having dangling bonds capable of covalent bonding to the adatoms) but not with subsurface atoms (being fully coordinated and hence incapable of covalent bonding). Exchange with *sub*surface atoms hence becomes unlikely in such a model. Recent LEED experiments and calculations[31] have independently shown that whereas the assumption of first-layer exchange[4,6] produces a very poor fit to the LEED profiles, models involving a lower-lying exchanged Al (subsurface layer) yield far better fits to the data.

(vi) Since Al(I) does have a small but negative binding energy to the substrate (Sec. IV), it is possible that for small arrival rates and low coverage and temperature such bonds would be formed. These will then provide an activation energy for cluster formation. Under these conditions one may expect that cluster formation will be supressed. (This suggestion is due to J. Van Laar, private communication.)

(vii) Since the chemical affinity of the Al_n clusters to the substrate atoms is far weaker than that of atomic Al, the present model is consistent with the fact that no low-temperature, low-coverage epitaxial growth of Al on GaAs(110) was ever observed. This is in sharp contrast with the known situation for Al growth on the GaAs(100) face[41,42] as well as for Al, Ag, and Au on InP(100) (Ref. 80): In this situation bonding to the ("metallic"-like) As lone-pair orbitals results in an epitaxial growth of AlAs layers on which Al continues to grow to form bulklike ordered layers. On the GaAs(100) face[41,42] Al was observed to grow at 20 °C in a (110) orientation as in the (100) orientation, depending on the surface preparation conditions and the nature of the exposed surface atom.[42] This phenomenon was explained by the existence of a very good epitaxial lattice matching if Al(110) is situated on GaAs(100) with GaAs[110] direction parallel to the Al[110] direction. Interestingly, whereas there also exists a good epitaxial relation for Al on the (110) face of GaAs,[78] no similar high-quality epitaxial growth on this face has as yet been reported. Instead, only a polycrystalline growth is observed with pyramidal clusters seen by TEM; for epitaxial growth to occur one needs to intentionally misorient the GaAs(110) surface.[78] This is consistent with the picture of Al_n clusters on the unreactive (110) face but not on the reactive (100) face. No TEM study exists on the morphology of the low-temperature, low-coverage deposition of Al on GaAs(110). Since the Schottky barrier is already nearly completed at these conditions, such a study may explain the nature of the particles present during the initial pinning of the Fermi level.

VI. THE EXCHANGED SURFACE

My previous discussion of Secs. IV and V pertained only to the low-coverage, low-temperature stage of the formation of the Al/GaAs(110) interface. We now consider the system's properties after annealing takes place. Central to our discussion here is the realization that different theoretical models are needed; one cannot expect to analyze the experimental data in both situations with a single theoretical model.[1-5]

From considerations of thermodynamic stability alone, one can imagine that Al will eventually react with the surface Ga to form the stabler AlAs compound (for GaAs at 298 K, $\Delta H = -19.5$ kcal/mol and $S = 15.3$ cal/deg mol, while for AlAs, $\Delta H = -29.3$ kcal/mol and $S = 14.4$ cal/deg mol[34(a)]). Previous attempts to explain the occurrence of surface exchange reactions[8-10] and adatom-induced surface defect formation[7] have, however, faced a common difficulty: In the absence of a large concentration of surface vacancies, or adatom clusters, the only source of energy that can activate the process (e.g., breaking the three surface bonds of Ga to its neighboring As atoms)—the thermal energy and the heat of condensation—are much lower than the estimated required activation energy (~ 2 eV).[38] Simple considerations of thermodynamic stabilities of the final reaction products[48(c),(d)] (i.e., compound heats of formation) are clearly insufficient to describe the system in the presence of high activation energy barriers. Furthermore, the covalent adatom—substrate bonding model assumes that bonding with the substrate occurs when the first impinging atoms land on the surface, releasing thereby their small deexcitation and adsorption energy (i.e., condensation energy). This does not explain the fact that chemical reactions do not occur immediately upon low-coverage adsorption but only after a certain coverage[9,10] (~ 2 ML) or temperature[11] (~ 450 °C) is attained. Clearly, the small increase in thermal energy attendant upon heating from room temperature to 450 °C is short of supplying the extra energy needed for activating a few—electron volt process. The cluster model provides, however, a natural explanation for this process: The excess binding energy $\Delta(n,m)$ of cluster formation is high enough (~ -2.5 eV) to promote locally surface chemical reactions. An increased temperature may be needed only to enhance the (low activation energy) surface diffusion and hence the probability of atom encounter and consequently the rate of cluster formation. These arguments suggest that the correlation between various interface characteristics (e.g., interface width, barrier heights) with the heat of formation of a substrate-adatom compounds[48] should be valid only above a few angstrom thick coverage and a high enough temperature where most activation barriers are overcome. At low coverages and temperatures no such correlation should hold as the predominant species are those formed in an activationless process (e.g., chemisorption bonds). For example, while the compound that In can form with GaAs (i.e., InAs) is less stable than the compound that Al can form (i.e., AlAs) this is of no consequence at very low coverages and temperatures: Al coverage will lead to cluster formation while In coverage may form chemisorption bonds.[5] The consideration of the end products alone, formed after a series of activated chemical reactions have taken place, disregards the importance of the internal configurational states[81] of the species which exist at the initial stage of barrier and interface formation.

