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THE ORIGIN OF SCHOTTKY BARRIERS ON THE CLEAVAGE PLANE OF III–V SEMICONDUCTORS: REVIEW OF SOME RECENT THEORETICAL WORK*

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Recent theoretical ideas on the origin of the Schottky barrier on the cleavage plane of III–V semiconductors are reviewed, using the Al/GaAs(110) system as a benchmark.

1. INTRODUCTION

In this paper I review four recent theoretical models that have focused on the formation of Schottky barriers on the (110) face of heteropolar semiconductors. I shall conclude this review by stating that the origin of Schottky barriers is not properly understood theoretically at this time. However, the recent experimental and theoretical advances in this field have eliminated a number of classical concepts and models and are now pointing to new directions of search for the origin of Schottky barriers. This article will summarize this state of affairs.

The theoretical progress in this field was made possible by a number of recent experimental advances. In particular, it was made possible by a new experimental methodology, which I choose to call "the principle of minimizing confusing evidence". Clearly, one could have continued to measure Schottky barriers under complex chemical and structural circumstances, *e.g.* in the presence of oxide layers, using less-than-perfect cleaves, after chemical pretreatment with ambient gases, or thermal treatments, at high metal coverages or for systems that are known to exhibit a high chemical reactivity or massive interdiffusion. While such experiments are important on their own, the complexity of these systems and the difficulty to isolate crucial physical parameters have often led to a situation where the results could best be summarized in terms of phenomenological correlations that systematize the data but provide little insight into causal mechanisms of barrier formation. Instead, the new experimental methodology has chosen to focus on systems and techniques that minimize "confusing evidence", yet providing Schottky barriers that are characteristic of those observed in actual devices. Perhaps the best-studied system in this respect is Al/GaAs(110). The experiments on this system (*e.g.* in refs. 1–8 and

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references cited therein) that have provided most of the impetus to theoretical studies were carried out at low coverages (0.5 monolayer (ML) or less), low temperatures (about 300 K or less), with high quality cleaves, high vacuum, no chemical pretreatments and with a system that was initially unpinned and showed a simple 1 × 1 low energy electron diffraction (LEED) pattern. The salient features of the experimental results could be summarized as follows.

(1) For a large range of adatoms, as diverse as cesium (a large and highly electropositive atom) and oxygen (a small and highly electronegative atom), the barrier heights on GaAs(110) are about the same: about 0.5 eV on p-type material and about 0.75 eV on n-type material[1] (gold may be an exception). Clearly, the adatom need not be a metal species to produce a barrier.

(2) About 80% or more of the barrier height is already formed at ultralow coverage (about 0.2 ML or less), *i.e.* when the "metal" adlayer is not a continuous metal but most probably has an insulating molecular structure[8].

(3) These barriers are observed at low coverage *before* the application of thermal treatment that is known to promote chemical reactions (*i.e.* Al–Ga exchange). In other words, the occurrence and development of the barrier can be observed before measurable chemical reactions are detected[5,6]. The latter are observed[3–5] at higher coverages, or after a thermal anneal, or in the presence of a poor cleave (even at low temperatures).

The three foregoing observations already indicate that many of the classical testbook concepts used in the past to understand Schottky barriers have to be revised. These observations point to the fact that the underlying phenomena have an *atomic scale*, implying that the proper intellectual tools to be used involve a quantum mechanical description, not a macroscopic electrical engineering model, a consideration of the local chemical potentials, not the bulk thermodynamic Fermi energies, a focus on the molecular species that exist at ultralow coverage, not the long-range strain fields associated with fully developed interfaces, and the consideration of the large activation energies for defect and bond formation, not the heat of formation of the final products.

(4) The LEED pattern of unannealed samples indicates that the substrate is still largely relaxed, much like the clean surface, and shows a diffused background, indicative of some disorder[7].

(5) No sharp and localized surface states are observed to move into the gap upon deposition: only a low intensity structureless tail is seen to linger in the gap region[5,6].

(6) The Ga 3d core level does not show a chemical shift over and beyond the band banding[5] (physical shift).

(7) The Ga 3d core exciton appears unshifted[5].

(8) The adatom core levels[1–8] (*e.g.* Al 2p) show chemical shifts; this chemical shift depends on the coverage even below 0.5 ML.

Not all of these experimental statements are universally accepted: for instance, statement 6 is still being debated[3–5]. The reason for this ambiguity appears to be the difficulty to delineate the experimental conditions under which no measurable chemical exchange occurs from the conditions under which some exchange occurs. Clearly, the temperature is not the only decisive factor: for a high quality cleave[5], a higher temperature (about 500 °C) may be needed to overcome reaction activation

barriers and to promote chemical exchange and a Ga 3d core shift, whereas, with less perfect cleaves, exchange reactions can occur even at room temperature. Hence caution would have to be exercised in interpreting these facts.

2. THEORETICAL TOOLS

In attempting to understand the formation of Schottky barriers on the cleavage plane of III–V semiconductors, we shall heavily rely on the available experimental data on the Al/GaAs(110) system and on related molecular and solid state species. I shall appeal to theoretical calculations only when the data are insufficient or inconclusive. The major theoretical tool will then be the self-consistent solution to the Schrödinger equation describing a model of the metal–semiconductor interface:

$$\left\{-\frac{1}{2}\nabla^2 + V_{ps}(\boldsymbol{r}) + V_{scr}(\boldsymbol{r})\right\}\psi_j(\boldsymbol{r}) = \varepsilon_j\psi_j(\boldsymbol{r}) \tag{1}$$

Here $V_{ps}(\boldsymbol{r})$ is the crystal pseudopotential which is given as a superposition of free-atom pseudopotentials $v_{ps}^{(L)}(\boldsymbol{r})$ of angular momentum L (*i.e.* "non-local" or L-dependent pseudopotentials). The assumed atomic positions at τ_α enter, therefore, in the expression

$$V_{ps}(\boldsymbol{r}) = \sum_{\tau_\alpha} v_{ps}(\boldsymbol{r}-\tau_\alpha) \tag{2}$$

The self-consistent response of the electronic system to this external potential is given by the screening potential $V_{scr}(\boldsymbol{r})$. It contains the interelectronic Coulomb as well as exchange and correlation interactions modeled by the density functional formalism[9]. In contrast with empirical pseudopotential or tight-binding approaches, in the first-principles pseudopotential approach $V_{scr}(\boldsymbol{r})$ is the output of the calculation, not the input. The boundary conditions used with eqn. (1) are those of a supercell (*e.g.* in ref. 10): a slab of a semiconductor (typically seven to nine layers) with a monolayer of metal atoms on each side is followed by a region of vacuum (typically three to five layers on each side) and repeated periodically through space. While this supercell construct allows us to use the standard techniques of band theory for solving eqn. (1), it also introduces a spurious adatom–adatom interaction between two adjacent supercells. An attempt is then made to minimize this interaction by using a sufficiently large supercell. Despite this, memory limitations of present-day computers still impose a non-vanishing (and unphysical) adatom–adatom interaction within this method (typically 0.1–0.2 eV). The wavefunctions $\psi_j(\boldsymbol{r})$ are usually expanded in a fixed set of plane waves.

The theoretical quantities calculated are the statistical distribution of orbital energies ε_j whose wavefunctions $\psi_j(\boldsymbol{r})$ have an amplitude on the surface layer (local density of states) and the total energy $E_{tot}(\tau_\alpha)$ of the system as a function of the atomic positions τ_α. Except for the most recent theoretical studies[11–13], all previous studies on extended semiconductor substrates have used a fixed set of atomic coordinates $\{\tau_\alpha\}$ (inspired by what appeared to be the correct experimental surface structure) and local semiempirical atomic pseudopotentials $v_{ps}(\boldsymbol{r})$. Recently, the physical accuracy of the semiempirical local pseudopotentials has been questioned[12]. In recent studies[12,13] researchers have varied $\{\tau_\alpha\}$ to deduce theoretical equilibrium

structures and have employed first-principles non-local pseudopotentials (*e.g.* those of ref. 14). I shall base my discussion on this more recent approach.

The first-principles self-consistent approach to the interface problem has been made possible largely by the advent of high speed large-memory computers, by the formulation of the density functional formalism to treat screening effects[9], by the invention of new and efficient strategies to achieve self-consistency[15] and to diagonalize huge hamiltonian matrices[16], by the development of accurate first-principles non-local pseudopotentials[14] and by the establishment of an efficient formalism to calculate the total energy E_{tot} from the solution of the single-particle problem in eqn. (1)[17]. When applied to simple bulk crystals, this approach produces physically accurate electronic charge densities, equilibrium lattice parameters and cohesive energies[18]. Further details can be found in the original papers.