When the Al/GaAs(110) is heated[11] to 450—500 °C (or prepared at room temperature with presumably more reactive substrates[8-10]), the thermal energy and lateral spreading pressure eventually overcome the activation barrier of cluster cohesion, the Al—Al bonds break, and Al is exchanged for the substrate Ga to form layers of the stabler species AlAs. Figure 1(d) shows the calculated surface density of states when only the first Ga layer is exchanged (unbroken line) and when the first two Ga layers are exchanged (dashed line); the exchanged Ga is assumed to escape.[11] The main effects are as follows.

(i) The high-energy tail of the second-layer cation state g''' is shifted from its surface counterpart g, somewhat increasing the heteropolar gap (a-g) with respect to GaAs.[11]

(ii) The substrate cation s state b''' (now an Al state) is shifted from the clean-surface g (a Ga state) by $\Delta_{b'''} \sim 1$ eV, as observed experimentally[10,11] and expected from atomic estimates $\Delta\epsilon_{ss}(\mathrm{Al}) = \epsilon_s[\mathrm{Ga(III)}] - \epsilon_s[\mathrm{Al(III)}] = 1.4$ eV.

(iii) The As dangling-bond states a''' and c''' are unchanged—the empty Ga state d''' is attenuated and replaced by a Ga-Al-like state which is exposed due to the larger band gap.

(iv) The calculated charge transfer suggests an increased ionization energy for Al and a much smaller decrease for the As core states.

These effects are consistent with the experimental data for high-coverage [≥ 2 ML (Refs. 9 and 10)] unheated surfaces or for low-coverage heated surfaces.[11] I conclude, therefore, that these results pertain to exchanged Ga and not to chemisorbed Al.

VII. SUMMARY AND IMPLICATIONS ON FERMI ENERGY PINNING

Different theoretical models that describe the low-temperature and low-coverage stage of the formation of the Al/GaAs(110) interface have been examined. Central to these models is the assumption that the basic physical properties of the interface (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[1] or covalent[2–5] chemisorption bonds between the adatoms and the substrate. The central 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 formation of the interface no such bonds occur but that Al_n clusters, which interact only weakly with the substrate prevail—is shown to be more likely. Analysis of the data leads to the following conclusions.

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

(ii) The good agreement between experiment and theory obtained previously within the epitaxially ordered, covalently bonded overlayer model was based on a far too short adatom—substrate bond length and an incomplete interpretation of the available experimental data. Quantitative as well as qualitative inaccuracies also occur with the previously used pseudopotentials.

(iii) Calculations for the epitaxially ordered, covalently bonded overlayer model using improved (*a priori* nonlocal) pseudopotentials and physically correct bond distances produce one-electron spectra that cannot be reconciled with the experimental photoemission and core shift data.

(iv) Stability arguments clearly suggest that interadatom interactions are comparable to or stronger than the adatom-surface interactions, leading to a preference for adatom cluster formation.

(v) The predictions of the weakly interacting cluster model have been examined in detail and found to agree with experimental data, where available. At the same time this model suggests a number of new predictions, including the occurrence of molecular cluster levels (not chemisorption bond states) between the VBM and E_F, the morphology of the overgrowth at its initial stage, the difficulty to obtain an epitaxy on the (110) surface, possible LEED geometries, as well as the trends in interface characteristics as one changes the adatom down column III.

(vi) The electronic structure of the annealed system can be understood in terms of an Al-Ga exchange taking place also at subsurface layers, as previously suggested. This system is fundamentally different from the low-coverage, low-temperature interface in its structural and electronic properties.