3. MODEL A: INTRINSIC SURFACE STATES PIN THE FERMI ENERGY

One of the first and best-studied models of Schottky barriers is due to Bardeen[19] and suggests that intrinsic surface states that exist before the adlayer is deposited are responsible for the pinning of the Fermi energy at the interface. This notion was widely used to rationalize the fact that barrier heights appear to scale with the difference between the metal and semiconductor work functions, with a coefficient S that increases with the semiconductor's ionicity[20]. Experimental studies in the early and mid-1970s have shown direct evidence for the existence of semiconductor surface states inside the band gap. These experiments for GaAs(110) included X-ray photoelectron spectroscopy (XPS)[21], partial yield[22], electron energy loss[23], ellipsometry[24] and photoyield[25] measurements. Similar experiments have indicated the existence of surface states in the band gaps of GaSb [22] and InP [26]. Concomitantly, early theoretical calculations, assuming an ideal surface structure, have all confirmed the existence of intrinsic surface states in the band gap, either empty[27,28] or both empty and filled[29,30]. Subsequent experiments in the mid- and late 1970s [31–33] have indicated that, with the exception of GaP, there are no gap surface states in III–V semiconductors. Previous assignments of spectral features as gap surface states were attributed to the failure to subtract the excitonic energy shift of the core states[31,32] and to the existence of surface defects and imperfections in poorly cleaved and impure crystals[33]. The early evidence[34] (in 1967!) of the absence of gap surface states in GaAs has been now confirmed and accepted. With the advent of LEED studies, it also became clear that the surface atoms undergo substantial structural rearrangements[35] (relaxation) relative to their positions in the bulk crystal. Subsequent theoretical calculations, now assuming the experimental (relaxed) surface geometry, have shown that the intrinsic surface states are eliminated from the gap upon surface relaxation[36–38]. Although it became evident that intrinsic surface states, or the Bardeen pinning, are not responsible for the formation of Schottky barriers on these systems, much has been learned from these studies on the properties of clean semiconductor surfaces and on the interplay between electronic structure and atomic geometries. In particular, theoretical studies[36–38], including the first application of a first-principles non-local pseudopotential approach to the problem[11], have revealed in great detail the dispersion,

parity and charge density distribution of many surface resonances. Whereas many of these structures have been first observed experimentally[39,40], some have been predicted first theoretically. In the mid- to late-1970s it hence became apparent that intrinsic surface states on the cleavage plane of heteropolar semiconductors do not hold the key to understanding Schottky barriers.

4. MODEL B: METAL-INDUCED GAP STATES PIN THE FERMI ENERGY

In 1965, Heine[41] suggested that the metallic tails of the wavefunctions of the adlayer penetrate the semiconductor and form new metal-induced gap states (MIGSs) that are capable of pinning the Fermi energy. This model has been revived in a series of semiempirical pseudopotential calculations[42] that have modeled the metallic adlayer by a rather thick layer of jellium bonded to an ideal unrelaxed semiconductor. These calculations have shown the disappearance of the semiconductor gap states and the appearance of MIGSs and have provided a correlation between the observed ionicity dependence of S and MIGSs. The focus has now shifted from considering the semiconductor states as the source of pinning to considering the metal states as the decisive factor. However, as indicated above, experimental evidence from photoemission studies suggested that the barrier heights are already developed at less than 0.5 ML coverage[1], *i.e.* when the adlayer is likely to be non-metallic. This was illustrated convincingly for gold overlayers where it was found[1] that at the coverage (about 0.2 ML) where the Fermi energy is already mostly stabilized the spin–orbit splitting of the Au 5d shell (1.9 eV) is still considerably 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 bulk like nor a free lattice gas of adatoms. Further, partial yield experiments showed that gap surface states (expected from an ideal unrelaxed surface) do not appear at low coverage[1,5], suggesting an essentially relaxed surface geometry. In agreement with this, LEED studies[7] at low coverage and room temperature (*i.e.* for unannealed samples) show intensity patterns that are characteristic of the clean (*i.e.* relaxed) surface, with an additional increased background signaling a disordered adlayer. This suggests that the model of a thick jellium layer over an unrelaxed substrate[42] is inappropriate for the system at hand. It may then be asked if the metallic bonding hypothesis can be tested by using a *thin* (0.5 ML or less) jellium layer on a *relaxed* surface. I have therefore solved eqn. (1) under these conditions. This self-consistent pseudopotential calculation[12] showed that under these conditions no Fermi-level-pinning MIGSs occur. In fact, such an ultrathin "metallic" layer is not even metallic; its bandwidth and electronic structure are substantially different from those of the bulk metal. MIGSs appear when the semiconductor initially has surface gap states (*i.e.* an unrelaxed substrate) which then hybridize with the well-developed tails of the metallic wavefunctions (*i.e.* a thick metallic layer). Hence I conclude that although the thick jellium model[42] 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. MIGSs are expected[42] and found[43] to be spectroscopically important at higher coverages but may not control barrier formation at the crucial initial stages.

5. MODEL C: ADATOM–SEMICONDUCTOR CHEMISORPTION BONDS CONTROL THE INTERFACE PROPERTIES

The inappropriateness of the intrinsic semiconductor surface state model A and the metal state model B to provide a complete explanation to barrier formation have naturally prompted the model C where both of the partners of the interface come to play. In this model[44–48] it is assumed that the adatoms form directional chemical bonds with the substrate atoms (chemisorption) and that at 0.5 ML the system can be described by an epitaxially ordered and covalently bonded array of such chemisorption bonds. The underlying assumption (the geometry was postulated and not predicted by total energy minimization) was that much of the surface characteristics (XPS spectra, chemical core shifts, barrier heights *etc.*) could be understood in terms of the quantum mechanics of these adatom–substrate chemisorption bonds. The various theoretical approaches applied to this model ranged from a tight-binding approach[45–47] to a semiempirical pseudopotential approach[44] and to coreless Hartree–Fock (HF) methods[48]. They differed in the choice of the surface atom to which the metal chemisorbs: gallium[48] or arsenic[44–47]. The chemisorption metal–semiconductor bond length was assumed[44–47] to be equal to the bulk GaAs or AlAs value of 2.43 Å. Reasonable agreement was obtained between the calculated and observed surface structures for the model advocating bonding to the gallium site.