A central point emerging from the experimental results of Spicer *et al.*,[7] Skeath *et al.*,[8] Brillson *et al.*,[9] and Bachrach *et al.*[10] is that the barriers are already established when as little as 10^{12} pinning states per cm^2 exist. There are three categories of surface-related energy levels that may be associated with Fermi energy pinning. (a) *Surface states* of the clean semiconductor (Bardeen's pinning). If present, their density is comparable to that of the surface atoms (e.g., 10^{15} cm^{-2}). (b) *Adsorption states,* i.e., the electronic states associated with either clusters or with adatom—substrate chemisorption bonds (e.g., MIGS or Heine's pinning). If no clustering occurs, their density is comparable to that of the adatom coverage (e.g., 10^{15} cm^{-2} for 1 ML). (c) *Adatom-induced defect states* (AIDS) associated with surface imperfections (vacancies, impurities, internal diffusion, compound formation, defect-induced relaxation, etc.). Since both the kinetics and the thermodynamics of surface defect production has, in general, a yield smaller than unity, the density of AIDS is only a fraction of the adatom density. Typically, for 1 ML coverage the density of AIDS may be $\sim 10^{13}$ cm^{-2} or 1% of the adatom density.

Previous theoretical models[1–5] have attempted to identify the pinning states as conventional adsorption states [category (b)]: either MIGS (Ref. 1) or covalent chemisorption states.[2–5] This was based, in part, on the recognition that surface states *per se* [category (a)] are not present in the band gaps of most III-IV semiconductors, as previously thought. Our foregoing discussion suggests that, in fact, no conventional chemisorption states are formed at low coverage of Al on GaAs(110). At the same time, experiments show that as few as $\sim 10^{12}$ states/cm^2 are needed for pinning. This suggests that conventional chemisorption states may not even be necessary to explain pinning states, as previously assumed.[1–5] This then opens the possibility that states of category (c) above, either AIDS or cluster states (both being *low-density species* rather than 1:1 chemisorption states), may be responsible for Fermi energy pinning. We briefly 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 Al_5, Al_9, Al_{19}, Al_{25}, and Al_{43} the calculated[68] band gaps are 0.14, 0.07, 0.05, 0.2, and 0.03 eV, respectively) cluster states are likely to overlap the semiconductor gap region. The low-energy density of cluster states (typically $1-5$ states/eV) and the low surface density of the clusters make their direct experimental identification difficult. The Fermi energy 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 *et al.*,[7] who suggested a low concentration ($\sim 10^{12}-10^{13}$ states/cm^2) of surface defects (e.g., anion and cation vacancies) as the source of pinning. I note, however, that while such a model does incorporate the essential physical features of the problem (e.g., the correct trend with the substrates ionicity,[82] noninterference with the substrate's valence-band spectra, semiquantitatively correct pinning energies[82]), at this time it is certainly incomplete. For example, an exhaustive theoretical search for *simple defect levels* that will explain the observed trends in barrier heights[83] (including both cation and anion surface vacancies and substitutional impurities such as B, Al, Ga, In, C, Si, Ge, Pb, O, N, S, Se, F, Cl, Br, and I in the semiconductors AlP, AlAs, GaP, GaAs, InP, InAs, InSb, CdSe, and ZnSe) failed to identify the source for the observed systematics in any simple manner. Further, most adatom clusters will have band gaps which are sufficiently small on the scale of the semiconductor band gap. Consequently, the density of cluster states in the semiconductor gap will be higher than that of the AIDS. The former states are then likely to dominate the Fermi-level stabilization.

Note added in proof. In a recent work by Ihm and Joannopoulos (private communication) the authors have applied the method of total energy minimization used here (Ref. 15) and similar first-principles nonlocal pseudopotentials to compute the binding energy of a number of additional Al/GaAs(110) configurations. They find the following. (1) For the idealized case of an ordered $\frac{1}{2}$ ML of chemisorbed Al where no strong $Al-Al$ bonds are permitted, the stable arrangement involves a twofold coordination of Al (or bonding to As) and an unrelaxed substrate. As indicated here, such an arrangement is only hypothetical since (i) the LEED data (Ref. 31) excludes an ordered epitaxial arrangement, (ii) photoemission studies (Refs. 7 and 11) exclude sharp chemisorption gap states expected from an unrelaxed system, and (iii) stability considerations (Sec. V A) prefer Al clustering to any chemisorption arrangement. (2) For the more realistic case of interacting $Al-Al$ particles at $\frac{1}{2}$ ML coverage, the authors confirm the basic conclusion of the present study that even the most stable configuration of ordered chemisorption is not stable with respect to the Al bulk or cluster formation. The entropy term is argued to further stabilize the cluster configuration over chemisorption. (3) In agreement with the present suggestions [Sec. V B, item (vi)] the authors indicate that at very low coverage ($<< \frac{1}{2}$ ML, before the pinning of the Fermi energy is established), the ultrasmall Al concentration will favor statistically independent chemisorption of Al. (4) The authors confirm the present conclusion (Sec. VI) that the heat released in Al bonding is likely to be responsible for formation of surface defects.