I shall discuss this chemisorption model by noting the following points.

(1) I shall argue that the chemisorption bond length guessed in previous calculations is about 25% too short, *i.e.* that the bond formed upon chemisorption between the essentially atomic aluminum and the substrate atoms is considerably weaker (and hence longer) than the bond between aluminum and arsenic as they exist in the bulk. I shall first use classical chemical considerations to suggest this and then show that a quantitative quantum mechanical energy minimization predicts a chemisorption bond length of 3.0 Å, considerably longer than the bulk value of 2.43 Å used in chemisorption calculations.

(2) Next I shall show by detailed calculations of the local density of states and comparison with photoemission results that if the physically correct chemisorption bond length is used the prediction of the chemisorption model, either for Al—Ga or for Al—As bonding, conflicts with experiment.

(3) I shall then show that the chemisorption model is likely to be incorrect not only because it disagrees with the photoemission data but also because stability considerations indicate that adatom–adatom clustering is stabler than chemisorption. I shall finally proceed in Section 6 to discuss the adatom cluster model, indicating which of its predictions have now been confirmed experimentally, and outline some of its other predictions which remain to be examined. More details were given in recent publications on this subject[12].

5.1. *Chemisorption adatom–substrate bond lengths*

Whereas the fourfold-coordinated aluminum atom in bulk AlAs has the nominal excited trivalent configuration s^1p^2 (denoted Al^{III}), a chemisorbed aluminum atom on top of gallium or arsenic is likely to maintain its monovalent ground state configuration s^2p^1 (denoted Al^{I}). From simple chemical

arguments[49,50] it appears that bonding of Al^{I} will be substantially different from bonding of Al^{III}. Considering group IIIa halides, thermodynamic data (see ref. 49 and ref. 12, Table I) indicates that whereas the monovalent forms are unstable at the top of the column in the periodic table (BF, BCl, AlF, AlCl) they are very stable at the bottom of the column (TlF, TlCl). In contrast, the trivalent forms are known to be stable at the top of the column (BF_3, BCl_3, AlF_3, $AlCl_3$) but less stable at the bottom of the column (TlF_3, $TlCl_3$). Clearly, the monovalent form is stable at the bottom of the column, whereas the trivalent form is stable at the top of the column. Boron and aluminum, at the top of column, are therefore likely to be unstable in a monovalent chemisorption configuration, or else to have a weak and long bond. This picture can be rationalized in terms of the increase in the atomic $s^2p^1 \rightarrow s^1p^2$ promotion energy with increasing atomic number Z: the smaller promotion energy for boron and aluminum is overcome to form the stabler trivalent multicoordinated forms, whereas the larger promotion energy of indium and thallium acts to favor the monovalent singly coordinated forms. Furthermore, the stability of the monovalent form decreases with the ionicity of the adatom[51] ($E(\text{AlF}) > E(\text{AlCl}) > E(\text{AlBr}) > E(\text{AlI})$). Only species that are far more electronegative than gallium or arsenic 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 $X \equiv Ga$ in the linear plot of the Al—X bond length (1.65 Å, 2.13 Å, 2.29 Å and 2.54 Å for $X \equiv$ F, Cl, Br and I respectively[51]) *versus* the X atom electronegativity (4.0, 3.0, 2.8 and 2.5 for $X \equiv$ F, Cl, Br and I respectively) yields an Al^{I}—Ga bond distance $d = 3.1$ Å, far larger than that previously inferred from Al^{III} bulk data (2.43 Å)[44–47]. Indeed, a cluster-type HF calculation[48] for Al^{I} bonded to gallium in a $GaAs_2$ cluster yielded d(Al—Ga) = 3.04 Å (and a small binding energy of between −0.4 and −0.6 eV).