The present results as well as the Hartree-Fock cluster calculation (Ref. 6) are, however, in conflict with the results of Ihm and Joannopoulos on the hypothetical geometry of independent Al chemisorption: The latter authors suggest that the $Al-$substrate bond length is close to the bulk value of 2.45 Å, far shorter than the bond length obtained here (3.1 Å) and in Ref. 6 (3.04 Å). The binding energy they obtain is more than twice the values obtained here and in Ref. 6. The reason for this discrepancy is not understood.

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ters (e.g., cutoff values) used in self-consistent calculations. If, for example, one performs a *fully converged calculation* with this pseudopotential (i.e., 169 plane waves in the basis set, including all nonzero components in the pseudopotential up to a momentum of $q_{\max}=3$ a.u.$^{-1}$ indicated in Table I of Ref. 23(a) and iterating over 10 special $\vec{k}$ points), one obtains [for an exchange coefficient $\alpha=0.8$ (Refs. 1, 2, 23, and 24)] an *indirect band gap* $\Gamma_{25,v}\rightarrow\Delta_{1c}$ of 0.95 eV. Experimentally, this material has a direct band gap $\Gamma_{25,v}\rightarrow\Gamma_{1,c}$ of 1.52 eV. More specifically, such a calculation produces the band energies (in eV, taken with respect to the valence-band maximum, internal precision of 0.03 eV): $\Gamma_{1v}(-12.14)$, $\Gamma_{1c}(1.31)$, $\Gamma_{15c}(3.56)$, $\Gamma_{1c}(7.17)$; $X_{1v}(-9.73)$, $X_{3v}(-6.64)$, $X_{5v}(-2.56)$, $X_{1c}(1.02)$, $X_{3C}(1.04)$, $X_{5c}(11.03)$; and $L_{1v}(-10.52)$, $L_{2v}(-6.51)$, $L_{3v}(-1.03)$, $L_{1c}(1.04)$, $L_{3c}(4.09)$. The experimental results are $\Gamma_{1v}[-13.1$ (Ref. 19), -13.8 (Ref. 20)], $\Gamma_{1c}[1.52,1.63$ (Ref. 19)], $\Gamma_{15c}[4.72$ (Ref. 19), 4.49 (Ref. 21)], $\Gamma_{1c}[8.33$ (Ref. 19)]; $X_{1v}[-10.7$ (Refs. 19 and 20)], $X_{3v}[-6.7$ (Ref. 19), -7.1 (Ref. 20)], $X_{5v}[-2.8$ (Ref. 19), -2.5 (Ref. 20)], $X_{1c}[2.18$ (Ref. 19), 1.95 (Ref. 21)], $X_{3c}[2.58$ (Ref. 19), 2.35 (Ref. 21)]; and $L_{1v}[-11.2$ (Ref. 19), -12 (Ref. 20)], $L_{2v}[-6.7$ (Ref. 19), -7.1 (Ref. 20)], $L_{3V}[-1.3$ (Ref. 19), -1.4 (Ref 20)], $L_{1c}[1.85$ (Ref. 19), 1.95 (Ref. 21)], $L_{3c}[5.6$ (Ref. 21)]. Clearly, the calculated lower conduction band is about 1 eV too low in the Δ and Λ directions. In practice, however, computer 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 $\Gamma_{25v}\rightarrow\Delta_{1c}$ band gap (0.6 eV) with $\Gamma_{1c}(1.30)$, $X_{1c}(0.69)$, and $L_{1c}(0.92)$. To get a physically correct band structure one needs to truncate the pseudopotential to include only the first six nonzero reciprocal-lattice vectors ($G^2=3$, 4, 8, 11, 12, and 16, equivalent to the first 65 plane waves, or $q_{\max}=2.36$ a.u.$^{-1}$) *but to artificially extend the screening potential to include the first* $\sim$*181 plane waves.* Using 27 plane waves in the basis, one then gets the "optimal" results $\Gamma_{1c}(1.53)$, $X_{1c}(1.42)$, and $L_{1c}(1.36)$; i.e., a $\Gamma_{25,v}\rightarrow\Lambda_c$ indirect band gap, but within ~ 0.2 eV of the magnitude of the direct gap. (This calculation has been checked independently by J. R. Chelikowsky who obtained 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 interface and surface calculations [e.g., Fig. 10 in Ref. 23(a) shows the lowest conduction band of GaAs to be erroneously below the conduction band of AlAs at $\bar{\Gamma}$]. The artificially low GaAs conduction band, resulting from a possible indirect gap along the Δ or Λ directions, may affect the nature and energy of conduction-band-derived interface states [e.g., the empty Ga surface state (Ref. 24) and the Ga/Al interface state (Ref. 2)]. I thank J. R. Chelikowsky, W. Pickett, and J. Ihm for comments on this footnote. Special thanks are due to J. R. Chelikowsky for repeating independently the underconverged calculation for bulk GaAs.

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