The expectations from these semiclassical arguments can be tested by a quantitative total energy minimization. In the first variational calculation of the equilibrium bond length of an adatom on an extended semiconductor substrate[12], $E_{tot}(d)$ was calculated self-consistently for a few distances d between aluminum and the substrate. Using distances d of 2.8, 3.0, 3.2 and 3.4 Å and a relaxed surface geometry, a total energy minimization was performed (by the method described in ref. 17) in a repeated-cell model for 0.5 ML of aluminum bonded to either gallium or arsenic, where aluminum is located in a symmetry plane perpendicular to the surface; positioning of aluminum 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 perturbation treatment) is sufficient to locate the minimum of the binding curve with a precision of ± 0.1 Å; however, the relative precision in the absolute binding energy is only ± 0.3 eV. This yielded at equilibrium d(Al—Ga) = 3.1 ± 0.1 Å and d(Al—As) = 3.0 ± 0.1 Å, in good agreement with the semiclassical estimates but in disagreement with the values ($d = 2.43$ Å) assumed in previous calculations. The binding energy to the gallium site at equilibrium is calculated to be -0.4 ± 0.3 eV, with a somewhat lower value of -0.3 ± 0.3 eV on the arsenic site, confirming the weakness of the bonds to the substrate.

This result raises an important question. It is known[1–5] that when the temperature is raised from about 30 °C to about 500 °C a surface Al–Ga exchange

reaction occurs. However, this thermal energy kT is two orders of magnitude lower than the activation energy required for such an exchange (*e.g.* formation of a gallium vacancy, requiring about 2 eV [52]). It has been previously suggested[1] that the source of energy available to overcome such barriers and to create surface defects or to promote surface reactions is the condensation energy. This energy involves the (very low) kinetic energy of the impinging particles plus the energy released upon their bonding to the surface. My calculation shows that this energy is considerably lower than the activation energy (the condensation energy of *monovalent* species such as cesium may be higher). What is then the source of energy at the surface and how is a small increase in kT sufficient to overcome an apparently large activation barrier? We shall see (Section 6) that the adatom cluster model provides a simple resolution to this dilemma.

5.2. Predictions of the chemisorption models with revised bond distances

To compare the predictions of the chemisorption model with experiment, I solved eqn. (1) self-consistently for 0.5 ML coverage of aluminum and used the first-principles non-local atomic pseudopotentials[14] and the predicted Al—Ga and Al—As equilibrium bond lengths to compute the local density of states. The results are depicted in Fig. 1. I shall now briefly summarize the main points of contradiction between these calculated results and experiment.

For aluminum bonded to arsenic (Fig. 1(b)) the points are as follows. (i) The peak b′ corresponds to an Al^{I}—Ga s state, localized on the adatoms Al^{I} and shifted to lower binding energy relative to the clean surface (Fig. 1(a)) gallium states corresponding to peaks g and b[5]. The calculated shift $\Delta_{b'g}$ is 2.8 eV for aluminum (3.5 eV for $d = 2.43$ Å [46]), 1.8 eV for gallium[45] and 1.5 eV for indium[47]. Experimentally, $\Delta_{b'g}$ was found to be 1.5 eV for indium (binding energy $E_{b'} = -5$ eV)[47] and 0.9–1.3 eV for gallium ($E_{b'} = -5.6$ eV)[45]. For aluminum, which is expected to have the largest shift, no shift has been observed by Spicer and coworkers[1] and Huijer *et al.*[5], whereas Chadi and Bachrach[45] found a weak structure at $E_{b'} = -6.1$ eV ($\Delta_{b'g} \approx 1.5$ eV) which was not reproduced in the other experiments[1,3]. However, even if experimentally $\Delta_{b'g} \neq 0$ for aluminum, the order of the observed binding energies $E_{b'} = -6.1$ eV, -5.6 eV and -5 eV for aluminum, gallium and indium respectively is reversed to that obtained in surface calculations. (ii) The peak c′ corresponds to an As—A^{I} p-like dangling bond state replacing the clean surface arsenic state corresponding to peak c. Experimentally, neither strong attenuation of c nor the appearance of a new peak c′ are observed upon deposition of aluminum, gallium or indium[1-3,47]. (iii) The state corresponding to the peak e′ is an interadatom p-like state appearing in pseudopotential calculations below the substrate cation state corresponding to the peak d′ and leading to pinning at 1 and 1.3 eV below the conduction band minimum (CBM) for $d = 2.43$ Å [45] and $d = 3.1$ Å respectively. The tight-binding model[45,46], failing to include any direct interadatom interactions, places e′ above d′ and hence leads to a fundamentally different pinning mechanism. Experimentally[1-3], however, no evidence is found in the photoemission spectra for sharp and partially occupied gap states such as those corresponding to d′ or e′; the calculated peaks would have to be attenuated by an unlikely factor of nearly two orders of magnitude (*e.g.* due to averaging over a number of surface layers) to explain their absence in the observed spectra.

For aluminum bonded to gallium (Fig. 1(c)) the major differences with the previous case are as follows. (i) The peak b″ is unshifted but has a somewhat increased intensity. (ii) The cation p-like bonding state corresponding to the peak d″ is now stabilized by bonding of Al^{I} to gallium and appears in the gap below e″, predicting pinning at energies that are much too low: 0.4 eV below the CBM for

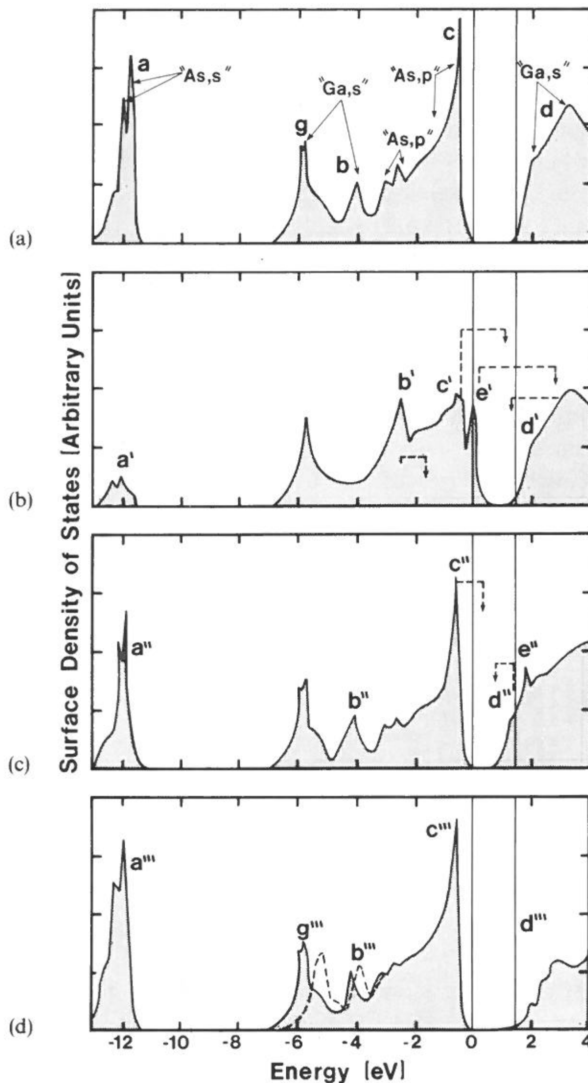

Fig. 1. Smoothed-surface density of states for different chemisorption models of aluminum on GaAs(110) obtained with a relaxed surface geometry and the calculated equilibrium Ga—Al and As—Al bond lengths[12]: (a) clean surface ($\Delta\{Q(\text{Ga})\} = \Delta\{Q(\text{As})\} = 0$); (b) aluminum on arsenic ($\Delta\{Q(\text{As})\} = -0.40e$; $\Delta\{Q(\text{Al})\} = 0.53e$); (c) aluminum on gallium ($\Delta\{Q(\text{Ga})\} = 0.28e$; $\Delta\{Q(\text{Al})\} = -0.41e$); (d) exchanged gallium ($\Delta\{Q(\text{As})\} = 0.09e$; $\Delta\{Q(\text{Al})\} = -0.11e$; ——, first layer; - - -, second layer). The broken arrows indicate the positions of the main structures for an unrelaxed surface geometry and shorter (bulk-like) adatom substrate bond lengths, used in previous calculations.

$d = 3.1$ Å. Because of its two-center (Al—Ga) nature (and resulting mixed angular momentum content) and substantial intensity, matrix element effects are not expected to reduce the bond strength below detection. Further, this strong bond to the surface gallium will tend to change considerably the Ga 3d exciton state occurring at the same final energy as d″. In contrast, however, d″ is not observed experimentally in the gap[1]; the Ga 3d exciton is unshifted in energy and unchanged in shape upon aluminum deposition[5].

The caption of Fig. 1 gives the calculated charge transfer ΔQ associated with surface atoms with respect to the clean surface and atomic aluminum (obtained by integrating the calculated charge densities in spheres). For Fig. 1(b) (negatively charged aluminum) a shift of the arsenic (aluminum) core states to higher (lower) ionization energies is expected whereas for Fig. 1(c) (positive aluminum) the arsenic (aluminum) core states are expected to shift to lower (higher) ionization energies. In contrast, Huijer *et al.*[5] have found that for approximately 0.33 ML of aluminum deposited at room temperature the substrate core emission and the surface-sensitive core exciton are weakened in intensity but remain unshifted (except for band bending) relative to the clean surface. The significant points here are that all theoretical models that assume either an adatom–substrate covalent bond (Figs. 1(b) and 1(c), model C) or a metallic bond (model B) predict a charge exchange between the substrate and adlayer and that this transfer has an opposite sign on the two sides of the interface. These models hence lead inevitably to (substantial[46,48]) core shifts, in opposite directions, in conflict with experiment.

TABLE I

Al—Al SEPARATIONS AND BINDING ENERGY PER ATOM FOR THREE SYSTEMS

System	*Al—Al distance* (Å)	*Binding energy* (eV atom^{-1})
Al/GaAs	3.96[a]	−0.45[a]
Al_2	2.50[a]	−0.85[a]
Al_∞	2.86[b]	−3.4[b]

[a] Calculated values.
[b] Experimental values for bulk aluminum.

5.3. *Stability of adatom clusters versus chemisorption geometries*

Table I compares the Al—Al bond lengths and binding energies of the hypothetical Al/GaAs chemisorption system, the Al_2 diatomic molecule and bulk aluminum. Clearly, for 0.5 ML of chemisorbed aluminum, the Al—Al bond length (next-nearest-neighbor substrate distance) and the binding energy are both well outside the range characteristic of stable aluminum-containing systems. This table alone suggests that the adlayer atoms would prefer to cluster, *i.e.* to reduce their interatomic distance and to increase their binding energy. The net clustering energy would equal the energy needed to desorb the initially chemisorbed aluminum atoms minus the binding energy of the clusters (the energy released upon cluster formation). In ref. 12 this energy was calculated to be in the neighborhood of 3 eV. A recent calculation by Ihm and Joannopoulos[13] has explored many more configurations than in the original study[12], and confirmed that *any* aluminum chemisorption

is unstable with respect to Al—Al bond formation. (In the calculation of ref. 13 cluster formation is predicted to be stabler than chemisorption even though the chemisorption energy was calculated to be ten times larger than that predicted by the HF cluster model[48] and the first-principles density functional model[12]. Ihm and Joannopoulos[13] have not explained the source of discrepancy between their results and previous results[12,48]. It is clear[53] that the discrepancy is not due to convergence difficulties in previous calculations[13]. It should be noted that the error introduced in supercell Al_n stability calculations due to the introduction of *two*[13] aluminum atoms over each surface unit cell (*i.e.* spurious interactions between aluminum on adjacent cells) has not been assessed at this time.)

The theoretical prediction of the stability of adatom clusters on GaAs(110)[12] (by about 3 eV) has the potential of resolving the dilemma posed at the end of Section 5.2. It suggests that the net energy of cluster formation is the energy available at the surface to promote defect formation and chemical reactions. It further explains why a small increase in kT is sufficient to induce reactions with large activation barriers: an increased temperature acts to overcome the small[13] barrier for surface diffusion, which in turn increases the probability of adatom–adatom encounter, and hence of cluster formation, with its attendant release of the cluster energy. We see that the heat of formation of adatom–substrate compounds[54] is not the key quantity for explaining the surface reactivity of this system, but instead the heat of formation of the precursor particles (Al_n) plays the central role.

Our simple stability arguments further predict an interesting "phase transition" between chemisorption and clustering, as a function of the position of the group III adatom in the periodic table. Let us recall that the affinity of a group III adatom to formation of a monovalent bond increases with increasing atomic number in group III (*e.g.* the stability sequence is TlBr > InBr > GaBr > AlBr > BBr [49–51]). However, the affinity of the adatom to itself, as measured by the elemental cohesive energy, decreases with increasing Z in group III (5.77 eV atom^{-2}, 3.39 eV atom^{-1}, 2.81 eV atom^{-1}, 2.52 eV atom^{-1} and 1.88 eV atom^{-1} for boron, aluminum, gallium, indium and thallium respectively). Hence it is expected that, whereas at the top of the column (boron, aluminum) there will be predominantly adatom clustering, at the bottom (indium, thallium) chemisorption might form the ground state of the system.

6. PREDICTIONS OF THE ADATOM CLUSTERING MODEL

In this section I summarize the predictions of the adatom cluster model and indicate which of them have been examined experimentally. The remaining predictions remain, in my view, interesting candidates for future experimental studies.

(1) Since the aluminum atoms in Al_n clusters are multicoordinated and have most of their bonds chemically saturated, it is expected 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 because of 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. The Ga 3d core level and core excitons are hence expected to be nearly unaffected by the deposition of the

adlayer. This is the only model so far which agrees on this issue with the observed valence band photoemission results.

(2) The model predicts that the core energy levels of the aluminum adlayer (*e.g.* 2p levels) will change with coverage between about 0.1 and about 0.5 ML, reflecting the changing chemical environment with the average cluster size n attained at each coverage and temperature. In contrast, the epitaxial covalent model[44–48] predicts a constant core level energy as the coverage changes from about 0.1 to 0.5 ML since more of the same aluminum–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. In contrast, the present model predicts this value to be above the bulk metallic value (72.6 eV) 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 that for a coalesced metallic phase, the Al 2p level is predicted to converge to the metallic limit. Daniels *et al.*[8] have responded to the challenge of this prediction and examined the development of the Al 2p emission as a function of coverage, starting at ultralow coverage. The observed shifts were entirely consistent with the predictions of the cluster model[8].

(3) There exists a rich theoretical and experimental literature on the properties of small metallic clusters. Much of the fingerprint phenomena observed there could be used to study the properties of the metal–semiconductor interface at low coverage. The phenomena include the following: the Debye temperature of small aluminum particles is considerably reduced relative to that of the bulk metal; surface-related phonon softening and an enhancement of the superconducting transition temperature are apparent[55]. The far-IR (0–150 cm^{-1}) absorption spectra of small aluminum particles[56–58] show an unusual parabolic frequency dependence possibly related to the Gorkov–Eliashberg theory of periodic frequency dependence of the electronic susceptibility of small metallic particles. Small Al_n clusters show in the visible spectrum an absorption band which does not occur in the free atom or the bulk metal[59]. 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[60]. The plasmons exhibited by small metallic particles are shifted to higher energies and show distinctive secondary structure above the plasma frequency[61]. Measurements of such phenomena at the early stages of metal deposition could shed light on the morphology and properties of the Schottky-barrier-forming states.

(4) Since in the cluster model the molecular species Al_n interact only weakly and largely non-directionally 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 LEED observations[7] at room temperature which show the same spot patterns as that for the clean (*i.e.* relaxed) surface except for a general decrease in intensity and an increased background, signaling motional disorder (presumably of the small clusters).

(5) Since aluminum does have a finite binding energy to the substrate, it is possible that for small arrival rates, low coverage and low temperature such chemisorption bonds will be formed. These will then provide an activation energy

for cluster formation. Under these conditions we may expect that cluster formation will be suppressed. Clearly, more experiments at low temperatures are called for, to establish the transition point between chemisorption and clustering.

(6) I have concluded that the chemical affinity of aluminum to bonding to the GaAs(110) face is weaker than the Al—Al affinity. This is consistent with the fact that despite an excellent lattice match, until recently, no successful molecular beam epitaxy (MBE) was possible on this lattice face. This is in sharp contrast with the situation on the GaAs(100) face, where good quality epitaxy is readily observed[62,63] due to the effective bonding to the "metallic-like" arsenic lone pair orbitals. The cluster model predicts that the clustering can be inhibited simply by lowering the temperature to the point where the lateral diffusion is sufficiently reduced. This would then open the way for chemisorption (point 5 above) and hence successful MBE. Recent experiments[64] have indicated that the previous failure to obtain an epitaxial growth at MBE temperatures resulted from an anomalously large (and hitherto unexplained) surface mobility of the weakly bonded aluminum species to the surface, leading to a preferential dendritic cluster formation of aluminum. This motion could be quenched at $-5\,^{\circ}$C, leading for the first time to a successful MBE growth on the (110) face[64].

(7) In general, the cluster model predicts a number of distinct structural regimes as a function of coverage and the type of adatom. Going from low to high coverages the following behavior is expected. (a) At a coverage θ_1, the ground state of the system involves chemisorption (*i.e.* at ultralow coverages clustering is statistically impossible). This regime is predicted to be the most important for adatoms from the high atomic number end of group III (indium, thallium) and to occur only at very low coverages $\theta_1 \lesssim 0.1$ ML for atoms from the low atomic number end of group III (boron, aluminum). For the latter case it appears[8] that only a small fraction of the final barrier height is attained (if at all) during chemisorption. (b) After a coverage θ_2 is attained, the predominant species are clusters. Their formation can promote chemical reactions. The adatom core states change with coverage. (c) At still higher coverages $\theta_3 \approx 1$ ML [8], the system consists of metallic drops of adatoms and exchanged atoms. (d) Finally, at even higher coverages $\theta_4 \approx 1$–20 ML [8], bulk aluminum is formed and exchange reactions and interdiffusion are dominant.

It appears to me that new experimental attempts are needed to establish the boundaries θ_1–θ_4 of these phases and their dependence on temperature and the choice of the adatoms. Not all phases are expected to occur in each case. However, it will be of great importance to establish how much of the Schottky barrier height is formed at each stage.

7. SUMMARIZING REMARKS

While the origin of Schottky barrier formation is not established at this time, it appears that intrinsic surface states, MIGSs and chemisorption bonds are not key factors. This leaves two major possibilities. (i) The electronic states of the clusters themselves pin the Fermi energy. We refer to these as "parent states". (ii) The formation of clusters provides sufficient energy to produce surface defects and surface reactions that produce the Fermi energy pinning states. We refer to these as "daughter states". The defect model of Spicer and coworkers[1] in this context

proposes daughter states, and so does Brillson's[54] model on interface-specific states induced by chemical reactions. Since the models involving daughter states are linked closer to the observed near-universality of barrier heights (Section 1, point 1), they appear more plausible at this time. However, the fact that the near-universality of barrier heights does not hold for many systems (*e.g.* InP), and that no simple defects (anion or cation vacancies, antisite defects) have been demonstrated to be the pinning species, indicate that further explorations of daughter state models are clearly needed. In my view, experimental and theoretical studies will have to continue to go hand in hand to elucidate the structure and properties of the ultralow coverage and low temperature parent and daughter states that exist at the initial stage of barrier formation.

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